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ANALYSIS OF GAS CONDENSATE

1. INTRODUCTION

Natural gas transported through the high pressure transmission systems has to fulfill the requirements on pipeline quality gas. Still transported gas contains trace amounts of impurities which can during the delivering of huge amounts of gas condensate or sediment in gas pipelines. As well as the impurities introduced during pipeline construction and repair works can be present. From that reason TSOs perform pipeline system cleaning regularly, generally twice a year. Presence of gas condensate or other impurities in system may cause severe difficulties during operation so it is necessary that cleaning is performed using so called pigs. Pipeline pigging removes impurities which increase pressure loss along the pipeline and reduce the gas volume flow.

Cleaning of high pressure pipelines is commonly performed prior to internal inspection of pipelines which are mainly focused on identification on material losses connected with corrosion or abrasion, cracking and laminations or to check condition of welds. However, the condensate or impurities pulled out of the pipeline system itself are source of useful information not only about the current condition of the pipeline but also about recent history.

Gas condensate or slug is generally composed of solid mechanical particles (clays, sand, and corrosion products) and liquid fractions as compressor oil, water and higher hydrocarbons which can dissolve in compressor oil or can simply condensate due to the changes in gas temperature and pressure. This effect is known as retrograde condensation [1, 2, 3].

2. RETROGRADE CONDENSATION

Phase equilibrium of natural gas with content of higher hydrocarbons (HHC) is strongly dependent on its composition/proportions of HHC mainly due to the different physical

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properties of each substance. The boundary between gaseous and liquid phase is described by the dew point curve. Passing this curve from the gaseous phase to the two phase region HHC start to condensate and simultaneously the composition of the gaseous phase is changing. Retrograde condensation occur under certain condition when during isothermal decreasing of pressure hydrocarbons start to condensate but along the further pressure decreasing it starts to evaporate.

Position of critical point in relation to cricondetherm (maximum temperature at which two phases can coexist) and cricondenbar (maximum pressure at which two phases can coexist) on phase envelope has the influence on further retrograde effects. Figure 1 shows that isobaric increase of temperature (from point 1 to 2) results in condensation (of HHC in this case) and therefore this behavior is called retrograde condensation. That means that increasing the gas temperature may not have been the proper solution of retrograde condensation in pipeline/system. Similarly the vaporization of liquid phase during either adiabatic temperature decrease or isothermal pressure decrease is called retrograde vaporization [6].

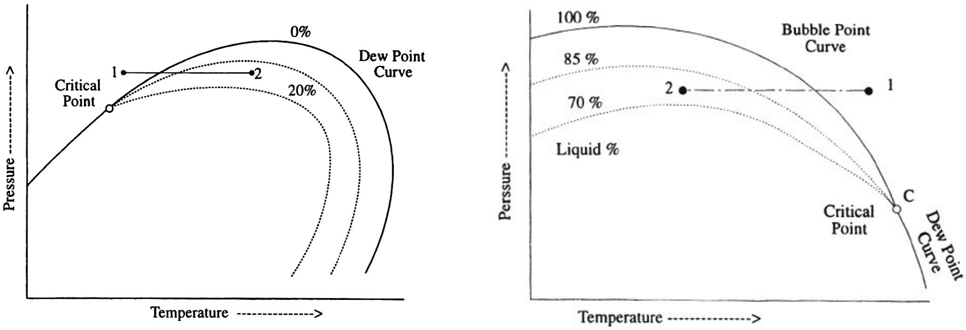


Fig. 1. Retrograde condensation and vaporization at constant pressure [6]

3. ANALYSIS OF CONDENSATES

During cleaning and inspection of gas transmission pipeline we can generally experience three different types of deposits. First, solid, apparently dry deposits which may contain various proportions of dust, clay, corrosion products, slug, etc. Second type is liquid condensate without dispersed solid particles which can be formed by several phases (oil phase, water, glycol phase). Logically, the third types of deposits represent mixtures of solid and liquid phases. As the proportion of liquid to solid phase is varying in wide range mud which is pulled off the pipeline is of variable consistency. Also the amount of obtained mud is dependent on local conditions and pipeline configuration for different parts of the same system it is possible to have one part completely dry and clean and other with deposit "yield" of tens of kilograms.

Apart from these typical components some other can be found which are rests from the construction or repair works on the system, e.g. rests of welding electrodes and debris of balloons.

Basic precondition for obtaining relevant results is representative sampling. This must be carefully performed directly after finishing of cleaning procedure as amateurish approach may devalue in laboratory obtained results.

Analysis of condensates is subdivided into several treatment procedures according to their character and subsequently treated sampled are analyzed.

3.1. Basic overview

Pipeline deposits/condensates are, based on their state (i.e. the ratio between solid and liquid phase), treated and series of analytical test are performed on such pretreated samples. Simplified scheme is given at Figure 2.

Following chapters are focused on individual analytical methods. The in tables or graphs presented results are mostly combinations of those which are common or typical together with some non-standard results which can be also identified. Presented results belong to a number of different samples so they are most of time not comparable to each other. For that reason samples are numbered wit series of letters (e.g. A, B, C).

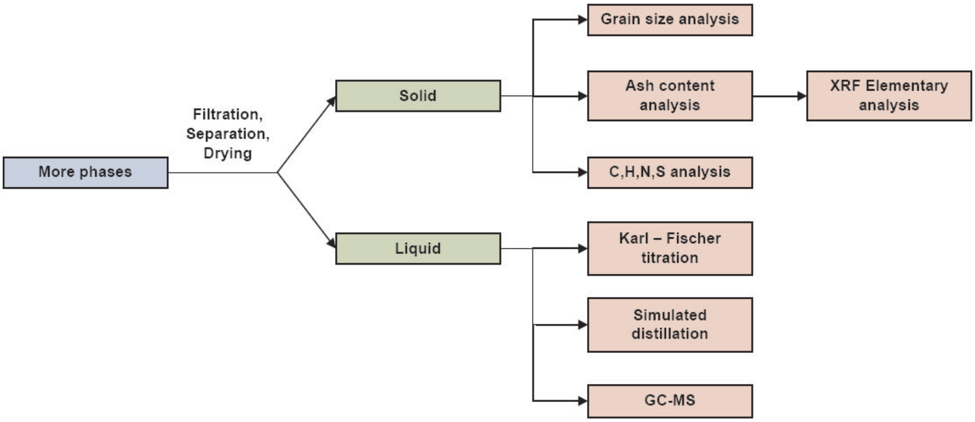


Fig. 2. Condensate analysis chain

3.2. Ash determination – Organic vs Inorganic content determination

The easiest approach is represented by dry solid samples. Such samples are treated like e.g. coal samples. Modified procedure has to be applied to solids dispersed either in oil or water phases creating mud or slug. Such samples are pretreated first by filtration then by “drying” on air on filtration paper for at least 24 hours. In order to obtain in some way representative sample, pretreated samples were used for “water like” determination, i.e. drying in the oven at 105 ^{o}C (according to the ISO 589) and can be adopted as determination of light hydrocarbons (LHC) with boiling point up to 105 ^{o}C together with possible water content. Water content in samples was later verified by KF titration.

Table 1

Determination of light hydrocarbons (LHC) and water

Sample	LHC and water [% mass.]
A	3.13
B	4.91
C	7.75

Samples after above mentioned determination were used as a basis for ash content determination. Ash determination is carried out by heating samples in an oven at 850 ^{o}C according to the ISO 1171. Light hydrocarbons content, ash content and C, H, N, S analysis are first steps for overall characterization of samples.

Table 2

Ash determination

Sample	Ash content [% hm.]
D	72.85
E	61.39
F	60.49

3.3. Elementary composition (C, H, N, S)

Method is useful for analysis both solid and liquid samples. Estimation of elementary composition is particularly suitable for determination of sulfur content in combustible part of the sample which can be important from the point of possible corrosion processes and of course to receive general overview on proportions of carbon, hydrogen and nitrogen in samples.

For determination of elementary composition quantitative combustion of samples in oxygen stream under high temperature (1200 ^{o}C) followed by identification of combustion products using TCD detector was used (Elementar Vario E1 III). Solid samples or samples after light hydrocarbons determination were used. Table 3 represents elementary composition of combustible part of two typical samples.

Table 3

CHNS determination

Sample	C [% mass.]	H [% mass.]	N [% mass.]	S [% mass.]
G	84.48	10.45	0.38	0.79
H	84.37	8.32	0.66	0.61

3.4. Elementary composition of inorganic part

The purpose of this determination is to identify the ratios of elements in inorganic part of the sample in order to identify source or possible sources of contamination.

Generally speaking there are two possible ways how to prepare or „pretreat“ samples for elementary composition determination. First samples after ash content determination can be used, i.e. the ash which remain after tests. Second, organic part of samples can be extracted using suitable liquid solvent and the rest is used for analysis. Optimal way of treatment should be chosen either on the basis of character of samples and the purpose of analysis or samples can be treated in both ways and obtained results are compared in order to discover changes in composition after combustion.

Samples were analyzed using X-Ray Fluorescence spectroscopy (ARL 9400 XP) which is particularly useful for qualitative and quantitative elementary composition of atoms with atomic number from 22 to 99 and lower than 22 in case when using vacuum.

Table 4 represents three samples with different composition. Fe content is important for identification of ongoing corrosion processes in pipeline. On the other hand e.g. high Si and Al may refer to contamination by soil or sand during repair works.

Table 4

Elementary composition of inorganic part (% mass.)

Element	Sample J	Sample K	Sample L
Na	0.88	0.3	–
Mg	5.02	0.37	–
Al	9.90	4.54	0.49
Si	26.56	10.46	2.90
P	0.14	–	–
S	2.65	0.68	0.62
K	2.63	0.75	–
Ca	1.32	1.19	0.90
Ti	0.54	0.27	–
Mn	0.83	1.24	1.01
Fe	50.79	79.33	93.35
Cu	–	–	0.13
Zn	0.22	0.13	–
Ba	–	0.21	–
Pb	–	0.19	–

3.5. Granulometry

In case of solid samples (and sometimes in case of mud samples) it can be useful to know the particle size distribution. Such analysis can provide e.g. information on efficiency of filtration equipment installed in the system.

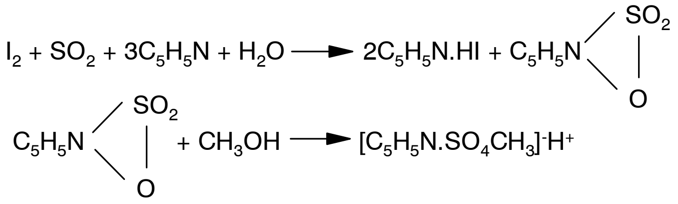
For estimation a procedure based on laser diffraction principle (Analysete 22 Nanotek) is used. Laser diffraction is an ensemble method where evaluation is based on Fraunhofer approximation.

3.6. Water content determination

Presence of water in transmission pipeline system is crucial from the point of corrosion and also represents the risk of gas hydrate formation. From this point of view water content of free or dissolved water in samples is determined.

One of the most suitable and universal method for water determination in solid, liquid and gaseous samples are analyzers based on Karl-Fischer titration, especially using coulometric titration which is capable of determining much lower water levels than volumetric titration.

The by Karl-Fischer proposed reaction scheme can be written as follows:



(1, 2)

For water content estimation a coulometric titrator (Mettler C30) was used. Several samples are given in Table 5. Again, several differences can be seen. Samples M, N, O represent water content dissolved in oils (typically in range 1–40 ppm). For samples P and Q it was proved that the rest to 100% was created by triethylene glycol (TEG) which is commonly used for gas dehydration at underground storages.

Table 5

Water content in selected liquid samples

Sample	Water content [mg/kg]
M	3
N	2
O	31
P	9,4%
Q	92,0%

3.7. Identification of liquid phases origin (Sim-Dist)

As oil phase creates significant part of slugs obtained from pipeline cleaning it is especially useful to focus on its detailed analysis. Recent methods based on chromatography connected with mass detectors are capable of identification of whole range of compounds which create the condensate. On the other hand a list of hundreds components is not a suitable outcome. This approach is useful when identifying specific compound in a mixture. Far more effective for getting overview on the sample is performing of so called simulated distillation.

Simulated distillation (Sim-Dist) is a gas chromatography based method which widely used in petro-chemical industry for characterization of oil fractions. Sim-dist uses stationary phase based on polymer of dimethylsiloxane on which individual components are separate on the basis of boiling points. The versatility of this method is given by the ability to measure distillation characteristics from light naphta to vacuum gas oil fraction.

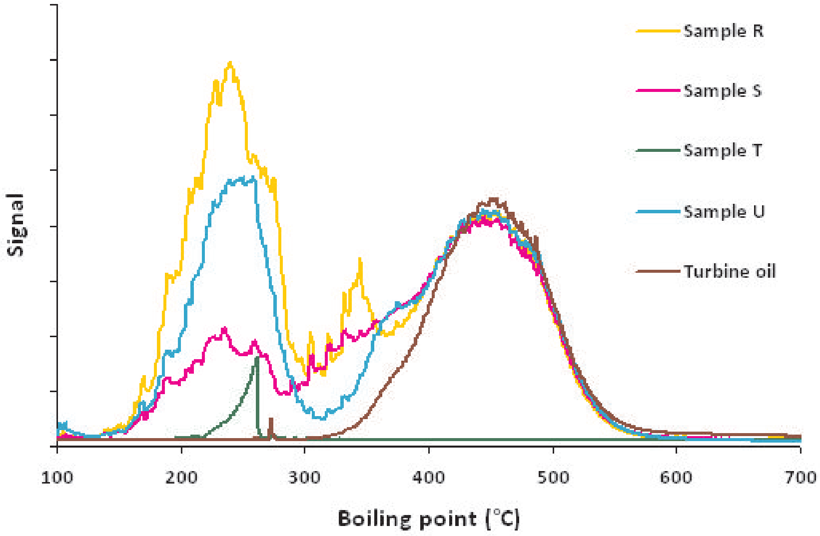


Fig. 3. Simulated distillation

Examples of analysis results are given in Figure 3. Basic information is the distillation curve of the pure compressor or turbine oil (in graph „Turbine oil“) which is used at compression stations along the transmission pipeline and which is commonly found in pipelines due to some minor leakages from compressor to the gas. Simply by comparison of distillation curves of turbine oil with curves of condensates from pipeline it is possible to detect character and proportions of different fraction without detailed knowledge on composition of the sample.

Boiling points of pure turbine oil are within 320 and 580 °C while the range of b.p. for gas condensate (gazoline or higher hydrocarbons) is within 120 and 300 °C. This can be seen on samples R, S and U on Figure 3. Atypical trend of the curve for sample T with maximum around 270 °C indicates that the sample is created with highest probability by triethylene glycol. Simulated distillation is also capable of estimation proportions of each group of components (peaks). This is shown in Table 6.

Table 6

Ratio of fractions in condensates (% mass.)

	Sample R	Sample S	Sample T	Sample U
Higher hydrocarbons/gazoline	54	25	100*	37
Turbine/compressor oil	46	75	0	63

* no HHC/gazoline but Glycol

3.8. Determination of glycol in selected liquid samples

Liquid condesates may contain also glycols especially when the pipeline system is connected to the underground storage where TEG dehydratation units are used. Glycols itself represent minimal risk for transmission pipelines but when entering distribution grid they are capable of damaging special technologies (e.g. gas turbines). Determination of glycols in liquid samples was performed using gas chromatography with mass detector (HP 6890 MSD 7393).

Table 7 shows some examples. Although generally the concentration of glycols is very low or glycols are missing completely in liquid condensates there are some cases where glycol is the main component. Identification of glycols in liquid condensate may also reveal operational problems with drying units (e.g. with mist separators).

Table 7

Glycol content in liquid samples

Sample	V	W	X	Generally
(g/l)	0.022	0.019	95%	< 0.001

4. CONCLUSION

Generally speaking, it is not necessary to perform the whole range of above mentioned tests. Any combination of these methods, of course based on expected results, can be used. During results evaluation it is particularly necessary to take into consideration also the total amount of slug/condensate pulled off the pipeline (relative to the pipe length) and the overall character of cleaned pipeline. Additionally some other tests not mentioned in this article can be applied. For example test for PCB content in liquid fractions as some older systems may still contain saturated lagoons with compressor oil with high content of polychlorinated biphenyls which were commonly used from 70ties to 80ties. For such determination gas chromatography using ECD is suitable.

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