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COMPARISON OF COMMERCIALLY AVAILABLE SOFTWARE PACKAGES FOR HYDROCARBON DEW POINT CALCULATION AGAINST EACH OTHER AND EXPERIMENTAL DATA

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Verwijderd: At this place all members of the GERG Working Group 1.52 should be mentioned.

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ABSTRACT

The hydrocarbon dew point of natural gas is an important parameter in regard to the potential formation of hydrocarbon liquids during normal operation of natural gas pipelines. One approach for its determination is to use a detailed gas analysis and phase calculation models. There are many software packages available on the market but due to differences in their calculation codes, including equation of state (EOS), physical parameters of natural gas compounds, binary interaction coefficients etc., they usually lead to different results. The way of handling heavy hydrocarbons, isomers, aromatic and cyclic compounds also influences the calculated hydrocarbon dew point of natural gas.

All these parameters have been studied separately by generating compositions derived from real natural gases. In order to make further comparison from these software packages, calculations were also performed with binary mixtures and synthetic gas compositions. Results of calculations were also compared with experimental data from the open literature and gas companies' laboratories.

Peng Robinson (PR) and Redlich Kwong Soave (RKS) equations of state were used in order to find out their applicability and show their limitations and discrepancies.

Software packages tested were: AGA Program, Gaspack™, GasVLe, Aspen HYSYS[®], Multiflash, PRO/II, PVTp and PVTSim.

The main conclusions of this study are:

- The cricondentherm temperatures calculated by the PR and RKS equations of state show significant but rather constant difference. Generally PR equation of state calculates cridondentherm temperatures which are 2 - 3 °C lower than calculated with the RKS equation of state. Conclusion is similar for cricondenbar pressures (generally PR 2 – 3 bars less than RKS)

- Aromatic and cyclic compounds (benzene, toluene, cyclohexane, methylcyclohexane) can have significant influence on hydrocarbon dew point

- In general, the measurement uncertainty in the gas composition resulting from the gas chromatographic analysis has only moderate impact on the calculated hydrocarbon dew point. However, this conclusion depends on the gas composition and the concentration of different compounds

- A good recommendation to check the suitability of a gas chromatographic analysis for hydrocarbon dewpoint calculations, is that the concentrations of two consecutive heavy hydrocarbons (probably C11 and C12) are both below 1 ppm. However, more information is required to draw definitive conclusions.

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1. INTRODUCTION

The GERG working group 1.52 is made up of 13 European gas companies: Advantica (UK), BEB (Germany), Enagas (Spain), E.ON Ruhrgas (Germany), Fluxys (Belgium), Gassco (Norway), Energinet.dk (Denmark), Gasunie (Netherlands), Gaz de France (France), Interconnector (UK), Snam Rete Gas (Italy), Statoil (Norway), Wingas (Germany). Gaz de France is the convenor of this working group.

The presence of hydrocarbon liquids in natural gas has been an issue for many years, as they may cause damages in the transmission and distribution networks, or consumer facilities. Two different sources of hydrocarbon liquids can be distinguished. The first source of hydrocarbon liquids can be lubricants and/or seal-oil originating from the compressors used in the transmission system. The other source is the condensation of heavy hydrocarbons from the natural gas itself. To prevent condensation of these heavy hydrocarbons, specifications on hydrocarbon dewpoint have been enforced in many countries in Europe. In the new context of a deregulated gas market in Europe, hydrocarbon dewpoint has become a key specification. However, it is still very difficult to determine the hydrocarbon dewpoint unambiguously, since no standard method is available.

The hydrocarbon dew point can be determined either by direct measurement or by calculation from a gas composition. Measurement methods are based on the chilled mirror principle, whereby the sampled gas passes a mirror surface that is cooled continuously. The hydrocarbon dew point temperature is reached when the very first amount of hydrocarbon liquid is detected either visually (manual devices) or optically (automatic devices) on the mirror surface. These direct measurement methods are economically advantageous and are easy to implement on location. However, the hydrocarbon dew point temperature determined by such a method is only available at a fixed measuring pressure and is often dependent on the observer. Calculation methods allow to draw a complete phase envelope but are more complex. First, it is necessary to have a detailed analysis of the natural gas available in which the heavy hydrocarbons (C11, C12…) are given at a sub-ppm level. Furthermore, the way of handling isomers of heavy hydrocarbons is crucial for the outcome of the calculation procedure. Also the calculation of the phase envelope is influenced by the thermodynamic parameters used, such as for example the equations of state implemented in the different software packages, the methods used for calculations of densities and the binary interaction coefficients.

The objective of the GERG working group is to compare the results of experimental and calculating techniques for hydrocarbon dew point and, if possible, to define a relation between both techniques. The project consists of 3 consecutive phases. The aim of phase 1 is to investigate and to compare commercial software packages used for the determination of phase envelopes and thus the hydrocarbon dewpoint. At the end of phase 1, the most suitable thermodynamic models are chosen. Subsequently, these models will be used in phases 2 and 3 of the project to compare the calculation results with the experimental data from automatic and manual devices.

This paper presents the main results of phase 1.

2. OBJECTIVES

This work started with an inventory of the current difficulties for calculating a phase envelope for a given natural gas composition. An ordinary user of a software package does not really know the optimum way to perform such a calculation. Some questions readily arise:

- Which equation of state is the best suited to predict the hydrocarbon dewpoint correctly?
- How should the various isomers in the gas analyses be grouped?
- …

Since no generally accepted recipe is available to perform these calculations, very different results can be obtained. The aim of this work is to present some recommendations and precautions for the calculation of hydrocarbon dew points.

The following methodology was applied during this study:

- Technical information on the software packages was gathered as completely as possible
- calculations were performed with many mixtures ranging from simple synthetic binary mixtures to real natural gases
- the way of considering components in the calculations was studied extensively
- the influence of a number of specific parameters was studied in more detail

To compare the various models, the phase envelopes (or P, T diagrams) were calculated for all the synthetic mixtures and real natural gases. For the more complex mixtures, special attention was paid to the cricondentherm and cricondenbar.

The following software packages were tested:

- GasVLe 5.0
- Multiflash 3.3.57
- PVTSim 13.1 (binary and synthetic mixtures) and 14.0 (real gases)
- Gaspack 5.0
- PVTp 6.5
- Aspen HYSYS 3.2
- AGA Program
- PRO/II 7.2

The results of these calculations are presented anonymously, identifying each software package by a unique letter.

Regarding the equation of states (EOS), calculations were performed with Peng Robinson (PR) and Redlich Kwong Soave (RKS) if available.

3. GAS COMPOSITIONS

3.1. Simple mixtures

First tests were completed with pure ethane and binary mixtures containing C1 and C3, and C3 and nC6. Experimental data are also collected on these mixtures from literature[1]. Experimental data on C3-nC6 mixtures are obtained from a static method to measure vapour pressure and the orthobaric densities of the liquid and vapor phases. Data on C1 and C3 mixtures are obtained experimentally from a chilled mirror technique.

3.2. Synthetic mixtures

Nine synthetic gases are used as input data for testing the various software packages. Experimental data from measurements with a manual chilled mirror carried out by Statoil as part of this project to determine the phase envelopes are also available. This information has been reported for information only and should not be considered as reference class data.

3.3. Real gases

Finally, tests were performed with 6 real gases compositions (see table 1) sampled by some of the participating companies mentioned above. These gases are representative for the natural gases transmitted in Europe and the hydrocarbon dew points are expected to vary between –30℃ and +20℃.

It is common practice in the gas chromatographic analysis of natural gases to group isomers according to their carbon number. To get the input data processed by the various software packages, all the isomers, including the n-alkane, having the same carbon number i, have been grouped together into a single fraction named "C_i". Depending on the possibilities of the software package, this fraction will be considered as "nC_i" or as a fraction "isomers C_i" depending on the input compounds available in the models. In the second case, fraction will include n-alkane.

Some assumptions have been made about real gases compositions before doing any test:

- O_2, H_2, He and Ar have no or little influence on the hydrocarbon dew point. If their concentrations were available, they have been intentionally added to N_2 fraction.
- N_2, C_1, CO_2, C_2, C_3, i- and n-C_4, i-, n- and neo-C_5 are considered separately
- All isomers of alkanes with carbon numbers above 5 (n-C_5) with the exception of the n-alkanes have been grouped into a single fraction even if these components were detected separately by chromatography like for example the C_6 isomers. The reason for lumping these isomers into a pseudo-component is that few software packages are able to use this detailed compositional information. Besides, for hydrocarbons containing more than six carbon atoms, it is impossible to separate all isomers. Moreover, the physical properties of these heavy isomers are not completely known. In order to make the calculations with a software package, all isomers are lumped into a single fraction. The fraction "Isomers C_6" for instance includes all the compounds that are eluted in the chromatogram between n-pentane and n-hexane.
- Some well-known isomers, which are also widely available in the software packages, have been treated separately if these components were given as separately in the detailed analysis: cyclopentane, cyclohexane, methylcyclohexane, benzene and toluene. Among the aromatic compounds, only benzene and toluene have been taken into account as separate components in the calculations. The amount of other aromatics in natural gas is very low, they are not systematically separated by chromatography, and most of models ignore them. For the same reason, among cyclic compounds, only cyclopentane, cyclohexane, and methycyclohexane have been taken into account if they were available from detailed analysis of the gas.

Verwijderd: The description of each software package has been based on the results of a questionnaire. The subjects covered in this questionnaire are the interface - user-friendliness, and the calculation procedures. The overview of the calculation procedures include the available equations of state (EOS) (with references if possible), the available input compounds (pure components and fractions) together with the critical temperatures, critical pressures, and acentric factors (ω), and the available binary interaction coefficients (BIC). Some models allow the user to define "pseudo-component" like fractions, with user-defined properties. This possibility has not been used in this study since this option requires additional know-how from the user, which is usually only available to an expert in this field.¶

Verwijderd: compounds

These rules have been established according to the recent recommendations of ISO FDIS 23874[2].

4. RESULTS

4.1. Pure ethane and binary mixtures

All phase envelopes, calculated with the various software packages, are in very good accordance with each other and with the experimental data, since discrepancies on cricondentherm temperatures are less than 1.5°C.

4.2. Synthetic mixtures

The synthetic mixtures are based on one basic composition (Gas1) including hydrocarbons from C_1 to C_4. Other compositions are derived by adding to this gas either 3000 ppm mol of cyclohexane (Gas2) or 3000 ppm mol of benzene (Gas3), or 2000 ppm mol of n-heptane (Gas4). Gas8 is similar to Gas1 but with higher level of ethane (10 mol-% instead of 3 mol-%) and propane (4 mol-% instead of 1 mol-%). Similarly, 3 compositions are derived from Gas8: Gas7 contains 3000 ppm mol of cyclohexane, Gas9 3000 ppm mol of benzene and Gas6 2000 ppm mol of n-heptane. Gas5 contains only C_1, C_4 and C_5. These compositions allowed studying the influence of benzene and cyclohexane in comparison with n-heptane, even if the concentrations of these compounds are higher than those generally observed in real gases. Values of cricondentherm temperatures obtained with PR are plotted in figure 1.

The main conclusions are:

- all software packages give similar results, with only few exceptions depending on the gas
- benzene and cyclohexane have almost the same influence on the cricondentherm temperature: the cricondentherm temperature changed from –19°C to about 10°C when adding 3000 ppm of benzene or cyclohexane into the gas. Benzene has a slightly greater influence
- the n-heptane concentration has more influence on the cricondentherm temperature: it changed from –19°C to about 14°C when adding only 2 000 ppm into the gas
- The concentrations ethane and propane have almost no effect on the cricondentherm temperature when higher hydrocarbons are present in the gas in significant concentrations

Difference between PR and RKS:

Difference of cricondentherms temperatures calculated with RKS or with PR are plotted in figure 2.

The difference in temperatures of the cricondentherms obtained with the RKS equation of state and with the PR equation of state varies between 1.5°C and 2.5°C,

Using the RKS equation of state always results in higher cricondentherm temperatures. The temperature difference depends on the gas composition and seems to be higher for gases containing heavy hydrocarbons (Gas4 for instance contains n-heptane). Experimental data seem to be better described for gases 1, 8 and 5, i.e. synthetic gases containing hydrocarbons from C_1 to C_4 and containing C_1, C_4 and C_5. The RKS equation of state seems to be the more suitable EOS for very lean gases, as already mentioned in literature[3].

RKS also results in higher cricondenbar pressures.

4.3. Real gases

General comments:

Factors like the exact formulation of the EOS used (for instance some software packages use automatically PR formulation of 1976 while others use the PR formulation of 1978, or chose one of these formulations depending on the value of omega), the physical properties of input compounds, the additional equations used to calculate densities etc… may influence the results of phase envelopes calculations.

The difference between cricondentherm temperatures calculated with the PR EOS and with the RKS EOS varies between 2.5°C and 4°C, and confi rms the observation found with synthetic mixtures. Using the RKS EOS always results in higher cricondentherm temperatures, and results on the influence of other parameters are similar. Consequently, in this paper, only the results with the PR EOS will be presented.

Influence of aromatic compounds:

To study the influence of aromatic components on the outcome of the software packages, only software packages having the possibility to use compositional data for both benzene and toluene separately as input have been taken into account. For each gas two calculations were performed: in

the first calculation the aromatics are treated separately; in the second calculation these components are lumped into the isomers C7 fraction (for benzene) or the isomers C8 fraction (toluene). The calculated temperatures of the cricondentherms and the calculated pressures of the cricondenbars obtained for these two variants were then compared for each gas.

It seems that the aromatic compounds have no significant influence on the outcome if their concentration is below 70 ppm, since the difference in temperatures of the cricondentherm is less than 0.5°C (See figure 3). However, it is difficult to d raw final conclusions since this influence depends on the complete gas composition (contents of C_6, C_7, and heavy hydrocarbons: C_{10}, C_{11}…). Obviously, if the dew point is determined by 'C_{10}' the concentration of the more volatile benzene has virtually no effect on the dew point until the amount is such that the dew point is determined by benzene. Given the possible influence of aromatics on the final results, it is advised to choose software packages that have a possibility to use benzene and toluene as input compounds, or software package where these compounds can be defined as specific user compounds.

Influence of cyclic compounds:

The study on the influence of cyclic components has been conducted according to the same procedure as used for the aromatic compounds. Only software packages having a possibility to use compositional data for both cyclohexane and methylcyclohexane separately as input have been taken into account. Cyclic compounds seem to have a larger influence on the outcome compared to the aromatics, independent of their concentrations. However, again it is difficult to draw a final conclusion since this influence depends on the complete gas composition (content of C_6, C_7, and heavy hydrocarbons: C_{10}, C_{11}…). Given the influence of cyclic components on the final results, it is advised to choose software packages that have cyclohexane and methylcyclohexane as input compounds, or software package where these compounds can be defined as specific user compounds.

Influence of heavy hydrocarbons:

To study the influence of the heavy hydrocarbons, various artificial compositions were diverted from the orginal composition. These compositions were obtained according to the following procedure:
Composition 1: truncated basic composition up to C_6 by cutting off the C_7^+ fraction. Normalization of the composition is carried out by adjusting the methane content;
Composition 2: truncated basic composition up to C_7 by cutting off C_8^+ fraction. Normalization of the composition is carried out by adjusting the methane content;
….etc. up to heaviest hydrocarbon analysed.
Graphs showing the evolution of cricondentherm, for each gas, according to the heaviest hydrocarbon group analysed, are given in figure 4. All software packages deliver similar results: the results are given for only one model.

Although the results depend heavily on the composition of the individual gases, the following observations seem to be more or less general for the investigated gases:

- For most European gases, it is not sufficient to perform gas analysis only up to C_8 to calculate hydrocarbon dew point
- However, for most gases, a gas analysis containing information on the concentrations up to C_{12} (+ isomers) seems to be sufficient to carry out reliable hydrocarbon dew point calculations. However, this observation cannot be generalized to all investigated gases. The suitability of a gas analysis for hydrocarbon dew point calculations merely seems to be determined by the concentrations of the last hydrocarbon analysed.

A suggestion would be to check the linearity within the gas composition by using a relationship between the concentration and the carbon number normally encountered in treated natural gases (log (ppm)= A + B* (no. of C atoms)). This check guarantees that the gas composition under consideration does not contain unexpected concentrations of heavy hydrocarbons. If the concentrations of the heavy hydrocarbons in the gas analysis do not fulfil the aforementioned linear relationship, the sampling and analysis procedure should be carefully investigated. Sometimes, it is necessary to extend the analysis to include the heavier hydrocarbons.
It seems difficult to draw a general conclusion to what extent the heavy hydrocarbons need to be analysed. A good recommendation could be to extend the analysis to those heavy hydrocarbons, for which applies that the concentrations of the two heavy consecutive hydrocarbons (probably C_{11} and C_{12}) are both below 1 ppm.

Influence of gas analysis uncertainty on hydrocarbon dew point:

In order to study the influence of the uncertainty of the gas analysis on the calculated hydrocarbon dew point, three compositions were generated:
- Composition 1: basic composition
- Composition 2: "maximum" composition in which all components with a concentration below 1000 ppm are maximized, i.e. for each of these components the estimated measurement uncertainty is added to the average concentration.

Opmerking [PvW3]: Pagina: 1 How is the y-axis defined in figure 3. Is the difference defined as (complete analysis – lumped analysis) or the other way around.

Verwijderd: ¶

Opmerking [R4]: Seite: 1 This sentence is not clear enough.

Verwijderd: benzene

Verwijderd: ¶

- Composition 3: "minimum" composition in which all compounds with a concentration below 1000 ppm are minimized, i.e. for each of these components the estimated measurement uncertainty is subtracted from the average concentration.

The uncertainty values used in this exercise are based on the experience of the participating companies. The uncertainty table below has been obtained by considering the maximum uncertainty that could be encountered in the given concentration range. The uncertainty estimates presented here are worst-case values. However, it should be noted that by using a non-suitable sampling technique, it is quite easy to introduce much larger deviations in the analysis.

Concentration range (ppm mol)	Estimated uncertainty
< 1	100%
1 to 10	20%
10 to 40	10%
40 to 100	5%
100 to 1000	2%

All software packages deliver similar results: the results are given for only one model in figure 5. The difference between the cricondentherm temperatures of the maximized and the basic composition is plotted in this figure, as well as the difference between the cricondentherm temperatures of the basic and the minimized composition.

Three gases show very small differences between the cricondentherm temperatures of the minimised and maximised compositions (about 1℃ to 2℃). For two gases, the influence of the uncertainty of the natural gas analysis is more distinct (a difference of 4℃ to 5℃ in the calculated cricondentherm temperature between the minimized and maximized compositions). For one gas only, a very large difference in the cricondentherm temperature (and also the cricondenbar pressure) is encountered (more than 10℃). However, it must be u nderlined that this large difference occurs when the heaviest hydrocarbons have a concentration below 1ppm. In such a case, the "minimum" concentration of those heavy hydrocarbons becomes zero, resulting in a different composition and thus a different cricondentherm temperature.

From this study, it can be concluded that it is important to be able to quantify the heaviest hydrocarbons in the natural gas at a level of 0.1-0.2 ppm mol. This corresponds for most transmission gases to C_{11} or C_{12}. Moreover, an uncertainty level of 100% is, even for concentration levels below 1 ppm mol, not acceptable. An uncertainty level of 50% would be the maximum acceptable.

5. CONCLUSIONS

The parameters that influence the calculation results of phase envelopes of natural gases have been identified. The main conclusions are:

- The cricondentherm temperatures calculated with PR equation of state and RKS equation of state show a significant and rather constant difference, in which the values calculated with the PR EOS are normally 2 - 3 ℃ lower than the values obt ained with the RKS EOS. Results are similar for cricondenbars (2-3 bars discrepancies)

- The aromatic and cyclic compounds (benzene, toluene, cyclohexane, methylcyclohexane) can have significant influence on hydrocarbon dew point

- The uncertainty in the gas composition resulting from the chromatographic analysis has only a minor influence on the outcome of hydrocarbon dew point calculations.

- A good recommendation to which extent information on the heavy hydrocarbons should be available for hydrocarbon dew point calculations, is to include those heavy hydrocarbons, for which the concentrations of two consecutive heavy hydrocarbons (probably C_{11} and C_{12}) are both below 1 ppm. However more information is required to draw up a final conclusion.

Next task planned in the GERG project is the comparison of measurements, carried out under fully controlled conditions, and calculations for a number of real natural gases. Hopefully, this additional information, makes it possible to confirm the preliminary results obtained in this first part of the project. Different devices for hydrocarbon dew point measurements will be tested: hydrocarbon dew point meters as well as process gas chromatographs.

REFERENCES
1. Pure C2: Friend D.G., Ingham H.and Ely J.F., Thermophysical Properties of Ethane, J.Phys.Chem. Ref. Data, 20(2):275-347, 1991
C3-nC6 mixture : W.B.Kay, Journal of Chem. and Eng. Data, Vol 16, No2, 1971. "Vapor-liquid equilibrium relationships of binary systems"

2. ISO FDIS 23874, "Gas chromatography requirements for hydrocarbon dew point calculations". No comparison with experimental data was made and software package were not the object of interest, contrary of this GERG group.

3. « Predicting natural gas dew points from 15 equations of states », K.Nasrifar, O.Bolland, M.Moshfeghian, Energy and Fuels, vol.19, pp.561-572 (2005).

LEGENDS TABLES/FIGURES

Table 1: Compositions of real gases

Figure 1: Synthetic mixtures - Cricondentherms calculated with PR

Figure 2: Difference of cricondentherms calculated with RKS or with PR

Figure 3: Influence of aromatic compounds on cricondentherm temperatures

Figure 4: Cricondentherm temperature as function of the carbon number taken into account (PR – one software package)

Figure 5: Uncertainty of analysis: Differences on cricondentherm temperatures

TABLES AND FIGURES

Table 1

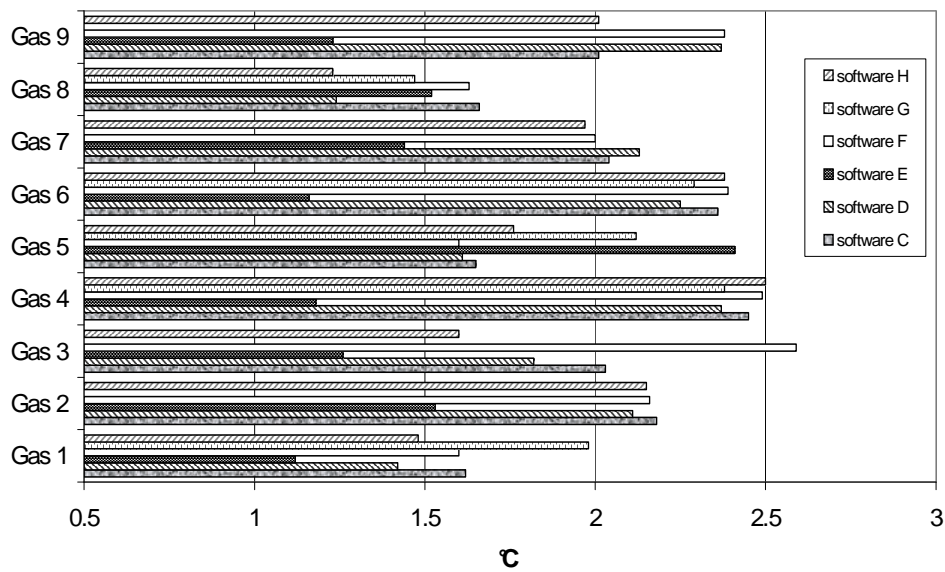|	Gas 1 mol %	Gas 2 mol %	Gas 3 mol %	Gas 4 mol %	Gas 5 mol %	Gas 6 mol %
N2	3.54	10.295	1.5284	0.861	1.629	0.485
CO2	1.3	1.641	0.821	1.81	0.35	1.69
C1	88.62	82.19	91.50	87.46	92.97	86.68
C2	4.73	4.40	4.50	8.65	3.80	6.54
C3	1.227	1.019	0.974	0.959	0.586	2.593
iC4	0.176	0.131	0.339	0.090	0.334	0.478
nC4	0.246	0.174	0.119	0.111	0.080	0.765
neoC5	0.0019	0	0.0041	0.0006	0.0065	0.0175
iC5	0.0600	0.0385	0.0596	0.0168	0.0652	0.2211
nC5	0.0539	0.0363	0.0243	0.0137	0.0185	0.1923
C6	0.0268	0.0288	0.0545	0.0107	0.0475	0.1402
Benzene	0.0135	0.0213	0.0009	0.0006	0.0002	0.0067
CycloC6	0.0012	0.0052	0.0194	0	0.0251	0.0401
MethylCycloC6	0.0022	0.0035	0.0119	0	0	0
Toluene	0.0009	0.0022	0.001	0.0004	0	0
C7	0.0041	0.0109	0.033	0.0058	0.0462	0.0920
C8	0.0008	0.0030	0.0050	0.0013	0.0364	0.0489
C9		0.00130	0.00147	0.00100	0.00610	0.00592
C10		0.00030	0.00027	0.00077	0.00077	0.00052
C11		0.00003		0.00052	0.00007	
C12		0.00002		0.00020	0.00005	
C13				0.00006	0.00002	

Figure 1
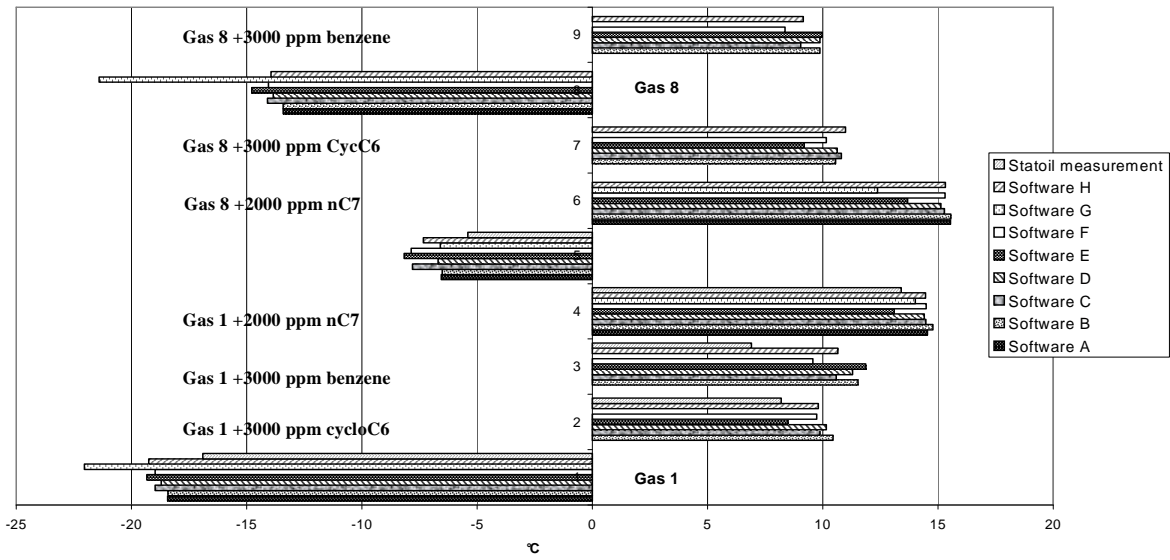
Figure 2

Figure 3

Figure 4
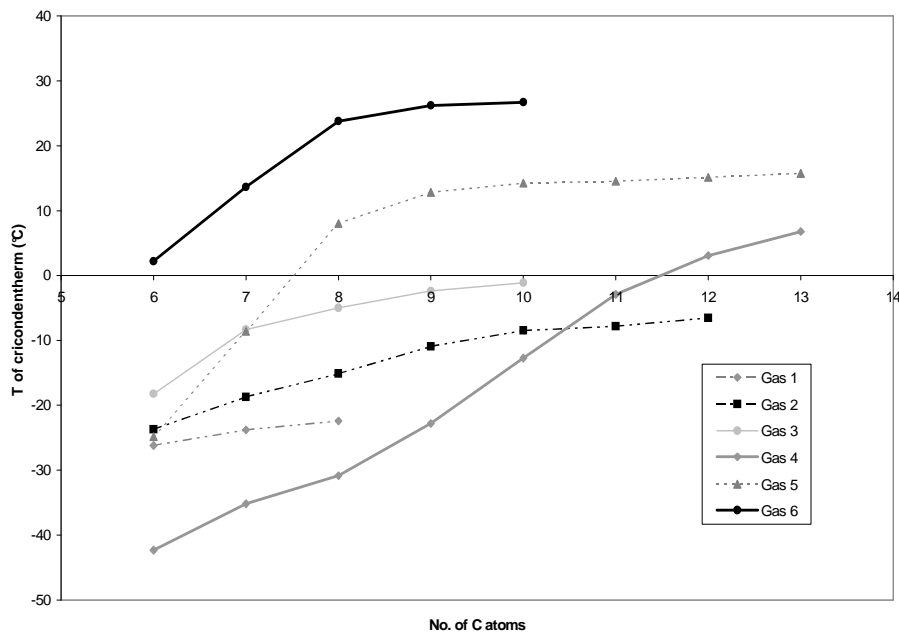
Figure 5