

NPL REPORT AS 3

Comparison of methods for the measurement of hydrocarbon dew point of natural gas

Andrew Brown
Martin Milton
Gergely Vargha
Richard Mounce
Chris Cowper
Andrew Stokes
Andy Benton
Mike Bannister
Andy Ridge
Dave Lander
Andrew Laughton

May 2007

Comparison of methods for the measurement of hydrocarbon dew point of natural gas

May 2007

Andrew Brown, Martin Milton, Gergely Vargha, Richard Mounce¹,
Chris Cowper¹, Andrew Stokes², Andy Benton², Mike Bannister²,
Andy Ridge³, Dave Lander⁴ and Andrew Laughton⁵

¹ EffecTech Ltd., Dove Fields, Uttoxeter, UK. ST14 8HU

² Michell Instruments Ltd., Nuffield Close, Cambridge, UK. CB4 1SS

³ Orbital Ltd, Cold Meece, Swynnerton, UK. ST15 0QN

⁴ National Grid, National Grid House, Warwick, UK. CV34 6DA

⁵ Advantica Ltd., Ashby Road, Loughborough, UK. LE11 3GR

© Crown Copyright 2007

Reproduced by permission of the Controller of HMSO
And Queen's Printer for Scotland

ISSN 1754-2928

National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

We gratefully acknowledge the financial support of the UK Department of Trade and Industry (Measurement for Innovators Programme and National Measurement System)

Approved on behalf of the Managing Director, NPL
by Dr Stuart Windsor, Business Leader, Analytical Science Team

EXECUTIVE SUMMARY

Measurement of the hydrocarbon dew point of natural gas is crucial when determining whether gas can be transported safely through national and international pipeline networks.

This report summarises the results of a study undertaken to compare the performance of direct and indirect methods for determining the hydrocarbon dew point of a wide range of real and synthetic natural gases. The results obtained from six analytical methods (one automatic chilled mirror instrument, one manual chilled mirror instrument, two laboratory gas chromatographs and two process gas chromatographs) are presented and the comparative results are compared in detail.

The conclusions from the work discuss the relative performance of the different methods and consider how they vary when used with real and synthetic gases of different compositions. The difficulties inherent in measuring a 'true' value of hydrocarbon dew point are also discussed.

CONTENTS

Executive Summary	3
1 Introduction	5
1.1 Hydrocarbon dew point	5
1.2 Measurement of hydrocarbon dew point	6
2 Experimental	7
2.1 Overview	7
2.2 Preparation of Primary Reference Gas Mixtures of synthetic natural gas	7
2.3 Sampling and stability of real natural gas mixtures	7
2.4 Automatic chilled mirror instrument	9
2.5 Manual chilled mirror instrument	11
2.6 Laboratory GC 1	11
2.7 Laboratory GC 2	12
2.8 Process GC 3	12
2.9 Process GC 4	13
2.10 Measurement of water content	13
2.11 Calculations	13
2.12 Use of different equations of state	14
3. Synthetic mixtures of natural gas	15
3.1 Introduction	15
3.2 Results	17
3.3 Discussion	23
4. Real samples of natural gas	26
4.1 Introduction	26
4.2 Results	27
4.3 Discussion	35
5. Conclusions	38
6. Further information	38
References	39
Annexes	
Annex A - Calibration and comparison of chilled mirror thermometer and pressure sensor	40
Annex B - Calculation of water dew curves for water vapour	42
Annex C - Composition of vapour and liquid phases of synthetic mixtures of natural gas	43

1. INTRODUCTION

1.1. Hydrocarbon dew point

Measurement of the hydrocarbon dew point of natural gas is crucial in determining whether gas can be transported safely through national and international pipeline networks. Maximum legislative levels for hydrocarbon dew point are set in order to prevent the formation of liquid condensate in the pipeline, which could have severe consequences for the safe transportation of natural gas.

The complex nature of the condensation process in a multi-component hydrocarbon mixture leads to there being several ways of defining the ‘hydrocarbon dew point’. The definition given by ISO 14532 [1] is the:

“Temperature above which no condensation of hydrocarbons occurs at a specified pressure.”

NOTE 1: At a given dew point temperature there is a pressure range within which retrograde condensation can occur. The cricondenthem defines the maximum temperature at which this condensation can occur.

NOTE 2: The dew point line is the locus of points for pressure and temperature which separates the single phase gas from the biphasic gas-liquid region.

An example of a hydrocarbon dew point curve for a typical natural gas mixture is shown in Figure 1.

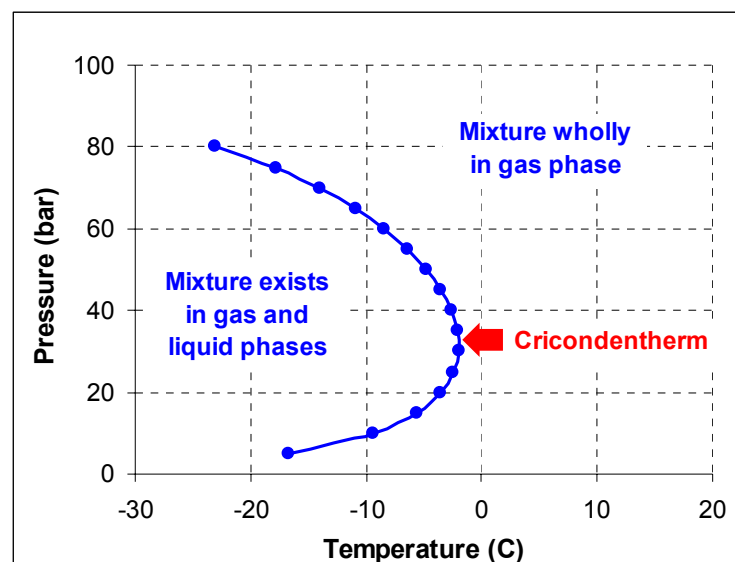


Figure 1. Typical hydrocarbon dew point curve. The cricondenthem (indicated by the red arrow) is defined as the maximum temperature at which condensation can occur (at any pressure).

If defined as above, the hydrocarbon dew point of a pre-specified gas cannot be measured in practice because detection of the onset of condensation requires the observation of the first molecule of liquid condensate - this is unachievable experimentally. Discussions are therefore ongoing within an ISO (International Organization for Standardization) committee (ISO/TC193/SC1) to redefine the dew point as a 'technical' or 'measurable' dew point. This is discussed in detail in Section 4.3.4.

1.2. Measurement of hydrocarbon dew point

The methods that can be used to measure the hydrocarbon dew point of natural gas may be classified as being direct methods or indirect methods.

The two 'direct' methods studied in this work, which used a manual chilled mirror instrument (MCMI) and an automatic chilled mirror instrument (ACMI), detect the formation of a film of liquid condensate on the cooled surface of a mirror. The MCMI method relies on a skilled operator to detect manually the formation of the film, whereas the ACMI is a fully automated process (see Section 2 for full details). An advantage of these methods is that they provide a direct observation of the formation of film on the mirror, but the measurement may be dependent on the operator of the manual instrument, or the sensitivity setting of the automatic instrument.

The most common 'indirect' method uses gas chromatography (GC) to determine the composition of the gas mixture. A thermodynamic equation of state (EoS) is then used to calculate the hydrocarbon dew curve. The measurement of the composition of the gas, which is usually automated, can be carried out to a high accuracy, but this method for determining dew point is heavily reliant on the validity of the equation of state used. Additionally, heavier (C_{11+}) hydrocarbon components (which affect the dew temperature significantly) may be present in very low quantities that are below the limit of detection of the instrument. Indirect methods, however, benefit from being able to provide a full dew curve, enabling determination of the hydrocarbon dew point at any pressure.

A further approach, not studied here, is the potential hydrocarbon liquid content (PHLC) method [2] which measures gravimetrically the amount of liquid condensate formed at a pre-defined pressure and temperature.

This report compares the performance of an ACMI, MCMI, and a series of laboratory and process GCs in determining the hydrocarbon dew point of a series of synthetic and real natural gases.

2. EXPERIMENTAL

2.1. Overview

The first part of the study determined the dew points of five synthetic natural gas mixtures of limited composition; the second part studied seven real natural gas mixtures sampled from gas fields around the British Isles. The experimental methods used in each part of the study are summarised in Table 1 and described in detail below.

Method	Synthetic gas mixtures	Real natural gases
ACMI	✓	✓
MCMI	✗	✓
Lab GC 1	✓	✓
Lab GC 2	✗	✓
Process GC 3	✗	✓
Process GC 4	✗	✓

Table 1. Summary of experimental methods used in the study.

2.2. Preparation of Primary Reference Gas Mixtures of synthetic natural gas

All synthetic standards were prepared gravimetrically using ‘pure’ gases and liquids, each component being added separately using either loop injection (for all liquids and those gaseous components with a required mass of < 15g) or direct gas transfer (for gaseous components with a required mass of > 15g), as described below:

- Loop injection: Transfer of the gas or liquid directly into the sample cylinder via a minimised-dead volume valve. To calculate the mass of gas or liquid added, the loop was weighed (against a tare loop) before and after transfer.
- Direct gas transfer: addition of the gas to the sample cylinder via $\frac{1}{16}$ " internal diameter Silcosteel-coated stainless steel tubing. The sample cylinder was weighed (against a tare cylinder) on a single-pan balance.

A full purity analysis was carried out on each ‘pure’ component and the gravimetric amount fraction of each component was calculated from the mass of each component added, its molecular mass and purity analysis. Uncertainties were calculated following ISO 6141 [3].

2.3. Sampling and stability of real natural gas mixtures

The samples were obtained using the evacuated cylinder method described in Annex F of ISO 10715 [4]. A schematic diagram of the sampling apparatus is shown in Figure 2 and a brief synopsis of the sampling method is given below:

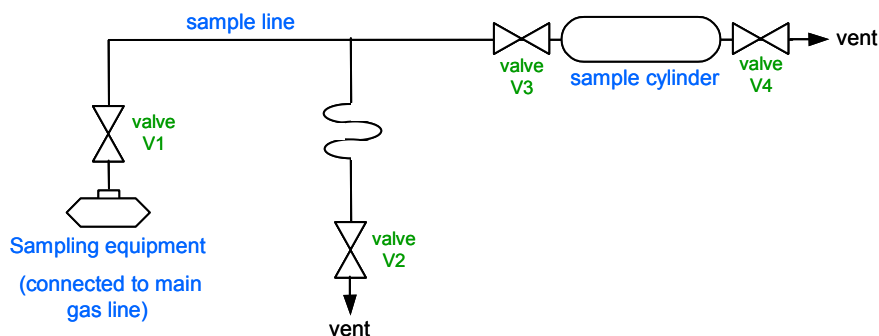


Figure 2. Schematic diagram of set-up used to sample real natural gases.

Synopsis of sampling method:

1. Purge V1 and the stub to the main gas line prior to connecting sampling equipment. Fully open and close five times, venting to atmosphere.
2. Connect the sampling equipment to V1.
3. Connect the evacuated sample cylinder with both V3 and V4 closed as received. Close V2. Check that the system is leak tight by partially opening and closing V1.
4. Purge the sample line five times: Ensuing that you stand on one side of the sampling system (not directly in line), fully open V1 to equalise the main gas line pressure into the sampling equipment. Close V1. Open V2 to release the pressure. Close V2.
5. With V2 closed, fully open V1.
6. Open V3 slowly, once only, until fully open.
7. Close V3. Close V1.
8. Open V2 to vent the sample gas to atmospheric pressure.
9. Disconnect the sample vessel from the sampling system and cap the vessel.
10. Disconnect the sampling equipment from V1.

In order to confirm that the composition of the real gas samples did not change during the course of the study (through contamination or decay), the samples were analysed using one of the GC methods (Lab GC 1) at the start and conclusion of the work. Figure 3 shows the calculated hydrocarbon dew curve for one of the samples before and after the study. For this, and all the other samples, no change in results was observed beyond any variation which can reasonably be expected from repeated analysis.

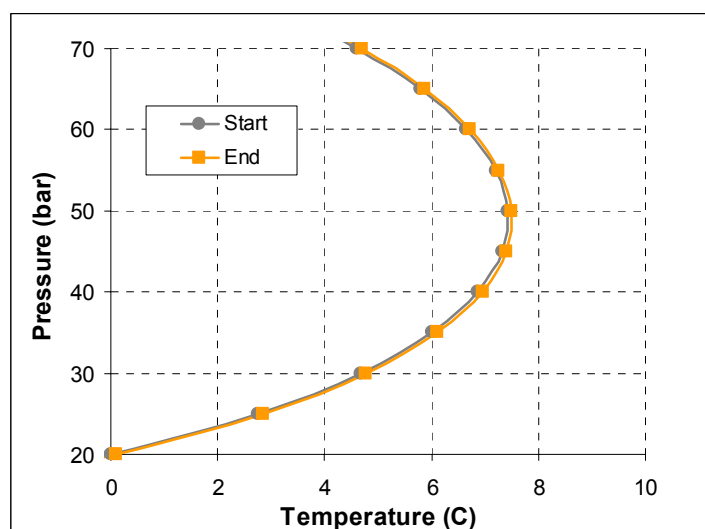


Figure 3. Calculated hydrocarbon dew curve of real Gas A measured at the start and end of the study. Both analyses were carried out using Lab GC 1.

2.4. Automatic chilled mirror instrument [Michell Condumax II]

2.4.1. Background to instrument development

The Condumax II instrument applies a unique optical detection method developed specifically for the measurement of hydrocarbon dew point in natural gas. This involves monitoring the decrease in intensity of scattered light from a conical, abraded metal surface, which achieves a very high sensitivity to the low surface tension film characteristic of hydrocarbon condensates. This patented detection method resulted from a project at Shell Thornton Research Centre and was first presented at the 1986 International Congress of Gas Quality [5].

Michell Instruments became the onward technical development and commercial partners to utilise this technology to provide on-line hydrocarbon dew point measurement solutions to the global natural gas industries. The first Michell version, model HDM100, designed for permanent site installation was sold in 1986. Further development of the analyser package, comprising safe area control electronics and field based sensor cell within the sampling system, resulted in the original Condumax and in September 2005 the introduction of Condumax II as a flameproof certified version suitable for wholly hazardous area installation.

The instrument has been designed to provide measurements of hydrocarbon dew point equivalent to those from a MCMI. Calculations have estimated that a condensate concentration of 70 mg.m^{-3} can be detected using a MCMI, and it is believed that the Condumax II instrument detects a similar concentration of condensate when operated at its standard sensitivity setting (see below).

2.4.2. Analysis

The ACMI was operated in two modes:

- *Standard (275 mV) sensitivity setting.* The default sensitivity setting chosen to provide results that are broadly equivalent to those from a MCMI.
- *Adaptive trigger point (ATP) mode.* The sensitivity of the instrument is varied by increasing the trigger level of the instrument linearly with pressure. It is proposed that this allows for the fact that there is more gas in the cell at higher pressures, meaning that if the sensitivity level remains constant, a thicker film of condensate is needed before being detected by the instrument. This approach allows reproduction of the retrograde behaviour of a hydrocarbon dew curve and is confirmed by experimental results [6].

The sensitivity calibration chart in Figure 4 shows the relationship between the chosen sensitivity setting of the instrument and the measured hydrocarbon dew point. At the standard sensitivity setting of 275 mV, good repeatability between analyses of the same gas is observed, whereas lower sensitivity settings show a larger variability in results, and much higher measured hydrocarbon dew points.

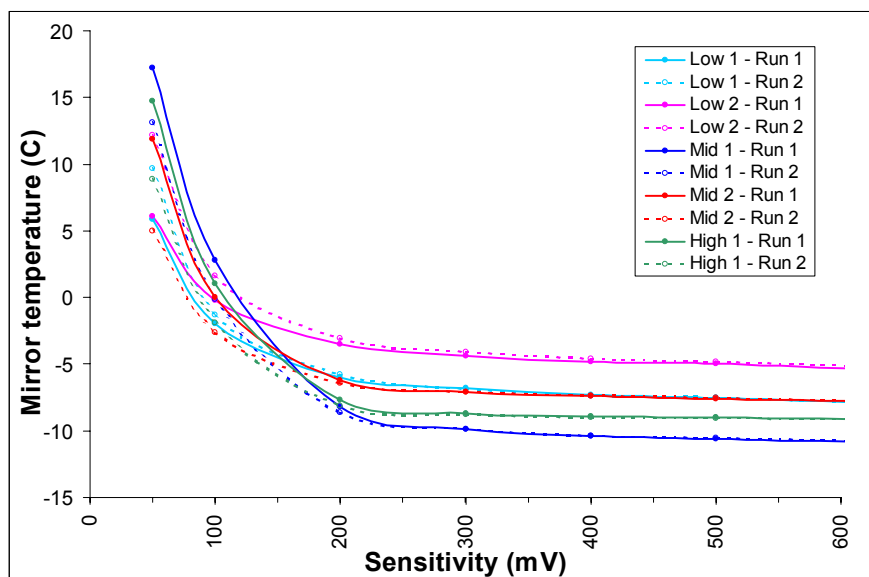


Figure 4. Mirror temperature as a function of signal response ('sensitivity') measured by the ACMI for the five synthetic natural gas mixtures. All data were recorded at a pressure of 27 bar (gauge). Note that the presence of elbows in the sensitivity curves is an artefact of plotting a line through a limited number of data points.

Key features of the procedure used with the ACMI were:

- Before analyses were carried out, the system was purged with the mixture under test (at a low flow rate) for 30-60 minutes.
- Measurements were carried out at a range of pressures, usually 20, 27, 35 and 45 bar (gauge). In general, a pressure of 27 bar (gauge) is used for field applications in the UK.
- 10-15 repeat analyses were carried out for each gas at each pressure.
- The rate of cooling of the mirror around the film formation point can be as low as $0.05\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$.
- The operation of the temperature sensor in the instrument was validated through measurement of a 10% *n*-butane in nitrogen gas standard (see Annex A).

2.5. Manual chilled mirror instrument [Chandler model A-2 Dew Point Tester]

2.5.1. Analysis

Key features of the procedure used with the MCMI were:

- Assessment of the film formation was carried out every 0.5 °C.
- The temperature was recorded using an alcohol in glass thermometer with a range of –100 °C to +10 °C with 1 °C graduations.
- The thermometer was calibrated by NPL to an expanded uncertainty of 0.5 °C and tested through measurement of a 10% *n*-butane in nitrogen gas standard (see Annex A).

2.6. Laboratory GC 1 ('Lab GC 1') [Danalyser 500 + HP 4890 GC]

2.6.1. Instrument

Danalyser 500 - configured as described in ISO 6974-5 [7] for measurement of N₂, CO₂, and C₁ to C₅ hydrocarbons. The instrument was calibrated using seven certified reference materials (CRMs) using the method described in ISO 6143 [8], generating a polynomial response function for each component.

HP 4890 GC - configured as described in ISO 23874 [9] for measurement of C₅ to C₁₂ hydrocarbons. This instrument, which had a flame ionisation detector (FID), was calibrated using a single CRM. Detailed experimental parameters are given below:

- 30 m non-polar methyl silicone phase (CP-Sil 5) capillary column. Internal diameter = 0.53 mm, film thickness = 2 µm.
- Column temperature program: 35 °C for 3.5 min, ramp to 200 °C at 6 °C.min⁻¹.
- Sample: 1 ml (split 1:3 column:vent).
- Valve temperature: 100 °C.
- FID temperature: 225 °C.

Due to GC baseline instability, a large expanded uncertainty (30-40%) should be applied to the C₁₁ & C₁₂ amount fractions. The HP 4890 GC showed a response to concentration ratio that was proportional to carbon number for components up to C₈. The C₉ and C₁₀ species showed responses that were high in proportion to the carbon number by about 8% and 15% (relative) respectively.

2.6.2. Analysis

Key features of the analytical procedure used with Lab GC 1 were:

- All components up to *n*-C₆, benzene, toluene, cyclohexane and methylcyclohexane were measured and reported individually.
- For the analysis of the synthetic natural gas mixtures, the *n*-alkanes *n*-C₇ to *n*-C₁₀ were measured by direct calibration against traceable reference gas mixtures standards.

- For the analysis of the natural gas samples, all other C₇₊ alkanes, and unidentified C₈₊ aromatics and naphthenes were grouped by carbon number fraction (with the assumption that all isomers had the same response factor as the *n*-alkanes present in the calibration gas). Each individual unidentified component within these fractions had a boiling point calculated on the basis of retention time. From this, the average boiling point of the fraction was calculated by weighting each measured quantity by its calculated boiling point, as described in ISO 23874 [9]. The fractions were allocated a specific gravity (SG) value identical to that of the relevant *n*-alkane.
- Helium, hydrogen and oxygen, when found, were measured by direct calibration.
- Four or five repeat analyses were carried out per mixture.
- The hydrocarbon dew curves were calculated by use of the composition data from the GC and the RKS equation of state [10].

2.7. Laboratory GC 2 ('Lab GC 2') [Danalyser 500 + Varian 3400 GC]

2.7.1. Instrument

Danalyser 500 unit - see Section 2.6.1 for full details.

Varian 3400 GC – configured in a similar manner to the HP 4890 GC (see Section 2.6.1 for the measurement of C₅ to C₁₂ hydrocarbons. The Varian GC showed good carbon counting behaviour with a maximum uncertainty of approximately 2% relative.

2.7.2. Analysis

Analysis and data processing were carried out in the same manner as for Lab GC 1 (section 2.6.2).

2.8. Process GC 3 [Danalyser 700]

2.8.1. Instrument

Process GC with thermal conductivity detector (TCD) and FID, and three valves (one 6-port and two 10-port). All components were fitted into a single oven operated isothermally at 80°C.

2.8.2. Analysis

Key features of the analytical procedure used with Process GC 3 were:

- All components up to *n*-C₆, benzene, toluene, cyclohexane and methyl cyclohexane were measured and reported individually.
- C₇ to C₉ hydrocarbons were measured as carbon number fraction groups.
- C₁₀₊ hydrocarbons were measured as one single backflushed group. The quantification of this group was found to be relatively poor due to a sloping baseline.
- The instrument was not optimised for multi-level calibration.
- Analysis time was < 10 min.

- Each fraction was assigned the same boiling point as calculated for Lab GC 1, and an SG value identical to that of the relevant *n*-alkane.
- The hydrocarbon dew curves were calculated by use of the composition data from the GC and the RKS equation of state.

2.9. Process GC 4 [Orbital ‘all in one’] system

2.9.1. Instrument

Process GC system based on a Siemens Maxus Edition II instrument with three detectors: TCD (for measurement of all components up to *n*-C₆), FID (for C₆ to C₁₂ hydrocarbons and flame photometric detector (FPD) (for sulphur containing species).

2.9.2. Analysis

Key features of the analytical procedure used with Process GC 4 were:

- All components up to *n*-C₆, benzene, toluene, cyclohexane and methyl cyclohexane were measured and reported individually.
- C₆ to C₁₂ hydrocarbons were measured as carbon number fraction groups. The boiling point and specific gravity of each fraction was calculated automatically.
- Hydrocarbon dew points were calculated automatically by the instrument’s software.

2.10. Measurement of water content

The water content of each real gas sample was determined using a solid-state silicon-based instrument Messer FM62 PRV instrument operated at atmospheric pressure. To avoid problems associated with obtaining a representative sample, all samples were purged for a sufficient period of time prior to analysis.

The water content of each sample was determined twice - before and after ‘push purge’ (re-zeroing of the instrument). It is the latter results that are used in this study. The response of the instrument to a dry zero gas and a range of gases with known water content (up to 120 µmol/mol) was determined before and after analysis of the real natural gases. Typically, a maximum of 2 µmol/mol difference was observed between these two analyses.

2.11. Calculations

For the Lab GC 1, Lab GC 2 and Process GC 3 instruments, hydrocarbon dew point calculations were carried out using GasVLe add-in version 2.0 and the RKS equation of state. The dew points determined by Process GC 4 were calculated automatically by the instrument’s software. All water dewlines were calculated using the RKS equation of state modified by setting all interaction parameters $K_{ij} = 0.5$.

Further discussion of the calculation of water dewlines can be found in Annex B.

2.12. Use of different equations of state

Figure 5 shows the hydrocarbon dew curve of one of the real gas mixture calculated by the RKS and two other commonly-used equations of state: PR (Peng Robinson) [11] and LRS (London Research Station [12] – a variant of RKS with different functional forms for some constants). All three equations of state are cubic in form..

At the cricondentherm, a difference of more than 2 °C is observed between the hydrocarbon dew points calculated by PR and other equations of state - this is due to the PR equation of state over-estimating the vapour pressure of the heavier components, hence giving a lower temperature for the onset of condensation. The 2 °C difference gives an indication of the uncertainty that the selection of an equation of state can contribute to the overall uncertainty of an indirect method of analysis.

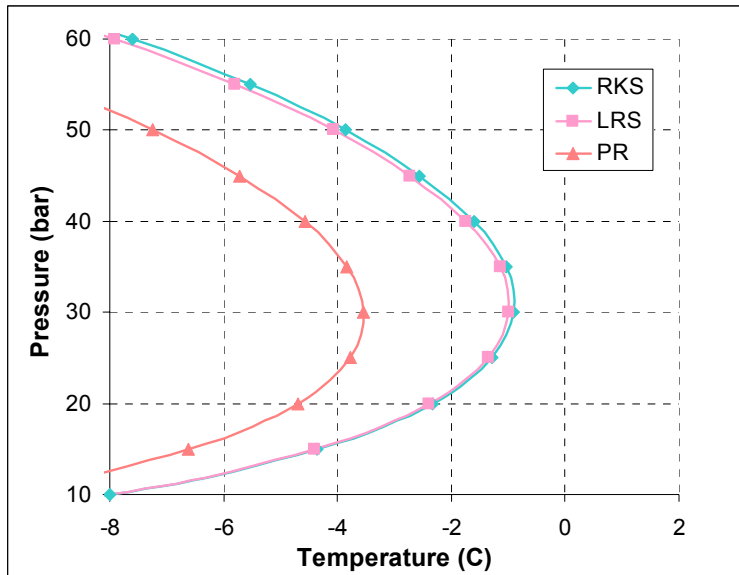


Figure 5. Hydrocarbon dew curve of a real natural gas mixture calculated using three equations of state: RKS, LRS & PR.

3. SYNTHETIC MIXTURES OF NATURAL GAS

3.1 Introduction

The composition of the synthetic gas mixtures used in the first part of the study was designed to encompass the hydrocarbon condensation rates of gases from gas fields across the British Isles, including those of the most extreme compositions. An example of the wide variation in condensation rates of typical natural gas samples from five off-shore fields is shown in Figure 6:

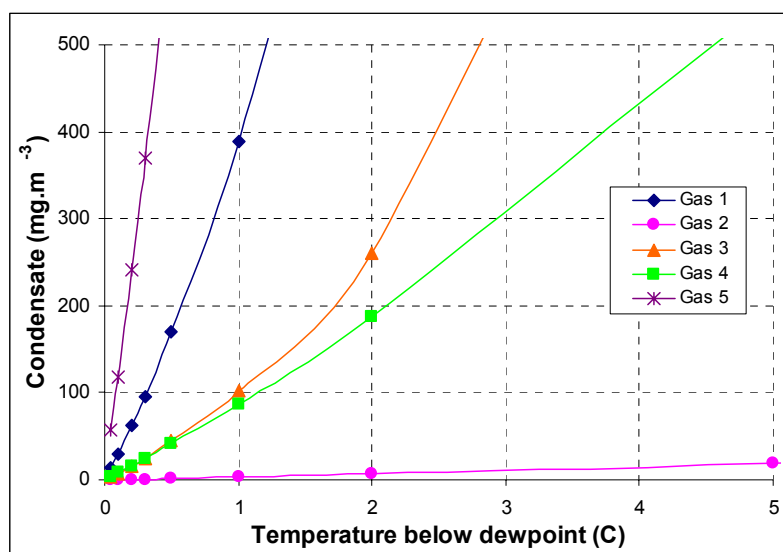


Figure 6. Calculated condensation rates of natural gases obtained from five different UK gas fields.

The mixtures prepared for the study were selected to represent three different rates of hydrocarbon condensation:

- ‘Mid’ condensation rate (two mixtures) – selected to be representative of the gases found in most UK gas fields.
- ‘High’ (one mixture) – selected to investigate whether, as envisaged, a high condensation rate leads to minimal differences between the dew points measured by the different analytical methods.
- ‘Low’ (two mixtures) – selected to be the most challenging mixtures.

The samples contained all (straight-chain) *n*-isomers from C₁ up to C₈, C₉ or C₁₀; benzene; toluene and cyclohexane – the gravimetric composition and expanded uncertainty of each mixture is shown in Tables 2a & 2b and the calculated hydrocarbon dew curves and condensation rate of each mixture is shown in Figures 7 and 8 respectively.

Component	Amount fraction ($\mu\text{mol/mol}$)				
	High	Mid 1	Mid 2	Low 1	Low 2
methane	902309	893411	922325	986879	973065
ethane	68677	77122	63712	7059	16081
propane	17107	22104	10492	4597	8781
<i>n</i> -butane	8480	5428	1582	782.1	904.7
<i>n</i> -pentane	2653	1326	946.3	358.2	533.9
<i>n</i> -hexane	514.2	319.6	440.4	99.11	294.9
benzene	61.03	41.90	139.8	35.36	97.86
toluene	24.63	32.25	85.88	30.05	58.53
cyclohexane	45.23	55.79	59.19	31.60	50.10
<i>n</i> -heptane	93.83	119.7	157.5	59.23	72.74
<i>n</i> -octane	12.17	13.61	32.20	34.86	24.90
<i>n</i> -nonane	<i>0.03</i>	10.18	15.85	21.75	17.63
<i>n</i> -decane	<i>0.01</i>	<i>0.03</i>	<i>0.05</i>	9.84	11.75

Table 2a. Composition of synthetic gas mixtures. The figures in italics are those components where the 'pure' component was not added to the mixtures – the content is made up entirely of impurities from other components.

Component	Expanded gravimetric uncertainty (% relative)				
	High	Mid 1	Mid 2	Low 1	Low 2
methane	0.011%	0.010%	0.010%	0.001%	0.001%
ethane	0.11%	0.10%	0.13%	0.06%	0.04%
propane	0.31%	0.24%	0.54%	0.06%	0.04%
<i>n</i> -butane	0.47%	0.04%	0.12%	0.25%	0.23%
<i>n</i> -pentane	0.08%	0.12%	0.16%	0.44%	0.32%
<i>n</i> -hexane	0.26%	0.37%	0.31%	0.18%	0.49%
benzene	0.18%	0.25%	0.09%	0.35%	0.14%
toluene	0.37%	0.28%	0.12%	0.36%	0.20%
cyclohexane	0.22%	0.18%	0.18%	0.37%	0.25%
<i>n</i> -heptane	0.15%	0.13%	0.67%	0.20%	0.18%
<i>n</i> -octane	0.60%	0.54%	0.26%	0.26%	0.37%
<i>n</i> -nonane	-	0.64%	0.45%	0.36%	0.47%
<i>n</i> -decane	-	-	-	0.70%	0.62%

Table 2b. Relative expanded uncertainty of each component in the synthetic gas mixtures.

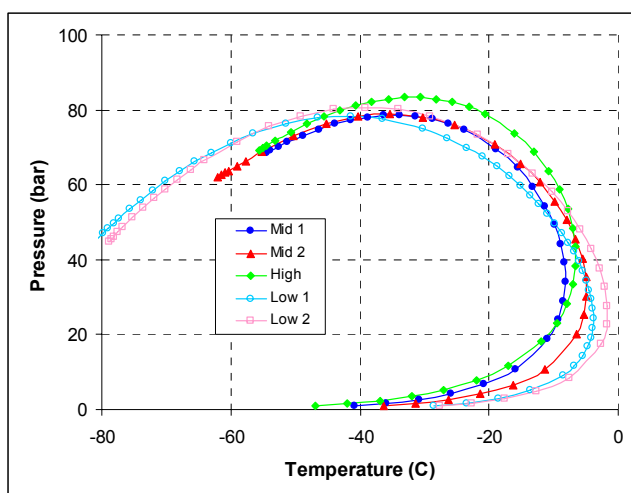


Figure 7. Calculated hydrocarbon dew curves of the synthetic natural gas mixtures.

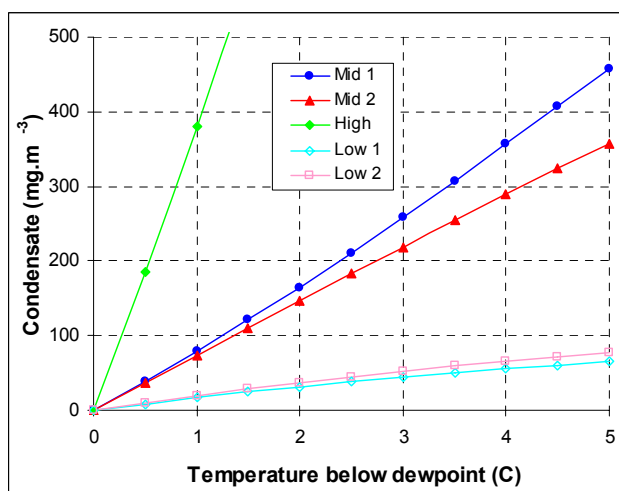


Figure 8. Calculated condensation rate of the synthetic natural gas mixtures.

3.2 Results

Each of the five synthetic mixtures were analysed by two methods, ACMI (operated at the standard (275 mV) sensitivity setting) and Lab GC 1 (operated as detailed in Section 2.6).

Figures 9 to 13 compare the results from these instruments with the dew curves calculated for the gravimetric compositions Table 2a, and the key findings for each gas are given beneath the charts. All data are plotted using pressures expressed as bar (absolute).

The expanded (right hand) plots for each gas also show an estimate for the expanded uncertainty of the Lab GC 1 results at the cricondentherm. However these uncertainties, which are typically between ± 0.2 °C and ± 0.4 °C, only account for the errors arising from the analytical procedure, and do not include any contribution from the calculation method. An indication of the uncertainty arising from the selected equation of state can be obtained by comparing the dew points calculated by different equations – see Section 2.12.

3.2.1 Results - High

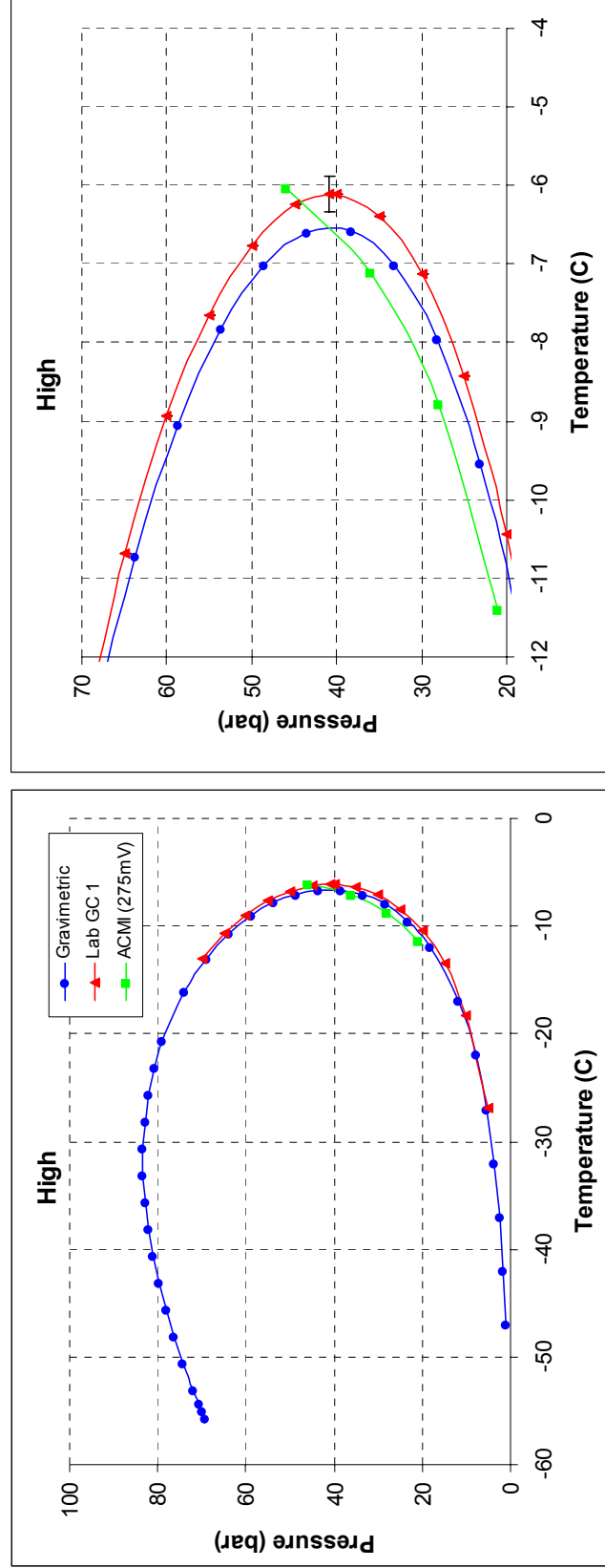


Figure 9. Results obtained for the analysis of synthetic mixture 'High'. The right-hand plot is an expansion of the left-hand plot.

Key findings

- This is the only mixture where the Lab GC 1 data give higher dew temperatures than the gravimetric data. The amount fraction measured by Lab GC 1 for $n\text{-C}_7$ is 2.5% higher than the gravimetric value (although the measured amount fraction of $n\text{-C}_8$ is 0.1% lower than the gravimetric value).
- The ACMI data shows unusual 'non-retrograde' behaviour around the cricondentherm. This was originally proposed to be due to inadequate flushing of heavier components between readings, or moisture interference, further investigation revealed the need the change the sensitivity of the instrument with increasing sample pressure. This 'adaptive trigger point' approach was not tested on the synthetic gas mixtures.

3.2.2 Results - Mid 1

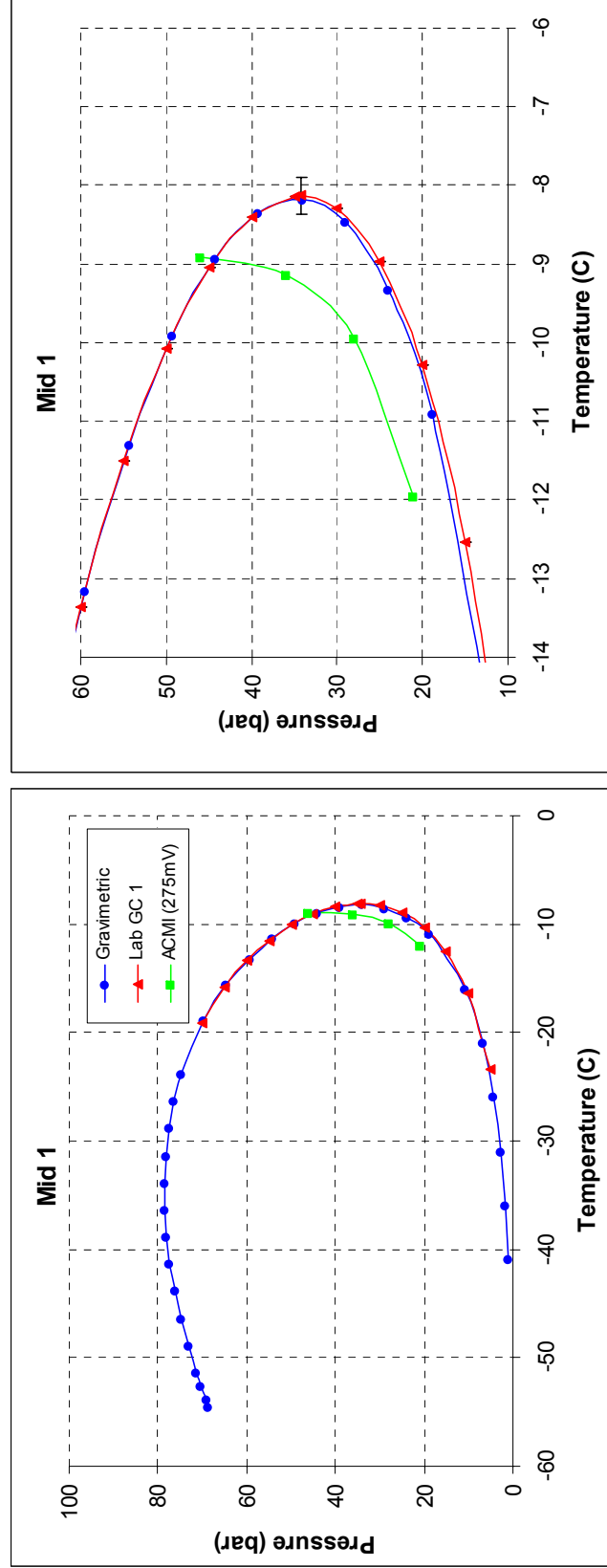


Figure 10. Results obtained for the analysis of synthetic mixture 'Mid 1'. The right-hand plot is an expansion of the left-hand plot.

Key findings

- Excellent agreement is observed between the Lab GC 1 and gravimetric data.
- The ACMI data shows non-retrograde behaviour around the cricondentherm - see comments for mixture High.

3.2.3 Results - Mid 2

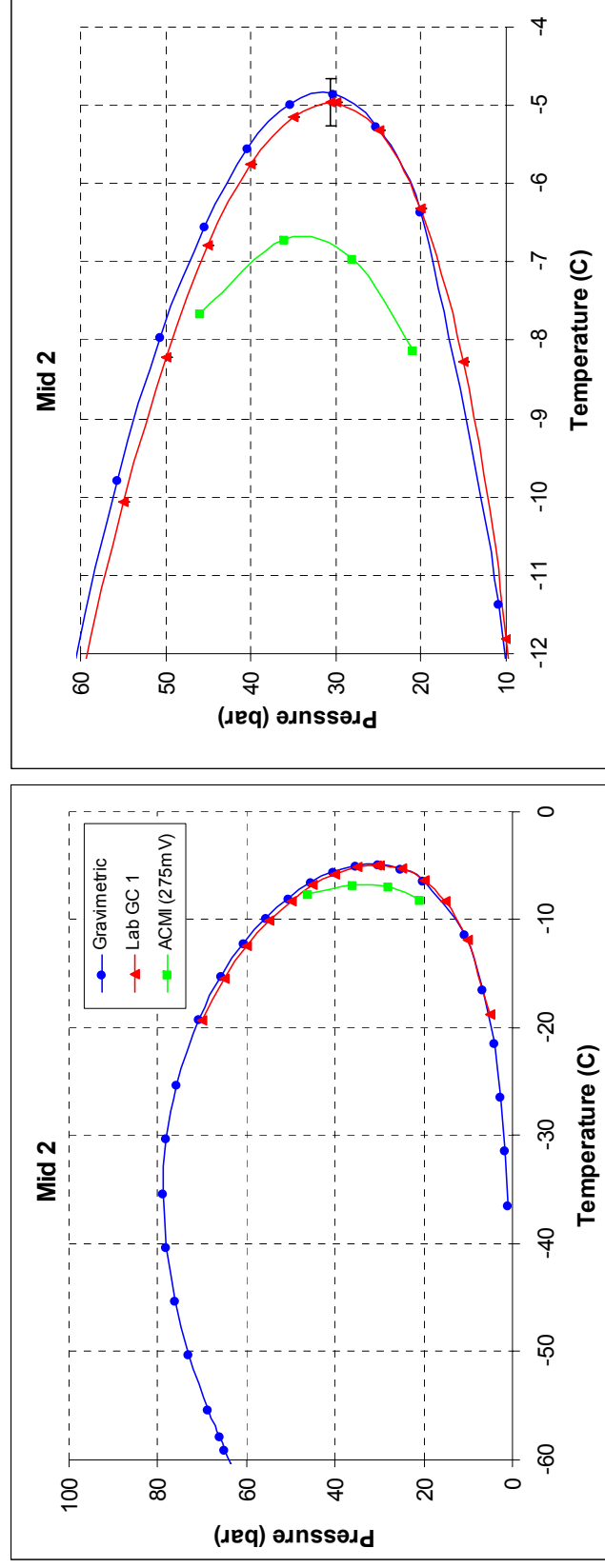


Figure 11. Results obtained for the analysis of synthetic mixture 'Mid 2'. The right-hand plot is an expansion of the left-hand plot.

Key findings

- This mixture has the largest difference between the dew point measured by the ACMI (275 mV) and the calculated dew point at 70 mg.m⁻³ of condensate.
- The ACMI analysis of this mixture revealed a very sharp transition from the gas phase to liquid film formation.

3.2.4 Results - Low 1

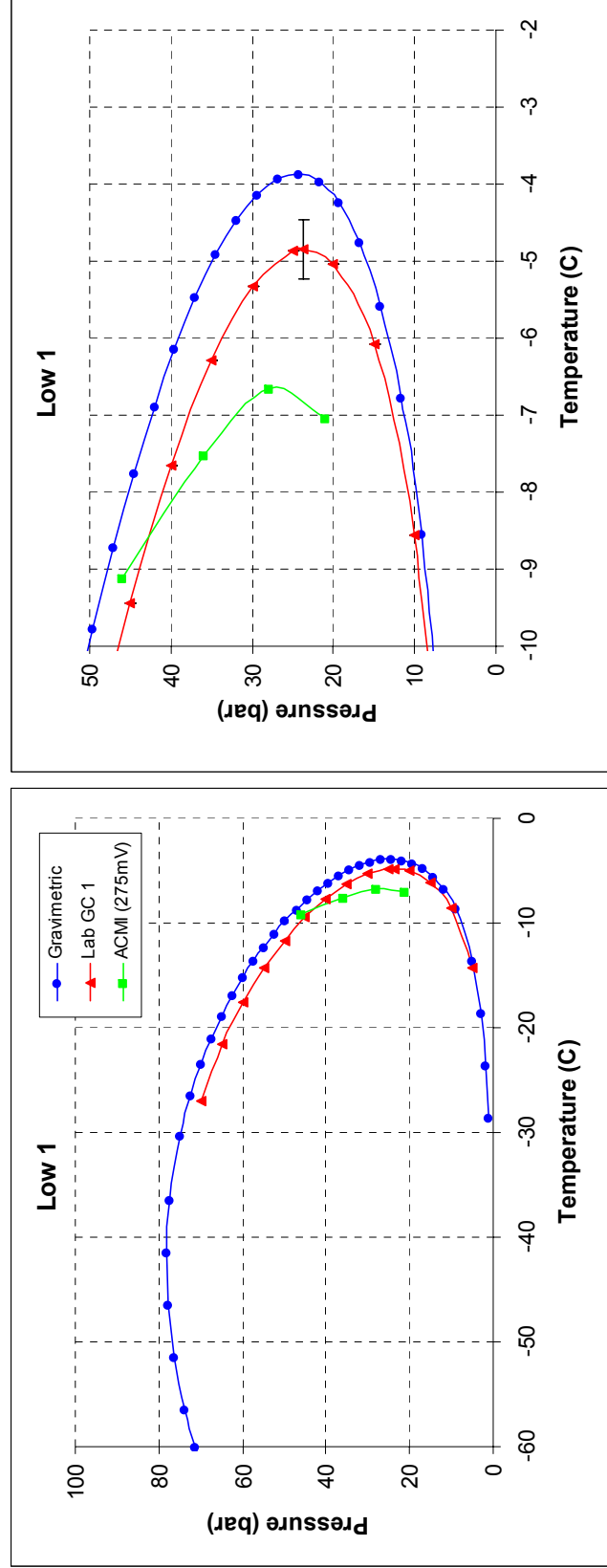


Figure 12. Results obtained for the analysis of synthetic mixture 'Low 1'. The right-hand plot is an expansion of the left-hand plot.

Key findings

- Mixtures Low 1 & Low 2 are the most difficult to sample due to the relatively high concentrations of C_9 & C_{10} .
- This mixture shows the largest deviation between the Lab GC 1 and gravimetric data. The amount fractions measured by Lab GC 1 for C_9 and C_{10} are 6.8% and 8.7% lower than the gravimetric values.
- The shape of the ACMI curve is significantly different than those of the calculated curves. This again points to 275 mV not being the optimum sensitivity setting at higher pressures.

3.2.5 Results - Low 2

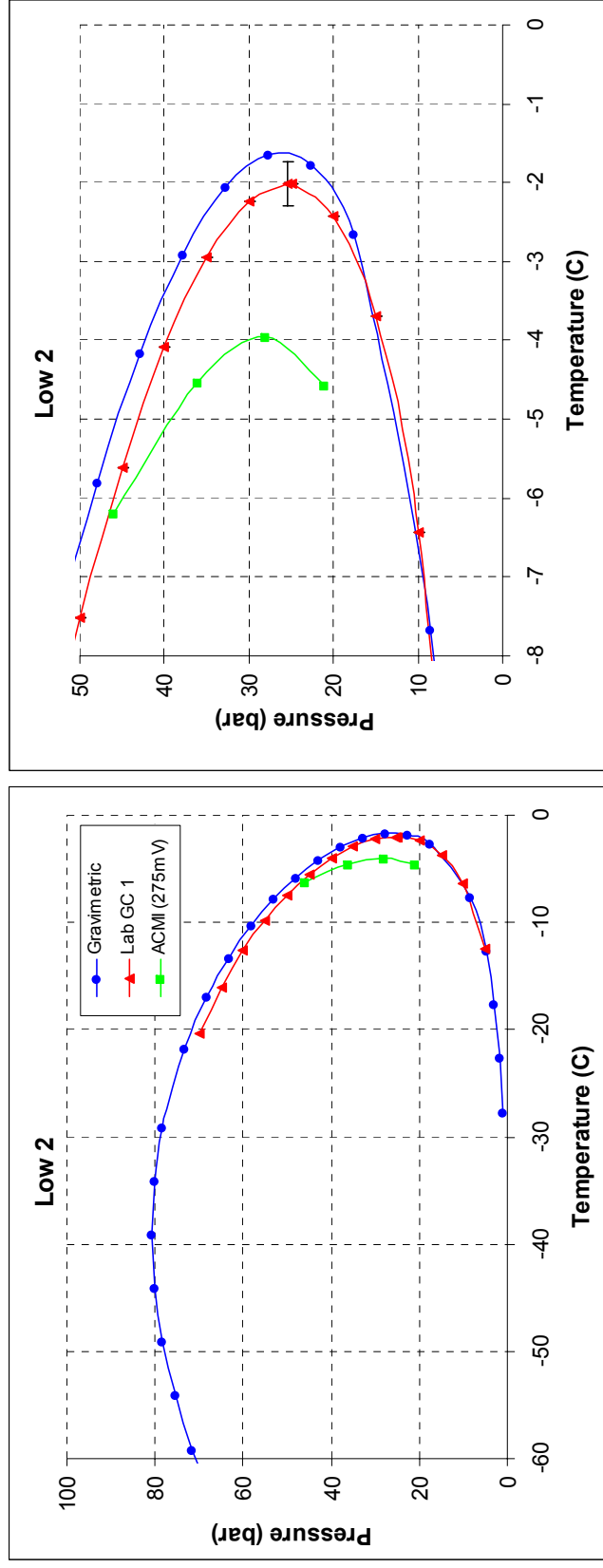


Figure 13. Results obtained for the analysis of synthetic mixture 'Low 2'. The right-hand plot is an expansion of the left-hand plot.

Key findings

- This mixture has the highest dew point of the five synthetic gases.
- Large variations were observed in the repeated analysis made using the ACMI. This may have been a consequence of the low gas pressure remaining in the cylinder at the time of analysis.
- The shape of the ACMI curve is again different than those of the calculated dew point curves.

3.2.6 Results - summary

Since it is common industry practice to measure hydrocarbon dew point at a pressure of 27 bar (gauge), the ACMI is optimised to measure the dew point at this pressure. The results obtained at this pressure are given in Table 3 (gauge):

Mixture	Hydrocarbon dew point / °C		
	Gravimetric	Lab GC 1	ACMI
High	-8.3	-7.9	-8.8
Mid 1	-8.7	-8.5	-10.0
Mid 2	-5.0	-4.6	-7.0
Low 1	-3.9	-4.4	-6.7
Low 2	-1.6	-1.5	-4.0

Table 3. Summary of results of analysis of synthetic gas mixtures. All analyses were carried out at a pressure of 27 bar.

3.3 Discussion

The above results show that the hydrocarbon dew points measured by Lab GC 1 agree well with those calculated from the gravimetric composition data – the average difference at the cricondenthem is only 0.3 °C

Good agreement is also observed between the results from the ACMI and the gravimetric data. The average difference at the cricondenthem is 1.9 °C, a value within the uncertainty of the measurement. (As shown in Section 2.12, the use of a different equation of state can lead to a change in calculated dew point of more than 2 °C.)

Even closer agreement is obtained when the ACMI results are compared to the theoretical temperature at which 70 mg.m⁻³ of condensate is formed (see Figure 14). This level of condensate corresponds approximately to the ACMI sensitivity setting of 275 mV used here (and would be equivalent to 10 µmol/mol of *n*-decane, 11 µmol/mol of *n*-nonane or 14 µmol/mol of *n*-octane). When these data are compared, the average difference at the cricondenthem is only 0.7 °C.

In conclusion, the data presented here from synthetic natural gas mixtures show that the two analytical methods used – an ACMI instrument and a laboratory GC - both reproduce the theoretical hydrocarbon dew curve well. The differences between the data sets are within the uncertainty of the experiment, which is greater than 2 °C.

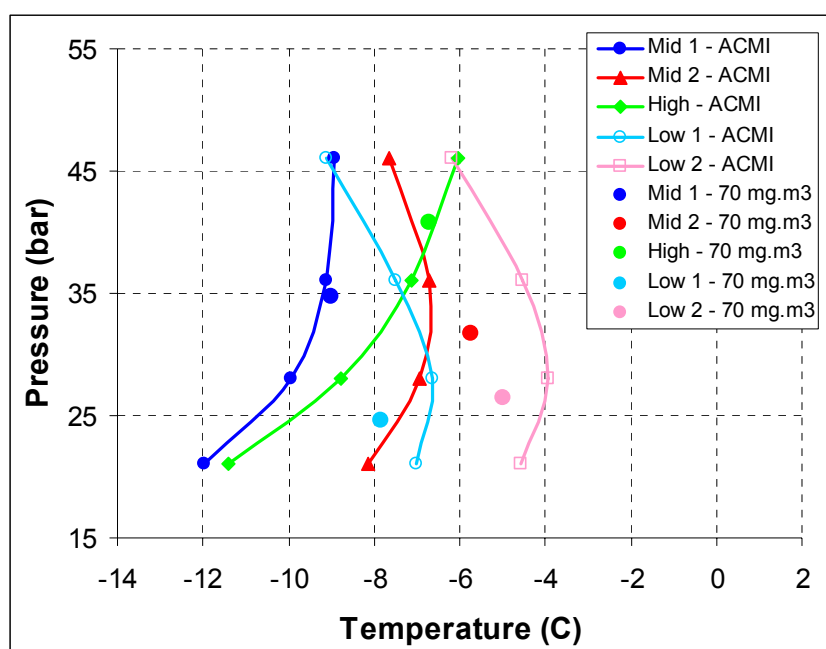


Figure 14. Comparison of ACMI results (lines) with the calculated cricondentherm temperature for the formation of 70 mg.m⁻³ of condensate (large circles) for all five synthetic gas mixtures.

To attempt to determine any trend between the data and the physical properties of the five mixtures, Table 4 shows the order of condensation rate and hydrocarbon dew point for each of the gases and compares this with the data in Figure 14.

Gas	Condensation rate	Hydrocarbon dew point	ACMI v theoretical 70 mg.m ⁻³ of condensate (Figure 14)
High	Highest	Low	Close
Mid 1	Mid	Lowest	Close
Mid 2	Mid	Mid	ACMI ~ 1 °C low
Low 2	Low	Highest	ACMI ~ 1 °C high
Low 1	Lowest	Mid	ACMI ~ 1 °C high

Table 4. Summary of results showing, for the five synthetic gas mixtures: (a) order of condensation rate, (b) order of hydrocarbon dew point, (c) closeness of agreement between the ACMI data and the theoretical dew point calculated for 70 mg.m⁻³ of condensate.

The two mixtures where the closest agreement is obtained between the ACMI data and the calculated dew point for 70 mg.m⁻³ of condensate are those with the two highest condensation rates. This supports the expectation that the dew points of fast-condensing gases are more straightforward to determine by direct observation methods.

Mid 2 is the only mixture where hydrocarbon dew point measured by the ACMI is noticeably lower than the calculated dew point for 70 mg.m⁻³ of condensate. This mixture has the longest ‘hydrocarbon tail’ and its unusual behaviour was proposed to possibly be a subtle consequence of the composition of the condensate, or sampling issues caused by the presence

of C₁₁ to C₁₂ species (with measured amount fractions of 50 nmol/mol and 30 nmol/mol respectively).

In order to investigate this possibility, the theoretical composition of the condensate (and vapour phase) for each of the synthetic gas mixtures was calculated at the cricondentherm pressure. The results are shown in Annex C by means of the following plots:

- Liquid phase amount fraction (plotted as a log scale);
- Liquid phase amount fraction (plotted as a fraction of the gravimetric amount fraction of that component in the gas mixture);
- Vapour phase amount fraction (plotted as a log scale);
- Vapour phase amount fraction (plotted as a fraction of the gravimetric amount fraction of that component in the gas mixture).

Some differences are observed between the gas mixtures, but the order of the amount fractions of most components in the condensate generally remains constant at all temperatures below the dew point - only the amount fractions of the heaviest components (C₈₊) decrease significantly at lower temperatures. It can therefore be concluded that composition of the condensate is unlikely to account for the small differences between measured and theoretical hydrocarbon dew point. Indeed, these differences are well within the best available estimate of the uncertainty of the data.

The data also show that, even at temperatures only a fraction of a degree below the cricondentherm, all components are present in the condensate. In fact, for mixtures High, Mid 1 and Mid 2, the most abundant species is methane. This is not intuitive and is a consequence of the fact that methane is at least an order of magnitude more abundant than any other species in the original gas mixtures. For mixtures Low 1 and Low 2 (which have the highest higher hydrocarbon content), the most abundant components in the liquid phase just below the cricondentherm are, in order, *n*-decane, *n*-nonane and methane.

4. REAL SAMPLES OF NATURAL GAS

4.1 Introduction

The second part of the work reported here studied a range of seven real natural gas mixtures taken from gas fields around the British Isles. Due to the highly complex nature of real gas mixtures, these samples provided a sterner challenge to the analytical methods than the synthetic mixtures discussed in Section 3.

The gases were selected to represent the extremes of composition that could be encountered in gases entering the UK network and are therefore not generally representative of those for which on-line are measurements carried out across the network. The composition of each sample (determined by Lab GC 1), along with the calculated cricondenthem pressure and temperature are shown in Table 5.

Component	Amount fraction ($\mu\text{mol/mol}$)						
	Gas A	Gas B	Gas C	Gas D	Gas E	Gas F	Gas G
Helium	319	470	420	329	30	80	120
Hydrogen	78	7.0	8.0	100	62	11	4.0
Oxygen + argon	269	40	60	160	30	50	40
Nitrogen	61120	41880	24600	71560	4450	8111	2600
Carbon dioxide	569	10020	4775	4713	17290	21730	6730
Methane	835100	892900	933100	859500	883200	880600	986900
Ethane	57600	39110	28140	43580	73150	62940	3360
Propane	23990	9790	5024	10650	17830	20370	130
<i>i</i> -butane	4863	1597	874	2253	1625	1801	30
<i>n</i> -butane	8909	2048	1113	3273	1968	3120	27
<i>neo</i> -pentane	94	49	31	101	0	0	0
<i>i</i> -pentane	2816	565	356	1240	216	420	7.5
<i>n</i> -pentane	2314	528	331	1040	143	430	7.4
2,2-dimethylbutane	85	42	39	105	1.5	5.8	1.8
2,3-dimethylbutane	121	34	29	66	5.5	23	3.4
2-methylpentane	546	124	100	307	11	57	2.1
3-methylpentane	309	63	57	173	5.3	27	1.4
<i>n</i> -hexane	327	161	144	399	10	69	3.8
Benzene	2.5	250	226	3.9	3.4	28	0.17
Cyclohexane	171	72	75	77	1.9	23	3.1
Toluene	0.31	32	53	0.8	0.51	6.9	0.12
Methylcyclohexane	56	56	77	46	0.61	10	2.9
Other C ₇ species	339	148	200	304	4.9	49	5.3
C ₈ fraction	22	35	88	40	0.17	4.9	1.9
C ₉ fraction	2.6	12	42	5.9	0.03	1.4	0.70
C ₁₀ fraction	0.03	1.2	4.8	0.35	0	0.09	0.33
C ₁₁ fraction	0	0.08	0.31	0.02	0	0	0.14
C ₁₂ fraction	0	0	0.002	0	0	0	0
Cricondenthem	Gas A	Gas B	Gas C	Gas D	Gas E	Gas F	Gas G
p / bar	48	33	31	38	45	37	15
T / °C	7.4	-8.4	-1.0	-3.7	-37.6	-23.6	-26.4

Table 5. Measured composition and cricondenthem point of the seven real natural samples used in the study (data obtained from Lab GC 1).

The condensation rate of each of the samples (calculated using the data in Table 5) is shown in Figure 15:

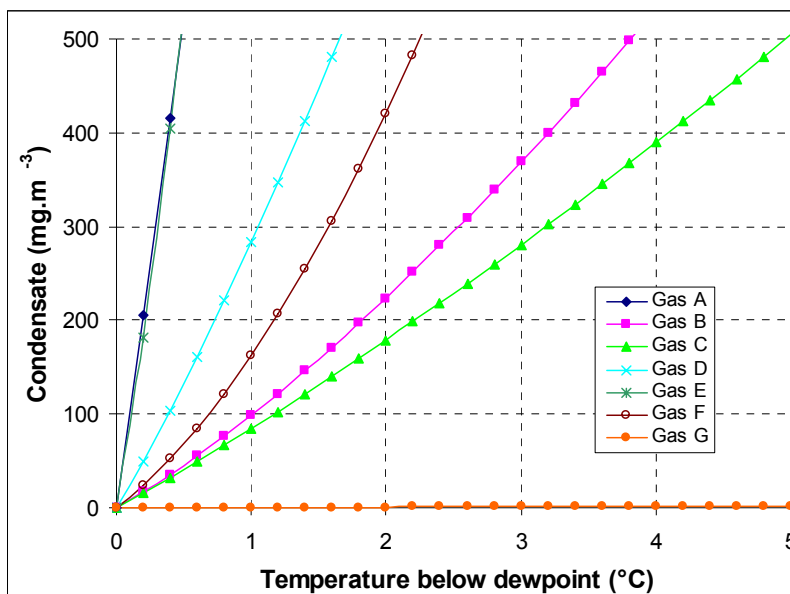


Figure 15. Calculated condensation rate of each of the real natural gas samples.

4.2 Results

As summarised in Table 1, the real natural gas samples were analysed by the full suite of methods available: MCMI, ACMI, laboratory GC (two instruments) and process GC (two instruments). The instruments were operated and the data processed as described in Sections 2.4 to 2.9.

Figures 16 to 22 summarise the results obtained, and the key findings for each gas are given beneath the charts. All data are plotted using pressures expressed as bar (absolute).

The data plotted for the ACMI are as follows:

- For Gas B, Gas C and Gas F, two sets of ACMI data are given, relating to operation of the instrument at the standard (275 mV) sensitivity setting and in adaptive trigger point mode (see Section 2.4).
- For Gas A and Gas D, only one set of ACMI data are given, relating to operation of the instrument at the standard (275 mV) sensitivity. These samples had insufficient pressure to investigate the retrograde behaviour of the dew curve by use of the adaptive trigger point mode.
- For Gas E and Gas G, no ACMI data is given as the hydrocarbon dew point of these mixtures are below the range of the instrument.

4.2.1. Results – Gas A

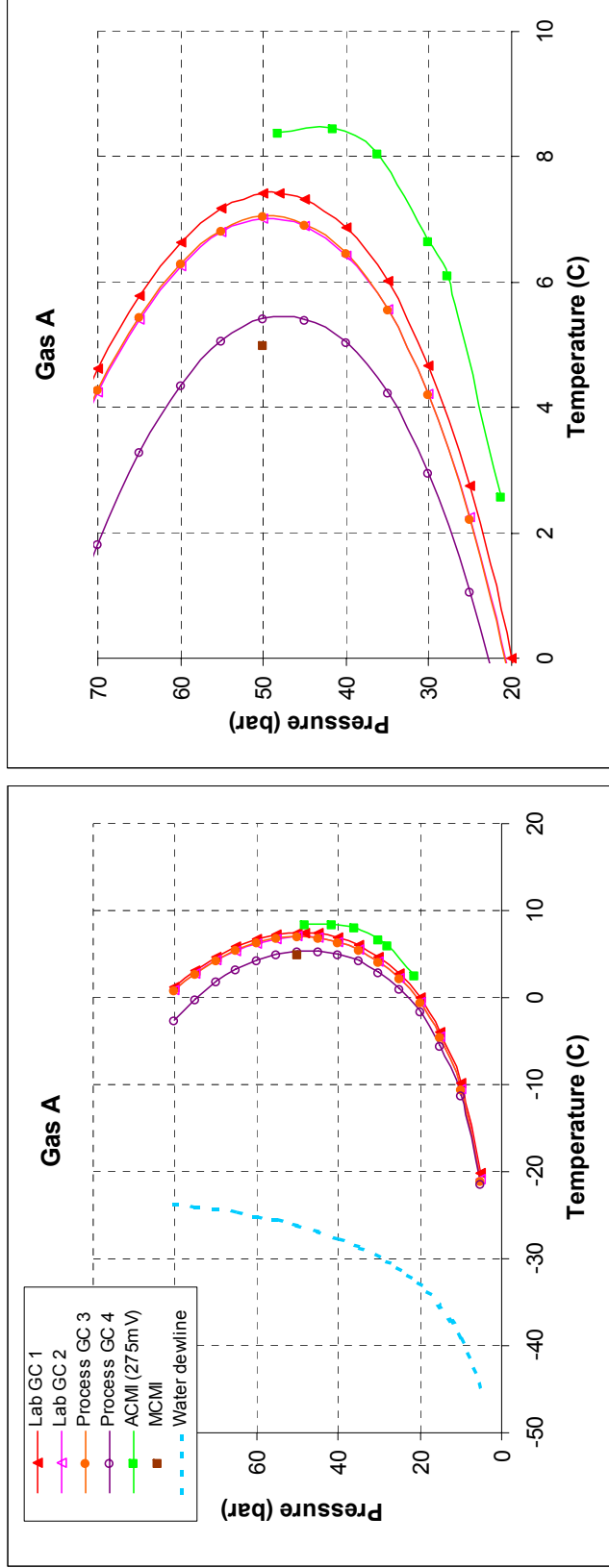


Figure 16. Results obtained for Gas A. The right-hand plot is an expansion of the left-hand plot.

Key findings

- Very good agreement is observed between three of the GC methods. Process GC 4 reports lower dew points.
- This mixture has the highest dew point, second highest condensation rate and one of the lowest high hydrocarbon (C_{10} to C_{12}) contents of the real samples. It is therefore relatively straightforward to analyse.
- This gas shows the second closest agreement between the MCM and Lab GC results (behind Gas D).

4.2.2. Results – Gas B

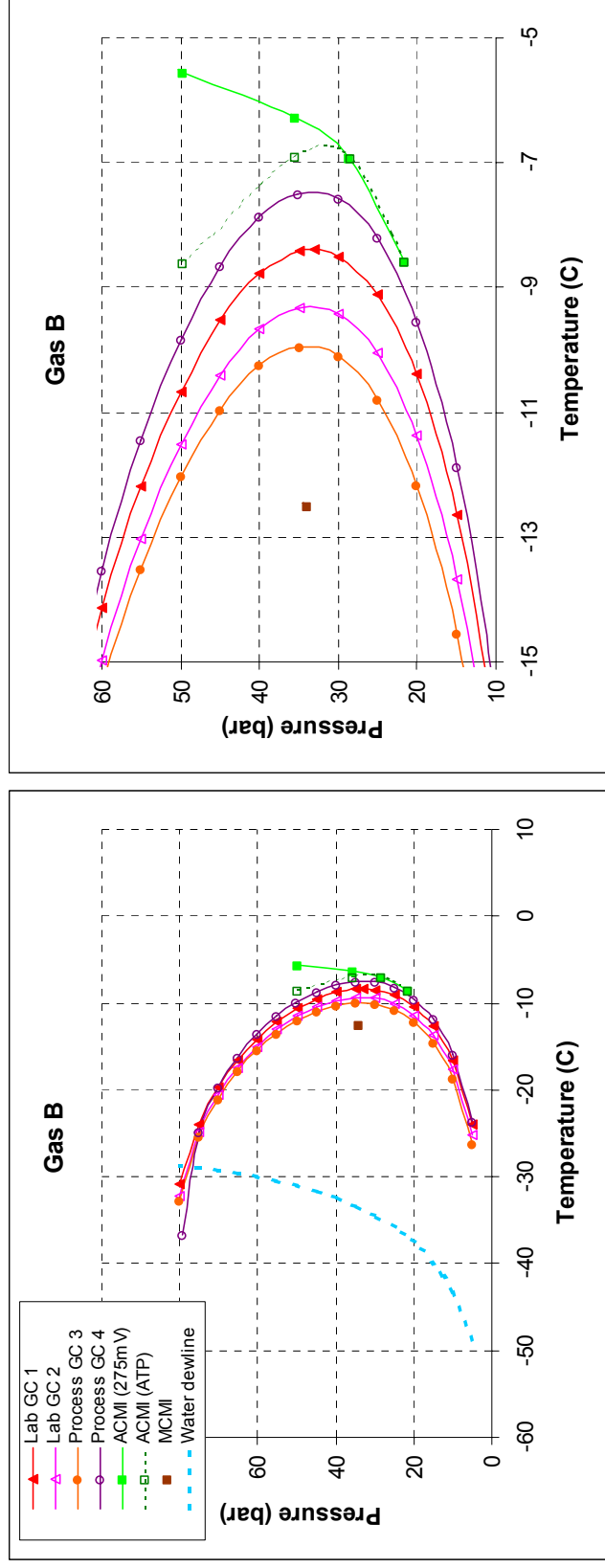


Figure 17. Results obtained for Gas B. The right-hand plot is an expansion of the left-hand plot.

Key findings.

- Non-retrograde behaviour is observed for the ACMI operating at a 275 mV sensitivity setting. Use of the ‘adaptive trigger point’ mode tracks the shapes of the curve more closely.
- A relatively large difference (approx 6 °C) is found between the MCM and ACMI data – see comments for Gas C.

4.2.3. Results – Gas C

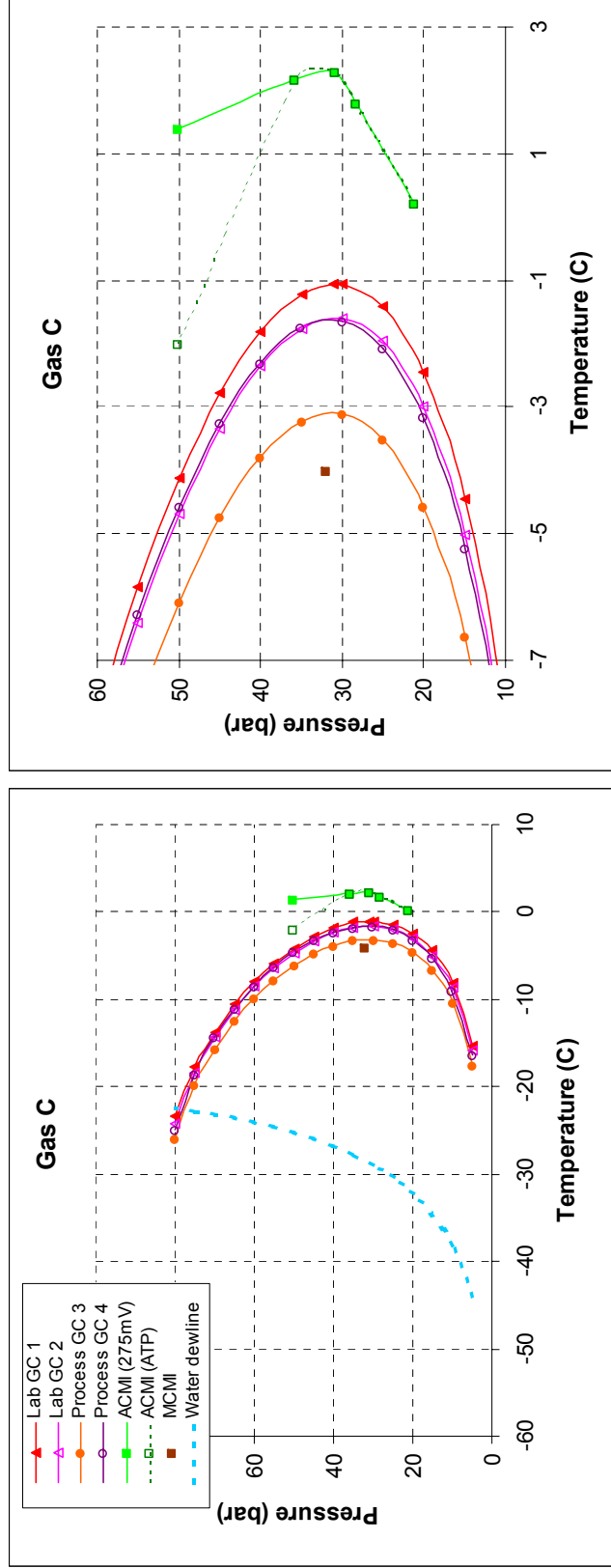


Figure 18. Results obtained for Gas C. The right-hand plot is an expansion of the left-hand plot.

Key findings

- Note that the cricondetherm pressure of this sample is close to 27 bar (gauge).
- This gas shows a relatively large difference between the MCMI and ACMI, and between the Lab GCs and the ACMI.
- Gases C & F show the closest agreement between Process GC 4 and Lab GCs. This gas has a dew point in the temperature region where determination by process GC is known to be the most accurate.
- Use of the ACMI in the adaptive trigger mode reproduces the retrograde shape of the dew curve.

4.2.4. Results – Gas D

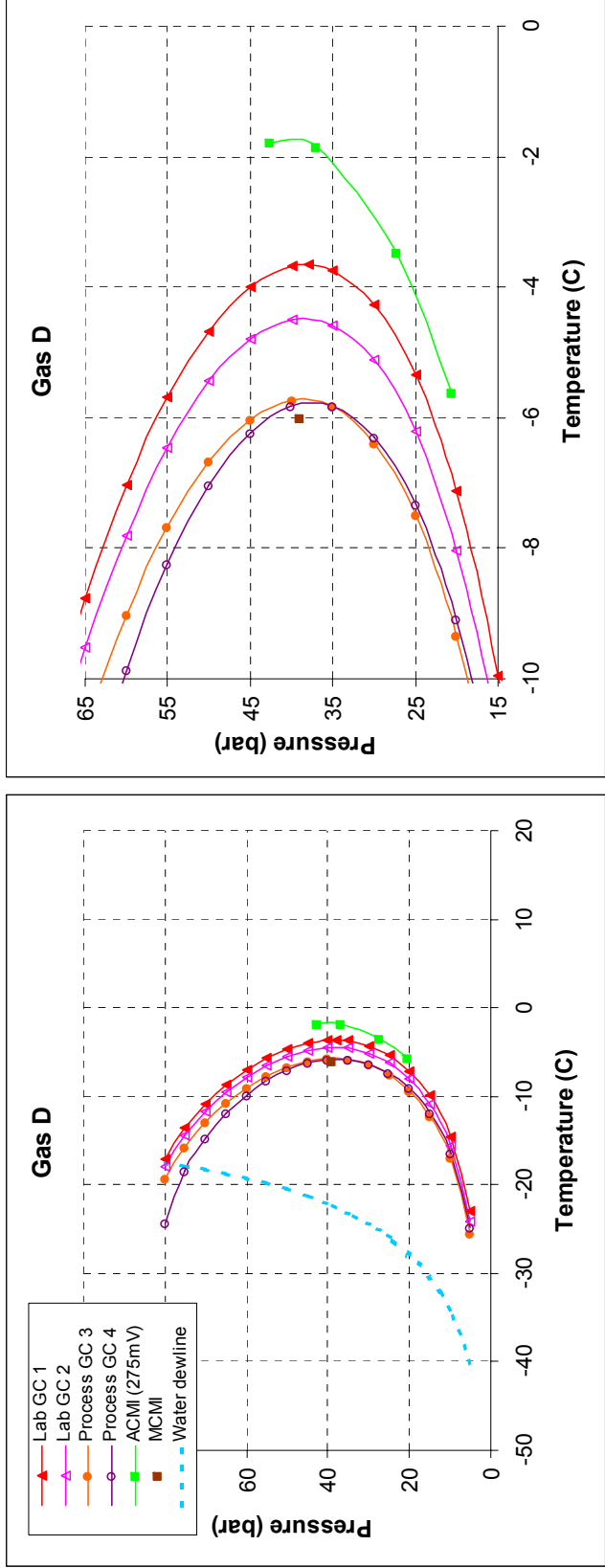


Figure 19. Results obtained for Gas D. The right-hand plot is an expansion of the left-hand plot.

Key findings

- The MCMl and two process GCs show extremely good agreement.
- The ACMI (275 mV) and two Lab GCs show good agreement.
- This gas shows the closest agreement between the MCMl and Lab GCs.

4.2.5. Results – Gas E

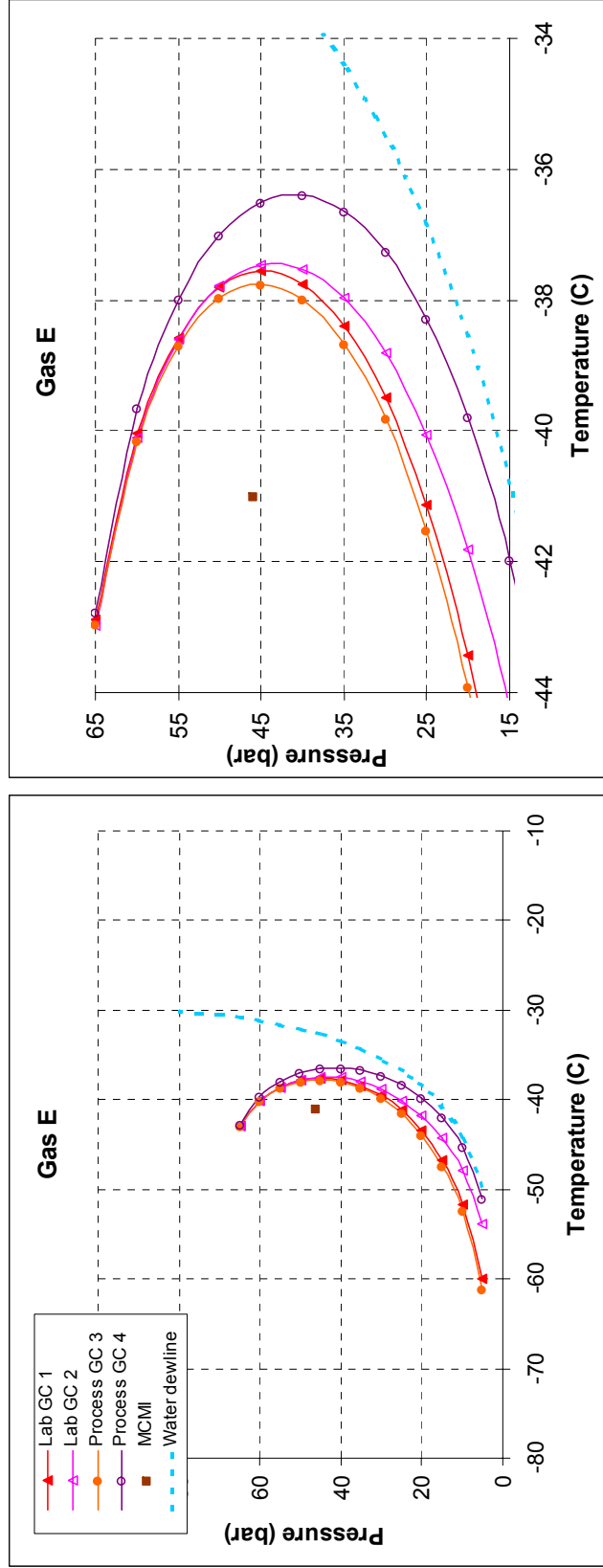


Figure 20. Results obtained for Gas E. The right-hand plot is an expansion of the left-hand plot.

Key findings

- Despite the unusually low hydrocarbon dew point of this gas, the four GC methods still report results that agree within 2 °C. The dew point is below the lower temperature range of the ACMI.
- Natural gases with dew points as low as this sample are of little concern to gas transporters and regulators.

4.2.6. Results – Gas F

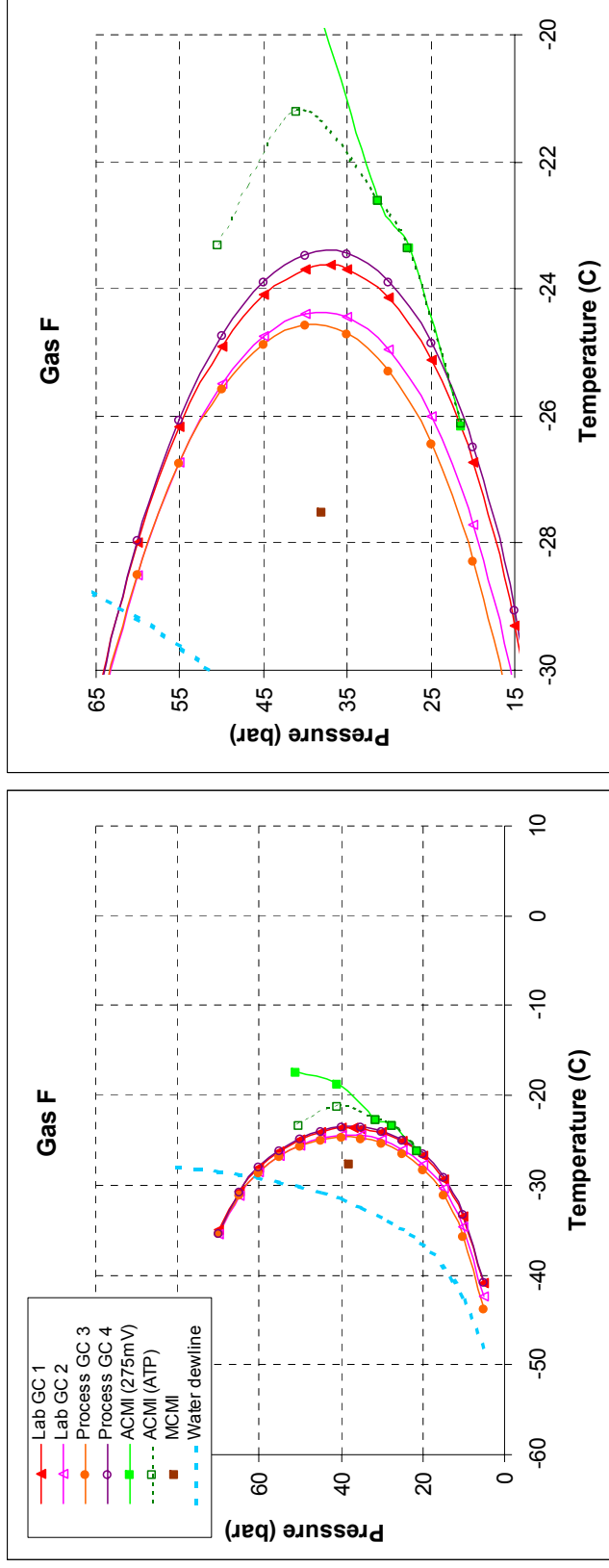


Figure 21. Results obtained for Gas F. The right-hand plot is an expansion of the left-hand plot.

Key findings

- Good agreement is observed between all four GC methods – the sample has a low heavy hydrocarbon content (but larger than that of Gas E).
- Gases C & F show the closest agreement between the results for Lab GC 1 and Process GC 4.
- Use of the ACMI in the adaptive trigger mode reproduces the retrograde shape of the dew curve.

4.2.7. Results – Gas G

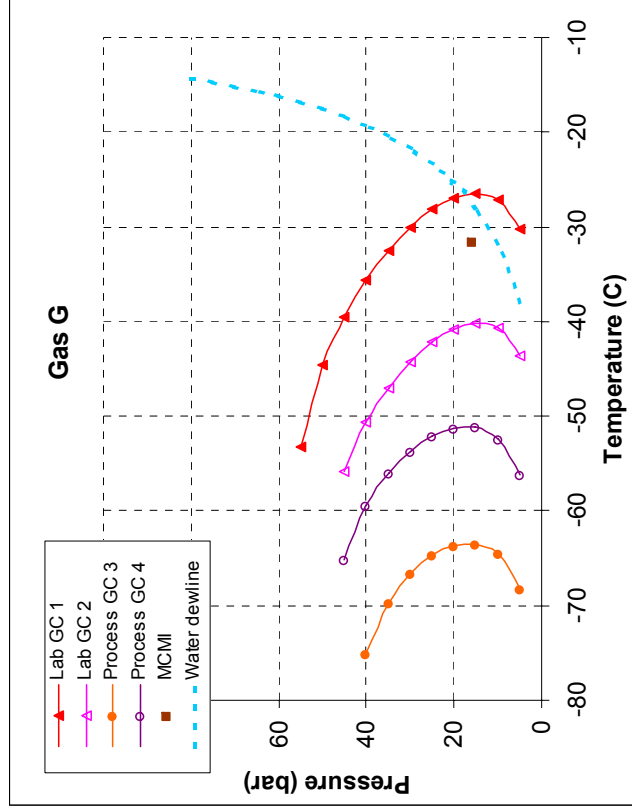


Figure 22. Results obtained for Gas G. The right-hand plot is an expansion of the left-hand plot.

Key findings

- This gas has a highly unusual composition (due to its long, but very flat hydrocarbon tail but a relatively low C₂ to C₅ content) and the lowest condensation rate.
- The data confirm that a long hydrocarbon tail results in a large spread of analytical results.
- The dew point of this gas is below the lower temperature range of the ACMI.

4.3. Discussion

4.3.1. Comparison of GC methods (lab GCs v process GCs)

The hydrocarbon dew points calculated by the four different GC methods at a pressure at or near to the cricondentherm are shown in Table 6:

Gas	Pressure (bar)	Measured hydrocarbon dew point (°C)			
		Lab GC 1	Lab GC 2	Process GC 3	Process GC 4
A	50	7.4	6.8	6.8	5.4
B	35	-8.4	-9.7	-10.0	-7.5
C	30	-1.1	-1.6	-3.1	-1.7
D	40	-3.7	-4.8	-5.7	-6.2
E	45	-37.6	-37.5	-37.8	-36.1
F	35	-23.7	-24.5	-24.7	-23.5
G	15	-26.4	-40.1	-63.5	-51.2

Table 6. The hydrocarbon dew point of each gas determined by the four GC instruments. For each gas, the pressure of the cricondentherm (to the nearest 5 bar) has been selected for comparison.

For the first three GCs, all the measured dew points are in the order Lab GC 1 > Lab GC 2 > Process GC 3. This order illustrates the relative sensitivity of each instrument to detect the higher hydrocarbon species – even small amounts of these species can have a large effect on the calculated hydrocarbon dew point. The dew points from these three instruments have all been calculated using the RKS equation of state using similar fraction boiling points and specific gravities.

The results for Process GC 4 do not follow a similar trend. This GC determined the hydrocarbon dew point (and the boiling point and specific gravity of each hydrocarbon fraction) automatically using its internal software. It is thought that the differences between the Process GC 4 results and those from the other instruments result from these differences in data processing.

Despite this difference, the Process GC 4 results generally agree with those from Process GC 3. Excluding Gas G (which has a highly unusual composition), the maximum difference in measured dew point at the cricondentherm is 2.5 °C. As discussed for the synthetic gas mixtures, these methods can be said to agree within a reasonable estimate of their uncertainties.

4.3.2. Comparison of dew point instruments (MCMI v ACMI)

Table 7 gives a comparison between the hydrocarbon dew points measured by the automatic and manual chilled mirror instruments. As the MCMI was only operated at a single pressure, the MCMI readings at this pressure have been compared to an ACMI result calculated by interpolation between the nearest two data points (using 275 mV sensitivity).

Gas	Pressure (bar)	Measured hydrocarbon dew point (°C)	
		ACMI (275 mV)	MCMI
A	50	8.2	5.0
B	34	-6.5	-12.5
C	32	2.3	-4.0
D	39	-1.8	-6.0
E	46	N/A	-41.0
F	38	-19.8	-27.5
G	13	N/A	-31.5

Table 7. The hydrocarbon dew point of each gas determined by the two chilled mirror instruments. For each gas, the pressure at which the measurement took place is given in brackets (all ACMI results are an interpolation between the nearest two readings). Gas E and Gas G were out of the range of the ACMI.

For all gases, the dew point measured by the ACMI is greater than that measured by the MCMI, the difference being between 3.2 °C and 7.7 °C. These differences are larger than might be expected to occur between the two methods because they both depend on direct observation of the formation of a hydrocarbon film. For Gas B and Gas F, slightly closer agreement is obtained when the ACMI is used in the adaptive trigger point mode, although the differences from the MCMI data are still 5.6 °C and 6.2 °C respectively.

However, the results from the comparison of temperature measurements using an *n*-butane in nitrogen standards (Annex A) showed that the results from the MCMI were typically 2 °C lower than those from the automatic instrument. When taking this into account, the difference between the two chilled mirror instruments reduces to between 1.2 °C and 5.7 °C. The differences at the upper end of this range are unexpectedly large and merit further investigation.

4.3.3. Comparison of 'process' instruments (process GCs v ACMI)

Comparison of the results between the ACMI and the GCs shows a difference in behaviour for real and synthetic gas mixtures.

For all seven real samples, the dew points measured by the ACMI are greater than those from the process GCs (and indeed from all the GCs). This difference would in fact be more pronounced if the GC data were used to calculate the theoretical dew point for the formation of 70 mg.m⁻³ of condensate (see Section 3.3 for this discussion for the synthetic mixtures).

This difference requires further investigation. One possible explanation is that it may be due to the complex nature of the real mixtures, the compositions of which are difficult to determine accurately by GC. In particular, the higher hydrocarbon species may be under-measured, not detected or misidentified. Also, unexpected components (such as very heavy oils or glycols) are likely to be not measured at all – any such species will have a disproportionately large effect on the calculated hydrocarbon dew point. Another possible cause of the difference may be factors related to the operation of the ACMI, such as the trigger point, cooling rate and cell construction.

In contrast, the dew points measured by the MCMI (which are lower than those determined by GC) show the opposite trend. The differences between the results from the two chilled mirror instrument are discussed in the section above.

For the synthetic gas mixtures, the opposite effect is observed for all gases, i.e. the GC dew points are higher than those reported by the ACMI. For these mixtures (which were not analysed by either of the process GCs), the Lab GC can be said to measure the ‘correct’ dew point, as the values agree very well with those determined from the known gravimetric composition. The slightly lower dew points recorded by the ACMI can be explained by the dynamic nature of the method which requires real condensate to be formed. The GC method calculated the ‘theoretical’ dew point (the point of formation of the first molecule of condensate) – a measurement which any direct observation method cannot carry out.

4.3.4. ‘True’ value of hydrocarbon dew point

In summary, the analysis of the real natural gases revealed a spread of results from the different analytical methods used – the dew points measured by the four GC methods agree within a reasonable estimate of their uncertainties, but more variability is exhibited with the chilled mirror instruments. The differences between results from method to method, and from gas to gas mean that no single method can be said to definitively measure the ‘true’ hydrocarbon dew point. For example, the GC methods may not measure trace quantities of higher hydrocarbons, or ‘unexpected’ components, whereas the chilled mirror instruments are dependent upon the detection of a liquid film, and other operational and instrumental factors.

Even for the synthetic mixtures, where the dew points measured by Lab GC 1 were shown to be in very good agreement with those calculated from the gravimetric composition data, some uncertainty exists regarding the validity of the equation of state used to perform the calculations.

As referred to in Section 1.1, the issue that the current definition of hydrocarbon dew point cannot be measured in practice is under discussion within ISO/TC193/SC1. The recommendation being put forward is that dew point should be redefined as a ‘technical’ or ‘measurable’ dew point to aid convergence of the determined value from the different methods of measurement. One approach would be to ensure that, when used in gas quality specifications, the term hydrocarbon dewpoint is appended by:

- the determined value, e.g. a maximum of $-2\text{ }^{\circ}\text{C}$ at pressures from 1 to 70 bar (gauge);
- a maximum permissible error, e.g. $\pm 1.5\text{ }^{\circ}\text{C}$ (from the accepted or true value); and
- the method of determination (in case of a disputed value should be stated).

It is therefore recommended that, until such time when an industry-standard method for measuring hydrocarbon dew point is adopted, reported dew points should also contain information about the analytical method used, and any assumptions made during the analysis.

5. CONCLUSIONS

The work presented in this report details the results of a comprehensive study of the measurement of the hydrocarbon dew point of real and synthetic natural gases. Six analytical methods were examined: one ACMI, one MCMI, two lab GCs and two process GCs.

Analysis of synthetic natural gas mixtures showed a good agreement between the dew points measured the methods used, one lab GC and the ACMI.

Although measurement of the real natural gases proved to be much more challenging, agreement was in most cases obtained between the dew points measured by the different analytical methods. The results from the four GC instruments differ by no more than 2.5 °C at the cricondentherm and can be said to agree within a reasonable estimate of their uncertainties. The chilled mirror methods show larger variability. An interesting difference in behaviour is observed when comparing the ACMI and GC results for the synthetic and real mixtures – it is proposed that this may be due to the complex nature of the real mixtures, or other effects, and merits further investigation.

The results from the analysis of the real gases also show that a ‘true’ value of hydrocarbon dew point is difficult to both measure and define. As discussed in Section 1.1, work is ongoing within ISO/TC193/SC1 to redefine the current definition of hydrocarbon dew point. The results from this study reveal that the measured dew point is dependent on the analytical method and it is suggested that any reported dew point should therefore be appended with the information on the analytical method used.

It is also concluded that the use of accurate synthetic gas mixtures is essential for the calibration of GC systems. Their role in the calibration of chilled mirror instruments is however, more limited. Using a *n*-butane in nitrogen standard to perform this task is straightforward and inexpensive, but the mixture forms an atypical, rapidly condensing, hydrocarbon film.

6. FURTHER INFORMATION

The data from the study can be downloaded, free of charge, from:
www.npl.co.uk/environment/hydrocarbondewpoint.html

REFERENCES

- [1] ISO 14532, *Natural gas – Vocabulary*.
- [2] ISO 6570, *Natural gas - Determination of potential hydrocarbon liquid content - Gravimetric methods*.
- [3] ISO 6141, *Gas analysis -- Requirements for certificates for calibration gases and gas mixtures*.
- [4] ISO 10715, *Natural gas - Sampling guidelines*.
- [5] J. L. K. Bannell, A. G. Dixon and T. P. Davies, *The monitoring of hydrocarbon dew point*, International Congress of Gas Quality, Groningen, The Netherlands, 1986.
- [6] H-J. Panneman, *A traceable calibration procedure for hydrocarbon dew point meters*, 23rd World Gas Conference, Amsterdam, The Netherlands, 2006.
- [7] ISO 6974-5, *Natural gas - Determination of composition with defined uncertainty by gas chromatography - Part 5: Determination of nitrogen, carbon dioxide and C₁ to C₅ and C₆₊ hydrocarbons for a laboratory and on-line process application using three columns*.
- [8] ISO 6143, *Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures*.
- [9] ISO 23874, *Natural gas - Gas chromatographic requirements for hydrocarbon dewpoint calculation*.
- [10] G. Soave, *Chem. Eng. Sci.*, 1972 (27), 1197.
- [11] D. Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fund.*, 1976 (15) 59.
- [12] R. M. Gibbons and A. P. Laughton, *J. Chem. Soc. Faraday Trans. 2*, 1984 (80) 1019.
- [13] ISO 18453, *Natural gas - Correlation between water content and water dew point*.

ANNEX A – CALIBRATION AND COMPARISON OF CHILLED MIRROR THERMOMETER AND PRESSURE SENSOR

A1. Comparison of automatic chilled mirror instrument temperature sensor and manual chilled mirror instrument thermometer

In order to validate the temperature calibration of the manual and automatic chilled mirror instruments, two Primary Reference Gas Mixtures were prepared at NPL at pressures of approximately 14 bar:

NG129: 10.028 % mol/mol *n*-butane in nitrogen – used for ACMI analysis;

NG130: 10.015 % mol/mol *n*-butane in nitrogen – used for MCMI analysis.

Measurements using the MCMI instrument were carried out at pressures of 100 and 140 psi (gauge); the ACMI was operated at a range of pressure between these values. The results are plotted below:

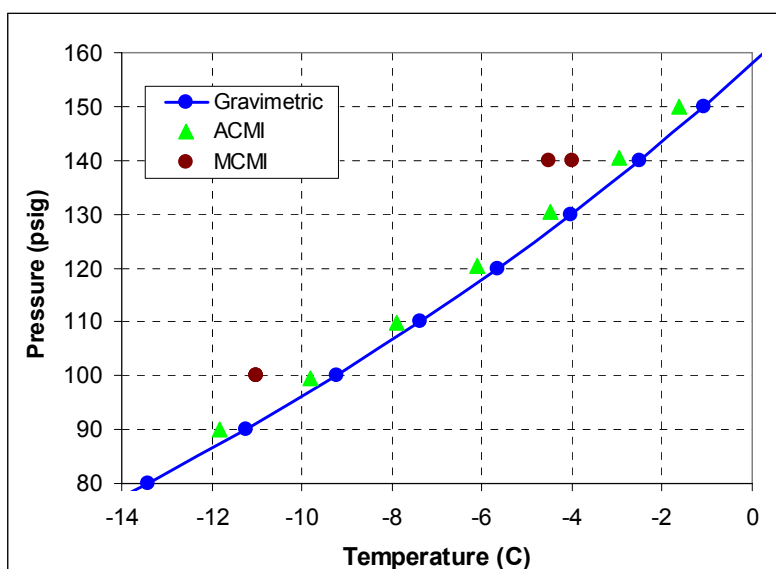


Figure A1. Measurement of the hydrocarbon dew point of a nominally 10% mol/mol *n*-butane in nitrogen standard by the chilled mirror instruments.

The dew curves of the two standards have been calculated using the RKS EoS. Due to the very similar compositions of the mixtures, the lines overlay each other when plotted on the scale above, so, for clarity, only one curve is plotted.

The gravimetric data takes into account the measured impurities in the constituent gases. For example, the *n*-butane used was determined to be 99.89 % pure, with the main impurities being *i*-butane (570 $\mu\text{mol/mol}$), water (380 $\mu\text{mol/mol}$) and propane (99 $\mu\text{mol/mol}$). These impurities affect the calculated hydrocarbon dew point by a maximum of 0.03 °C.

The data show strong agreement between the ACMI and gravimetric dew points, with all differences typically around 0.5 °C. This can be taken to be a ‘pure case’ as the gas mixture is

simple, of known composition and has an easily-measured hydrocarbon dew point – the condensate will flood the chilled mirror at the dew point.

The differences between the MCMI and theoretical data are larger – typically 2 °C.

A2. Calibration of manual chilled mirror instrument thermometer

The thermometer used in the MCMI underwent calibration at NPL. A subset of the results is shown in Table A1 (reproduced from NPL certificate PM07/E07010117/1).

Thermometer reading / °C	Emergent column temperature / °C	Correction / °C	Corrected thermometer reading / °C
-50.0	15	0.0	-50.0
-40.0	17	-0.2	-40.2
-30.0	20	0.0	-30.0
-20.0	20	-0.2	-20.2
-10.0	20	+0.2	-9.8
0.0	19	0.0	0.0
10.0	22	-0.2	9.8

Table A1. Results from calibration of the thermometer used in the MCMI.

NOTES

- The expanded uncertainty of the test from –50 °C to + 10 °C is ± 0.5 °C.
- To account for differences in immersion conditions, the certified correction should be amended by adding the quantity $10.4 \times 10^{-4} N (t_l - t_2)$ where N is the length of the emergent liquid column (elc) expressed in °C, t_l the elc temperature given in the certificate and t_2 the elc temperature in use. See Appendix A of the certificate for further information.

ANNEX B – CALCULATION OF DEW CURVES FOR WATER VAPOUR

In order to investigate an example of the retrograde behaviour of a water dewline calculated using the RKS equation of state in an earlier version of this report, five methods of calculation were compared, namely:

- LRS
- PR
- ISOW (modified PR equation of state for the calculation of water dew point according to ISO 18453 [13])
- RKS with $K_{ij} = 0$ (full composition) – the default option for the software used
- RKS with $K_{ij} = 0.5$ (full composition)
- RKS with $K_{ij} = 0.5$ (simplified composition)

Gas A was used in the calculation, its composition taken from the Lab GC 1 analysis (for all species except water), with the water content calculated to achieve the National Grid National Transmission System indicative specification of a water dew point of $-10\text{ }^{\circ}\text{C}$ at 85 bar. (The actual amount fraction of water therefore differed slightly between each equation of state). The ‘simplified composition’ assumes that all hydrocarbons from C_2 to C_{12} could be represented by C_2 , and that N_2 , O_2 , He and H_2 could be represented by N_2 .

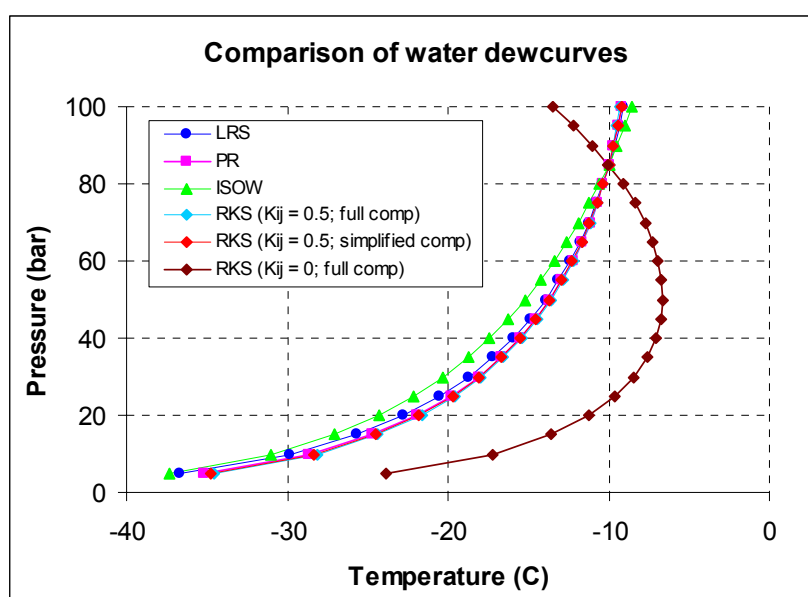


Figure B1. Comparison of water dewlines plotted using different equations of state. Note that all the curves converge at a pressure of 85 bar due to the use of the NTS indicative water specification

The results (Figure B1) show that the use of an RKS equation of state with $K_{ij} = 0$ would clearly be an erroneous approach – the curve shows retrograde behaviour which is uncharacteristic of a water dew curve.

The two RKS ($K_{ij} = 0.5$) curves show good agreement, but a large difference is shown by the ISOW curve. This is due to the phase of the condensed water in the equation – the LRS, PR & RKS EoS assumes water to be in the liquid phase, but the ISOW EoS gives the condensed phase of water below 0°C as ice (i.e. in the solid phase).

ANNEX C – COMPOSITION OF VAPOUR AND LIQUID PHASES OF SYNTHETIC MIXTURES OF NATURAL GAS

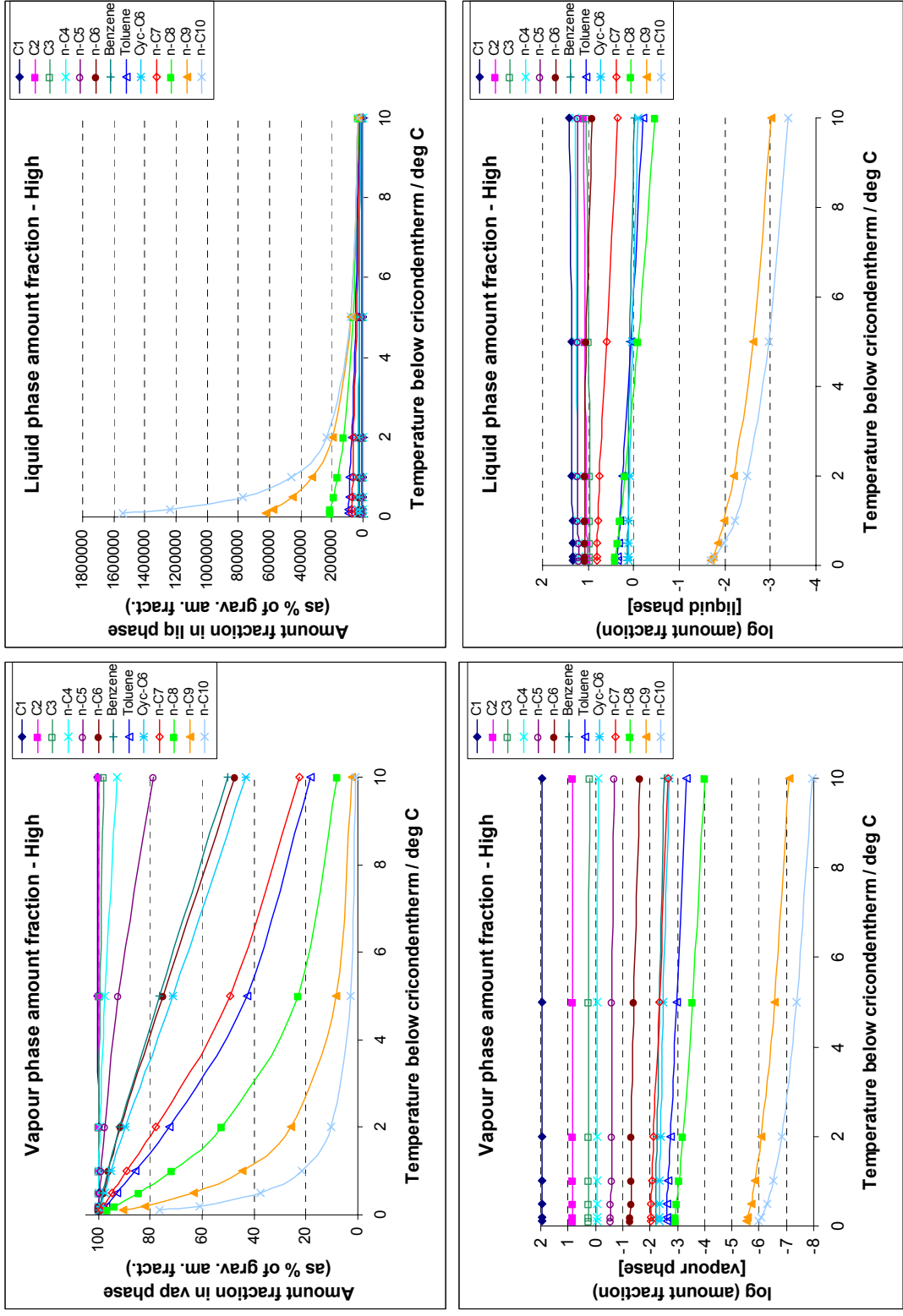


Figure C1. Comparison of liquid and vapour phases of mixture High at temperatures below the cricondentherm. Note that: $n\text{-C}_9$ and $n\text{-C}_{10}$ are present in the mixture as an impurity only.

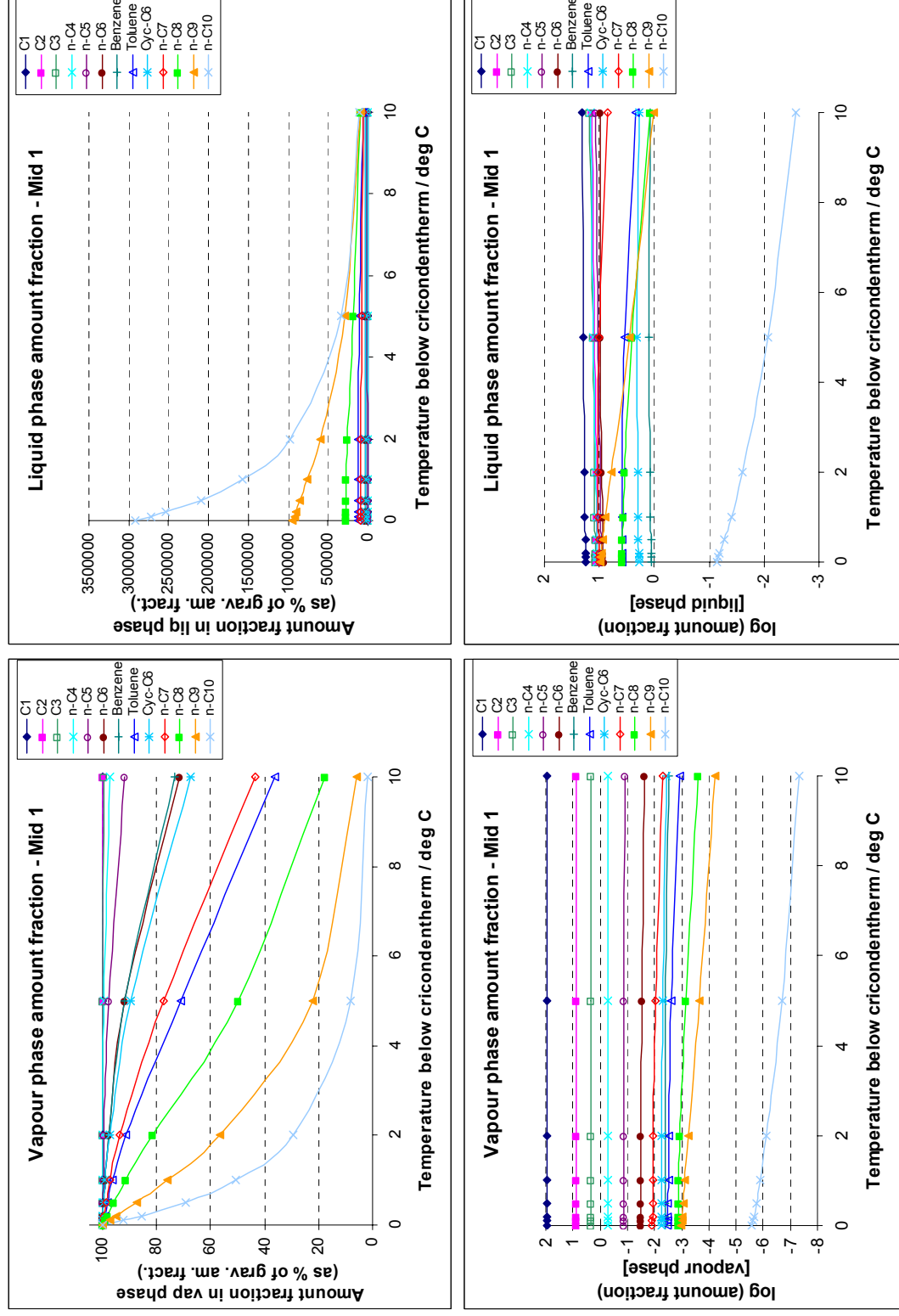


Figure C2. Comparison of liquid and vapour phases of mixture Mid1 at temperatures below the cricondentherm. Note that: $n\text{-C}_{10}$ is present in the mixture as an impurity only.

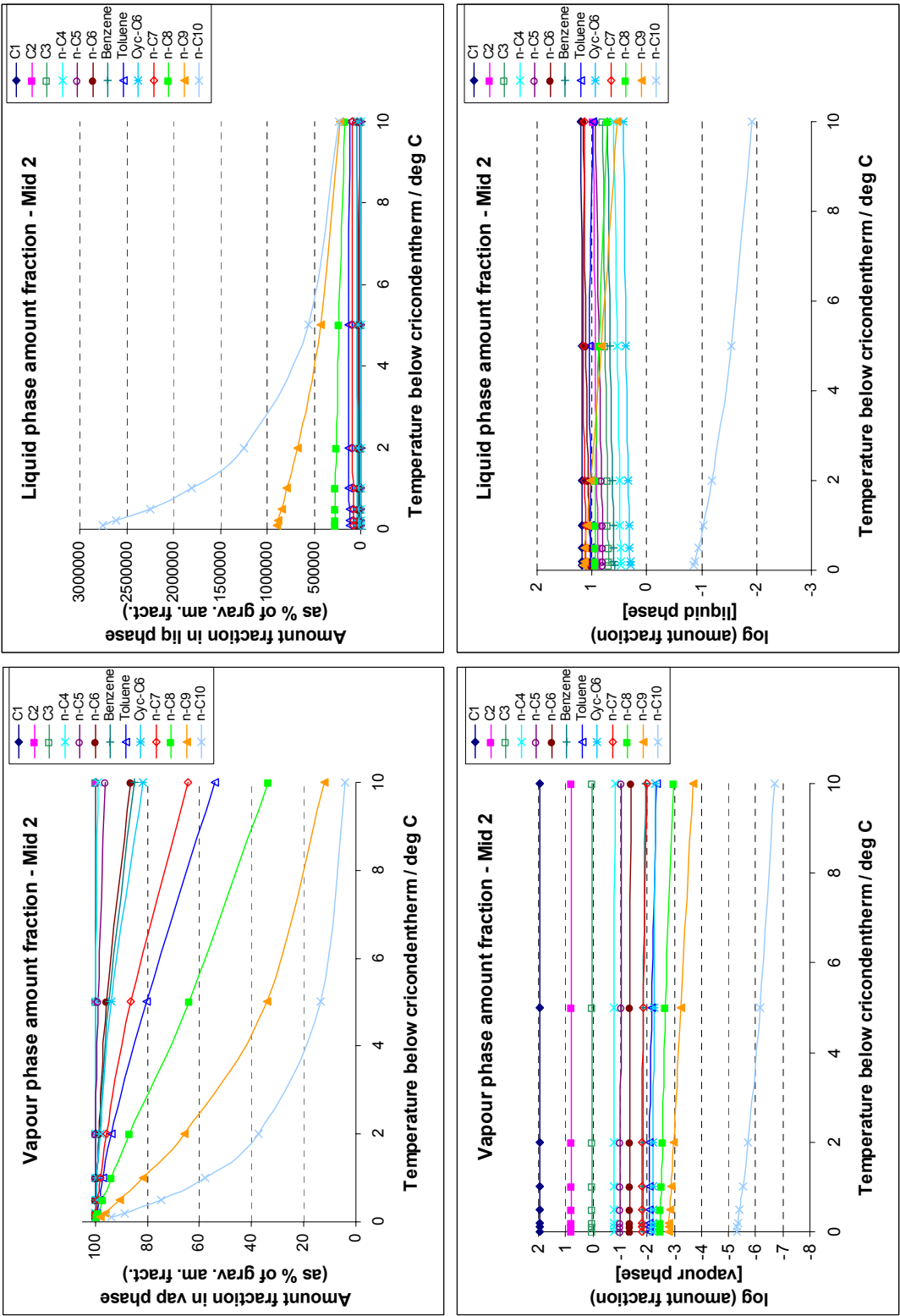


Figure C3. Comparison of liquid and vapour phases of mixture Mid 2 at temperatures below the cricondentherm. Note that: $n\text{-C}_{10}$ is present in the mixture as an impurity only.

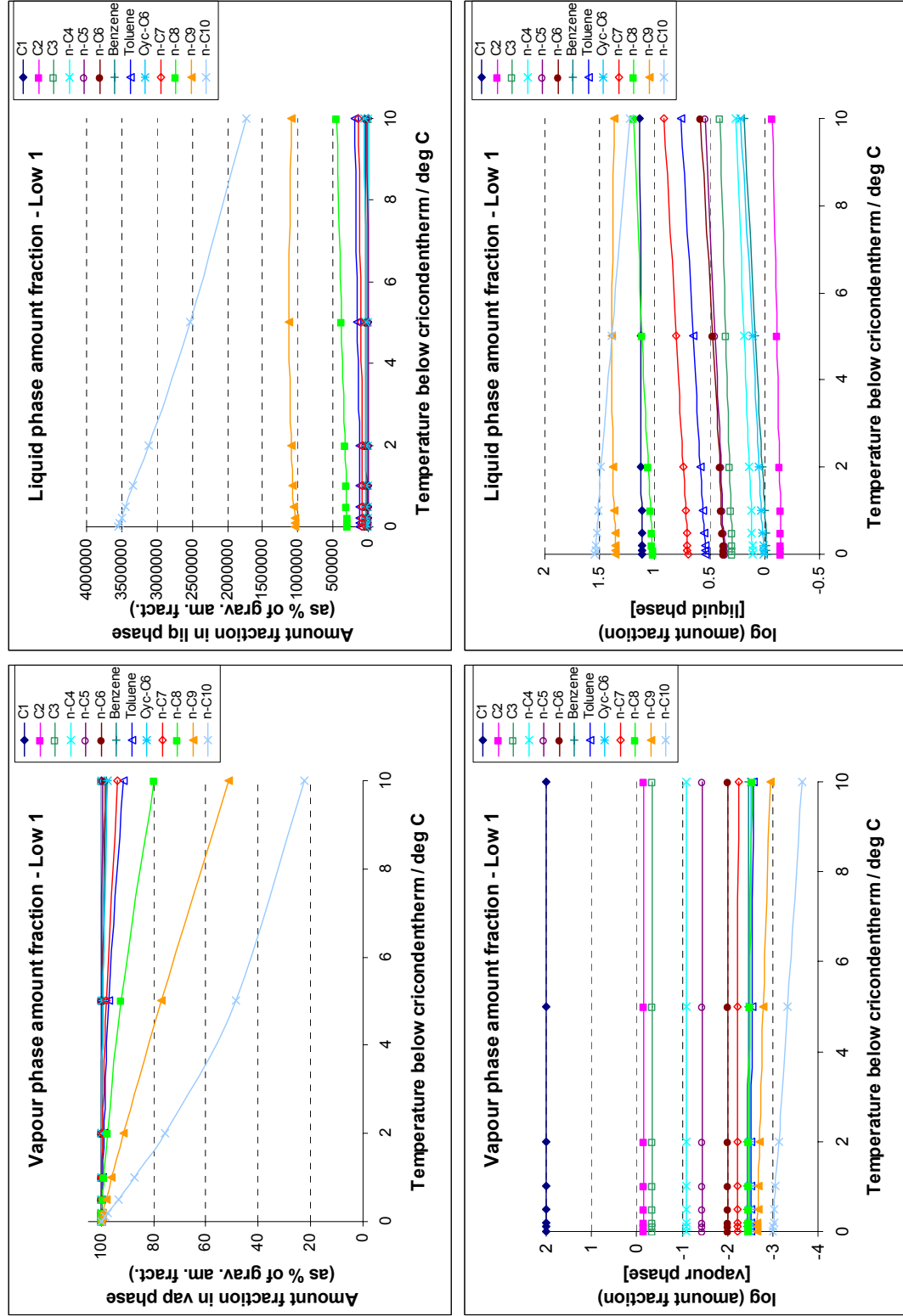


Figure C4. Comparison of liquid and vapour phases of mixture Low 1 at temperatures below the cricondentherm

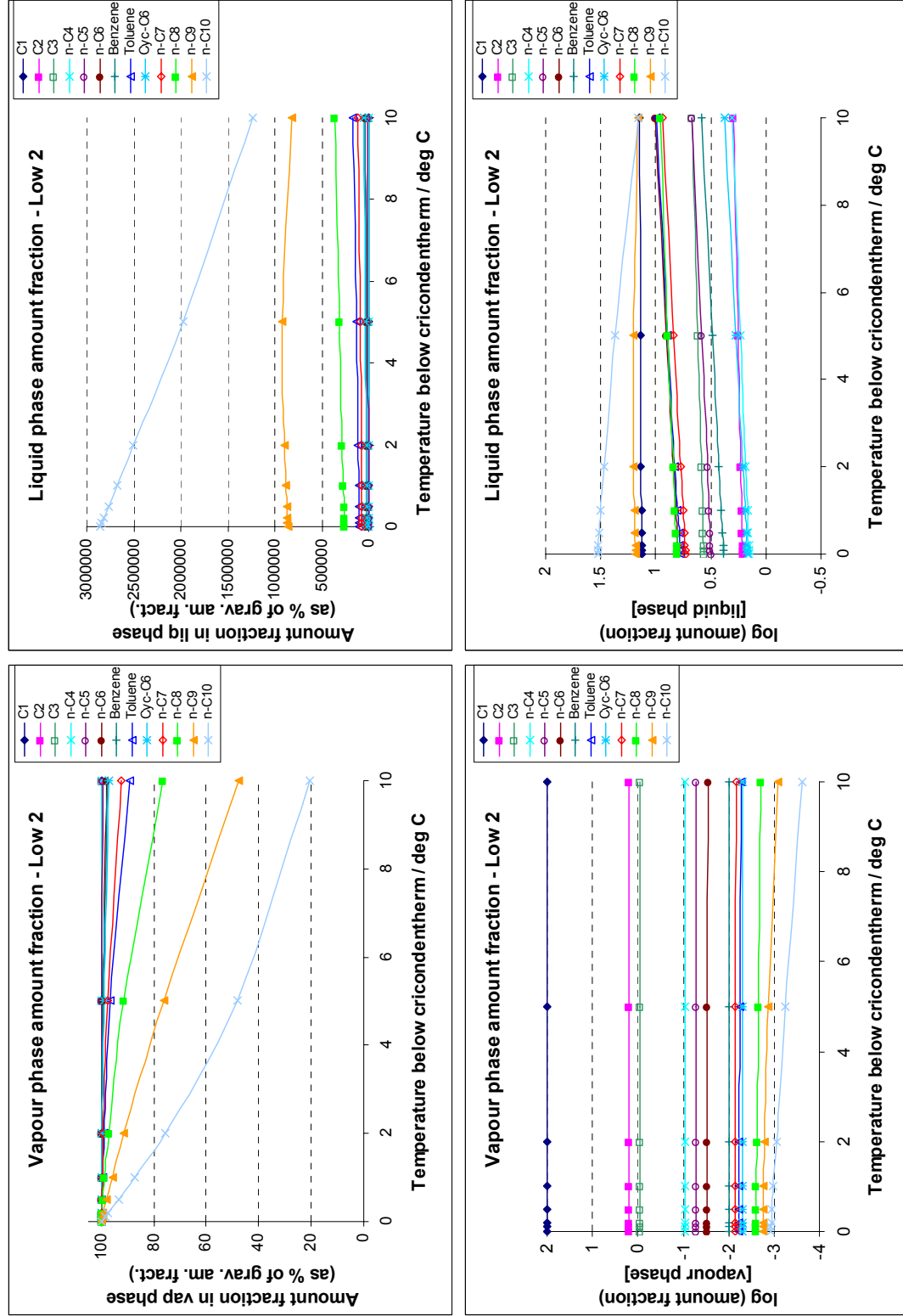


Figure C5. Comparison of liquid and vapour phases of mixture Low 2 at temperatures below the cricondentherm