

# A new approach of splitting C6+ composition of pipeline gas for hydrocarbon dew point determination

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**Abstract** Hydrocarbon dew point (HCDP) is a critical consideration for pipeline operations. Equation of state (EOS) method combined with Gas Chromatograph analysis is one of the methods used for HCDP determination. Most of the GCs on pipeline gas and in end-user installations are generally C6+ design and a few are C9+ design. In applying a HCDP limit using C6+ data, it is prudent to use an appropriate split of the C6+ composition. Though several fixed ratios of C6+ composition splits have been published in a Gas Processors Association standard and by leading chromatograph manufacturers for application, but may not truly reflect the C6+ composition of a particular gas. This work therefore presents a very simple procedure for splitting C6+ component into C6/C7/C8 for any particular pipeline gas provided that the specific gravity of the C6+ data is known. The method involves; determination of the molecular weights of C6/C7/C8 using three well-established hydrocarbon physical properties correlations, solution of the algebraic equations of the apparent molecular weight of C6+ using matrix notation, and application of logarithmic distribution to the calculated “quasi-mole fraction” of the individual C6+ components. An application of this approach to a field C6+ data is presented. In order to show the capabilities of the new approach, results comparison of calculated HCDP as well as cricondentherm (using HYSYS<sup>®</sup> with Peng Robinson EOS) between the

new approach and some common C6+ composition splits is made.

**Keywords** C6+ splits · Pipeline gas · Hydrocarbon dew point

## Introduction

Hydrocarbon dew point (HCDP) defines whether the natural gas stream in a pipeline at a given pressure and temperature consists of a single gas phase or two phases, gas and liquid. Figure 1 shows a phase diagram depicting the HCDP for a typical natural gas.

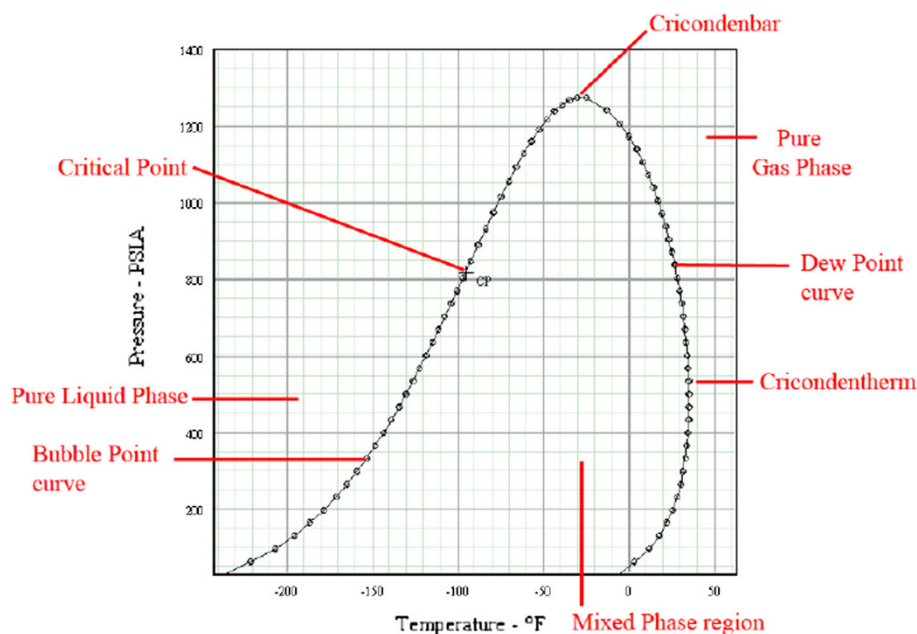
When natural gas is processed, the heavier components are removed in order to supply high quality gas to the market and also to ensure the safety and reliability of the pipeline system. For example, gas turbine generator plants have a written requirement in their warranties that the fuel gas must be totally gaseous. In order to comply with this requirement, the gas is superheated to a minimum of 50 °F/28 °C above the highest dew point of the gas at the pressure regulators located ahead of the burner section.

The two methods currently in use for determining HCDP are; the manual visual dewpoint approach and the equation of state (EOS) method using Gas Chromatograph (GC) analysis. The manual method was developed by the US Department of Interior, Bureau of Mines and has been codified into a standard test method by the American Society of Testing and Materials (ASTM D 1142-95 1995). It uses a chilled mirror or dew point tester. This approach is labour intensive. Although automated continuous units are available, they are expensive and, unlike GCs, are currently not part of most existing gas transmission facilities

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**Fig. 1** A phase diagram for a typical natural gas (source: Shane 2000, Emerson Process Management, class # 5300)



(NGC-GPA 2005). In addition, the determination of the phase envelope or the cricondentherm would be difficult using this method since it is a periodic spot checking only. The indirect method uses a GC for compositional analysis in conjunction with an EOS to estimate the dew point as well as the cricondentherm and phase envelope if desired. As the HCDP is the condition when the heavy components begin to drop out into the liquid phase, the accurate measurement of the heavier components is critical for meaningful determination of the HCDP. The composition of the pipeline gas for custody metering is determined by the use of GCs, most of these analyzers are generally C6+ and a few are C9+ design (Jack 2010). The GC C6+ design measures the individual hydrocarbons up to normal-pentane using GPA 2261 (2000) procedure and then report the heavier components as a combined C6+ measurement.

In the absence of detailed analytical data for hydrocarbon plus fractions in a hydrocarbon mixture, erroneous predictions and conclusions can result if the plus fraction is used directly as a single component in the mixture phase behaviour calculations. Numerous authors have indicated that these errors can be substantially reduced by splitting or breaking down the plus fraction into a manageable number of fractions for equation of state calculations.

For energy calculation and HCDP calculation, many gas processors and end-users are now applying equation of state, either a Peng–Robinson (PR) or Soave–Redlich–Kwong (SRK) equation of state, to pipeline gas composition; the C6+ component is split into a fixed ratio of *n*-hexane, *n*-heptane and *n*-octane. Some commonly used percentage C6+ composition splits, based on empirical studies of most pipeline gases, are published in a GPA

standard (NGC-GPA 2005): GPA 60 % C6, 30 % C7, 10 % C8; Daniels 47 % C6, 36 % C7, 17 % C8; GPA 50 % C6, 25 % C7, 25 % C8. Application of any of these fixed ratios for a particular delivery point of natural gas may not be a truly representative of the measured gas because the specific gravity of C6+ generated with the fixed ratios may likely deviate from that of the measured gas. Even with the most recent approach, used by gas processors and end-users to determine the percentage characterization of C6+ for a given pipeline, which is by taken the weighted average compositions of the regional supply on that pipeline, the ability of the average characterization to reflect the true composition of a particular gas within a region greatly depends on the variance of the individual components of all gases throughout the region (NGC-GPA 2005). Though, the traditional C6+ analysis provides insufficient data for a valid HCDP calculation (Ernst and Pettigrew 2005), improving on the repeatability of the prediction capability of the C6+ characterisation is essential.

This work presents a very simple and practical procedure for extending the percentage distribution of C6+ composition of pipeline gas into C6/C7/C8 in order to improve HCDP determination. An illustrative example in which the new procedure is applied to field C6+ data is also presented. In order to show the capabilities of the new approach, results comparison of calculated HCDP as well as cricondentherm (using HYSYS® with Peng Robinson EOS) between the new approach and some common C6+ composition splits is made.

Using C6+ data for HCDP limit application on a particular pipeline gas, it is prudent that an appropriate split be employed. If we consider the specific gravity, molecular

weight, mole fraction of C6+ of a gas are known, the challenge facing the gas processor or end-user becomes one of splitting the C6+ fraction into C6/C7/C8 that can be used to predict the HCDP and phase behaviour of the gas by equation of state. Based on the observation reported by several researchers (Katz 1983; Lorenz et al. 1964; Pedersen et al. 1982; Ahmed et al. 1985) that lighter hydrocarbon systems exhibit exponential molar distribution, an equation is therefore formulated which could be used to appropriately split the C6+ data after the calculation of the “quasi-mole fraction” of the individual C6+ pseudocomponents from the application of three well-established hydrocarbon physical properties correlations.

The procedure employed to generate an appropriate percentage distribution of C6+ composition of a gas is summarized below:

- The apparent molecular weight of the C6+ composition, if characterized into C6/C7/C8, is defined mathematically by the following equation;

$$(M_a)_{C6+} = \sum_{i=6}^8 y_i M_i \tag{1}$$

- If the specific gravity of C6+ ( $\gamma_{C6+}$ ) is considered, Eq. (1) can then be expressed as:

$$\gamma_{C6+} = \frac{(M_a)_{C6+}}{M_{air}} = \sum_{i=6}^8 y_i M_i \tag{2}$$

$$\gamma_{C6+} M_{air} = \sum_{i=6}^8 y_i M_i \tag{2}$$

- Expanding the equation and inserting the value, 28.96, of the apparent molecular weight of air ( $M_{air}$ ) gives;

$$28.96\gamma_{C6+} = y_6 M_6 + y_7 M_7 + y_8 M_8 \tag{3}$$

$M_i$ , molecular weight of the  $i$ th component in the C6+;  $y_i$ , “quasi-mole fraction” of the component  $i$  in the C6+.

Though there are many correlations for estimating the molecular weight of petroleum fractions, most of which use specific gravity and boiling point as correlation parameters, three well-established hydrocarbon physical properties

correlations (Katz and Firoozabadi 1978; Ahmed 1985; Robinson and Peng 1978) have been chosen for the determination of the molecular weights of C6/C7/C8; in so doing three forms of Eq. (3) are generated. Table 1 presents the approximate molecular weight values of C6/C7/C8 from the chosen correlations.

The three forms of Eq. (3) are thus;

$$28.96\gamma_{C6+} = 84y_6 + 96y_7 + 107y_8 \tag{4}$$

$$28.96\gamma_{C6+} = 85y_6 + 94y_7 + 106y_8 \tag{5}$$

$$28.96\gamma_{C6+} = 86y_6 + 100y_7 + 114y_8 \tag{6}$$

Note: Katz and Firoozabadi (1978) proposed a set of tabulated properties. Ahmed (1985) correlated Katz–Firoozabadi-tabulated physical properties with the number of carbon atoms of the fraction. The generalized equation is of the form:

$$\theta = a_1 + a_2n + a_3n^2 + a_4n^3 + (a_5/n) \tag{7}$$

where  $\theta$  = any physical properties, but for this work, it represents the molecular weight;  $n$  = number of carbon atoms, i.e. 6,7, ..., 45;  $a_1$ – $a_5$  = coefficients of the equation given Table 2.

Robinson and Peng (1978) put forward a correlation for the determination of the molecular weight of the paraffinic group of hydrocarbon system. The equation is of the form;

$$\text{For Paraffinic group : } MW = 14.026n + 2.016 \tag{8}$$

MW = molecular weight;  $n$  = number of carbon atoms.

Equation (4) through (6) can be written in matrix form as follows;

$$\begin{bmatrix} 84 & 96 & 107 \\ 85 & 94 & 106 \\ 86 & 100 & 114 \end{bmatrix} \begin{bmatrix} y_6 \\ y_7 \\ y_8 \end{bmatrix} = \begin{bmatrix} 28.96\gamma_{C6+} \\ 28.96\gamma_{C6+} \\ 28.96\gamma_{C6+} \end{bmatrix} \tag{9}$$

- To solve the matrix expression requires that the specific gravity of the C6+ must be known.
- The calculated “quasi-mole fraction”, that is  $\gamma_6, \gamma_7, \gamma_8$ , of the individual C6+ pseudocomponents from the application of three well-established hydrocarbon physical properties correlations are then expressed in an exponential molar distribution percentage pattern. The equation is of the form;

**Table 1** Approximate values of the molecular weight of C6/C7/C8

Katz and Firoozabadi (1978)	Component	C6	C7	C8
	Molecular weight, $M$	84	96	107
Ahmed (1985)	Component	C6	C7	C8
	Molecular weight, $M$	85	94	106
Robinson and Peng (1978)	Component	C6	C7	C8
	Molecular weight, $M$	86	100	114

**Table 2** Coefficients of Ahmed for calculating hydrocarbon molecular weight

$\theta$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$
Molecular weight, $M$	-131.11375	24.96156	-0.34079022	$2.4941184 \times 10^{-3}$	468.32575

$$\% \text{ mole distribution, } z_i = \frac{\text{Exp}(y_i)}{\sum_{i=6}^8 (\text{Exp}(y_i))} \times 100 \quad (10)$$

Equations (9) and (10) are therefore the proposed equations to be used for the splitting of C6+ composition of any given pipeline gas provided that the C6+ specific gravity is known.

### Application to field C6+ data

The first example uses a gas sample from Queensland Gas Pipeline reported by Jemena Asset Management (Queensland Gas Pipeline Measurement Manual, GTS-199-PR-GM-001 2011). The gas sample was analyzed online by a C6+ gas chromatography for its bulk molecular compositions. The sample information, gas molecular compositions and sample properties are presented in Table 3. The C6+ has a 0.0304 mol%. If we assume the specific gravity of 0.6245 reported to be that of the C6+ data, then the molar percentage distribution of the C6+ data can be determined using Eqs. (9) and (10). Equation (9) therefore becomes;

$$\begin{bmatrix} 84 & 96 & 107 \\ 85 & 94 & 106 \\ 86 & 100 & 114 \end{bmatrix} \begin{bmatrix} y_6 \\ y_7 \\ y_8 \end{bmatrix} = \begin{bmatrix} 28.96(0.625) \\ 28.96(0.625) \\ 28.96(0.625) \end{bmatrix}$$

$$\begin{bmatrix} 84 & 96 & 107 \\ 85 & 94 & 106 \\ 86 & 100 & 114 \end{bmatrix} \begin{bmatrix} y_6 \\ y_7 \\ y_8 \end{bmatrix} = \begin{bmatrix} 18.085 \\ 18.085 \\ 18.085 \end{bmatrix}$$

Using MATLAB, the above matrix algebra can be solved. Thus, the results of the ‘quasi-mole’ fraction, i.e.

**Table 3** Queensland gas pipeline gas sample

Components	Composition, mol%
N <sub>2</sub>	2.4910
CO <sub>2</sub>	0.9960
C1	89.9510
C2	4.9800
C3	0.9940
<i>i</i> -C4	0.3080
<i>n</i> -C4	0.3090
<i>i</i> -C5	0.1001
<i>n</i> -C5	0.1002
C6+	0.0304
Specific gravity (air = 1)	0.6245

$\gamma_6, \gamma_7, \gamma_8$  are 0.2133, 0.1919, -0.1706 respectively. To obtain the actual percentage molar distribution of the C6+ composition, the ‘quasi-mole’ fraction are expressed in exponential pattern using Eq. (10);

$$z_i = \frac{\text{Exp}(y_i)}{\sum_{i=6}^8 (\text{Exp}(y_i))} \times 100$$

$$\sum_{i=6}^8 (\text{Exp}(y_i)) = \text{Exp}(y_6) + \text{Exp}(y_7) + \text{Exp}(y_8)$$

$$= \text{Exp}(0.2133) + \text{Exp}(0.1919) + \text{Exp}(-0.1706)$$

$$= 1.2378 + 1.2115 + 0.8432$$

$$= 3.2925$$

Thus, the percentage split of the C6+ components are;

$$z_6 = \frac{1.2378}{3.2925} \times 100 = 37.593 \% \approx 37.59 \%$$

$$z_7 = \frac{1.2115}{3.2925} \times 100 = 36.798 \% \approx 36.80 \%$$

$$z_8 = \frac{0.8432}{3.2925} \times 100 = 25.609 \% \approx 25.61 \%$$

The percentage distribution of the C6+ component of the gas sample from Queensland Gas Pipeline with specific gravity of 0.6245 is approximately; 37.59 % C6, 36.80 % C7, and 25.61 % C8. Thus, Table 4 illustrates the resulting distributions of the concentration of hexanes, heptanes, octanes using common composition splits (of the C6+ percentage mole of 0.0304) similar to using a company, contract or historical characterization assumption, and the new method.

For the C6+ data compositions in Table 4, calculation of the HCDPs as well as cricondentherm, using HYSYS<sup>®</sup> with Peng Robinson EOS, were performed. (Note that: in the case of C6+ data with no split, the C6+ is treated as a single cut; its normal boiling point of 311.98 °F R was estimated using the correlation by Riazi and Daubert (1987). The predicted HCDPs, at a pipeline pressure of 215 psia, for the five C6+ data are presented in Table 5. A comparison of the HCDP results, at the pipeline operating pressure, shows a slight variance between the new method and the traditional C6+ split ratios (Daniels 47/35/17, GPA 50/25/25 and the GPA 60/30/10). The predicted HCDP ranges from as low as -40 °F for the C6+ data with no split ratio to 2.861 °F for the new split method. The HCDP results for Daniels 47/35/17, GPA 50/25/25 and the new split method are -2.151, 1.038 and 2.861 °F respectively; this shows that the new split method has the maximum HCDP value.

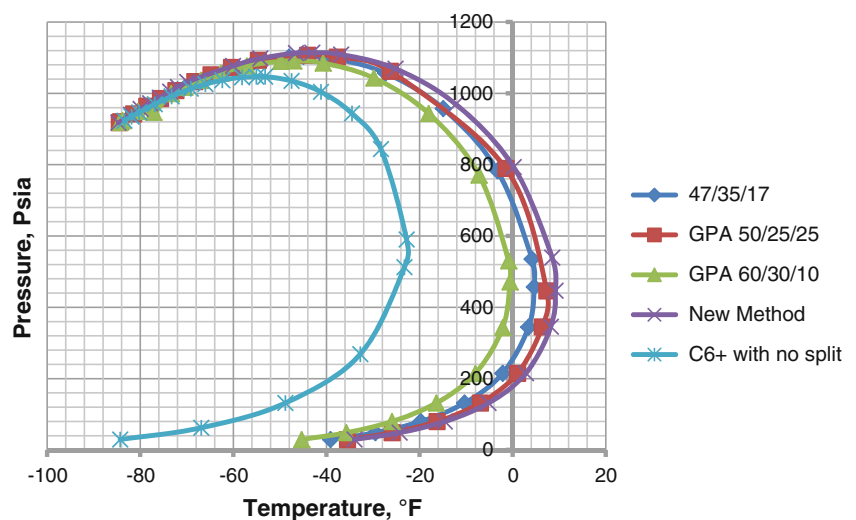
**Table 4** Illustration of the resulting distribution of C6/C7/C8 for various common splits

Component	C6+ data with no split (composition, mol%)	C6+ data with the new method split ratio (composition, mol%)	C6+ data with 47/35/17 split ratio (composition, mol%)	C6+ data with GPA 2261 split ratio (50/25/25) (composition, mol%)	C6+ data with GPA 2261 split ratio (60/30/10) (composition, mol%)
N <sub>2</sub>	2.4910	2.4910	2.4910	2.4910	2.4910
CO <sub>2</sub>	0.9960	0.9960	0.9960	0.9960	0.9960
C1	89.9510	89.9510	89.9510	89.9510	89.9510
C2	4.9800	4.9800	4.9800	4.9800	4.9800
C3	0.9940	0.9940	0.9940	0.9940	0.9940
<i>i</i> -C4	0.3080	0.3080	0.3080	0.3080	0.3080
<i>n</i> -C4	0.3090	0.3090	0.3090	0.3090	0.3090
<i>i</i> -C5	0.1001	0.1001	0.1001	0.1001	0.1001
<i>n</i> -C5	0.1002	0.1002	0.1002	0.1002	0.1002
C6+	0.0304	–	–	–	–
C6		0.01143	0.014432	0.0152	0.01824
C7		0.01130	0.010747	0.0076	0.00912
C8		0.00786	0.00522	0.0076	0.00304
Total	100	100	100	100	100

**Table 5** Comparisons of hydrocarbon dew point predictions and cricondenthem along with cricondenbar

	C6+ data with no split	C6+ data with 47/35/17 split ratio	C6+ data with the new method split	C6+ data with GPA 2261 split ratio (50/25/25)	C6+ data with GPA 2261 split ratio (60/30/10)
Hydrocarbon dew point prediction at 215 psia (°F)	–40	–2.151	2.861	1.038	–8.0140
Cricondenthem (°F)	–22.78	4.627	9.204	7.334	–0.5866
Cricondenbar (psia)	1,047	1,104	1,114	1,107	1,091

**Fig. 2** Different phase envelopes, dew point curve portions, using different C6+ characterisation methods of a pipeline gas with specific gravity of 0.6245



Also, comparison of the predicted cricondenthem using the various C6+ characterisation approaches shows significant variation. Table 5 also presents the comparison of

the predicted cricondenthem values. Figure 2 shows the comparison of the phase envelopes (of the dew point curve portions) for the various C6+ data compositions. The

**Table 6** Typical union gas sample

Components	Composition, mol%
N <sub>2</sub>	2.4910
CO <sub>2</sub>	0.9960
O <sub>2</sub>	0.02
C1	95.2
C2	2.50
C3	0.20
<i>i</i> -C4	0.03
<i>n</i> -C4	0.03
<i>i</i> -C5	0.01
<i>n</i> -C5	0.01
C6+	0.01
Specific gravity (air = 1)	0.58

phase envelope of the new split ratio is above those of the traditional C6+ split ratios (Daniels 47/35/17, GPA 50/25/25, and GPA 60/30/10). The worst case seems to be the C6+ with no split which is far below all split methods (Table 5).

Performing similar calculations, using Eqs. (9) and (10), for the typical pipeline gas on the Union Gas system given in Table 6 (Chemical Composition of Natural Gas (2005, <http://www.uniongas.com>) with specific gravity of 0.58 gives the following C6+ percentage distributions; (37.303 % C6, 36.568 % C7, 26.130 % C8. The ratio of the split of the C6+ component of the typical pipeline gas

with specific gravity of 0.58 is approximately; 37.3 % C6, 36.6 % C7, and 26.1 % C8. Thus, Table 7 presents the resulting distributions of the concentration of hexanes, heptanes, octanes and nonanes using common composition splits (of the C6+ percentage mole of 0.010) similar to using a company, contract or historical characterization assumption, and the new method.

Figure 3 shows the comparison of the phase envelopes (of the dew point curve portions) for the various split methods of the C6+ data compositions of the Union Gas system. The phase envelope of the new split ratio gives the maximum cricondenterm value. There is a slight difference in the phase envelope predicted using GPA 50/25/25, Daniels 47/35/17 and the new split ratio. However, for this example, the GPA 50/25/25 dew point curve tends to be closer to that of the new split ratio than the dew point curve predicted by the Daniels 47/35/17 split ratio. The phase envelope of the C6+ data with no split appears to be far away from that of the other split methods.

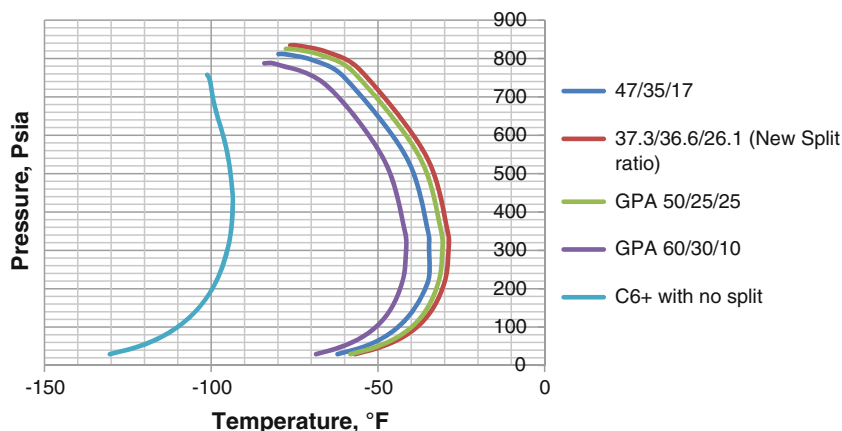
## Conclusions

Monitoring of HCDP of a pipeline gas is very important in order to ensure that high quality gas is supplied by gas processor/pipeline operators to the end-users. It is prudent to use an appropriate split of the C6+ composition when applying a HCDP limit using C6+ data. Therefore, a very simple and practical procedure for the estimation of the

**Table 7** Illustration of the resulting distribution of C6/C7/C8 for various common splits

Component	C6+ data with no split (composition, mol%)	C6+ data with 47/35/17 split ratio (composition, mol%)	C6+ data with the new method split ratio (37.3/36.6/26.1) (composition, mol%)	C6+ data with GPA 2261 split ratio (50/25/25) (composition, mol%)	C6+ data with GPA 2261 split ratio (60/30/10) (composition, mol%)
N <sub>2</sub>	2.4910	1.3	1.3	1.3	1.3
CO <sub>2</sub>	0.9960	0.70	0.70	0.70	0.70
O <sub>2</sub>	0.02	0.02	0.02	0.02	0.02
C1	95.2	95.2	95.2	95.2	95.2
C2	2.50	2.50	2.50	2.50	2.50
C3	0.20	0.20	0.20	0.20	0.20
<i>i</i> -C4	0.03	0.03	0.03	0.03	0.03
<i>n</i> -C4	0.03	0.03	0.03	0.03	0.03
<i>i</i> -C5	0.01	0.01	0.01	0.01	0.01
<i>n</i> -C5	0.01	0.01	0.01	0.01	0.01
C6+	0.01				
C6		0.004747	0.00373	0.005	0.006
C7		0.003535	0.00366	0.0025	0.003
C8		0.001717	0.00261	0.0025	0.001
Total	100	100	100	100	100

**Fig. 3** Different phase envelopes, dew point curve portions, using different C6+ characterisation of the union gas system with specific gravity of 0.58



percentage distribution of C6+ composition for any particular pipeline gas with a known C6+ specific gravity in order to improve HCDP determination has been formulated. The appropriate percentage distribution of C6+ pipeline gas composition may hover around 37–38 % C6, 36–37 % C7 and 24–26 % C8. Based on the field C6+ data examples, the new split method has the maximum HCDP value when compared to the HCDP predictions of some common C6+ split ratios. Application of this new method to split the C6+ data may therefore represent and also enhance the prediction of HCDP of any particular gas.

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