Development of Accurate Methods for Predicting Hydrocarbon Dew Points

FINAL REPORT

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Abstract

Many different calculational methods are available for computing hydrocarbon dew points of natural gas streams from gas chromatograph analyses. These various methods often produce results that are inconsistent from one method to another, and for some gas streams, have been found to significantly underpredict hydrocarbon dew point temperatures. Several approaches have been evaluated for predicting hydrocarbon dew points of natural gas streams using compositional data available from field gas chromatographs, particularly GC data reported as a lumped C_{6+} fraction. The primary objectives were to evaluate the accuracy of several C_{6+} characterization methods used with generic equations of state to predict dew points for a wide range of production, transmission, and distribution gases, and to identify the characterization methods that produce the most accurate predictions for this range of gas compositions. Characterizations were tested using the GERG-2004 equation of state, and the Peng-Robinson and Soave-Redlich-Kwong (SRK) cubic equations of state.

Approximately 1800 comparisons were performed using the various characterization methods, equations of state, and documented gas compositions and dew points. The SRK equation of state was found to have advantages over the other equations in predicting dew points. An adaptation of a Gaussian characterization method used by the petroleum industry was recommended, as it best simulated actual distributions of hexane and heavier components. A method of adjusting the Gaussian characterizations to predict dew points within ±5°F was pursued. However, limited experimental dew point data from the literature prevented the research from successfully creating a generally acceptable method. It is recommended that users gather field dew point data for their own gas streams to tune their characterizations and predict the most accurate dew points using the Gauss-gamma characterization method. Additional research is needed to collect more dew point data with defensible uncertainties to resolve remaining hydrocarbon dew point prediction issues.

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Acknowledgments

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1. INTRODUCTION

1.1 BACKGROUND AND INDUSTRY NEEDS

Hydrocarbon dew points are often used as a measure of the quality of a natural gas stream, and as a criterion for assessing compliance with transportation tariffs. Accurate hydrocarbon dew points will be crucial in the future in accommodating the introduction of LNG and marginal gas supplies into the natural gas transmission network. The hydrocarbon dew point of a gas stream can be determined either experimentally, using a chilled mirror dew point tester, or analytically, using composition data from a gas chromatograph and an equation-of-state model.

The use of data from an on-site gas chromatograph (GC) is often faster and more convenient, since portable chilled mirror dew point testers must be taken to a particular test site and used by a trained operator. Many different methods are available to the gas industry for calculating hydrocarbon dew points from GC analyses. These include different equations of state, different software packages, and different characterizations used to complete "extended" GC analyses of the heavy hydrocarbon components in the gas blend. Unfortunately, these various calculational methods often produce results that are inconsistent from one method or heavy component characterization to another. The sampling equipment heating requirements in the recent revision of the American Petroleum Institute (API) Manual of Petroleum Measurement Standards (MPMS), Chapter 14.1 (American Petroleum Institute, 2006), reflect the potential for disagreement and error between these different methods.

Clearly, there is a critical need to know how well these different approaches can predict dew points that agree with existing experimental data over the full range of natural gas mixtures handled by the gas industry. Research beginning in 2001 sought to assess the accuracy of various analytical methods used to determine the hydrocarbon dew points of production, transmission, and distribution natural gas mixtures. Initial evaluations were limited by the amount of acceptable phase behavior data available for comparisons. A small set of hydrocarbon dew point data was collected through a literature search in 2002 and 2003 and used to evaluate common methods of computing hydrocarbon dew points (George *et al.*, 2005a). The data were used to evaluate the accuracy of the Peng-Robinson and Soave-Redlich-Kwong equations of state using several different methods of characterizing heavy hydrocarbons and various commercial software packages. While a universal characterization method for the heavier hydrocarbon components in a gas blend was not identified, several methods were found to consistently produce inaccurate results. The choice of characterization method was identified as the largest source of potential error, much more so than the equation of state or software package used to compute dew points.

Research sponsored by Gas Technology Institute (GTI), Pipeline Research Council International (PRCI) and the United States Department of Energy (DOE) in 2004 and early 2005 expanded the existing database to include experimental data on test gases ranging in heating value from approximately 1,050 to 1,525 Btu/scf. The expanded database was published and made available to the natural gas research community, along with initial comparisons of the data to common equations of state (George *et al.*, 2005b; George and Burkey, 2005c). However, much work remained to determine those methods of characterizing heavy hydrocarbons that produce the most accurate dew point predictions.

The research reported here completes the evaluation of analytical dew point determination methods begun earlier under the sponsorship of GTI and PRCI through the FERC funding mechanism. The study has used the results of experiments conducted under that program, as well as experimental data published elsewhere, to help complete a study of the accuracy of common equations of state in predicting hydrocarbon dew points. The study focuses primarily on "characterization methods," methods of correctly approximating the individual percentages of the heavier hydrocarbon components in a given gas blend in order to produce the most accurate predictions.

1.2 PROJECT OBJECTIVES

The objectives of this project were as follows:

- Evaluate the accuracy of several characterization methods as used with generic equations of state in predicting hydrocarbon dew points for a wide range of production, transmission, and distribution gases, using the results of the GTI/PRCI experiments and other experimental data from the literature.
- Identify methods of characterizing heavy hydrocarbons that produce the most accurate dew point predictions for a wide range of natural gases from limited compositional data. In particular, identify characterization methods appropriate for production gases that have previously shown disagreement with results of earlier characterizations. If no existing methods are found with acceptable uncertainties, identify the information needed to derive an accurate characterization method for gases of interest.
- Provide guidance for the preparation of an American Petroleum Institute standard for calculating hydrocarbon dew points.

A common technique in the petroleum industry is to tune the properties of each component used in a heavy hydrocarbon characterization, so that calculations with the new component distribution and component properties best match observed data. Unfortunately, not all equation of state software packages available to the natural gas industry allow the user to tune component properties. Instead, the approach of this study is to find characterizations of normal paraffins that best reproduce observed hydrocarbon dew points using standard properties and parameters in most EOS software. Therefore, the development of improved interaction parameters or new equations of state for HDP predictions were not included in the scope of work.

1.3 TECHNICAL APPROACH

This work was divided into several phases, each of which is discussed in a separate chapter of the report. Hydrocarbon dew points have been calculated using two common equations of state and several methods for characterizing the distribution of heavy hydrocarbons beyond hexane (C_6). The results have been compared to the data obtained in the experiments sponsored by GTI/PRCI and DOE, and data gathered from the open literature. The comparisons of calculated and experimental data have been used to identify the most accurate calculational methods, and an approach to select the most accurate methods has been created. This approach will be recommended to the API Chapter 14.1 Working Group and the natural gas industry.

Phase 1A of the project, discussed in Chapter 2, involved a literature review of technical journals, conference proceedings, and other literature sources to gather several types of data. A search was performed for additional experimental measurements of natural gas hydrocarbon dew points (HDPs) to be compared to calculated HDP values later in the project. A brief literature review was performed as part of the previous GTI/PRCI-sponsored research (George *et al.*, 2005a), but this only produced data on a limited number of gas compositions and measured pressures. Chapter 2 documents the literature search during this project for other HDP data on gases of interest to the production, transmission, and distribution industries. Unfortunately, despite an extensive search, only two new datasets were found with the necessary uncertainty information, and those toward the very end of the project. The data from the original literature review and the results of the GTI/PRCI-sponsored research (George *et al.*, 2005a and 2005b; George and Burkey, 2005c) were combined to form a "reference dataset" for the characterization methods tested here. The reference dataset was used to develop the characterization method recommended in this report; the new data discovered at the end of the project were used to validate the method and assess its uncertainty.

To investigate possible causes of errors in predicted dew points, Phase 1B reviewed the data used to derive the parameters in the original Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) equations of state. These data were used to determine the range of validity of these common equations of state, and possible uncertainties in dew points computed using them. Where values calculated from these equations disagree with experimental HDP data, the results of this search helped to determine the cause. The results of this study are described in Chapter 3.

Phase 2 of the project, covered in Chapter 4, describes work to identify the characterization methods with the most potential for accurate HDP prediction. "Characterization methods" are methods of assigning amounts of heavy hydrocarbons (usually C_{6+} components) to a natural gas mixture when the true and complete C_{6+} distribution is unknown. During the GTI/PRCI-sponsored research on dew point calculations, several characterization methods were evaluated, but none produced accurate HDP estimates in all cases. Those methods that accurately predicted experimental dew points in at least some cases were evaluated further during this research. A literature review was also performed for previously unknown characterization methods, to ensure that the research thoroughly evaluated the state of the art.

Chapter 5 describes the results of Phase 3 of the project, in which the PR and SRK equations of state were used with the characterization methods identified in Chapter 4 to compute HDP curves for the gas compositions in the reference dataset documented in Chapter 2. Confidence intervals on the calculated curves were found using the uncertainties in the documented gas compositions. The results were compared to the measured HDP values in the reference dataset. The accuracy of the various characterization methods have been judged based on the overlap in the confidence intervals of the calculated and measured dew points.

Chapter 6 covers Phase 4 of the project, in which the experimental and calculational comparisons have been used to try to develop a general hydrocarbon dew point prediction method for the natural gas industry. The prediction method was intended to accurately predict HDPs of a wide range of gases when compositional data are limited to C_{6+} grouped data typical of common field gas chromatographs. The method was created in part by identifying those gas compositions and HDP conditions for which the recommended characterization method(s) consistently predict experimental results most accurately. This chapter describes:

- the trial method for deriving an appropriate characterization for HDP calculations using an occasional extended analysis of a gas stream, and using this method later when extended analyses are not available;
- the minimum set of natural gas components to be included in the characterization, and threshold values of other components that require their inclusion in the characterization;
- expected uncertainties in dew point values computed using the trial method; and
- additional data and information proposed to improve the accuracy of the trial method.

Finally, Chapter 7 summarizes the findings of this report, recommends an interim method of predicting dew points using equations of state and field dew point measurements, and recommends additional work to improve the HDP prediction method and equation of state accuracy in general.

2. CREATION OF A HYDROCARBON DEW POINT REFERENCE DATASET

The overall goal of this project is to evaluate approaches for predicting natural gas hydrocarbon dew points (HDPs). Validation of any prediction method or model requires reliable data, preferably experimental data, with which to check the method results. The first phase of this project involved a review of technical journals, conference proceedings, and other literature sources to find experimental measurements of HDPs to be compared to calculated HDP values.

A limited review of industry literature was performed as part of the previous GTI/PRCI-sponsored research (George *et al.*, 2005a). However, only three useful datasets were found during that work, involving a total of 15 gas compositions with a limited range of heavy hydrocarbon content and measured pressures. The GTI/PRCI research (George *et al.*, 2005a and 2005b; George and Burkey, 2005c) produced dew point data on four additional gas compositions ranging in heating value from 1,050 to 1,525 Btu/scf. These data were unique at the time in that they include HDP data at multiple pressures for each gas composition. Still, it was desired to obtain more data to expand the reference dataset if possible.

This first section of this chapter summarizes the literature search for other HDP data on gases of interest to the production, transmission, and distribution industries. To be useful in this study, HDP data must include gas compositions, measured dew point pressures and temperatures, and stated uncertainties in these values. The uncertainty information is needed to determine whether differences in calculated and experimental HDPs are statistically significant. Unfortunately, no additional data was found during the literature search phase that met these criteria.

The data from the original literature review and the results of the GTI/PRCI-sponsored research were combined to form a reference dataset. That dataset was used to evaluate the characterization methods tested in the research and develop a correlation for a general characterization method in Chapter 6. The final reference dataset, containing a total of 45 combinations of gas composition and pressure, is described at the end of this chapter. Two new sets of dew point data, one of them similar to the data from the GTI/PRCI-sponsored research, became available toward the end of this project, well after the literature search and most other work on the project had been completed. Those data, described in Chapter 6, were not used to develop the general characterization method, but were instead used in a “validation dataset” to determine how the general characterization method would perform on gases which had not been used in its development.

2.1 RESULTS OF THE LITERATURE SURVEY FOR REFERENCE-QUALITY DATA

The literature review began with a search of relevant technical journals. A review of the journal *Fluid Phase Equilibria* identified over 80 articles published since 1975 on the topics of HDP algorithms, vapor-liquid equilibria, and experimental data on natural gases. As the study of these articles progressed, many were found to contain no relevant data, but they in turn referred to other potentially useful articles. It became evident that an exhaustive review would be far outside the scope of this project. The task was narrowed to selectively review those articles most likely to contain relevant HDP data. Appendix A contains a list of these articles, along with brief descriptions of their contents. This section lists key findings of the review.

Several publications refer to data from Hoffmann *et al.* (1953) and Pedersen *et al.* (1988), consisting of liquid condensation measurements of North Sea reservoir fluids and other natural gases. Data on amounts of liquid condensate can be extrapolated to a value of zero condensate to obtain a hydrocarbon dew point at a given pressure. Unfortunately, the compositions in these references are only explicit in hydrocarbons through hexane (C_6), with heavier components reported in terms of "lumped fractions" having measured densities and average molecular weights. This characterization is commonly used in the petroleum distillation industry when gas chromatography is not available. The lack of data on explicit C_{7+} isomers for these gas compositions, along with a lack of uncertainties in the data, makes the data unsuitable for the reference dataset. This was a common reason for the rejection of much of the data found during the literature search.

Other experimental HDP data in the literature was taken from simple hydrocarbon blends that did not represent the multi-component gases encountered in the field. For instance, the Thermodynamics Research Center at Texas A&M University maintains a database of gas properties (Skrzecz, 1997) that was reviewed for useful data on natural gases. To date, the database contains vapor-liquid equilibrium (VLE) data on binary and ternary (three-component) systems, but contains no data on multi-component systems representative of natural gases encountered by the industry. One reference (Avila *et al.*, 2002) contained HDP data for five liquefied natural gases delivered by pipelines in Spain. However, as with typical LNG compositions, the gases contained no hydrocarbons heavier than hexane. Since the characterization of heavy hydrocarbons above C_6 is of primary interest in this research, the data was not useful for validating characterization methods.

Recently, the GERG-2004 equation of state (Wagner, 2005) was developed in Germany for use in computing gas, liquid, and VLE conditions, including hydrocarbon dew points. Personnel from the National Institute of Standards and Technology (NIST) in the U.S. assisted in the development of this equation of state, and discussed the origins of its supporting data with SwRI personnel (Lemmon, 2006). The majority of the hydrocarbon dew point data used to create GERG-2004 was gathered on prepared gas blends containing only two or three hydrocarbon compounds, or in a few cases, five hydrocarbons. Since these simple prepared blends are not representative of production, transmission or distribution gases, they could not be included in the reference dataset.

Shariati *et al.* (1999) contains data on 15 different gas compositions, including seven petroleum fractions, but these datasets were either measurements of the bubble point (instead of the dew point) or data on compositions that were lumped into fractions above C_6, rather than explicit compositions. Sivaraman *et al.* (2005) reported phase change data on natural gases that either contained only hydrocarbons through C_5, or that reported lumped "plus fraction" compositions instead of explicit amounts of C_7 and heavier components. Dohrn and Brunner (1995) published a review of 380 separate papers containing phase equilibria data, including a table of compositions, experimental methods for gathering data, and temperature and pressure conditions. Of these, only one paper contained phase data on natural gases, but the data was limited to gases high in hydrogen sulfide, and was again of no interest to this work.

It was concluded from the literature search that hydrocarbon dew point data of the quality needed for this study – that is, data including explicit compositional data beyond hexane, with uncertainties in composition, pressure and temperature – is very limited. At the time the reference dataset listed in the next section was created, the four datasets identified and produced during the GTI/PRCI-sponsored research were the only data known to meet these criteria.

2.2 CONTENTS OF THE REFERENCE DATASET

This section presents the hydrocarbon dew point data used to identify accurate characterization methods for this study. Three of these datasets were identified during a literature review for the GTI/PRCI-sponsored research (George *et al.*, 2005a), while the fourth was developed during testing for eventual use in this work (George *et al.*, 2005b; George and Burkey, 2005c). Each dataset is tabulated here, and its origins are briefly described. A comparison of the entire dataset to gases and pipeline conditions of interest to the natural gas industry is shown at the end of the chapter.

2.2.1 ARCO Research on Chilled Mirror Accuracy

Warner *et* al. (2001) presented the results of research on the comparative accuracy of measured and calculated hydrocarbon dew points. Two round robin studies were conducted as part of that research: (1) an extended GC analysis study comparing the results of extended natural gas analyses performed at various commercial laboratories, and (2) a study investigating the results of hydrocarbon dew point measurements made using a dew scope. For the ten gases tested in the study, the paper compared hydrocarbon dew points calculated using an equation of state and an extended GC analysis of each gas with hydrocarbon dew points measured on the same gas with a Bureau of Mines chilled mirror device at a single pressure.

Compositions with uncertainties and measured dew point data with uncertainties were available for three of the gases, making them appropriate for the reference dataset. The three compositions of interest are shown in Table 2-1, along with measured dew points and uncertainties. Note that for C_6 and heavier hydrocarbons, the components are listed as “hexanes,” “heptanes,” and so on, suggesting that these amounts contain both normal alkanes and non-normal hydrocarbons of the same carbon number. Since more detailed compositions were not available, it was necessary for some characterizations to assume that the entire component was composed solely of the normal alkane associated with that carbon number. This procedure would be recommended for use with EOS software packages that contain only data for the normal isomers.

The ARCO research results showed that the combined bias and precision uncertainty of dew points determined with the chilled mirror, including measurements by several different operators with different levels of training, was on the order of ±2.4ºF under laboratory conditions. The accuracy and repeatability values for measurements from most individual dew scope users were found to be smaller than this value. By comparison, the reproducibility of HDP values calculated from extended GC analyses from the different gas laboratories in the study was ±33.3ºF, and the overall accuracy was determined to be ±33.9ºF.

Table 2-1. Gravimetric natural gas compositions and HDP measurements from the round robin study by Warner *et al.* (2001). Component values are in units of mole percent.

	Warner #2		Warner #3		Warner #4	
Compositional data	Gravimetric value	95% confidence interval	Gravimetric value	95% confidence interval	Gravimetric value	95% confidence interval
CO_2	9.439	0.094	9.465	0.095	9.449	0.094
Nitrogen	0.621	0.027	0.614	0.027	0.611	0.027
Methane	87.205	0.174	87.049	0.174	87.102	0.174
Ethane	1.853	0.096	1.863	0.097	1.860	0.097
Propane	0.439	0.014	0.450	0.014	0.447	0.014
Isobutane	0.091	0.007	0.096	0.007	0.093	0.007
n-butane	0.083	0.004	0.091	0.005	0.089	0.005
Isopentane	0.026	0.003	0.030	0.003	0.029	0.003
n-pentane	0.020	0.003	0.025	0.004	0.023	0.004
Hexanes	0.047	0.013	0.059	0.016	0.058	0.016
Heptanes	0.133	0.029	0.191	0.041	0.180	0.039
Octanes	0.036	0.013	0.058	0.021	0.051	0.019
Nonanes	0.006	0.006	0.009	0.009	0.006	0.006
Decanes	0.001	0.002	0.001	0.002	0.001	0.002
Total	100.000		100.001		99.999	
Total C_{6+}	0.223		0.318		0.296	
Total diluents	10.060		10.079		10.060	
H_v (Btu/scf)	1100.2		1105.2		1104.2	
HDP data	Measured value	95% confidence interval	Measured value	95% confidence interval	Measured value	95% confidence interval
Temp. (°F)	53.9	0.6	72.2	2.2	71.4	1.6
Pressure (psia)	564.696		564.696		564.696	

2.2.2 Gasunie Research on Potential Hydrocarbon Liquid Content

In the early 1990’s, researchers from Gasunie and Delft University of the Netherlands collaborated in experimental measurements of the behavior of hydrocarbon gases just inside the hydrocarbon phase boundary (Derks *et al.*, 1993; Voulgaris *et al.*, 1994). They documented desorption measurements of the mass of liquid that condensed from a flowing gas stream at various temperatures below the HDP. Their goal was to obtain data on the vapor/liquid equilibrium behavior of each gas and characterize the potential hydrocarbon liquid content (PHLC) of the stream – that is, the potential mass of liquid that could condense from a unit volume of flowing gas. The PHLC is defined mathematically as

$$PHLC = 10^6 \frac{LF}{1-LF} \frac{MW_L P_n}{Z_n R T_n} \quad \left\{ \frac{\text{mg}}{\text{m}^3\,\text{(normal)}} \right\} \qquad (2\text{-}1)$$

where

LF = liquefied fraction, the number of moles in the liquid phase relative to the total number of moles in both phases,

MW_L = average molecular weight of the liquid phase {kg/kmol},

P_n = normal pressure = 101.325 kPa,

T_n = normal temperature = 273.15 K,

Z_n = compressibility factor of the gas at normal pressure and temperature,

R = universal gas constant = 8.3144 kJ/kmol.

PHLC would be useful in the definition of “operational” dew points, defined as temperatures at which a predetermined quantity of liquid – beyond tariff or contract limits or harmful to the operation of compressors and equipment – would condense from a flowing gas stream. By definition, the PHLC approaches zero as conditions approach the hydrocarbon dew point from within the two-phase region. Therefore, while Derks et al. did not directly measure hydrocarbon dew points, useful HDP data can be extrapolated from their PHLC data. The study included only two well-characterized natural gas mixtures (Table 2-2), and each gas was tested at only one pressure. However, the data on these gases included uncertainties in the analytical compositions and measured temperatures, and were of sufficient quality for use in this study.

As with the Warner data, several components in the Derks compositions are given general names such as “non-normal C_7 isomers.” Since more detailed information on their composition was not available, these isomers were assigned to the normal alkane associated with the same carbon number if a detailed composition was needed. It is recommended here that this procedure be used with EOS software packages that contain only data for the normal isomers.

Table 2-2. Analytical natural gas compositions and PHLC measurements from the Gasunie study (Derks *et al.*, 1993). Component values are in units of parts per million.

	Derks gas A		Derks gas B	
Compositional data	Analytical value	95% confidence interval	Analytical value	95% confidence interval
Helium	508.4	5.9	515.5	4.9
Nitrogen	142690	1300	24579	310
Methane	810800	7200	740000	5900
CO_2	9854	150	206470	4200
Ethane	28000	400	27477	140
Propane	3917	37	4368	24
2-methylpropane	646	7.2	790.5	5.6
Butane	695.5	7.2	788.3	5.3
2,2-dimethylpropane	80.32	0.76	36.46	0.3
2-methylbutane	180.9	1.7	325	3.8
Pentane	176.4	1.6	217.7	3.2
Cyclopentane	0.7	0.3	0	0
2,2-dimethylbutane	63.53	0.65	29.24	0.57
2,3-dimethylbutane + 2-methylpentane	54.05	0.61	109.5	1.9
3-methylpentane	23.97	0.28	45.42	0.8
Hexane	66.91	0.8	87.2	1.7
Benzene	154.1	2.2	258.7	12
Cyclohexane	38.4	2	68.2	2
Non-normal C_7 isomers	55.2	1.8	96.5	3
Heptane	33.75	0.97	38.6	2.1
Methylcyclohexane	25	1	70.3	3.7
Toluene	33.1	1.4	45.4	2.6
Non-normal C_8 isomers	39.3	1.6	54.5	3.5
Octane	15.82	0.71	11.33	0.74
Non-normal C_9 isomers	33.9	1.6	28.4	2.4
Nonane	7.63	0.74	3.24	0.37
Non-normal C_{10} isomers	15.15	0.94	4.9	0.92
Decane	2.86	0.32	0.501	0.083
Non-normal C_{11} isomers	4.76	0.57	0.554	0.11
Undecane	0.959	0.11	0.095	0.019
Non-normal C_{12} isomers	1.26	0.17	0.114	0.048
Dodecane	0.318	0.048	0	0
Non-normal C_{13} isomers	0.342	0.085	0	0
Tridecane	0.105	0.033	0	0
Non-normal C_{14} isomers	0.083	0.039	0	0
Tetradecane	0.044	0.014	0	0
Pentadecane	0.0203	0.0062	0	0
Hexadecane	0.0101	0.0017	0	0
Total	998219.791		1006520.154	
Total C_{6+}	670.5714		952.6940	
Total diluents	153052.4		231564.5	
H_v (Btu/scf)	991.8		1108.8	

Table 2-2 (continued).

	Derks gas A		Derks gas B	
PHLC data at 4100 kPa	Temperature (K)	PHLC (mg/m^3)	Temperature (K)	PHLC (mg/m^3)
	277.75	21.6	263.65	27.3
	277.65	22.1	263.64	25.2
	275.15	37.6	263.24	42.1
	273.75	52.0	263.14	45.2
	273.75	52.9	262.17	94.3
	272.15	69.3	262.08	95.4
	269.65	95.0	261.23	150.7
	269.65	96.1	261.16	153.3
	268.65	113.4	261.15	159.6
	265.25	184.7	261.11	158.2
	264.65	188.5	261.11	163.3
	264.65	198.3	261.11	172.0
			261.09	157.3
			260.21	252.3
			260.18	251.4

2.2.3 EffecTech Research

A recent study by EffecTech (Cowper, 2002a) that assessed the sensitivity of calculated dew points to measured gas compositions also provided useful experimental data for the reference dataset. The study used a detailed analytical procedure that became the basis for an international standard on to analytical requirements for dew point calculations (ISO, 2006). The study quantified the errors that resulted when successive groups of heavy hydrocarbons, ranging from C_{15} to C_9, were discarded from an analytical composition used to compute dew points. The paper also included theoretical calculations to determine the minimum volume of condensate detectable by a chilled mirror device, based on the composition of the gas, the properties of visible light and the dimensions of a typical chilled mirror. These last two topics provided additional information useful in assigning uncertainties to the calculated and measured dew points in the study.

To compare the accuracy of calculational and experimental HDP methods, EffecTech measured dew point temperatures for a series of ten gases using a manual chilled mirror dew point tester, and calculated dew points using analyses of the same gases from three different types of gas chromatographs. The test gases included compositions with diluent mole percents from 2.2% to 7.5%, and C_{6+} content from 0.005% to 0.155% (Table 2-3). The tests produced dew point temperature measurements and calculations of each test gas only at the expected cricondentherm pressure, the pressure at which the maximum dew point temperature occurs over all gas pressures. The results showed that the spread between measured and calculated dew point temperatures in the study varied between 1.3 and 3.8ºC (2.3 and 10.1ºF) for each gas. Unlike the study by Warner *et al.* (2001), this study concluded that with sufficient detail and resolution, dew point calculation via GC analysis is capable of accurate results. However, to match the accuracy of a chilled mirror device would require an extended analysis through C_{11} with an accuracy of 1 ppm, well beyond the capability of current field gas chromatographs and many laboratory GCs in use by the industry.

Discussions were held with Chris Cowper, the author of the EffecTech paper, who graciously provided the measured dew points from the study and an uncertainty analysis of the data. Both the pressure and temperature data included measurement uncertainties; typical repeatability values in the temperature measurements were ±0.5ºC (±0.8ºF). [Notably, Warner *et al.* (2001) reported an overall reproducibility of ±2.3°F, but this figure includes the effects of different operators and repeat measurements.] Uncertainties in the EffecTech gas compositions were also provided, having been computed using GC calibration data and uncertainties in relative response factors. It was decided to use the data from all ten gases listed in Table 2-3 in the reference dataset. The C_9 and heavier components were tabulated only in total amounts; as with the Warner and Derks datasets, these amounts were assigned to the normal alkane of the same carbon number where required by the characterization method.

Table 2-3. Analytical natural gas compositions and HDP data from the EffecTech study (Cowper, 2002a). Component values are in units of mole percent.

	Gas 1		Gas 2		Gas 3	
Compositional data	Analytical value	95% confidence interval	Analytical value	95% confidence interval	Analytical value	95% confidence interval
Nitrogen	3.430	0.02058	2.818	0.01691	0.803	0.00482
CO_2	0.859	0.00601	0.629	0.00440	2.981	0.02087
Methane	89.992	0.26998	92.465	0.27740	85.730	0.25719
Ethane	4.061	0.02843	3.042	0.02130	7.567	0.05297
Propane	1.027	0.00719	0.600	0.00420	2.189	0.01532
i-Butane	0.172	0.00120	0.105	0.00073	0.182	0.00127
n-Butane	0.217	0.00174	0.132	0.00106	0.364	0.00291
neo-Pentane	0.005	0.00008	0.004	0.00007	0.000	0.00000
i-Pentane	0.063	0.00088	0.042	0.00058	0.061	0.00085
n-Pentane	0.056	0.00079	0.039	0.00055	0.068	0.00095
2,2-dimethyl-C_4	0.0045	0.00022	0.0042	0.00021	0.0010	0.00007
2,3-dimethyl-C_4	0.0038	0.00019	0.0032	0.00017	0.0038	0.00019
2-methyl-C_5	0.0142	0.00056	0.0116	0.00048	0.0099	0.00041
3-methyl-C_5	0.0073	0.00032	0.0064	0.00029	0.0048	0.00023
n-C_6	0.0182	0.00069	0.0165	0.00065	0.0125	0.00050
Benzene	0.0267	0.00098	0.0243	0.00092	0.0042	0.00021
Cyclohexane	0.0083	0.00035	0.0080	0.00035	0.0039	0.00019
C_7 alkanes	0.0179	0.00068	0.0219	0.00084	0.0096	0.00040
Toluene	0.0036	0.00018	0.0052	0.00025	0.0013	0.00009
Methylcyclohexane	0.0063	0.00028	0.0081	0.00035	0.0019	0.00011
C_8 alkanes	0.0045	0.00022	0.0090	0.00039	0.0014	0.00009
Total C_9	0.0016	9.9168E-05	0.0042	0.00021	0.0006	5.37822E-05
Total C_{10}	0.0002	2.73662E-05	0.0007	5.78435E-05	0.0002	2.30415E-05
Total C_{11}	1.30E-05	4.84459E-06	5.17725E-05	1.11922E-05	5.18779E-06	2.78645E-06
Total C_{12}	0		0		0	
Total	100.0000		100.0000		100.0000	
Total C_{6+}	0.1171		0.1234		0.0551	
Total diluents	4.289		3.447		3.784	
H_v (Btu/scf)	1074.4		1056.4		1144.1	
HDP data	Measured value	95% confidence interval	Measured value	95% confidence interval	Measured value	95% confidence interval
Temp. (°F)	16.7	0.9	23.9	0.9	0.5	0.9
Pressure (psia)	406.1		406.1		406.1	

Table 2-3 (continued).

	Gas 4		Gas 5		Gas 6	
Compositional data	Analytical value	95% confidence interval	Analytical value	95% confidence interval	Analytical value	95% confidence interval
Nitrogen	7.118	0.04271	3.587	0.02152	0.982	0.00589
CO$_2$	0.421	0.00295	0.153	0.00107	2.067	0.01447
Methane	86.188	0.25856	87.968	0.26390	84.750	0.25425
Ethane	4.348	0.03043	5.006	0.03504	8.525	0.05967
Propane	1.042	0.00730	1.577	0.01104	2.672	0.01871
i-Butane	0.213	0.00149	0.437	0.00306	0.295	0.00206
n-Butane	0.301	0.00241	0.733	0.00587	0.501	0.00401
neo-Pentane	0.008	0.00013	0.010	0.00016	0.000	0.00000
i-Pentane	0.111	0.00155	0.246	0.00344	0.081	0.00113
n-Pentane	0.094	0.00131	0.162	0.00227	0.078	0.00110
2,2-dimethyl-C$_4$	0.0098	0.00040	0.0077	0.00032	0.0011	0.00008
2,3-dimethyl-C$_4$	0.0054	0.00025	0.0080	0.00033	0.0039	0.00019
2-methyl-C$_5$	0.0297	0.00106	0.0397	0.00136	0.0097	0.00040
3-methyl-C$_5$	0.0163	0.00062	0.0237	0.00085	0.0047	0.00022
n-C$_6$	0.0389	0.00135	0.0092	0.00038	0.0112	0.00045
Benzene	0.0004	0.00004	0.0001	0.00002	0.0045	0.00021
Cyclohexane	0.0075	0.00032	0.0082	0.00034	0.0032	0.00016
C$_7$ alkanes	0.0347	0.00122	0.0200	0.00073	0.0075	0.00032
Toluene	0.0001	0.00002	0.0000	0.00001	0.0010	0.00007
Methylcyclohexane	0.0053	0.00024	0.0022	0.00012	0.0015	0.00009
C$_8$ alkanes	0.0059	0.00027	0.0013	0.00009	0.0007	0.00006
Total C$_9$	0.0012	0.00008	0.0001	2.08251E-05	0.0002	2.72373E-05
Total C$_{10}$	0.0002	2.49995E-05	7.08E-06	3.36031E-06	1.21783E-05	4.65735E-06
Total C$_{11}$	6.71037E-06	3.25277E-06	1.66903E-06	1.40948E-06	0	
Total C$_{12}$	1.06122E-06	1.07395E-06	0		0	
Total	100.0000		100.0000		100.0000	
Total C$_{6+}$	0.1554		0.1202		0.0492	
Total diluents	7.539		3.740		3.049	
H$_v$ (Btu/scf)	1066.0		1114.6		1160.6	

HDP data	Measured value	95% confidence interval	Measured value	95% confidence interval	Measured value	95% confidence interval
Temp. (°F)	23.9	0.9	23.0	0.9	-0.4	0.9
Pressure (psia)	406.1		406.1		406.1	

Table 2-3 (continued).

	Gas 7		Gas 8		Gas 9	
Compositional data	Analytical value	95% confidence interval	Analytical value	95% confidence interval	Analytical value	95% confidence interval
Nitrogen	0.917	0.00550	8.131	0.04878	0.983	0.00590
CO_2	4.935	0.03455	0.189	0.00132	2.266	0.01586
Methane	80.795	0.24239	83.758	0.25127	86.499	0.25950
Ethane	9.465	0.06625	4.786	0.03350	9.004	0.06303
Propane	3.020	0.02114	1.515	0.01061	1.070	0.00749
i-Butane	0.211	0.00148	0.418	0.00292	0.065	0.00045
n-Butane	0.473	0.00378	0.690	0.00552	0.091	0.00073
neo-Pentane	0.000	0.00000	0.011	0.00018	0.000	0.00000
i-Pentane	0.064	0.00089	0.232	0.00324	0.009	0.00013
n-Pentane	0.069	0.00097	0.155	0.00217	0.008	0.00012
2,2-dimethyl-C_4	0.0005	0.00005	0.0070	0.00030	0.0001	0.00002
2,3-dimethyl-C_4	0.0040	0.00020	0.0070	0.00030	0.0004	0.00004
2-methyl-C_5	0.0089	0.00037	0.0370	0.00127	0.0009	0.00007
3-methyl-C_5	0.0043	0.00021	0.0217	0.00079	0.0004	0.00004
n-C_6	0.0113	0.00046	0.0119	0.00047	0.0010	0.00008
Benzene	0.0032	0.00017	0.0002	0.00003	0.0005	0.00005
Cyclohexane	0.0035	0.00018	0.0077	0.00033	0.0003	0.00004
C_7 alkanes	0.0095	0.00039	0.0190	0.00070	0.0009	0.00007
Toluene	0.0015	0.00010	0.0000	0.00001	0.0002	0.00002
Methylcyclohexane	0.0019	0.00011	0.0021	0.00012	0.0002	0.00003
C_8 alkanes	0.0014	0.00009	0.0012	0.00008	0.0002	0.00002
Total C_9	0.0006	5.33885E-05	0.0001	1.98587E-05	0.0001	1.81874E-05
Total C_{10}	0.0001	1.49752E-05	7.13E-06	3.37359E-06	3.68E-05	9.13776E-06
Total C_{11}	3.49696E-06	2.1982E-06	1.02843E-06	1.05389E-06	1.65194E-06	1.40149E-06
Total C_{12}	0		0		0	
Total	100.0000		100.0000		100.0000	
Total C_{6+}	0.0507		0.1149		0.0052	
Total diluents	5.852		8.320		3.249	
H_v (Btu/scf)	1182.7		1088.1		1117.6	

HDP data	Measured value	95% confidence interval	Measured value	95% confidence interval	Measured value	95% confidence interval
Temp. (°F)	5.9	0.9	16.7	0.9	-47.2	0.9
Pressure (psia)	406.1		356.8		406.1	

Table 2-3 (continued).

	Gas 10	
Compositional data	Analytical value	95% confidence interval
Nitrogen	0.917	0.00550
CO_2	4.935	0.03455
Methane	80.795	0.24239
Ethane	9.465	0.06625
Propane	3.020	0.02114
i-Butane	0.211	0.00148
n-Butane	0.473	0.00378
neo-Pentane	0.000	0.00000
i-Pentane	0.064	0.00089
n-Pentane	0.069	0.00097
2,2-dimethyl-C_4	0.0005	0.00005
2,3-dimethyl-C_4	0.0040	0.00020
2-methyl-C_5	0.0089	0.00037
3-methyl-C_5	0.0043	0.00021
n-C_6	0.0113	0.00046
Benzene	0.0032	0.00017
Cyclohexane	0.0035	0.00018
C_7 alkanes	0.0095	0.00039
Toluene	0.0015	0.00010
Methylcyclohexane	0.0019	0.00011
C_8 alkanes	0.0014	0.00009
Total C_9	0.0006	5.33885E-05
Total C_{10}	0.0001	1.49752E-05
Total C_{11}	3.49696E-06	2.1982E-06
Total C_{12}	0	
Total	100.0000	
Total C_{6+}	0.0507	
Total diluents	5.852	
H_v (Btu/scf)	1182.7	
HDP data	Measured value	95% confidence interval
Temp. (°F)	-7.6	0.9
Pressure (psia)	406.1	

2.2.4 SwRI Research

Two projects to obtain qualified hydrocarbon dew point data, funded by GTI, PRCI and DOE, were performed at Southwest Research Institute from 2003 through 2005 (George *et al.*, 2005a and 2005b; George and Burkey, 2005c). Because of the scarcity of documented dew point data with uncertainties, a series of experiments was performed to measure the dew points of well-characterized natural gas blends with a range of heavy hydrocarbon content and dew point temperatures. The data from these experiments, along with the data from the ARCO, Gasunie and EffecTech research, were used to evaluate dew point calculational methods.

Comparisons of the experimental dew point data to calculational predictions revealed that both the Peng-Robinson and Soave-Redlich-Kwong equations of state tended to underpredict the hydrocarbon dew points of the gas as the line pressure and the heating value of the gas stream increased. No single combination of an equation of state and characterization method consistently predicted all the experimental dew point temperatures to within their measurement uncertainties. By far, the calculational variable with the largest influence was the method of characterizing heavy hydrocarbons. Using a C_{6+} characterization instead of a full characterization beyond C_9 was found to influence the computed dew point by over 70ºF. This was a factor of three larger than the effects of other choices in dew point calculation, including different equation of state, different software programs and different binary interaction parameters.

The gas mixtures tested were selected, with guidance from the American Petroleum Institute Chapter 14.1 Working Group, to expand the heating values and C_{6+} contents for which useful experimental data would be available. The prepared gas blends cover a range of production-grade and transmission-grade gases with heating values from 1,050 to 1,523 Btu/scf and C_{6+} fractions ranging from 0.1% to 0.8%. Similarly, the test conditions were chosen to expand the range of pressures over which useful data would be available. The SwRI data is notable in that it is the only data in the reference set to contain measurements of dew points at multiple pressures for a given gas composition, both above and below the cricondentherm. During the 2003 research, tests were performed on three different nominal gas blends; the 2005 research repeated tests on these nominal compositions and added a fourth composition. Table 2-4 through Table 2-10 list the compositions and measured dew points, with uncertainties on all quantities, for these seven data sets.

Table 2-4. Analytical natural gas compositions and HDP data for the 1,050 Btu/scf test gas of George *et al.* (2005a). Component values are in units of mole percent.

Component	Certified concentration	99.5% confidence interval	Run number	Measured temperature (ºF)	95% conf. interval (ºF)	Measured pressure (psia)	95% conf. interval (psia)
Methane	94.737	0.365	1	31.0	0.2	805.83	2.44
Ethane	2.022	0.002	2	30.2	0.2	805.23	2.47
Propane	0.746	0.001	3	32.8	0.2	804.48	2.41
Isobutane	0.299	0.001	4	33.5	0.2	803.14	2.41
N-Butane	0.302	0.001	5	34.5	0.2	607.51	6.53
Isopentane	0.151	0.001	6	35.4	0.2	607.52	6.53
N-Pentane	0.150	0.001	7	35.5	0.2	607.27	6.54
2,2-Dimethylbutane	0.001	0.002	8	35.5	0.2	606.85	6.53
2-Methylpentane	0.016	0.008	9	35.6	0.2	606.47	6.52
2,3-Dimethylbutane	0.002	0.003	10	31.0	0.2	208.66	3.19
3-Methylpentane	0.006	0.005	11	29.9	0.2	208.68	3.18
Hexane	0.032	0.011	12	31.4	0.2	208.66	3.19
Methylcyclopentane	0.001	0.002	13	36.7	0.2	208.62	3.19
Heptane	0.030	0.011	14	32.9	0.2	208.64	3.18
Methylcyclohexane	0.000	0.001	15	33.2	0.2	208.63	3.19
Octane	0.009	0.006					
Nonane	0.001	0.002					
Decane	0.001	0.002					
CO_2	0.501	0.001					
Nitrogen	0.993	0.002					
Total	100.000						
Total C_{6+}	0.099						
Total diluents	1.494						

Table 2-5. Analytical natural gas compositions and HDP data for the 1,145 Btu/scf test gas of George *et al.* (2005a). Component values are in units of mole percent.

Component	Certified concentration	99.5% confidence interval	Run number	Measured temperature (°F)	95% conf. interval (°F)	Measured pressure (psia)	95% conf. interval (psia)
Methane	85.500	0.272	1	70.1	0.2	1146.35	2.58
Ethane	4.896	0.023	2	70.7	0.2	1138.20	2.44
Propane	2.959	0.001	3	70.8	0.2	1133.93	2.52
Isobutane	0.985	0.001	4	71.7	0.2	1127.24	2.42
N-Butane	0.986	0.001	5	78.2	0.2	715.45	7.55
Isopentane	0.481	0.001	6	77.5	0.2	709.58	7.49
N-Pentane	0.494	0.001	7	78.1	0.2	707.57	7.48
2,2-Dimethylbutane	0.002	0.001	8	77.6	0.2	699.23	7.42
2-Methylpentane	0.039	0.004	9	77.5	0.2	693.83	7.34
2,3-Dimethylbutane	0.005	0.001	10	77.7	0.2	689.13	7.31
3-Methylpentane	0.015	0.002	11	59.8	0.2	256.62	3.52
Hexane	0.079	0.005	12	60.1	0.2	255.97	3.51
Methylcyclopentane	0.003	0.001	13	60.2	0.2	255.92	3.51
Heptane	0.074	0.005	14	60.2	0.2	254.94	3.52
Methylcyclohexane	0.000	0.000	15	45.75	0.45	99.65	2.61
Octane	0.022	0.003					
Nonane	0.003	0.001					
Decane	0.003	0.001					
CO_2	0.984	0.001					
Nitrogen	2.432	0.002					
Total	99.961						
Total C_{6+}	0.245						
Total diluents	3.416						

Table 2-6. Analytical natural gas compositions and HDP data for the 1,325 Btu/scf test gas of George *et al.* (2005a). Component values are in units of mole percent.

Component	Certified concentration	99.5% confidence interval	Run number	Measured temperature (°F)	95% conf. interval (°F)	Measured pressure (psia)	95% conf. interval (psia)
Methane	69.818	0.619	1	137.0	0.2	1261.13	2.73
Ethane	9.093	0.003	2	138.4	0.2	1244.81	2.63
Propane	6.003	0.002	3	138.6	0.2	1229.38	2.53
Isobutane	2.998	0.002	4	131.0	0.2	860.40	2.76
N-Butane	2.999	0.002	5	133.2	0.2	856.68	2.74
Isopentane	1.003	0.001	6	131.6	0.2	854.04	2.51
N-Pentane	1.005	0.001	7	131.7	0.2	846.00	2.72
2,2-Dimethylbutane	0.002	0.001	8	132.0	0.2	845.17	2.55
2-Methylpentane	0.064	0.007	9	115.8	0.2	406.32	4.76
2,3-Dimethylbutane	0.008	0.002	10	115.5	0.2	402.99	4.73
3-Methylpentane	0.025	0.004	11	116.4	0.2	398.56	4.65
Hexane	0.130	0.010	12	115.3	0.2	395.69	4.65
Methylcyclopentane	0.005	0.002	13	115.7	0.2	392.21	4.62
Benzene	0.049	0.000	14	68.9	0.2	104.64	2.62
Heptane	0.121	0.009	15	68.8	0.2	105.07	2.65
Methylcyclohexane	0.000	0.001	16	68.5	0.2	105.65	2.63
Toluene	0.050	0.000	17	68.8	0.2	105.90	2.66
Octane	0.036	0.005	18	69.0	0.2	105.95	2.63
Nonane	0.005	0.002					
Decane	0.004	0.002					
CO_2	1.520	0.002					
Nitrogen	5.060	0.004					
Total	100.000						
Total C_{6+}	0.499						
Total diluents	6.580						

Table 2-7. Analytical natural gas compositions and HDP data for the 1,050 Btu/scf test gas of George *et al.* (2005b). Component values are in units of mole percent.

Component	Certified concentration	99.5% confidence interval	Run number	Measured temperature (ºF)	Measured pressure (psia)
Methane	94.748	0.131000	1	22.6	809.5
Ethane	1.997	0.000697	2	22.8	809.5
Propane	0.756	0.000475	3	23.0	808.5
Isobutane	0.301	0.000361	4	23.0	806.5
N-Butane	0.297	0.000359	5	24.3	805.5
Isopentane	0.150	0.000290	6	24.0	812.5
N-Pentane	0.150	0.000290	7	24.2	820.5
2,2-Dimethylbutane	0.00062	0.000552	8	29.1	598.5
2-Methylpentane	0.01602	0.002795	9	28.6	619.0
2,3-Dimethylbutane	0.00211	0.001015	10	28.5	616.5
3-Methylpentane	0.00625	0.001746	11	29.6	614.5
Hexane	0.03271	0.003993	12	29.3	612.5
Methylcyclopentane	0.00136	0.000815	13	29.5	611.5
Heptane	0.03047	0.003854	14	30.2	466.4
Methylcyclohexane	0.00012	0.000238	***15***	***21.8***	***455.4***
Octane	0.00896	0.002089	***16***	***22.1***	***463.4***
Nonane	0.00134	0.000810	17	28.3	465.4
Decane	0.00104	0.000710	18	28.6	465.3
CO$_2$	0.503	0.000476	19	26.5	456.3
Nitrogen	0.997	0.000754	20	26.5	469.3
Total	100.000		21	21.4	215.9
Total C$_{6+}$	0.101		22	21.8	216.0
Total diluents	1.500		23	21.6	216.0
			24	21.0	215.7
Data points 15 and 16 were judged to be outliers and removed from the final dataset.			25	21.2	215.8
			26	20.3	215.8
			27	29.6	392.2
			28	27.7	393.3
			29	30.0	390.7
			30	28.9	389.8
95% confidence interval on measured pressures	6 psia		31	28.4	390.1
			32	28.6	389.8
			33	22.7	809.5
95% confidence interval on measured temperatures	≤2.2ºF		34	23.9	819.3
			35	29.9	813.3
			36	24.8	814.3
			37	25.0	813.3
			38	23.6	814.3
			39	29.3	616.3
			40	30.0	613.4
			41	29.9	613.4

Table 2-8. Analytical natural gas compositions and HDP data for the 1,145 Btu/scf test gas of George *et al.* (2005b). Component values are in units of mole percent.

Component	Certified concentration	99.5% confidence interval	Run number	Measured temperature (ºF)	Measured pressure (psia)
Methane	85.224	0.136000	1	57.2	1429.8
Ethane	4.995	0.000726	2	56.7	1433.5
Propane	2.997	0.000495	3	54.6	1444.3
Isobutane	1.005	0.000376	4	56.6	1430.4
N-Butane	1.001	0.000374	5	56.3	1425.7
Isopentane	0.503	0.000302	6	58.8	1382.9
N-Pentane	0.502	0.000302	7	89.6	706.6
2,2-Dimethylbutane	0.00155	0.000365	8	86.7	700.4
2-Methylpentane	0.03965	0.001848	9	83.6	700.2
2,3-Dimethylbutane	0.00523	0.000671	10	86.8	699.9
3-Methylpentane	0.01548	0.001155	11	87.7	699.5
Hexane	0.08096	0.002640	12	86.6	699.0
Methylcyclopentane	0.00337	0.000539	13	68.9	1164.7
Heptane	0.07542	0.002548	14	69.1	1156.1
Methylcyclohexane	0.00029	0.000157	15	70.4	1162.4
Octane	0.02217	0.001382	16	70.5	1150.7
Nonane	0.00333	0.000535	17	70.1	1151.6
Decane	0.00256	0.000470	18	70.6	1152.1
CO_2	1.006	0.000496	19	67.5	266.1
Oxygen	0.011	0.000003	20	67.4	265.9
Nitrogen	2.506	0.000783	21	66.3	265.8
Total	100.000		22	66.9	265.7
Total C_{6+}	0.250		23	67.6	265.8
Total diluents	3.523		24	68.5	265.8
			25	80.5	748.0
95% confidence interval			26	80.3	739.5
on measured pressures	6 psia		27	80.2	738.0
			28	85.3	744.9
95% confidence interval			29	87.8	749.3
on measured temperatures	≤2.2ºF		30	89.2	740.3
			31	64.7	267.0
			32	67.6	268.0
			33	53.5	159.7
			34	54.4	159.9
			35	54.6	159.8
			36	54.1	159.8
			37	54.6	159.9
			38	54.4	160.0

Table 2-9. Analytical natural gas compositions and HDP data for the 1,325 Btu/scf test gas of George and Burkey (2005c). Component values are in units of mole percent.

Component	Certified concentration	99.5% confidence interval	Run number	Measured temperature (°F)	Measured pressure (psia)
Methane	69.410	0.210000	*1*	*106.5*	*399.6*
Ethane	9.222	0.001120	2	109.5	399.8
Propane	6.117	0.000763	3	110.7	399.7
Isobutane	3.028	0.000579	4	110.8	399.8
N-Butane	3.022	0.000577	5	110.8	399.7
Isopentane	1.008	0.000465	6	111.7	399.6
N-Pentane	1.016	0.000466	7	132.3	852.4
2,2-Dimethylbutane	0.00250	0.000443	8	132.1	858.1
2-Methylpentane	0.06408	0.002243	9	132.5	851.1
2,3-Dimethylbutane	0.00846	0.000815	10	132.0	853.5
3-Methylpentane	0.02502	0.001402	11	131.0	849.4
Hexane	0.13082	0.003205	12	131.4	851.1
Methylcyclopentane	0.00545	0.000654	13	136.7	1248.4
Benzene	0.049	0.000043	14	136.8	1248.6
Heptane	0.12187	0.003094	15	137.2	1249.5
Methylcyclohexane	0.00046	0.000191	16	142.2	1251.1
Toluene	0.047	0.000037	17	145.6	1250.3
Octane	0.03582	0.001677	18	144.1	1251.2
Nonane	0.00538	0.000650	19	142.4	1250.4
Decane	0.00414	0.000570	20	131.9	854.4
CO_2	1.556	0.00076	21	109.4	398.7
Nitrogen	5.121	0.00120	22	109.6	399.2
Total	100.000		*23*	*123.9*	*98.8*
Total C_{6+}	0.500		24	64.8	98.7
Total diluents	6.677		25	65.1	98.5
			26	65.2	98.6
Data points 1 and 23 were judged to be outliers and removed from the final dataset.			27	65.0	98.5
			28	65.0	98.5
			29	65.0	98.5
95% confidence interval on measured pressures	6 psia				
95% confidence interval on measured temperatures	≤1.6°F				

Table 2-10. Analytical natural gas compositions and HDP data for the 1,523 Btu/scf test gas of George and Burkey (2005c). Component values are in units of mole percent.

Component	Certified concentration	99.5% confidence interval	Analyzed concentration (500 psia post-test)	95% confidence interval	Run number	Measured temperature (ºF)	Measured pressure (psia)
Methane	65.529	1.069000	65.5485	1.964	1	152.1	499.4
Ethane	10.228	0.005700	10.3483	0.316	2	152.9	500.0
Propane	7.907	0.003880	7.9513	0.239	3	156.4	498.6
Isobutane	2.101	0.002970	2.0712	0.022	4	154.7	496.7
N-Butane	6.207	0.002940	6.1480	0.066	5	155.2	499.8
Isopentane	1.810	0.002370	1.7822	0.018	6	155.3	496.9
N-Pentane	2.212	0.002370	2.1872	0.023	7	174.4	999.6
2,3-dimethylbutane			0.0064	0.00012	8	176.9	1000.3
3-methylpentane			0.0055	0.0004	9	176.1	998.6
Hexane	0.382	0.001890	0.3733	0.0058	10	175.7	998.7
Methylcyclopentane			0.0124	0.00070	11	174.9	999.5
Benzene	0.102	0.000219	0.0988	0.00173	12	174.0	999.8
Heptane	0.136	0.001700	0.1364	0.00264	13	107.1	122.1
Toluene	0.100	0.000185	0.0948	0.00275	14	105.4	122.0
Methylcyclohexane			0.0002	0.00004	15	104.1	122.0
Octane	0.060	0.000147	0.0591	0.00191	16	104.3	121.7
Nonane	0.015	0.000137	0.0122	0.00098	17	106.9	121.8
Decane	0.006	0.000119	0.0071	0.00105	18	108.0	121.9
CO_2	1.200	0.00389	1.2031	0.037	19	174.9	1247.8
Nitrogen	2.005	0.00614	2.0600	0.086	*20*	*190.0*	*1245.3*
Total	100.000		100.1060		21	170.0	1247.6
Total C_{6+}	0.801		0.8062				
Total diluents	3.205		3.2631				
Data point 20 was judged to be an outlier and removed from the dataset.							
95% confidence interval on measured pressures				6 psia			
95% confidence interval on measured temperatures				≤1.6ºF			

2.2.5 Distribution of Gases in the Reference Dataset

Figure 2-1 and Figure 2-2 present the range of gas compositions and test conditions of the reference dataset. The figures plot four key quantities: mole percent and molecular weight of the C_{6+} fraction, mole percent total diluents, and test pressures. As Figure 2-1 shows, the dataset contains a wide range of total diluent content, ranging from 2% to 23%. Most of the EffecTech and SwRI data were gathered on gases with diluent levels below 5%, a typical maximum for gases in the transmission industry. The remaining data from these sources, and all the ARCO and Gasunie data, came from gases with higher diluent contents typical of production gases before processing. The SwRI tests provided the data both above 600 psig and below 300 psig needed to cover the entire range of pressures of interest.

Figure 2-2 shows the characteristics of the heavy hydrocarbons found in each gas. For a given C_{6+} mole fraction, a heavier C_{6+} molecular weight indicates that the distribution within the fraction tends toward heavier hydrocarbons. The ARCO gases are unique in their high concentration of the heaviest hydrocarbons, resulting in C_{6+} molecular weights above 100. Most of the test gases fall below 0.4 mol % C_{6+}, levels typically of interest to the transmission industry, while the 1,325 and 1,523 Btu/scf gases from George *et al.* best represent production gases.

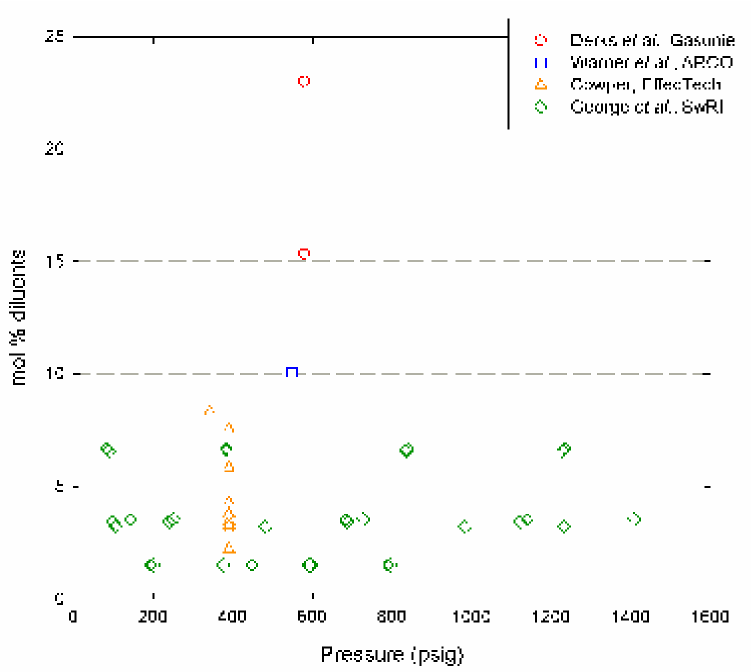

Figure 2-1. Ranges of pressures and diluent content of test data used in the reference dataset.

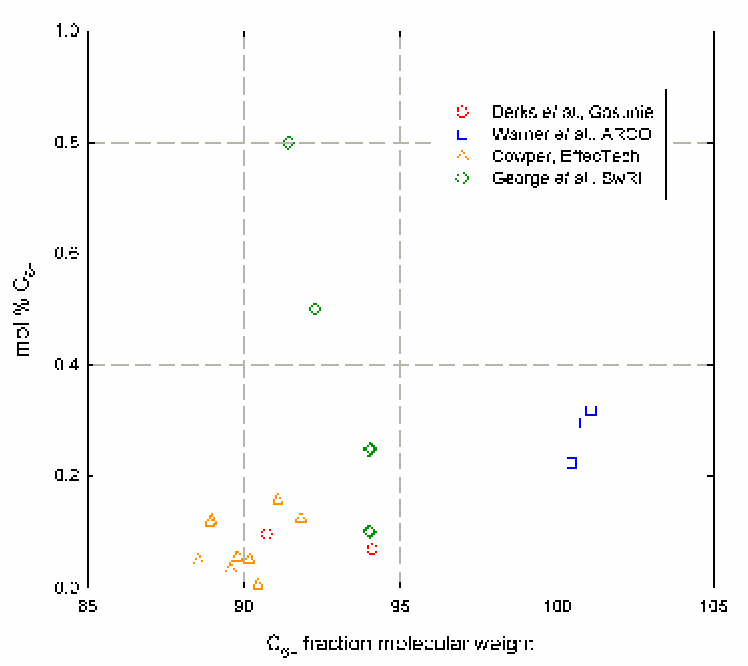

Figure 2-2. Properties of C_{6+} fractions of gases in the reference dataset.

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3. REVIEW OF EQUATIONS OF STATE AND ASSOCIATED PARAMETERS

As stated in the Introduction, many different equations of state, software packages, and heavy hydrocarbon characterizations are available to compute hydrocarbon dew points. The choice of characterization method has been identified as the largest source of potential error, much more so than the equation of state or software package used to compute dew points. Ideally, an actual natural gas composition determined gravimetrically or from GC analysis should yield an accurate HDP prediction from an equation of state (EOS). However, as found repeatedly by George *et al.* (2005a and 2005b), the use of the actual gas composition with common cubic equations can consistently underpredict dew point temperatures for rich gases at high pressures, sometimes by as much as 25°F. This suggests that the EOS parameters for various natural gas components may be inaccurate, or may not be valid for all the compositions or conditions of interest.

As part of this research, published parameters for the Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) equations of state have been reviewed, along with some of the data used to derive these parameters. The goal of this task was to determine the range of validity of these common equations of state, and if possible, determine uncertainties in dew points computed from them. Where experimental HDP data are in disagreement with HDP values calculated from these equations, it was hoped that this review would determine whether the disagreement is partly due to use of the equations outside their regions of validity, or to uncertainties in the values of the parameters themselves. Section 3.1 presents the results and conclusions of this review.

During this project, a new equation of state from Germany was introduced to the natural gas community. This EOS, known as GERG-2004, is intended for use in computing gas, liquid, and vapor-liquid equilibrium conditions, and is being considered by the industry for use in hydrocarbon dew point prediction. At the request of the Project Advisory Committee, this equation was also evaluated for its accuracy in predicting observed dew points. Section 3.2 briefly reviews this equation of state and its range of validity.

3.1 CUBIC EQUATIONS OF STATE

Two of the most common equations in use by the natural gas industry, both of which were applied in this work, are the Peng-Robinson EOS (Peng and Robinson, 1976) and the Soave-Redlich-Kwong EOS (Soave, 1972). Both are referred to as "cubic equations" because they can be rewritten as cubic polynomials in the specific volume term v. Indeed, both of these equations can be written in the same algebraic form, simply using different values for some of the parametric coefficients. This section reviews the origins of these common EOS and the parameters that appear in them for hydrocarbon mixtures. The following introduction to cubic equations of state is adapted from several references (Barrufet, 1998a; Pedersen *et al.*, 1989; Wang and Pope, 2001; Poling *et al.*, 2001; George *et al.*, 2005a; Riazi, 2005), and the reader is encouraged to locate these references for further information.

3.1.1 Derivation of the Cubic Equations of State

The cubic equations of state are based on the ideal gas law, but add various terms to correct for the non-ideal behavior of real gases. The ideal gas law itself can be expressed in several forms; Equations 3-1 and 3-2 are often used as a starting point for deriving other equations of state.

$$Pv = RT \tag{3-1}$$

$$v = \frac{RT}{P} \tag{3-2}$$

Here, P is the pressure of the gas, v is its specific molar volume (volume per mole of gas), R is the universal gas constant, and T is the absolute temperature of the gas. The compressibility factor, Z, is an example of a simple correction to the ideal gas law for non-ideal behavior:

$$Pv = ZRT\,. \tag{3-3}$$

The compressibility factor is determined using equations of state when phase change is not of concern, such as in the AGA-8 EOS (Poling *et al.*, 2001; American Gas Association, 1994). The compressibility factor itself is not constant, but varies with gas composition, pressure, and temperature.

Other corrections to the ideal gas law based on the physical behavior of the gas are made when phase changes must be characterized. For instance, as gases are cooled and the molecules move closer together, the molar volume, v, does not completely go to zero as the temperature approaches zero, but liquefaction occurs at some point in the cooling process. A common adjustment to account for the repulsive forces between molecules that lead to the nonzero volume of the liquid phase is to add a constant “zero temperature volume,” b, to the equation of state.

$$v = \frac{RT}{P} + b \tag{3-4}$$

Rearranging gives

$$P = \frac{RT}{v-b}\,. \tag{3-5}$$

On the other hand, attractive forces between molecules, proportional to $1/v^2$, tend to make gas pressure lower than predicted by the ideal gas law. A subtractive term corrects the gas pressure to account for these forces.

$$P = \frac{RT}{v-b} - \frac{a_c}{v^2} \tag{3-6}$$

The parameter a_c varies with the attractive forces between molecules. This equation is commonly known as the van der Waals equation of state (van der Waals, 1890), one of the first equations proposed to accurately characterize the behavior of real gases.

The van der Waals EOS and many more recent equations can be generalized to a common form that includes five parameters and is cubic in *v*. It has been shown that this cubic equation of state is required to describe both the gas and liquid behavior of a substance (Poling *et al.*, 2001). Both the Peng-Robinson EOS and the Soave-Redlich-Kwong EOS are cubic equations of the same form, shown in Equation 3-7.

$$P = \frac{RT}{v-b} - \frac{a_c a^2}{(v-b_1)(v-b_2)} \tag{3-7}$$

The attractive force parameter, a_c, and the repulsive force parameter, *b*, are fit to experimental data on the behavior of pure gases. These parameters are a function of the gas' critical temperature, T_c, critical pressure, P_c, and acentric factor, *w* (itself a function of the gas' critical pressure and vapor pressure at a specific temperature). The two equations use different values for some of the parametric coefficients, and thus produce slightly different dew point predictions given the same gas composition. Table 3-1 compares the values and algebraic forms of the attractive and repulsive parameters for the two equations of state, while Equations 3-8 and 3-9 compare the formulas for the acentric parameter, *a* (a function of the acentric factor, *w*), used in each equation.

$$a_{PR} = 1 + \left(0.37464 + 1.54226w - 0.26992w^2\right)\left(1 - \sqrt{T/T_c}\right) \tag{3-8}$$

$$a_{SRK} = 1 + \left(0.480 + 1.547w - 0.176w^2\right)\left(1 - \sqrt{T/T_c}\right) \tag{3-9}$$

Table 3-1. Parameters for the Peng-Robinson and Soave-Redlich-Kwong equations of state (Barrufet, 1998a; Peng and Robinson, 1976; Soave, 1972).

Equation	a_c	b	b_1	b_2
Peng-Robinson	$\frac{0.45724R^2T_c^2}{P_c}$	$\frac{0.07780RT_c}{P_c}$	$-b\left(1+\sqrt{2}\right)$	$-b\left(1-\sqrt{2}\right)$
Soave-Redlich-Kwong	$\frac{0.42748R^2T_c^2}{P_c}$	$\frac{0.08664RT_c}{P_c}$	$-b$	0

For pure gases, the values of the attractive and repulsive force parameters in the PR and SRK equations of state are based on experimental data, as mentioned earlier. To implement these equations for multi-component mixtures, the attraction and repulsion parameters must be modified to account for interactions between dissimilar molecules. Weighted averages of the values for pure substances are typically computed from Equations 3-10 through 3-12 and used in the equations of state to predict the behavior of mixtures:

$$a_{c,\,mixture} = \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} x_i x_j \sqrt{a_i a_j} \left(1 - k_{ij}\right) \tag{3-10}$$

$$a_i = a_{ci} a_i^2 \tag{3-11}$$

$$b_{mixture} = \sum_{i=1}^{N} x_i b_i \tag{3-12}$$

where

i,j = component indices,

N = total number of components in the mixture,

x_i = mole fraction of component i in the mixture,

k_{ij} = binary interaction parameter (weighting factor for interactions between components i and j),

a_{ci} = attractive force parameter for pure component i,

a_i = acentric parameter for pure component i, and

b_i = repulsive force parameter for pure component i.

While published values of a_c and b for pure substances have been generally accepted, the extension to mixtures through the binary interaction parameters, k_{ij}, and Equations 3-10 through 3-12 is still a topic of current research. Still, this method is commonly used in current software packages to predict the phase behavior and properties of hydrocarbon mixtures.

3.1.2 Range of Validity of Cubic Equation Parameters

This section reviews the source data used to derive the parameters in the Peng-Robinson and SRK equations of state. The source material is divided into three groups:

- source data for the attractive and repulsive force parameters, a_c and b;
- source data for the acentric parameter a, which is derived from correlations for vapor pressure;
- experimental VLE data used to determine the binary interaction parameters (BIPs), k_{ij}.

As expected, different sets of experimental data were used to generate parameters for the two equations. The Van der Waals parameters and acentric factors in the SRK equation of state were generated from data collected prior to 1950, while these same parameters in the Peng-Robinson equation of state were generated from data compiled through the early 1970s.

No uncertainty information was found in any of the source data, so it was not possible to perform an error propagation study or to determine uncertainties in predicted dew points due to uncertainties in the parameters themselves. However, it was found that the range of pressures and temperatures for which binary interaction parameters are valid is likely to be insufficient for determining HDPs over the range of interest to the natural gas industry.

Attractive and repulsive force parameters. Riazi (2005) and Pedersen *et al.* (1989) describe two ways in which the attractive and repulsive force parameters a_c and b can be determined. Analytically, values for the parameters can be determined by imposing the critical point conditions on the equation of state. At the critical point, where $T = T_c$ and $P = P_c$, the properties of the liquid and vapor phases are identical, and the first and second partial derivatives of pressure with respect to volume at constant temperature are zero.

$$\left(\frac{\partial P}{\partial v}\right)_{T_c,P_c} = \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c,P_c} = 0 \tag{3-13}$$

Applying the conditions of Eq. 3-13 to the generic cubic EOS, Eq. 3-7, produces expressions for both a_c and b that depend only on the critical pressure and temperature and the universal gas constant R (see Table 3-1). These critical values are constants for a given component. Therefore, if the critical pressure and temperature values are correct, the attractive and repulsive force parameters will be valid over the entire range of pressures and temperatures where the EOS might be applied.

Experimentally, values for a_c and b can be determined from critical pressure and temperature data. Soave (1972) based the parameters for the SRK equation on data from Redlich and Kwong (1949), but that reference does not give the critical values used in the original Redlich-Kwong equation. Similarly, Peng and Robinson (1976) do not give the source of the critical values used in their derivation. Values for T_c and P_c for many natural gas components can be found in any number of references (for example, Reid *et al.*, 1977 and 1987; American Petroleum Institute, 1978; Pedersen *et al.*, 1999; Poling *et al.*, 2001). None of the values found during this research include uncertainty information, however, so that uncertainties in computed dew points caused by uncertainties in T_c and P_c (or a_c and b) cannot be determined at this time.

Acentric factor. The acentric factor, w, is a defined parameter rather than a measurable quantity. Each natural gas component has a specific value of w, and by definition, the acentric factor increases as the molecule of interest becomes more non-spherical. For example, $w = 0$ for argon, 0.001 for methane, and 0.489 for decane (Riazi, 2005; Pedersen *et al.*, 1989). The acentric factor for component i is defined as a function of its critical pressure and temperature, and its vapor pressure P_{vi} at a temperature of 0.7 times the absolute critical temperature (Pitzer, 1955):

$$w_i = -\log_{10}\left(\frac{P_{vi}(T_i = 0.7T_{ci})}{P_{ci}}\right) - 1 \tag{3-14}$$

SRK acentric factors. The acentric factors for pure components used in the SRK equation of state (Soave, 1972) were obtained from data in API Research Report 44 (American Petroleum Institute, 1978). Specifically, reference values of vapor pressures, critical pressures and critical temperatures from this report were used to derive the acentric parameters for SRK. The vapor pressures, in turn, were derived from the Antoine equation, first proposed in 1888 and now commonly used to estimate the vapor pressure of pure compounds at a given absolute temperature T (Riazi, 2005):

$$\ln P_{vi} = A_i - \frac{B_i}{T + C_i} \tag{3-15}$$

The parameters A_i, B_i and C_i listed in API Research Report 44 (API 44) were generated from fits to published data. The report does not include the published data itself, but lists the data sources, which were far too numerous to be reviewed as part of this project.

It was decided at this point to determine whether the use of the curve-fit Antoine parameters A_i, B_i and C_i to derive P_{vi} and w_i may be responsible for the underprediction of dew points. Along with the Antoine parameters, API 44 contains values of P_{vi} computed from these parameters and Equation 3-15, tabulated as a function of temperature. Although not explicitly stated in API 44, it was assumed for this validity check that the temperature ranges of the tabulated values of P_{vi} correspond to the ranges of experimental data used to derive the Antoine coefficients for each component. If P_{vi} was calculated for a component at a temperature T_i outside the temperature range of the table, it would indicate that the Antoine curve fit for that component was extrapolated to obtain P_{vi}, increasing the likelihood of errors in P_{vi} and w_i.

Table 3-2 lists these temperature ranges for many hydrocarbon components of interest. The table also lists the normal boiling temperatures T_{bi} and critical temperatures T_{ci} of each component (Poling *et al.*, 2001), and the temperature $T_i = 0.7T_c$ at which the vapor pressure was computed to obtain w_i. The table shows that values of P_{vi} at T_i are indeed extrapolations of Equation 3-15 to the experimental data for several components. The extrapolation occurs for the C_1 through C_4 hydrocarbons, cyclopentane and methylcyclopentane, and the aromatics benzene and toluene. For the majority of the pentanes and heavier hydrocarbons, the use of the API 44 data to compute acentric factors does not appear to involve extrapolation of the Antoine curve fits. Since the underprediction of dew points occurs in richer gases where the heavy hydrocarbons are in greater amounts, it is concluded here that use of the Antoine curve fits is not the cause of the underprediction.

Table 3-2. Validity analysis of acentric factors used in the SRK equation of state. Evaluation temperatures outside the assumed range of validity of the Antoine parameters are marked in bold.

	Valid range of Antoine coefficients		Normal boiling temperature	Critical temperature	P_{vi} evaluation temperature
Component	T_{min} (°F)	T_{max} (°F)	T_{bi} (°F)	T_{ci} (°F)	T_i (°F)
methane	-320	-240	-258.68	-116.66	**-219.56**
ethane	-225	-100	-127.48	89.91	**-74.97**
propane	-150	-15	-43.83	206.02	**6.32**
n-butane	-125	65	31.12	305.55	**75.98**
isobutane	-125	45	10.74	274.46	**54.22**
n-pentane	-70	135	96.93	385.79	132.15
isopentane	-70	120	82.11	369.03	120.42
neopentane	5	85	49.10	321.08	86.86
cyclopentane	-40	165	120.61	461.21	**184.95**
n-hexane	-45	200	155.71	454.01	179.91
2-methylpentane	-45	185	140.45	435.83	167.18
3-methylpentane	-45	190	145.85	448.25	175.87
2,2-dimethylbutane	-45	170	121.50	419.99	156.09
2,3-dimethylbutane	-45	180	136.35	440.15	170.20
methylcyclopentane	-10	205	161.29	499.35	**211.65**
benzene	45	220	176.16	552.02	**248.51**
n-heptane	30	255	209.16	512.69	220.98
2-methylhexane	15	240	194.05	494.51	208.26
3-methylhexane	15	240	197.33	503.69	214.68
2,2-dimethylpentane	0	225	174.51	477.05	196.03
2,3-dimethylpentane	15	240	193.57	507.47	217.33
ethylcyclopentane	30	265	218.19	565.43	257.90
toluene	45	280	231.15	605.48	**285.94**
n-octane	65	305	258.21	563.99	256.89
2-methylheptane	55	295	243.77	547.61	245.43
3-methylheptane	55	295	246.07	554.81	250.47
n-nonane	100	355	303.48	610.61	289.53

PR acentric factors. Peng and Robinson (1976) note that the acentric factors in their derivation of the PR EOS were determined using vapor pressure data (see, *e.g.*, Reamer *et al.*, 1942; Starling, 1973) extending from the normal boiling point to the critical point, rather than only the vapor pressure calculated at $T = 0.7T_c$. In this case, Table 3-2 shows that the normal boiling points of all the hexanes and heavier components are well above the temperature range typically of interest to the natural gas industry (below 100°F). The use of Peng-Robinson w_i for these heavy components when their partial pressures are low, such as in natural gas blends at temperatures below 100°F, could be considered extrapolation of the data to lower temperatures. As such, this may be one cause (but not the only cause) of underpredicted hydrocarbon dew points.

Binary interaction parameters. Many references have noted a lack of experimental data with which C_{6+}-C_{6+} binary interaction parameters (BIPs) can be determined [see, for example, Avila *et al.* (2002) and Starling (2003)]. This may explain why some software packages include zero values for these BIPs, and may also explain the tendency of the Peng-Robinson and SRK equations of state to underpredict hydrocarbon dew points of rich natural gases containing significant amounts of these components.

To determine whether BIPs used with the PR and SRK equations cover the range of conditions of interest to the industry, the origins of these parameters were researched. Values for binary interaction parameters can be found in many references; common sources include Whitson and Brulé (2000) and Reid *et al.* (1977). However, the Dechema Data Series published in Germany (Knapp *et al.*, 1982) is often the original source of the binary interaction parameters tabulated in these references. Volume VI of the Dechema Data Series is the definitive source of BIPs used by equation of state software. This volume lists recommended values of BIPs, along with an exhaustive table and bibliography of published data used to derive the BIPs.

The tabulated source data from gas mixtures including CO_2, nitrogen, and hydrocarbons from methane to decane were reviewed to determine the range of pressures and temperatures for which the BIPs are valid. Table 3-3 on the following pages presents the results of this review. Each cell in the chart lists the minimum and maximum pressures and temperatures for data on a component pair. The ranges of data for a particular component pair are identified by locating the column for one component and the row for the other, then finding their intersection on the chart. For example, the Dechema data used to create BIPs for the CO_2-ethane pair covers a temperature range from -60°F to +77°F and a pressure range from 80.1 to 961.6 psia. Blank cells indicate component pairs for which no data is listed in the Dechema Data Series.

It was assumed for this review that the conditions of interest to the natural gas industry range from 50 to 90°F and from 100 to 1,250 psia. Bold numbers in Table 3-3 indicate limits on data that do not extend beyond these conditions of interest. It can be seen from the table that only 9 of 72 BIPs are valid over this range of interest. Data is also lacking for many BIPs for hydrocarbon pairs involving isobutane, normal butane, and heavier hydrocarbons up through decane. A standard procedure is to assume a BIP of zero for hydrocarbon-hydrocarbon interactions, but clearly, no data exists to support this assumption for the heavier hydrocarbon pairs. It has been concluded that the binary interaction parameters used by many equation-of-state software packages are not valid over common pipeline conditions, and their use may be responsible for the underpredictions of hydrocarbon dew points for rich natural gases by these equations.

As an aside, most experimental data used to generate EOS parameters is for pure substances and binary and ternary mixtures, and equations of state would be expected to recreate this data accurately. With little data available on mixtures of four or more components, it would not be surprising for equations of state to exhibit larger errors on properties of multicomponent natural gas streams. Therefore, where recent research has tried to improve the agreement of equations of state with reference data, binary interaction parameters (BIPs) and mixing rules have received a majority of the attention.

Several variations on the linear mixing rule of Equation 3-10 have been successfully tried, such as quadratic formulas (Arnaud *et al.*, 1996; Nishiumi and Arai, 1988). Knudsen *et al.* (1993) evaluated five different mixing rules for the SRK EOS, both with and without temperature-dependent parameters, and recommended a method using exponential weighting functions. Twu *et al.* (2002) discuss several of these variations, many involving asymmetric mixing rules where $k_{ij} \neq k_{ji}$. Implementing most of these approaches requires software more flexible than most packages available to the natural gas industry, however.

Table 3-3. Chart of valid temperatures and pressures for common binary interaction parameters (Knapp *et al.*, 1982).

	methane		CO_2		ethane		propane	
CO_2	-184	**28**						
	84.3	**1234.3**				Legend:	Tmin (°F)	Tmax (°F)
ethane	-226	**50**	-60	**77**			Pmin (psia)	Pmax (psia)
	0.1	**964.5**	80.1	**961.6**				
propane	-226	188	-40	203	-1	199		
	0.0	1464.9	14.9	**1002.2**	37.9	**751.3**		
isobutane	**98**	219	32	250	**100**	250	19	250
	80.1	1667.9	22.8	**1041.4**	73.0	**778.9**	17.8	**604.8**
n-butane	-200	278	-51	278	-47	295	**140**	302
	0.0	1914.5	4.8	**1183.5**	99.9	**839.8**	92.8	**588.9**
isopentane	**160**	349	39	219			32	356
	398.9	**999.3**	6.1	1289.4			4.8	**664.3**
n-pentane	-143	368	39	381	39	340	**160**	368
	0.0	2480.1	4.4	1396.7	4.4	**989.2**	42.4	**649.8**
benzene	**151**	442	**77**	104	32	536	**98**	399
	99.9	4786.2	**129.7**	**1124.0**	**112.5**	**1199.5**	3.2	**849.9**
cyclohexane	**70**	340	**392**	500	-40	500		
	1.6	4090.1	**192.9**	1871.0	0.9	1299.5		
n-hexane	-132	302	**77**	104	**77**	349	**140**	428
	0.0	2842.7	64.4	**1109.5**	13.6	**1145.8**	11.0	**699.1**
toluene	**300**	518	**100**	399				
	291.5	3655.0	48.4	2204.6				
n-heptane	-101	**-1**	**98**	399	-46	484	**140**	500
	99.9	2987.8	27.0	1929.0	99.9	1277.8	4.1	**699.1**
n-octane	-58	302			32	212		
	146.5	3959.5			58.7	**762.9**		
n-nonane	-58	302						
	146.5	4684.7						
n-decane	-20	590	39	458	39	458	39	458
	20.0	5235.9	0.0	2726.7	0.0	1711.4	0.0	**1026.9**
nitrogen	-301	**-121**	-67	**68**	-211	**62**	-202	176
	1.7	**729.5**	**184.2**	2422.1	0.4	1943.5	1.0	3176.3

Table 3-3 (continued).

	isobutane		n-butane		isopentane		n-pentane	
n-butane	32	**32**						
	15.1	**22.8**						
isopentane								
n-pentane			**77**	**77**	**131**	232		
			10.6	**15.7**	33.9	**114.0**		
benzene							-1	176
							1.0	**14.6**
cyclohexane							**97**	176
							14.6	**14.6**
n-hexane			**185**	428				
			146.5	**535.2**				
toluene								
n-heptane			**179**	509			**266**	487
			99.9	**574.3**			**146.5**	**443.8**
n-octane							**64**	320
							7.4	**220.5**
n-nonane								
n-decane			**98**	458				
			0.1	**713.6**				
nitrogen	-1	250	**98**	300	39	219	39	219
	33.6	3002.3	**235.0**	4017.5	26.5	3002.3	36.3	3002.3

	benzene		cyclohexane		n-hexane		toluene	
cyclohexane								
n-hexane	**77**	176						
	2.2	**14.6**						
toluene								
n-heptane	**140**	208			**86**	122		
	4.6	**14.6**			1.2	**7.7**		
n-octane	**176**	257						
	14.6	**14.6**						
n-nonane								
n-decane								
nitrogen	**167**	257			**98**	340		
	900.7	4452.7			**249.5**	4989.3		

Table 3-3 (continued).

	n-heptane		n-octane		n-nonane		n-decane	
n-octane								
n-nonane								
n-decane								
nitrogen	**89**	359	**122**	212			**100**	280
	1019.6	10022.1	**2190.1**	3669.5			**249.5**	4989.3

3.2 GERG EQUATION OF STATE

During this project, a new equation of state was identified by the Project Advisory Group and recommended for study. This equation, developed at Ruhr-Universität Bochum (the University of Bochum) in Germany and known as GERG-2004, is intended for use in computing gas, liquid, and vapor-liquid equilibrium properties, including hydrocarbon dew point conditions. With the help of Prof. Wolfgang Wagner of the University of Bochum, SwRI staff obtained a copy of the GERG-2004 software package for the project.

Discussions were also held with Eric Lemmon of NIST about REFPROP, an equation of state package published by NIST. Mr. Lemmon noted that the GERG-2004 equation of state would be incorporated into REFPROP 8 for distribution in the United States. Because of the long lead time required, REFPROP 8 was not available in time for the project. However, Mr. Lemmon provided useful information on the data used to generate the GERG-2004 equation of state (Lemmon, 2006). The data covered a wide range of pure gases and mixtures, including two-component, three-component and five-component mixtures. None of this data was representative of the multi-component gases delivered by the natural gas industry, and no phase behavior data was identified that could be included in the reference dataset in Chapter 2. However, the range of validity and accuracy of the equation has been determined from knowledge of this source data. This section briefly describes the GERG EOS, its range of validity, and its accuracy; the reader is referred to Jaeschke *et al.* (2003), Jaeschke (2005), and Wagner (2005, 2006) for details.

The GERG-2004 equation of state is based on a multi-fluid approximation which is explicit in the reduced Helmholtz energy a (not to be confused with the acentric parameter a of the cubic equations of state). The Helmholtz energy is a thermodynamic property dependent on gas composition $\bar{x}$, density r, and temperature T. All other fluid properties of interest can be derived from the Helmholtz energy using thermodynamic principles.

The basic structure of the multi-fluid approximation (Wagner, 2006) divides the Helmholtz energy formula into three terms: one term to account for ideal gas behavior, a second term describing the contributions of pure substances to the real behavior, and a departure function. For a gas containing N components,

$$a(d,t,\bar{x}) = \text{ideal gas term} + \text{pure substance EOS term} + \text{departure function}$$

$$= a^{o}(r,T,\bar{x}) + \sum_{i=1}^{N} x_i a_{0i}^{r}(d,t) + \Delta a^{r}(d,t,\bar{x}) \tag{3-16}$$

where the reduced density and inverse reduced temperature are

$$d = r / r_n(\bar{x}) \tag{3-17}$$

$$t = T_n(\bar{x})/T \,. \tag{3-18}$$

The reducing functions r_n and T_n, and the departure function Δa^r, are specific to the GERG implementation and were created to better describe mixture behavior. For pure substances, the reducing functions are equal to the critical properties r_c and T_c, respectively. The departure function is a summation of specific departure functions for all binary subsystems within the mixture.

$$\Delta a^{r}(d,t,\bar{x}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \Delta a_{ij}^{r}(d,t,\bar{x}) \tag{3-19}$$

As reported in the documentation (Wagner, 2005), the range of applicability of the GERG-2004 EOS is divided into a normal range and an extended range corresponding to different levels of accuracy. Table 3-4 lists the accuracy of computed properties in these ranges; the vapor pressure uncertainties are of interest for HDP calculations. The version of GERG-2004 evaluated during this project incorporates data on eighteen gas components, but hydrocarbon components are limited to normal hydrocarbons from C_1 through C_8, isobutane and isopentane. Because GERG-2004 does not yet contain data on nonane and heavier hydrocarbons, it is currently incapable of implementing many of the characterization methods described in Chapter 4. Data on nonane and decane is expected to be included in GERG during 2007 (Lemmon, 2006), and it is recommended that GERG be re-evaluated once the additional data is included.

Table 3-4. Uncertainties of properties calculated by the GERG-2004 equation of state (Wagner, 2005).

			Uncertainties in computed properties			
Range of validity	Temperature range	Pressure range	Gas density	Gas sound speed	Liquid density	Vapor pressures
Normal	-298°F ≤ T ≤ 350°F	P ≤ 5,075 psia	< 0.1%	< 0.1%	0.1% to 0.5%	1% to 3%
Extended	-352°F ≤ T ≤ 800°F	P ≤ 10,150 psia	0.2% to 0.5%			

4. CHARACTERIZATION METHODS EXAMINED IN THIS WORK

As stated in the Introduction, the primary goal of this work was to evaluate the accuracy of several characterization methods in predicting hydrocarbon dew points for a wide range of gas compositions. Because of the limited number of field gas chromatographs capable of analyzing a gas stream beyond C_6, this project focused on methods that could produce an extended component distribution using only the total C_{6+} fraction and other available data on the gas stream.

It is generally agreed by the industry that accurate dew point predictions require compositional data at least through C_9. Dixon and Ebbrell (1986) cite studies from the late 1960’s that demonstrated how retrograde dew points are sensitive to trace quantities of C_{10+}. Cowper (2004) showed that compositional data out to C_9 are sufficient for computing natural gas dew points at or below 0ºC, but states that the components must be measured to a precision of 0.1 ppm. For gases with even higher dew points, Cowper advocates obtaining analyses through C_{12}. Similarly, Pettigrew (2004) found that HDPs computed with data from a C_{9+} GC analysis were consistent with online dew scope measurements to within ±2ºC, and obtained ±1ºC agreement when samples were analyzed to C_{10}. The majority of the methods tested in this research can produce characterizations containing C_9 or heavier components from a lumped C_{6+} total, if needed for an accurate dew point calculation.

At the outset of the project, a list of possible characterization methods was presented to the PRCI/API Project Advisory Subcommittee for approval. Some of these methods were developed to accurately determine the heating value of a gas stream from limited compositional data, but have historically been used by natural gas companies to determine hydrocarbon dew points as well. The original list included:

- Lumped C_{9+} method
- Logarithmic or exponential characterizations in C_{6+} fraction
- Whitson’s gamma distribution method (Whitson *et al.*, 1989)
- C_{6+} – GPM method (Natural Gas Council, 2005)
- GPA 60/30/10 $C_6/C_7/C_8$ distribution (GPA, 2000)
- 47/36/17 $C_6/C_7/C_8$ distribution

Testing of the GPA 60/30/10 distribution was rejected by the subcommittee, based on its inability to accurately predict dew points in a previous study (George *et al.*, 2005a). Further study of Whitson’s gamma distribution method found the complete characterization method to be impractical, as will be explained later in this chapter.

A literature search was conducted for other characterization methods that could be applied by the natural gas industry to compute hydrocarbon dew points. Shariati *et al.* (1999) provided a brief history of characterization methods; a recent text by Riazi (2005) was found to contain an exhaustive survey of characterizations used by the petroleum industry, and some characterizations described in the book were adapted for use with natural gases and tested. A new ISO standard (ISO, 2006), published in final form just before this report was issued, also contains a characterization method of interest that was tested here.

In all, seven characterizations were found to fit the intent of the study and were tested in this work. This chapter presents the results of the search for practical characterization methods, and describes both methods that were tested and methods that were considered for testing but set aside as impractical for use by the natural gas industry. Included with the description of each tested characterization method are formulas for calculating the uncertainties of component values in the characterizations. The accuracy and uncertainties of the computed dew points themselves will be reviewed in Chapter 5.

4.1 METHODS SELECTED FOR TESTING

Dew points were computed in this study using seven characterization methods as well as the complete composition of the test gas. The characterization methods fall into two categories.

- The first category requires some information on individual hydrocarbon components above C_6. These methods include the lumped C_{9+} fraction method, which requires data on individual components up through nonane, and the ISO 23874 method, which recommends the use of a chromatographic analysis of the gas through C_{12} if possible.
- The second category requires data that is easily found from references or can be generally assumed, and requires no *a priori* knowledge of the heavy hydrocarbon composition beyond C_6. This category includes the 47/36/17 $C_6/C_7/C_8$ distribution, the Katz exponential distribution, and two methods using a Gaussian quadrature splitting scheme. The C_{6+}-GPM correlation for predicting dew points introduced in a recent NGC+ White Paper involves the use of several $C_6/C_7/C_8$ distributions, and is also placed in this category.

The category 1 methods will be described first, followed by the category 2 methods.

In this chapter, the following symbols are used:

x_i = known or measured mole fraction of any component, including non-normal hydrocarbons, aromatics, cyclic hydrocarbons, etc.;

x_n = known or measured mole fraction of a normal hydrocarbon with carbon number n;

y_n = mole fraction of normal hydrocarbon with carbon number n, computed as part of a characterization; and

s_{xi} = uncertainty in mole fraction x_i.

The subscript n is also used to indicate a specific carbon number in summations with other subscripts. For example, $\sum_{n\geq 6} x_i$ represents the sum of the mole fractions of all components with carbon numbers greater than or equal to 6. A number used as a subscript refers to hydrocarbons of a specific carbon number; y_9, for example, is the characterized mole fraction of normal nonane.

4.1.1 Lumped C_{9+} Method

This characterization requires that amounts of individual components with carbon numbers through C_8 be known. These components are entered explicitly into the equation of state software for dew point calculations. The amounts of all components with nine or more carbon atoms per molecule are added, and the sum is assigned to normal nonane. This method is automatically implemented by gas chromatographs that perform extended analyses up to C_9 and report the amount of nonanes and heavier components as a lumped C_{9+} fraction.

$$y_9 = \sum_{n\geq 9} x_i \; . \tag{4-1}$$

The uncertainty in the lumped C_{9+} fraction can be computed using the principle of error propagation. If some quantity p is a function of the independent variables q, r, and s,

$$p = f(q,r,s) \tag{4-2}$$

then the uncertainty s_p in the quantity p is computed by the error propagation formula (ISO, 1995)

$$s_p^2 = \left(\frac{\partial p}{\partial q}\right)^2 s_q^2 + \left(\frac{\partial p}{\partial r}\right)^2 s_r^2 + \left(\frac{\partial p}{\partial s}\right)^2 s_s^2 \, . \tag{4-3}$$

In this case, y_9 is a simple summation of known mole fractions, so the error propagation formula applied to Equation 4-1 becomes

$$s_{y9}^2 = \sum_{n\geq 9} s_{xi}^2 \; . \tag{4-4}$$

4.1.2 ISO 23874 Method

A standard has recently been issued (ISO, 2006) to compute hydrocarbon dew points from gas chromatographic data. The approach is based on a technique developed by Chris Cowper of the UK that generally requires the use of a GC with a flame ionization detector and linear temperature programming. The method is useful for computing dew points of gases when the GC analysis produces peaks that cannot be identified with known components.

Suppose that a GC analysis produces a chromatogram with multiple peaks between n-octane and n-nonane (Figure 4-1). If the components cannot be identified directly, property data on the components such as boiling point temperatures cannot be assigned to the component from the data library associated with the equation of state software. The ISO method assumes that boiling points of the unknown components can be found from the boiling points of the known normal alkanes and a linear interpolation in retention time. For unknown component *i*, eluting at time t_i between normal components *n* and *n* + 1, the boiling point temperature T_{bi} is approximated by

$$T_{bi} = T_{bn} + \frac{(t_i - t_n)(T_{b,n+1} - T_{bn})}{t_{n+1} - t_n}. \tag{4-5}$$

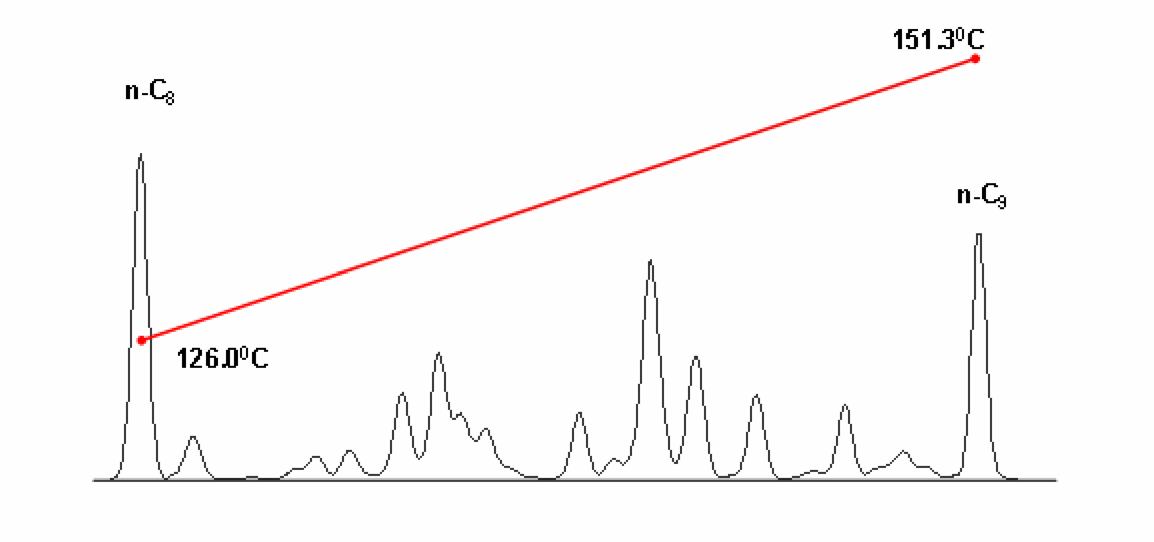

Figure 4-1. Example of a chromatogram with multiple peaks for non-normal isomers between peaks for normal isomers with known boiling points (Cowper, 2002b).

The analyzed mole fractions for the unidentified peaks are added together, and the total is added to the mole fraction for the next normal alkane with a higher retention time (C_9 in the figure).

$$y_{n+1} = \sum_{t_n < t \le t_{n+1}} x_i \tag{4-6}$$

The boiling point of the newly defined lumped component is taken as the weighted average of the boiling points of the lumped components.

$$T_{b,y_{n+1}} = \frac{\sum\limits_{t_n < t \le t_{n+1}} T_{bi} x_i}{\sum\limits_{t_n < t \le t_{n+1}} x_i}. \tag{4-7}$$

The density of the new component must also be assigned, but the ISO standard notes that the densities of isomers deviate little from one another, so that the density of the *n* + 1 alkane is assigned to the new component. Finally, the uncertainty in each characterized mole fraction y_{n+1} is determined from the uncertainties in the mole fractions x_i used to compute it, via Equations 4-3 and 4-6.

$$s_{y,n+1}^{2} = \sum_{t_n < t \leq t_{n+1}} s_{xi}^{2} \tag{4-8}$$

The ISO standard advocates this method to define properties of lumped components with carbon numbers of 7 or higher, as a method of accurately computing dew points from extended analyses when not all components are known. Several obstacles to the use of this method by the U.S. natural gas industry have been identified:

- The U.S. natural gas industry has few field GCs that can identify isomers beyond C_6 and provide the detailed chromatograms needed for this approach. The method appears to be intended for laboratory GCs with flame ionization detectors and temperature programming capabilities. These are used by the natural gas industry only occasionally for extended analyses.

- It was noted by members of the project advisory committee that the ISO method assumes a direct correlation between elution time of a component from a chromatographic column and its boiling point. Different columns may elute components in different orders, potentially violating this assumption.

- This approach requires an equation of state software package that can accept or define new components with new properties. Few commercially available packages have this capability, the Multiflash software package (Infochem, 2006) used in this research being an exception.

Despite these potential obstacles to the immediate use of the ISO method in the U.S., the method was tested on gases in the reference dataset. For each gas, lumped amounts of hexane and heavier normal alkanes were calculated from the reference compositions. For the 2005 GTI/PRCI/DOE experimental data (George *et al.*, 2005b and 2005c), archived chromatograms provided the retention times used to compute the boiling points of the lumped components. For the other reference gases, retention times for a hexadecane/hexadecene/KEL-F column described by McNair and Bonelli (1969) were applied in the calculations of T_b for component y_{n+1}.

4.1.3 Modified Exponential Method of Katz

During the GTI/PRCI research (George *et al.*, 2005a), a simple logarithmic characterization was tested and found to poorly predict observed dew points. Other logarithmic and exponential distributions were sought during this research, and an exponential distribution by Katz (1983) to describe petroleum fractions was identified and tested for the natural gases in the reference database. The method requires no ***a priori*** knowledge of the heavy hydrocarbon properties beyond C_{7+}, only information on the heaviest component to be included in the characterization.

As described in Riazi (2005), the model assumes that mole fractions of successive normal alkane lumped components (called single carbon number groups or SCNs by Riazi) follow an exponential decay curve. The model starts the curve at heptane and proceeds up through the heaviest carbon number for which data is known on the petroleum fraction. In the natural gas industry, however, most field GCs will provide data on individual components up through the pentanes, and an assumption must be made about the amounts of hexane and heavier components in the C_{6+} fraction. It was decided to apply this method to natural gas characterizations by placing the starting point of the curve at C_6 rather than C_7, effectively extrapolating the Katz curve backward to hexane. The original Katz model also determines the molecular weight and specific gravity of the heaviest lumped component. Similar to the ISO 23874 method, the use of this information would require an equation of state software package that can accept or define new properties for components. Since the majority of software assumes fixed properties for each component, these properties were determined using default values in Multiflash rather than the Katz model.

As applied to natural gas in this study, the Katz characterization is formulated as follows:

$$y_n\big|_{6\le n<n\,\max} = 1.38205\exp(-0.25903n)\sum_{n\ge 6} x_i \tag{4-9}$$

This formula applies fixed fractions to successive components, leaving a "remainder" that must be assigned to one component. In the original formulation, mole fractions y_6 through $y_{n\max-1}$ are computed from Equation 4-9, and the remainder of x_{6+} is assigned to $y_{n\max}$ via Equation 4-10.

$$y_{n\,\max} = \sum_{n\ge 6} x_i - \sum_{n=6}^{n\,\max-1} y_n \tag{4-10}$$

At the suggestion of the project advisory subcommittee, a second approach was tested in which the remainder of the mole fraction was assigned to the light end of the distribution, rather than the heavy end. In this version, y_7 through $y_{n\max}$ were computed from Equation 4-9, and the remainder of the x_{6+} fraction is assigned to y_6.

$$y_6 = \sum_{n\ge 6} x_i - \sum_{n=7}^{n\,\max} y_n \tag{4-11}$$

The distribution can be extended up to a maximum of C_{11}, since Equation 4-9 produces negative mole fractions for components C_{12} and heavier.

The uncertainties in the amounts of each lumped component, found from error propagation, are as follows:

$$s^2_{yn}\big|_{6\le n<n\,\max} = [1.38205\exp(-0.25903n)]^2 \sum_{n\ge 6} s^2_{xi}\ . \tag{4-12}$$

$$s^2_{yn\,\max} = \left\{1 - \sum_{n=6}^{n\,\max-1}[1.38205\exp(-0.25903n)]\right\}^2 \sum_{n\ge 6} s^2_{xi}\ . \tag{4-13}$$

4.1.4 47/36/17 C_6/C_7/C_8 Method

This characterization, like the GPA 60/30/10 characterization, splits the total C_{6+} fraction into constant amounts of hexane, heptane and octane. The ratios of the various components in this case were based on analyses of gases historically produced off the Gulf Coast. The exact proportions are 47.466% C_6, 35.34% C_7, and 17.194% C_8.

$$y_6 = 0.47466 \sum_{n \geq 6} x_i \tag{4-14}$$

$$y_7 = 0.3534 \sum_{n \geq 6} x_i \tag{4-15}$$

$$y_8 = 0.17194 \sum_{n \geq 6} x_i \tag{4-16}$$

The constants propagate through the uncertainty formulas as shown.

$$s_{y6}^2 = (0.47466)^2 \sum_{n \geq 6} s_{xi}^2 \tag{4-17}$$

$$s_{y7}^2 = (0.3534)^2 \sum_{n \geq 6} s_{xi}^2 \tag{4-18}$$

$$s_{y8}^2 = (0.17194)^2 \sum_{n \geq 6} s_{xi}^2 \tag{4-19}$$

4.1.5 C_{6+}–GPM Distribution

A common measure of gas quality is "natural gas liquids," or the volume of liquid that may be produced when the heavier hydrocarbons condense from a natural gas stream. This quantity is a common measure of whether a gas stream is too rich to flow through a pipeline system without producing unwanted hydrocarbon condensates. The theoretical volume of natural gas liquids (NGLs) that can be produced by a known gas stream may be calculated using reference data (GPA, 2003) that converts a given volume of each pure gas component in the stream to the equivalent volume of condensate. Depending upon the application, the lightest hydrocarbon included in a theoretical NGL calculation may be chosen as hexane, pentane, or in some cases, ethane. NGL units are gallons per thousand cubic feet of gas, abbreviated GPM.

A correlation was recently developed between the GPM value of a gas computed using its C_{6+} components and the cricondentherm hydrocarbon dew point (CHDP) of the gas (Natural Gas Council, 2005; Poellnitz, 2002). The correlation was developed as a way to control liquid dropout in pipelines; the C_{6+} fraction was selected for the correlation because of its large effect on computed dew points as opposed to the C_{5+} fraction. A series of 55 gas samples from the Gulf of Mexico were analyzed up to C_{6+}, and their cricondentherms were computed using the Peng-Robinson equation of state, the HYSYS software package (HYSYS, 2003) and an assumed distribution for the C_{6+} fraction of 40% C_6, 40% C_7, and 20% C_8. The C_{6+} GPM was also computed using this 40/40/20 split. The resulting correlation was reported as

$$\text{CHDP (°F)} = 392 \times (\text{C}_{6+}\text{GPM})^{0.159} - 210\,. \tag{4-20}$$

The largest absolute deviation between cricondentherms computed by HYSYS and by the correlation was 7.2°F. No other uncertainty analysis was reported with the correlation, however.

In this project, results of the correlation were compared to experimental cricondentherm data for three of the reference gases (George *et al.*, 2005b and 2005c). The NGC+ White Paper suggested the use of the 60/30/10, 47/36/17 and/or 40/40/20 $C_6/C_7/C_8$ splits to compute the GPM values input to the correlation. In the comparisons, all three of these characterizations and the complete gas compositions were used to compute GPM amounts for input to Equation 4-20. Data to convert the mole fractions of the C_{6+} components to liquid volume were taken from GPA 2145-03 (GPA, 2003).

4.1.6 Gaussian Quadrature Splitting Schemes

Gaussian quadrature (Press *et al.*, 1992) is a method of numerically integrating a function f by evaluating the function at only a few points. The exact shape of the function need not be known – for instance, the function may be experimental data from a process that is not yet completely understood – but if something is known about its mathematical form, its integral can be numerically evaluated more accurately. The method proceeds as follows:

- The function f is evaluated at certain values of the independent variable (abscissa), z. The evaluation values z_j are chosen based upon an assumed form for the function.
- Each result $f(z_j)$ is multiplied by a weighting function w_j. The value of w_j corresponding to each value of the abscissa z_j is also based upon the assumed form of the function.
- Finally, all the weighted results $w_j \times f(z_j)$ are added together to determine the integral over the region of interest.

As an example, if a function is assumed to follow an exponential form, the normalized integral of the function could be expressed as

$$\int_0^{\infty} f(z) e^{-z} dz = \sum_{j=1}^{N} w_j f(z_j) = 1 . \tag{4-21}$$

This form of Gaussian quadrature is named Gauss-Laguerre quadrature, after the French mathematician who identified the polynomials upon which the weights w_i are based.

Riazi (2005) discusses many approaches to breaking a lumped fraction of heavy petroleum components, such as the C_{6+} or C_{7+} fraction, into “pseudocomponents.” To best describe the phase behavior of the petroleum mixture, both the mole fractions of each pseudocomponent and its properties (such as molecular weight and boiling point) are determined by various mathematical splitting schemes. One such splitting approach assumes a continuous distribution of plus-fraction properties that (1) follows an exponential form, and (2) can be integrated numerically using Gaussian quadrature. Each distribution of pseudocomponent properties, such as molar distribution or molecular weight, can be described by an appropriate function $f(z)$ integrated on the left-hand side of Equation 4-21. The number of pseudocomponents in the characterization is the same as the number of quadrature points used to integrate the property function. Various forms for the property density function are described by Riazi (2005), complete with expressions for the mole fractions and properties of pseudocomponents (pseudo-C_7, pseudo-C_8, etc.). Two forms of the property density function are discussed in this section.

It should be emphasized again here that the Gaussian quadrature splitting approach is a variation on a common characterization technique in the petroleum industry. This technique defines a distribution using pseudocomponents, with the properties of each pseudocomponent tuned so that calculations with the characterization match boiling point data measured from distilled petroleum fractions. Unfortunately, not all EOS software packages available to the natural gas industry allow the user to tune component properties, and even when tuning is possible, the natural gas industry will probably not have fractional boiling point data available. Instead, the approach of this study is to find characterizations of normal paraffins which best reproduce observed hydrocarbon dew points using standard properties and parameters. Here, the mole fraction distributions described by Riazi for use with pseudocomponents are assigned to normal paraffins with known properties, and methods to determine properties of the pseudocomponents have been set aside.

Riazi component distribution. Riazi (1997, 2005) proposes a generalized property distribution of the form

$$\frac{P_n - P_0}{P_0} = \left[\frac{A}{B}\ln\frac{1}{1-x_{cum,n}}\right]^{1/B} = P^*, \tag{4-22}$$

where

P_n = property of interest of pseudocomponent n,

P_0 = property of interest of the lightest component in the gas mixture,

$x_{cum,n}$ = cumulative mole fraction of the mixture from methane to pseudocomponent n, and

A, B = parameters fit on data for the lumped component fraction.

To follow the Gaussian distribution model, each pseudocomponent property must satisfy Equation 4-21, so that

$$\int_0^\infty F(P^*)dP^* = \int_0^\infty f(z)e^{-z}dz = 1. \tag{4-23}$$

Riazi shows that this distribution function will conform to the Gauss-Laguerre distribution if

$$z = \frac{B}{A}\left(P^*\right)^B, \tag{4-24}$$

$$f(z) = 1, \tag{4-25}$$

and (assuming that the characterization is applied to a C_{6+} lumped fraction)

$$y_n = w_{n-6+1} \sum_{n \geq 6} x_i \ . \tag{4-26}$$

In effect, the quadrature weights become the mole fraction of each pseudocomponent *n*, normalized by the total mole fraction of the lumped component being characterized. Since the quadrature weights are constants, they propagate through the uncertainty calculations in the same manner as the constants in the 47/36/17 $C_6/C_7/C_8$ method.

$$s_{yn}^2 = w_{n-6+1}^2 \sum_{n \geq 6} s_{xi}^2 \ . \tag{4-27}$$

Equation 4-26 can be applied directly to determine the mole fractions of normal hydrocarbons in the C_{6+} fraction characterization. This method will be referred to as the "Gauss-Riazi" characterization in the rest of this report.

Table 4-1 on the next page shows several sets of weights used in Gauss-Laguerre quadrature (Abramowitz and Stegun, 1965), each using a different number of abscissas *N*. The values of w_j used to distribute components in a characterization depend on the highest normal hydrocarbon used. In the Gauss-Riazi method, if a C_{6+} lumped mole fraction were characterized to include only n-C_6, n-C_7, and n-C_8, then the parameters for $N = 3$ would be used, and the total C_{6+} fraction would be redistributed as 71.11% C_6, 27.85% C_7, and 1.04% C_8. Since a typical GC analysis of a gas stream will only identify components out to C_{6+}, and heavier components must be included for an accurate dew point calculation, an assumption must be made to select the heaviest component in the C_{6+} characterization, hence the value of *N*. A method of selecting the heaviest component will be discussed in Chapter 6.

Whitson's gamma function component distribution. Another property distribution function used by the petroleum industry is the gamma function, which has been used to describe the molar distribution of a wide range of reservoir fluids. The gamma function is defined as (Abramowitz and Stegun, 1965; Poling *et al.*, 1992)

$$\Gamma(g) = \int_0^\infty s^{g-1} e^{-s} ds \, , \tag{4-28}$$

where *s* is an integration variable and *g* is the independent variable at which the gamma function is evaluated. Use of this distribution function to determine mole fractions, molecular weights and boiling points was first proposed and discussed in detail by Whitson (see, *e.g.*, Whitson and Brulé, 2000). When this function is applied to the Gaussian quadrature splitting scheme, the distribution function and the mole fraction of each pseudocomponent are given by

$$f(z) = \frac{z^{g-1}}{\Gamma(g)} \tag{4-29}$$

and (again assuming that the characterization is applied to a C_{6+} lumped fraction)

Table 4-1. Gauss-Laguerre quadrature abscissas and weights used to assign mole fractions in Gaussian characterization methods (Abramowitz and Stegun, 1965).

N	z_j	w_j	N	z_j	w_j
2	0.58579	8.53553×10^{-1}	6	0.22285	4.58965×10^{-1}
	3.41421	1.46447×10^{-1}		1.18893	4.17001×10^{-1}
				2.99274	1.13373×10^{-1}
3	0.41577	7.11093×10^{-1}		5.77514	1.03992×10^{-2}
	2.29428	2.78518×10^{-1}		9.83747	2.61017×10^{-4}
	6.28995	1.03893×10^{-2}		15.98287	8.98548×10^{-7}
4	0.32255	6.03154×10^{-1}	7	0.19304	4.09319×10^{-1}
	1.74576	3.57419×10^{-1}		1.02666	4.21831×10^{-1}
	4.53662	3.88879×10^{-2}		2.56788	1.47126×10^{-1}
	9.39507	5.39295×10^{-4}		4.90035	2.06335×10^{-2}
				8.18215	1.07401×10^{-3}
5	0.26356	5.21756×10^{-1}		12.73418	1.58655×10^{-5}
	1.41340	3.98667×10^{-1}		19.39573	3.17032×10^{-8}
	3.59643	7.59424×10^{-2}			
	7.08581	3.61176×10^{-3}			
	12.64080	2.33700×10^{-5}			

$$y_n = w_{n-6+1} \frac{z_{n-6+1}^{g-1}}{\Gamma(g)} \sum_{n\geq 6} x_i \; . \tag{4-30}$$

Recall that z is the abscissa for the evaluation of the distribution function f, while g is the independent parameter in the gamma function. Values of z_i can also be found in Table 4-1 with the associated quadrature weights w_i.

In Whitson's approach, g is dependent on the properties of the lumped component fraction for which the distribution is being derived. Whitson *et al.* (1990) note an approximate relationship between g and $h_{\min}$, the lowest value of molecular weight in the lumped component fraction:

$$h_{\min} = 110\left(1 - \frac{1}{1 + 4.043 g^{-0.723}}\right). \tag{4-31}$$

Rearranging to obtain g as a function of $h_{\min}$ yields

$$g = \left[\frac{h_{\min}}{4.043\left(110 - h_{\min}\right)}\right]^{-1.383} . \tag{4-32}$$

Since this method is being examined for use by the natural gas industry to characterize C_{6+} fractions, $h_{\min}$ would logically be assigned the molecular weight for normal hexane. In this work, however, another approximation by Pedersen *et al.* (1989) for molecular weight is used to incorporate knowledge from successful petroleum characterizations, and for other reasons that will be discussed shortly. The formula was developed for characterizations using single carbon number groups (SCNs), and is a simple linear function of the carbon number *n*:

$$h = 14n - 4\,. \tag{4-33}$$

Using the Pedersen *et al.* approximation, $h_{\min} = 80$, $g = 1.77819$, and $\Gamma(g) = 0.92578$.

Finally, to ensure that the characterized mole fractions add to the original lumped C_{6+} mole fraction, each y_n is normalized by the sum of all y_n, so that Equation 4-30 becomes

$$y_n = \frac{w_{n-6+1} z_{n-6+1}^{0.77819}}{\sum_{n=6}^{n\max}\left(w_{n-6+1} z_{n-6+1}^{0.77819}\right)} \sum_{n\geq 6} x_i\,. \tag{4-34}$$

Since the Gaussian quadrature abscissas and weights are deterministic constants, they propagate directly through the uncertainty formulas.

$$s_{yn}^{2} = \left(\frac{w_{n-6+1} z_{n-6+1}^{0.77819}}{\sum_{n=6}^{n\max}\left(w_{n-6+1} z_{n-6+1}^{0.77819}\right)}\right)^{2} \sum_{n\geq 6} s_{xi}^{2} \tag{4-35}$$

Although the constant value of $\Gamma(g) = 0.92578$ is eliminated from Equation 4-34 by the normalization of Equation 4-30, the presence of z^{g-1} in the expression is still influenced by the choice of the gamma function to describe the mole fraction distribution. Hence, this will be referred to as the "Gauss-gamma" characterization in this report. Note that the value of the abscissa exponent g -1 depends directly on the choice of minimum molecular weight $h_{\min}$ for the lumped C_{6+} fraction in Equation 4-32. Using $h_{\min} = 80$ from the Pedersen approximation produced an exponent of 0.77819. If the reference molecular weight for hexane of 86.175 (GPA, 2003) were used for $h_{\min}$, the exponent would change to 0.16649. An abscissa exponent of 0, corresponding to $h_{\min} = 88.188$, would reduce Equation 4-34 to the Gauss-Riazi characterization of Equation 4-26. (By definition, the sum of all Gaussian weights w_i for a given value of N is 1, so the term in the denominator of Equation 4-34 would become unity.) The Pedersen approximation for h was chosen in part to create a second Gaussian splitting scheme significantly different from the Gauss-Riazi method. The use of $h_{\min}$ as an adjustable parameter will be proposed as an avenue for further characterization research.

4.2 METHODS NOT TESTED IN THIS STUDY

During the search for characterization methods, several were identified but set aside as impractical for use by the natural gas industry. Barrufet (1998b), in a review of characterization methods for the petroleum industry, notes that a constraint in defining pseudocomponents for petroleum characterizations is that the molecular weight and specific gravity of the characterized mixture must equal the measured properties for the heavy hydrocarbon fraction being characterized. This has led to many correlations for estimating properties of the heavy fraction, most of which require data on specific gravity, molecular weight and/or normal boiling points as input. Such measured fraction properties would be available during a petroleum distillation process, but not from a GC analysis of a natural gas stream. As a result, most petroleum characterization methods cannot be used by the natural gas industry, or must be significantly modified to use only available data, and were rejected for use here. For completeness, this section briefly describes methods not tested and explains the reason for their exclusion.

4.2.1 Exponential Characterizations

The exponential distribution by Katz described in Section 4.1.3 was included in the tests because it requires no *a priori* knowledge of properties of heavy hydrocarbons in the C_{6+} fraction. Two similar distributions were identified but not included due to input requirements. One method by Yarborough (1978) and Pedersen *et al.* (1984, 1988) assumes a logarithmic distribution of the mole fraction y_n versus carbon number n of the form

$$\ln y_n \big|_{6 \le n < n\max} = A + Bn \,. \tag{4-36}$$

The constants A and B are determined for each lumped fraction, but the equation is otherwise similar to the Katz model of Equation 4-9. The constants must be determined using either data or assumptions about the characteristics of the components in the C_{6+} fraction. For instance, if the Pedersen approximation for molecular weight versus carbon number (Equation 4-33) is employed, Equation 4-36 is modified to become

$$y_n \big|_{6 \le n < n\max} = A' \exp(B' h_n) \,. \tag{4-37}$$

However, this approach requires a regression of the mole fraction to molecular weights of individual components, and a value for the molecular weight of the C_{6+} fraction itself. Measurements of these values are readily available to the petroleum industry, but the natural gas industry must rely upon assumed values or correlations. A relationship such as Equation 4-33 can be assumed for molecular weights of the individual components, but without knowledge of the actual component distribution in the C_{6+} fraction, a value of h for the total C_{6+} fraction cannot be obtained, and the correlation cannot be completed. For this reason, the Yarborough-Pedersen *et al.* logarithmic model was set aside.

Whitson and Brulé (2000) also propose a correlation between characterized mole fraction and carbon number similar to Equations 4-9 and 4-35. They employ a variation on the Pedersen molecular weight approximation to obtain values of h for each component. A value of h for the total C_{6+} fraction is again needed to uniquely define the distribution, however, which would not be available from a field GC analysis up to C_{6+}.

4.2.2 Whitson's Gamma Distribution

The gamma distribution put forward by Whitson *et al.* (1989, 1990, 2000) is used regularly to determine molecular weights and boiling points of components in petroleum characterizations, and is routinely available as part of some EOS software packages, including the Multiflash software used in this work. Use of this characterization requires the molecular weight of the C_{6+} fraction as input. As with the exponential characterizations discussed above, this information would not be available as part of a field GC C_{6+} analysis, so it was decided not to evaluate the gamma characterization method *per se*. In Section 4.1.6, however, Whitson's gamma distribution was used to define the property distribution function for one of the two Gaussian quadrature splitting methods tested.

Also, as with many characterizations, Whitson's gamma distribution method determines the properties of each pseudocomponent fraction, and its use requires an EOS software package that can accept or define new components with new properties. The Multiflash software package used in this research has this capability, but other commercially available packages do not, making the gamma characterization method impractical at present.

4.2.3 Generalized Distribution Model of Riazi

The generalized distribution model of Riazi (1997, 2005) was also used to define the property distribution function for one of the two Gaussian quadrature splitting schemes described in Section 4.1.6. Equation 4-22 describes the basic equation for each property defined by the model. The parameters P_0, A and B must be defined by trial and error and curve fitting using data on each component fraction produced by the distillation process, such as molecular weight, boiling point, or specific gravity. Again, such an extensive data set would not be available for a natural gas stream, and most EOS software cannot define new properties for new components, so the model was not evaluated here.

4.2.4 PNA Method

One characterization method discussed extensively in the literature characterizes the heavy hydrocarbon fraction as three specific groups of hydrocarbons: paraffins (P), naphthenes (N), and aromatics (A). The PNA method uses measurements of density, molecular weight and boiling points of distilled petroleum fractions to define the pseudocomponents and their properties. By solving simultaneous equations, a characterization is created from appropriate amounts of the pseudocomponents that will recreate the observed phase behavior of the petroleum fractions in equation-of-state calculations. References describing the PNA method include Bergman *et al.* (1975), Riazi and Daubert (1980) and Whitson (1984).

Again, not all commercially available EOS software is capable of defining the properties of pseudocomponents, making the PNA method impractical for the natural gas industry. One variation on the PNA method (Shariati *et al.*, 1999) uses experimental data to create a characterization from actual PNA hydrocarbons, such as n-octane or toluene, instead of pseudocomponents. This variation on the PNA method could be applied by the majority of software packages, but the unavailability of measured fraction properties for natural gas makes the PNA method impractical in general.

4.2.5 Corresponding States Principle

Mansoori *et al.* (1980) describe a method known as the “corresponding states principle.” This was developed as a method of using known critical properties of reference substances to predict properties of a mixture for which no experimental data exists. Using parameters for intermolecular potential or critical temperature and volume for two reference substances, the paper demonstrates how molar volume, viscosity and thermal conductivity can be predicted for related substances at a given state. A third parameter, whose contribution is small, is used to correct predictions for simple molecules to model properties of complex molecules. The method is able to predict thermodynamic properties such as molar density, viscosity and thermal conductivity accurately. However, the method has not yet been applied to predicting hydrocarbon dew points, and the work required to do so was beyond the scope of work and budget for this project, so the principle was not included in the characterization methods tested here.

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5. COMPARISON OF PREDICTED AND EXPERIMENTAL HYDROCARBON DEW POINTS

Chapters 2, 3 and 4 reviewed the information gathered for this evaluation project. This chapter summarizes the comparisons of experimental HDPs from the reference dataset to HDPs predicted using various equations of state, characterizations and parameters. Each characterization method is assessed for its ability to reproduce the experimental data, and explanations are given where possible for the good or poor agreement between calculations and reference data. The criterion for an "accurate" characterization method, as defined by the project advisory subcommittee, is one that can predict experimental HDP values to within ±2.3°F, the uncertainty of an industry-standard chilled mirror device (George *et al.*, 2005a).

Dew points were calculated using generic versions of the Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) equations of state, which are used most often by the natural gas industry. These equations were tested using Multiflash version 3.5 (Infochem, 2006), which is capable of computing both hydrocarbon dew points and amounts of liquid condensate within the region of two-phase behavior. Previous research (George *et al.*, 2005a) has shown that differences in commercial software packages have much less of an effect on computed dew points than the selection of a characterization method, so the use of other cubic EOS software was not considered necessary. An Excel spreadsheet template was created containing a Multiflash interface and the characterizations of interest. Using the spreadsheet, all characterizations could be tested with a new equation of state or a new reference gas by changing inputs at a few locations, minimizing potential errors. As discussed in Chapter 2, the GERG equation of state was also tested using the software available from the University of Bochum in Germany (Wagner, 2005). For GERG, the DOS interface was found to be more efficient than the Excel interface, so separate input files to the DOS software were created for each characterization and test gas.

George *et al.* (2005a) also found that changes in binary interaction parameters (BIPs) had a small effect on computed dew points relative to changes in characterization methods, so this research did not set out to evaluate different BIP sets. However, as time allowed, calculations with the cubic equations of state were performed with two component property datasets. The default dataset within Multiflash is based on data from several accepted references, including Reid *et al.* (1977 and 1987), Riazi and Daubert (1980), Knapp *et al.* (1982), and Whitson and Brulé (2000). The DIPPR database of chemical properties produced by AIChE (1991) was also available for use with Multiflash, and HDPs were calculated using DIPPR data also. Differences in dew points computed using the default parameters and the DIPPR parameters were 0.1°F or 0.2°F in the majority of cases, and never more than 0.6°F. The results using the DIPPR parameters will not be reported here, as they do not affect the conclusions of the study.

Peng-Robinson and SRK dew points were computed using the characterization methods described in Chapter 4, and with the full compositions from the reference dataset tabulated in Chapter 2. Multiple calculations were performed using the Katz exponential characterization and the two Gaussian quadrature splitting schemes, since they can be extended to different values of the maximum carbon number, $n_{\max}$. Calculations were performed at values of $n_{\max}$ from 7 to 11 for the Katz method, and from 7 to 12 for the Gaussian methods. Because the

GERG database does not currently include data on hydrocarbons beyond C_8, the project advisory subcommittee agreed that tests of GERG-2004 should be limited to characterizations containing hydrocarbons no heavier than octane. Methods tested with GERG include a C_{8+} characterization, the 47/36/17 $C_6/C_7/C_8$ distribution, and the Gauss-Riazi and Gauss-gamma characterizations using $n_{\text{max}} = 8$.

5.1 EXAMPLE COMPARISONS

Approximately 1,800 comparisons were performed among the various combinations of equations of state, characterizations and reference points. This section presents example graphs comparing computed dew points to reference data. A summary of the comparisons can be found in Section 5.2.

5.1.1 Comparisons to Warner Gas #2

The first group of graphs compares computed and experimental dew points for Warner Gas #2, listed in Table 2-1. In Figure 5-1, the horizontal line represents the measured dew point from the reference dataset. The dashed horizontal lines represent experimental uncertainties on the reference measurement. The symbols represent dew points computed using the indicated equations of state and parameter sets. The error bars on each point were determined by setting hexanes and heavier components to the upper and lower 95% confidence intervals, and computing dew points for the redistributed compositions. The next four figures present similar comparisons for the Katz and Gaussian characterizations, with results for different values of the maximum carbon number.

Figure 5-1 shows that Peng-Robinson calculations with the complete gas composition and the lumped C_{9+} method overpredict the measured value by about 12°F, while SRK calculations overpredict by about 16°F. The large confidence intervals on the calculated values overlap the data, however, so while these differences are well outside the target margin of ±2.3°F, they are not considered statistically significant. The 46/36/17 characterization results are in excellent agreement with the data, within ±3°F when the cubic equations of state are used, and within 4°F when GERG is used as the EOS. This good agreement may be explained by the fact that the composition of Warner gas #2 resembles a Gulf Coast gas, which was used as the basis for the 46/36/17 split ratios.

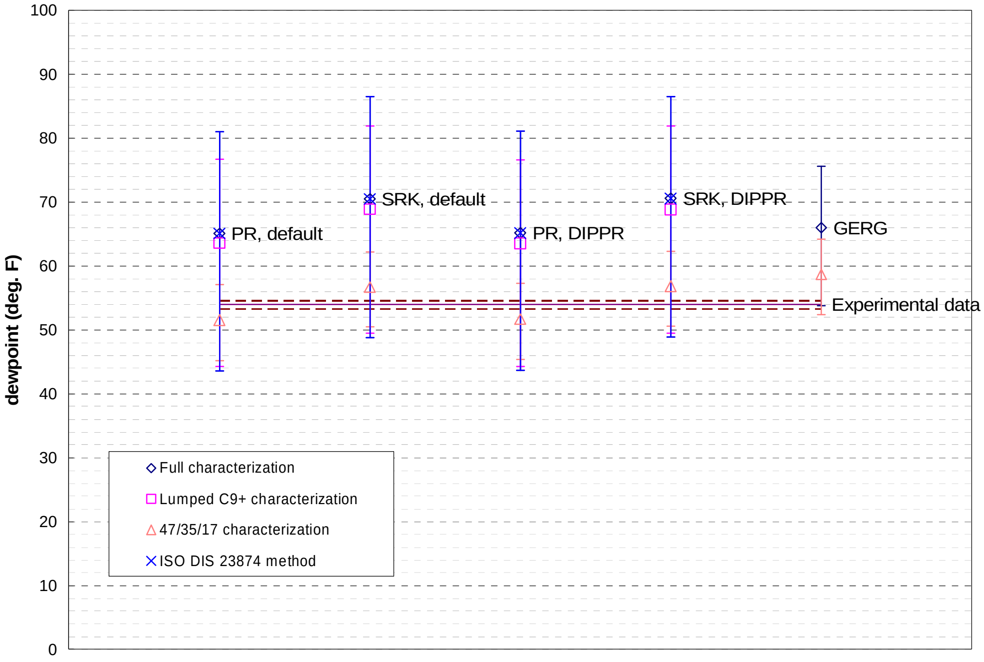

Figure 5-1. Comparison of reference data for Warner gas #2 to HDPs computed using the lumped C_{9+}, 47/36/17 and ISO 23874 characterizations and the reference gas composition.

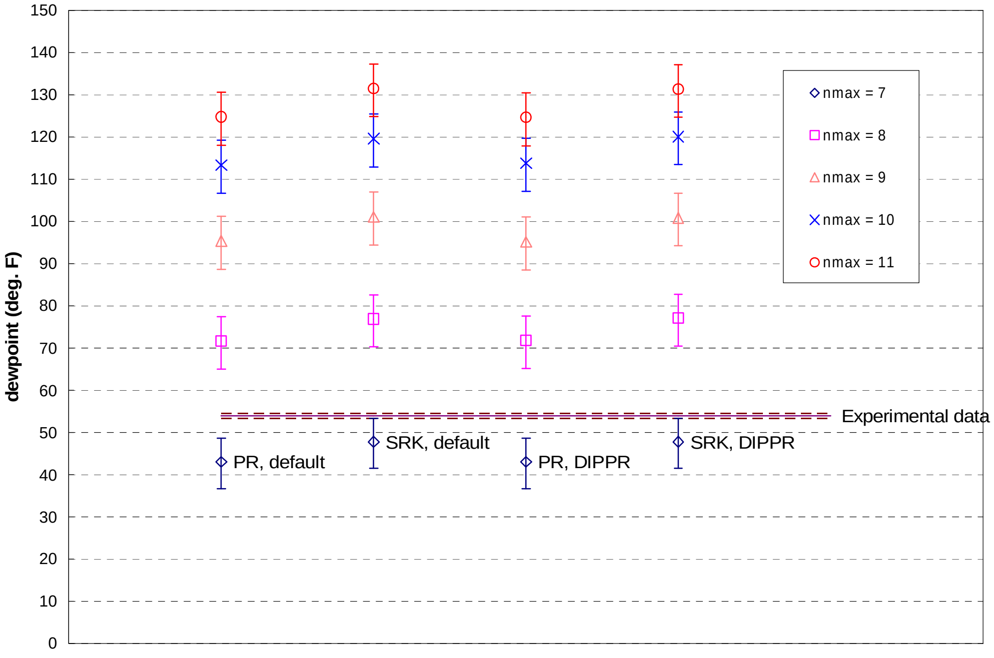

Figure 5-2. Comparison of reference data for Warner gas #2 to HDPs computed using the Katz exponential characterization with the remainder assigned to the heaviest component.

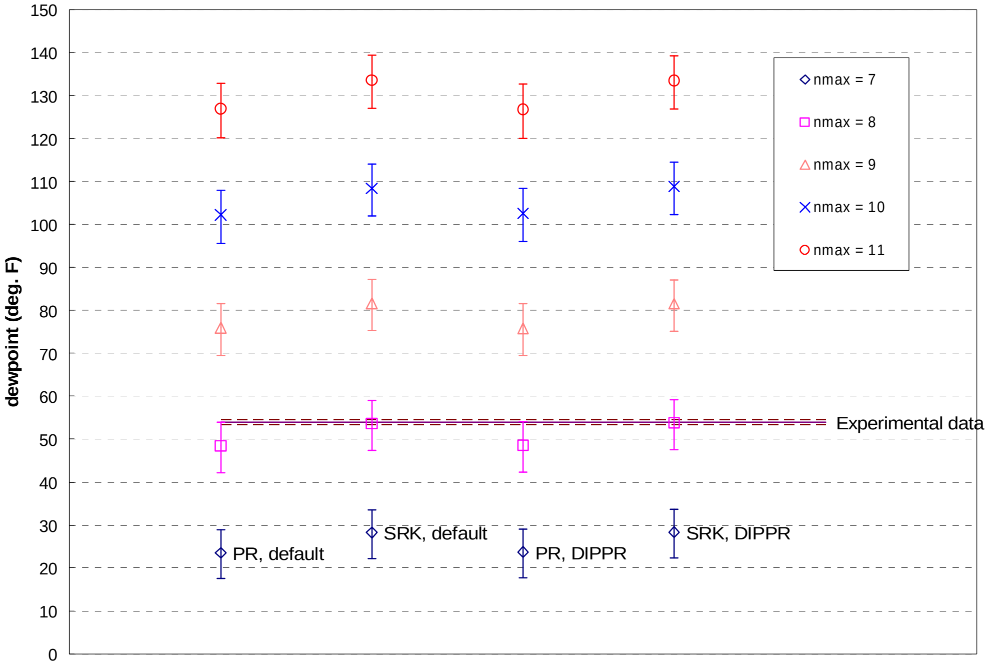

Figure 5-3. Comparison of reference data for Warner gas #2 to HDPs computed using the Katz exponential characterization with the remainder assigned to C_6.

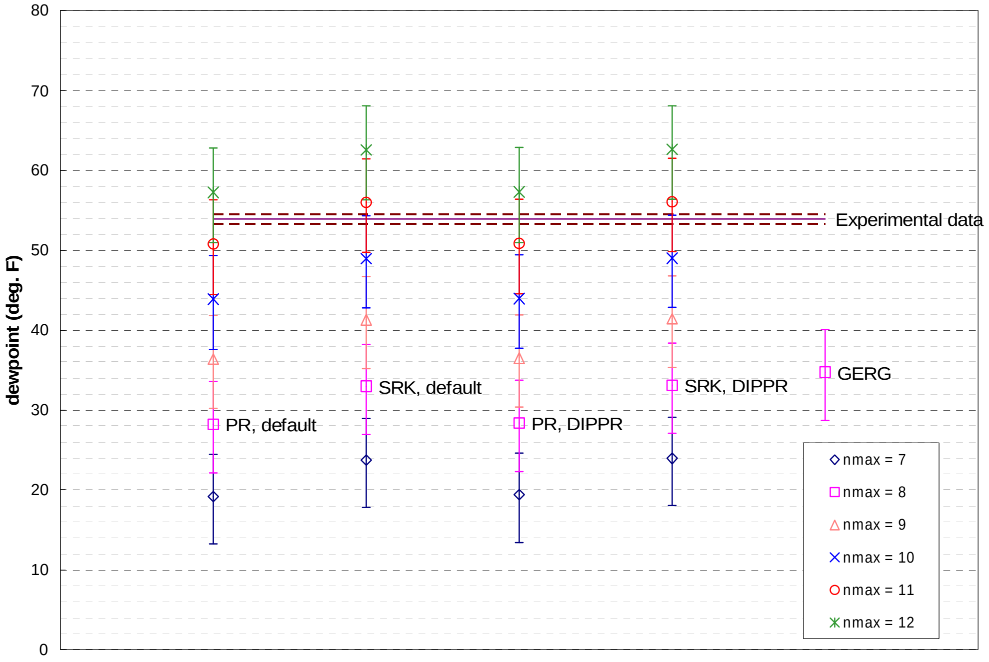

Figure 5-4. Comparison of reference data for Warner gas #2 to HDPs computed using the Gaussian quadrature splitting scheme with the Riazi distribution.

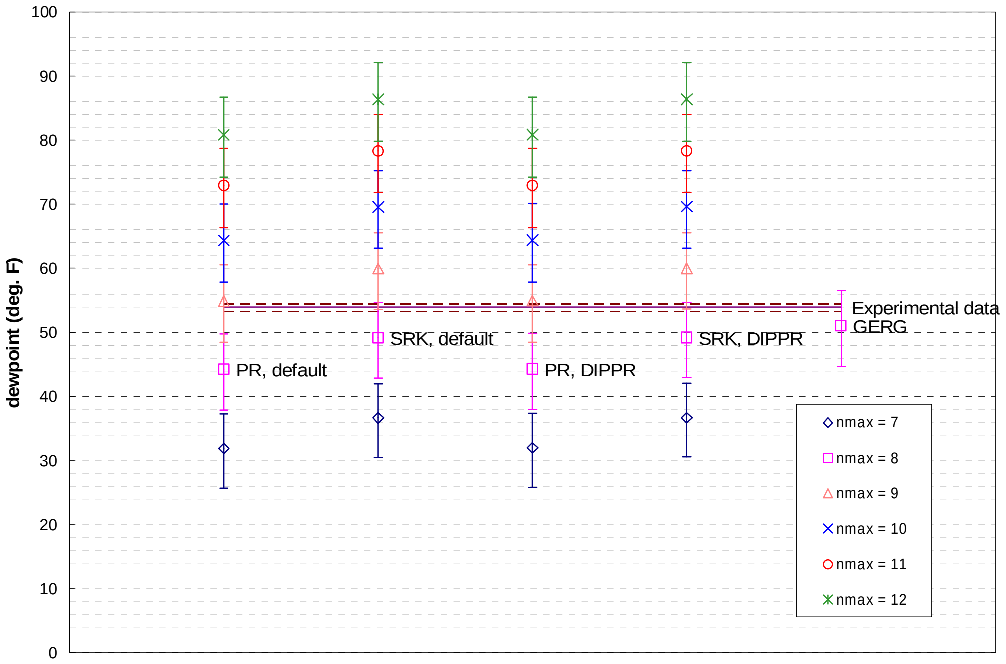

Figure 5-5. Comparison of reference data for Warner gas #2 to HDPs computed using the Gaussian quadrature splitting scheme with Whitson's gamma distribution.

Figure 5-2 and Figure 5-3 show that depending upon the number of components used, the Katz logarithmic characterization with the "remainder" fraction assigned to the heaviest component either underpredicts or overpredicts the data significantly, regardless of the equation of state used. When the remainder is assigned to C_6, the Katz characterization with $n_{max} = 8$ predicts the experimental dew point to within 6°F, the differences not being statistically significant. Other values of n_{max} again severely overpredict or underpredict the measured value. In Figure 5-4, it is seen that the Gauss-Legendre method with Riazi's weights predicts the experimental values to within ±3°F if the characterization is extended to C_{11}. Figure 5-5 shows that for the Gauss-Legendre method with gamma weights, a characterization to C_8 or C_9 comes to within ±5°F, again depending upon the equation of state used.

One reason for the closer agreement of the Gaussian results can be seen in Figure 5-6 through Figure 5-9, which compare the mole fraction distributions of the reference gases to the Katz and Gaussian characterizations. The Gaussian distributions produce profiles of the correct shape, and depending on the heaviest hydrocarbon in the characterization, yield amounts of each component of the correct order of magnitude as the true gas composition. By comparison, the fixed profile created by the Katz characterization does not represent the actual mole fraction trend of the Warner gas, and overestimates the amounts of C_{9+} components. A possible explanation is that the Katz formula was developed for characterizing gas condensate systems rather than gas streams. If condensed liquid phases of several gas/liquid systems were analyzed to create the formula, the majority of the C_{9+} components may have existed in the condensed liquid phase, skewing its use for characterizing a gas stream. Riazi (2005) gives another example in which the Katz characterization underpredicts the amounts of lighter components and overpredicts the heavier component distribution.

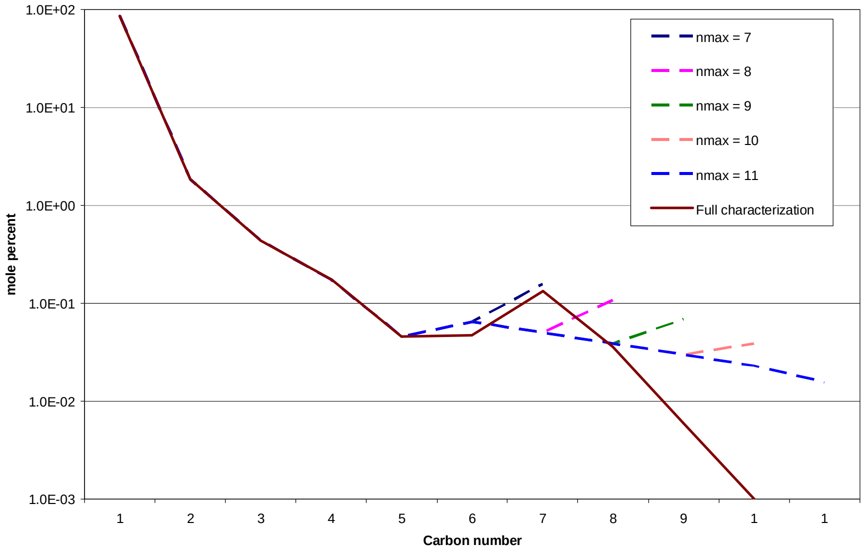

Figure 5-6. Comparison of reference gas composition for Warner gas #2 to characterizations computed using the Katz exponential characterization with the remainder assigned to the heaviest component.

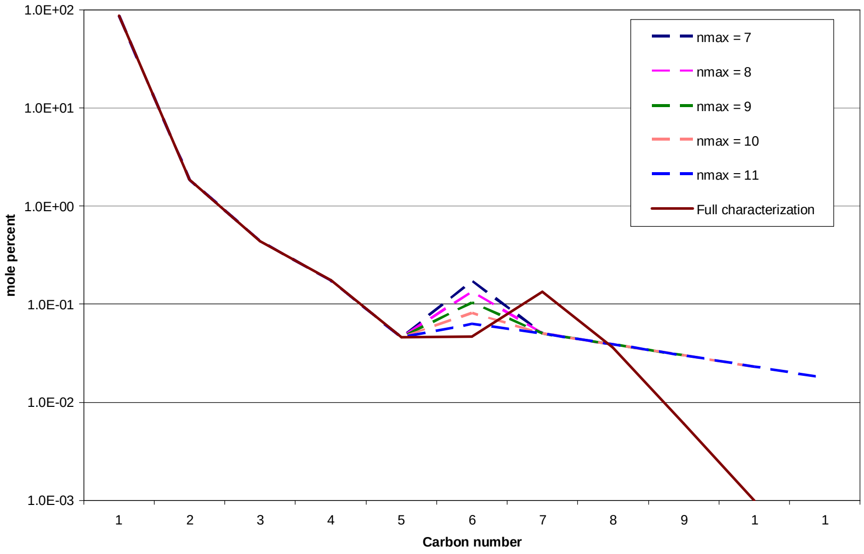

Figure 5-7. Comparison of reference gas composition for Warner gas #2 to characterizations computed using the Katz exponential characterization with the remainder assigned to C_6.

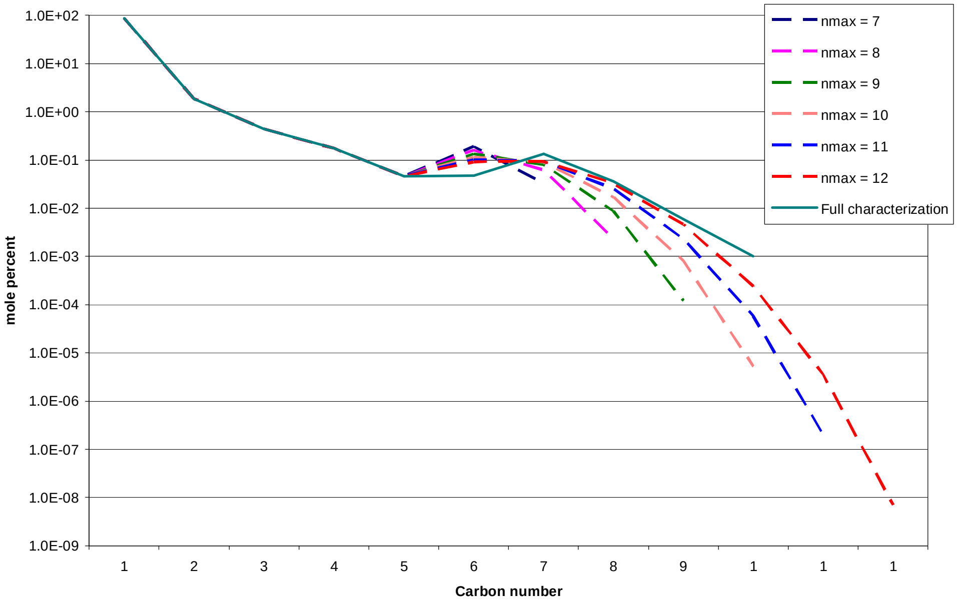

Figure 5-8. Comparison of reference gas composition for Warner gas #2 to characterizations computed using the Gaussian quadrature splitting scheme with the Riazi distribution.

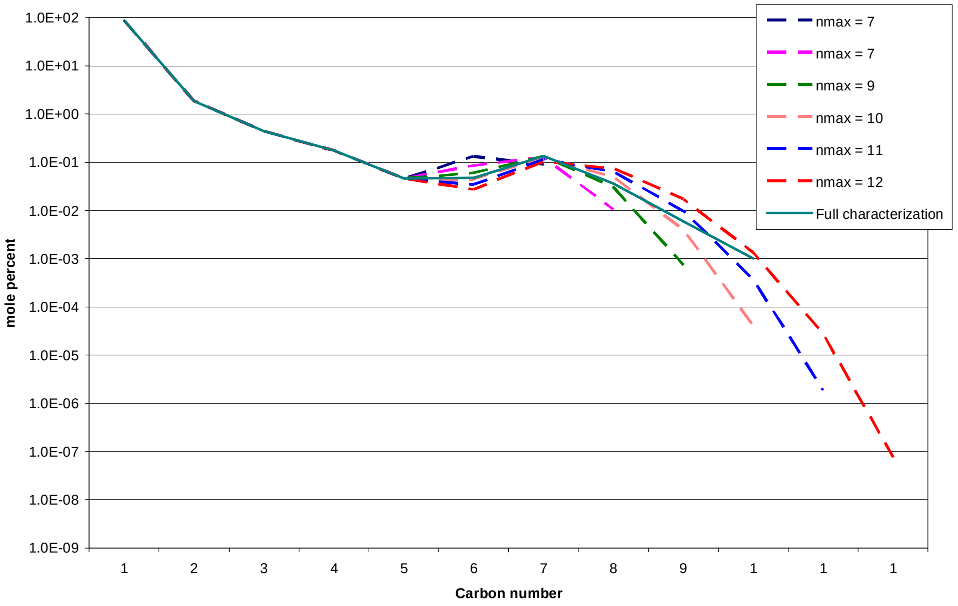

Figure 5-9. Comparison of reference gas composition for Warner gas #2 to characterizations computed using the Gaussian quadrature splitting scheme with Whitson's gamma distribution.

5.1.2 Comparisons to SwRI 1,523 Btu/scf Gas

The next set of graphs compares computed and experimental dew points for the 1,523 Btu/scf gas used in the DOE-sponsored tests at Southwest Research Institute (SwRI) (George and Burkey, 2005c), whose composition is listed in Table 2-10. Because measurements were taken at SwRI of each gas at multiple pressures, comparisons for each equation of state and characterization require a separate graph. In this set of plots, experimental data for the 1,523 Btu/scf gas are compared to dew point curves computed with the SRK equation of state and various characterization methods. The dew point curves were computed using the indicated characterization methods; the symbols represent the measured dew points from the reference dataset, with 95% confidence intervals on measured pressure and temperature shown as error bars. Confidence intervals were produced for the computed dew point curves, determined (as before) by setting hexanes and heavier components to their upper and lower 95% confidence intervals and computing dew points for the redistributed compositions. However, because of the large amounts of C_9 and C_{10} in the certified test gas composition and the relatively small uncertainties in their amounts, the 95% confidence intervals on the curves are very narrow and indistinguishable on the graph from the curves themselves.

Figure 5-10 shows that for the 1,523 Btu gas, curves calculated using the complete certified composition, the C_{9+} characterization and the 47/36/17 characterization are almost identical and consistently underpredict the measured dew points at all pressures. The ISO 23874 characterization produces a curve that intersects the measured dew points at the two lower pressures, but again underpredicts the dew points at higher pressures. In Figure 5-11, the data are compared to results from the Katz characterization with the “remainder” assigned to the heaviest component. Depending on the pressure of interest, the data is either predicted well using $n_{\max} = 8$, or straddled by characterization using $n_{\max} = 7$, 8 or 9. Figure 5-12 and Figure 5-13 compare predictions from the Gauss-Riazi and Gauss-gamma characterizations, respectively. The Gauss-Riazi characterization with $n_{\max} = 12$ performs similarly to the ISO characterization, while the Gauss-gamma characterization will accurately predict observed dew points at various pressures using $n_{\max}$ values ranging from 9 to 12.

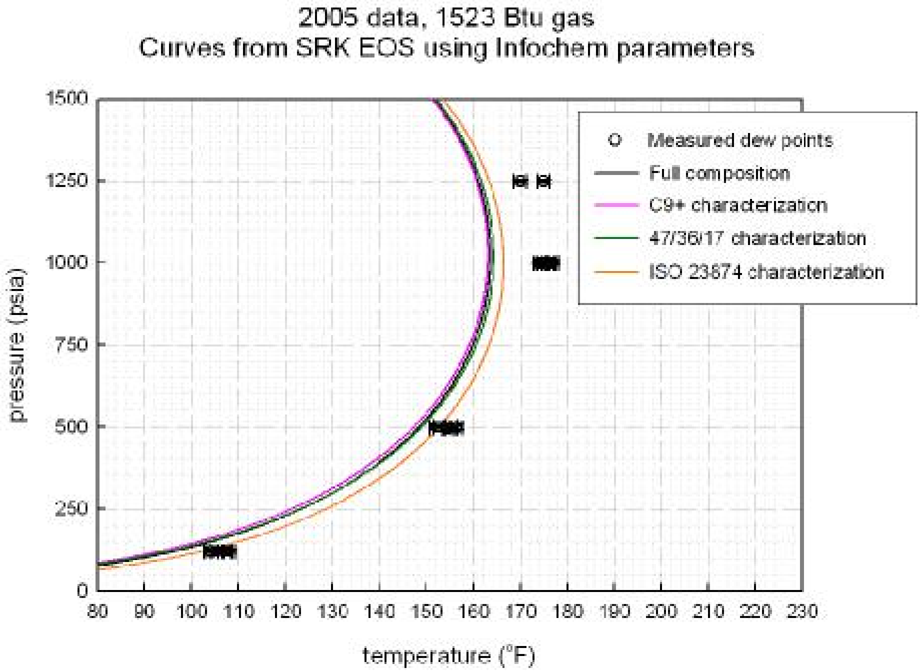

Figure 5-10. Comparison of reference data for the 2005 SwRI 1,523 Btu/scf test gas to HDPs computed using the lumped C_{9+}, 47/36/17 and ISO 23874 characterizations and the reference gas composition.

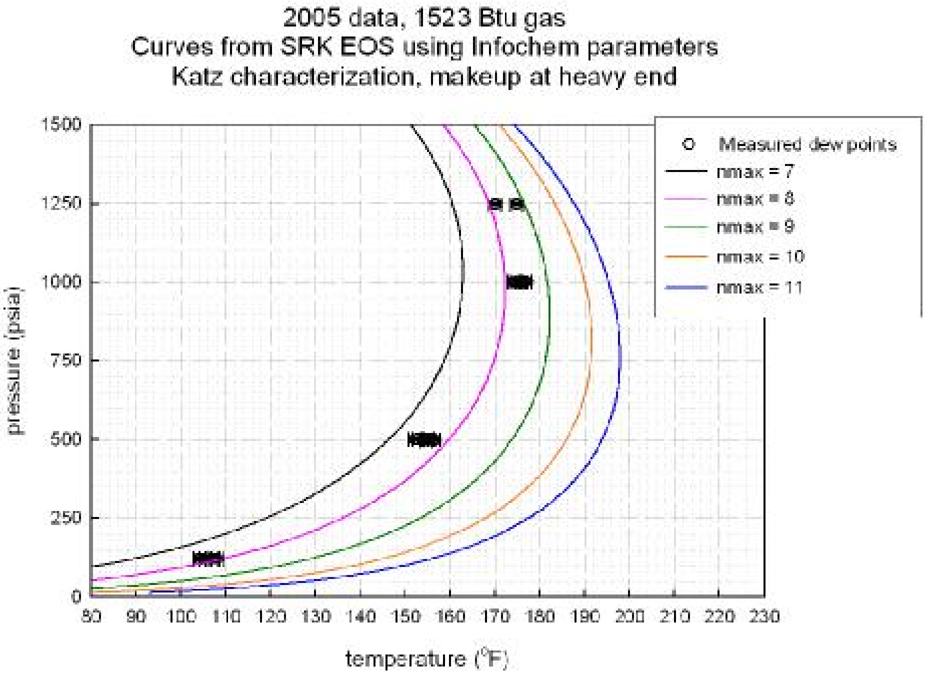

Figure 5-11. Comparison of reference data for the 2005 SwRI 1,523 Btu/scf test gas to HDPs computed using the Katz exponential characterization with the remainder assigned to the heaviest component.

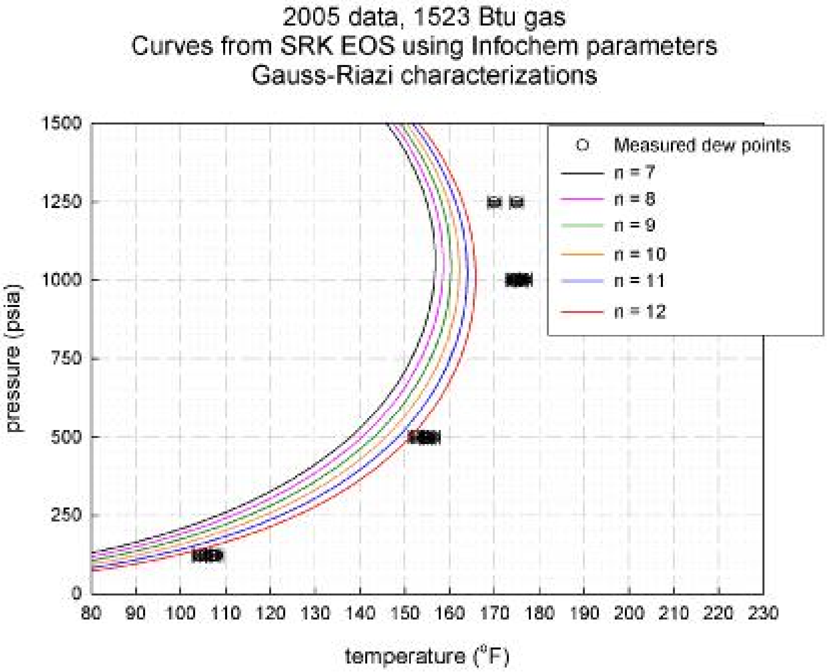

Figure 5-12. Comparison of reference data for the 2005 SwRI 1,523 Btu/scf test gas to HDPs computed using the Gaussian quadrature splitting scheme with the Riazi distribution.

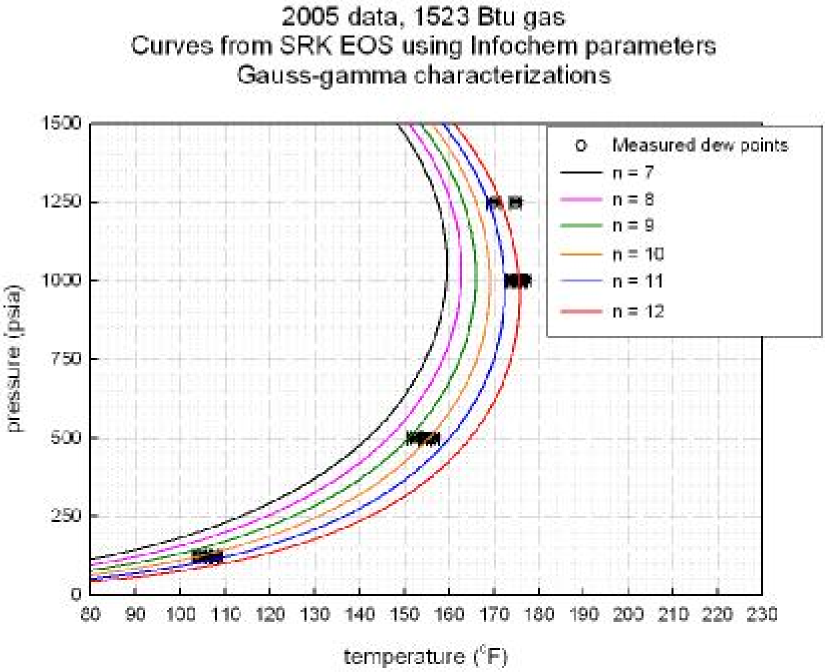

Figure 5-13. Comparison of reference data for the 2005 SwRI 1,523 Btu/scf test gas to HDPs computed using the Gaussian quadrature splitting scheme with Whitson’s gamma distribution.

These figures exemplify a trend found in comparisons to much of the SwRI data, which include measurements at multiple pressures on the same gas. Data at all pressures for a given gas composition, particularly the 1,325 and 1,523 Btu gases, cannot be reproduced by a single characterization method. The root cause may be related to the temperature dependence of the EOS parameters, and ideally, modification of the parameters would allow one characterization to acceptably predict actual dew point behavior at all pressures. In the next chapter, however, it will be shown that the Katz or Gaussian characterizations can be adapted to predict actual phase behavior by selecting different values of $n_{\max}$ at different pressures.

5.1.3 Comparisons to PHLC Data from Derks Gas A

The two Derks datasets are composed solely of measurements of potential hydrocarbon liquid condensate (PHLC), a quantity analogous to liquid dropout defined in Section 2.2.2. By definition, the PHLC approaches zero as conditions approach the hydrocarbon dew point from within the two-phase region. All equations of state (Peng-Robinson, SRK and GERG-2004) were used to compute both dew points and PHLC values for the Derks test gases at the pressures of interest. The experimental data was extrapolated to a value of zero using a cubic curve fit to provide an HDP estimate to be compared to calculated HDP values.

Because measurements were taken of PHLC at multiple temperatures below the dew point, each graph is limited to comparisons for a given equation of state and no more than six characterizations. The final set of graphs in this section compare the experimental PHLC values for Derks gas A to the calculated values from various characterizations using the Peng-Robinson equation of state. Differences in results between gas A and gas B are noted separately in the text.

Figure 5-14 compares experimental PHLC data to curves computed using the category 1 characterizations (lumped C_{9+} and ISO 23874), the 47/36/17 $C_6/C_7/C_8$ distribution, and the complete reference composition. Calculations with the cubic equations of state using either the complete gas composition or the ISO 23874 characterization (based on GC retention times) most closely predict the extrapolated HDP. These are also the only characterizations that predict the nonlinear trends in PHLC with temperature also seen in the experimental data. The next four figures compare the data to curves computed using the Katz and Gaussian characterizations. None of these methods accurately reproduce the nonlinear trends in PHLC. However, when extrapolated to zero PHLC to determine a dew point, the Gauss-Riazi characterizations with different limits on carbon number tend to bracket the extrapolated dew points for gas A. The Gauss-gamma characterizations up through the maximum carbon number tested ($n_{\max} = 12$) underpredict the extrapolated dew points, but it is expected from Figure 5-18 that the Gauss-gamma method with $n_{\max} = 12$ and 13 will bracket the extrapolated value.

As with all other comparisons, the SRK equation of state produces dew points and PHLC curves shifted toward temperatures a few degrees higher. For Derks gas A, this brings the C_{9+} results into closer agreement with the reference data; for the Katz and Gaussian characterizations, the value of $n_{\max}$ that produces best agreement with the reference data decreases by 1 in two comparisons.

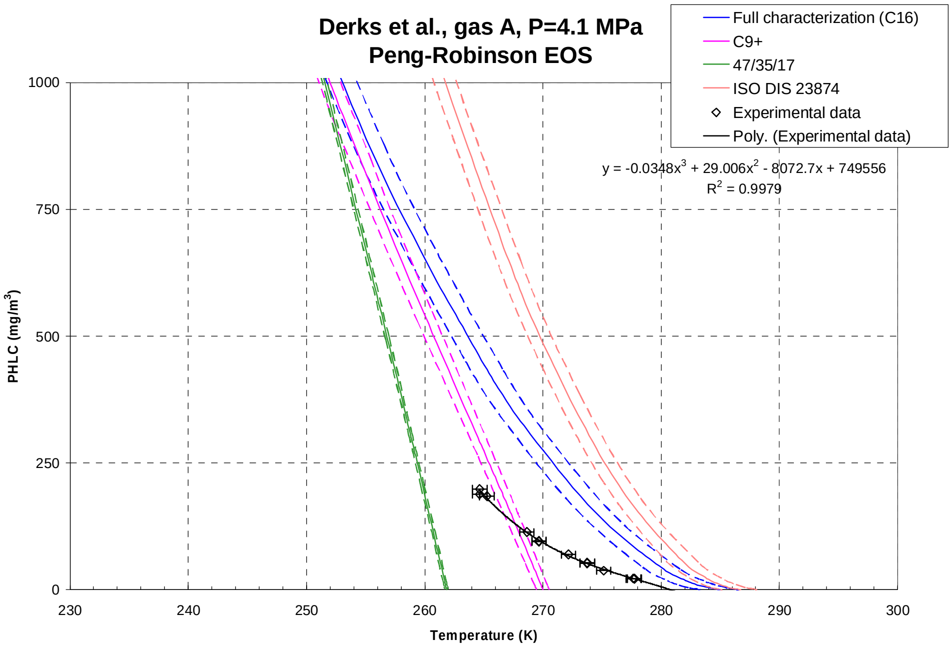

Figure 5-14. Comparison of reference data for Derks gas A to PHLC and dew point values computed using the Peng-Robinson EOS with the lumped C_{9+}, 47/36/17 and ISO 23874 characterizations and the complete reference gas composition through C_{16}.

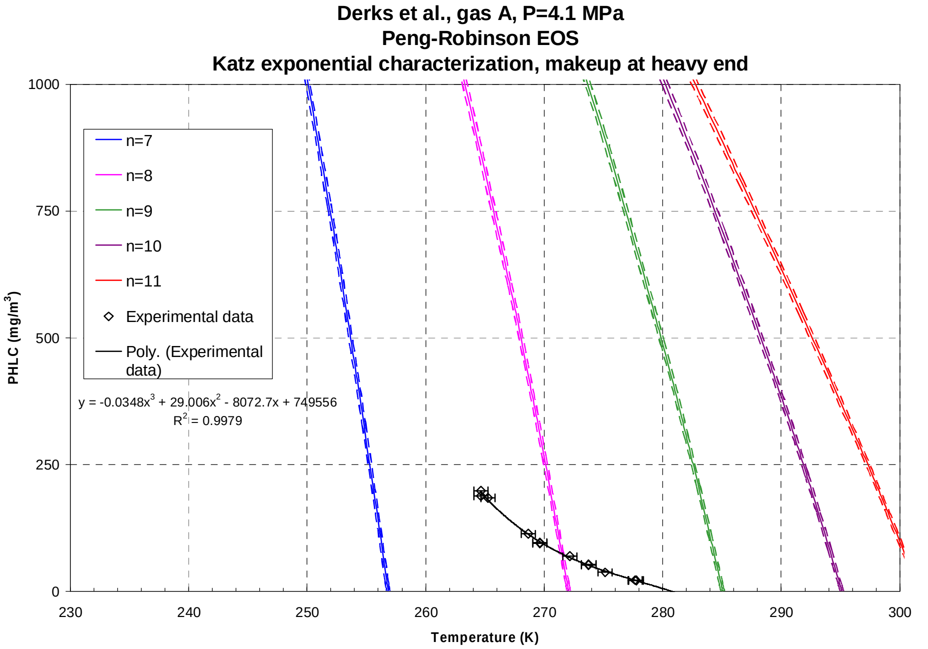

Figure 5-15. Comparison of reference data for Derks gas A to PHLC and dew point values computed using the Peng-Robinson EOS and the Katz exponential characterization, with the remainder assigned to the heaviest component.

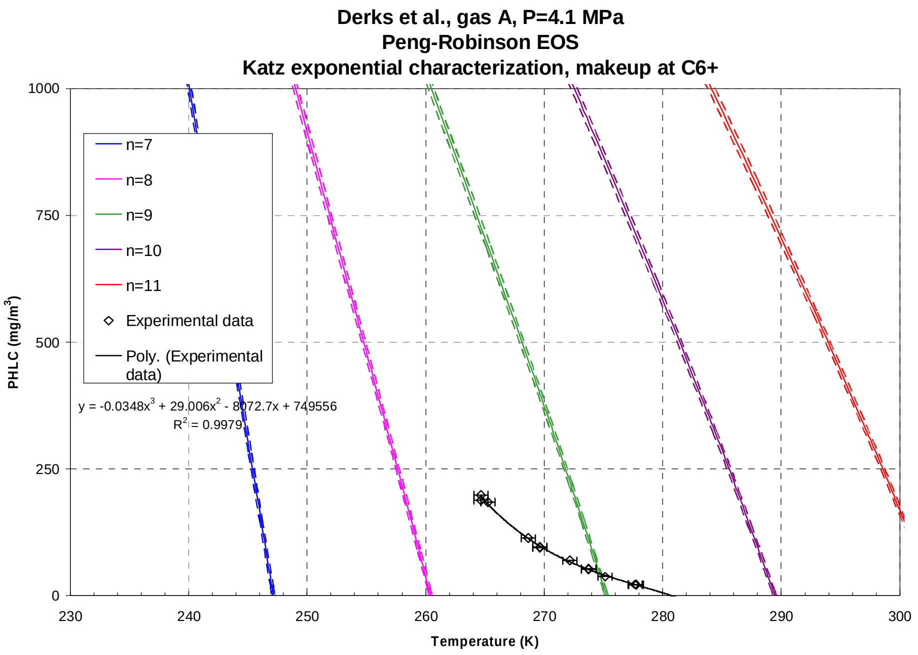

Figure 5-16. Comparison of reference data for Derks gas A to PHLC and dew point values computed using the Peng-Robinson EOS and the Katz exponential characterization, with the remainder assigned to hexane.

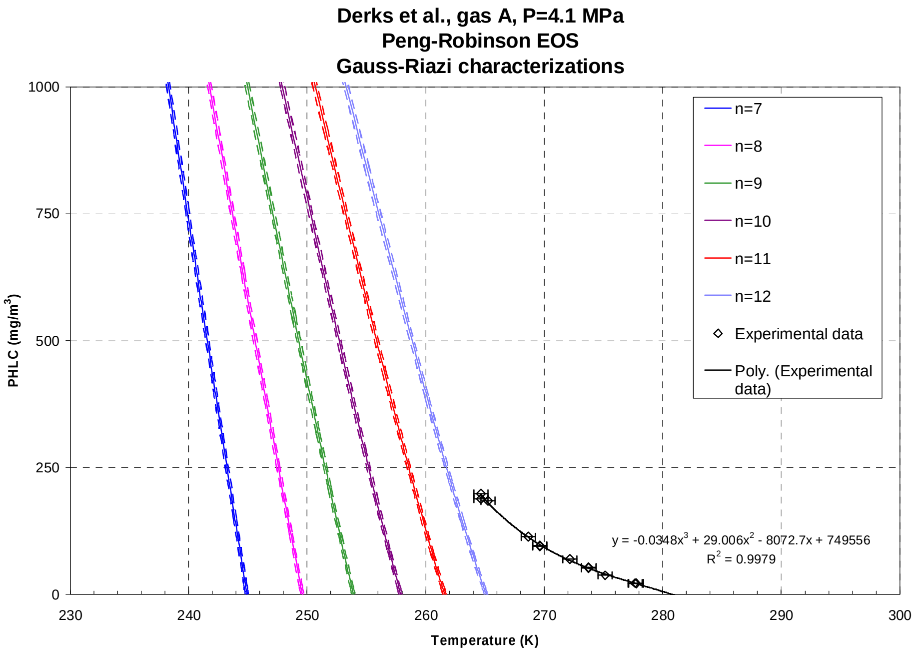

Figure 5-17. Comparison of reference data for Derks gas A to PHLC and dew point values computed using the Peng-Robinson EOS and the Gaussian quadrature splitting scheme with the Riazi distribution.

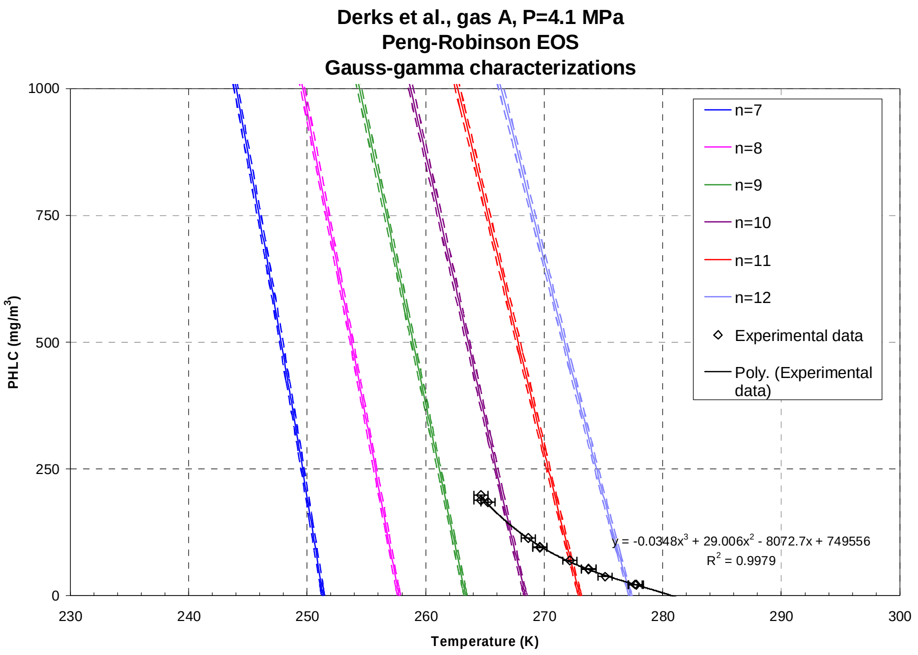

Figure 5-18. Comparison of reference data for Derks gas A to PHLC and dew point values computed using the Peng-Robinson EOS and the Gaussian quadrature splitting scheme with Whitson's gamma distribution.

Derks gas B is a richer gas in propane and heavier hydrocarbons than gas A, so it can be expected that the same characterization methods will produce different results. For gas B, dew points computed using the complete gas composition and the C_{9+}, 47/35/17, and ISO DIS 23874 characterizations consistently overpredict the HDP extrapolated from the experimental data. While dew points from only the Gauss-Riazi characterizations bracket the experimental results for gas A, both the Gauss-Riazi and Gauss-gamma characterizations with different values of $n_{\max}$ bracket the extrapolated dew points for gas B.

5.2 SUMMARY OF COMPARISONS BETWEEN CALCULATED AND EXPERIMENTAL DEW POINTS

It became clear as the comparisons progressed through the various equations of state, characterization methods and database gases that no single characterization method could consistently predict the measured hydrocarbon dew points for the entire reference dataset to within calculational and experimental uncertainties. Certain characterizations had a higher "success rate" than others, making them candidates for use in a general procedure. Acceptable accuracy for a computed hydrocarbon dew point, as defined by the Project Advisory Group, is agreement with an experimental HDP value to within the uncertainties of an industry-standard chilled mirror device (±2.3°F).

In all, dew point comparisons were made for 45 combinations of gas composition and pressure, using the PR, SRK and GERG equations of state (EOS), and using eight chosen characterization methods. In this section, the general performance of the various equations and methods will be discussed, and the final choice of characterization and equation of state for the procedure will be explained.

5.2.1 Results of the Lumped C_{9+} Method

Results from the lumped C_{9+} characterization method, and dew points computed using the complete certified gas composition from the reference dataset, generally overpredicted the reference data. Of 45 reference dew points, neither characterization met the accuracy criteria for more than 12 of the dew points. The C_{9+} characterization method overpredicted the Warner dew points and six of the ten EffecTech gases by 3 to 15°F. For EffecTech gases 5 through 9, the C_{9+} characterization used with the Peng-Robinson EOS predicted the measured dew points to within the desired accuracy, but the same characterization input to the SRK EOS met the accuracy criterion only for EffecTech gas 5. For Derks gas A, the lumped C_{9+} method underpredicted the measured dew points by 7 to 11°F, but overpredicted values for Derks gas B by 3 to 7°F. Finally, for the SwRI gases, the lumped C_{9+} method was successful in some cases, but followed no pattern other than underpredicting the measured dew points, particularly for the 1,325 and 1,523 Btu gases. This fits the observation that current EOS predictions tend to underpredict dew points for richer gases at higher pressures.

5.2.2 Results of the ISO 23874 Method

The method described in ISO document 23874 requires chromatographs to associate elution times with boiling point data. Chromatographs were available for the 2005 SwRI test gases, but for the other reference gases, retention times described by McNair and Bonelli (1969) were used in the calculations. The ISO predictions met the accuracy criteria for only 9 of 45 compositions and pressures when used with the PR equation, but 15 of 45 compositions and pressures when used with the SRK equation. Notably, agreement to within the target of ±2.3°F was obtained only for SwRI gases (which make up 30 of the 45 data points), but with measurements from both the 2003 and 2005 tests.

For the Warner, EffecTech and Derks gases, the ISO method consistently overpredicted the measured dew points. Notably, only the Warner, EffecTech and Derks gas compositions (see Chapter 2) include “lumped” amounts such as “total C_9” or “non-normal C_9 isomers.” These lumped amounts include components which have the same carbon number as the associated normal alkane, but which most likely have lower boiling points than the normal alkane. Without detailed information on the non-normal components, it was necessary to assign the total mole fraction to the normal alkane of the same carbon number, as would be recommended for EOS software containing only data on the normal hydrocarbons. It is possible that the distribution of these total amounts to normal alkanes may have caused the overpredictions for these gases using the ISO characterization method. No judgment of the overall performance of the method will be made here as a result. However, because of its poor performance with gases for which only limited compositional data is available, it was not considered further for the general characterization procedure.

5.2.3 Results of the 47/36/17 $C_6/C_7/C_8$ Method

Since the 47/36/17 method uses only normal hydrocarbons up to octane to characterize the C_{6+} fraction, it can be used with the GERG equation of state as well as the Multiflash software package and the cubic equations. In fact, this characterization method was most successful when used with the GERG EOS, predicting approximately half of the experimental dew points for the SwRI test gases and dew points for two of the three Warner gases to within the target criterion of ±2.3°F. However, the method consistently overpredicted the measured dew points for the EffecTech gases, typically by about 20°F, and underpredicted the dew points for Derks gas A by 15 to 20°F. In all, the method met the accuracy requirements for only 16 of 45 test cases when used with the GERG EOS, and fewer still with the Peng-Robinson and SRK equations of state.

5.2.4 Cricondentherm Predictions Using the C_{6+}–GPM Method

The C_{6+}–GPM method was used to calculate cricondentherm hydrocarbon dew points (CHDPs) for the three gases in the SwRI database on which CHDPs were measured. Using a 40/40/20 $C_6/C_7/C_8$ split to compute the molecular weight of the C_{6+} fraction, as recommended in the NGC+ White Paper (Natural Gas Council, 2005), yields a predicted CHDP for the 1,050 Btu/scf gas of 29.8°F, in agreement with the measured values ranging from 27.7°F to 30.0°F. However, the same combination of equation of state and characterization underpredicted the measured CHDPs for the 1,145 Btu/scf gas by 17°F, and underpredicted the CHDP for the 1,523 Btu/scf gas by 50°F. The NGC+ White Paper also suggested the use of the 47/36/17 and 60/30/10 $C_6/C_7/C_8$ split to compute the C_{6+} molecular weight. Molecular weights were recomputed using these characterizations, as well as using the complete gas compositions listed in Chapter 2. With each characterization, the method predicted the 1,050 Btu/scf cricondentherm to within experimental values, but underpredicted the measured CHDPs for the other gases by similar amounts as before.

It was suspected that the two richer SwRI gases were beyond the range of compositions used to create the correlation, so that its use on these gases was an attempt to "extrapolate" the correlation unsuccessfully. The gases used to create the correlation (Poellnitz, 2002) had C_{6+} contents ranging from 0.10% to 0.56% and C_{6+} GPM values ranging from 0.04 to 0.25 gallons per thousand cubic feet of gas. For the 1,050, 1,145 and 1,523 Btu/scf gases, the C_{6+} contents were 0.10%, 0.25%, and 0.81%, respectively; the C_{6+} GPM values computed using the 40/40/20 split were 0.05, 0.11, and 0.36 gallons per thousand cubic feet, respectively. The richest SwRI gas clearly falls outside the valid range of the correlation, which explains its failure to predict the cricondentherm temperature for this gas, but the 1,145 Btu/scf gas appears to fall within the limits of the correlation database. No explanation can be given at this time for the large underprediction of CHDP for the 1,145 Btu/scf gas.

5.2.5 Results of the Katz and Gaussian Characterizations

Unlike the other characterization methods tested in this work, the Katz and Gaussian characterization methods allow the option of choosing the heaviest normal hydrocarbon in the distribution. This flexibility of choosing the heaviest component led to a higher "success rate" for the Katz and Gaussian characterization methods in accurately predicting HDPs when used with the cubic equations of state. With the proper choice of $n_{\max}$, both methods met the accuracy criterion of ±2.3°F in predicted hydrocarbon dew points much more often than the C_{9+} method, the 47/36/17 C_6/C_7/C_8 method or the ISO 23874 method.

Recall that the Derks, Warner, and Cowper reference datasets contain dew points measured at a single pressure for each gas composition Among these 15 test gases documented in these three references, the Gauss-Riazi characterization with a proper limit on carbon number and the correct choice of equation of state met the ±2.3°F accuracy criterion for 14 of the 15 gases. The Gauss-gamma characterization met the criterion for 11 gases, given the correct value of $n_{\max}$ between 7 and 12 and the correct choice of EOS. For the Katz characterization, the success rates were 3 of 15 gases when the heaviest component was used as the "makeup" component and 8 of 15 when C_6 was used as the "makeup."

The SwRI database contains dew points measured at multiple pressures for each gas along their respective dew point curves, so that the characterization methods can be evaluated at several conditions for the same gas. For 25 of 30 combinations of composition and pressure, dew points were predicted to within ±2.3°F using the Gauss-Riazi characterization with one of the cubic equations of state and a properly selected carbon number limit. The four exceptions occurred for the 1,325 Btu/scf gases at a pressure of 1,250 psi, and for the 1,523 Btu/scf gas at all pressures except 500 psi. Even better results were obtained with the Gauss-gamma characterization; dew points at all 30 combinations of composition and pressure were predicted to within ±2.3°F using one or more combinations of cubic EOS and value of $n_{\max}$. For the Katz characterization, the equivalent success rates were 18 of 30 with the heaviest component as "makeup," and 24 of 30 with C_6 as the "makeup" component.

The Gauss-Riazi and Gauss-gamma characterizations met the accuracy criteria more often than the Katz characterizations due to two advantages:

- Incrementing the carbon number of the heaviest component used in the Gaussian methods produces smaller increments in computed dew point than similar increments in the Katz characterization methods. An example of this can be seen by comparing Figure 5-11, Figure 5-12 and Figure 5-13, where an increment in $n_{\max}$ of 1 increases the predicted dew point by as much as 10°F for the Katz method, but only by 2 or 3°F for the Gaussian methods.
- The Gaussian characterizations more realistically simulate the actual component distributions for the test gases than the exponential Katz characterizations, as explained in Section 5.1.1.

While an optimum value of $n_{\max}$ may be determined from data on the gas composition, it was decided to choose a single equation of state for the prediction method developed in the next chapter from a practicality standpoint. For both Gaussian characterization methods, a higher success rate was obtained with the SRK equation than the PR equation. This is explained by the fact that SRK consistently predicts higher hydrocarbon dew points for a given composition than the PR equation. Also, using SRK, most dew points were accurately predicted using a maximum carbon number $n_{\max}$ between 8 and 10 for the Gauss-gamma characterization and a maximum $n_{\max}$ of 10 to 12 for the Gauss-Riazi distribution. Using the Peng-Robinson EOS, higher carbon numbers are needed to accurately predict dew points, and in many cases, $n_{\max}$ was beyond 10, the maximum carbon number for which many commercial software packages contain property data.

5.2.6 Predictions using GERG-2004 EOS

As discussed earlier, because of its limited gas property database, the GERG-2004 EOS was tested only with characterizations limited to hydrocarbons through C_8. The list of characterizations tested with the GERG equation included a lumped C_{8+} characterization, in which octane and heavier components are added together into a single amount assigned to octane; the 47/36/17 $C_6/C_7/C_8$ method; and the Gauss-Riazi and Gauss-gamma characterization, tested only using $n_{\max} = 8$.

The GERG EOS and the four tested characterization methods typically predicted hydrocarbon dew points to within ±2.3°F in only one-third of all test cases. With the EffecTech reference gases, the tested characterizations overpredicted the measured dew points by 7 to 25°F in a large majority of cases; reducing $n_{\max}$ to 7 in the case of the Gaussian characterizations would not bring the results to within the ±2.3°F acceptability limits. For the Warner test gases and Derks gas A, the Gaussian methods underpredict the measured dew points by double-digit amounts, indicating that values of $n_{\max}$ greater than 8 would be required to accurately reproduce the experimental data. Because of the limitation of $n_{\max} \leq 8$, therefore, the GERG-2004 EOS was not considered for the dew point prediction developed in the next chapter.

5.2.7 Summary Tables

Table 5-1 through Table 5-4 summarize the results of all calculations, marking those characterizations which successfully predicted the experimental dew points for each reference gas. In the case of the Katz and Gaussian characterizations, the value(s) of $n_{\max}$ that accurately predicted the dew points are listed. The criterion for an "accurate" characterization method, as defined by the Project Advisory Group, is one which can predict experimental HDP values to within the uncertainties of an industry-standard chilled mirror device (±2.3°F). In all, dew point comparisons were made for 45 combinations of gas composition and pressure, using the PR, SRK and GERG equations of state (EOS), and using eight chosen characterization methods.

Based upon their success rates, the Gauss-Riazi and Gauss-gamma characterization methods were judged the best candidates for characterizing heavy hydrocarbons in dew point calculations. The measured dew points for the SwRI gases are often "bracketed" by values computed using the Gauss-Riazi and Gauss-gamma distributions with successive values of $n_{\max}$, the carbon number of the heaviest normal alkane in the characterization. In a few cases, the measured dew points fell just beyond the curve computed using the Gauss-Riazi distribution extended to C_{12}, but the same dew points were bracketed by values of $n_{\max}$ below 12 for the Gauss-gamma distribution.

The most promising candidate is the characterization method using the SRK equation of state, Gaussian quadrature weights and the gamma function distribution. While both the Gauss-Riazi and Gauss-gamma characterizations were able to predict about 80% of experimental dew points to within the target accuracy of ±2.3°F, the Gauss-gamma characterizations did so using lower values of $n_{\max}$, often between 8 and 10. Since few equation-of-state software packages used for dew point prediction have data on hydrocarbons beyond decane, the use of the Gauss-gamma characterizations would be more practical for use with common software, and was chosen for the procedure developed in the next chapter.

Table 5-1. Summary of results for dew points predicted using the Peng-Robinson equation of state.

Validation gas	Gas ID or pressure	Characterization							
		Full composition	Lumped C9+	47/36/17 C6/C7/C8	ISO DIS 23874	Katz method, makeup at heavy end	Katz method, makeup at C6	Gauss-Riazi distribution	Gauss-gamma distribution
Warner gases	2								**9**
	3							**12**	
	4								
EffecTech gases	1							**9**	**7**
	2					**7**		**10**	**8**
	3							**8**	**7**
	4							**8**	**7**
	5	**X**	**X**				**7**		
	6	**X**	**X**				**7**	**7, 8**	
	7	**X**	**X**					**9**	
	8	**X**	**X**					**7**	
	9		**X**			**7**		**10**	**8**
	10						**7**	**8**	**7**
Derks gases	A								
	B					**7**	**8**	**10**	**8**
2003 SwRI 1050 Btu gas	800 psi								**10**
	600 psi				**X**			**12**	
	200 psi	**X**			**X**			**12**	**10**
2003 SwRI 1145 Btu gas	1140 psi								**10**
	700 psi				**X**			**12**	**9**
	250 psi		**X**	**X**			**8**	**11**	
	100 psi								**10**
2003 SwRI 1325 Btu gas	1250 psi						**10**		
	850 psi					**8**	**9**		**10, 11**
	400 psi				**X**				**10**
	105 psi	**X**						**12**	**9**
2005 SwRI 1050 Btu gas	815 psi	**X**	**X**	**X**	**X**		**8**	**11**	**9**
	610 psi	**X**	**X**	**X**			**8**	**11**	
	465 psi		**X**	**X**		**7**	**8**	**10, 11**	**8**
	400 psi		**X**	**X**			**8**	**11**	
	215 psi		**X**	**X**			**8**	**11**	
2005 SwRI 1145 Btu gas	1415 psi					**8**	**9**		**11**
	1160 psi								**10**
	745 psi					**8**	**9**	**12**	**9, 10, 11**
	705 psi					**8**	**9**		**10, 11**
	265 psi	**X**		**X**	**X**			**11, 12**	**9**
	160 psi	**X**			**X**			**12**	**9**
2005 SwRI 1325 Btu gas	1250 psi					**9, 10, 11**	**10**		
	850 psi					**8**	**9**		**10, 11**
	400 psi	**X**		**X**	**X**		**8**	**11, 12**	**9**
	100 psi	**X**		**X**				**11**	**9**
2005 SwRI 1523 Btu gas	1255 psi					**9, 10**	**10**		
	1000 psi					**9**	**10**		
	500 psi				**X**	**8**	**9**		**10, 11**
	120 psi					**8**			**10, 11**
Successful predictions		12	11	9	9	14	21	26	29

X = measured dew point predicted successfully (to within ±2.3°F)
Bold numbers indicate the value(s) of nmax used in the successful characterization

Table 5-2. Summary of results for dew points predicted using the SRK equation of state.

		Characterization							
Validation gas	Gas ID or pressure	Full composition	Lumped C9+	47/36/17 C6/C7/C8	ISO DIS 23874	Katz method, makeup at heavy end	Katz method, makeup at C6	Gauss-Riazi distribution	Gauss-gamma distribution
Warner gases	2						**8**	**11**	
	3			**X**					**9**
	4							**12**	**9**
EffecTech gases	1							**8**	**7**
	2							**9**	
	3						**7**	**8**	
	4						**7**		
	5	**X**	**X**					**7**	
	6							**7**	
	7							**8**	**7**
	8								
	9					**7**		**9**	**7**
	10						**7**	**7**	
Derks gases	A						**9**		**12**
	B					**7**		**9, 10**	**8**
2003 SwRI 1050 Btu gas	800 psi	**X**		**X**	**X**			**11, 12**	**9**
	600 psi	**X**	**X**	**X**			**8**	**11**	**9**
	200 psi	**X**			**X**			**12**	**9, 10**
2003 SwRI 1145 Btu gas	1140 psi	**X**		**X**	**X**			**11, 12**	**9**
	700 psi	**X**	**X**	**X**	**X**		**8**	**11**	**8**
	250 psi		**X**			**7**	**8**	**10**	**8**
	100 psi	**X**			**X**			**12**	
2003 SwRI 1325 Btu gas	1250 psi								**12**
	850 psi				**X**			**12**	**9, 10**
	400 psi				**X**			**12**	**9**
	105 psi	**X**		**X**			**8**	**11**	**9**
2005 SwRI 1050 Btu gas	815 psi		**X**			**7**	**8**	**10**	**8**
	610 psi					**7**		**10**	**8**
	465 psi					**7**		**10**	**8**
	400 psi					**7**		**10**	**8**
	215 psi					**7**		**10**	**8**
2005 SwRI 1145 Btu gas	1415 psi			**X**	**X**			**11. 12**	**9**
	1160 psi	**X**	**X**	**X**	**X**	**7**	**8**	**11, 12**	**8, 9**
	745 psi	**X**		**X**	**X**		**8**	**11, 12**	**9, 10**
	705 psi				**X**			**12**	**9, 10**
	265 psi	**X**	**X**	**X**	**X**		**8**	**11, 12**	**9**
	160 psi		**X**	**X**			**8**	**11**	**9**
2005 SwRI 1325 Btu gas	1250 psi					**9**	**10**		**12**
	850 psi				**X**			**12**	**9, 10**
	400 psi	**X**	**X**	**X**		**7**	**8**	**10, 11**	**8**
	100 psi		**X**	**X**			**8**	**11**	
2005 SwRI 1523 Btu gas	1255 psi					**8, 9**	**10**		**11, 12**
	1000 psi					**8**			**11, 12**
	500 psi				**X**			**12**	**9, 10**
	120 psi				**X**	**8**			**10, 11**
Successful predictions		12	10	13	15	14	18	36	35

X = measured dew point predicted successfully (to within ±2.3°F)
Bold numbers indicate the value(s) of nmax used in the successful characterization

Table 5-3. Summary of results for dew points predicted using the GERG-2004 equation of state.

Validation gas	Gas ID or pressure	Lumped C8+	47/36/17 C6/C7/C8	Gauss-Riazi distribution, nmax = 8	Gauss-gamma distribution, nmax = 8
Warner gases	2				
	3		**X**		
	4		**X**		
EffecTech gases	1			**X**	
	2				
	3				
	4				
	5				
	6				
	7			**X**	
	8				
	9			**X**	
	10				
Derks gases	A				
	B				**X**
2003 SwRI 1050 Btu gas	800 psi	**X**	**X**		**X**
	600 psi	**X**	**X**		
	200 psi				
2003 SwRI 1145 Btu gas	1140 psi	**X**			**X**
	700 psi	**X**			**X**
	250 psi	**X**			**X**
	100 psi				
2003 SwRI 1325 Btu gas	1250 psi				
	850 psi	**X**	**X**		**X**
	400 psi	**X**	**X**		
	105 psi	**X**	**X**		
2005 SwRI 1050 Btu gas	815 psi				
	610 psi				**X**
	465 psi	**X**			**X**
	400 psi	**X**			**X**
	215 psi	**X**			**X**
2005 SwRI 1145 Btu gas	1415 psi	**X**		**X**	**X**
	1160 psi			**X**	
	745 psi	**X**	**X**		**X**
	705 psi		**X**		
	265 psi		**X**		
	160 psi		**X**		
2005 SwRI 1325 Btu gas	1250 psi				
	850 psi	**X**	**X**		**X**
	400 psi		**X**		**X**
	100 psi	**X**	**X**		
2005 SwRI 1523 Btu gas	1255 psi	**X**	**X**		
	1000 psi				
	500 psi	**X**	**X**		
	120 psi				
Successful predictions		17	16	5	14

X = measured dew point predicted successfully (to within ±2.3°F)
Bold numbers indicate the value(s) of nmax used in the successful characterization

Table 5-4. Summary of results for cricondentherm dew points predicted using the C_{6+}–GPM method.

		Validation gases		
		2005 SwRI 1050 Btu gas P = 400 psi	2005 SwRI 1145 Btu gas P = 705 psi	2005 SwRI 1523 Btu gas P = 1000 psi
Validation data (measured values in °F)	minimum CHDP	27.7	83.6	174.0
	maximum CHDP	30.0	89.6	176.9
C_{6+} MW calculated using full composition	calculated CHDP	28.8	65.8	118.0
	error	**1.1 to -1.2**	-17.8	-56.0
C_{6+} MW calculated using 60/30/10 C_6/C_7/C_8	calculated CHDP	28.5	65.5	121.9
	error	**0.8 to -1.5**	-18.1	-52.1
C_{6+} MW calculated using 47/36/17 C_6/C_7/C_8	calculated CHDP	29.4	66.5	123.1
	error	**1.7 to -0.6**	-17.1	-50.9
C_{6+} MW calculated using 40/40/20 C_6/C_7/C_8	calculated CHDP	29.8	67.0	123.7
	error	**2.1 to -0.2**	-16.6	-50.3

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6. DEVELOPMENT OF A GENERAL HYDROCARBON DEW POINT PREDICTION METHOD

The primary objectives of this project were to evaluate the accuracy of heavy hydrocarbon characterization methods and generic equations of state for predicting HDPs of a wide range of natural gases, and to identify specific characterization methods that produce the most accurate dew point predictions from limited compositional data. In the previous chapter, the most accurate approach was found to be the use of a Gaussian quadrature splitting scheme and the gamma distribution function to determine mole fractions, and the SRK equation of state to determine dew points. However, the accuracy of the method depended on the carbon number $n_{\max}$ of the heaviest hydrocarbon included in the characterization. The optimum value of $n_{\max}$ varied from one reference test gas to another, and varied from one pressure to another for the same test gas.

The fact that $n_{\max}$ varied in this way suggested that a generalized method for predicting hydrocarbon dew points would require a means of choosing the best value of $n_{\max}$ from the limited compositional data available to the user. It was theorized that the best choice of $n_{\max}$ for a particular gas was likely to depend in some way on its heavy hydrocarbon distribution, not simply the total C_{6+} fraction. This was suggested by the following evidence:

- For the lighter gases in the database – generally but not always gases with heating values below 1,200 Btu/scf – calculations using the complete gas composition and the C_{9+} characterization came closest to measured values, faring better than characterizations that extended only to C_8 or used constant, unvarying component ratios.

- For the SwRI 1,325 and 1,523 Btu/scf gases, particularly at higher pressures, dew points calculated with the full composition tended to underpredict measured dew points, but artificial extension of the characterization to higher values of $n_{\max}$ yielded better agreement with experimental data.

Unfortunately, the natural gas industry typically uses field gas chromatographs that analyze gas streams out to C_{6+}, and only occasionally sends gas samples to laboratories for extended analyses to C_9 and beyond. While it is acknowledged that the goal of the project was to develop a characterization method using only a C_{6+} analysis, the results of Chapter 5 indicate that an occasional extended analysis will be needed to select values of $n_{\max}$ for accurate dew point prediction.

In this chapter, a correlation is developed to determine the optimum value of $n_{\max}$ from available data. The correlation is then tested on a separate set of validation gas compositions and measured dew points. Finally, a general procedure is presented for predicting dew points using selected field information, the Gauss-gamma characterization method and the SRK equation of state, and its expected accuracy is given.

6.1 DEVELOPMENT OF CORRELATIONS FOR THE MAXIMUM CARBON NUMBER IN THE CHARACTERIZATION

6.1.1 Initial Selection of Independent Variables

Work on the correlation began with the selection of gas properties against which the optimum values of n_{max} would be correlated. An obvious independent variable for the correlation is the total C_{6+} mole percent. Another variable correlated to n_{max} was the line pressure at which the dew point is to be determined. This was included to compensate for the current inability of equations of state to accurately predict the shape of hydrocarbon dew point curves for richer gases. Figure 5-13 shows how different HDP curves, generated using different values of n_{max} for the same characterization, agree with data at different pressures for the same gas. Line pressure was included as an independent variable in the correlation primarily to compensate for this flaw in the existing equations of state.

A review of lab analyses of common production and transmission gases found that the average molecular weight (MW) of the C_{6+} fraction does not correlate well to the amount of the C_{6+} fraction itself (Figure 6-1). However, the C_{6+} average molecular weight does depend on the distribution of components within that fraction, and in theory could be correlated to the best value of n_{max} for a Gauss-gamma characterization. To test this, the average C_{6+} molecular weight was computed from each reference gas composition, and was used as an independent variable to correlate n_{max}. The values of average C_{6+} molecular weight used in the correlation are derived from the actual gas compositions, not from assumed splits of the C_{6+} fraction. The 60/30/10 $C_6/C_7/C_8$ split, for example, will always produce a value of C_{6+} MW = 93.19, while actual values of C_{6+} MW for the reference gases range from 88.54 to 101.08 and better reflect the actual heavy hydrocarbon distributions. In actual use, an accurate value of the stream's molecular weight must be obtained from extended analysis of a gas sample; the result can be considered reliable if the gas stream composition is relatively constant. Table 6-1 shows the values of C_{6+} mole percent, pressure and C_{6+} MW for each reference gas used as input to the correlation.

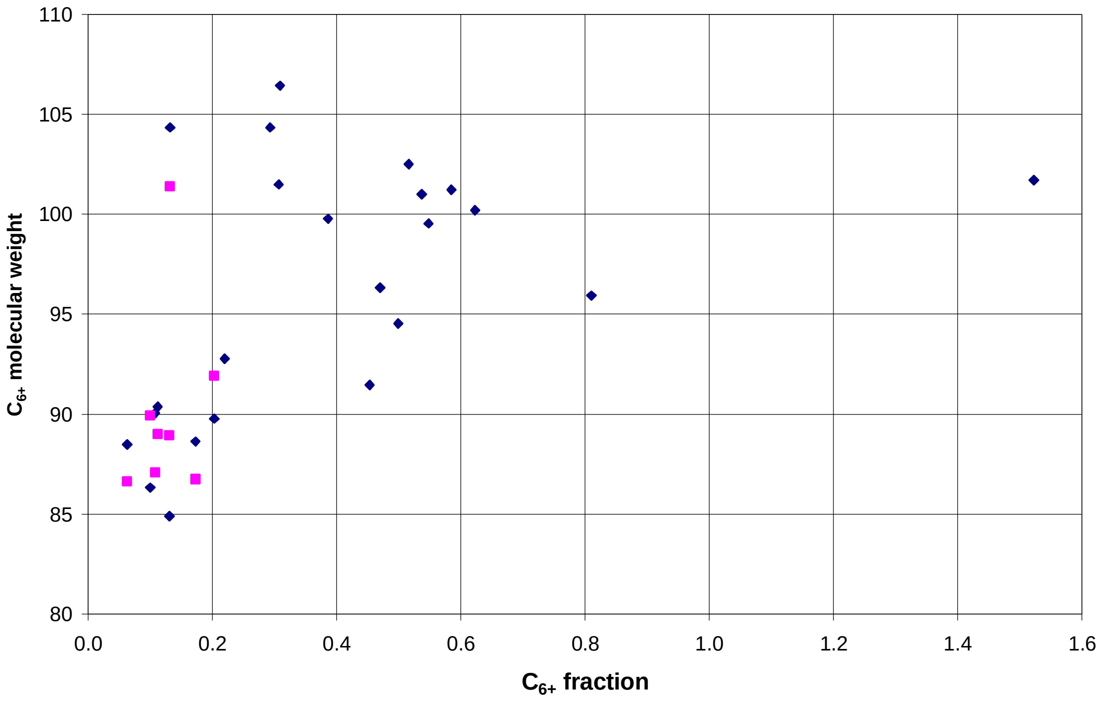

Figure 6-1. Comparison of average molecular weights of C_{6+} fractions to amounts of C_{6+} fractions for a random sample of production and transmission gases.

Table 6-1. Values of correlated independent variables and dependent variable $n_{max,0}$ for each reference gas.

Dataset	Gas ID or pressure	Measured or midpoint HDP pressure (psia)	Measured, extrapolated or midpoint HDP temperature (°F)	Mole % lumped C_{6+}	Average C_{6+} molecular weight	$n_{max,0}$ for Gauss-gamma characterization
Warner	2	564.7	53.9	0.2230	100.454	8.5
	3	564.7	72.2	0.3180	101.084	9.0
	4	564.7	71.4	0.2960	100.581	9.2
EffecTech	1	406.1	16.7	0.1170	88.930	6.6
	2	406.1	23.9	0.1233	91.811	7.4
	3	406.1	0.5	0.0550	89.790	6.5
	4	406.1	23.9	0.1555	91.073	6.2
	5	406.1	23.0	0.1202	88.950	5.9
	6	406.1	-0.4	0.0492	88.537	6.0
	7	406.1	5.9	0.0508	90.170	6.9
	8	356.8	16.7	0.1151	88.911	5.5
	9	406.1	-47.2	0.0053	90.439	7.4
	10	406.1	-7.6	0.0346	89.567	6.3
Derks gas	A	594.7	45.7	0.0672	94.093	11.9
	B	594.7	16.0	0.0947	90.714	7.6
2003 SwRI 1050 Btu gas	800 psi	804.5	31.9	0.0990	94.016	9.0
	600 psi	607.0	35.1	0.0990	94.016	8.8
	200 psi	208.7	33.3	0.0990	94.016	9.7
2003 SwRI 1145 Btu gas	1140 psi	1136.8	70.9	0.2440	94.016	8.8
	700 psi	702.3	77.9	0.2440	94.016	8.4
	250 psi	255.5	60.2	0.2440	94.016	8.2
	100 psi	99.7	45.8	0.2440	94.016	9.5
2003 SwRI 1325 Btu gas	1250 psi	1245.3	137.8	0.5010	92.274	12.8
	850 psi	852.8	132.1	0.5010	92.274	9.6
	400 psi	399.3	115.9	0.5010	92.274	9.3
	105 psi	105.3	68.8	0.5010	92.274	8.8
2005 SwRI 1050 Btu gas	815 psi	813.0	23.8	0.1010	94.019	8.0
	610 psi	608.7	29.3	0.1010	94.019	8.0
	465 psi	462.8	28.4	0.1010	94.019	7.9
	215 psi	215.9	21.1	0.1010	94.019	8.1
	400 psi	391.5	28.9	0.1010	94.019	8.0
2005 SwRI 1145 Btu gas	1415 psi	1413.6	56.7	0.2500	94.016	9.1
	1160 psi	1157.7	69.7	0.2500	94.016	8.5
	745 psi	743.6	84.7	0.2500	94.016	9.3
	705 psi	702.8	86.6	0.2500	94.016	9.6
	265 psi	266.9	66.6	0.2500	94.016	8.8
	160 psi	159.9	54.0	0.2500	94.016	8.9
2005 SwRI 1325 Btu gas	850 psi	853.7	131.8	0.5000	92.281	9.5
	1250 psi	1249.8	141.2	0.5000	92.281	13.8
	400 psi	399.3	110.5	0.5000	92.281	8.4
	100 psi	98.6	65.0	0.5000	92.281	8.6
2005 SwRI 1523 Btu gas	500 psi	498.4	154.3	0.8062	91.421	9.7
	1000 psi	999.5	175.4	0.8062	91.421	11.9
	120 psi	121.9	106.0	0.8062	91.421	10.4
	1255 psi	1247.7	172.5	0.8062	91.421	12.3

6.1.2 Determination of $n_{max,0}$ for Reference Gases

The next step in developing the correlation was to obtain values of the dependent variable, the optimum value of Gauss-gamma $n_{\max}$, for each gas in the reference dataset. Recall that dew point calculations were performed in Chapter 5 for each of the 45 combinations of reference gas compositions and pressures, using values of $n_{\max}$ from 7 to 12. Errors in predicted dew points relative to the measured dew points for each of the 45 gases were found to be a linear function of $n_{\max}$, with r^2 correlation coefficients of 0.993 or better. Interpolation or extrapolation on these linear fits of error versus $n_{\max}$ produced a "theoretical" optimum value of $n_{\max,0}$ for zero dew point error. Table 6-1 also shows the interpolated or extrapolated zero-error values of $n_{\max,0}$ for each reference gas. To prevent round-off error from skewing any results, it was decided to retain decimal portions of the interpolated values of $n_{\max,0}$ as they are used to create correlations in this chapter. Obviously, any final values of $n_{\max,0}$ used eventually to select the heaviest component in a gas characterization will need to be rounded to an integer value.

6.1.3 Correlation for $n_{max,0}$ for Lighter Gases

The first correlation to determine the best $n_{\max,0}$ values for zero-error dew point predictions included values for all 45 reference data points, correlated to the three independent variables of total C_{6+} mole percent, average molecular weight of the C_{6+} fraction (C_{6+} MW), and pressure in psia (P). Partial regression statistics (Miller, 1997) were used to select the correlations that best predicted $n_{\max,0}$. Linear regressions were used, with the variables taken to various powers (for example, P, P^2, $P^{½}$, and P^{-1}). A goal was set to obtain a curve fit with an r^2 correlation coefficient of 0.9 or better. However, the best correlation to the data for all 45 cases produced a value of $r^2 = 0.724$, which was not considered acceptable.

In an effort to improve the correlation, plots of $n_{\max,0}$ versus the independent variables were studied, and a helpful trend was found in the data. Figure 6-2 shows the values of $n_{\max,0}$ for the 45 reference gases plotted versus C_{6+} MW. The data suggest a trend in characterizations of the gases with C_{6+} molecular weights below about 93, namely that the value of $n_{\max,0}$ increases with increasing molecular weight. These gases include the EffecTech gases, one of the Derks gases, and the richer SwRI gases. Several values of $n_{\max,0}$ are found at values of C_{6+} MW = 91.4 and 92.3; these correspond to the SwRI 1,325 and 1,523 Btu/scf gases and reflect changes in $n_{\max,0}$ with pressure. When this effect of pressure is accounted for, the trend of increasing $n_{\max,0}$ with increasing C_{6+} MW becomes clearer. On the other hand, the data for gases with C_{6+} molecular weights above 93, which includes gases from Warner, Derks and SwRI, do not show such a trend. This suggested that separate correlations for gases with C_{6+} molecular weights above and below 93 might better predict the zero-error values of $n_{\max}$. Separate correlations were therefore investigated for the 23 compositions and pressures with C_{6+} MW $\leq$ 92.281 and the 22 compositions and pressures with C_{6+} MW $\geq$ 94.

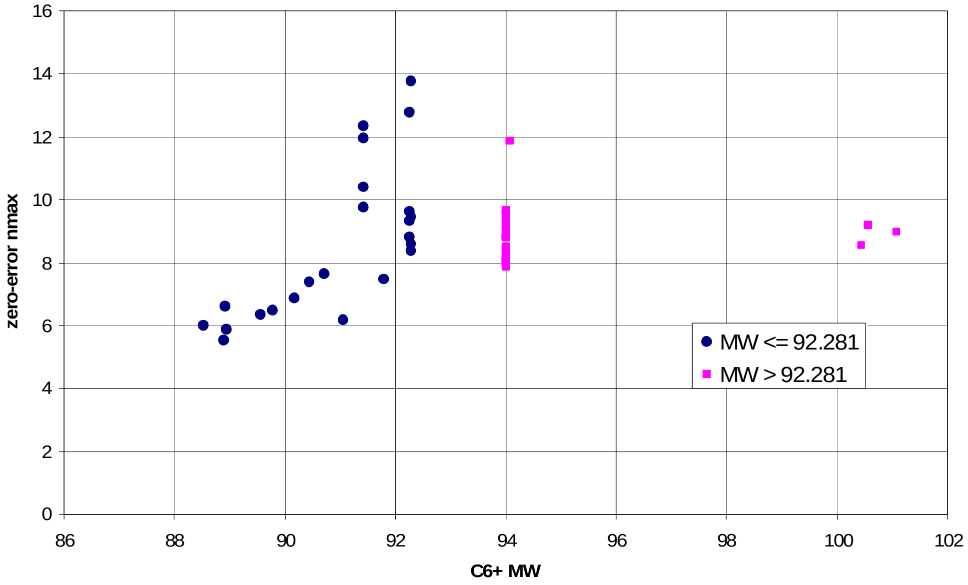

Figure 6-2. Trends in $n_{\max,0}$ versus C_{6+} molecular weight.

For the lighter gases, a correlation was obtained with an acceptable r^2 of 0.954 and a tractable number of terms:

$$n_{\max,0} = \frac{P^2}{197593} - \frac{P}{279.492} + 7.75288\left(C_{6+}\ \text{mol\%}\right) - 5.50132\sqrt{C_{6+}\ \text{mol\%}} - \frac{4196.11}{\left(C_{6+}\text{MW}\right)} + 54.7346 \qquad \text{(6-1)}$$

This correlation suggests a second-order relationship between $n_{\max,0}$ and pressure, and as suggested by the plot of Figure 6-2, produces increasing values of $n_{\max,0}$ with increasing C_{6+} molecular weight. [Note that the term proportional to 1/(C_{6+} MW) is subtracted in the expression, so as C_{6+} molecular weight increases, the reciprocal term decreases, and the value subtracted from $n_{\max,0}$ becomes smaller.] Section 6.2 will present results of tests of this correlation and the predicted dew points obtained from it.

A correlation to the same independent variables was attempted for the gases with C_{6+} MW ≥ 94, but the best correlation ($r^2 \approx 0.9$) required nine terms. A justifiable correlation should indicate a clear relationship between the independent and dependent variables, but the terms in the correlation for the heavier reference gases did not do so, so it was rejected in favor of the correlation introduced in the next two subsections.

6.1.4 Application of Mole Percent Threshold

To find a better correlation for $n_{\max,0}$ for the heavier gases, the general behavior of hydrocarbon dew points was considered. Dew point temperatures of actual gas blends will increase as the amount of a heavy hydrocarbon component increases, or as a new heavier hydrocarbon component is added to the mixture. Computed dew point temperatures will also increase as the same changes are made to the input gas composition. It should be expected that, in order to predict a dew point accurately, the best $n_{\max,0}$ for an "adjustable" characterization must increase as the mole fractions of heavy components in the actual gas composition rise.

If a value of $n_{\max,0}$ for a gas stream were found to increase from $(n - 1)$ to n when the amount of hydrocarbons in the stream with carbon number n rose above a certain threshold amount, defining these thresholds would be extremely useful in selecting the best $n_{\max,0}$ for the characterization. Thresholds for amounts of each carbon number n in the gas could be determined from known properties of the gas, such as molecular weight. The actual extended analysis of the gas could then be compared to these thresholds. One or more components whose actual amount exceeded a threshold would then determine the heaviest hydrocarbon in the characterization (*i.e.*, the value of $n_{\max,0}$). As with the use of C_{6+} molecular weight, this approach would require an extended analysis of the gas stream, which is outside the original scope of work to develop a characterization method using only a C_{6+} analysis. However, the results in Chapter 5 indicate that extended analysis will be needed for accurate dew point prediction, and many natural gas companies perform occasional extended analyses that would provide this information.

To pursue this approach, the compositions of the reference gases were reviewed. "Values" of $n_{\max,0}$ that would produce the most accurate dew points for each reference gas were reported in Table 6-1. As discussed in Section 6.1.2, these numbers are interpolated or extrapolated from computed dew point errors and associated carbon numbers. They are not integers, and do not represent actual carbon numbers, but rather describe trends in the characterizations and dew points that may be useful here in determining mole percent thresholds.

For most of the reference gases, the actual mole percents of hydrocarbons of each carbon number n follow a logarithmic trend in n (see, for example, Figure 5-6 through Figure 5-9). Based on this, logarithmic interpolation was used to assign a mole percent value $x_{n_{\max,0}}$ to each value of $n_{\max,0}$ for the reference gases.

$$\ln\left(\frac{x_{n_{\max,0}}}{x_n}\right) = \left(\frac{n_{\max,0} - n}{(n+1) - n}\right)\ln\left(\frac{x_{n+1}}{x_n}\right) = \left(n_{\max,0} - n\right)\ln\left(\frac{x_{n+1}}{x_n}\right), \quad n \le n_{\max,0} \le n+1 \qquad (6\text{-}2)$$

This logarithmic interpolation formula uses only mole percent values for components with values of n on either side of $n_{\max,0}$, so that trends in component amount x over all carbon numbers and all reference data should not be influenced by the interpolation method.

The interpolated values of $x_{n_{\max,0}}$, graphed versus $n_{\max,0}$ in Figure 6-3, do indeed display a trend across all reference gases, and reinforce the idea of a correlation between the best maximum carbon number for a characterization and the mole percent of components with that carbon number in the characterized stream. The correlation itself is determined in the next section.

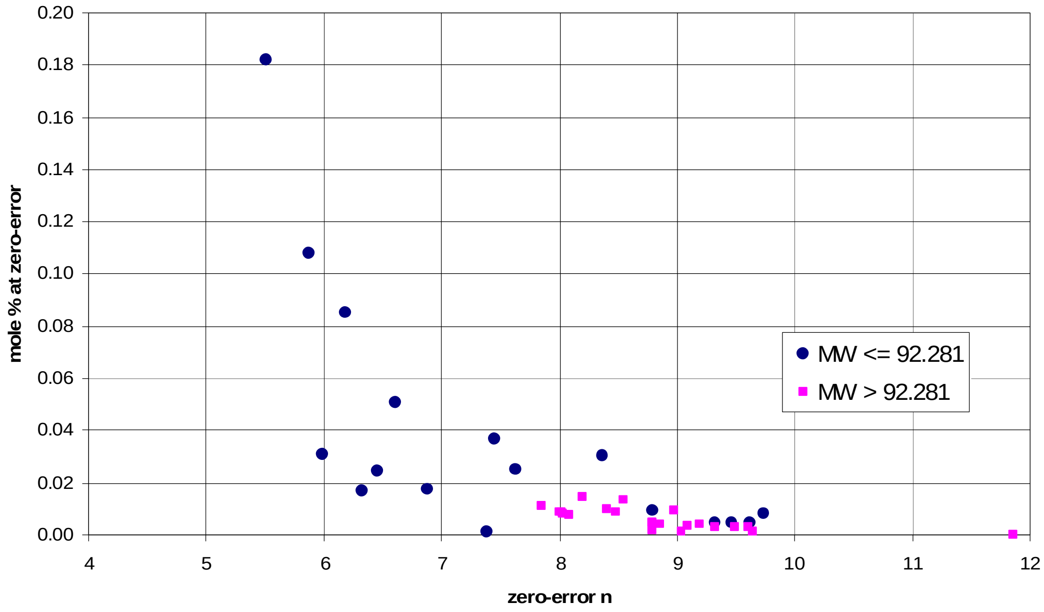

Figure 6-3. Trends in mole percent of gas composition at $n_{\max,0}$ for the reference gases.

6.1.5 Correlation for Mole Percent Thresholds for Heavier Gases

Work to develop the correlation for $n_{\max,0}$ for heavier gases began with creation of the correlation for mole percent thresholds. For simplicity, the approach requires that amounts of all components in a reference gas composition with the same carbon number n be added together. The total mole fraction for n is then compared to the threshold value from the correlation.

Because of the relationship apparent in Figure 6-3, it was decided to correlate $x_{n_{\max,0}}$ to $n_{\max,0}$ as well as to the other independent variables used previously (C_{6+} molecular weight, C_{6+} mole percent, and dew point pressure). This correlation would then be used as a model to predict threshold values of $x_{\lim,n}$ for a range of carbon numbers in a given gas composition. Partial regression statistics were again used to derive the optimum correlations for gases in the database with C_{6+} MW $\geq$ 94. These gases included the Warner gases, one gas from Derks, and the lean SwRI gases. Pressure was not found to affect the threshold mole fractions, and does not appear in the final correlations. This is not surprising, since the 1,050 and 1,145 Btu/scf gases SwRI in the C_{6+} MW $\geq$ 94 subset did not exhibit deviations from predicted dew point curves that varied with pressure, as the richer SwRI gases did.

A five-term correlation for $x_{\lim,n}$ including n, C_{6+} molecular weight and C_{6+} mole %, produced an r^2 correlation coefficient of 0.862, while a seven-term correlation including the same variables had a correlation coefficient of $r^2 = 0.915$.

$$x_{\lim,n} = \frac{n^2}{1418.13} + \frac{1.47894}{n} - \frac{1558.39}{(\mathrm{C}_{6+}\ \text{mole}\,\%)} - \frac{4.56799}{(\mathrm{C}_{6+}\ \mathrm{MW})} - 0.16543 \qquad (6\text{-}3)$$

$$x_{\lim,n} = \frac{n^2}{728.739} + \frac{2.3183}{n} - \frac{164.721}{(\mathrm{C}_{6+}\ \text{mole}\,\%)} - 0.177272\sqrt{\mathrm{C}_{6+}\ \text{mole}\,\%} + \frac{(\mathrm{C}_{6+}\ \mathrm{MW})^2}{1941.2} + \frac{940.53}{(\mathrm{C}_{6+}\ \mathrm{MW})} - 14.8087 \qquad (6\text{-}4)$$

While the seven-term correlation appears to correlate more strongly to the data, the five-term correlation is simpler to use. Both correlations were used to predict dew points for gases with C_{6+} MW ≥ 94; the results and comparisons to reference data are presented in the next section.

6.2 EVALUATION OF DEW POINTS COMPUTED USING CORRELATIONS

The correlations were checked for accuracy by using them to compute dew points for the 45 gases in the reference dataset, as well as dew points for validation gases not used to create the correlations. The validation data included both measured hydrocarbon dew points and analytical gas compositions.

6.2.1 Comparisons to Dew Points in the Reference Dataset

Values of $n_{\max,0}$ were computed for each of the 23 “light” gases in the reference dataset with C_{6+} molecular weights less than or equal to 92.281, using the correlation of Equation 6.1. These values of $n_{\max,0}$ were used as the heaviest component in the Gauss-gamma characterization for each gas. The resulting characterization was then used with the SRK equation of state to compute a hydrocarbon dew point for each gas.

Table 6-2 compares the computed and measured dew points for the 23 gases. Recall that the goal of the research is to develop a method of predicting dew points that is accurate to within the established accuracy of a Bureau of Mines manual chilled mirror dew scope, ±2.3°F. The characterizations selected using Equation 6.1 meet this target accuracy for only 10 of the 23 gases. However, for 20 of the 23 gases, the computed dew points agree with the reference dew points to within ±5.0°F. This is comparable to the magnitude of dew point uncertainties caused by selecting different binary interaction parameters or using different software packages when computing dew points (George *et al.*, 2005a).

Table 6-2. Comparison of measured dew points for reference gases with C_{6+} MW ≤ 92.281 to dew points computed using characterizations selected using Equation 6-1.

				Results of correlation			
Dataset	Gas ID or pressure	Measured or midpoint HDP pressure (psia)	Measured, extrapolated or midpoint HDP temperature (°F)	Gauss-gamma n_{max} producing smallest error	Gauss-gamma n_{max} predicted by Equation 6-1	Computed HDP temperature (°F)	Median error of computed temperature (°F)
EffecTech	1	406.1	16.7	7	6	-0.3	-17.0
	2	406.1	23.9	8	8	29.6	5.7
	3	406.1	0.5	7	7	4.0	3.5
	4	406.1	23.9	7	8	40.6	16.7
	5	406.1	23.0	6	6	18.9	-4.1
	6	406.1	-0.4	6	6	-3.1	-2.7
	7	406.1	5.9	7	7	6.5	0.6
	8	356.8	16.7	6	6	15.0	-1.7
	9	406.1	-47.2	8	8	-43.6	3.6
	10	406.1	-7.6	7	7	-3.2	4.4
Derks	B	594.7	16.0	8	8	19.7	3.7
2003 SwRI 1325 Btu gas	1250 psi	1245.3	137.8	13	13	138.7	0.9
	850 psi	852.8	132.1	10	10	133.7	1.6
	400 psi	399.3	115.9	10	9	114.0	-1.8
	105 psi	105.3	68.8	9	9	70.8	2.0
2005 SwRI 1325 Btu gas	850 psi	853.7	131.8	10	10	134.0	2.2
	1250 psi	1249.8	141.2	14	13	138.8	-2.4
	400 psi	399.3	110.5	9	9	114.2	3.7
	100 psi	98.6	65.0	9	9	68.7	3.7
2005 SwRI 1523 Btu gas	500 psi	498.4	154.3	10	10	155.4	1.2
	1000 psi	999.5	175.4	12	12	175.6	0.2
	120 psi	121.9	106.0	11	10	103.8	-2.3
	1255 psi	1247.7	172.5	13	14	177.3	4.8

For the reference gases with higher molecular weights (C_{6+} MW > 92.281), both Equations 6-3 and 6-4 were used to compute threshold mole percentages of each component of the gas in question. Next, these thresholds were compared to the actual amounts of x_n in each reference gas composition. The component with the lowest carbon number for which the threshold was exceeded was chosen as the heaviest component in the characterization, defining n_{max}. Finally, the gas was re-characterized using the Gauss-gamma method with the defined value of n_{max}, and a hydrocarbon dew point for the reference gas was computed from the characterization.

Table 6-3 compares the computed and measured dew points for the 22 heavier reference gases. The results of the two correlations, Equations 6-3 and 6-4, were identical for all reference gases except Warner gases 3 and 4. Where the two correlations produced different characterizations, the results from Equation 6-4 are listed in the table in parentheses; otherwise, the tabulated results were obtained from both correlations. The characterizations selected using either correlation meet the target accuracy of ±2.3°F for only 12 of the 22 “heavy” gases, but for 16 of the 22 gases, the computed dew points agree with the reference dew points to within

±5.0°F. When combined with the correlation for the lighter gases, the approach developed here is able to predict hydrocarbon dew points to within ±5.0°F for 36 of 45 reference gases (80%).

Table 6-3. Comparison of measured dew points for reference gases with C_{6+} MW ≥ 94 to dew points computed using characterizations selected using Equations 6-3 and 6-4.

					Results of correlation		
Dataset	Gas ID or pressure	Measured or midpoint HDP pressure (psia)	Measured, extrapolated or midpoint HDP temperature (°F)	Gauss-gamma n_{max} yielding smallest error	Gauss-gamma n_{max} predicted by Equation 6-3 or (6-4)	Computed HDP temperature (°F)	Median error of computed temperature (°F)
Warner	2	564.7	53.9	9	9	60.0	6.1
	3	564.7	72.2	9	10 (9)	83.8 (74.0)	11.6 (1.8)
	4	564.7	71.4	9	9 (10)	71.1 (80.8)	-0.3 (9.4)
Derks	A	594.7	45.7	12	12	45.6	-0.1
2003 SwRI 1050 Btu gas	800 psi	804.5	31.9	9	8	23.7	-8.2
	600 psi	607.0	35.1	9	8	28.8	-6.3
	200 psi	208.7	33.3	10	8	19.5	-13.8
2003 SwRI 1145 Btu gas	1140 psi	1136.8	70.9	9	9	72.0	1.1
	700 psi	702.3	77.9	8	9	81.7	3.9
	250 psi	255.5	60.2	8	9	66.6	6.5
	100 psi	99.7	45.8	9	9	42.4	-3.3
2005 SwRI 1050 Btu gas	815 psi	813.0	23.8	8	8	23.9	0.1
	610 psi	608.7	29.3	8	8	29.3	0.0
	465 psi	462.8	28.4	8	8	29.8	1.4
	215 psi	215.9	21.1	8	8	20.6	-0.5
	400 psi	391.5	28.9	8	8	28.8	-0.1
2005 SwRI 1145 Btu gas	1415 psi	1413.6	56.7	9	9	56.1	-0.5
	1160 psi	1157.7	69.7	8	9	72.6	2.8
	745 psi	743.6	84.7	9	9	82.8	-1.9
	705 psi	702.8	86.6	10	9	82.9	-3.7
	265 psi	266.9	66.6	9	9	68.6	2.0
	160 psi	159.9	54.0	9	9	55.7	1.7

6.2.2 Comparisons to Dew Points from External Validation Data

To be most useful, the method developed here must be able to predict dew points of new gas compositions encountered by the natural gas industry. A validation dataset was created from blind field data provided by Dave Bromley of BP and Dave Dannhaus of Fesco, participants in the Project Advisory Group. The dataset, listed in Table 6-4, was collected on gas streams sampled at field pipeline sites. Dew point temperatures were measured using a Bureau of Mines chilled mirror device, and are assigned the measurement uncertainty of ±2.3°F reported by George *et al.* (2005a). Samples collected at the sites were analyzed by laboratory GC, and the compositions in the lab reports were used to create characterizations for calculating dew points. Values of average C_{6+} molecular weight were also taken from the lab reports.

Table 6-4. Analytical gas compositions and field HDP data from the Bromley/Dannhaus validation dataset. Component values are in units of mole percent.

Compositional data	Gas D7	Gas D8	Gas E1	Gas E2	Gas E3
Nitrogen	0.343	0.275	0.7171	0.1801	0.7821
CO_2	0.175	0.160	2.1897	2.8921	1.0425
Oxygen					
Methane	93.834	94.389	95.2104	84.2129	83.8044
Ethane	3.366	3.164	1.1583	8.1466	7.1031
Propane	1.107	0.965	0.3977	2.7099	3.8542
Isobutane	0.516	0.444	0.0891	0.5798	1.0586
n-Butane	0.334	0.287	0.0972	0.6159	1.1639
Neopentane	0.019	0.031			
Isopentane	0.148	0.124	0.0392	0.2151	0.4531
n-Pentane	0.080	0.072	0.0273	0.1647	0.3335
2,2-Dimethylbutane	0.010	0.011			
2,3-Dimethylbutane	0.006	0.006			
2-Methylpentane	0.016	0.017			
3-Methylpentane	0.007	0.008			
n-Hexane	0.013	0.015	0.0287	0.1465	0.2247
Methylcyclopentane	0.003	0.004			
Benzene	0.005	0.006			
Cyclohexane	0.004	0.005	0.7171	0.1801	
Dimethylpentanes	0.003	0.003			
2-Methylhexane	0.002	0.002			
3-Methylhexane	0.001	0.002			
Heptanes	0.003	0.004	0.0257	0.0892	0.1311
Methylcyclohexane	0.002	0.003			
Toluene					
Octanes		0.002	0.0169	0.0438	0.046
Nonanes			0.0027	0.0035	0.0027
Total	99.997	99.999	100.0000	100.0001	99.9999
Total C_{6+}	0.075	0.088	0.0740	0.2830	0.4045
Average C_{6+} MW	88.710	88.381	91.421	95.459	94.192
Total diluents	0.518	0.435	2.9068	3.0722	1.8246
HDP data					
Temp. (°F)	0.4	-1.25	27.5	54.8	67.3
Pressure (psia)	780	804	701	696	369

The procedure developed in the previous section was used with the composition and property data of Table 6-4 to predict dew points for the five validation gases. Unfortunately, the results in Table 6-5 show that this methodology tends to overpredict dew points for these validation gases by more than 5°F. Note that gases D7, D8 and E1 required the use of Equation 6-1 for “light” gases, while gases E2 and E3 were used with the correlations for “heavy” gases. Overprediction of dew points is preferable, since it would ensure that equipment would be heated well above the actual hydrocarbon dew point. However, the margins of overprediction in this case are as much as 22°F when the five-term correlation for $x_{\mathrm{lim},n}$ of heavy gases is used (Equation 6-3), and approach 45°F when the seven-term correlation is used (Equation 6-4). This case suggests that the five-term correlation is more accurate in identifying thresholds for mole fractions, though neither correlation leads to computed dew points within ±5°F of measured values.

Table 6-5. Comparison of measured dew points for Bromley/Dannhaus validation gases to dew points computed using selected characterizations.

Dataset	Pressure (psia)	Temperature (°F)	n_{max} yielding smallest error	Correlation equation	Predicted Gauss-gamma n_{max}	Predicted HDP temperature (°F)	Error in predicted temperature (°F)
D7	780	0.4	6	Eq. 6-1	7	8.7	8.3
D8	804	-1.25	6	Eq. 6-1	7	13.3	14.6
E1	701	27.5	10	Eq. 6-1	8	7.5	-20.0
E2	696	54.8	7	Eq. 6-3	9	75.6	20.8
				Eq. 6-4	12	98.5	43.8
E3	369	67.3	7	Eq. 6-3	9	89.3	22.0
				Eq. 6-4	12	111.9	44.7

At the time this report was being completed, a study was published describing the accuracy of manual and automated chilled mirror devices in measuring hydrocarbon dew points (Brown *et al.*, 2007). The study tested the devices on a variety of prepared gas blends and pipeline gas samples. For five prepared gas blends, dew points were measured by an automated chilled mirror device, and the test gases were analyzed by GC to confirm their certified compositions. This data was used as a second validation dataset for the dew point prediction methods developed here; this validation dataset is shown in Table 6-6. Like the SwRI data, measurements were made at multiple pressures on each gas blend, providing a total of thirty combinations of pressure and gas composition in the validation dataset.

Table 6-6. Analytical gas compositions and measured HDP data from the NPL study (Brown *et al.*, 2007). Component values are in units of mole percent.

	Mid 1		Mid 2		High	
Compositional data	Analytical value	95% confidence interval	Analytical value	95% confidence interval	Analytical value	95% confidence interval
Nitrogen	0.007	0.008	0.011	0.008	0.014	0.008
CO_2	0.000	0	0.000	0	0.001	0.006
Methane	89.372	0.09	92.261	0.10	90.242	0.10
Ethane	7.679	0.031	6.338	0.026	6.845	0.028
Propane	2.214	0.009	1.054	0.005	1.719	0.007
n-Butane	0.5390	0.0033	0.1575	0.0013	0.8418	0.0051
n-Pentane	0.1316	0.0016	0.0936	0.0012	0.2630	0.0033
2,2-dimethylbutane	0.1309	0.0018	0.0946	0.0012	0.2646	0.0052
Cyclopentane	0.000016	0.000006	0.000046	0.000007	0.000021	0.000018
2-methylpentane	0.000146	0.000013	0.000107	0.000018	0.000252	0.000139
3-methylpentane	0.000015	0.000003	0.000020	0.000005	0.000019	0.000012
n-C_6	0.000087	0.000004	0.000121	0.000005	0.000123	0.000069
Benzene	0.031874	0.001022	0.044034	0.001385	0.052199	0.001812
Cyclohexane	0.004247	0.000140	0.014209	0.000450	0.006309	0.000218
n-C_7	0.005574	0.000185	0.005967	0.000193	0.004632	0.000165
Toluene	0.012056	0.000389	0.015865	0.000502	0.009672	0.000338
Methylcyclohexane	0.003243	0.000118	0.008597	0.000284	0.002495	0.000085
n-C_8	0.000036	0.000005	0.000035	0.000022	0.000019	0.000006
n-C_9	0.001361	0.000043	0.003184	0.000110	0.001223	0.000043
n-C_{10}	0.000989	0.000048	0.001546	0.000084	0.000002	0.000001
n-C_{11}	0.000008	0.000003	0.000018	0.000011	0.000006	0.000003
n-C_{12}	0.000003	0.000002	0.000005	0.000001	0.000002	0.000001
Total	100.001543		100.009829		100.004396	
Total C_{6+}	0.05951		0.09365		0.0551	
Average C_{6+} MW	89.939		89.418		87.812	
Total diluents	0.007		0.011		0.07672	
Measured HDP data	Temperature (°F)	Pressure (psia)	Temperature (°F)	Pressure (psia)	Temperature (°F)	Pressure (psia)
	10.5	304.9	17.4	303.6	11.5	305.2
	14.1	405.5	19.5	405.6	16.2	406.1
	15.6	522.3	19.9	521.0	19.2	520.6
	15.9	664.4	18.2	666.0	21.1	668.7
	15.2	403.8	22.4	405.2	17.6	416.7
	16.1	522.5	22.0	463.1	20.6	597.6

95% confidence interval on measured temperatures: <2°F

Table 6-6 (continued).

	Low 1		Low 2	
Compositional data	Analytical value	95% confidence interval	Analytical value	95% confidence interval
Nitrogen	0.005	0.008	0.012	0.007
CO_2	0.000	0	0.000	0
Methane	98.716	0.10	97.299	0.10
Ethane	0.705	0.006	1.607	0.009
Propane	0.460	0.003	0.884	0.004
n-Butane	0.0780	0.0011	0.0905	0.0011
n-Pentane	0.0362	0.0009	0.0538	0.0009
2,2-dimethylbutane			0.000002	0.000004
Cyclopentane	0.000042	0.000002	0.000058	0.000004
2-methylpentane				
3-methylpentane	0.000015	0.000003	0.000039	0.000001
n-C_6	0.010132	0.000371	0.029911	0.000971
Benzene	0.003633	0.000137	0.009954	0.000322
Cyclohexane	0.003202	0.000120	0.005063	0.000168
n-C_7	0.006084	0.000219	0.007440	0.000239
Toluene	0.002989	0.000122	0.005886	0.000188
Methylcyclohexane	0.000012	0.000003	0.000017	0.000009
n-C_8	0.003455	0.000135	0.002515	0.000078
n-C_9	0.002061	0.000096	0.001747	0.000061
n-C_{10}	0.000914	0.000052	0.001168	0.000049
n-C_{11}	0.000002	0.000001	0.000001	2.58×10^{-7}
n-C_{12}	0.000001	0.000001	0.000001	3.04×10^{-7}
Total	100.032761		100.010121	
Total C_{6+}	0.03250		0.06374	
Average C_{6+} MW	95.492		90.239	
Total diluents	0.005		0.012	
Measured HDP data	Temperature (°F)	Pressure (psia)	Temperature (°F)	Pressure (psia)
	19.3	308.4	23.8	303.9
	20.0	408.8	24.8	404.0
	18.5	522.9	23.8	525.4
	15.6	666.8	20.9	663.3
	24.4	364.8	27.5	387.4
	24.2	366.0	27.1	383.4

95% confidence interval on measured temperatures: <2°F

As before, the procedure developed in Section 6.1 was used with the composition and property data of Table 6-6 to predict dew points for the five validation gases at each of the six pressures. The gases labeled “Mid 1,” “Mid 2,” “High” and “Low 2” all have average C_{6+} molecular weights below 92.281, while “Low 1” has an average C_{6+} MW above 94, so that both correlations could again be tested. As Table 6-7 shows, the method suggests values of $n_{\max}$ for all but one condition that consistently produce dew points in error by more than 5°F. Calculations for the lighter gases using Equation 6-1 to set $n_{\max}$ underpredict the dew points in all cases, typically by 7 to 11°F. For the heavy gas “Low 1,” Equation 6-3 recommended values of $n_{\max}$ that overpredict the dew points by 13 to 18°F. As with the Bromley/Dannhaus data, results obtained with Equation 6-4 suggest even higher values of $n_{\max}$ (16 in this case) that lead to even larger overpredictions, so those results are not included in the table.

Table 6-7. Comparison of measured dew points for NPL validation gases to dew points computed using selected characterizations.

Dataset	Pressure (psia)	Temperature (°F)	n_{max} yielding smallest error	Correlation equation	Predicted Gauss-gamma n_{max}	Predicted HDP temperature (°F)	Error in predicted temperature (°F)
Mid 1	304.9	10.5	8	Eq. 6-1	7	3.5	-7.0
	405.5	14.1	8		7	6.7	-7.4
	522.3	15.6	8		7	7.8	-7.7
	664.4	15.9	8		8	13.5	-2.4
	403.8	15.2	8		7	6.7	-8.6
	522.5	16.1	8		7	7.8	-8.2
Mid 2	303.6	17.4	8	Eq. 6-1	7	8.8	-8.6
	405.6	19.5	8		7	11.1	-8.4
	521.0	19.9	8		7	11.1	-8.8
	666.0	18.2	8		7	8.0	-10.2
	405.2	22.4	8		7	11.1	-11.2
	463.1	22.0	8		7	11.4	-10.5
High	305.2	11.5	7	Eq. 6-1	6	3.0	-8.4
	406.1	16.2	7		6	7.9	-8.2
	520.6	19.2	7		6	10.7	-8.5
	668.7	21.1	7		6	11.2	-10.0
	416.7	17.6	7		6	8.3	-9.3
	597.6	20.6	7		6	11.4	-9.3
Low 1	308.4	19.3	11	Eq. 6-3	14	37.2	17.8
	408.8	20.0	11		14	37.6	17.6
	522.9	18.5	12		14	35.9	17.5
	666.8	15.6	12		14	31.2	15.6
	364.8	24.4	12		14	37.7	13.3
	366.0	24.2	12		14	37.7	13.5
Low 2	303.9	23.8	10	Eq. 6-1	7	-3.7	-27.5
	404.0	24.8	10		7	-2.2	-27.1
	525.4	23.8	10		7	-3.2	-27.1
	663.3	20.9	10		8	4.1	-16.8
	387.4	27.5	10		7	-2.3	-29.8
	383.4	27.1	10		7	-2.3	-29.4

In summary, the correlations of Equations 6-1 and 6-3 can be used to closely predict the dew points of the reference gases used to create the correlations themselves, but they are considerably less accurate in predicting dew points for other gases. As shown in Chapter 5, when the best value of the heaviest carbon number is chosen, the Gauss-gamma characterization is capable of predicting hydrocarbon dew points of 80% of the reference cases to within ±2.3°F. For the validation gases described in Table 6-4 and Table 6-6, all tabulated values of n_{max} yielding the smallest errors lead to dew points in agreement with measured values to within ±5°F. However, the correlations do not yield these same low-error values of n_{max} for the validation gases, and therefore do not produce dew points of the best accuracy.

The correlated variables – pressure, C_{6+} fraction average molecular weight and total C_{6+} mole fraction – do not appear to have captured all the natural gas characteristics necessary to characterize the dew point behavior for a wider range of gas compositions. Clearly, additional work is needed to improve the method for determining $n_{\max}$. This would require an analysis of a much larger database of gas compositions, to identify other gas properties that are easily determined by the industry with its current equipment. Additional data is clearly needed to make the method as robust as possible, applicable to the widest range of compositions that the natural gas industry may encounter. Without such data, the method of selecting $n_{\max}$ cannot yet be recommended for general use.

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7. CONCLUSIONS

This project evaluated the accuracy of several characterization methods, used with common equations of state, in predicting hydrocarbon dew points for a wide range of production, transmission, and distribution gases. A primary goal was to identify characterization methods that could produce accurate dew point predictions from compositional data only through C_6, as would be available from common field gas chromatographs. The characterization methods were created and tested using reference hydrocarbon dew point data and gas compositions from the literature. This data included production-quality gases for which dew points computed using the complete gas compositions are known to disagree with measured dew points.

As part of this research, published parameters for the Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) equations of state were reviewed, along with some of the data used to derive these parameters. The goal was to determine the range of validity of these common equations of state, and determine if the parameters were responsible for the observed errors in dew points for production-type gases computed using all available compositional data. It was concluded that the pressures and temperatures of the data used to derive binary interaction parameters do not fully represent common pipeline conditions. Further, little experimental data exists to derive valid C_{6+}-C_{6+} binary interaction parameters, so that many software packages default to a value of 0 for these pairs. These facts may explain the tendency of the Peng-Robinson and SRK equations of state to underpredict hydrocarbon dew points of rich natural gases, particularly at higher pressures. More experimental data on natural gas blends is needed, over a larger range of pressures and temperatures and at higher C_{6+} content, to resolve these problems. This is recommended as a long-term industry goal, outside the scope of work of this project.

The GERG-2004 equation of state was also reviewed in this work. Currently, the GERG software package contains data only on components through C_8. Because of this, many of the useful characterization methods identified here cannot be applied in the GERG-2004 software. The University of Bochum and NIST are currently working to add data on C_9 and C_{10}, and a new version is expected to be released in 2007. Until then, no judgment can be made on the ability of this equation to accurately predict hydrocarbon dew points of gas compositions of interest.

A variety of characterization methods were tested during this work to find those capable of accurate dew point predictions. The methods were tested with the Peng-Robinson and SRK equations of state, and where possible, the GERG-2004 equation of state. Based on the results of this work, the SRK equation of state is generally recommended for dew point calculations. This is based on the observation that SRK consistently predicts slightly higher dew points than Peng-Robinson for a given gas composition. As a result, for the cases of richer gases and higher pressures, characterizations using lower carbon numbers can be used with SRK to predict accurate dew points, and common software packages that only include data out through C_{10} are more likely to have the required hydrocarbon data. An adaptation of the Gaussian characterization method is recommended for describing the hydrocarbon distribution beyond hexane, because of its ability to realistically simulate actual component distributions, and because of the ability of the user to adjust the computed dew point in small increments by changing the heaviest hydrocarbon in the characterization.

With the observed errors in predicted dew points, particularly of rich natural gases at higher pressures, a search began for a method to adapt the Gauss-gamma characterization to correct for these errors. The success of the Gauss-gamma characterization hinges on the correct selection of the heaviest hydrocarbon in the distribution. Using the reference dataset of gas compositions and dew points, a correlation was attempted between the best maximum carbon number in the characterization, $n_{\max}$, and easily obtained properties such as C_{6+} mole percent, C_{6+} molecular weight, and dew point pressure. For 36 of 45 combinations of composition and pressure in the reference dataset, the correlation produced values of $n_{\max}$ for the characterization that predicted the observed dew points to within ±5°F. However, when other gases not used to create the correlation were tested, most values of $n_{\max}$ from the correlation led to predicted dew points in error by 20°F.

In summary, where an extended analysis of a natural gas stream is not available or fails to accurately predict the observed HDP of the stream, the Gauss-gamma characterization and the SRK equation of state are recommended for predicting dew points from a C_{6+} analysis of the stream. If all relevant gas properties of the stream can be identified and used to select the maximum carbon number $n_{\max}$ for the characterization, the uncertainty in dew points computed by this method is expected to be smaller than ±5°F at the one-sigma level. If the method for choosing $n_{\max}$ is not adequate, uncertainties approaching ±45°F in predicted dew points may result.

Clearly, not all gas properties dictating the best choice of $n_{\max}$ for the Gauss-gamma characterization were identified. As stated earlier, a primary research goal was to identify characterization methods that could work with field compositional data up through a lumped C_{6+} fraction. While the Gauss-gamma characterization can be generally recommended for this, the selection of $n_{\max}$ may require more data than would be available from a C_{6+} analysis by a field GC. The average C_{6+} molecular weight, for example, would need to be determined by occasional extended analyses through C_{9+} of spot or composite samples sent to a laboratory. This dependence on other gas properties poses an obstacle to the original goal of the characterization study. Given the known dependence of dew points on the presence of heavy hydrocarbons, however, occasional extended analyses are deemed necessary for now.

It is also suggested that users gather field dew point data for their own gas streams to "tune" their characterizations and predict the most accurate dew points. It may be that the tuned characterizations will have higher or lower values of $n_{\max}$ than the true gas composition, but this may be necessary to accurately predict the dew point and alleviate the errors caused by the binary interaction parameters.

What follows is a recommended procedure for predicting hydrocarbon dew points of a pipeline gas stream using the Gauss-gamma characterization, C_{6+} analyses from a field GC, and field dew point measurements.

1. During a scheduled field site visit, measure the hydrocarbon dew point of the gas stream using a Bureau of Mines chilled mirror device. Take measurements at multiple pressures if possible.

2. If a current field GC analysis of the stream at that location is available, record the C_{6+} or C_{9+} analysis from the GC.

3. Use the measured dew points to determine if heating of sampling equipment is necessary, and then obtain a spot sample of the stream for extended laboratory analysis to C_{9+}, or out to C_{12+} if possible.

4. Use the C_{9+} laboratory analysis, along with the SRK equation of state, to compute dew points for the gas stream. No one software package is recommended over another, but the default binary interaction parameters should be used.

5. If the computed dew points of Step 4 predict the measured dew points with sufficient accuracy, use the distribution of hexane and heavier components from the lab analysis as the C_{6+} fraction characterization to predict dew points from future C_{6+} GC data.

6. If the C_{9+} laboratory analysis does not reproduce the measured data to within the desired accuracy, use the C_{6+} field analysis of the gas stream and the Gauss-gamma method to characterize the stream composition for $n_{\max}$ values of 7 and higher. Repeat the dew point calculations using these Gauss-gamma characterizations.

7. Compare dew points computed using the various Gauss-gamma distributions to the measured dew points. Select the characterization (the value of $n_{\max}$) that most closely predicts the observed dew points. Use this characterization with future C_{6+} GC analyses to predict dew points at this location.

8. If any indications are found that the heavy hydrocarbon composition has changed at this location, the process should be repeated.

A common thread through this research has been the lack of experimental hydrocarbon dew point data. Clearly, additional research is needed to collect more data with defensible uncertainties for solving the remaining issues with dew point predictions. More dew point data is needed, for example, to identify the additional compositional properties and characteristics that define the best value of $n_{\max}$ for the proposed Gauss-gamma characterization method. It was also confirmed during this research that many of the binary interaction parameters in common use with the cubic equations of state are being applied outside their valid pressure and temperature ranges. Additional experimental data could be used to derive C_{6+}-C_{6+} binary interaction parameters that would be accurate at pipeline transmission conditions, potentially resolving the tendency of current equations to underpredict dew point temperatures for gases with high C_{6+} content. Some researchers have suggested creating entirely new equations of state to address dew point accuracy issues, a goal which would also require new dew point data. Additional data is also a necessity for assessing methods of measuring hydrocarbon dew points, such as automated devices now entering the natural gas marketplace.

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APPENDIX A: LITERATURE REVIEW OF NATURAL GAS HYDROCARBON DEW POINT DATA

The following is a summary of key journal articles reviewed during this research in a search for experimental hydrocarbon dew point data. To be useful in this study, HDP data must include gas compositions, measured dew point pressures and temperatures, and stated uncertainties in these values. The uncertainty information is needed to determine whether differences in calculated and experimental HDPs are statistically significant. Many of the references contain HDP data on gas compositions that do not represent typical production, transmission or distribution gases, or do not include the required uncertainty information. However, the review has been included in this Appendix for the benefit of the natural gas community at large.

Table A-1. Key results of literature search for natural gas hydrocarbon dew point data.

Reference	Notes
Aasberg-Petersen and Stenby, 1991	Compares results from a variation on the ALS EOS and a logarithmic characterization method by Pedersen *et al.* [1985] to experimental liquid dropout data for several reservoir fluids obtained from other references. However, experimental compositions from these sources are known only through C_6.
Arnaud *et al.*, 1996	Describes an experimental apparatus used for PVT and phase characterizations of deep reservoir fluids (crude oil or natural gas) at conditions between 255 and 470 K and pressures up to 150 MPa. Tests were performed on methane and n-tetracosane, separately and in four binary mixtures, to evaluate the device. Cites several other sources of dew point data, but all for methane – n-alkane binary mixtures.
Diller and Magee, 2000	Original experimental phase equilibrium data is cited for 28 binary systems and 16 ternary systems. Only four binary and two ternary systems listed do not contain nitrogen or CO_2.
Hoffmann *et al.*, 1953	Analyses are given of several reservoir fluids, and in one case the condensate-gas ratio vs. pressure is extrapolated to determine a dew point. However, compositions are only given with lumped fractions of C_7 and higher.
Ng, 1997	Examines the behavior of natural gas condensation curves as a function of C_{7+} fraction (not explicit component values) and water content. Also reviews limitations on experimental HDP determination and compositional analysis. Several test apparatus are described, including PVT cells and an apparatus that uses sample interaction with microwaves to determine phase boundaries.

Panneman *et al.*, 2003	Manual and automated methods for measuring Potential Hydrocarbon Liquid Condensate (PHLC) conforming to ISO 6570 were applied. Six gases were tested, characteristic of transmission and distribution gases in Europe and taken from various sources. Control charts identified heavy HCs in some analyses that did not originate from the gas field itself. It was concluded that a stable gas quality is difficult to reach during a complete measurement, and only one gas stream produced reliable data.
Pedersen *et al.*, 1985	Presents experimental data for phase behavior of five North Sea reservoir fluids, along with evaluation of a new characterization procedure for C_{7+} fractions. However, compositions are reported explicitly only to C_6, and the remaining data (to C_{10} or C_{20}) is given as fractions. Twelve other North Sea reservoir fluids were used to estimate parameters for the characterizations, but no data or compositions are tabulated. Results are compared against the data from Hoffmann *et al.* [1953].
Sage *et al.*, 1934	Detailed discussion of a method for gathering dew point curves of a methane-propane binary mixture.
Savidge, 1995	The paper describes an apparatus to determine phase boundaries, incorporating a "spherical resonator to determine sound speed, reentrant cavity and concentric cylinder to determine relative permittivity, and electromagnetic circulating pump." Dew point measurements of an ethane-CO_2 mixture are compared to data reported in two other references.
Shariati *et al.*, 1999	This paper introduces the PNA technique for characterizing C_{6+} fractions using an equation of state. Results are compared to 15 sets of experimental data in the literature, including eight synthetic mixtures and seven real petroleum fractions. However, the experimental data involves either bubble points instead of dew points, or involves compositions known explicitly only up to C_6.
Sivaraman *et al.*, 2005	Measured sound speeds of three natural gas mixtures along isobaric and isochoric lines. The mixtures were typical of hydrate field gases in the Gulf of Mexico. The blends contained only hydrocarbons through n-C_5. Sudden changes in sound speed were used to determine HDPs. No uncertainty information is given on composition or pressure or temperature measurements.
Skrzecz, 1997	Discusses collections of experimental data available from the Thermodynamics Research Center (TRC) at Texas A&M University. The collection includes some gas-liquid phase equilibria data and cites sources of solubility data, including NIST and DECHEMA. The TRC Data Bank only includes vapor-liquid equilibrium (VLE) data on binary and ternary systems, however.