University of Southern Queensland
Faculty of Engineering & Surveying

Improvement of Hydrocarbon Dew Point Determination via Gas Chromatography

A dissertation submitted by

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Abstract

A gas chromatograph is the most common method to continuously determine the hydrocarbon dew point of export natural gas. It is used to ascertain the composition of the natural gas mixture which is applied to a thermodynamic equation of state. Due to the inherent design of the process type gas chromatograph there are limitations to the computation of the gas mixture in the C_6 to C_8 carbon groups.

It was found that process type C_{9+} gas chromatographs determine a higher hydrocarbon dew point than actual, because it summates all the chromatogram hydrocarbon peaks within the respective carbon group into the normalised alkane of that carbon group. The reason for this, is that the process type gas chromatograph does not have a method to identify these species between the normalised alkane components in the C_6 to C_8 carbon groups.

Therefore the aim of this project was to research the ‘equations of state’ used to calculate natural gas hydrocarbon dew point from constituent analysis by Gas Chromatography and to develop a methodology to improve Gas Chromatography hydrocarbon dew point determination.

One important characteristic of the gas chromatograph, is that the measurement of carbon fractions greater than pentane, $n - C_5$, is based on the relationship of component elution time and hydrocarbon boiling point. The International Standard Organistation standard 23874 (ISO 23874, 2007) uses this relationship to calculate the boiling points of unidentified hydrocarbon components by linear interpolation between the normalised alkanes. The limitation of the ISO 23874 standard is that it is only applicable for laboratory analysis type gas chromatographs.

In order to exploit the boiling point and hydrocarbon component elution time relationship to identify unknown components using a process gas chromatograph, the author developed his own method and a modified method of the ISO 23874 standard.

Trials on export natural gas, using the equation of state software program, GasVLE, a manual chilled mirror instrument and a Daniel 500 C_{9+} gas chromatograph proved that the Grygorcewicz method is a valid characterisation method for further research and use in improving the hydrocarbon dew point determination of export natural gas when applied to a process gas chromatograph on a custody transfer station or pipeline.

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Certification of Dissertation

I certify that the ideas, designs and experimental work, results, analyses and conclusions set out in this dissertation are entirely my own effort, except where otherwise indicated and acknowledged.

I further certify that the work is original and has not been previously submitted for assessment in any other course or institution, except where specifically stated.

Jon-Paul Frederick Grygorcewicz

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Signature

Date

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Nomenclature

Abbreviations

ACMI	Automatic Chilled Mirror Instrument
AEMO	Australian Energy Market Operator
CNG	Compressed Natural Gas
EOS	Equation of State
GC	Gas chromatograph
GERG	Groupe Europeen de Recherches Gazieres
GPSA	Gas Producers Suppliers Association
HCDP	Hydrocarbon Dew Point
HHV	Higher Heating Value
ISOW	Modified PR equation of state
JT	Joules-Thomson effect
LRS	London Research Station equation of state
MBWR	Modified Benedict-Webb-Rubin equation of state
MCMI	Manual Chilled Mirror Instrument
PHLC	Potential Hyrocarbon Liquid Content
PR	Peng-Robinson equation of state
RKS	Redlich Kwong Soave equation of state a.k.a SRK
SW	Schmidt Wenzel equation of state
VLE	Vapour Liquid Equalibrium
WDP	Water Dew Point
WSVP	Wong-Sandler with Wagner saturated vapour pressure equation

Component Abbreviations and Chemical Formulas

CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane
C_5H_{12}	Pentane
C_6H_{14}	Hexane
C_7H_{16}	Heptane
C_8H_{18}	Octane
C_9H_{20}	Nonane
C_{6+}	C_6 refers to all compounds in the hexane group.The addition of + is a term of art used in analytical chemistry that refers to a grouping of compounds (or fraction). For example C_{6+} represents $n - C_6$, $n - C_7$, $n - C_8$ and higher molecular weight hydrocarbons.
C_7	refers to all compounds in the heptane group.
C_8	refers to all compounds in the octane group.
C_{9+}	C_9 refers to all compounds in the nonane group. The addition of + is a term of art used in analytical chemistry that refers to a grouping of compounds (or fraction). For example C_{9+} represents $n - C_9$, $n - C_{10}$, $n - C_{11}$ and higher molecular weight hydrocarbons.
CO_2	Carbon dioxide
$i - C_4$	Isobutane (2-Methylpropane)
$i - C_5$	Isopentane (2-Methylbutane)
$n - C_4$	n-Butane
$n - C_5$	n-Pentane
$n - C_6$	n-Hexane
$n - C_7$	n-Heptane
$n - C_8$	n-Octane
$n - C_9$	n-Nonane
C_5H_{12}	neopentane
N_2	Nitrogen
C_5H_{12}	$2,2 - dimethylpropane$, also known as neopentane
C_6H_{14}	$2,2 - dimethylbutane$, also known as neohexane

Glossary of Terms

Associated gas	(GPSA, 2004) Gaseous hydrocarbons occurring as a free-gas phase under original oil-reservoir conditions of temperature and pressure.
Bubble point	(GPSA, 2004) The temperature at a specified pressure at which the first stable vapour forms above a liquid.
Chromatography	(GPSA, 2004) A technique for separating a mixture into individual components by repeated adsorption and desorption on a confined solid bed. It is used for analysis of natural gas and NGL.
Compressibility factor	(GPSA, 2004) A factor, usually expressed as Z, which gives the ratio of the actual volume of gas at a given temperature and pressure to the volume of gas when calculated by the ideal gas law.
Condensate	(GPSA, 2004) The liquid formed by the condensation of vapour or gas; specifically, the hydrocarbon liquid separated from natural gas because of changes in temperature and pressure when the gas from the reservoir was delivered to the surface separators. In a steam system it may be water that is condensed and returned to the boilers.
Convergence pressure	(GPSA, 2004) The pressure at a given temperature for a hydrocarbon system of fixed composition at which the vapour liquid equilibrium K-values of the various components in the system become or tend to become, unity. The convergence pressure is used to adjust vapour liquid equilibrium K-values to the particular system under consideration.

Glossary of Terms *continued*

Cricondenbar	(GPSA, 2004) The highest pressure at which liquid and vapour phases can exist at equilibrium in a multi component system.
Cricondentherm	(ISO 11150: 2007) defines the maximum temperature at which the hydrocarbon dew point can occur. (Herring, 2008) The derivation of the word is Critical condensation thermal curve. Also called the phase envelope. The cricondentherm is the point on the phase envelope curve where the pressure and temperature indicate that the maximum hydrocarbon dew point is the be found.
Critical point	(ISO 7504: 2001) single point in pressure and temperature phase diagram at which the composition and properties of the gas and liquid phases in equilibrium are identical. Note: The pressure at his point is known as the critical pressure and the temperature as the critical temperature.
Critical pressure	(GPSA, 2004) the vapour pressure of a substance at its critical temperature.
Critical temperature	(GPSA, 2004) For a pure component, the maximum temperature at which the component can exist as a liquid.
Equation of state	(ISO 7504: 2001) mathematical relationship between the state variables (pressure and temperature) of a gas or gas mixture and the volume occupied by a given amount of substance.

Glossary of Terms *continued*

Gas processing	(GPSA, 2004) The separation of constituents from natural gas for the purpose of making saleable products and also for treating the residue gas to meet required specifications.
Gas processing plant	(GPSA, 2004) A plant which processes natural gas for recovery of natural gas liquids and sometimes other substances such as sulfur.
GPM	(GPSA, 2004) GPM Preferably Gal/Mcf (gallons per thousand cubic feet): This term refers to the content in natural gas of components which are recoverable or recovered as liquid products.
Higher Heating Value	(AS4564: 2005) The amount of energy in MJ/sm^3 relesaaed when one cubic metre of dry gas, at standard conditions, is completely burnt in aur with the products of combustion brought to standard conditions and with the water produced by combustion condensed to the liquid state. Note: Higher heating value is also known as gross heating value, superior heating value or calorific value.
Hydrocarbon dew point	(ISO 11150: 2007) the temperature above which no condensation of hydrocarbons occurs at a specified pressure.
Joule-Thomson effect	(GPSA, 2004) The change in gas temperature which occurs when the gas is expanded at constant enthalpy from a higher pressure to a lower pressure. The effect for most gases at normal pressure, except hydrogen and helium, is a cooling of the gas.

Glossary of Terms *continued*

Natural Gas	(AS4564)A gaseous fule consisting of a mixture of hydrocarbons of the alkane series, primarily methane but which may also include ethane, propane and higher hydrocarbons in much smaller amounts. It amy also include some inert gases, plus minor amounts of other constituents including odourising agents. Natural gas remains in the gaseous state under the temperature and pressure conditions normally found in service.
Natural Gas Liquid	(GPSA, 2004) Natural gas liquids are those hydrocarbons liquefied at the surface n field facilities or in gas processing plants. Natural gas liquids include ethane, propane, butanes, and natural gasoline.
Potential hydrocarbon liquid content	(ISO 11150: 2007) the amount of liquid potentially condensable per unit volume of gas at a given temperature and pressure.
Retrograde Condensate	(ISO 11150: 2007) phenomenon associated with the non-ideal behaviour of a hydrocarbon mixture in the critical region wherein, at a constant temperature, the vapour phase in contact with the liquid may be condensed by a decrease in pressure; or at a constant pressure, the vapour is condensed by an increase in temperature. Note: retrograde condensate in natural gas is the formation of liquid when gas is heated or pressure is reduced.
Slug Catcher	(AEMO: 2010a) Device used to collect and remove slugs of liquid from pipelines.

Chapter 1

Introduction

1.1 Introduction

In the custody transfer of natural gas, hydrocarbon dew point is being used by energy traders worldwide to measure the quality of a natural gas stream and as a criteria for assessing compliance with export and transportation tariffs.

Gas Chromatography is the most common method to continuously determine the hydrocarbon dew point of export natural gas at custody transfer skids. Due to the inherent design of the process type gas chromatograph, there are limitations to these instruments which consequently determine a higher hydrocarbon dew point when compared with a direct method chilled mirror instrument. Since the onus of meeting the export criteria is placed on the gas producer; if the hydrocarbon dew point is determined higher than actual, then the process is operated with greater energy loss than required. This has both short term and long term economic consequences.

Thus, this dissertation is based on an instrument problem dealing with a chemical measurement and equation of state. To overcome this instrument problem many characterisation methods have been developed, however from research they require a detailed gas analysis that can only be achieved by a laboratory type gas chromatograph.

Therefore, this research develops a novel characterisation method that allows the user to view a process chromatogram for export natural gas and identify and quantify unidentified hydrocarbon components, in order to produce a detailed like analysis that can be applied to an equation of state to improve the hydrocarbon dew point determination.

1.2 Research Aims and Objectives

The aim of this work was to research the ‘equations of state’ used to calculate natural gas hydrocarbon dew point from constituent analysis by Gas Chromatography and to develop a methodology to improve Gas Chromatography hydrocarbon dew point determination.

1.2.1 Specific Research Objectives

The research set out to address the following objectives:

1. Research Gas Chromatography operation and equipment applicable to natural gas pipelines and custody transfer stations.
2. Research gas hydrocarbon dew point measurement methods, both: Direct and Indirect.
3. Research the major factors that contribute to current best practices for measuring hydrocarbon dew point in natural gas.
4. Research natural gas hydrocarbon components to develop a methodology to identify unknown hydrocarbon species using process gas chromatography, in order to provide users with a detailed gas composition required to assist with hydrocarbon dew point determination using an equation of state.
5. Develop a process to more accurately measure, or sufficiently model, the natural gas hydrocarbon dew point using gas chromatographs and the equation of state.

If time and resources permit:

1. Implementation of the above developed methodology to improve hydrocarbon analysis and dew point determination results during on-line gas chromatography operation.

1.3 Dissertation Outline

This dissertation is organized as follows:

Chapter 2 explains the rationale of this project. It will define hydrocarbon dew point and provide an overview of the purpose of measuring it in the natural gas industry. It will also explain the Australian requirements for hydrocarbon dew point measurement at custody transfer points.

Chapter 3 provides an overview of the methods used for determining hydrocarbon dew point of natural gas and includes the advantages and disadvantages of each method.

Chapter 4 provides an overview of gas chromatography, the principle of operation and its main components.

Chapter 5 provides an overview of the development of equations of state, from the first equation of Boyle's Law to the modern day. This chapter also provides a detailed explanation of the two equations of state that this research focuses on, namely the Redlich Kwong Soave and Peng Robinson. This chapter also provides information on the equation of state software used in this research.

Chapter 6 outlines three characterisation methods: The ISO 23874 method, the authors own method and the authors adapted ISO 23874 method. The two characterisation methods developed by the author have specific application for process type gas chromatographs and these novel methods are explained.

Chapter 7 documents the results obtained from the application of the authors characterisation method and the authors adapted ISO 23874 method both in software and a gas chromatograph. The purpose of this chapter is to validate if the methods should be researched further as potential characterisations for adoption in the natural gas industry.

Chapter 8 discusses the results of the authors characterisation method and authors adapted ISO 23874 method for improving the hydrocarbon dew point determination of process gas chromatographs used on custody transfer stations.

Chapter 9 documents the achievements of the project objectives and discusses further work required to validate and have recognised the authors characterisation method.

Appendix A details the project specification.

Appendix B provides for reference, the chromatograms collected from the gas chromatographs for the two gas analysis samples.

Appendix C provides additional hydrocarbon dew point curves produced, that compare the various equations of state that were available in the GasVLE equation of state software.

Appendix D explains to the reader the basic nomenclature of hydrocarbon organic chemistry, the types of hydrocarbons found in the natural gas industry and their structural formula. This will assist the reader in understanding the terminology used when identifying unknown hydrocarbons on the gas chromatograph chromatogram.

Chapter 2

Project Rationale

2.1 Chapter Overview

This chapter explains the rationale of this project. It also defines hydrocarbon dew point and provides an overview of the purpose of measuring it in the natural gas industry.

This chapter also explains the Australian requirements for hydrocarbon dew point measurement at custody transfer points. In particular interest to this research are the relevant gas quality standards and operating procedures published by the Australian Energy Market Operator in accordance with AS 4564: 2005 Specification for general purpose natural gas, as it is beneficial to understand the regulators criteria and guidelines when accessing methods to improve the hydrocarbon dew point determination using a gas chromatograph.

2.2 Rationale

This project is based on an instrument problem dealing with a chemical measurement and equations of state calculations. To explain the rationale, the following case study is presented.

A Victorian gas producer conducted a laboratory extended gas analysis of their export gas. The laboratory results determined the hydrocarbon dew point to be -9°C. In comparison the gas producers custody transfer gas chromatographs determined the hydrocarbon dew point, using the Peng-Robinson equation of state at -3.5°C and the Redlich Kwong Soave equation of state at 1.0°C. This is a difference of 5.5°C and 8°C respectively. To verify the laboratory extended analysis hydrocarbon dew point determination, a manual chilled mirror instrument was used to measure the export gas hydrocarbon dew point. The manual chilled mirror instrument also measured the hydrocarbon dew point at -9°C at 3500 kPag. Determining a higher hydrocarbon dew point means that end users and pipeline operators have a substantial safety margin, however this is at the cost of the gas producer who is over processing the gas when it is not required.

To control the hydrocarbon dew point, the gas producer uses a dew point control unit that employees the Joule-Thomson (JT) valve method. To achieve the above mentioned gas chromatograph determined hydrocarbon dew point temperature, the differential pressure across the JT valve is 2500 kPag. A trial was conducted using a manual chilled mirror instrument to measure the export gas hydrocarbon dew point at 3500 kPag, while the differential pressure across the JT valve was reduced. The objective of this trial was to determine the required differential pressure to obtain a measured hydrocarbon dew point of -2°C using the manual chilled mirror instrument.

The results of the trial showed that a differential pressure of 1500 kPag across the JT valve was required to achieve a consistent manual chilled mirror instrument measured hydrocarbon dew point of -3°C at 3500 kPag. This means the gas producer has a potential process energy saving of 1000 kPag.

This result has great impact on the current and future operation of the plant. Straight away the gas producer has the potential to reduce the cost of operating the compression system and conserve the energy potential of the gas reservoir. This change also impacts future capital expenditure. As gas reservoirs decline in pressure, there is a point when the JT valve can no longer control the dew point due to the low differential pressure across it. Therefore either capital expenditure is required for reservoir gas compression or a change of dew point control unit type.

Based on these factors it was determined that research should be conducted to determine why the custody transfer gas chromatographs determine a higher hydrocarbon dew point than the laboratory gas chromatograph and the manual chilled mirror instrument, and a method to improve the determination.

2.3 Hydrocarbon Dew Point

Hydrocarbon dew point is defined in the International Standard Organisation (ISO) 11150: 2007 and ISO 14532: 2005 as the:

temperature above which no condensation of hydrocarbons occurs at a specified pressure.

The American Petroleum Institute (API) Chapter 14 Section 1 (API 14.1, 2006), defines hydrocarbon dew point as the:

the temperature at which hydrocarbon condensates first begin to form a visible deposit of droplets on a surface, when the gas is cooled at a constant pressure.

The hydrocarbon dew point is normally given based on temperature, however it can also be related to pressure. For instance (George et al., 2006), if the temperature of a natural gas mixture is reduced while the pressure remains constant, the temperature at which hydrocarbon condensation begins to occur is the hydrocarbon dew point temperature. Likewise if the pressure of a natural gas is increased while the temperature remains constant, the pressure at which hydrocarbon condensation occurs is the hydrocarbon dew point pressure.

Phase behaviour in hydrocarbon mixtures (ISO11150, 2007), such as natural gas is highly non-ideal. Retrograde condensation (ISO11150, 2007; George et al., 2006) is a phenomenon that occurs in natural gas mixtures. It is characterised by the presence of two hydrocarbon dew points at a given pressure or temperature. Retrograde condensation can occur during isobaric temperature increases, or during isothermal pressure reductions. The word retrograde means moving backward and this phenomenon was given the name because it is contradictory to the phase behaviour of pure components, which condense with increasing pressure and or decreasing temperature.

The hydrocarbon dew point (HCDP) curve of natural gas is typically displayed on a phase diagram. Figure 2.1 shows a phase diagram (API14.1, 2006) for a typical natural gas mixture and it is explained as follows:

- The line A-B is the section of the phase diagram known as the bubble point curve. When the pressure is lowered isothermally to the bubble point, an infinitesimal amount of gas begins to evolve. As the pressure is reduced further, more and more gas is liberated from the mixture, increasing the total concentration of gas in the two phase mixture.
- The line B-E is the dew point curve. This section of the phase diagram represents the pressures and temperatures associated with the condensation of an infinitesimal amount of liquid from the gas mixture.
- The line C-D is sometimes referred to as the retrograde dew point line. The dew points along the C-D are referred to as the upper or retrograde dew points.
- The line D-E is sometimes referred to as the normal dew point curve. The dew points along line D-E are referred to as the lower or normal dew points.
- Point C is the cricondenbar. It is the highest pressure on the phase envelope.
- Point D is the cricondentherm. it is the highest temperature on the phase envelope.

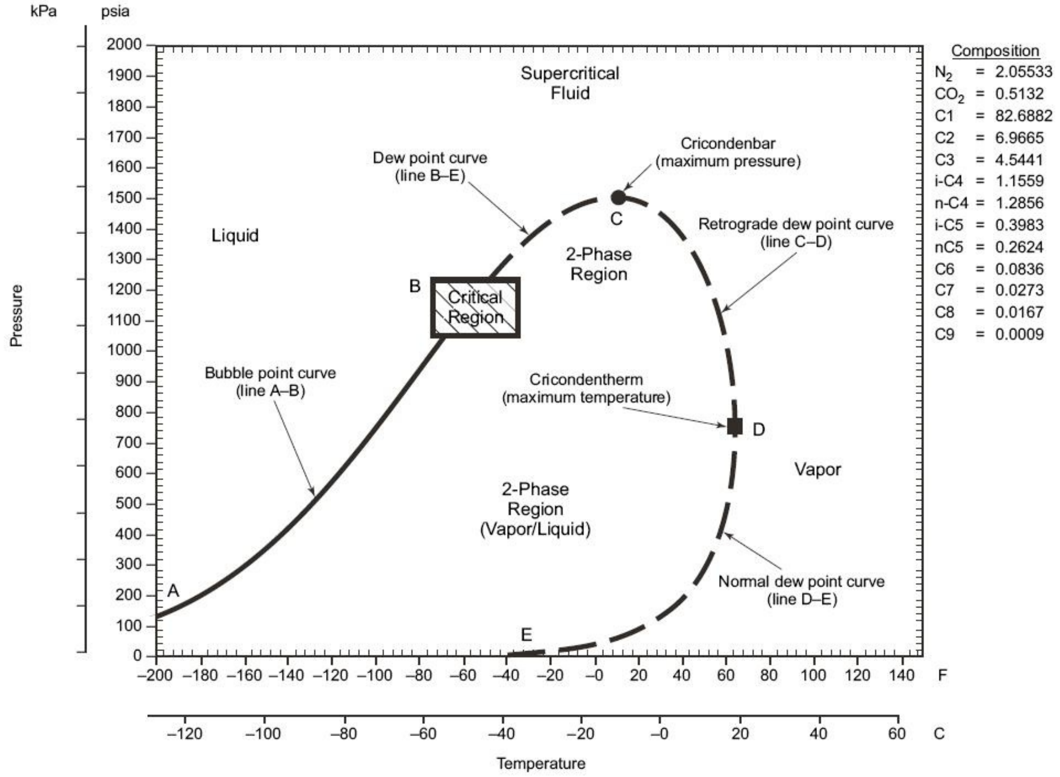

Figure 2.1: A typical natural gas phase diagram, showing bubble point curve, critical point and hydrocarbon dew point curve (adapted from API 14.1, 2006)

2.4 Purpose of hydrocarbon dew point measurement

The two primary reasons for measuring hydrocarbon dew point are safety and commercial value. Secondary reasons for measuring hydrocarbon dew point include the economics of processing, for both gas producers and shippers, and sustainability.

2.4.1 Safety

Accurate measurement (Brown et al, 2008) of the highest temperature at which hydrocarbons in natural gas condense is essential to ensure that it can be safely transported through pipelines. All natural gas producers must comply with specifications for hydrocarbon dew point in order to prevent the formation of hazardous liquid condensate in pipelines. Hydrocarbon liquids produce the following safety concerns in pipeline distribution systems (Dustman et al n.d.; NGC 2005; ISO1150: 2001; Herring 2008; AEMO: 2010a):

- It can degrade performance of burner systems, discharge out through the burner ports and either cause a large uncontrolled flame or extinguish the flame altogether and form a hydrocarbon liquid pool in the hot appliance, with the potential to explosively reignite.
- In fuel gas for Gas Turbines hydrocarbon liquids can result in over firing causing hot spots on the turbine blades resulting in embrittlement, as shown in Figure 2.2. If liquids are not burnt they can also impact on the turbine blades causing damage.
- It can cause erratic pressure variations in the delivered pipeline pressure. The variations can impact nearby regulating stations upsetting large portions of a gas distribution system. This results in potential adverse impacts on system reliability or safety including overpressure protection devices. Note: In the Victorian Gas Transmission System (Australia) there are relatively few purpose built permanent liquid ‘slug catchers’ or withdrawal points, thus even small quantities of liquid may create problems.

- Hydrocarbon liquids also cause odourant removal from the gas phase. The presence of both hydrocarbons and odourant in the liquid phase can cause degradation of the rubber components of regulating stations.

- It can impact on the long term strength of polyethylene piping, components and joining methodologies. It has been shown that aliphatic gaseous fuels of higher molecular weights tend to be absorbed to a small extent by polyethylene. This absorption reduces the long term strength of polyethylene pipe materials by up to 40%.

- Gas hydrates can form when the pressure is reduced at pressure reduction stations along the gas distribution network. It is possible that a pressure reduction is enough to chill the gas below the corresponding hydrocarbon dew point, thereby causing liquids to fall out and the potential for hydrates to form. A gas hydrate, as shown in Figure 2.3 and Figure 2.4, is the formation of a solid mass of water and hydrocarbons. Gas hydrates limit pipeline capacity and damage compressors and valves.

Figure 2.2: Turbine blade embrittlement caused by over firing. (adapted by Accident and Failure Analysis Consultants)

Figure 2.3: An example of a natural gas hydrate plug. (adapted by Harriot Watt Institute of Petroleum Engineering)

2.4.2 Commercial Value

Natural Gas is sold at the custody transfer point in energy content, primarily in Giga Joules (GJ). The energy content calculation is based on the volumetric flow, pressure, temperature and heating value of the export gas(AEMO, 2007). The heating value is based on the hydrocarbon content of the gas.

At custody transfer skids analysers are used to measure gas properties. If the sample temperature drops below the hydrocarbon dew point temperature, a significant loss in hydrocarbon content can occur, resulting in errors in gas property calculations such as the heating value. This is because hydrocarbon constituents condense, preferentially in order of decreasing molecular weight (heaviest components first) (George et al., 2006). Therefore a small amount of liquid condensation is associated with a large decrease in heating value. From the gas producers prospective, this results in a loss of revenue as more gas is required for export to provide the agreed energy content contracted for the fiscal gas day.

From the gas transmission company's perspective, (NGC, 2005) any portion of gas condensed into liquid will not only cause operational or safety problems, but may also

Figure 2.4: An example of a natural gas hydrate form in a gas distribution pipe. (adapted by Benton, A., 2010)

result in the loss of that portion of the energy quantity, heating value (MJ/sm^3), in the process of transportation. The shipper will take receipt of the gas heating value contracted for with the pipeline. Energy lost during transportation because of liquid drop out must be made up by the pipeline in the short term. Where the liquids accumulate in the pipeline or associated equipment, the pipeline operator experiences shortages that must be made up to meet the natural gas demand. This results in lost and unaccounted for gas.

2.4.3 Economics of Processing – Gas Producers

The control measures to meet the hydrocarbon dew point specification will be dependent on the natural gas mixture from the gas reservoir. If a dew point control system is required, then the capital and operating cost must be assessed based on the net profit value from gas and gas-liquid sales.

There are several types of refrigeration systems used to control the hydrocarbon dew point (Campbell, 1992). They are:

1. Absorption refrigeration,
2. Compression refrigeration,
3. Expansion across a turbine, and
4. Expansion across a valve.

The ‘expansion across a valve’ method is a relatively simple hydrocarbon dew point control system used in gas producing plants where a pressure drop is available and very low temperatures are not required. The pressure drop across the valve causes the gas to expand and subsequently cools it. This is known as the Joule-Thomson effect and hence the valve is known as a Joule-Thomson valve or abbreviated to JT valve. The produced liquids primarily pentane components, C_5, are recovered in a low temperature separator. Along with this water condensation is also removed. Thus the process can accomplish dew point control for both water and hydrocarbon in a single unit. A typical schematic of a JT valve dew point control unit is shown in Figure 2.5 and a unit installed at a gas processing facility is shown in Figure 2.6.

The pressure drop across the JT valve is an energy loss in the process. With reference to Figure 2.7, the process requires gas compression to increase the gas pressure in order to export into the pipeline. Therefore if the hydrocarbon dew point is measured higher than actual, then the process is operated with greater energy loss than required. This is an additional operating cost for the Gas Producer. In additional to this, as gas reserviours decrease in pressure then additional capital expenditure is required for front end compression and or changing the dew point control unit from a JT valve to an absorption or compression type refrigeration system.

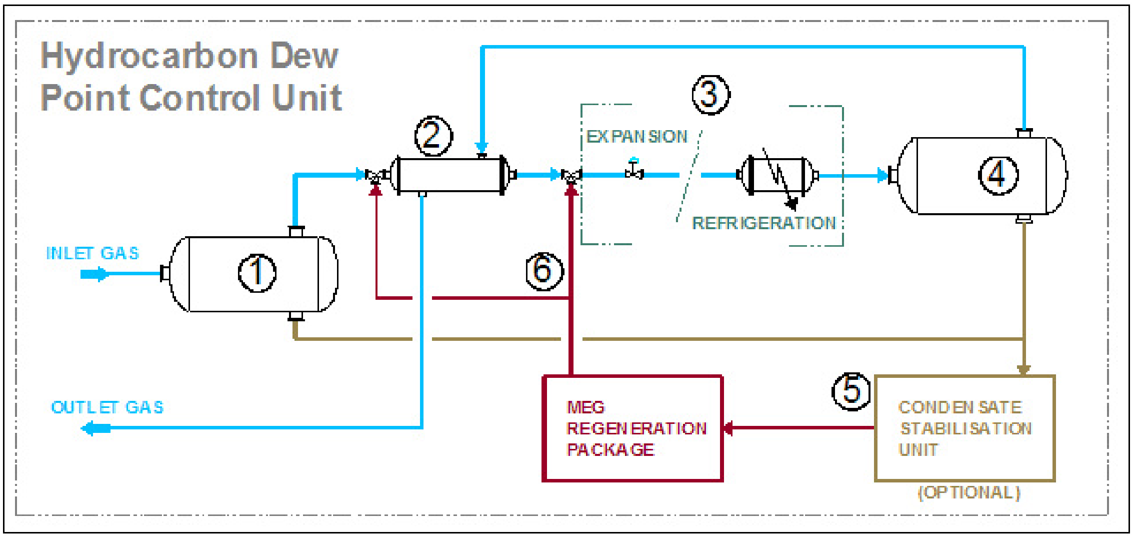

Figure 2.5: A typical schematic of a JT valve dew point control system, that uses monoethylene glycol injection to inhibit hydrate formation. (adapted by Process Group, 2004)

2.4.4 Economics of Processing – Pipeline Operators

In the USA and Australia, transmission lines have moderate to low separation capabilities (Dustmann, n.d). The primary impact of liquids to the economics of processing for Pipeline Operators are(NGC, 2005):

- Increased pipeline compression costs due to increased pressure drops.
- Decreased throughput leading to decrease in gas supplied to customers and increased maintenance cost due to frequency of pipeline cleaning, known as pigging.
- Increase in capital and operating expenditure for equipment to prevent liquid formation. Such equipment includes gas heaters, liquid knock out vessels and separation equipment.
- Transmission line shutdowns, due to hydrate formation or erratic pressure variations in the pipeline pressure, resulting in disruptions to the gas distribution supply impacting on gas fired power stations and end users.

Figure 2.6: A dew point control unit installed at a gas processing facility. The JT valve is positioned at the bottom left of the photo. (adapted by Process Group, 2004)

2.4.5 Sustainability

Two aspects of sustainability this project deals with is energy conservation and emissions control.

Energy Conservation

All turbine manufacturers generally specify that the incoming natural gas fuel meet several criteria and one of these is termed superheat. Superheat is defined as an inlet gas temperature of 28°C above the hydrocarbon dew point and water dew point temperature (Balevic, 2004). If the hydrocarbon dew point is not accurate or not used, then overheating of the inlet gas occurs. For a General Electric (GE) Frame 7 gas turbine, 28°C of superheat amounts to about 740 kW, which means energy costs can be as high as $324,120 per year. But if the gas is well above its dew point under normal conditions, the additional heating is wasteful (Tiras, 2001).

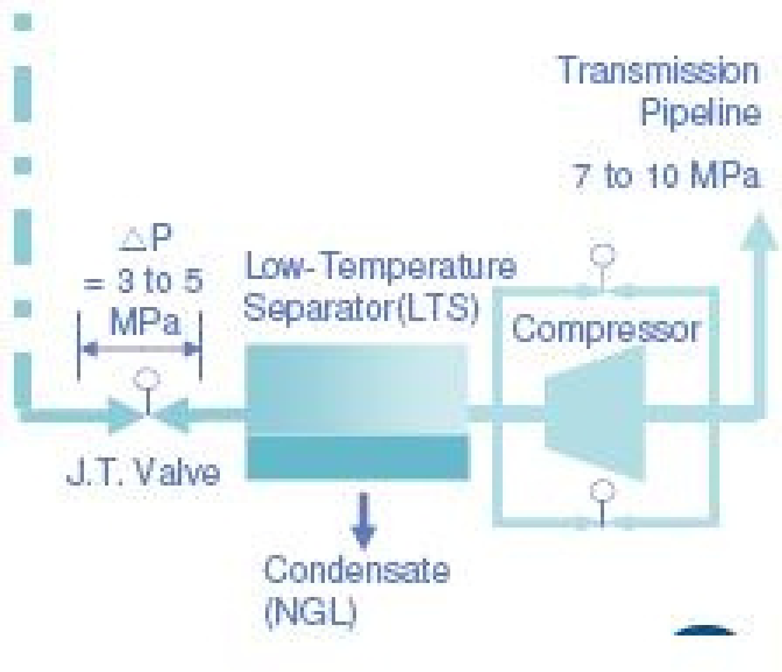

Figure 2.7: A schematic of a JT valve demonstating the process pressure energy loss and subsequent gas compression required to boost pressure for export (adapted by Benton, A., 2010).

Emissions Control

The National Gas Councils White Paper on Natural Gas Interchangeability (2005) advised that varying natural gas composition beyond acceptable limits can have the following effects in combustion equipment. In appliances, it can result in soot formation, elevated levels of carbon monoxide and pollutant emissions and yellow tipping. It can also shorten heat exchanger life and cause nuisance shutdowns from extinguished pilots or tripping safety switches. In industrial boilers, furnaces and heaters, it can result in degraded performance, damage to heat transfer equipment and non compliance with emissions requirements. Along with this (Herring, 2008) if liquid hydrocarbons impact the turbine hot section there will be a proportionate increase in Nitrous Oxide emissions.

2.5 Australian Requirements for Hydrocarbon Dew Point

The Australian Energy Market Operator (AEMO) was established in 2009 by the Council of Australian Governments (COAG) and developed under the guidance of the Ministerial Council on Energy. AEMO is an amalgamation of the previous energy services and provides a consistent framework of operational rules and underlying systems to ensure maximum efficiency, combined with maximum integrity and energy resource development.

In particular interest to this research are the relevant gas quality standards and operating procedures published by AEMO and in accordance with AS 4564: 2005 Specification for general purpose natural gas. The AEMO Gas Quality Standard for system injection points, Table 1, specifies that the hydrocarbon dew point maximum temperature is 2.0°C at 3500 kPa gauge.

The AEMO Operating Procedure for Gas Quality Guidelines (2010) outlines the hydrocarbon dew point limits. The curtailment limit of 5°C is based on a hydrocarbon dew point that is 7°C below Victoria's winter ground temperature (12°C). The 7°C margin between the winter ground temperature and the curtailment limit is to allow for Joule-Thompson cooling that may occur at regulator stations, which may cool the gas significantly below 12°C and the actual dew point at pressures other than 3500 kPa may be slightly higher. Note, that the maximum dew point temperature (cricondentherm) may not be at the 3500 kPa pressure.

The AEMO Operating Procedure for Gas Quality Measurement Requirements (2009) outlines the specification and minimum AEMO requirements for measuring hydrocarbon dew point. The Gas Quality Regulations do not specify the method for monitoring hydrocarbon dew point, however where it is based on gas chromatography, the gas chromatograph must be capable of measuring up to at least C_{9+}. The gas chromatograph must be calibrated using gravimetrically prepared reference standard gases. Automatic calibration once every 48 hours is usually acceptable and sampling greater than once every 15 minutes must be used to ensure adequate representation of average composition.

The calculation of the hydrocarbon dew point (at 3500 kPag) must be carried out using an internationally recognised equation of state (e.g. Peng-Robinson or Redlich Kwong Soave). The methodology for the characterisation of the C_{9+} components and choice of equation of state must be supplied to AEMO for approval.

Where chilled mirror type instruments are used, the calibration procedures must include appropriate calibration of the temperature sensing device and inspection of the cleanliness of the chilled surface regardless of the dew sensing technology. The response of the chilled mirror type instrument must be such that readings are available more than once every 15 minutes.

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Chapter 3

Hydrocarbon Dew Point Determination

3.1 Chapter Overview

The two methods for determining hydrocarbon dew point of natural gas are direct and indirect. Direct methods for measuring hydrocarbon dew point (HCDP) rely on the formation of a condensate film on the surface of a mirror as the gas temperature is reduced at a set pressure. Indirect methods calculate the conditions under which a condensate will form using data from other measurements such as a gas chromatograph.

This chapter outlines the methods for determining hydrocarbon dew point in the natural gas industry and that would be applied on a custody transfer skid.

3.2 Direct Methods of Hydrocarbon Dew Point Determination

The direct methods for measuring hydrocarbon dew point (HCDP) rely on the formation of a condensate film on the surface of a mirror as the gas temperature is reduced at a set pressure (Brown et al, 2009). Therefore direct methods are used to spot check the HCDP of the pipeline gas at a predetermined pressure. In Australia the HCDP is referenced at 3500 kPag (AEMO, 2009) and in Europe the pressure is 2760 kPag (400 psig) (ISO 11150, 2007).

There are two types of direct method instruments: the manual chilled mirror instrument (MCMI) and the automatic chilled mirror instrument (ACMI). Although all chilled mirror instruments detect the onset of the condensation process directly, they depend on the availability of sufficient material in the vapour phase to form a detectable liquid film. This is quantified by the condensation rate of the mixture, which is the amount of condensate in milligrams of liquid per cubic metre of gas (i.e. the potential hydrocarbon liquid content (PHLC)) formed per Kelvin of temperature change below the hydrocarbon dew point.

3.2.1 Manual Chilled Mirror Instrument

The MCMI for determining the dew point of gas under pressure was first published by Deaton and Frost (ISO 11150, 2007). The method was further developed by the U.S Department of Interior, Bureau of Mines and has been codified into a standard test method by the American Society of Testing and Materials (ASTM). The MCMI method has been in use since the 1940s (Brown et al, 2008) and was widely adopted, as it was the only method available, and by default became the de facto standard.

The dew point of the gas is determined by cooling a mirror, over which a slow stream of the gas is passed. The dew point is recorded as the temperature at which a film of condensate just appears on the mirror (ISO 11150, 2007).

The general layout of equipment is common to the different MCMI's employed. The instrument, refer to Figure 3.1, consists of a cylinder divided by a stainless steel mirror. A slow stream of gas is passed through the part of the cylinder on the reflecting side of the mirror, which can be viewed through an eye piece. To assist, a torch can be added for illumination. A refrigerant (carbon dioxide) is passed into the other part of the cylinder, cooling the back of the mirror. The temperature of the mirror is measured by a thermometer. A fine needle valve controls the flow of refrigerant. The apparatus is fitted with inlet and outlet gas valves and a gas pressure gauge. The instrument is connected to the sample point via a high pressure hose or tube and the sampled gas is expelled to the atmosphere.

Figure 3.1: A Chandler MCMI in operation measuring the HCDP of an export natural gas. (Authors own photo)

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The MCMI has been in operation throughout the world for many years in the gas industry (ISO 11150, 2007). A measurement can be made relatively quickly and reproducibly by different trained operators. Like most measurement techniques it is dynamic. That is a sample of natural gas has to be cooled and the result can be dependent on cooling rate. Detection of the first formation of liquid is subjective and trained operators must be able to characterize the type of dew detected as hydrocarbon, water, glycol or methanol, as each of these compounds exhibit differing characteristics of dew formation.

Critical factors considered in the operating procedure are the flows of gases and refrigerants in order to achieve a slow (1°C/min) cooling rate just prior (ca 3.5°C) to the appearance of liquid. The test methodology requires the dew points on cooling and on heating to be different by no more than 1°C. The reported dew point under this condition is the dew point on cooling.

The advantages of the MCMI are:

- Condensation of liquid is clearly demonstrated.
- It is the de facto standard method and experienced operators can achieve good agreement when using it.
- The MCMI is portable.

The disadvantages of the MCMI are:

- A defined amount of liquid needs to condense before it becomes visible. This will occur at a temperature below the theoretical dew point temperature (the first molecule) and the extent of the difference varies between gases.
- The rate at which liquid condensate forms as a function of the temperature below the theoretical dew point depends on the composition of the gas.

3.2.2 Automatic Chilled Mirror Instrument

While there are variations in the specific measurement principles employed, virtually all ACMI employ the following generic techniques. A natural gas sample stream is connected from the pipeline to the analyser at pipeline pressure. The pressure is regulated to the defined pressure required for analysis. The sample gas is usually filtered to remove entrained liquids and solids which would contaminate the sample cell and measuring surface. The measuring surface is cyclically cooled and heated to allow dew to form for dew point detection and to evaporate to clean the surface for the next measuring cycle. An optical system consisting of a light source, the measuring surface and detector is employed to detect when dew forms on the cooled surface. A beam of light is projected by the light source on to the measuring surface. When the surface is free of dew, little if any light is transmitted to the detector, resulting in a corresponding low signal from the detector. When dew forms on the surface, the condensate directs the light to the detector resulting in an increased signal from the detector, indicating the presence of dew. A highly accurate thermocouple is used to constantly relay the temperature of the surface. The temperature at which the detector sees light is then reported as the hydrocarbon dew point temperature.

The accuracy of an ACMI depends on several factors: the accuracy of the temperature measuring device, the amount of dew formation required to trigger the detector and the temperature gradient between the temperature measuring device and the measuring surface where the dew forms.

Verification of the accuracy of the ACMI can be achieved by challenging the device with a hydrocarbon of known dew point such as pure propane at a controlled pressure. However this does not reflect the complex behaviour of real natural gas and its retrograde nature.

3.3 Indirect Methods of Hydrocarbon Dew Point Determination

Indirect methods calculate the conditions under which a condensate will form using data from other measurements (Brown et al., 2009). A gas chromatograph is used to determine the composition of the natural gas mixture and then a thermodynamic equation of state to calculate the condensation curve. An overview of gas chromatographs and equations of state used on custody transfer stations will be outlined in Chapter 4 and 5 respectively.

Gas chromatographys are divided into two groups: laboratory and process. The advantages of the laboratory GC analysis are (ISO 11150, 2007):

- Gas chromatography using capillary columns, temperature programming and a flame ionisation detector (FID) is well established for the range of components, and has sufficient sensitivity to be applied to subparts per million levels.
- Pre-concentration techniques allow measurement of parts per billion levels

The disadvantages of the laboratory GC analysis are (ISO 11150, 2007):

- The quality of the result is totally reliant on the quality of the sample. Great care must be taken to ensure that the sample is representative, with no components lost in whole or in part and no cross contamination from previous use.
- Quantitative data is usually calculated using the assumption that the FID is a carbon counter. Components are then quantified relative to a component, such as butane or pentane, which means that it is important to ensure this calibration is correct.
- As with any laboratory measurement, there is an inevitable delay between sampling and reporting.

The advantages of the process GC analysis are (ISO 11150, 2007):

- With properly designed sampling system, the analyser will be presented with a representative sample, in the same way that physical dew point methods are.
- There is little delay between sampling and reporting.
- An analyser set up for dew point determination will also be capable of providing data for other physical properties, such as higher heating value, density, Wobbe index and compressibility factor.

The disadvantages of the process GC analysis are (ISO 11150, 2007):

- Temperature programming is not available on process analysers.
- It is impossible with isothermal detectors to achieve the same performance as that of a laboratory GC.
- In the absence of an FID, the thermal conductivity detector (TCD) can be used with capillary columns, but it cannot match the range and sensitivity of the FID.
- There is less available information about hydrocarbon responses from a TCD and so the need for certified mixtures to check performance is all the greater.

Other limitations of the process GC, used on custody transfer stations measuring up to $C-9+$ are:

- Limited to C_{9+} analysis
- Cannot provide a laboratory extended analysis or similar chromatogram.
- All fractions of the carbon group are lumped in the normalise alkane causing a higher hydrocarbon dew point determination.
- The accuracy is dependent on the sampling system and the certified reference gas.

The first two limitations cannot be changed because they are inherent to the instrument, however the last two limitations will be investigated further in order to develop a method in which to improve the hydrocarbon dew point determination using gas chromatography.

Chapter 4

Gas Chromatography Overview

4.1 Chapter Overview

Gas Chromatography has been developed into a key analytical tool for the petroleum and petrochemical industry. Chromatography (Grob et al., 2004) is the physical separation of sample components in which these components distribute themselves between two phases, one stationary and the other mobile. This chapter will outline the principle of operation for the process gas chromatograph and explain the its main components.

4.2 Principle of Operation

A gas chromatographs primary function is to separate a gas sample into its individual components and then calculate the concentration of each component measure. A sample of gas to be analysed is taken from the process stream and conditioned before analysis by the gas chromatograph.

The chromatographic separation of the sample gas into its components is accomplished in the analyser in the following manner. A precise volume of sample gas is injected into one of the units analytical columns. The column contains a stationary phase (packing) that is either an active solid (adsorption partitioning) or an inert solid support that is coated with a liquid phase (absorption partitioning). The sample gas is moved through the column by means of a mobile phase (carrier gas). Selective retardation of the components of the sample takes place in the column, that causes each component to move through the column at different rates. This action separates the sample into its constituent gases and vapours. A detector located at the outlet of the analytical column sense the elution of components from the column and produces electrical outputs proportional to the concentration of each component. The analysers controller then calculates the concentration of each component providing a detailed analysis of the gas mixture[Daniel manual 2002; Grob et al 2004].

The most common chromatograph found in field applications uses a combination of columns to analyse for methane through pentane and then treats all compounds with molecular weights greater than pentane, i.e. hexane and upwards on the hydrocarbon chain, as a C_{6+} fraction. This chromatogram is referred to as a C_{6+} chromatograph (NGC 2005). A C_{9+} chromatograph is an extension of the C_{6+}. It has a second detector that measures hexane through to octane with C_{9+} components being back flushed and the remaining components (C_6 –C_8) eluting from a single boiling point column (Ernst et al., 2005). Real natural gas contains many isomers other than the straight chain normal components. It is important to note that analysis on the second detector is by carbon number grouping and boiling point.

The C_{9+} gas chromatograph is researched and used in this project, as this type of GC is required in Australian if it is used to determine hydrocarbon dew point.

4.3 Sample System

The sample system is the most critical part of the process analyser. It is designed to provide a constant flow of sample and this includes conditioning the sample so that a representative sample can be injected into the chromatograph.

The sample stream originates from the process through a sample probe. It is recommended (George et al., 2006; API 14.1, 2006) that the probe be mounted vertically at the top of a straight run of horizontal pipe. If the gas stream is not near its hydrocarbon dew point, any probe location within a meter run is satisfactory provided it doesnot interfere with the performance of the the metering element. Straight cut probes are preferred over probes with beveled openings. In order to provide a representative sample the API standard 14.1 (2006) recommends that the sampling equipment be maintained at least 17 °C above the expected hydroarbon dew point.

Most sample streams require filtration to remove particulates. Phase separation may also be required for removal of condensed liquid droplets from vapours or immiscible droplets from liquids. Automatic valve switching is used to provide flow to the sample valve for injection into the GC. Valve switching is also used to sample multiple streams with a single analyser. Variable area flow meters are installed in the sample line to regulate the sample flow rate to the GC.

4.4 Analyser

The analyser section of the gas chromatograph comprises of multiport valves, columns, carrier gas and the detector. Figure 4.1 is an animated schematic of the Daniel 500 C_{9+} gas chromatograph, showing valves, columns and detectors and Figure 4.2 is a photo of the GC.

4.4.1 Multiport Valves

Figure 4.1 shows five chromatograph valves in the Daniel 500 C_{9+} GC. Valve 1 and 4 are used to inject a sample into the analyser and valves 2, 3 and 5 are used to direct the carrier gas flow in order to direct the hydrocarbon sample through the columns in the correct sequence. The controller is used to program the switching time of the valves as this directly affects the elution time of the components.

4.4.2 Columns

The Daniel 500 C_{9+} gas chromatograph uses packed columns to separate the hydrocarbon components. A packed column consists, (Grob et al., 2004), of three basic components: tubing in which packing material is placed, packing retainers inserted into the ends of the tubing to hold the packing in place and thirdly, the packing material. The stationary phase is an inert solid particle which adsorbs components as they pass over the columns stationary phase. This slows down the progression of the hydrocarbon components through the columns.

Referring to Figure 4.1 top section, which is for detector one:

- Column 1 is used to separate hexane (C_{6+}) so that it can be flushed to the detector.
- Column 2 is used to separate propane, iso-butane, neopentane, iso-pentane and normal pentane.
- Column 3 is used to separate nitrogen, methane, carbon dioxide and ethane.
- Column 4 is used to move the hexane (C_{6+}) peak away from a valve upset.

Referring to Figure 4.1 bottom section, which is for detector two:

- Column 5 is used to separate nonane (C_{9+}) so that it can be flushed to the detector.
- Column 5 and 6 is used to separate C_6, C_7 and C_8 and this is determined by the hydrocarbon boiling point. Methane through to pentane, including nitrogen and carbon dioxide is moved through as one lump and not measured for analysis purposes.

4.4.3 Carrier Gas

Commonly used carrier gas is helium (H_e), nitrogen (N_2) or hydrogen (H_2). In this application helium is the used as the carrier gas. Helium is the second lightest elemental gas next to hydrogen. The smallest of all molecules, it has the lowest boiling point of any element. It is colourless, odourless, tasteless and nontoxic, chemically inert, helium is non-flammable, only slightly soluble in water and has a high thermal conductivity.

4.4.4 Detector

The detectors used in the Daniel 500 C_{9+} GC are thermal conductivity (TCD). The thermal conductivity detector is a universal, nondestructive detection system (Grob et al., 2004). Since the thermal conductivity is a bulk physical property, the TCD is also identified as a bulk property detector, because it responds to some difference in the thermal conductivity of the carrier gas caused by the presence of the eluted components.

The Daniel 500 C_{9+} TCD consists of a balanced bridge network with heat sensitive thermistors in each leg of a Wheatstone bridge circuit. Each thermistor is enclosed in a separate chamber of the detector block. One thermistor is designated the reference element and the other the measurement element. In the quiescent condition (prior to sample injection) both legs of the bridge are exposed to pure carrier gas. In this condition the bridge is balanced and the bridge output is electrically nulled. As components elute from the column, the temperature of the measurement element changes based on the thermal conductivity of the hydrocarbon component. The temperature change unbalances the bridge and produces an electrical output proportional to the component concentration.

4.4.5 Controller

The the Daniel 500 C_{9+} controller is a microprocessor based device that provides the analyser with highly accurate timing, precision calculations, report generation and an interface with other devices.

The controller generates the gas composition analysis, chromatogram component elution times and peak areas and provides calculates for heating values, density and compressibility. Along with this the controller uses the gas analysis and applies it to either the Peng Robinson or Redlich Kwong Soave thermodynamic equation of state. The Dew Point calculation DewCalc is an additional program that can be utilised by the operator to enter detailed gas analysis in order to determine a more accurate hydrocarbon dew point. This program is used by this project to apply the authors characterisation method.

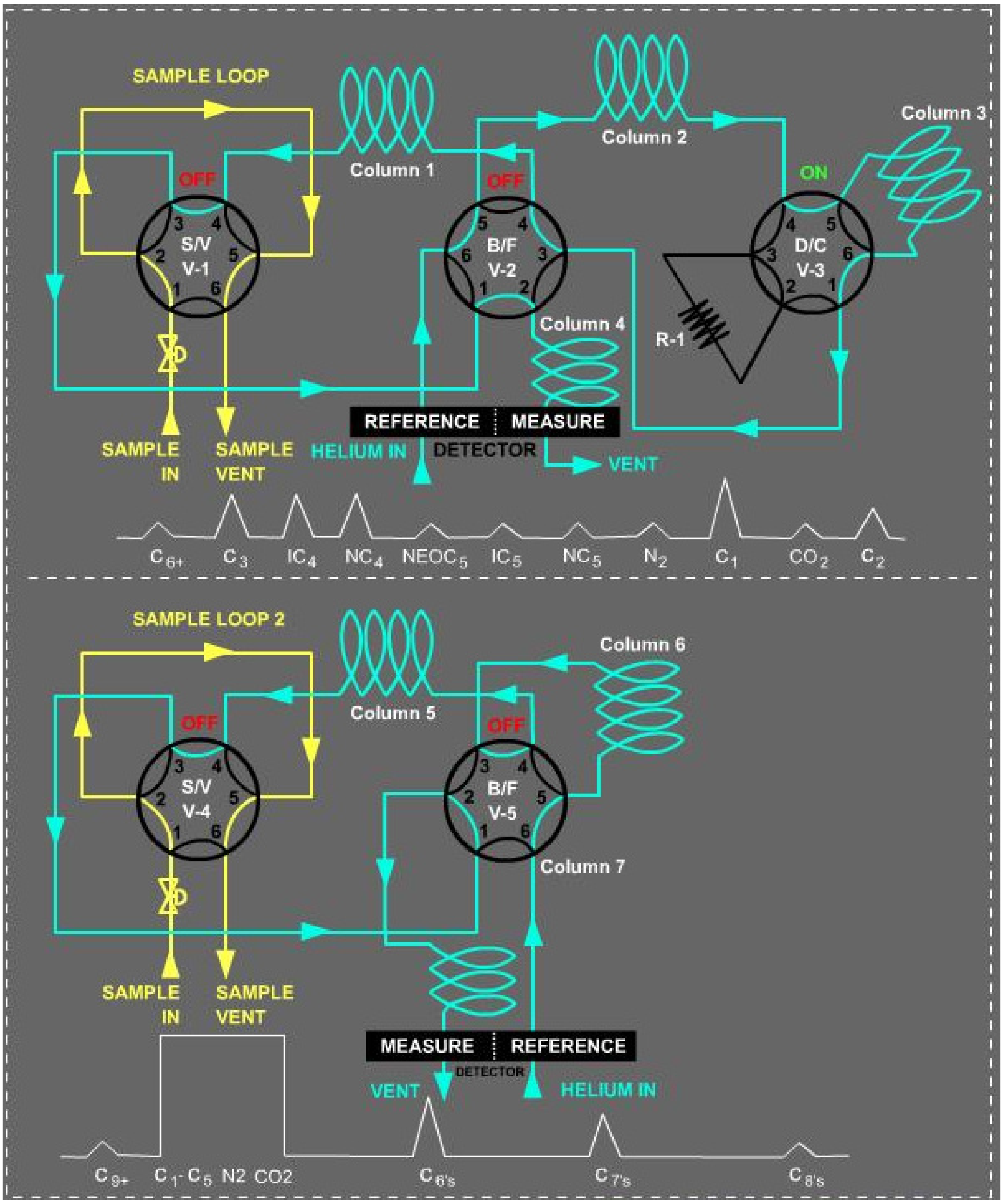

Figure 4.1: A schematic animation of the Daniel 500 C_{9+} gas chromatograph, showing valves, columns and detectors.

Figure 4.2: A Daniel 500 C_{9+} gas chromatograph, (authors own photo).

Chapter 5

Equations of State

5.1 Chapter Overview

The hydrocarbon dew point determination is calculated by applying thermodynamic principles and accepted equations of state using the detailed gas analysis from the gas chromatogram. An equation of state is an analytical calculation to express the pressure, volume and temperature (PVT) behaviour of gases and liquids. The Peng-Robinson and Soave-Redlich-Kwong are the two most commonly accepted sets of state equations used with custody transfer natural gas chromatography (NGC 2005).

This chapter provides an overview of the development of equations of state, from the first equation of Boyle's Law to the modern day. This chapter also provides a detailed explaination of the two equations of state that this research focuses on, namely the Redlich Kwong Soave and Peng Robinson. This chapter also provides information on the equation of state software used in this research.

5.2 Equation of state development

In 1662 Boyle's Law, Equation 5.1, was the first expression of an equation of state. Boyle's Law expressed the observation that te volume of a gas decreases as the pressure increases. Work on the equations of state for gases progressed by Charles, Gay-Lussac, Dalton and Claypeyron to produce the ideal gas law, Equation 5.2.

$$\frac{V}{V_0} = \frac{P_0}{P} \tag{5.1}$$

where

V is the gas volume,

P is the gas pressure,

V_0 is the gas volume at standard conditions,

P_0 is the gas pressure at standard conditions,

$$Pv = RT \tag{5.2}$$

where

P is the gas pressure,

v is the specific molar volume,

n is the number of moles of gas,

R is the universal gas constant,

T is the absolute temperature of the gas.

In 1873 van der Waals (Valderrama, 2003) introduced the first equation of state, Equation 5.3, capable of representing vapour-liquid coexistence. It was derived from the assumption of a finite volume occupied by the constituent molecules.

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \tag{5.3}$$

The parameter a is a measure of the attractive forces between molecules and the parameter b is a measure of the size of the molecules. Both parameters are adjustable and can be obtained from the critical properties of the fluid.

More complex and more accurate equations of state have been proposed through the years and several theories have been devised to better represent PVT properties and vapour liquid equilibrium (Valderrama, 2003). Advances in equations of state have taken three paths (Valderrama, 2003):

1. those following on from the van der Waals equation of state,
2. molecular based equations of state, and
3. virial type equations of state.

By the time of the proposal of Redlich and Kwong in 1948 there were about 200 equations of state (Valderrama, 2003; Redlich et al 1948). Redlich and Kwong were very much concerned about the limiting behaviour of the van der Waals equation of state and wanted to correct representations at low and high densities. They proposed an equation of state containing two individual coefficients and a dependence on the coefficients of the composition which furnished satisfactory results above the critical temperature for any pressure (Redlich et al 1948). Their equation did not have a strong theoretical back ground and was essentially empirical (Valderrama, 2003; Redlich et al 1948), but it provided good results for many gaseous systems.

In 1972 Soave proposed a modification to the Redlich-Kwong equation of state which introduced a third parameter, the acentric factor, and a temperature dependency into the cohesion energy term to account for the effect of nonsphericity on fluid PVT properties (Graboski, 1978). The Redlich-Kwong-Soave equation rapidly gained acceptance in the hydrocarbon processing industry because of its relative simplicity and capability for generating reasonably accurate equilibrium ratios in vapour-liquid equilibrium (VLE) (Peng et al, 1976).

Peng and Robinson improved upon Soaves equation by recalculating the dimensionless function of reduced temperature and acentric factor and by modifying the volume dependency of the attractive term. These changes allowed them to obtain better results for liquid volumes and better representations of vapour liquid equilibrium for many gas mixtures (Valderrama, 2003; Peng et al, 1976).

The Redlich Kwong Soave and the Peng Robinson equations of state are the most popular cubic equations used currently in research, simulations and optimisations in which thermodynamic and vapour liquid equilibrium properties are required (Valderrama, 2003; Bolland et al 2004; Laughton et al 2006). The Peng-Robinson and Soave-Redlich-Kwong are also the two most commonly accepted sets of state equations used with gas chromatography (NGC 2005). Trends in research on cubic equations of state after Soaves and Peng and Robinsons contribution have following three main routes (Valderrama, 2003):

1. modifications to the temperature dependant function in the Redlich Kwong Soave and Peng Robinson equations,
2. modifications to the volume dependence of the attractive pressure term, and
3. use of a third substance dependant parameter.

There are however, factors that influence the determining of hydrocarbon dew point from indirect methods and much research has been conducted in this area (Bolland et al 2004; Brown et al 2007; Brown et al 2008; Ernst et al 2005; George at al 2005; George 2007; George et al API). These factors primarily relate to the composition of the gas and the validity of the equation of state used and this will form the foundation of this project.

George et al (2005) found that hydrocarbon dew point predictions depended on obtaining and using accurate gas composition data especially up to nonane. Brown et al

(2008) agreed with George et al (2005), as he found that the hydrocarbon dew point of natural gas is highly sensitive to the composition of the gas, particularly the amount of fraction components with six or more carbon atoms. Another large impact on accuracy is the method used to characterise the distribution of heavy hydrocarbons in the gas stream when the exact composition beyond hexane, C_6, cannot be resolved by field gas chromatography (George et al 2005).

5.3 Equations of state used in this research

The two primary equations of state used in this research are the Redlich Kwong Soave and the Peng Robinson. Secondary equations of state used for comparison were the London Research Station equation of state, the Schmidt Wenzel equation of state, the Wong Sandler with Wagner saturated vapour pressure equation of state and the modified Benedict Webb Rubin equation of state.

As mentioned previously, the Redlich Kwong Soave and the Peng Robinson equations of state are the most popular cubic equations used currently in research, simulations and optimisations in which thermodynamic and vapour liquid equilibrium properties are required (Valderrama, 2003; Bolland et al 2004; Laughton et al 2006). Both are referred to as cubic equations (George, 2007; Modisette, 2000; Valderrama, 2003) because they can rewritten as cubic polynomials in the specific volume term v. The advantage of these equations are that they can accurately and easily represent the relation among temperature, pressure and phase composition in binary and multicomponent systems.

5.3.1 Redlich Kwong Soave and Peng Robinson Equation of State

The Redlich Kwong Soave and the Peng Robinson equations of state are cubic equations of the same form, shown in Equation 5.4.

$$P = \frac{RT}{v-b} - \frac{a_c\alpha^2}{(v-b_1)(v-b_2)} \tag{5.4}$$

George (2007) explains that the attractive force parameter, a_c and the replusive force parameter, b, are fit to experimental data on the behaviour of pure gases. These parameters are a function of the gases critical temperature, T_c, critucal pressure, P_c, and accentric factor, ω (itself a function of the gases critical pressure and vapour 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 for the same gas composition. The formulas for the acentric parameter, α (a function of the acentric factor, ω) used in each equation are given in Equation 5.5 and Equation 5.7.

Peng Robinson accentric parameter equation

$$\alpha_{PR} = 1 + (0.37644 + 1.54226\omega - 0.26992\omega^2)(1 - \sqrt{\frac{T}{T_c}}) \tag{5.5}$$

where

$$a_c = \frac{0.45724R^2T_c^2}{P_c}, b = \frac{0.07780RT_c^2}{P_c}, b_1 = -b(1+\sqrt{2}), b_2 = -b(1-\sqrt{2}) \tag{5.6}$$

Redlich Kwong Soave accentric parameter equation

$$\alpha_{RKS} = 1 + (0.480 + 1.547\omega - 0.176\omega^2)(1 - \sqrt{\frac{T}{T_c}}) \tag{5.7}$$

where

$$a_c = \frac{0.42748R^2T_c^2}{P_c}, b = \frac{0.08664RT_c^2}{P_c}, b_1 = -b, b_2 = 0 \tag{5.8}$$

For pure gases, (George, 2007; Modisette, 2000; Valderrama, 2003) the values of the attractive and repulsive force parameters in the Peng Robinson and Redlich Kwong Soave equations of state are based on experimental data. 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 5.9 to Equation 5.11 and used in the equations of state to presict the bahaviour of mixtures:

$$a_{c,mixture} = \sum_{i=1}^{N} \sum_{i=1 j\neq i}^{N} x_i x_j \sqrt{a_i a_j}(1 - k_{ij}) \tag{5.9}$$

$$a_i = a_{ci}\alpha_i^2 \tag{5.10}$$

$$b_{mixture} = \sum_{i=1}^{N} x_i b_i \tag{5.11}$$

where

ij are component indices,

N total number of components inthe 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 forpure components i,

α_i acentric parameter for pure components i, and

b_i repulsive force parameter for pure component i.

5.4 Equation of state software

Equation of state software programs are a useful tool for modeling the behaviour of natural gas in custody transfer and sampling system. There (Laughton et al 2006) are many software packages available on the market but due to differences in their calculation codes, including equaitons of state, physical parameters of natural gas compounds, binary interaction coefficients they usually lead to different results.

In this research project the GasVLe 5.0 software program by GL Nobel Denton was used. The choice software was based on availability; it was provided as a free trial for the research period.

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Chapter 6

Method to improve hydrocarbon dew point measurement via gas chromatography

6.1 Chapter Overview

This chapter outlines three characterisation methods: The ISO 23874 method, the authors own method and the authors adapted ISO 23874 method.

The ISO 23874 method is primarily based on laboratory type gas chromatographs. However, its equation for the calculation of unknown species boiling point using interpolation, has been adapted into the authors own method.

The two characterisation methods developed by the author have specific application for process type gas chromatographs and these novel methods are explained in this chapter. It is not the intention of the authors methods to produce the most accurate dew point characterisation curve.

The aim of these methods are to:

- establish an improved hydrocarbon dew point that provides benefits for gas producers, while maintaining a safety margin for pipeline operators and end users.
- help someone look at a process gas chromatogram for export natural gas and identify and quantify unknown hydrocarbon species in order to produce a detailed like gas analysis for implementation with an equation of state software program, either stand only or within a gas chromatograph controller.

6.2 ISO 23874 Method

ISO 23874:2006 Natural Gas – Gas chromatographic requirements for hydrocarbon dew point calculation, describes the performance requirements for analysis of treated natural gas of transmission or pipeline quality in sufficient detail so that the hydrocarbon dew point temperature can be calculated using an appropriate equation of state. The procedure covers the measurement of hydrocarbons in the range C_5 to C_{12}. n-Pentane, which is quantitatively measured using ISO 6974 (all parts), is used as a bridge component and all C_6 and higher hydrocarbons are measured relative to n-pentane.

The gas analysis is performed in two parts. Major components (nitrogen, carbon dioxide and hydrocarbons from C_1 to C_5) are analyzed according to ISO 6974 (all parts) and higher hydrocarbons (C_5 to C_{12}) are analyzed using the requirements of ISO 23874.

ISO 23874 determines that it is not possible to identify all the measured higher hydrocarbons, nor is it possible to obtain reference gas mixture that contains more than a few representatives of the higher hydrocarbons. The analytical data are, therefore, handled with a number of simplifying assumptions:

- Unidentified components are allocated a carbon number or molar mass according to their positions in the chromatogram with respect to identified *n-alkanes.*
- Alkanes of carbon number 7 and above are summed by carbon number and treated as fractions for input to the dew point calculation.

- Average boiling points and densities of fractions are calculated from the individual boiling points and quantities of the components that comprise them; individual component boiling points are calculated by interpolation between the bracketing *n-alkanes*.
- Sample components are quantified by comparison with n-pentane, which has been measured according to ISO 6974 (all parts), using relative response factors based on their allocated carbon numbers.

6.2.1 Calculation of the composition

The qualitative information is derived by comparing the response of unknown components with that of n-pentane. When using a flame ionization detector, relative response factors, F_{RR}, are claimed to be proportional to the carbon number. This is verified by using calibration gas of known composition to check the relative response factors. This method is also applied for other types of GC detectors.

Components are measured relative to the peak for n-pentane. The quality of n-pentane is derived from analysis in accordance with ISO 6974. The quality of each component, c_i, is calculated with Equation 6.1.

$$c_i = \frac{5 \times R_i \times c_{n-C_5} \times F_{RR,i,n-C_5}}{N \times R_{n-C_5}} \tag{6.1}$$

where:

R_i is the instrument response to component i in the sample,

R_{n-C_5} is the instrument response to n-pentane in the sample,

c_{n-C_5} is the quantity of n-pentane in the sample, determined according to ISO 6974,

$F_{RR,c,i,n-C_5}$ is the relative carbon response factor of component i to that of n-pentane,

N is the carbon number of i.

6.2.2 Calculation of the fraction quantities and properties

Other than the n-alkanes, benzene, cyclohexane, toluene and methylcyclohexane, most peaks measured in the C_7 to C_{12} part of the chromatogram are unidentified. They can be accounted for by using the widely accepted assumption that (with the exception of aromatics and some cycloalkanes) all components eluting between the n-alkanes $n-C_x$ and $n-C_{x+1}$ are iso-alkanes of the carbon number $x+1$. This means that the same carbon number can be applied to those components as is used for $n-C_{x+1}$ and so quantitative values can be derived for unidentified components.

The unidentified components are summed as fractions by carbon number. Such fractions can be input into an equation of state used for dew point calculation, along side individual identified components. Critical properties for individual components are available in the equation of state database, whereas those for fractions can be calculated from the average boiling points and densities of the fractions.

Individual peaks measured on the chromatogram are calculated according to Equation 6.1. The calculated quantities of unidentified peaks that elute immediately after $n-C_x$ up to including $n-C_{x+1}$ are summed and the total allocated to the fraction $x+1$. Any peaks that are separately identified in this region, such as benzene and cyclohexane in the C_7 fraction and methylcyclohexane and toluene in the C_8 fraction are not included in the summation because they are accounted for separately.

The ISO method calculates the boiling points of unidentified components (ISO23874, 2006, George, 2007) on the assumption that the boiling points of individual unidentified components can be calculated by linear interpolation between the values for the bracketing *n-alkanes*. This is checked by using known data for *n-alkanes*. Thus, the boiling point, $T_{BP},_y$, of a component y, which elutes between $n-C_x$ and $n-C_{x+1}$, is calculated using Equation 6.2.

$$T_{BP,y} = T_{BP,n-C_x} + \frac{(t_{R,y} - t_{R,n-C_x}) \times (T_{BP,n-C_{x+1}} - T_{BP,n-C_x})}{(t_{R,n-C_{x+1}} - t_{Rn-C_x})} \tag{6.2}$$

where:

$t_{R,y}$ is the retention time of component y.

$t_{R,n-C_x}$ is the retention time of the n-alkane $n - C_x$,

$t_{R,n-C_{x+1}}$ is the retention time of the n-alkane $n - C_{x+1}$,

$T_{BP,n-C_x}$ is the boiling point of the n-alkane $n - C_x$,

$T_{BP,n-C_{x+1}}$ is the boiling point of the n-alkane $n - C_{x+1}$.

The boiling point of the fraction, $T_{BP,FR}$, is then found by weighting the quantity of each component in the group by its boiling point, summing the total and dividing by the total quantity, according to Equation 6.3.

$$T_{BP,FR} = \frac{\sum(R_i \times T_{BP,i})}{\sum(t_{R,i})} \tag{6.3}$$

where:

R_i is the instrument response to component i in the sample.

$t_{R,i}$ is the retention time of component i in the sample.

6.3 Grygorcewicz Method

The authors method, for identifying and quantifying unknown hydrocarbon species on a gas chromatogram, is based on the relationship of elution time and hydrocarbon component boiling point and is a modified version of the lumped C_{9+} characterization method.

The authors method is designed to help someone look at a process gas chromatogram for export natural gas and identify and quantify unknown hydrocarbon species in order to produce a detailed like gas analysis for implementation with an equation of state software program, either stand only or within a gas chromatograph controller.

The lumped C_{9+} characterization method (George, 2007) requires that amounts of individual components with carbon numbers through to C_8 be known. These components are entered into the equation of state software for hydrocarbon dew point calculation. The amounts of all components higher than C_8 are added together and the sum assigned to the normal nonane. This method can be automatically implemented by GC's that perform extended analysis up to C_9 and report the amount of nonane and heavier components as a lumped C_{9+} fraction.

The issue with this method is that GC's on custody transfer points, that measure a lumped C_{9+}, do not identify the individual components up to C_8 for the dew point equation of state calculation. Instead they add all peaks within the respective carbon group and the sum assigned to the normal alkane of that carbon group. This includes benzene and cyclohexane in the C_7 fraction and toluene and methyl cyclohexane in the C_8 fraction. This is the case for the Daniel C_{9+} GC and the authors method described is based on this GC. The process for the authors characterisation method is as follows:

1. The Daniel C_{9+} GC does not reference the n-pentane as per the ISO 23874 method. Instead it uses two detectors, the first analyses C_1 to C_5 with nitrogen and carbon dioxide and the second analyses C_6 to C_8 with lumped C_{9+} peak. Since n-pentane cannot be referenced as the starting point, then for the C_6 group $2,2-dimethylbutane$ is used as the starting reference.

2. Using a certified calibration gas as the reference for the normalised alkanes, the reference gas chromatogram is compared to the sample gas chromatogram. This provides a visual of the peaks that the GC has identified between the normalised alkanes for C_6 to C_8. The GC raw data report is obtained for the retention time and peak area of each detected peak on the chromatogram.

3. The ISO 23874 method equation 6.2, is used to calculate the boiling point of the respective peaks identified on the chromatogram in the C_6 to C_8 groups. The only difference for the calculation is the C_6 fraction which uses $2,2-dimethylbutane$ instead of C_5 as the starting reference. $2,2-dimethylbutane$ is the first component in the C_6 group eluted from the GC and is a component in the calibration gas, therefore it can be validated and used as an alternative reference point in the equation 6.2.

4. The unknown components are identified by referencing the resultant boiling points to an accredited reference source, such as NIST Chemistry WebBook, Beilstein Crossfire database or GPSA engineering data handbook. If the boiling point of two compounds are close together and the retention time fails between them, then the compound with the higher boiling point will be used, unless it is an aromatic or naphthenes. The identified components should be compared to an laboratory extended analysis of the sample gas, for comparison of results and to determine and quantify any aromatics and naphthenes found in the sample gas.

5. The Daniel $C-9+$ GC summates all the peaks within the carbon group and assigns the result to the respective n-alkane. To determine the molecular percentage (mole %) of the newly identified component peak, the component peak area is divided by the summated peak area and multiplied by the resultant n-alkane. The quantity of each component, c_i, is calculated using equation 6.4.

$$c_i = \frac{A_{p,i}}{\sum_{n=z} A_{p,n-C_n+1}} \times \sum_{n=z} x_i \tag{6.4}$$

where

$A_{p,i}$ is the instrument response peak area to component i in the sample,

$A_{p,n-C_n+1}$ is the summed instrument peak area of the carbon number group,

x_i is the summed mol % of the carbon number group,

z is the number of peaks identified in the carbon number group.

6. The identified hydrocarbon components and calculated concentrations are applied to the GC equation of state to determine the hydrocarbon dew point. The Peng-Robinson and Soave Redlich Kwong equations of state should be used and compared to the MCMI results. In order to determine the accuracy of the equation of state calculation, it is beneficial to determine the dew point curve of the gas PVT phase envelope. This can be achieved by the MCMI and determining the HCDP at 3500 kPa and various pressure up to the transmission or pipeline pressure. The equation of state that is closest to the MCMI HCDP results should be applied in the GC dew point equation of state calculation software.

6.4 Adapted ISO 23874 Method

The requirements of ISO23874 to measure C_5 to C_{12} cannot be achieved by the custody transfer station GC used in this research. The following methodology is an adaptation of the ISO23874 Annex E so it can be applied to a Daniel C_{9+} GC.

1. The retention time for each peak in the C_6 to C_8 group is recorded and equation 6.2 is applied to obtain the calculated boiling points. As per the Grygorcewicz method, pentane cannot be used as the starting reference and this is substituted for $2,2-dimethylbutane$. The C_9 group is not included in this method as all components are lumped into a C_{9+} peak.
2. The calculated boiling points for the peaks in the C_6 group between $2,2-dimethylbutane$ and $n-hexane$ are referenced to an accredited reference source and identified individually for use in the EOS software.
3. The aromatics and cycloalkanes are identified as per the Grygorcewicz method using an accredited reference source or by means of an laboratory extended analysis. This is important as they will not be used in the calculation for the average boiling point of the C_n group fraction.
4. Each peak in the carbon group that is an isomer is assigned a letter to designate its order in the group.
5. The calculated boiling point is multiplied by teh component peak area and totalised.
6. The peak area of each isomer peak in the carbon group is totalised.
7. The total (Area x BP) is divided by the total peak area to obtain the average boiling point of the carbon group fraction.
8. As explained in the Grygorcewicz method, the Daniel C_{9+} GC doesnot measure components relative to the $n-pentane$ peak. This means that equation 6.4 is applied to determine the mole % of each unidentified isomer in the arbon group. The results are totalised and applied to the carbon group fraction. Equation 6.4 is also applied to determine the mole % quantity for aromatics and cycloalkanes.

9. The identified hydrocarbon alkanes in the C_6 group along with the aromatics, cycloalkanes and the average boiling point carbon group fractions of the C_7 and C_8 group are applied to the EOS software with all other gas sample data to determine the HCDP.

6.5 Chapter Summary

This chapter described the process of three charaterisation methods, the ISO 23874 method, the authors own method and the authors adapted ISO 23874 method.

In summary:

- the ISO 23874 provided an important equation that interpolates the boiling point for unknown peaks between the normalised alkane.
- this equation has been integrated with the Grygorcewicz method to identify unknown hydrocarbons within the C_6 to C_8 carbon groups to produce a detailed like gas analysis that can be implemented with an equation of state software program.
- the authors adapted ISO 23874 method was developed to apply the ISO 23874 method to a process type gas chromatograph measuring up to C_{9+}, which is typical of custody transfer gas chromatographs used in Australia to determine hydrocarbon dew point.

The purpose of both of the authors methods, is to provide a characterisation that the user can apply with the information from a process gas chromatograph rather than a laboratory extended analysis. Both these characterisation methods are novel and will be trialled in the next chapter.

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Chapter 7

Hydrocarbon dew point measurement improvement results

7.1 Chapter Overview

This chapter documents the results obtained from the application of the authors characterisation method and the authors adapted ISO 23874 method.

The chapter follows a systematic path. The first step taken was to gather initial data concerning the:

- actual hydrocarbon dew point, using a direct method instrument,
- the process gas chromatograph analysis and chromatograms, and
- the detailed gas analysis and chromatogram from a laboratory gas chromatograph.

This information is required to establish a basis for which to compare the results of the authors characterisation methods.

The next step involved the implementation of the data and this was conducted over two trials. The first trial compares the Grygorcewicz method and the authors adapted ISO 23874 method to the equation of state software, GasVLE. The second trial then implements both characterisation methods into the gas chromatograph dew point software and compares the results to the GasVLE software and MCMI.

7.2 Manual Chilled Mirror Instrument Results

A manual chilled mirror instrument (MCMI) was used to measure the hydrocarbon dew point (HCDP) of the export natural gas used in this research. The MCMI was used to produce a baseline direct method HCDP phase envelope curve in which to compare the results determined from the authors method and the authors adapted ISO 23874 method. The MCMI results are recorded in Table 7.1.

The MCMI used was a Chandler DewScope. The calibrated thermometer had 0.5°C graduations and the tests were verified by two trained operators.

Table 7.1: MCMI HCDP results for the export natural gas used in this research

Pressure (bar)	HCDP Temperature (°C)
16.0	-10.5
25.5	-9.5
34.0	-9.0
37.0	-8.5
39.5	-9.5
46.5	-10.5
60.0	-15.5
70.0	-16.5
79.0	-18.0

7.3 Custody Transfer Gas Chromatograph

The process gas chromatograph (GC) used in these experiments was the Daniel 500 C_{9+} GC with 2350 controller. The GC detectors are thermal conductivity (TCD).

7.3.1 Gas Chromatograph Sample Data

The custody transfer gas chromatograph sample data was obtained while the MCMI HCDP measurements were conducted. Table 7.2 provides the GC component analysis report of the export gas and Table 7.3 provides the raw data report that establishes the retention time and peak area. This data is use to calculate the boiling point and concentration for both the authors method and the authors adapted ISO 23874 method. Table 7.4 provides data related to the gas properties and Table 7.5 records the resultant HCDP temperatures at predefined pressures determined by the GC using the Peng Robinson equation of state.

7.3.2 Gas Chromatograph Sample Data Hydrocarbon Dew Point Determination

The results of Table 7.2 were applied to the GasVLE equation of state software to determine the HCDP curves for the Peng Robinson and Redlich Kwong Soave equations of state. Figure 7.1 is a comparison of the HCDP curves produced by: the equation of state software, the gas chromatograph (Table 7.5) and the MCMI results of Table 7.1. A comparison of other equations of state to the Peng Robinson and Redlich Kwong Soave for this gas sample can be referred too in Figure C.1.

It should be noted that the resultant HCDP curves and temperature results are based on the GC analysis providing all component results as the normalised alkane.

Table 7.2: GC analysis report of the export natural gas used in this research

Component Name	Symbol	Mole Percent
Nitrogen	N_2	0.9964
Carbon Dioxide	CO_2	1.8106
Methane	CH_4	93.6975
Ethane	C_2H_6	2.2300
Propane	C_3H_8	0.8115
i-Butane	$i - C_4$	0.1089
n-Butane	$n - C_4$	0.1756
Neopentane	C_5H_{12}	0.00174
i-Pentane	$i - C_5$	0.0445
n-Pentane	$n - C_5$	0.0406
C6 Group	C_6	0.0343
C7 Group	C_7	0.0347
C8 Group	C_8	0.0121
C9+ Group	C_{9+}	0.00156
TOTAL		100.0000

7.3.3 Gas Chromatograph Chromatograms

The export gas analysis chromatograms were obtained from the custody transfer GC at the time the MCMI HCDP measurement was conducted. The chromatograms can be referenced in Appendix B, Figure B.1 to Figure B.4

7.3.4 Discussion of Results

The MCMI measured the HCDP cricondentherm of the export gas at -8.5°C at 37 bar.

The GC using the Peng Robinson equation of state reported the HCDP cricondentherm at -3.25°C at 29.3 bar. At the same pressure, the MCMI measured -9.0°C. This is a difference of 5.75°C.

Table 7.3: GC raw data report highlighting retention times and peak areas for C_6 to C_8

Carbon Group	Retention Time (sec)	Peak Area
C_6	79.1	94712
	87.2	1483636
	91.6	395892
	97.1	972932
C_7	109.8	957912
	127.4	1315440
	133.9	801676
	143.1	255400
	150.3	340968
C_8	171.9	882072
	214.9	31280
	234.4	339456
	261.0	77864

The gas analysis was applied to the equation of state software, GasVLE. The Peng Robinson equation of state results were aligned with the GC Peng Robinson HCDP temperatures. The Redlich Kwong Soave equation of state reported a higher HCDP cricondentherm of -0.56°C at 28.8 bar.

This highlights two points:

1. that by using the normalised alkane in the C_6 to C_8 group, as in this case, then a higher than actual HCDP determination will result.
2. that there is a need to develop a method that can easily produce a laboratory extended analysis like composition in which to apply to the equaiton of state in order to produce HCDP determinations similar to the actual HCDP measured by the MCMI.

Table 7.4: GC gas property results for the export natural gas used in this research

Property	Value	Unit
Compressibility factor (Z)	0.99774	–
Heating Value	38.2924	MJ/m^3
Relative density	0.6034	–
Gas density	0.7394	kg/m^3
Wobbie Index	49.2949	MJ/m^3

Table 7.5: GC HCDP Peng Robinson results for the export natural gas used in this research

Pressure (bar)	HCDP Temperature (°C)
14.0	-6.0
24.0	-3.2
28.5	-3.0
35.0	-3.4
44.0	-5.3

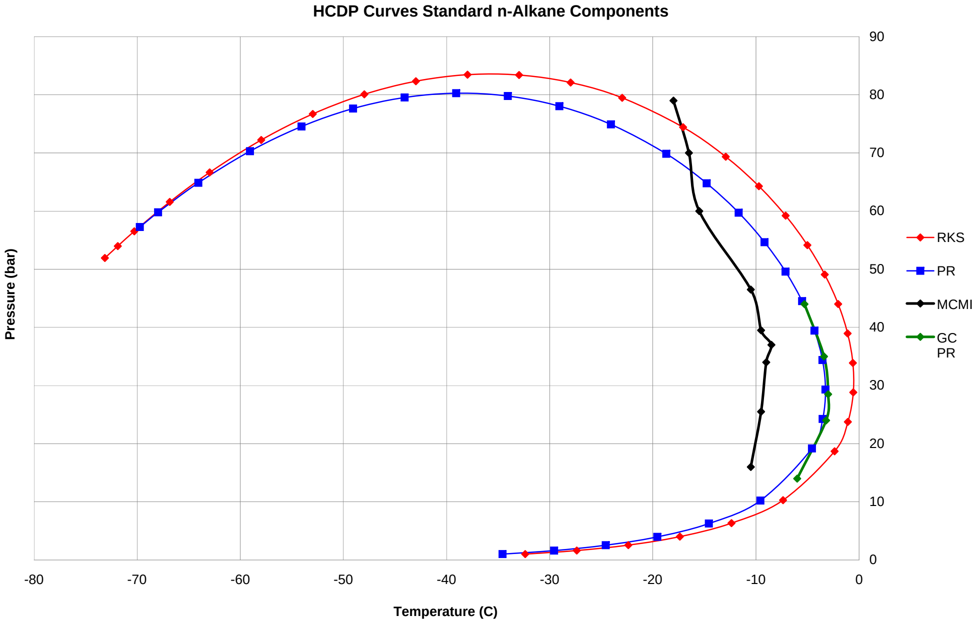

Figure 7.1: A comparison of the HCDP curves obtained by the PR and RKS EoS using the GC analysis of standard n-alkanes from Table 7.2 and the MCMI

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7.4 Laboratory Extended Analysis

A laboratory extended analysis of the export natural gas used in this research was completed. The purpose of the laboratory extended analysis was to verify the correct identification of the unknown hydrocarbon isomers, aromatics and cycloalkanes shown on the custody transfer chromatogram (Figure B.1) when applying the authors characterisation methods. The results of the extended analysis are shown in Table 7.6 and the corresponding determined HCDP temperatures are recorded in Table 7.7. The laboratory chromatogram is included in Figure 7.2. In regard to Figure 7.2:

1. all peaks are referenced to n-pentane (abbreviated as $n5$ on the chromatogram),
2. the aromatics and cycloalkanes have been identified and abbreviated on the chromatogram as:
    - Benzene is BZ,
    - Cyclohexane is CH,
    - Methylcyclohexane is MCH
    - Toluene is TOL

The laboratory gas chromatograph used, was an Agilent 6890N with Flame Ionisation Detector (FID), SGE-BP1 capillary column and 28 minute runtime. The laboratory extended analysis determined the HCDP using the Peng Robinson equation of state with the 'AGA' computer program as modified by the Murdoch University Gas Group. The components specified in the equation of state software are: C_1, C_2, C_3, $i-C_4$, $n-C_4$, $i-C_5$, $n-C_5$, $n-C_6$, $n-C_7$, $n-C_8$, $n-C_9$, $n-C_{10}$, N_2, CO_2, H_2S, $toluene$. It should be noted that the laboratory extended analysis is still using the normalised alkanes to determine the HCDP, which inevitable determines a higher result.

7.4.1 Discussion of Results

The laboratory extended analysis using the Peng Robinson equaiton of state determined the HCDP cricondentherm at -4.43°C at 30.7 bar. This is still 4°C higher than the

Table 7.6: Laboratory GC extended analysis report

Component Name	Mole Percent
Nitrogen	0.91
Carbon Dioxide	1.76
Methane	93.77
Ethane	2.34
Propane	0.74
i-Butane	0.10
n-Butane	0.17
i-Pentane	0.05
n-Pentane	0.041
C6 Group	0.0343
Benzene	0.0059
Cyclohexane	0.018
C7 Group	0.030
Methylcyclohexane	0.014
Toluene	<0.0001
C8 Group	0.0121
Ethylbenzene + Xylene	0.0004
C9 Group	0.0015
C10 Group	<0.0001
C11 Group	<0.0001
C12 Group	<0.0001
C13 Group	<0.0001
C14+ Group	<0.0001

Table 7.7: Laboratory GC HCDP results using Peng Robinson equation of state for the export natural gas used in this research.

Pressure (bar)	HCDP Temperature (°C)
10.0	-10.88
16.9	-6.63
23.8	-4.82
30.7	-4.43
35.0	-4.70
44.5	-6.42
51.4	-8.58
58.2	-11.55
65.1	-15.52

MCMI HCDP cricondentherm. The higher HCDP determination is due to the fact that the laboratory extended analysis is still using the n-alkanes to calculate the HCDP and therefore determines a higher HCDP temperature.

The laboratory extended analysis was beneficial for this research. It identified benzene and cyclohexane in the C_7 group and methylcyclohexane and toluene in the C_8 group The identification of these aromatics and cycloalkanes and their position on the chromatogram will be used in the experiments for the authors methods.

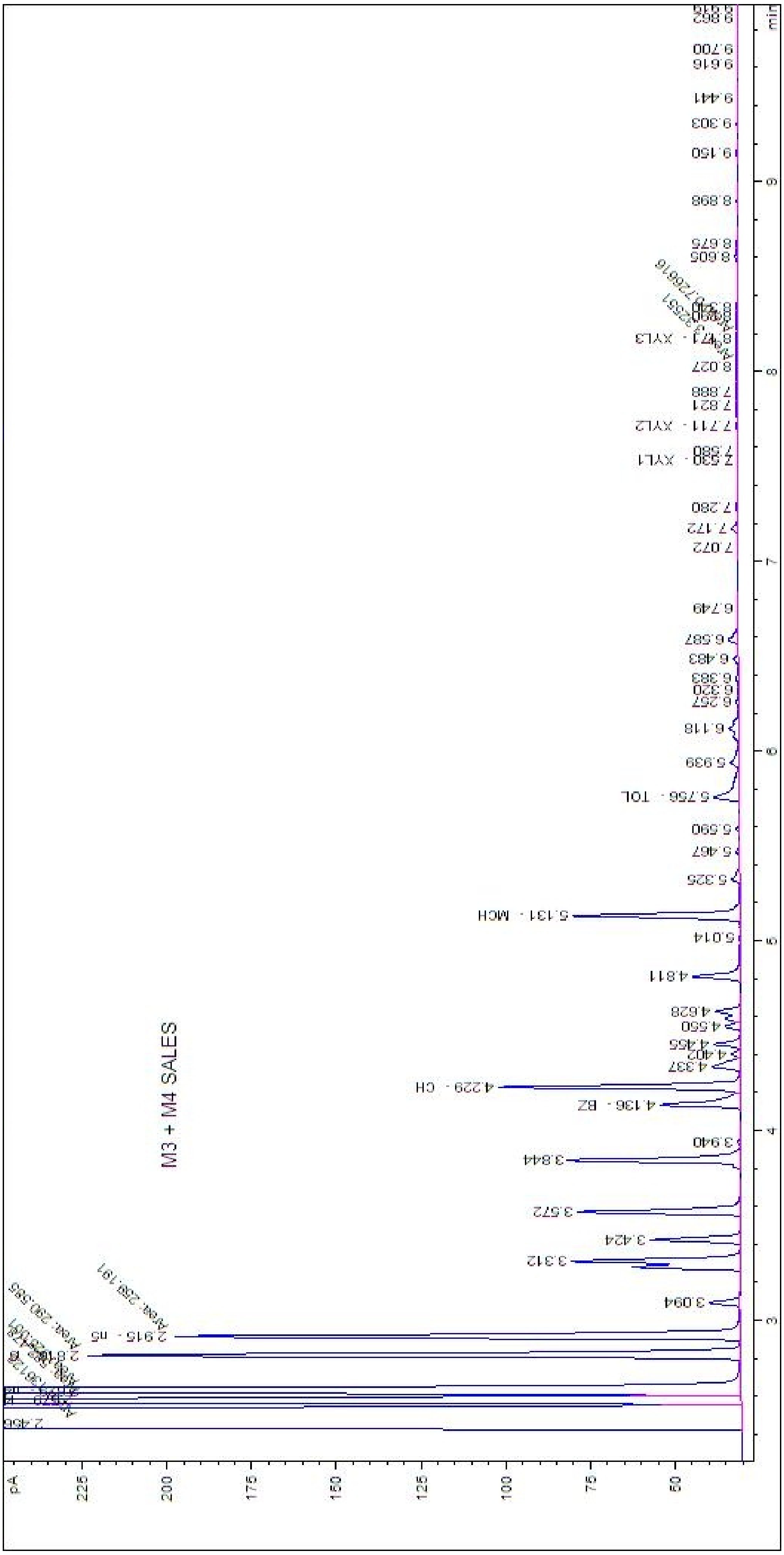

Figure 7.2: Laboratory GC extend analysis chromatogram. The aromatics and cycloalkanes have been identified and abbreviated above their respective peak.

7.5 Grygorcewicz Method Results

This section details the data and results of six experiments conducted using the authors method, that was developed in Section 6.3.

In each set of results, the hydrocarbon species are identified from the interpolated boiling point. The mole % concentrations are calculated and the data applied to the GasVLE equation of state software. The resultant hydrocarbon dew point curves for the Peng Robinson and Redlich Kwong Soave equations of state are compared to the manual chilled mirror instrument to assess the validity of the authors method.

The purpose of conducting six experiments was to ensure that all valid combinations of hydrocarbon species were tested and to determine the importance of correctly identifying the hydrocarbon species.

7.5.1 Boiling Point Calculation Results

The boiling point of each unknown hydrocarbon component is interpolated using Equation 6.2 and recorded in Table 7.8.

Table 7.8: Calculated hydrocarbon boiling point of unidentified peaks in the C_6 to C_8 group on the chromatogram.

Carbon Group	Retention Time (sec)	Boiling Point (°C)	Calculated Boiling Point (°C)
C_6	79.1	49.80	–
	87.2		58.35
	91.6		62.99
	97.1	68.80	–
C_7	109.8		75.89
	127.4		85.72
	133.9		89.34
	143.1		94.48
	150.3	98.50	–
C_8	171.9		103.79
	214.9		114.31
	234.4		119.09
	261.0	125.6	–

7.5.2 Hydrocarbon Dew Point Determination Result Set One

The hydrocarbon components identified in this result set are based on boiling point data only and do not consider the laboratory extended analysis.

Hydrocarbon Component Identification

The calculated boiling points are referenced to the National Institute of Standards and Technology (NIST) Chemistry Webbook to identify the hydrocarbon components found on the chromatogram. The identified hydrocarbon components are recorded in Table 7.9.

Table 7.9: Identification of hydrocarbon peaks in the C_6 to C_8 group – Result Set One.

Carbon Group	Retention Time (sec)	Calculated Boiling Point (°C)	Referenced Boiling Point (°C)	Component
C_6	79.1	49.80	49.80	2,2-dimethylbutane
	87.2	58.35	58.10	2,3-dimethylbutane
	91.6	62.99	63.30	3-methylpentane
	97.1	68.80	68.80	n-hexane
C_7	109.8	75.89	79.20	2,2-dimethylpentane
	127.4	85.72	86.10	3,3-dimethylpentane
	133.9	89.34	89.80	2,3-dimethylpentane
	143.1	94.48	93.50	3-ethylpentane
	150.3	98.50	98.50	n-heptane
C_8	171.9	103.79	103.45	ethylcyclopentane
	214.9	114.31	114.70	2,3,3-trimethylpentane
	234.4	119.09	118.90	3-methylheptane
	261.0	125.60	125.60	n-octane

Hydrocarbon Component Concentration

The hydrocarbon concentration for each component in the C_6 to C_8 carbon groups were calculated by applying the results of Table 7.2 and Table 7.3 to Equation 6.4 and recorded in Table 7.10.

Table 7.10: Identified hydrocarbon component concentration in the C_6 to C_8 groups – Result Set One.

Carbon Group	Component	Component Concentration *mole%*
C_6	2,2-dimethylbutane	0.001372
	2,3-dimethylbutane	0.01715
	3-methylpentane	0.004459
	n-hexane	0.011319
C_7	2,2-dimethylpentane	0.009022
	3,3-dimethylpentane	0.012492
	2,3-dimethylpentane	0.007634
	3-ethylpentane	0.002429
	n-heptane	0.003123
C_8	ethylcyclopentane	0.007986
	2,3,3-trimethylpentane	0.000242
	3-methylheptane	0.003146
	n-octane	0.000726

Hydrocarbon Dew Point Curves

The results recorded in Table 7.10 are used to substitute the normalised alkane from C_6 to C_8 in Table 7.2. The new detailed gas composition, Table 7.11, was entered into the GasVLE equation of state software to determine the hydrocarbon dew point curves for the Peng Robinson and Redlich Kwong Soave equations of state. These curves are displayed in Figure 7.3 and the MCMI results have been included to provide a baseline, in order to compare the theoretical determined HCDP with that actually measured. For a comparison of other equations of state for this gas composition refer to Figure C.2.

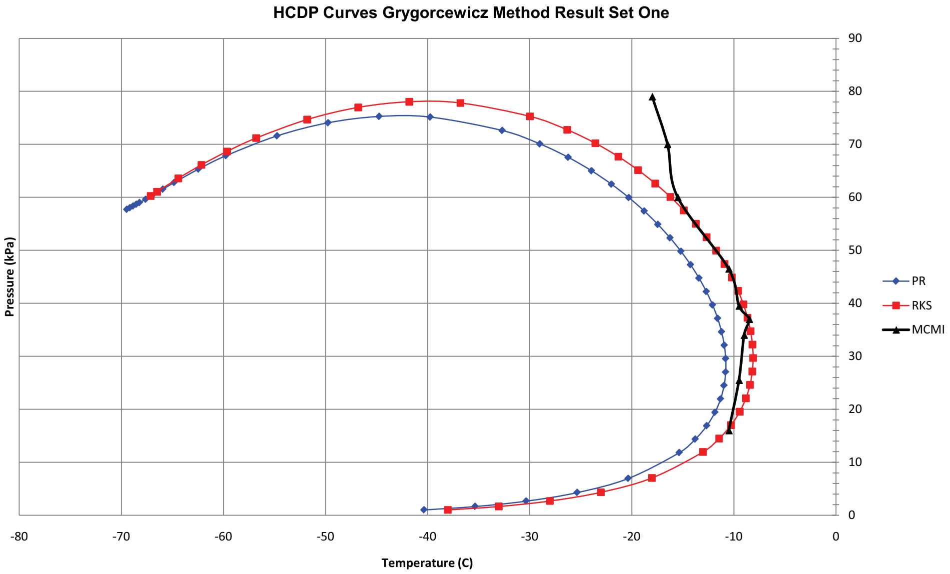

Figure 7.3: A comparison of the HCDP curves obtained by the PR and RKS EoS using the identified components from Table 7.11 and the MCMI

.

Discussion of Results

The identified hydrocarbon components from the referenced boiling points in Table 7.9 are all isomers of the normalised alkane and do not contain any aromatic or cycloalkane components.

Referring to Figure 7.3. The Peng Robinson HCDP curve is on average 2.5°C lower than the MCMI and Redlich Kwong Soave HCDP curves. In the pressure range of 35 to 60 bar, *the retrograde dew point line*, the Redlich Kwong Soave equation of state HCDP curve is aligned with the MCMI results. In the region 14 to 35 bar, *the normal dew point line*, the Redlich Kwong Soave HCDP curve determines a cricondentherm of -8.12°C at 29.7 bar and determined a higher HCDP temperature of +1°C to the MCMI at the same pressure. This result is good. This composition improved the HCDP temperature by -4.96°C compared to the GC result and maintained the theoretical HCDP curve higher than the actual dew point measured. With reference to the ISO and API definitions in Section 2.3, the theoretical HCDP needs to be higher than the actual as condensation has formed, meaning that the curve has been crossed.

Table 7.11: Gas analysis used with the GasVLE Equation of State software for Result Set One

Component Name	GasVLE Component Code	Mole Percent
Nitrogen	$N2$	0.9964
Carbon Dioxide	$CO2$	1.8106
Methane	$C1$	93.6975
Ethane	$C2$	2.2300
Propane	$C3$	0.8115
i-Butane	$iC4$	0.1089
n-Butane	$nC4$	0.1756
Neopentane	$neoC5$	0.00174
i-Pentane	$iC5$	0.0445
n-Pentane	$nC5$	0.0406
2,2-dimethylbutane	$22DMB$	0.001372
2,3-dimethylbutane	$23DMB$	0.017150
3-methylpentane	$3MC5$	0.004459
n-hexane	$nC6$	0.011319
2,2-dimethylpentane	$22DMC5$	0.009022
3,3-dimethylpentane	$33DMC5$	0.012492
2,3-dimethylpentane	$23DMC5$	0.007634
3-ethylpentane	$3EC5$	0.002429
n-heptane	$nC7$	0.003123
ethylcyclopentane	$EtCyc5$	0.007986
2,3,3-trimethylpentane	$233TMC5$	0.000242
3-methylheptane	$3MC7$	0.003146
n-octane	$nC8$	0.000726
n-nonane	$nC9$	0.00156

7.5.3 Hydrocarbon Component Identification Result Set Two

The hydrocarbon components identified in this result set are based on boiling point data and the laboratory extended analysis. The laboratory extended analysis found benzene and cyclohexane in the C_7 group and methylcyclohexane and toluene in the C_8 group for the export natural gas used in this research.

Hydrocarbon Component Identification

The calculated boiling points are referenced to the National Institute of Standards and Technology (NIST) Chemistry Webbook to identify the hydrocarbon components found on the chromatogram. The identified hydrocarbon components are recorded in Table 7.12.

The boiling point of benzene and cyclohexane is 80.15°C and 80.75°C respectively and the first peak in the C_7 group has a calculated boiling point of 75.89°C. Since this boiling point is less than the referenced boiling point it was decided to replace 2,2-dimethylpentane with benzene and cyclohexane. A benzene and cyclohexane component concentration split of 50:50 was chosen to determine the effect on the HCDP curve.

The boiling point of methylcyclohexane is 100.85°C and the calculated boiling point of the first peak in the C_8 group is 103.79°C. Eventhough the calculated boiling point is higher than the referenced, the laboratory extended analysis identified methylcyclohexane, so ethylcyclopentane was replaced with methylcyclohexane. Likewise the same applied for toluene. Its boiling point is 110.65°C compared to the boiling point of the second peak (114.21°C). However it was identified on the laboratory extended analysis, so 2,3,3-trimethylpentane was replaced with toluene.

Hydrocarbon Component Concentration

The hydrocarbon concentration for each component in the C_6 to C_8 carbon groups were calculated by applying the results of Table 7.2 and Table 7.3 to Equation 6.4 and

Table 7.12: Identification of hydrocarbon peaks in the C_6 to C_8 group – Result Set Two.

Carbon Group	Retention Time (sec)	Calculated Boiling Point (°C)	Referenced Boiling Point (°C)	Component
C_6	79.1	49.80	49.80	2,2-dimethylbutane
	87.2	58.35	58.10	2,3-dimethylbutane
	91.6	62.99	63.30	3-methylpentane
	97.1	68.80	68.80	n-hexane
C_7	109.8	75.89	80.15	benzene
			80.75	cyclohexane
	127.4	85.72	86.10	3,3-dimethylpentane
	133.9	89.34	89.80	2,3-dimethylpentane
	143.1	94.48	93.50	3-ethylpentane
	150.3	98.50	98.50	n-heptane
C_8	171.9	103.79	100.85	methylcyclohexane
	214.9	114.31	110.65	toluene
	234.4	119.09	118.90	3-methylheptane
	261.0	125.60	125.60	n-octane

recorded in Table 7.13.

Hydrocarbon Dew Point Curves

The results recorded in Table 7.13 are used to substitute the normalised alkane from C_6 to C_8 in Table 7.2. The new detailed gas composition, Table 7.14, was entered into the GasVLE equation of state software to determine the hydrocarbon dew point curves for the Peng Robinson and Redlich Kwong Soave equations of state. These curves are displayed in Figure 7.4 and the MCMI results have been included to provide a baseline, in order to compare the theoretical determined HCDP with that actually measured. For a comparison of other equations of state for this gas composition refer to Figure C.3.

Table 7.13: Identified hydrocarbon component concentration in the C_6 to C_8 group – Result Set Two.

Carbon Group	Component	Component Concentration $mole\%$
C_6	2,2-dimethylbutane	0.001372
	2,3-dimethylbutane	0.01715
	3-methylpentane	0.004459
	n-hexane	0.011319
C_7	benzene	0.004511
	cyclohexane	0.004511
	3,3-dimethylpentane	0.012492
	2,3-dimethylpentane	0.007634
	3-ethylpentane	0.002429
	n-heptane	0.003123
C_8	methylcyclohexane	0.007986
	toluene	0.000242
	3-methylheptane	0.003146
	n-octane	0.000726

Discussion of Results

The position of benzene and cyclohexane at the first peak was based on the boiling point and not the peak position on the laboratory extended analysis chromatogram in Figure 7.2. Referring to Figure 7.2, there is another peak before benzene and cyclohexane in the C_7 group and this will be explored in another set of experiments.

Eventhough the boiling points of methylcyclohexane and toluene are lower than that calculated for the first and second peak in the C_8 group, they were included because the extended laboratory analysis identified them.

Referring to Figure 7.4. The Peng Robinson HCDP curve is on average 2.5°C lower than the Redlich Kwong Soave and the MCMI results. The Redlich Kwong Soave HCDP curve is more aligned to the MCMI than result set one. The MCMI cricondentherm is

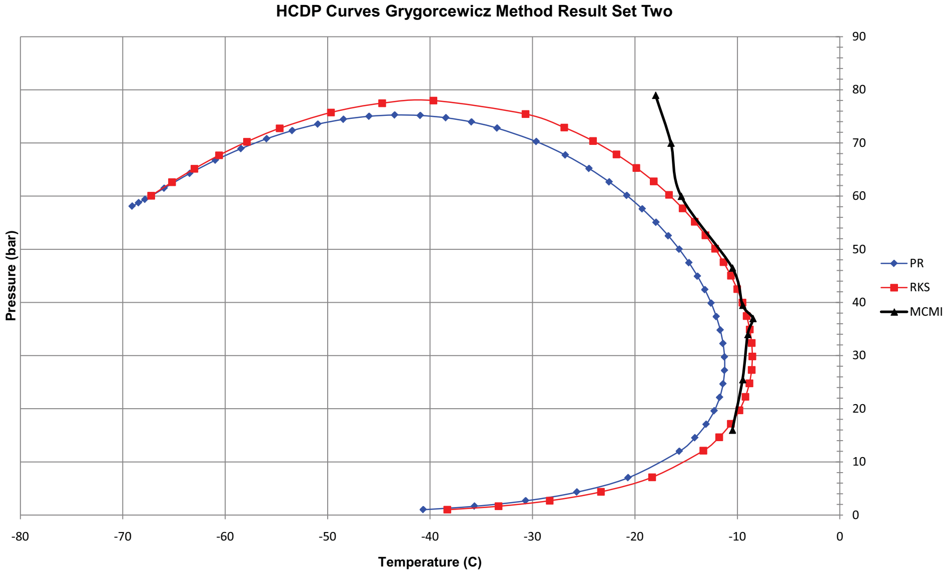

Figure 7.4: A comparison of the HCDP curves obtained by the PR and RKS EoS using the identified components from Table 7.14 and the MCMI

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-8.5°C at 37 bar, whereas the Redlich Kwong Soave equation of state determined the cricondentherm at -8.5°C at 29.8 bar. In the 35 to 60 bar pressure range, *the retrograde dew point line*, the Redlich Kwong Soave HCDP curve is approximately 0.5°C lower than the MCMI at the same pressure. In the 14 to 35 bar pressure range, *the normal dew point line*, the Redlich Kwong Soave determines a higher HCDP temperature of 0.7°C to the MCMI at the same pressure. This is a better result when compared to result set one. This composition improved the HCDP temperature by 5.1°C compared to the GC result and maintained the theoretical HCDP curve higher than the actual dew point measured.

Table 7.14: Gas analysis used with the GasVLE Equation of State software for Result Set Two

Component Name	GasVLE Component Code	Mole Percent
Nitrogen	$N2$	0.9964
Carbon Dioxide	$CO2$	1.8106
Methane	$C1$	93.6975
Ethane	$C2$	2.2300
Propane	$C3$	0.8115
i-Butane	$iC4$	0.1089
n-Butane	$nC4$	0.1756
Neopentane	$neoC5$	0.00174
i-Pentane	$iC5$	0.0445
n-Pentane	$nC5$	0.0406
2,2-dimethylbutane	$22DMB$	0.001372
2,3-dimethylbutane	$23DMB$	0.017150
3-methylpentane	$3MC5$	0.004459
n-hexane	$nC6$	0.011319
benzene	$Benz$	0.004511
cyclohexane	$Cyc6$	0.004511
3,3-dimethylpentane	$33DMC5$	0.012492
2,3-dimethylpentane	$23DMC5$	0.007634
3-ethylpentane	$3EC5$	0.002429
n-heptane	$nC7$	0.003123
methylcyclohexane	$MeCyc6$	0.007986
toluene	Tol	0.000242
3-methylheptane	$3MC7$	0.003146
n-octane	$nC8$	0.000726
n-nonane	$nC9$	0.00156

7.5.4 Hydrocarbon Component Identification Result Set Three

The hydrocarbon components identified are the same as result set two, except that the benzene and cyclohexane component concentration split was changed from 50:50 to 25:75 respectively.

Hydrocarbon Component Identification

The calculated boiling points are referenced to the National Institute of Standards and Technology (NIST) Chemistry Webbook to identify the hydrocarbon components found on the chromatogram. The identified hydrocarbon components are recorded in Table 7.15.

Table 7.15: Identification of hydrocarbon peaks in the C_6 to C_8 group – Result Set Three.

Carbon Group	Retention Time (sec)	Calculated Boiling Point (°C)	Referenced Boiling Point (°C)	Component
C_6	79.1	49.80	49.80	2,2-dimethylbutane
	87.2	58.35	58.10	2,3-dimethylbutane
	91.6	62.99	63.30	3-methylpentane
	97.1	68.80	68.80	n-hexane
C_7	109.8	75.89	80.15	benzene
			80.75	cyclohexane
	127.4	85.72	86.10	3,3-dimethylpentane
	133.9	89.34	89.80	2,3-dimethylpentane
	143.1	94.48	93.50	3-ethylpentane
	150.3	98.50	98.50	n-heptane
C_8	171.9	103.79	100.85	methylcyclohexane
	214.9	114.31	110.65	toluene
	234.4	119.09	118.90	3-methylheptane
	261.0	125.60	125.60	n-octane

Hydrocarbon Component Concentration

The hydrocarbon concentration for each component in the C_6 to C_8 carbon groups were calculated by applying the results of Table 7.2 and Table 7.3 to Equation 6.4 and recorded in Table 7.16.

In Table 7.6, the benzene and cyclohexane concentration split by analysis is 33:67 respectively. However the component concentration split of 25:75 was chosen after taking into consideration the average of all historical extended analysis results. It was interesting to note that all previous extended analysis results showed that cyclohexane remained constant and that benzene was variable, sometimes as low as 6% compared to cyclohexane.

Table 7.16: Identified hydrocarbon component concentration in the C_6 to C_8 group – Result Set Three.

Carbon Group	Component	Component Concentration $mole\%$
C_6	2,2-dimethylbutane	0.001372
	2,3-dimethylbutane	0.01715
	3-methylpentane	0.004459
	n-hexane	0.011319
C_7	benzene	0.002256
	cyclohexane	0.006767
	3,3-dimethylpentane	0.012492
	2,3-dimethylpentane	0.007634
	3-ethylpentane	0.002429
	n-heptane	0.003123
C_8	methylcyclohexane	0.007986
	toluene	0.000242
	3-methylheptane	0.003146
	n-octane	0.000726

Hydrocarbon Dew Point Curves

The results recorded in Table 7.16 are used to substitute the normalised alkane from C_6 to C_8 in Table 7.2. The new detailed gas composition, Table 7.17, was entered into the GasVLE equation of state software to determine the hydrocarbon dew point curves for the Peng Robinson and Redlich Kwong Soave equations of state. These curves are displayed in Figure 7.5 and the MCMI results have been included to provide a baseline, in order to compare the theoretical determined HCDP with that actually measured. For a comparison of other equations of state for this gas composition refer to Figure C.4.

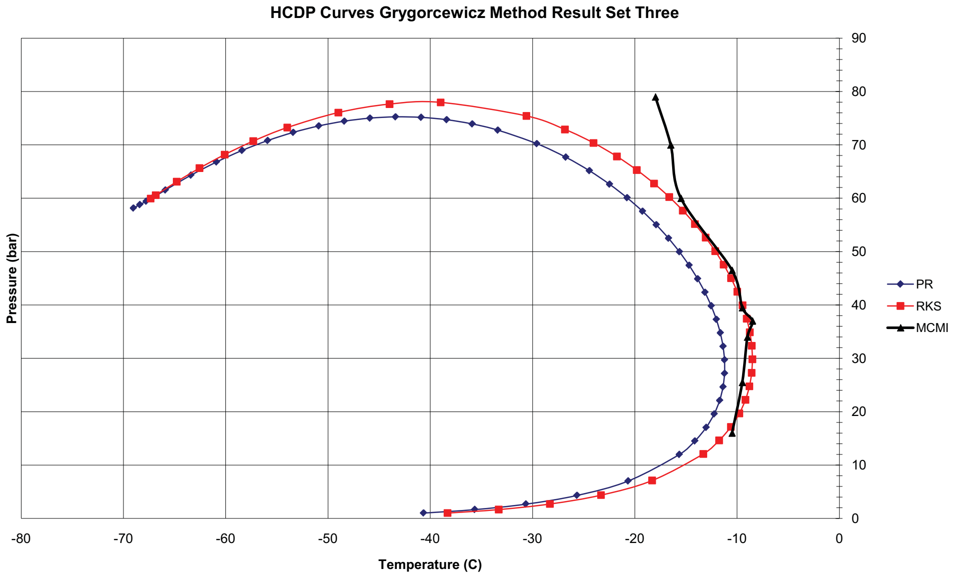

Figure 7.5: A comparison of the HCDP curves obtained by the PR and RKS EoS using the identified components from Table 7.17 and the MCMI

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Discussion of Results

Changing the concentration split of benzene and cyclohexane from 50:50 to 25:75 respectively in this detailed gas composition had no effect on the results and there was no change from the results derived in set two.

Referring to Figure 7.5. The Peng Robinson HCDP curve is on average 2.5°C lower than the Redlich Kwong Soave and the MCMI results. The Redlich Kwong Soave HCDP curve is more aligned to the MCMI than result set one. The MCMI cricondentherm is -8.5°C at 37 bar, whereas the Redlich Kwong Soave equation of state determined the cricondentherm at -8.5°C at 29.8 bar. In the 35 to 60 bar pressure range, *the retrograde dew point line*, the Redlich Kwong Soave HCDP curve is approximately 0.5°C lower than the MCMI at the same pressure. In the 14 to 35 bar pressure range, *the normal dew point line*, the Redlich Kwong Soave determines a higher HCDP temperature of 0.7°C to the MCMI at the same pressure. This is a better result when compared to result set one and the same as result set two. This composition improved the HCDP temperature by 5.1°C compared to the GC result and maintained the theoretical HCDP curve higher than the actual dew point measured in the lower pressure region.

Table 7.17: Gas analysis used with the GasVLE Equation of State software for Result Set Three

Component Name	GasVLE Component Code	Mole Percent
Nitrogen	$N2$	0.9964
Carbon Dioxide	$CO2$	1.8106
Methane	$C1$	93.6975
Ethane	$C2$	2.2300
Propane	$C3$	0.8115
i-Butane	$iC4$	0.1089
n-Butane	$nC4$	0.1756
Neopentane	$neoC5$	0.00174
i-Pentane	$iC5$	0.0445
n-Pentane	$nC5$	0.0406
2,2-dimethylbutane	$22DMB$	0.001372
2,3-dimethylbutane	$23DMB$	0.017150
3-methylpentane	$3MC5$	0.004459
n-hexane	$nC6$	0.011319
benzene	$Benz$	0.002256
cyclohexane	$Cyc6$	0.006767
3,3-dimethylpentane	$33DMC5$	0.012492
2,3-dimethylpentane	$23DMC5$	0.007634
3-ethylpentane	$3EC5$	0.002429
n-heptane	$nC7$	0.003123
methylcyclohexane	$MeCyc6$	0.007986
toluene	Tol	0.000242
3-methylheptane	$3MC7$	0.003146
n-octane	$nC8$	0.000726
n-nonane	$nC9$	0.00156

7.5.5 Hydrocarbon Component Identification Result Four

The hydrocarbon components identified in this result set are based on boiling point data and the laboratory extended analysis. The laboratory extended analysis found benzene and cyclohexane in the C_7 group, however the extended analysis chromatogram detected a peak between n-hexane and benzene. This would indicate that 2,2-dimethylpentane is being detected. For this result set 2,2-dimethylpentane is inserted as the first peak and benzene and cyclohexane are moved to the second peak in the C_7 group.

Hydrocarbon Component Identification

The calculated boiling points are referenced to the National Institute of Standards and Technology (NIST) Chemistry Webbook to identify the hydrocarbon components found on the chromatogram. The identified hydrocarbon components are recorded in Table 7.18.

The position of benzene and cyclohexane at the first peak was based on the boiling point and not the peak position on the laboratory extended analysis chromatogram in Figure 7.2. Referring to Figure 7.2, there is another peak before benzene in the C_7 group. Based on the calculated boiling point, 75.89°C, the closest C_7 isomer is 2,2-dimethylpentane with a boiling point of 79.20°C. Therefore benzene and cyclohexane are moved to the second peak in the C_7 group, replacing 3,3-dimethylpentane. As per result set three benzene and cyclohexane are split 25:75 respectively.

Hydrocarbon Component Concentration

The hydrocarbon concentration for each component in the C_6 to C_8 carbon groups were calculated by applying the results of Table 7.2 and Table 7.3 to Equation 6.4 and recorded in Table 7.19.

Table 7.18: Identification of hydrocarbon peaks in the C_6 to C_8 group – Result Four.

Carbon Group	Retention Time (sec)	Calculated Boiling Point (°C)	Referenced Boiling Point (°C)	Component
C_6	79.1	49.80	49.80	2,2-dimethylbutane
	87.2	58.35	58.10	2,3-dimethylbutane
	91.6	62.99	63.30	3-methylpentane
	97.1	68.80	68.80	n-hexane
C_7	109.8	75.89	79.20	2,2-dimethylpentane
	127.4	85.72	80.15	benzene
			80.75	cyclohexane
	133.9	89.34	89.80	2,3-dimethylpentane
	143.1	94.48	93.50	3-ethylpentane
	150.3	98.50	98.50	n-heptane
C_8	171.9	103.79	100.85	methylcyclohexane
	214.9	114.31	110.65	toluene
	234.4	119.09	118.90	3-methylheptane
	261.0	125.60	125.60	n-octane

Hydrocarbon Dew Point Curves

The results recorded in Table 7.19 are used to substitute the normalised alkane from C_6 to C_8 in Table 7.2. The new detailed gas composition, Table 7.20, was entered into the GasVLE equation of state software to determine the hydrocarbon dew point curves for the Peng Robinson and Redlich Kwong Soave equations of state. These curves are displayed in Figure 7.6 and the MCMI results have been included to provide a baseline, in order to compare the theoretical determined HCDP with that actually measured. For a comparison of other equations of state for this gas composition refer to Figure C.5.

Table 7.19: Identified hydrocarbon component concentration in the C_6 to C_8 group – Result Four.

Carbon Group	Component	Component Concentration $mole\%$
C_6	2,2-dimethylbutane	0.001372
	2,3-dimethylbutane	0.01715
	3-methylpentane	0.004459
	n-hexane	0.011319
C_7	2,2-dimethylpentane	0.009022
	benzene	0.003123
	cyclohexane	0.009369
	2,3-dimethylpentane	0.007634
	3-ethylpentane	0.002429
	n-heptane	0.003123
C_8	methylcyclohexane	0.007986
	toluene	0.000242
	3-methylheptane	0.003146
	n-octane	0.000726

Discussion of Results

Referring to Figure 7.6. The Peng Robinson HCDP curve is on average 2.5°C lower than the Redlich Kwong Soave and the MCMI results. The MCMI cricondentherm is -8.5°C at 37 bar, whereas the Redlich Kwong Soave equation of state determined the cricondentherm at -8.93°C at 27.5 bar. In the 35 to 60 bar pressure range, *the retrograde dew point line*, the Redlich Kwong Soave HCDP curve is approximately 1.0°C lower than the MCMI at the same pressure. In the 14 to 35 bar pressure range, *the normal dew point line*, the Redlich Kwong Soave determines a higher HCDP temperature of 0.3°C to the MCMI at the same pressure. This is a better result in the lower pressure range when compared to the previous results. This composition improved the HCDP temperature by -5.8°C compared to the GC result and maintained the theoretical HCDP curve higher than the actual dew point measured in the lower pressure region.

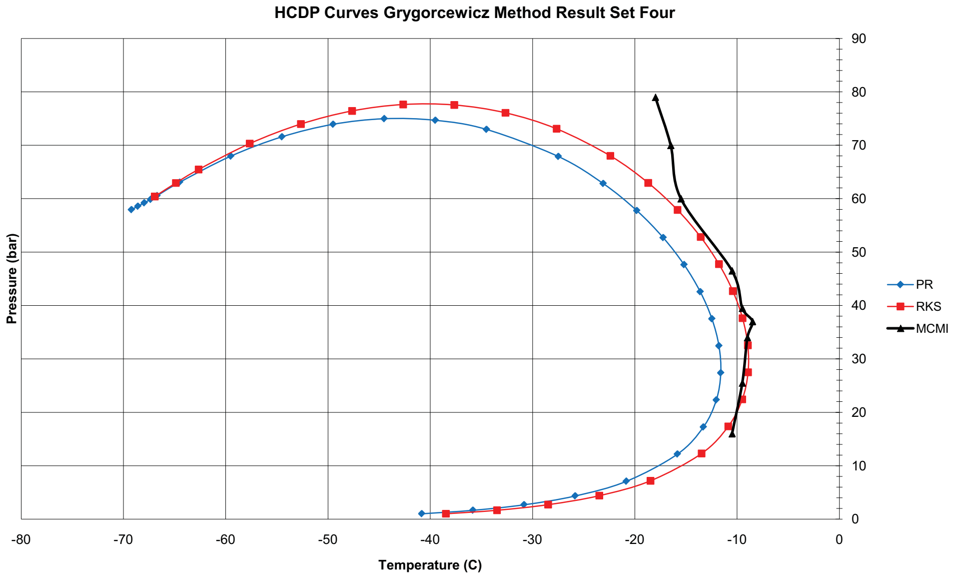

Figure 7.6: A comparison of the HCDP curves obtained by the PR and RKS EoS using the identified components from Table 7.20 and the MCMI

.

Table 7.20: Gas analysis used with the GasVLE Equation of State software for Result Set Four

Component Name	GasVLE Component Code	Mole Percent
Nitrogen	$N2$	0.9964
Carbon Dioxide	$CO2$	1.8106
Methane	$C1$	93.6975
Ethane	$C2$	2.2300
Propane	$C3$	0.8115
i-Butane	$iC4$	0.1089
n-Butane	$nC4$	0.1756
Neopentane	$neoC5$	0.00174
i-Pentane	$iC5$	0.0445
n-Pentane	$nC5$	0.0406
2,2-dimethylbutane	$22DMB$	0.001372
2,3-dimethylbutane	$23DMB$	0.017150
3-methylpentane	$3MC5$	0.004459
n-hexane	$nC6$	0.011319
2,2-dimethylpentane	$22DMC5$	0.009022
benzene	$Benz$	0.003123
cyclohexane	$Cyc6$	0.009369
2,3-dimethylpentane	$23DMC5$	0.007634
3-ethylpentane	$3EC5$	0.002429
n-heptane	$nC7$	0.003123
methylcyclohexane	$MeCyc6$	0.007986
toluene	Tol	0.000242
3-methylheptane	$3MC7$	0.003146
n-octane	$nC8$	0.000726
n-nonane	$nC9$	0.00156

7.5.6 Hydrocarbon Component Identification Result Set Five

The hydrocarbon components identified in this result set are based on boiling point data and the laboratory extended analysis. The only change in this result group is that methylcyclohexane is replaced with ethylcyclopentane in the C_8 carbon group.

Hydrocarbon Component Identification

The calculated boiling points are referenced to the National Institute of Standards and Technology (NIST) Chemistry Webbook to identify the hydrocarbon components found on the chromatogram. The identified hydrocarbon components are recorded in Table 7.21.

The calculated boiling point of the first peak in the C_8 carbon group is 103.78°C and the C_8 isomer closest to this boiling point is ethylcyclopentane. Eventhough the laboratory extended analysis found methylcyclohexane it was changed to ethylcyclopentane to determine the effect it would have on the resultant HCDP curves.

Hydrocarbon Component Concentration

The hydrocarbon concentration for each component in the C_6 to C_8 carbon groups were calculated by applying the results of Table 7.2 and Table 7.3 to Equation 6.4 and recorded in Table 7.22.

Hydrocarbon Dew Point Curves

The results recorded in Table 7.22 are used to substitute the normalised alkane from C_6 to C_8 in Table 7.2. The new detailed gas composition, Table 7.23, was entered into the GasVLE equation of state software to determine the hydrocarbon dew point curves for the Peng Robinson and Redlich Kwong Soave equations of state. These curves are displayed in Figure 7.7 and the MCMI results have been included to provide a baseline, in order to compare the theoretical determined HCDP with that actually

Table 7.21: Identification of hydrocarbon peaks in the C_6 to C_8 group – Result Set Five.

Carbon Group	Retention Time (sec)	Calculated Boiling Point (°C)	Referenced Boiling Point (°C)	Component
C_6	79.1	49.80	49.80	2,2-dimethylbutane
	87.2	58.35	58.10	2,3-dimethylbutane
	91.6	62.99	63.30	3-methylpentane
	97.1	68.80	68.80	n-hexane
C_7	109.8	75.89	79.20	2,2-dimethylpentane
	127.4	85.72	80.15	benzene
			80.75	cyclohexane
	133.9	89.34	89.80	2,3-dimethylpentane
	143.1	94.48	93.50	3-ethylpentane
	150.3	98.50	98.50	n-heptane
C_8	171.9	103.79	103.45	ethylcyclopentane
	214.9	114.31	110.65	toluene
	234.4	119.09	118.90	3-methylheptane
	261.0	125.60	125.60	n-octane

measured. For a comparison of other equations of state for this gas composition refer to Figure C.6.

Discussion of Results

Referring to Figure 7.7. The Peng Robinson HCDP curve is on average 2.5°C lower than the Redlich Kwong Soave and the MCMI results. The MCMI cricondentherm is -8.5°C at 37 bar, whereas the Redlich Kwong Soave equation of state determined the cricondentherm at -8.5°C at 29.8 bar. In the 35 to 60 bar pressure range, *teh retrograde dew point lien*, the Redlich Kwong Soave HCDP curve is approximately 0.4°C lower than the MCMI at the same pressure. In the 14 to 35 bar pressure range, *the normal dew point line*, the Redlich Kwong Soave determines a higher HCDP temperature of 0.75°C to the MCMI at the same pressure. These results are the same as result set two

Table 7.22: Identified hydrocarbon component concentration in the C_6 to C_8 group – Result Set Five.

Carbon Group	Component	Component Concentration $mole\%$
C_6	2,2-dimethylbutane	0.001372
	2,3-dimethylbutane	0.01715
	3-methylpentane	0.004459
	n-hexane	0.011319
C_7	2,2-dimethylpentane	0.009022
	benzene	0.003123
	cyclohexane	0.009369
	2,3-dimethylpentane	0.007634
	3-ethylpentane	0.002429
	n-heptane	0.003123
C_8	ethylcyclopentane	0.007986
	toluene	0.000242
	3-methylheptane	0.003146
	n-octane	0.000726

and three. This composition improved the HCDP temperature by -5.1°C compared to the GC result and maintained the theoretical HCDP curve higher than the actual dew point measured in the lower pressure region.

Therefore changing methylcyclohexane to ethylcyclopentane decreased the hydrocarbon dew point by 0.4°C, when compared to result set two adn three.

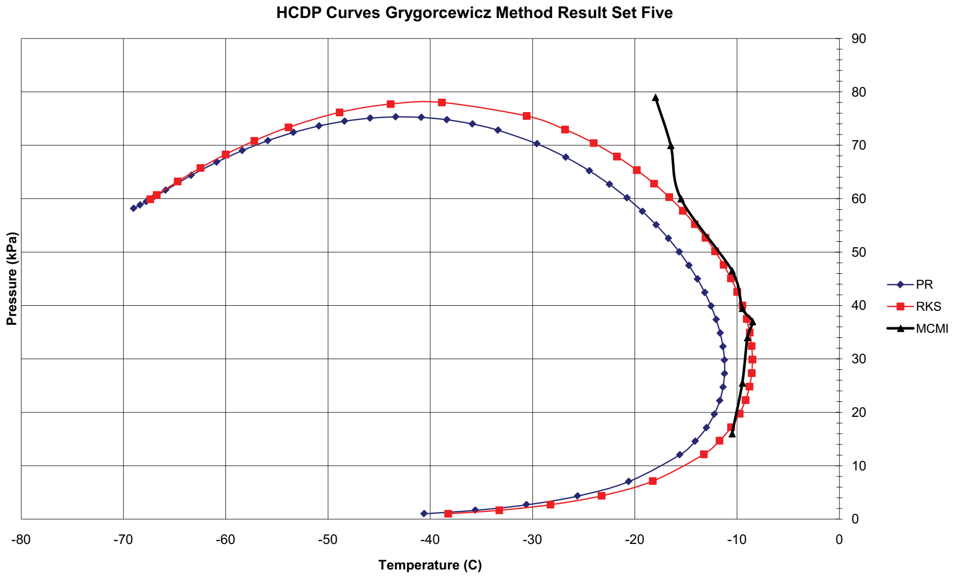

Figure 7.7: A comparison of the HCDP curves obtained by the PR and RKS EoS using the identified components from Table 7.23 and the MCMI

.

Table 7.23: Gas analysis used with the GasVLE Equation of State software for Result Set Five

Component Name	GasVLE Component Code	Mole Percent
Nitrogen	$N2$	0.9964
Carbon Dioxide	$CO2$	1.8106
Methane	$C1$	93.6975
Ethane	$C2$	2.2300
Propane	$C3$	0.8115
i-Butane	$iC4$	0.1089
n-Butane	$nC4$	0.1756
Neopentane	$neoC5$	0.00174
i-Pentane	$iC5$	0.0445
n-Pentane	$nC5$	0.0406
2,2-dimethylbutane	$22DMB$	0.001372
2,3-dimethylbutane	$23DMB$	0.017150
3-methylpentane	$3MC5$	0.004459
n-hexane	$nC6$	0.011319
2,2-dimethylpentane	$22DMC5$	0.009022
benzene	$Benz$	0.003123
cyclohexane	$Cyc6$	0.009369
2,3-dimethylpentane	$23DMC5$	0.007634
3-ethylpentane	$3EC5$	0.002429
n-heptane	$nC7$	0.003123
ethylcyclopentane	$EtCyc5$	0.007986
toluene	Tol	0.000242
3-methylheptane	$3MC7$	0.003146
n-octane	$nC8$	0.000726
n-nonane	$nC9$	0.00156

7.5.7 Hydrocarbon Component Identification Result Six

The hydrocarbon components identified in this result set are based on boiling point data and the laboratory extended analysis. The only change in this result group is that ethylcyclopentane is replaced with methylcyclohexane and toluene is replaced with 2,3,3-trimethylpentane in the C_8 carbon group.

Hydrocarbon Component Identification

The calculated boiling points are referenced to the National Institute of Standards and Technology (NIST) Chemistry Webbook to identify the hydrocarbon components found on the chromatogram. The identified hydrocarbon components are recorded in Table 7.24.

The first peak in the C_8 carbon group is changed back to methylcyclohexane, eventhough its boiling point is lower than that calculated. The calculated boiling point of the second peak is is 104.3°C and the the C_8 isomer closest to this boiling point is 2,3,3-trimethylpentane. Eventhough the laboratory extended analysis found toluene it was changed to 2,3,3-trimethylpentane to determine the effect it would have on the resultant HCDP curves.

Hydrocarbon Component Concentration

The hydrocarbon concentration for each component in the C_6 to C_8 carbon groups were calculated by applying the results of Table 7.2 and Table 7.3 to Equation 6.4 and recorded in Table 7.25.

Hydrocarbon Dew Point Curves

The results recorded in Table 7.25 are used to substitute the normalised alkane from C_6 to C_8 in Table 7.2. The new detailed gas composition, Table 7.26, was entered into the GasVLE equation of state software to determine the hydrocarbon dew point

Table 7.24: Identification of hydrocarbon peaks in the C_6 to C_8 group – Result Six.

Carbon Group	Retention Time (sec)	Calculated Boiling Point (°C)	Referenced Boiling Point (°C)	Component
C_6	79.1	49.80	49.80	2,2-dimethylbutane
	87.2	58.35	58.10	2,3-dimethylbutane
	91.6	62.99	63.30	3-methylpentane
	97.1	68.80	68.80	n-hexane
C_7	109.8	75.89	79.20	2,2-dimethylpentane
	127.4	85.72	80.15	benzene
			80.75	cyclohexane
	133.9	89.34	89.80	2,3-dimethylpentane
	143.1	94.48	93.50	3-ethylpentane
	150.3	98.50	98.50	n-heptane
C_8	171.9	103.79	100.85	methylcyclohexane
	214.9	114.31	114.70	2,3,3-trimethylpentane
	234.4	119.09	118.90	3-methylheptane
	261.0	125.60	125.60	n-octane

curves for the Peng Robinson and Redlich Kwong Soave equations of state. These curves are displayed in Figure 7.8 and the MCMI results have been included to provide a baseline, in order to compare the theoretical determined HCDP with that actually measured. For a comparison of other equations of state for this gas composition refer to Figure C.7.

Discussion of Results

Referring to Figure 7.8. The Peng Robinson HCDP curve is on average 2.5°C lower than the Redlich Kwong Soave and the MCMI results. The MCMI cricondentherm is -8.5°C at 37 bar, whereas the Redlich Kwong Soave equation of state determined the cricondentherm at -8.91°C at 27.5 bar. In the 35 to 60 bar pressure range, *the retrograde dew point line*, the Redlich Kwong Soave HCDP curve is approximately 1.0°C lower

Table 7.25: Identified hydrocarbon component concentration in the C_6 to C_8 group – Result Six.

Carbon Group	Component	Component Concentration *mole%*
C_6	2,2-dimethylbutane	0.001372
	2,3-dimethylbutane	0.01715
	3-methylpentane	0.004459
	n-hexane	0.011319
C_7	2,2-dimethylpentane	0.009022
	benzene	0.003123
	cyclohexane	0.009369
	2,3-dimethylpentane	0.007634
	3-ethylpentane	0.002429
	n-heptane	0.003123
C_8	methylcyclohexane	0.007986
	2,3,3-trimethylpentane	0.000242
	3-methylheptane	0.003146
	n-octane	0.000726

than the MCMI at the same pressure. In the 14 to 35 bar pressure range, *the normal dew point line*, the Redlich Kwong Soave determines a higher HCDP temperature of 0.3°C to the MCMI at the same pressure. This is the same result as result set four. This composition improved the HCDP temperature by -5.8°C compared to the GC result and maintained the theoretical HCDP curve higher than the actual dew point measured in the lower pressure region.

Therefore by replacing toluene with 2,3,3-trimethylpentane, the hydrocarbon dew point made no change to the determination. Either 2,3,3-trimethylpentane has the same affect as toluene or the quantity is not enough to influence the determination.

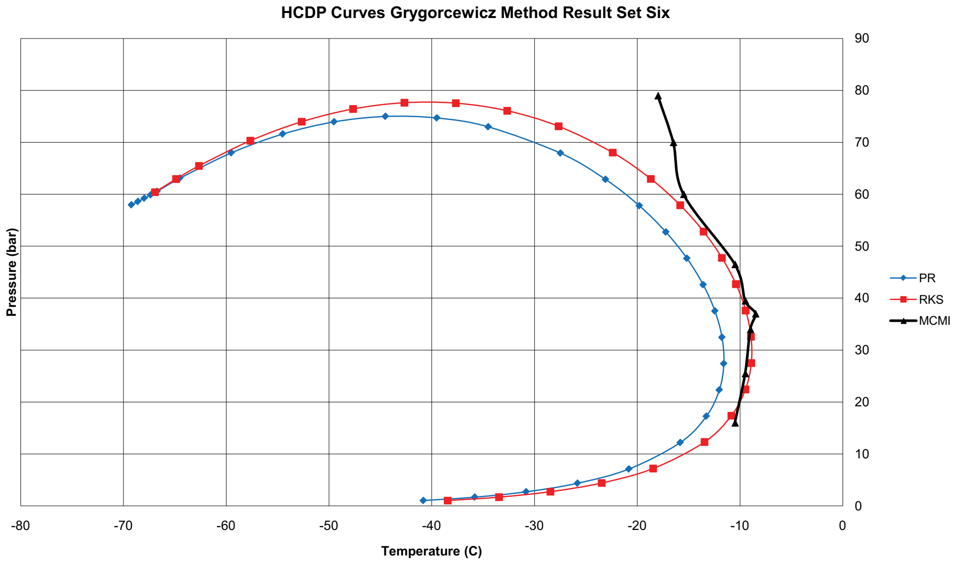

Figure 7.8: A comparison of the HCDP curves obtained by the PR and RKS EoS using the identified components from Table 7.26 and the MCMI

.

Table 7.26: Gas analysis used with the GasVLE Equation of State software for Result Set Six

Component Name	GasVLE Component Code	Mole Percent
Nitrogen	$N2$	0.9964
Carbon Dioxide	$CO2$	1.8106
Methane	$C1$	93.6975
Ethane	$C2$	2.2300
Propane	$C3$	0.8115
i-Butane	$iC4$	0.1089
n-Butane	$nC4$	0.1756
Neopentane	$neoC5$	0.00174
i-Pentane	$iC5$	0.0445
n-Pentane	$nC5$	0.0406
2,2-dimethylbutane	$22DMB$	0.001372
2,3-dimethylbutane	$23DMB$	0.017150
3-methylpentane	$3MC5$	0.004459
n-hexane	$nC6$	0.011319
2,2-dimethylpentane	$22DMC5$	0.009022
benzene	$Benz$	0.003123
cyclohexane	$Cyc6$	0.009369
2,3-dimethylpentane	$23DMC5$	0.007634
3-ethylpentane	$3EC5$	0.002429
n-heptane	$nC7$	0.003123
methylcyclohexane	$MeCyc5$	0.007986
2,3,3-trimethylpentane	$233TMC5$	0.000242
3-methylheptane	$3MC7$	0.003146
n-octane	$nC8$	0.000726
n-nonane	$nC9$	0.00156

7.6 Adapted ISO 23874 Method Results

This section details the data and results of the authors adapted ISO 23874 method, that was developed in Section 6.4.

Only one set of results were obtained for this method. Table 7.27 was produced to determine the average boiling point of the carbon group fractions for C_7 and C_8. The mole % concentration is then calculated and the data applied to the GasVLE equation of state software. The resultant hydrocarbon dew point curves for the Peng Robinson and Redlich Kwong Soave equations of state are compared to the manual chilled mirror instrument to assess the validity of the authors adapted ISO 23874 method.

Hydrocarbon Component Identification and Concentration

The calculated boiling points and the average boiling point of the carbon group fractions are referenced to the National Institute of Standards and Technology (NIST) Chemistry Webbook to identify the hydrocarbon components to be used in the adapted ISO 23874 method detailed gas analysis. The results are recorded in Table 7.27.

Hydrocarbon Dew Point Curves

The results recorded in Table 7.27 are used to substitute the normalised alkane from C_6 to C_8 in Table 7.2. The new detailed gas composition, Table 7.28, was entered into the GasVLE equation of state software to determine the hydrocarbon dew point curves for the Peng Robinson and Redlich Kwong Soave equations of state. These curves are displayed in Figure 7.9 and the MCMI results have been included to provide a baseline, in order to compare the theoretical determined HCDP with that actually measured. For a comparison of other equations of state for this gas composition refer to Figure C.8.

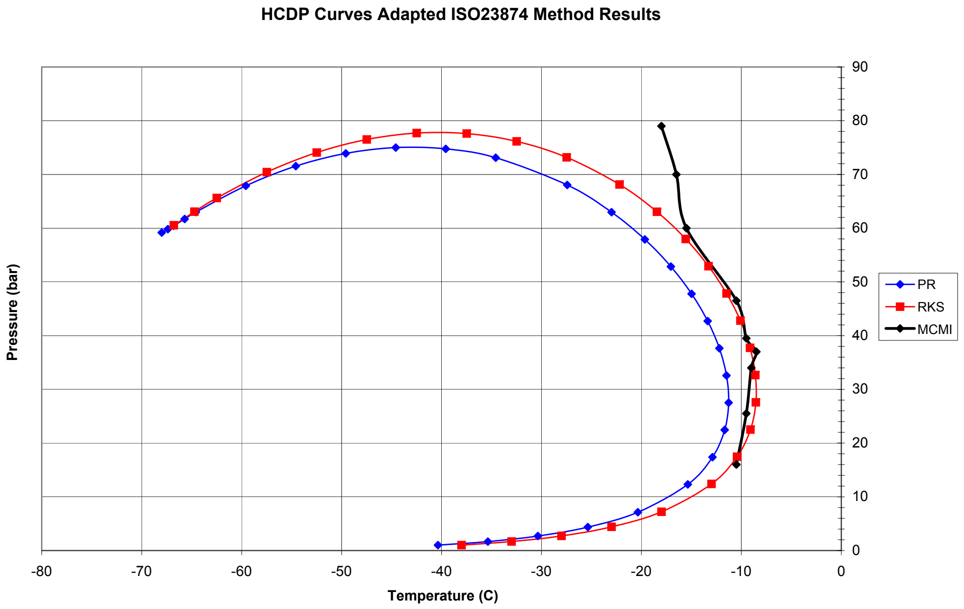

Figure 7.9: A comparison of the HCDP curves obtained by the PR and RKS EoS using the the adapted ISO 23874 method identified components from Table 7.28 and the MCMI

.

Discussion of Results

There is no change to the hydrocarbon components identified for the C_6 group. Using the adapted ISO 23874 method the new boiling point fraction for C_7 is 3,3-dimethylpentane and for C_8 is n-octane.

Referring to Figure 7.9. The Peng Robinson HCDP curve is on average 2.5°C lower than the Redlich Kwong Soave and the MCMI results. The MCMI cricondentherm is -8.5°C at 37 bar, whereas the Redlich Kwong Soave equation of state determined the cricondentherm at -8.54°C at 27.6 bar. In the 35 to 60 bar pressure range the Redlich Kwong Soave HCDP curve is approximately 1.0°C lower than the MCMI at the same pressure. In the 14 to 35 bar pressure range the Redlich Kwong Soave determines a higher HCDP temperature of 0.6°C to the MCMI at the same pressure. The results produced are very similar to result set three using the Grygorcewicz method. This composition improved the HCDP temperature by -5.1°C compared to the GC result and maintained the theoretical HCDP curve higher than the actual dew point measured in the lower pressure region.

Table 7.27: Identification of hydrocarbon peaks and carbon group fractions using the adapted ISO 23874 method in the C_6 to C_8 group.

Carbon Group	Retention Time (sec)	Calculated Boiling Point (°C)	Referenced Boiling Point (°C)	Peak Area	Area x BP	Component
C_6	79.1	49.80	49.80	92296	4795541	2,2-dimethylbutane
	87.2	58.35	58.10	1485360	86670756	2,3-dimethylbutane
	91.6	62.99	63.30	974508	61388547	3-methylpentane
	97.1	68.80	68.80	974508	67046150	n-hexane
C_7						
C7(a)	109.8	75.89	–	957912	72695942	–
	127.4	85.72	86.10	1315440	–	benzene
					–	cyclohexane
C7(b)	133.9	89.34	–	801676	71624941	–
C7(c)	143.1	94.48	–	255400	24130320	–
n-C7	150.3	98.50	98.50	340968	33585348	n-heptane
totals for C7				2355956	202036550	
BP FR7		85.76				3,3-dimethylpentane
C_8						
C8(a)	171.9	103.79	–	882072	–	methylcyclohexane
	214.9	114.31	110.65	31280	–	toluene
C8(b)	234.4	119.09	–	339456	40425204	–
	261.0	125.60	125.60	77864	9779718	n-octane
totals for C8				417320	50204922	
BP FR8		120.30				n-octane

Table 7.28: Gas analysis used with the GasVLE Equation of State software for adapted ISO 23874

Component Name	GasVLE Component Code	Mole Percent
Nitrogen	$N2$	0.9964
Carbon Dioxide	$CO2$	1.8106
Methane	$C1$	93.6975
Ethane	$C2$	2.2300
Propane	$C3$	0.8115
i-Butane	$iC4$	0.1089
n-Butane	$nC4$	0.1756
Neopentane	$neoC5$	0.00174
i-Pentane	$iC5$	0.0445
n-Pentane	$nC5$	0.0406
2,2-dimethylbutane	$22DMB$	0.001372
2,3-dimethylbutane	$23DMB$	0.017150
3-methylpentane	$3MC5$	0.004459
n-hexane	$nC6$	0.011319
benzene	$Benz$	0.003123
cyclohexane	$Cyc6$	0.009369
3,3-dimethylpentane	$33DMC5$	0.022208
methylcyclohexane	$MeCyc6$	0.007986
toluene	Tol	0.000242
n-octane	$nC8$	0.003872
n-nonane	$nC9$	0.00156

7.7 Reference Gas Specification Results

ASTM D1945-96 recommends that the concentration of a component in the reference standard gas should not be less than one half nor more than twice the concentration of the corresponding component in the sample gas. It is assummed that this recommendation is to improve or ensure the measurement accuracy of the gas chromatograph. To test the ASTM D1945-96 recommendation, a reference gas specific to the composition of the export gas used in this research was produced and tabulated in Table 7.29. For comparison the standard reference calibration gas composition is included.

The results of the gas chromatograph analysis before and after calibration using the specific reference gas is recorded in Table 7.30. The results show only an improvement of 2 ppm for C_9 and this resulted in a change of -0.5 °C for the hydrocarbon dew point temperature.

Table 7.29: GC reference gas composition

Component Name	Specific Concentration Mole %	Standard Concentration Mole %
Nitrogen	0.9901	2.507
Carbon Dioxide	1.7370	0.9998
Methane	93.8224	89.5031
Ethane	2.2120	4.970
Propane	0.7984	1.004
i-Butane	0.1000	0.3123
n-Butane	0.1739	0.3020
Neopentane	0.0022	0.1012
i-Pentane	0.0440	0.1000
n-Pentane	0.0401	0.1003
C6 Group	0.0330	0.0500
C7 Group	0.0337	0.0251
C8 Group	0.0119	0.0151
C9+ Group	0.0013	0.0101

Table 7.30: GC analysis report

Component Name	Before Calibration Mole %	After Calibration Mole %
Nitrogen	1.0026	0.9291
Carbon Dioxide	1.7350	1.7352
Methane	93.7816	93.8777
Ethane	2.2179	2.2021
Propane	0.8060	0.8000
i-Butane	0.1101	0.1096
n-Butane	0.1744	0.1741
Neopentane	0.00195	0.00174
i-Pentane	0.0450	0.0447
n-Pentane	0.0404	0.0406
C6 Group	0.0340	0.0346
C7 Group	0.0366	0.0366
C8 Group	0.0127	0.0126
C9+ Group	0.00177	0.00155
HCDP °C at 3500 kPa PR EoS	-2.5	-2.9

7.8 Daniel GC Dew Point Determination Trial Results

A second gas chromatograph, Daniel GC500 with 2350 controller, on the same export custody transfer station was used for this trial.

The export gas analysis chromatogram was captured for the application of the Grygorcewicz method and the authors adapted ISO 23874 method to identify the unknown hydrocarbon components and calculate the concentration. The chromatograms can be referenced in Appendix B, Figure B.5 to Figure B.7. The gas chromatograph analysis and raw data reports were obtained to calculate the component concentration. Refer to Table 7.30, after calibration column, for the concentration in mole percentage results and Table 7.31 for the raw data result.

To verify the Daniel DewCalc results using the Grygorcewicz method and adapted ISO 23874 method, a new set of hydrocarbon dew point testing was conducted using the Chandler DewScope MCMI. The results of the MCMI are recorded in Table 7.32.

Table 7.31: GC raw data report highlighting retention times and peak areas for C_6 to C_8

Carbon Group	Retention Time (sec)	Peak Area
C_6	79.1	94712
	87.2	1483636
	91.6	395892
	97.1	972932
C_7	109.8	957912
	127.4	1315440
	133.9	801676
	143.1	255400
	150.3	340968
C_8	171.9	882072
	214.9	31280
	234.4	339456
	261.0	77864

Table 7.32: MCMI HCDP results for the export natural gas conducted during the Daniel GC DewCalc trial

Pressure (bar)	HCDP Temperature (°C)
25.0	-9.5
30.0	-8.5
35.0	-9.0
40.0	-10.0
50.0	-11.5

7.8.1 Application of the Grygorcewicz Method

The Grygorcewicz method, as outlined in Section 6.3, was applied to Table 7.30 and Table 7.31 to produce Table 7.33 and Table 7.34 to identifiy the unknown hydrocarbon species and concentration.

The data from Table 7.36 was then entered into the Daniel 2350 controller Dew2 software user defined numeric parameter table. Gas samples were analysed and the hydrocarbon dew point calculations completed for both the Peng Robinson and Redlich Kwong Soave equation of state. The GC HCDP results are obtained from the Daniel 2350 controller Dewcalc Data Report.

Hydrocarbon Component Identification

The calculated boiling points are referenced to the National Institute of Standards and Technology (NIST) Chemistry Webbook to identify the hydrocarbon components found on the chromatogram. The identified hydrocarbon components are recorded in Table 7.33.

The hydrocarbon components identified in this result set are based on boiling point data and the laboratory extended analysis.

Hydrocarbon Component Concentration

The hydrocarbon concentration for each component in the C_6 to C_8 carbon groups were calculated by applying the results of Table 7.30 and Table 7.31 to Equation 6.4 and recorded in Table 7.34.

Daniel DewCalc Results

The data from Table 7.36 was entered into the Daniel Dew2 software and the results of the Daniel GC DewCalc report using the Grygorcewicz method are recorded in

Table 7.33: Identification of hydrocarbon peaks in the C_6 to C_8 group – GC DewCalc Trial.

Carbon Group	Retention Time (sec)	Calculated Boiling Point (°C)	Referenced Boiling Point (°C)	Component
C_6	78.2	49.80	49.80	2,2-dimethylbutane
	85.3	58.03	58.10	2,3-dimethylbutane
	89.7	63.12	63.30	3-methylpentane
	94.6	68.80	68.80	n-hexane
C_7	106.4	75.10	79.20	2,2-dimethylpentane
	122.8	83.84	80.15	benzene
			80.75	cyclohexane
	–	–	–	–
	137.6	91.73	91.8	3-methylhexane
	150.3	98.50	98.50	n-heptane
C_8	164.4	102.48	100.85	methylcyclohexane
	204.6	113.81	110.65	toluene
	212.3	115.98	117.60	2-methylheptane
	246.4	125.60	125.60	n-octane

Table 7.35.

Hydrocarbon Dew Point Curves

The results recorded in Table 7.34 are used to substitute the normalised alkane from C_6 to C_8 in Table 7.30. The new detailed gas composition, Table 7.36, was entered into the GasVLE equation of state software to determine the hydrocarbon dew point curves for the Peng Robinson and Redlich Kwong Soave equations of state. These curves are displayed in Figure 7.10 and the MCMI results have been included to provide a baseline, in order to compare the theoretical determined HCDP with that actually measured. The Daniel GC dew point calculation results, DewCalc, from Table 7.35 have also been included to determine if the Grygorcewicz method can be applied to the Daniel Dew2 software application to determine the HCDP.

Table 7.34: Identified hydrocarbon component concentration in the C_6 to C_8 group – GC DewCalc Trial.

Carbon Group	Component	Component Concentration *mole%*
C_6	2,2-dimethylbutane	0.00108
	2,3-dimethylbutane	0.01713
	3-methylpentane	0.00497
	n-hexane	0.01142
C_7	2,2-dimethylpentane	0.00967
	benzene	0.005079
	cyclohexane	0.015236
	–	–
	3-methylhexane	0.00302
	n-heptane	0.0036
C_8	methylcyclohexane	0.00847
	toluene	0.00041
	2-methylheptane	0.00294
	n-octane	0.000777

Discussion of Results

The results showed that the Grygorcewicz method can produce valid HCDP determination results when applied to the Daniel GC 2350 controller Dew2 software user defined numeric parameter table.

Figure 7.10 shows that:

- The GC DewCalc report and GasVLE HCDP determation results are aligned for both the Peng Robinson and Redlich Kwong Soave equations of state.
- The MCMI and Redlich Kwong Soave equation of state are aligned for the pressure range measured in the trial. This included teh retrograde dew point line and the normal dew point line.

Table 7.35: Daniel GC DewCalc results using the Grygorcewicz method and applied equations of state for the export natural gas used in this research

Pressure (bar)	PR EoS HCDP Temperature (°C)	RKS Eos HCDP Temperature (°C)
14.0	-14.3	-12.1
24.0	-11.8	-9.3
27.0	-11.6	
29.0		-9.0
35.0	-12.2	-9.3
44.0	-14.2	-11

- The MCMI measured cricondentherm was -8.5°C at 30 bar. The Redlich Kwong Soave GasVLE determined cricondentherm was -9.14°C at 27.6 bar. The Redlich Kwong Soave DewCalc report determined cricondentherm was -9.0°C at 29 bar.
- The only difference occurs at 30 bar where the Redlich Kwong Soave result is 0.5°C lower than the MCMI.

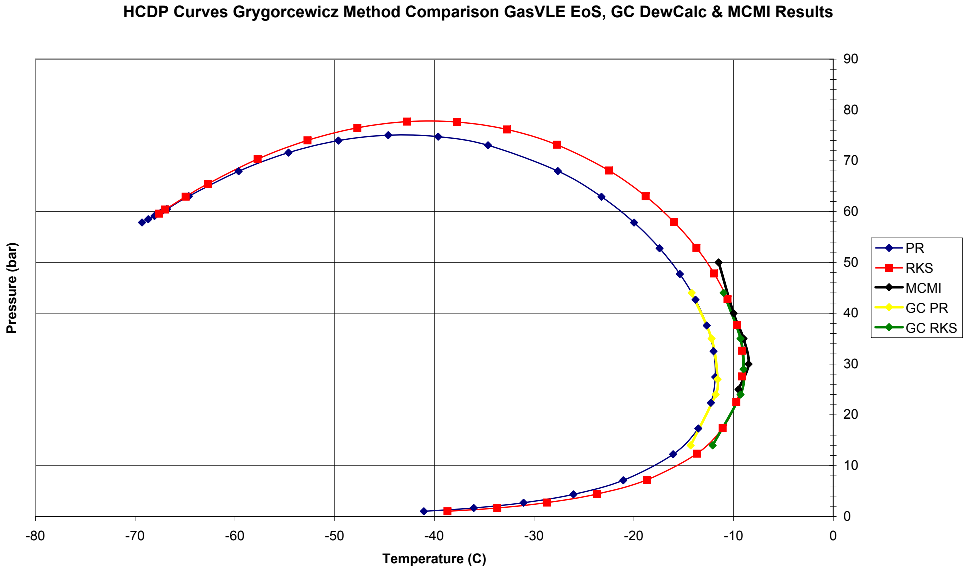

Figure 7.10: A comparison of the HCDP curves obtained by the GasVLE, GC DewCalc and MCMI results

.

Table 7.36: Gas analysis used with the GasVLE Equation of State software for GC DewCalc Trial

Component Name	GasVLE Component Code	Mole Percent
Nitrogen	$N2$	0.9291
Carbon Dioxide	$CO2$	1.7352
Methane	$C1$	93.8777
Ethane	$C2$	2.2021
Propane	$C3$	0.8000
i-Butane	$iC4$	0.1096
n-Butane	$nC4$	0.1741
Neopentane	$neoC5$	0.00171
i-Pentane	$iC5$	0.0447
n-Pentane	$nC5$	0.0406
2,2-dimethylbutane	$22DMB$	0.00108
2,3-dimethylbutane	$23DMB$	0.01713
3-methylpentane	$3MC5$	0.00497
n-hexane	$nC6$	0.01142
2,2-dimethylpentane	$22DMC5$	0.00967
benzene	$Benz$	0.005079
cyclohexane	$Cyc6$	0.015236
–	–	–
3-methylhexane	$3MC6$	0.00302
n-heptane	$nC7$	0.0036
methylcyclohexane	$MeCyc6$	0.00847
toluene	Tol	0.00041
2-methylheptane	$2MC7$	0.00294
n-octane	$nC8$	0.000777
n-nonane	$nC9$	0.00155

7.8.2 Application of the Adapted ISO 23874 Method

The authors adapted ISO 23874 method, as outlined in Section 6.4, was applied to Table 7.30 and Table 7.31 to produce Table 7.37 to identifiy the unknown hydrocarbon species, average boiling point fractions and concentration.

The data from Table 7.39 was then entered into the Daniel 2350 controller Dew2 software user defined numeric parameter table. Gas samples were analysed and the hydrocarbon dew point calculations completed for both the Peng Robinson and Redlich Kwong Soave equation of state. The GC HCDP results are obtained from the Daniel 2350 controller Dewcalc Data Report.

Hydrocarbon Component Identification and Concentration

The calculated boiling points and the average boiling point of the carbon group fractions are referenced to the National Institute of Standards and Technology (NIST) Chemistry Webbook to identify the hydrocarbon components to be used in the adapted ISO 23874 method detailed gas analysis. The results are recorded in Table 7.37.

Daniel DewCalc Results

The data from Table 7.39 was entered into the Daniel Dew2 software and the results of the authors adapted ISO 23874 method are recorded in Table 7.38.

Hydrocarbon Dew Point Curves

The results recorded in Table 7.37 are used to substitute the normalised alkane from C_6 to C_8 in Table 7.30. The new detailed gas composition, Table 7.39, was entered into the GasVLE equation of state software to determine the hydrocarbon dew point curves for the Peng Robinson and Redlich Kwong Soave equations of state. These curves are displayed in Figure 7.11 and the MCMI results have been included to provide a baseline, in order to compare the theoretical determined HCDP with that actually measured.

The Daniel GC dew point calculation results, DewCalc, from Table 7.38 have also been included to determine if the authors adapted ISO 23874 method can be applied to the Daniel Dew2 software application to determine the HCDP.

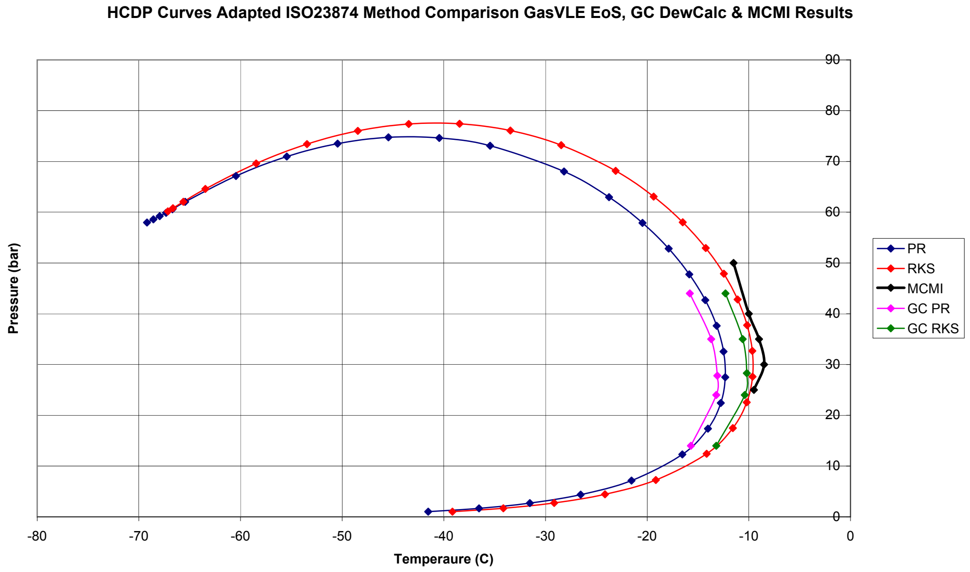

Figure 7.11: A comparison of the HCDP curves obtained by the GasVLE, GC DewCalc and MCMI results

.

Discussion of Results

The results showed that the adapted ISO 23874 method did not produce valid HCDP determination results when applied to the Daniel GC 2350 controller Dew2 software user defined numeric parameter table. It should be noted that instead of 3-ethylhexane, 3-methylheptane was used as the boiling point fraction for C_8 as this component was available in the Daniel Dew Point calculation user defined table for C_7 isomers.

Table 7.37: Identification of hydrocarbon peaks and carbon group fractions using the adapted ISO 23874 method in the C_6 to C_8 group – DewCalc Trial.

Carbon Group	Retention Time (sec)	Calculated Boiling Point (°C)	Referenced Boiling Point (°C)	Peak Area	Area x BP	Component
C_6	78.2	49.80	49.80	70152	3493570	2,2-dimethylbutane
	85.3	58.03	58.10	1113048	64590175	2,3-dimethylbutane
	91.6	63.12	63.30	322920	20382710	3-methylpentane
	94.6	68.80	68.80	742176	51061709	n-hexane
C_7						
C7(a)	106.4	75.10	–	751748	56465275	–
	122.8	83.84	86.10	–	–	benzene
					–	cyclohexane
	–	–	–	–	–	–
C7(b)	137.6	91.73	–	234548	21515088	–
n-C7	150.3	98.50	98.50	280064	27515088	n-heptane
totals for C7				1266360	105557667	
BP FR7		83.36				3,3-dimethylpentane
C_8						
C8(a)	164.4	102.48	110.85	–	–	methylcyclohexane
	204.6	113.81	110.65	–	–	toluene
C8(b)	212.3	115.98	–	242648	28142315	–
	246.4	125.60	125.60	64072	8047443	n-octane
totals for C8				306720	36189758	
BP FR8		118.0				3-methylheptane

Table 7.38: Daniel GC DewCalc results using the adapted ISO 23874 method and applied equations of state for the export natural gas used in this research

Pressure (bar)	PR EoS HCDP Temperature (°C)	RKS Eos HCDP Temperature (°C)
14.0	-15.7	-13.2
24.0	-13.2	-10.4
27.8	-13.1	
28.3		-10.2
35.0	-13.7	-10.6
44.0	-15.8	-12.3

Table 7.39: Gas analysis used with the GasVLE Equation of State software for adapted ISO 23874 in DewCalc Trial

Component Name	GasVLE Component Code	Mole Percent
Nitrogen	$N2$	0.9291
Carbon Dioxide	$CO2$	1.7352
Methane	$C1$	93.8777
Ethane	$C2$	2.2021
Propane	$C3$	0.8000
i-Butane	$iC4$	0.1096
n-Butane	$nC4$	0.1741
Neopentane	$neoC5$	0.00174
i-Pentane	$iC5$	0.0447
n-Pentane	$nC5$	0.0406
2,2-dimethylbutane	$22DMB$	0.00108
2,3-dimethylbutane	$23DMB$	0.01713
3-methylpentane	$3MC5$	0.00497
n-hexane	$nC6$	0.01142
benzene	$Benz$	0.005079
cyclohexane	$Cyc6$	0.015236
3,3-dimethylpentane	$33DMC5$	0.016285
methylcyclohexane	$MeCyc6$	0.00847
toluene	Tol	0.00041
3-dimethylheptane	$3MC7$	0.00372
n-nonane	$nC9$	0.00155

Figure 7.11 shows that:

- The MCMI measured cricondentherm was -8.5°C at 30 bar. The Redlich Kwong Soave GasVLE determined cricondentherm was -9.63°C at 27.6 bar. The Redlich Kwong Soave DewCalc report determined cricondentherm was -10.3°C at 28.3 bar.
- The Peng Robinson and the Redlich Kwong Soave equation of state HCDP curves for both the GasVLE and DewCalc determined the HCDP temperatures lower than the MCMI.
- The Daniel DewCalc Peng Robinson and Redlich Kwong Soave determined HCDP temperatures did not align with the GasVLE determined HCDP curves and for both equations of state the DewCalc results determined lower HCDP temperatures.

7.9 Chapter Summary

This chapter documented the results of the authors characterisation method and authors adapted ISO 23874 method. Discussion of the results is covered in the next chapter. However in brief, the results showed that the authors method is consistent and a valid method that can be used for application in a process type gas chromatograph. The results of the authors adapted ISO 23874 method were not consistent over the two separate trials, as the calculation of the average boiling point fraction is affected more by concentration changes.

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Chapter 8

Discussion of results

8.1 Chapter Overview

This chapter discusses the results of the authors characterisation method and the authors adapted ISO 23874 method and their validity as a characterisation method for improving the hydrocarbon determination of process gas chromatographs used on custody transfer stations.

8.2 Discussion of Results

Much research has been conducted into the factors that influence the determining of hydrocarbon dew point from indirect methods (Bolland et al 2004; Brown et al., 2007; Brown et al., 2008; Ernst et al., 2005; George at al., 2005; George et al., 2006;George, 2007). These factors primarily relate to the composition of the gas and the validity of the equation of state used and this formed the foundation of this project.

George et al. (2005), found that hydrocarbon dew point predictions depended on obtaining and using accurate gas composition data especially up to nonane. Brown et al., (2008), agreed with George et al., (2005), as he found that the hydrocarbon dew point of natural gas is highly sensitive to the composition of the gas, particularly the amount of fraction components with six or more carbon atoms. Another large impact on accuracy is the method used to characterise the distribution of heavy hydrocarbons in the gas stream when the exact composition beyond hexane, C_6, cannot be resolved by field gas chromatography (George et al 2005).

It should be noted, as mentioned in Chapter 6, that it is not the intention of the authors methods to produce the most accurate hydrocarbon dew point characterisation curve. The aim of the characterisation methods presented is to established an improved hydrocarbon dew point determination that can be produced from data obtained from the process gas chromatograph and consequently result in an improved hydrocarbon dew point determination that provides benefits in lowering hydrocarbon dew point temperature for gas producers, while maintaining a safety margin for pipeline operators and end users.

8.2.1 Grygorcewicz Method

To test the influence of the gas composition and the validity of the equation of state, six experiments were conducted using the Grygorcewicz method. In these experiments the composition was varied to document its influence on the hydrocarbon dew point curve when using the Peng Robinson and the Redlich Kwong Soave equation of state. This was compared to the direct method MCMI, which was considered the baseline, as it measured the actual temperature that condensation was first sighted.

In review of the Peng Robinson and Redlich Kwong Soave equations of state results obtained from the six tests, varying the composition with valid changes based on component boiling point and position on the chromatogram had a less than 1°C difference for both equations of state. Figure 8.1 highlights that for each test method using the Peng Robinson equation of state the difference at 35 bar was 0.85°C and for the Redlich Kwong Soave equation of state the difference at 35 bar was 0.80°C. For both equations of state the difference in results occurred between 15 and 40 bar, which is the normal dew point line.

The results also highlight that if the boiling points are used to identify the unknown hydrocarbon species without referring to an extended analysis, that a detailed gas composition can be still be produced that will provide a verifiable HCDP curve using the Redlich Kwong Soave equation of state. This indicates that emphasis should not be placed solely on getting the components identified correctly, but should be placed on the distribution of components over the hydrocarbon group, instead of summing all into the normalised alkane.

Therefore by applying the authors method, a laboratory extended gas analysis is not required to produce an improved hydrocarbon dew point determination. The authors method provides an adequate detailed like analysis that can be confidently used.

For all the result sets, using the Grygorcewicz characterisation method, the Redlich Kwong Soave equation of state produced the best hydrocarbon dew point curves when compared to the MCMI. Figure 8.2 shows that in the lower pressure region, *the normal dew point line*, between 14 and 35 bar, the Redlich Kwong Soave hydrocarbon dew point curves was higher in temperature than the MCMI, but within an acceptable range. This point will increase the acceptance of the characterisation by regulators as it still provides a safety margin for pipeline transmission companies, while still providing a gain in hydrocarbon dew point temperature for the gas producer.

The authors characterisation method was applied to a Daniel 500 C_{9+} gas chromatograph. This was a different chromatograph, but on the same export line. The experiment was conducted three months after the initial gas sample data capture. It was noted on this chromatogram that a peak in the C_7 groups was not detected when compared with the initial trial. The result showed that the authors method was not affected by these variances, as it identified the peaks that are detected by the gas chromatograph. The resultant hydrocarbon dew point curves using the Redlich Kwong Soave equation of state were in accordance with the GasVLE equation of state software and the MCMI results.

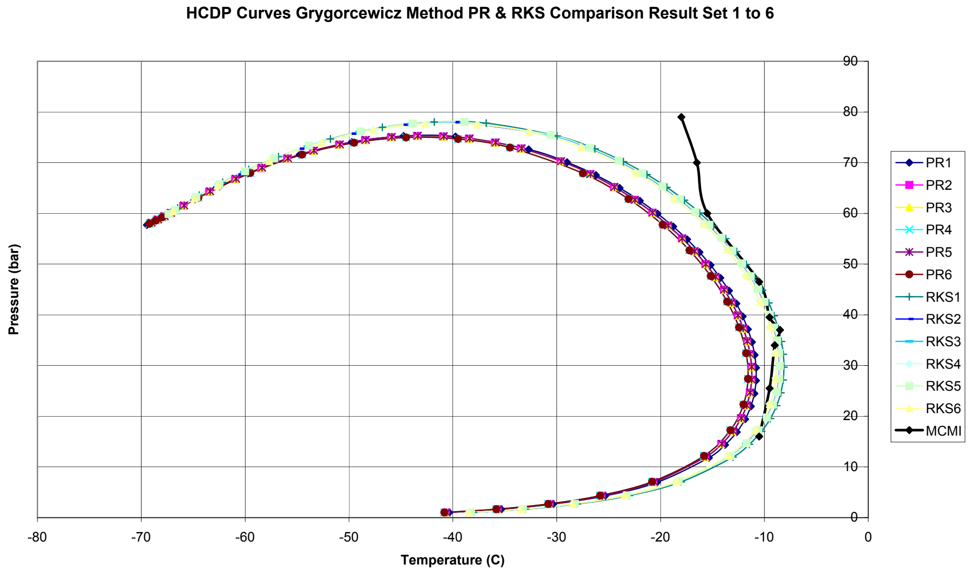

Figure 8.1: A comparison of the HCDP curves obtained by the PR and RKS EoS for test results 1 to 6 using the Grygorcewicz method, included is the MCMI

.

8.2.2 Adapted ISO 23874 Method

The ISO 23874 method concentrates on the average boiling point fraction and hence it is not critical to identify each isomer in the relevant group. However, it is important to identify the aromatics and cycloalkanes as they are not used in the calculation. This is an important point that will affect the HCDP determination.

For the natural gas used in this research the adapted ISO 23874 method produced acceptable results for the initial GC sample analysis results. However in the second trial the method produced unacceptable results as the HCDP temperatures determined were -1.1°C lower than the MCMI, using the Redlich Kwong Soave equation of state. The only notable difference between the two GC samples was the removal of a peak on the chromatogram in the C_7 group. However this did not affect the determination of the average boiling fraction in that group as it remained unchanged as 3,3-dimethylpentane.

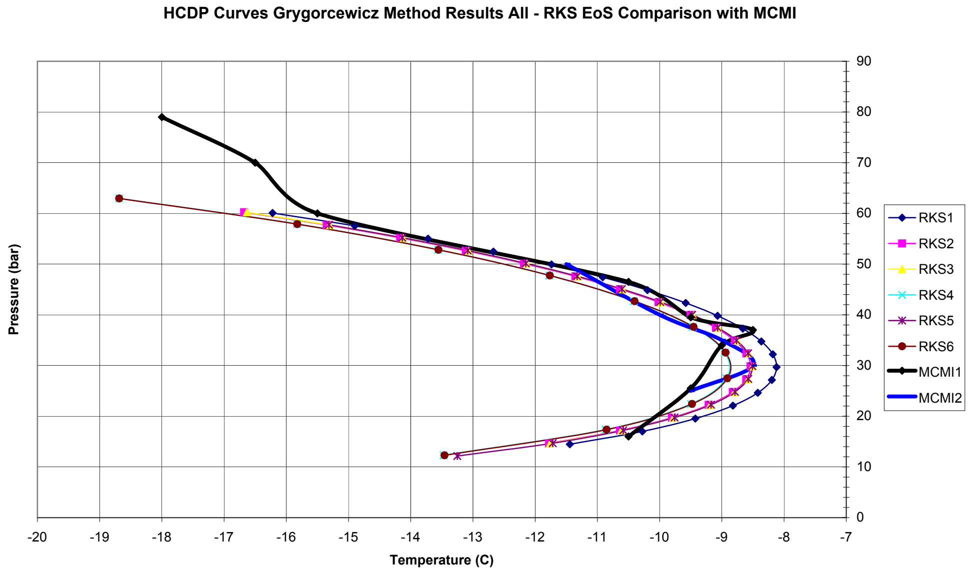

Figure 8.2: A comparison of the HCDP curves obtained by the RKS EoS for test results 1 to 6 using the Grygorcewicz method, included is the MCMI results from both trials

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This means that the adapted ISO 23874 method is affected by changes in the isomers identified on the chromatogram as it adversely affects the average boiling point fraction calculation.

8.2.3 Reference Gas Specification

Another area of focus for improving hydrocarbon dew point concerns the calibration reference gas. As mentioned in the overview, factors that influence the hydrocarbon dew point related to the composition of the gas. It was proposed that by producing a reference gas composition that is similar in concentration to the sample then an improvement in accuracy would be achieved, resulting in an improvement in hydrocarbon dew point determination.

The results of our experiment showed that for the Daniel 500 C_{9+} gas chromatogram no improvement in accuracy was gained for C_1 to C_8. The C_9, which is a lumped C_{9+}, peak improved by 2 ppm and this resulted in a -0.5°C improvement. It was concluded that it is not warranted to use a calibration reference gas similar to the gas composition being analysed as the improvement is only minor when compared to the improvement made by the authors characterisation method.

Chapter 9

Conclusions and Further Work

9.1 Achievement of Project Objectives

The following objectives have been addressed:

Gas Chromatograph operation and equipment Chapter 4 presented a summary of the principle of operation and the equipment applicable to natural gas pipelines and custody transfer stations.

Hydrocarbon dew point determination methods Chapter 3 provided an overview of the direct and indirect methods used to determine hydrocarbon dew point in the natural gas industry. The direct chilled mirror method, although the de facto standard can not provide continuous measurement. The indirect method, by means of a process gas chromatograph is the most common method as it provides other important gas property data required for fiscal metering. This chapter also explained the advantages and disadvantages of both methods.

Best practice for hydrocarbon dew point measurement Both chapter 3 and 4 reviewed the major factors that contribute to current best practices for measuring and determining hydrocarbon dew point in natural gas.

Identification of unknown hydrocarbon species Chapter 6 presented a novel method for identifying unknown peaks on a process gas chromatogram. This method used the relationship of hydrocarbon boiling point and component elution time to interpolate the boiling point of unidentified chromatogram peaks between the normalised alkanes. Appendix D was included to explain the basic nomenclature of hydrocarbon organic chemistry, the types of hydrocarbons found in the natural gas industry and their structural formula.

Develop a process to more accurately determine HCDP Chapter 6 also presented a novel characterisation method developed by the author and Chapter 7 recorded the results of the characterisation methods experiments. It was proven that the authors characterisation can be used to identify unknown hydrocarbon species detected on a process gas chromatogram. This data is used to produce a detailed like gas analysis that when applied to an equation of state does improve the hydrocarbon dew point determine to an acceptable temperature when compared to a direct method instrument.

Implementation to on-line process gas chromatograph The project was extended and the authors characterisation method was applied to a process gas chromatograph measuring natural gas on a custody transfer skid. The results showed that the authors method does in fact improve the hydrocarbon dew point determination to an acceptable temperature that provides benefits for gas producers, while still maintaining a safety margin for pipeline operators and end users.

9.2 Conclusion

Gas chromatography is used worldwide to determine the hydrocarbon dew point of export natural gas. In Australia it is a requirement that these gas chromatographs be able to measure up to C_{9+}. It was found that an inherent design issue in these gas chromatographs, limits the computation of the gas mixture in the C_6 to C_8 carbon groups resulting in a higher hydrocarbon dew point determination than actual.

To solve this problem a novel characterisation method was developed by the author. This method allows the user to view a process gas chromatograph chromatogram for export natural gas and identify and quantify unidentified hydrocarbon components. The authors method produces a detailed like analysis that, when applied to a thermodynamic equation of state improves the hydrocarbon dew point determination. When applied to the Redlich Kwong Soave equation of state the characterisation method proved comparable to the direct method manual chilled mirror instrument. The authors characterisation method was further proven when applied to an on-line process gas chromatograph in which it produced the same results as the equation of state software, GasVLE.

The aim of this work was to research the 'equations of state' used to calculate natural gas hydrocarbon dew point from constituent analysis by Gas Chromatography and to develop a methodology to improve Gas Chromatography hydrocarbon dew point determination. Therefore it can be stated that the aim of this project has been met.

9.3 Further Work

The following further work is required to validate and have recognised in the natural gas industry, the authors hydrocarbon dew point determination improvement method:

- trial the authors method at other export custody transfer stations and or pipelines that have different gas compositions up to C_{9+}
- discuss with the Australian Energy Market Operator the acceptance of the authors method as a characterisation that can be applied to gas chromatographs that are used to measure the hydrocarbon dew point of C_{9+} gas compositions.

The following current and further research is required by industry to improve hydrocarbon dew point determination:

The Gas Processors Association co-operative research projects for 2010 had two projects related to hydrocarbon dew point of natural gas. The first project titled 'testing of methods for measuring hydrocarbon dew points is a continuation of research proposed to Pipeline Research Council International (PRCI) for 2005. The primary goal is to identify cost effective instruments capable of repeatable, objective dew point measurements that can easily replace the Bureau of Mines manual chilled mirror device. A secondary goal is to identify and evaluate or develop alternative methods to the Bureau of Mines dew scope for detecting hydrocarbon dew points. The second project titled 'industrial natural gas dew point by equation of state method is an ongoing project to develop a 'practical industrial natural gas dew point using equation of state prediction that can easily replace and or supplement the Bureau of Mines chilled mirror method.

Inline with this (George et al., 2006) current research is reviewing several equations of state and heavy hydrocarbon characterisation methods to find possible causes and solutions to the problem of dew point under prediction for rich gas blends.

The National Gas Council Liquid Hydrocarbon Dropout Task Group (2005) in a white paper on liquid hydrocarbon dropout in natural gas infrastructure recommended that additional research be conducted in the following areas:

1. build the database to support use of C6+ split assumptions for heavier hydrocarbons, develop better correlation between direct and indirect hydrocarbon dew point determination and to improve the accuracy of commonly used equations of state.
2. develop a cost effective hydrocarbon specific direct reading dew point analyser because a conventional chilled mirror direct measurement instrument in general can be subjective to operator variability and interferences including but not limited to water vapour.

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Chapter 10

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Appendix A

Project Specification

ENG 4111/2 Research Project

Project Specification

For:	**Jon-Paul Frederick GRYGORCEWICZ**
Topic:	IMPROVEMENT OF HYDROCARBON DEW POINT DETERMINATION VIA GAS CHROMATOGRAPHY
Supervisors:	Dr Andrew Maxwell, Dr Nigel Hancock (*USQ*) Mr Alfi Zakhari, (*BHP Billiton Petroleum*)
Project Aim:	To research the 'equations of state' used to calculate natural gas hydrocarbon dew point from constituent analysis by Gas Chromatography and to develop a methodology to improve Gas Chromatography hydrocarbon dew point determination.

Program:

1. Research Gas Chromatography operation and equipment applicable to natural gas pipelines and custody transfer stations.
2. Research gas hydrocarbon dew point measurement methods, both: Direct and Indirect.
3. Research the major factors that contribute to current best practices for measuring hydrocarbon dew point in natural gas.
4. Research natural gas hydrocarbon components to develop a methodology to identify unknown hydrocarbon species using process gas chromatography, in order to provide users with a detailed gas composition required to assist with hydrocarbon dew point determination using an equation of state.
5. Develop a process to more accurately measure, or sufficiently model, the natural gas hydrocarbon dew point using gas chromatographs and the equation of state.

If time and resources permit:

1. Implementation of the above developed methodology to improve hydrocarbon analysis and dew point determination results during online gas chromatography operation.

Agreed:

Student Name:	Jon-Paul Grygorcewicz
Date:	12-05-2010
Supervisor Name:	Dr A. Maxwell
	Dr N. Hancock
Date:	12-05-2010
Examiner/Co-Examiner:	Dr A. Apan
Date:	12-05-2010

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Appendix B

Gas Chromatograph Chromatograms

B.1 Introduction

Appendix B is provided for referencing the gas chromatograph chromatograms collected during this project.

B.2 Initial Gas Sample Chromatograms

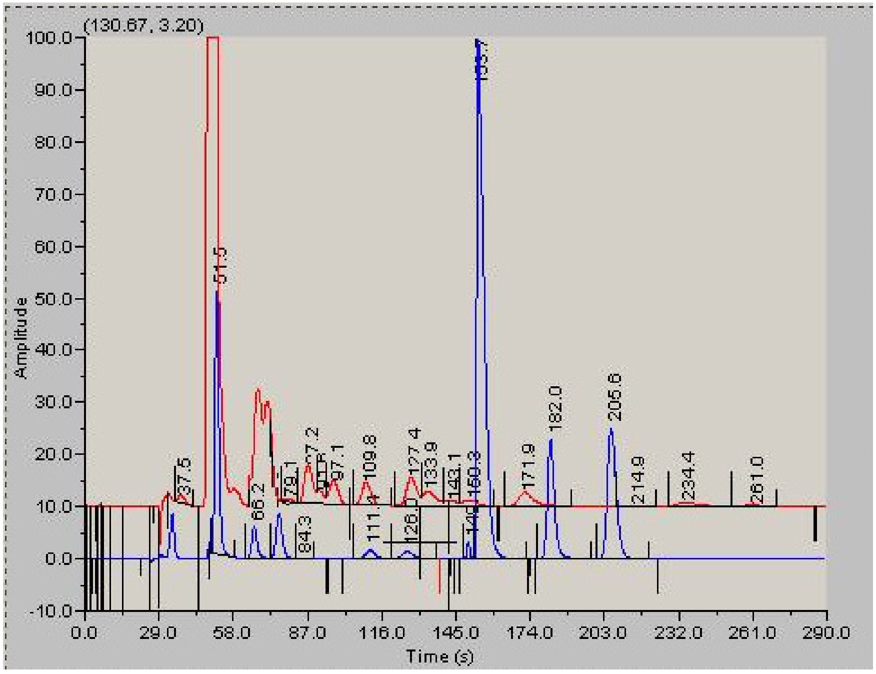

Figure B.1: Custody Transfer GC analysis chromatogram. The blue line is methane to pentane with nitrogen and carbon dioxide.The red line is C6 to C9.

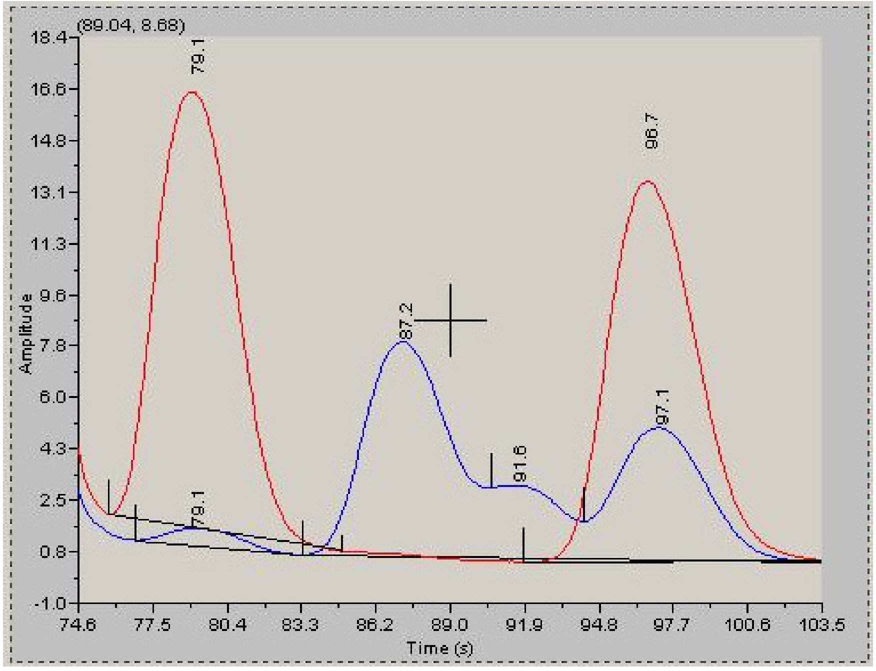

Figure B.2: Custody Transfer GC analysis chromatogram C6 Group. The blue line is the sample.The red line is the certified reference gas.

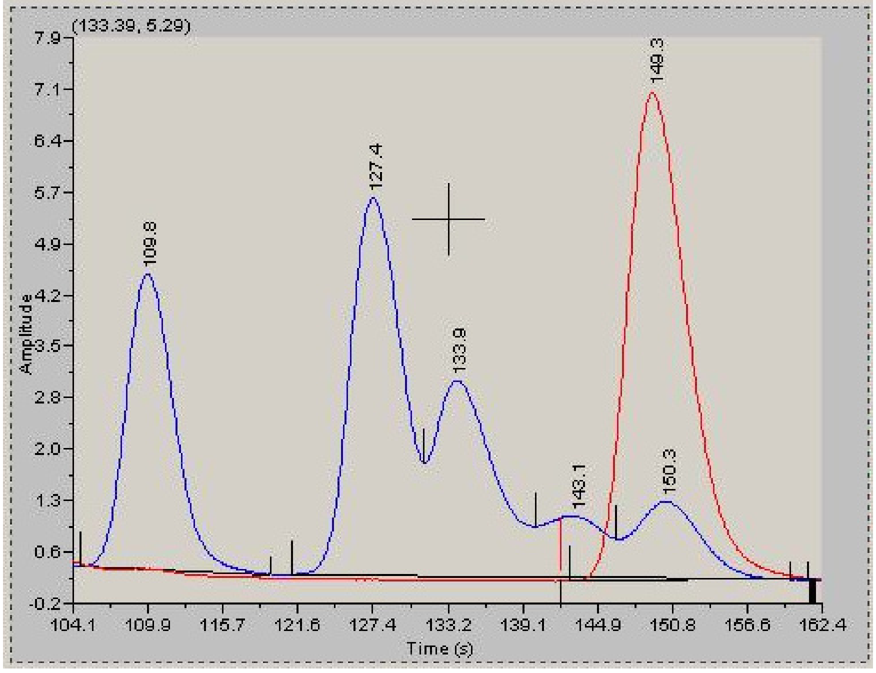

Figure B.3: Custody Transfer GC analysis chromatogram C7 Group. The blue line is the sample.The red line is the certified reference gas.

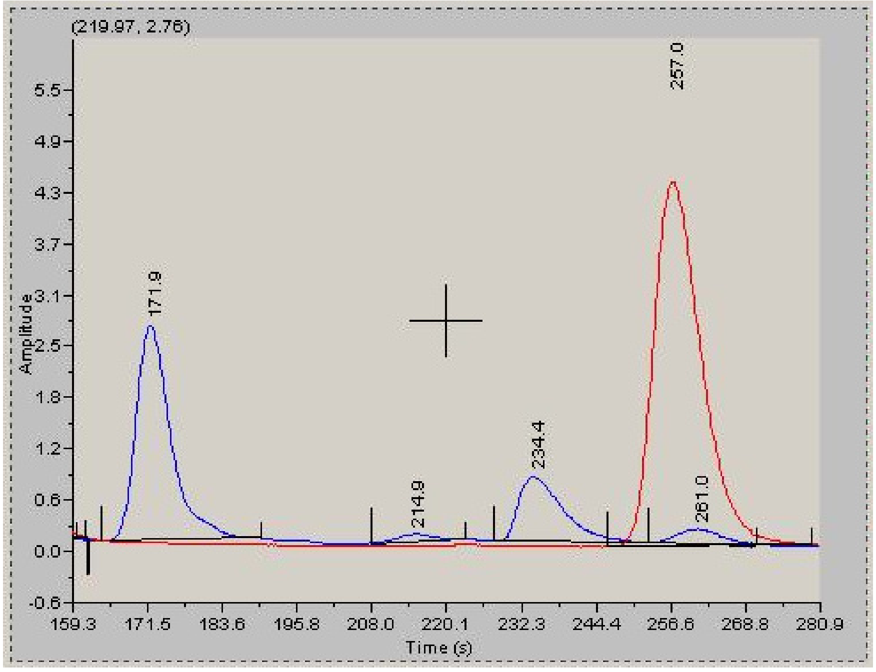

Figure B.4: Custody Transfer GC analysis chromatogram C8 Group. The blue line is the sample.The red line is the certified reference gas.

B.3 DewCalc Trial Chromatograms

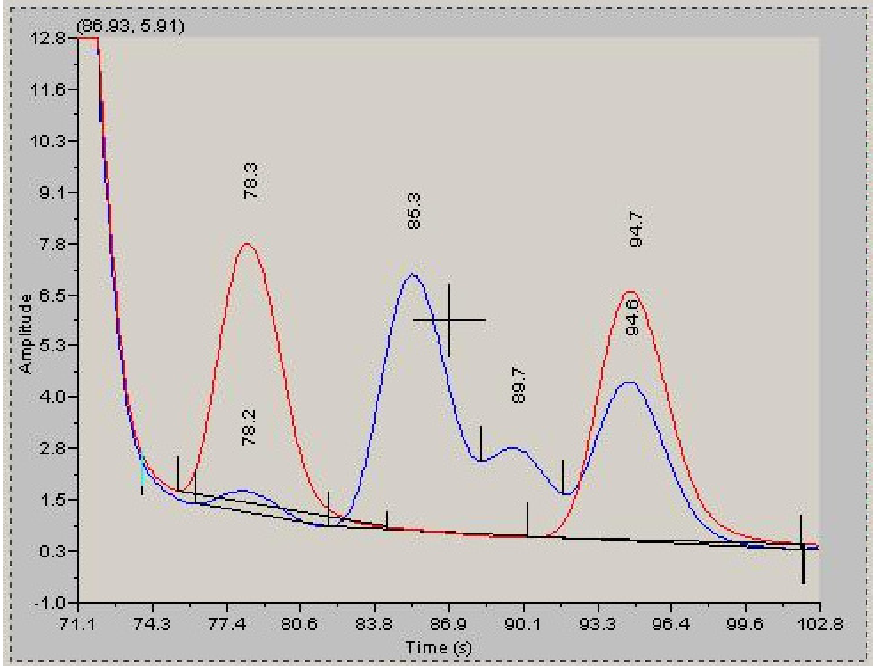

Figure B.5: Custody Transfer GC analysis chromatogram C6 Group. The blue line is the sample.The red line is certified reference gas.

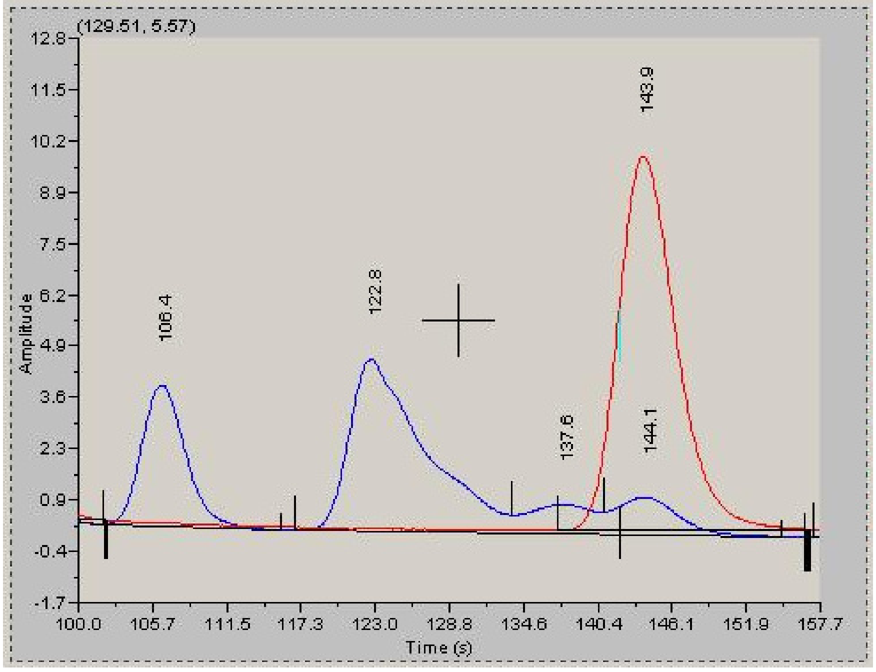

Figure B.6: Custody Transfer GC analysis chromatogram C7 Group. The blue line is the sample.The red line is certified reference gas.

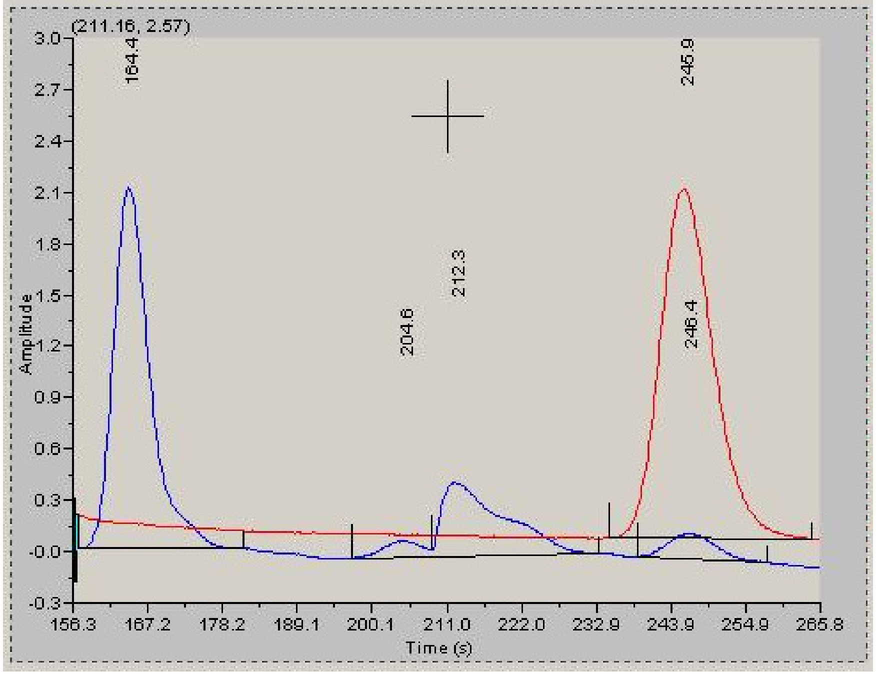

Figure B.7: Custody Transfer GC analysis chromatogram C8 Group. The blue line is the sample.The red line is certified reference gas.

Appendix C

Hydrocarbon Dew Point Curves

C.1 Introduction

Appendix C is provided for referencing the additional hydrocarbon dew point curves produced using the GasVLE equation of state software for this project. The following figures compare the hydrocarbon dew point curves produced by each of the equations of state for the sample indicated.

C.2 Project Hydrocarbon Dew Point Curves

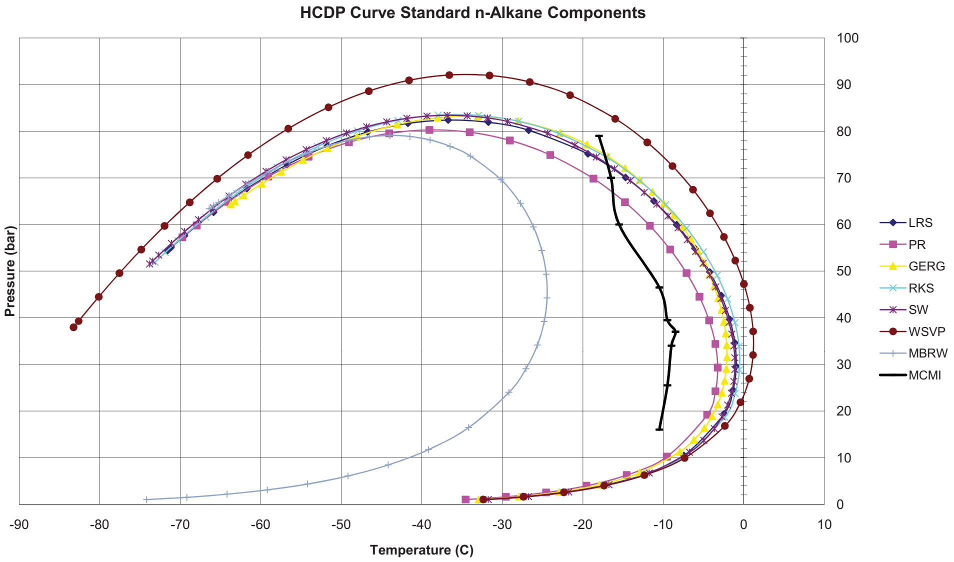

Figure C.1: A comparison of the HCDP curves obtained by the EoS using the GC analysis of standard n-alkanes from Table 7.2 and the MCMI

.

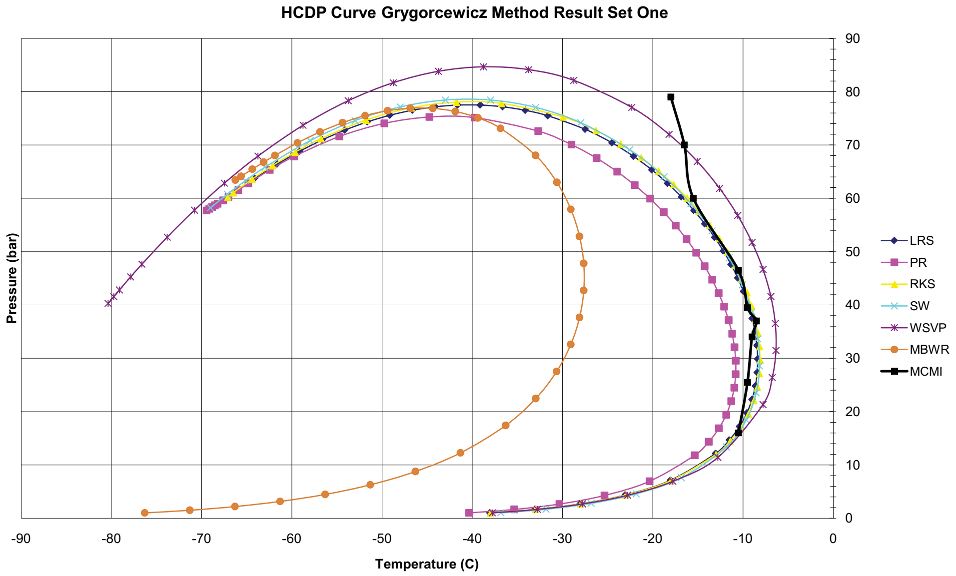

Figure C.2: A comparison of the HCDP curves obtained by the EoS using the gas analysis from Table 7.11 and the MCMI

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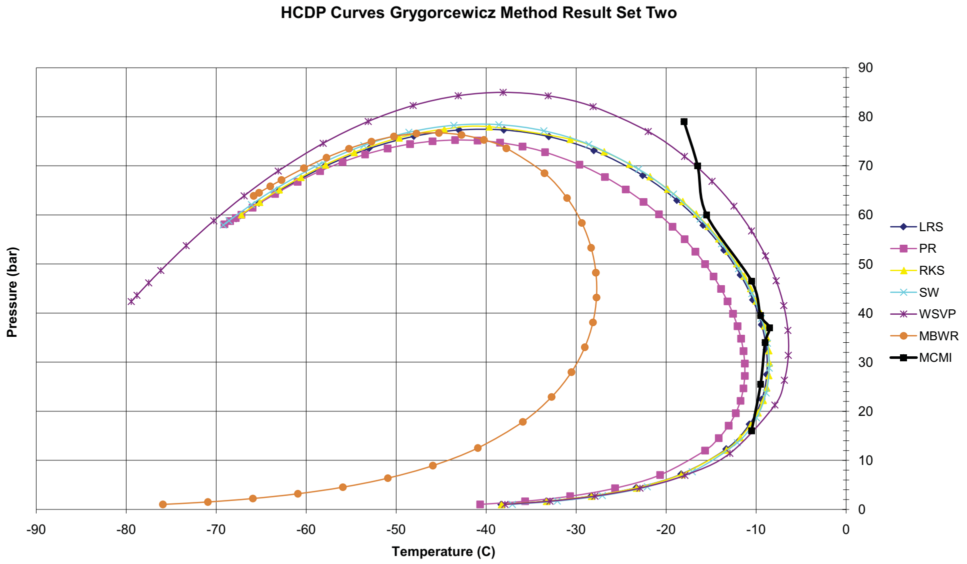

Figure C.3: A comparison of the HCDP curves obtained by the EoS using the gas analysis from Table 7.14 and the MCMI

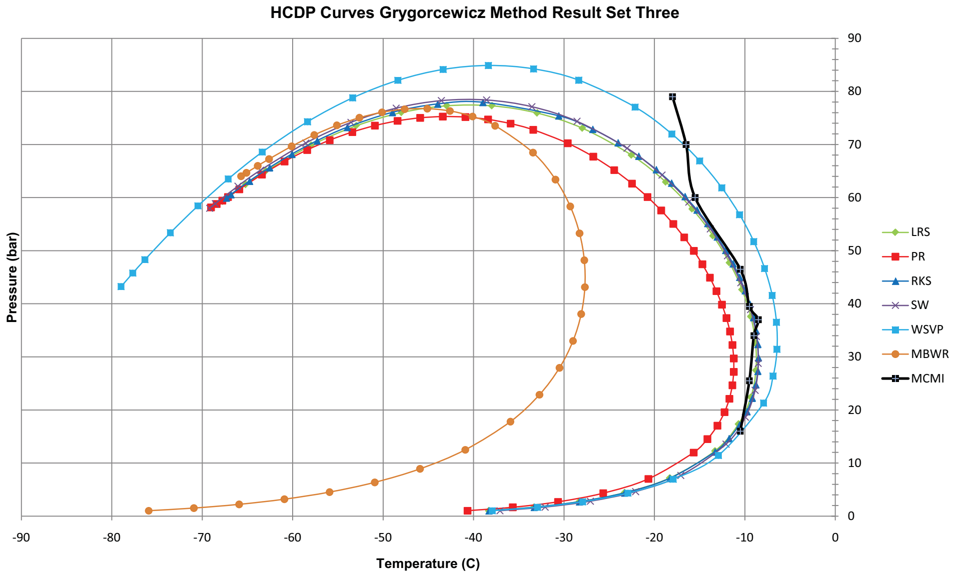

Figure C.4: A comparison of the HCDP curves obtained by the EoS using the gas analysis from Table 7.17 and the MCMI

.

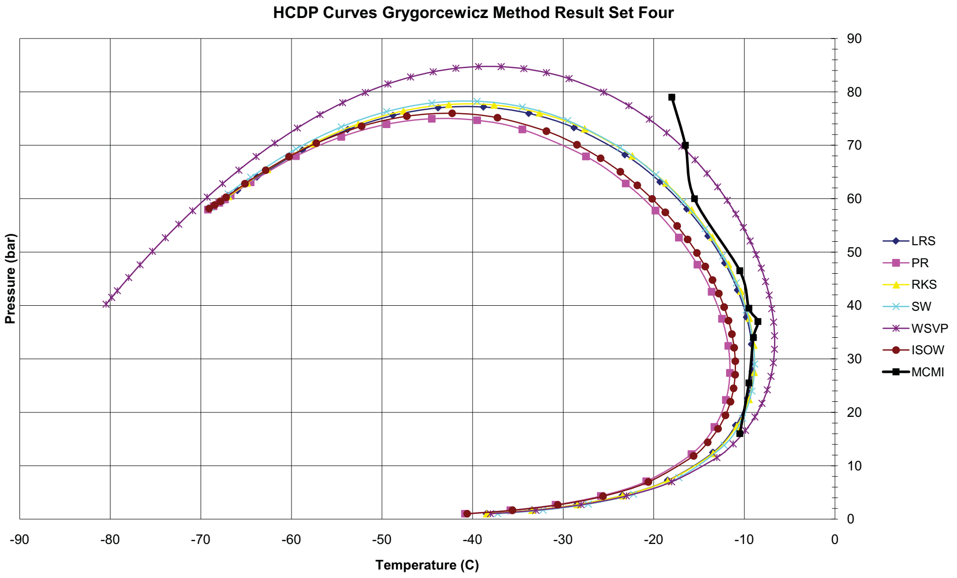

Figure C.5: A comparison of the HCDP curves obtained by the EoS using the gas analysis from Table 7.20 and the MCMI

.

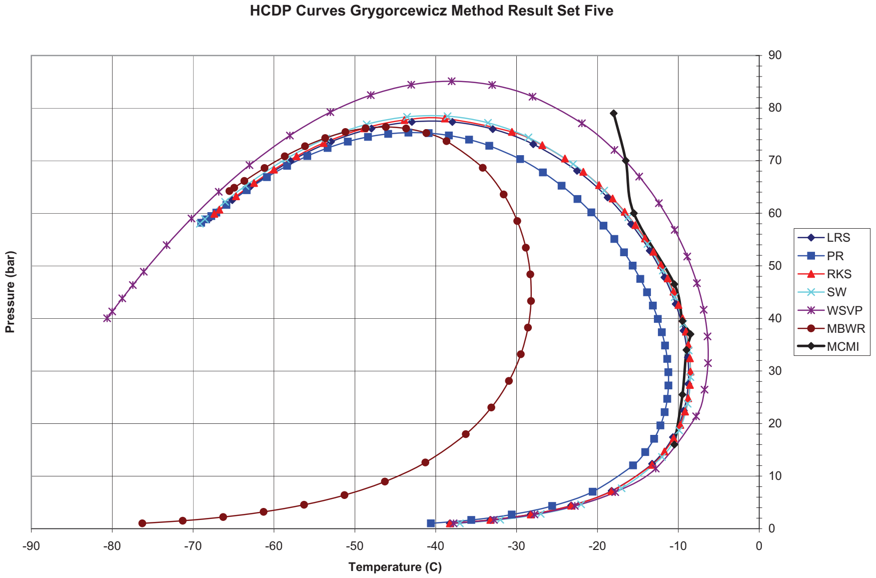

Figure C.6: A comparison of the HCDP curves obtained by the EoS using the gas analysis from Table 7.23 and the MCMI

.

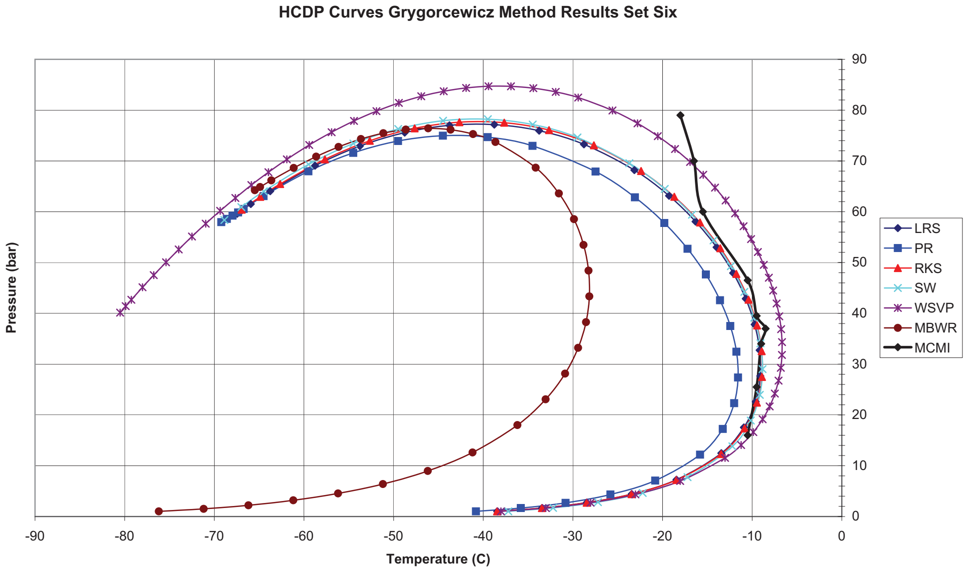

Figure C.7: A comparison of the HCDP curves obtained by the EoS using the gas analysis from Table 7.26 and the MCMI

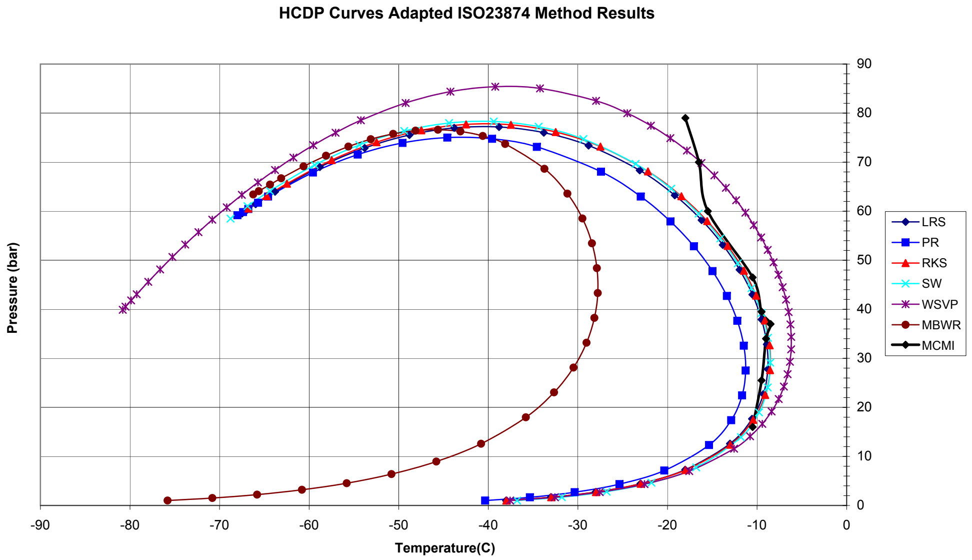

Figure C.8: A comparison of the HCDP curves obtained by the GasVLE EoS software using the GC analysis and adapted ISO23874 method composition from Table 7.28 and the MCMI

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Appendix D

Hydrocarbon Nomenclature

D.1 Chapter Overview

The purpose of this chapter is to explain to the reader the basic nomenclature of hydrocarbon organic chemistry, the types of hydrocarbons found in the natural gas industry and their structural formula. This will assist the reader in understanding the terminology used when identifying unknown hydrocarbons on the gas chromatograph chromatogram.

D.2 Basic Hydrocarbon Nomenclature

Natural gas (Whitmans, S., n.d.) is a mixture of many compounds which can be classified into three groups: hydrocarbons, inerts and miscellaneous trace compounds. A hydrocarbon, by definition (Moss et al., 1995), is any compound composed solely of carbon and hydrogen. Hydrocarbons are further classified as being aliphatic or aromatic. Aliphatic groups include alkanes, alkenes, alkynes and cycloalkanes.

To help eliminate the proliferation of many names of compounds (Moss et al., 1995), a systematic naming system was derived by the *International Union of Pure and Applied Chemistry* (IUPAC). In general compounds are classified and named by consideration of:

- the number and type of atoms that are present,
- the bond types in the molecule, and
- the geometry of the molecule

After pentane the following rules apply:

1. Name the longest continuous carbon chain in the molecule as the parent name.
2. Identify the side groups attached to this chain and place them before the parent name in alphabetical order. In general side groups can be regarded as an alkane that is deficient in a hydrogen atom.

3. If several groups of the same kind are attached to the main chain, list the groups only once using the appropriate numerical prefix di, tri, tetra, penta, hexa, hepta, octa, nona, deca, etc. to indicate how many times that side group appears.

4. Assign a number to each of the side groups to indicate where the group is attached to the main chain. Start the numbering of the main chain from whichever end of the main chain will give the lowest set of numbers. The lowest set of numbers is selected on the basis of the lowest number at the first point of difference.

5.
   - hyphens must separate numbers and letters,
   - commas must separate numbers,
   - the di, tri, tetra, etc. are not included in the alphabetizing process,
   - *n*, *s* and *t* are not included in the alphabetizing process, but *iso* is,
   - the prefix *cyclo* is used for cyclic alkanes

D.2.1 Alkanes

Alkanes (Moss et al., 1995) are acyclic branched or unbranched hydrocarbons having the general formula C_nH_{2n+2} and therefore consist entirely of hydrogen atoms and saturated carbon atoms. *Paraffins* is an obsolescent term for saturated hydrocarbons, commonly but not necessarily acyclic. The term paraffins is still widely used in the petrochemical industry, where it designates acyclic saturated hydrocarbons and stands in contradistinction to naphthenes.

Alkanes are the most fundamental types of organic compounds. According to the IUPAC naming convention, the first two and most elementary rules for naming alkanes are: to identify the length of the carbon chain, start the name with the appropriate Greek prefix and end the name with the suffix -ane.

Alkane Isomers are compounds that have the same chemical formula but different atomic structure. For example butane, C_4H_{10} has the normal structure, as shown in Figure D.1. The adjective *normal* is used to designate a molecule wherein all of the carbon atoms are in a straight line and it is often abbreviated to *n*. That is $n-butane$.

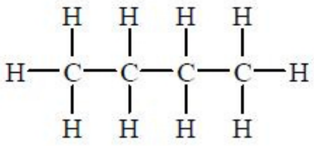

Figure D.1: Structural formula of normal butane. Note the normal chain structure. (adapted from (Campbell, J., 1984)).

Isomers are formed when branching occurs. The compound in Figure D.2 also has the formula C_4H_{10}, however it is given the designation *isobutane* to signify an isomer and it is often abbreviated to i. That is $i - butane$.

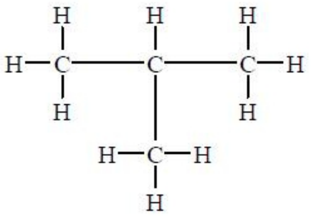

Figure D.2: Structural formula of isobutane. Note the branch off the middle carbon atom. (adapted from (Campbell, J., 1984)).

D.2.2 Alkenes

Alkenes (Moss et al., 1995) are acyclic branched and unbranched hydrocarbons having one carbon carbon double bond and the general formula C_nH_{2n}. Acyclic branched or unbranched hydrocarbons having two double carbon bonds are alkadienes and three double bonds are alkatrienes.

The Olefin group subsumes alkenes and cycloalkanes and the corresponding polymers. Hydrocarbons in this series combine easily with other atoms, without the replacement of a hydrogen atom. Since they are reactive, Olefin's are thus called unsaturated hydrocarbons. The structural formula for olefin's uses a double line to indicate the double carbon linkage and this is the most reactive point in the molecule. The amount of olefin's in natural gas is usually small. Figure D.3 shows the structural formula of

Table D.1: Alkane Nomenclature.

Carbon No.	Formula	Name	Mol. Wt.
1	CH_4	Methane	16
2	C_2H_6	Ethane	30
3	C_3H_8	Propane	44
4	C_4H_{10}	Butane	58
5	C_5H_{12}	Pentane	72
6	C_6H_{14}	Hexane	86
7	C_7H_{16}	Heptane	100
8	C_8H_{18}	Octane	114
9	C_9H_{20}	Nonane	128
10	$C_{10}H_{22}$	Decane	142

the alkene, ethylene.

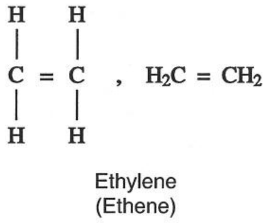

Figure D.3: Structural formula of Ethylene showing the double carbon bond. (adapted from (Campbell, J., 1984)).

D.2.3 Alkynes

Alkynes (Moss et al., 1995) are acyclic branched or unbranched hydrocarbons having a carbon carbon triple bond with the general formula C_nH_{2n-2}. Acyclic branched or unbranched hydrocarbons having two triple carbon bonds are alkadiynes and three triple bonds are alkatriynes.

The alkyne series of hydrocarbons are of basic importance only in certain refining and petrochemical applications. Acetylene is the most important member of this series.

D.2.4 Aromatic Compounds

Historically, the term aromatic originally (Moss et al., 1995) referred to the smell of selected compounds that later were found to contain benzene or fused benzene rings in the structure. In a structural sense, it designates compounds that, in accordance with the theory of *Hückel*, have a cyclic, delocalised $(4n+2)$ pi-electron system. This includes arenes and their substitution products, for example: benzene, naphthalene and toluene. Aromatics have the general formula C_nH_{2n-6}. Benzene the parent compound of this series has the structural formula of C_6H_6. The structural formula of the aromatic compound benzene is shown in Figure D.4.

Since aromatics (Campbell, J., 1984) are unsaturated, they react readily and may be oxidized to form organic acid. Aromatics also promote foaming and other operational problems in the production and handling of crude oil and natural gas. Most natural gas fields only contain traces of aromatics.

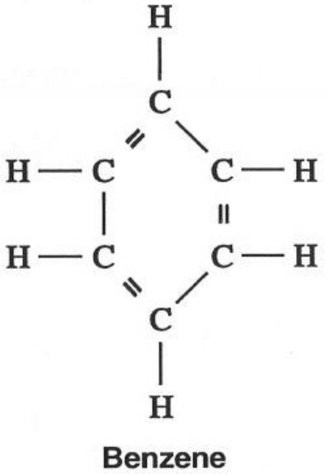

Figure D.4: Structural formula of benzene showing the carbon atoms in a ring, a cyclic compound. (adapted from (Campbell, J., 1984)).

D.2.5 Cycloalkanes

Cycloalkanes (Moss et al., 1995) are saturated mono cyclic hydrocarbons with the general formula C_nH_{2n}. The term naphthenes is used in the petrochemical industry to signify cycloalkanes. The most common cycloakanes are cyclopentane and cyclohexane. Cyclohexane is similar to benzene except that it is saturated. The structural formula for cyclohexane is shown in Figure D.5.

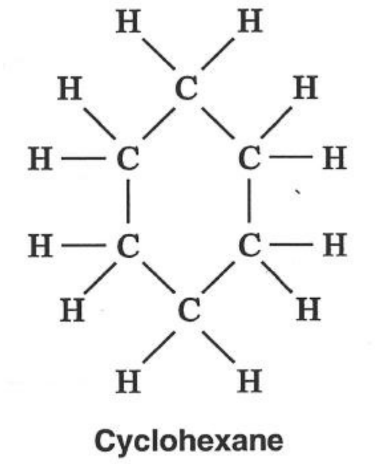

Figure D.5: Structural formula of Cyclohexane showing the carbon atoms in a saturated ring. (adapted from (Campbell, J., 1984).