SENSITIVITY ANALYSIS OF PETROLEUM PHASE BEHAVIOR PREDICTION

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PREFACE

This work focuses on the phase behavior of a hydrocarbon system including a Cn+ fraction. The sensitivity to changes in critical properties, number of hypothetical components, and also to the last boiling point is studied and summarized. First, a characterization of the Cn+ fraction is carried out and the phase behavior predicted; second, advanced characterization is used to improve the phase behavior; and third, the initial characterization is changed within the degrees of freedom given in the experimental distillation data. The phase behavior is predicted for every modification and compared to the initial phase behavior and the available experimental data. Also, the change in volumetric properties, in terms of liquid drop out for a gas and gas to oil ratio for an oil, is predicted and noted.

I wish to thank my adviser, Dr. Jan Wagner, for his help and moral support through this study. I also extend thanks to him and his family for their honest concern and friendship during my entire stay at OSU. I appreciate the assistance given by Mrs. Ellen Stange, Dr. Ali Majeed and Dr. Robert L. Robinson, Jr. Special thanks is given to Mr. Arild Wilson and Norsk Hydro for making my stay at OSU possible, and for providing the experimental data needed in my project. I am thankful to Mr. Carlos Ruiz and Dr. Ruth Erbar for their kind support and friendship. Heartfelt thanks is expressed to my friend Dan Friedemann for his patience, encouragement, love and understanding on days when the school work seemed to never end.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

The task of describing higher boiling petroleum fractions for successful use in models to simulate pressure-volume-temperature (PVT) data is difficult, and numerous methods of variable quality have been tried during the past few years. Many methods have been successfully used for specific fluids but fail once they are applied to a slightly different type of hydrocarbon mixture.

The aim of this work has been to investigate the sensitivity of the phase behavior of a hydrocarbon fluid containing a Cn+ fraction. The sensitivity to changes in the critical properties as characterization and advanced characterization are performed is studied. Characterization is defined here as the description of the Cn+ fraction in terms of hypothetical components with thermophysical properties similar to those for real components. The advanced characterization is the manipulation of critical temperature (Tc) and/or critical pressure (Pc) of the hypothetical components with the aim of achieving a set of critical properties that give a better agreement between predicted and experimental phase behavior.

The sensitivity of the hydrocarbon fluid phase behavior has also been investigated as a function of the number of hypothetical components and the 100% distilled off boiling point [T(100)] in the experimental distillation. The changes in volumetric properties in terms of liquid drop out for a gas and gas to oil ratio (GOR) for an oil have been predicted, but no effort has been made to tune the volumetric properties to the experimental data. The changes that are observed in these properties are therefore due solely to the manipulations performed to improve the phase behavior.

A set of guidelines for achieving the best possible predictions of phase-behavior when experimental data are available is outlined as a result of the individual steps in this work.

Four different fluids have been studied; two synthetic gas mixtures consisting of the most common components in a light gas reservoir; and two real hydrocarbon fluids sampled from different reservoirs in the North Sea, one of them a gas the other an oil.

The two real fluids have been characterized based upon an experimental distillation including the normal boiling point, molecular weight and specific gravity of each fraction. The data needed to characterize the synthetic mixture were simulated from the known components and thermophysical properties of the mixture. The "experimental" data for the synthetic mixture is therefore model specific.

An example phase envelope is shown in Figure 1.

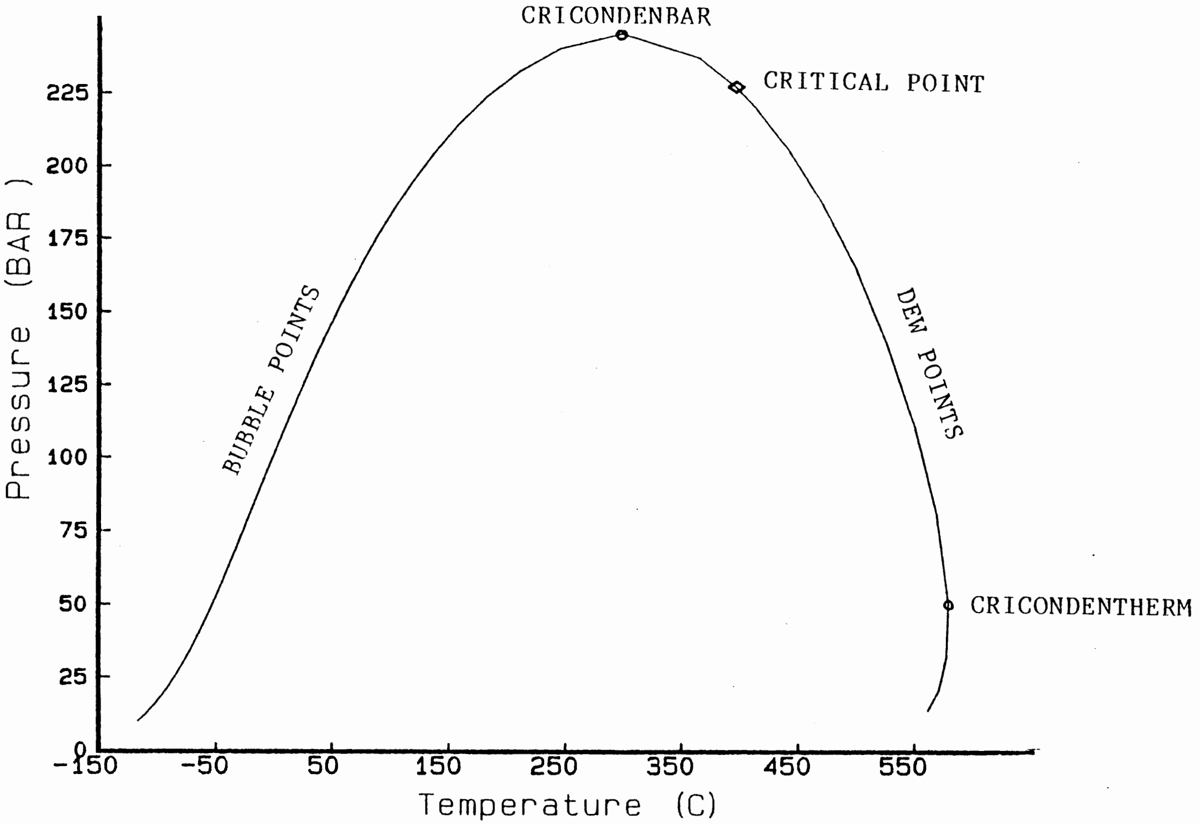

Figure 1. Example Phase Envelope.

CHAPTER II

LITERATURE REVIEW

The simplest method of describing a petroleum fluid, including higher boiling hydrocarbons, is to perform a component-by-component analysis on the lighter components, and then to "lump" the remaining components into one fraction. The residue fraction is assigned a molecular weight (MWT), specific gravity (SG), and critical properties (Tc,Pc) from the literature for some known higher boiling n-paraffin. Or somewhat better, the MWT and SG are measured experimentally, and Tc and Pc are correlated from these values. This method of describing higher boiling hydrocarbon fluids is still in wide use for characterizing hydrocarbon fluids due to its simplicity and low cost. Unfortunately, the method has been shown to create significant errors when used as input for a model to simulate phase behavior, to determine heat duties and compressor requirements, and to size process equipment (Maddox and Erbar, 1982; Petree and Hankinson, 1984). Other techniques for describing the Cn+ fraction have been developed and published; some of them are significantly better, and almost all of them are more complicated, time consuming and expensive.

Simulated boiling point analysis using a gas chromatographic (GC) technique are widely used. The components are separated and quantified up to and including five hydrocarbons. Beyond these components only the n-paraffins are identified, and all components eluting between the n-paraffins are qualified as the next higher boiling n-paraffin. Such components are assigned the same boiling point, MWT, SG and critical properties as the equivalent n-paraffins. Several more accurate versions of this technique have been used. The improvements are that MWT and SG are computed from the analysis using selected mixing rules. Further, Tc and Pc are correlated using conventional techniques. Other adjustments to improve predictions may or may not be performed (Dale, 1984; Austad et al., 1983).

A more valid approach to describing hydrocarbon fluids is to perform a component by component analysis up to some Cn, followed by a boiling point analysis of the Cn+ fraction and measurement of MWT and SG for every distillate fraction including the residue. The paraffinic-naphthenic-aromatic (PNA) distribution can also be utilized when available, but is not required. The experimental information is then used to correlate EOS parameters for use in a model to predict phase behavior. A well known method based on this kind of experimental work is to break down the boiling point curve into a finite number of narrow boiling fractions and to define hypothetical components with normal boiling point, SG, MWT and critical properties for use in the EOS (Wilson, Maddox and Erbar, 1978; Maddox and Erbar, 1982).

The boiling point curve has also been discretized on the basis of the boiling points of the n-paraffins with one subfraction for each carbon number, (Pedersen, Thomassen, and Fredenslund, 1982).

Another variant based on the same type of experimental data is to group the fractions together on a weight basis so that all the fractions contain approximately the same weight of fluid. The necessary EOS parameters are correlated for each of these weight fractions. This method also lumps together the light components as fractions. (Pedersen, Thomassen, and Fredenslund, 1983).

A statistical approach to describe the Cn+ fraction using the carbon numbers as a basis has been described for use when there is insufficient experimental data to adequately characterize the Cn+ fraction (Whitson, 1983). The technique uses the three parameter gamma function to describe the molar distribution and physical properties of the Cn+ fraction. In addition, the assumption is made that adjustments to the generated distributions are necessary to match the experimental PVT data.

Another technique that utilizes the TBP data and the PNA distribution of distillate fractions is based on a group contribution approach. Model compounds for each fraction are defined by assuming that the total composition can be represented in terms of common groups such as -CH3, -CH2-, and A-CH. The number of each group in each fraction is then adjusted to match the average boiling point in each fraction. MWT, SG and parameters for use in the model are estimated using conventional methods (Ruzicka, Fredenslund, and Rasmussen, 1983).

Several attempts have been made to describe the Cn+ fraction using the theory of continuous thermodynamics. The Cn+ fraction is treated as an infinite number of components that can be described by a continuous distribution function as opposed to a finite number of hypothetical components (Cotterman, Bender and Prausnitz, 1985; Briano and Glandt, 1983; Ratzsch and Kehlen, 1983).

Only a few of the reviewed methods to describe heavy petroleum fractions have been used with success for a wide variety of mixtures, and all of them do require some kind of an adjustment procedure to match experimental PVT data. Unfortunately, the procedure for successfully adjusting the characterization to match the experimental PVT measurements is often omitted, and the investigators successfully tune the correlations to give a good match to the specific fluid of their interest. Problems arise when these correlations are applied to other types of hydrocarbon fluids.

CHAPTER III

DESCRIPTION OF HEAVY PETROLEUM FRACTIONS

Experimental Data

Literature suggests that the experimental data for characterizing the Cn+ fraction is a true boiling point (TBP) distillation of the stabilized crude or condensate (Maddox and Erbar, 1982). Traditionally, the TBP distillation was taken as the distillation procedures described by the American Society for Testing and Materials (ASTM). These procedures are specified in standard D-2892 which represents the distillation at atmospheric pressure and standard D-1160 which gives specifications for the part of the distillation carried out at reduced pressure to avoid cracking of the higher boiling hydrocarbon molecules. More recently, the laboratory distillation techniques have increased in popularity, and several different techniques that do not meet the specification in the ASTM standards have been claimed to produce TBP data. These techniques have been widely used during the last few years, mainly because they are less expensive, require less sample and are quicker. There are small discrepancies in the normal boiling point data produced from different apparatus. Not enough research has been done on comparing the different methods to state that the TBP data are significantly better than the normal boiling point data produced from alternative apparatus. Boiling point data will be referred to as TBP data only if they are obtained on an ASTM specified apparatus, and as normal boiling point data otherwise.

The experimental data used in the present work are proprietary data, and the fluids will therefore be labeled as Gasmix1 and Oilmix1. The data are as follows:

(1) Distillations of the stabilized crude and the condensate are reported. The normal boiling point at the endpoint of every distillate fraction is reported. Also, the average molecular weight and the specific gravity are measured and reported for every fraction including the residue.

The end of the boiling curve will never be determined experimentally due to cracking problems of the heavy hydrocarbons and must be predicted from some suitable correlation or from experience. The end of the boiling curve therefore represents a degree of freedom in the characterization of the Cn+ fraction that must be carefully monitored throughout the work.

(2) A pressure-volume-temperature (PVT) study has been carried out at the reservoir temperature. The experimental data of particular importance for phase behavior predictions are the experimental dew points and bubble points. The volumetric data of interest are the liquid drop out for the gas stream as it undergoes a constant-volume-depletion (CVD) study, and the solution gas to oil ratio (R_s) for the oil as it undergoes a differential liberation of gas.

Prediction of Phase Behavior and Volumetric Properties

The vapor-liquid-equilibrium (VLE) calculations were performed via the Soave-Redlich-Kwong (SRK) equation of state (EOS) which is a cubic

EOS widely used in the petroleum industry. The equation uses the critical properties and the acentric factor of each component in the prediction of phase behavior. Hence, the quality of these data are crucial for matching the predicted phase behavior with experimental data. Binary interaction parameters are also introduced to the EOS to improve the predicted phase behavior (Reid, et al., 1977). The goodness of the predictions will vary from fluid to fluid, but almost always the parameters used in the EOS have to be tuned to get a best possible match to the experimental data. This tuning is called advanced characterization, and the most common method is to adjust one or more of the desired parameters, i.e. Tc and/or Pc for the hypothetical components, or keep Tc and Pc constant while the binary interaction parameters are adjusted.

The technique of adjusting Tc and/or Pc for the hypothetical components will often improve the phase behavior predictions, and usually a very good match to the experimental data can be achieved. Most often only one or a few experimental points on the phase boundary are known, and there is no way to check the predicted phase envelope against the experimental phase envelope at all points.

As in other empirical methods, extrapolation may not be accurate. Fitting a few data points exactly does not guarantee an exact match of the complete envelope. Unfortunately, experimental data for the whole phase envelope are rare. Therefore, the overall expected fit to the experimental envelope is not commonly known. One can aim for agreement of 3.5 to 7 bar over a temperature range of 30 to 50°C when several points are known in the region (Maddox and Erbar, 1982). These values are for oil systems, and the expected agreement for a gas system will normally be poorer.

The vapor phase density predicted from the SRK EOS will normally agree well with the experimental data at pressures and temperatures away from the critical region. The accuracy is expected to be within 2-4% for most systems based on experience.

The liquid phase densities have been predicted by the Corresponding States Liquid Density method, COSTALD, (Hankinson and Thomson, 1979). Hankinson and Thomson report that this correlation gives very good agreement with experimental data for pure components and mixtures. The average absolute error is reported to be within 1.5%. However, experience with fluids sampled from both oil and gas reservoirs in North Sea have shown that the agreement between experimental and correlated values is not very good for hydrocarbon mixtures containing heavy hydrocarbons. The COSTALD method includes Tc and Pc in the correlation, the volumetric properties are therefore expected to change as these parameters are adjusted: The predicted liquid volume will increase with increasing Tc and/or decreasing Pc and decrease with decreasing Tc and/or increasing Pc.

Characterization of the Cn+ Fraction

The heavy end of the hydrocarbon reservoir fluid is composed of a very large number of components, and todays experimental techniques do not detect and quantify all these components. Even if detection of all components was possible, the information would be far too detailed to handle.

The information needed for the simulations must be more condensed than a component-by-component analysis of the whole stream. The method chosen in this work is the one first developed by Erbar (Maddox and Erbar, 1982) and is a combination of a component-by-component analysis of the light end of the hydrocarbon stream and a discretization of the crude oil or the condensate into a finite number of hypothetical components. The technique of discretizing the unknown number of heavy hydrocarbons into a finite set of hypothetical components is called characterization. The minimum required experimental data are the average molecular weight and the specific gravity of the stabilized crude oil or condensate. The result will improve when more experimental data are available, and the recommendation is to use a TBP distillation of the stabilized crude oil or condensate as a basis for the characterization work. A TBP distillation should report the normal boiling point temperature of each fraction distilled and also the average molecular weight and the specific gravity for each fraction. In addition, an analysis of the PNA distribution can be used when available. However, the accuracy of the PNA data are often questionable for the higher hydrocarbons, and these data are sometimes omitted.

The characterization procedure is commonly started from and including normal-hexane, but the characterization can also start at some higher hydrocarbon as long as all the information needed for the simulation is known for all lighter components. Some of the newer gas chromatographic separation techniques have succeeded in separating and detecting all the isomers of hydrocarbons up to and including nine carbon atoms. All characterizations carried out in this work have the starting point at normal hexane and will be referred to as C6+ characterization.

Given the experimental data as an input, the characterization procedure generates a set of hypothetical components and all the thermophysical properties needed for the phase behavior calculations. The defined C6+ fraction can then be added to the other components in the stream, and the fluid will be fully defined with normal boiling point, molecular weight, specific gravity and critical properties for all components, including the hypothetical ones. The acentric factor also needed for the prediction of phase behavior is found from the SRK EOS when all other parameters are known.

Improving the Characterization

Why Adjust EOS Parameters?

Predicted phase behavior often does not agree with experimental PVT data. This discrepancy between theory and experiment is the result of several limiting factors:

- Insufficient experimental data.
- Inaccurate experimental data.
- Improper characterization of the C6+ fraction.
- Improper model selection.
- Invalid correlations/parameters used in the model.

Even when the best available model is chosen for the application, the model does not work equally well for all mixtures; the same is true for the correlations used to predict parameters in the model. In addition the models are never better than the experimental data used as a basis for the computations. To account for deficiencies in the models, selected model parameters (for example Tc and Pc) may be adjusted to achieve a closer match between experimental and predicted phase behavior. Another approach is to modify the initial correlation of T(100) from the experimental boiling point curve, since this last point never is an experimental point.

Techniques Used

The technique chosen to improve the predicted phase behavior depends on the models that are used and also the type and amount of experimental data available. When there are insufficient experimental data available to define the composition of the fluid properly, the degrees of freedom are numerous, and a consistent way to reach the desired match is difficult to find. However, given a reasonable model and experimental data, there are several systematic approaches that can be taken to improve initial estimates of phase behavior. These include: (1) Modification of the initial characterization of the C6+ fraction by changing the number of hypothetical components and/or by modifying the initially correlated T(100), and (2) Adjusting EOS parameters such as critical properties, binary interaction parameters, or other parameters that may contribute in the model.

Normally only one or two of the parameters in the EOS are allowed to be adjustable, while the others are fixed at the correlated or preset values. The adjustments that are mentioned here are primarily carried out to improve the phase behavior predictions, but improvements in other properties, such as volume, may also result since Tc and Pc are also involved in predictions of both vapor and liquid volumes.

Two different approaches to achieve improved predictions of phase behavior were used in this study. First, the EOS parameters Tc and Pc were allowed to be adjustable (advanced characterization), second, the initial characterization of the C6+ fraction was modified by changing the number of hypothetical components, and by changing the 100% distilled off boiling point of the experimental distillation. The binary interaction parameters were not allowed to change, but kept at the specific values set in the model (Reid et al., 1977).

The advanced characterization was performed using the guidelines given by Maddox and Erbar (Maddox and Erbar, 1982):

(1) Increasing Tc and/or decreasing Pc results in a lower predicted saturation pressure at constant temperature. Decreasing Tc and/or increasing Pc increases saturation pressure.

(2) Changing Tc and/or Pc for the heaviest components influences dew points more than bubble points, since the dew point is controlled by the heavier components.

(3) Changing all the Tc's and/or Pc's simultaneously may influence the whole phase envelope.

(4) The Tc and/or Pc adjustments should be carried out in such a way that the ratio Tc/Tb as a function of Tb remains a monotonic curve; or for the case when Pc is changed the curve ln(Pc) versus ln(MWT) must remain monotonic.

The desired match to the experimental phase boundary may be achieved through these adjustments, but there is a limit to the magnitude of the adjustments. This limit can be estimated from the curves described in item (4) in the above list and the normal boiling point of every hypothetical component. The boiling point must not exceed the critical point. In addition, the boiling range of the whole C6+ fraction is a limiting factor; the more narrow boiling the C6+ fraction, the less effective the advanced characterization.

CHAPTER IV

PROCEDURE FOR DESCRIPTION OF HEAVY PETROLEUM FRACTIONS

Selection of Fluids

Four fluids have been investigated in this work: Two synthetic fluids and two real fluids from different reservoirs in North Sea.

Synthetic Fluids

The compositions of both the synthetic fluids were based on a North Sea gas reservoir. Although a real mixture may have thousands of different components in the C6+ fraction, the C6+ fraction of the synthetic fluids was composed of only a few different components. This was done to make the synthetic mixture fairly ideal and also to use components with known thermophysical properties. In addition the model had a limit of 25 components. The synthetic fluids were included to create a case where the entire phase envelope was known.

Real Fluids

In addition to the synthetic mixtures, two fluids from different reservoirs were studied. One fluid was an oil sampled at the wellhead during a drill stem test (DST) of an exploration well. The other fluid was from a gas reservoir and was recombined in the laboratory from separate gas and liquid samples collected at the test separator during a

DST of the exploration well. Both fluids were assumed to be representative of the fluid from the respective reservoirs.

Experimental data

The "experimental" data for the synthetic fluids were actually generated from the SRK EOS as explained below from the knowledge of the composition and thermophysical properties of all the components in the mixtures. Since the data are generated, they are model (SRK) specific. Their value was to furnish a base case from which sensitivities to changes in the characterization could be evaluated on a well described mixture.

(1) A single flash calculation was performed for the fluid to standard temperature and pressure (STP is here defined at 15°C and 1 atmosphere absolute). The liquid was then taken as the stabilized condensate.

(2) A series of flash calculations at constant atmospheric pressure was then performed on the liquid to obtain a boiling point curve for the condensate.

(3) The vapor (distillate) was removed after each flash, and a bubble point or a flash computation was carried out on this product to determine the specific gravity of each distillate fraction. The molecular weight was also recorded for each distillate fraction.

The series of flash calculations was continued until most of the liquid was collected as overhead product, leaving only a very small fraction as bottom product (residue). In this way the whole boiling point curve was generated for the synthetic condensate, unlike the real mixtures where T(100) of the boiling point curves had to be correlated due to the cracking problems of the heavy hydrocarbons at high temperatures.

All PVT data of interest were generated from the known properties of the mixtures. The properties along with the components used in the simulations for the two synthetic fluids are shown in Table I (Erbar et al., 1986).

The same type of information was then available for all four fluids and can be summarized as follows:

A distillation with reported normal boiling point, molecular weight and specific gravity for each fraction.

A PVT study from which one or more points on the phase boundary were known, in addition to liquid drop out or GOR.

Characterization

The four fluids were characterized using Erbar's method (Maddox and Erbar, 1982) and the available experimental data. First, five different methods to predict the critical properties were evaluated. The methods were (1) Lee and Kesler (1976), (2) Riazi and Daubert (1980), (3) Cavett (1962), (4) Twu (1984) and (5) Winn (1957). The method proposed by Riazi and Daubert was then chosen for the rest of the work since it seemed to give a better, or equally good, match to the experimental PVT data before any adjustment procedures were carried out. The Raizi and Daubert correlation is included in Appendix A. The phase boundary was predicted and compared to the experimental data for each fluid. In addition, the GOR was predicted for the oil and the liquid drop out was predicted for the gas.

TABLE I

PURE COMPONENT PROPERTIES OF THE SYNTHETIC MIXTURES

Component Name	Tc DEG C	Pc BAR	Omega (SRK)	NBPT DEG C	Mol Wt	Liq. Density KG/M3
N2	-146.95	33.94	0.03346	-195.80	28.02	805.57
CO2	30.95	73.75	0.22500	-78.51	44.01	824.47
CH4	-82.57	46.04	0.00389	-161.52	16.04	299.55
C2H6	32.27	48.80	0.09440	-88.60	30.07	356.57
C3H8	96.67	42.50	0.14967	-42.10	44.10	505.70
IC4H10	135.00	36.48	0.18070	-11.73	58.12	561.45
NC4H10	152.03	37.97	0.19713	-0.50	58.12	582.91
IC5H12	187.28	33.81	0.22505	27.85	72.15	622.96
NC5H12	196.55	33.69	0.24901	36.07	72.15	629.37
NC6H14	234.35	30.12	0.29731	68.73	86.17	663.64
C6H6	289.01	48.98	0.20884	80.09	78.11	882.55
NC7H16	267.15	27.36	0.34754	98.43	100.20	686.39
o C7H8	318.64	41.04	0.26064	110.63	92.13	869.95
NC8H18	295.68	24.87	0.39741	125.67	114.22	704.97
o EB	344.05	36.00	0.30008	136.19	106.17	869.80
O-Xylene	357.15	37.30	0.30834	144.43	106.17	882.79

TABLE I (Continued)

Component Name	Tc DEG C	Pc BAR	Omega (SRK)	NBPT DEG C	Mol Wt	Liq. Density KG/M3
NC9H20	321.46	22.88	0.44563	150.82	128.25	719.87
NC10H22	344.55	21.04	0.49077	174.15	142.28	732.36
NC11H24	365.65	19.66	0.53975	195.93	156.31	742.13
NC12H26	385.05	18.24	0.58072	216.32	170.34	750.30
NC13H28	402.85	17.23	0.62920	235.47	184.37	757.83
NC14H30	419.85	16.20	0.66748	253.58	198.40	764.40
NC15H32	433.91	15.17	0.71899	270.61	212.42	769.85
NC16H34	448.85	14.20	0.74677	286.86	226.45	774.97
NC17H36	459.85	13.17	0.80037	302.17	240.48	779.30
* Diphenyl	516.00	38.00	0.35621	255.00	154.20	1028.98
* C20H42	494.00	11.00	0.01125	344.00	283.00	777.23

Erbar et. al., 1986

o = Only Synthetic Mixture 1

* = Only Synthetic Mixture 2 (Reid et al., 1977)

EB = Ethyl Benzene

Characterizations were carried out using HYPO*S, (Johannesen and Stange, 1986), the PVT predictions were performed by MAXI*SIM (Erbar, Johannesen and Majeed, 1986), and the phase envelopes used to visualize changes in the phase behavior were generated by TERMO (Pedersen, 1983).

Adjustments to the Initial Characterization

The characterization was adjusted by changing Tc, Pc, T(100), and the number of hypothetical components. Figure 2 show a flowchart of the adjustment procedure. The phase boundary and volumetric properties were predicted and compared to the experimental data and the initial predictions after each adjustment.

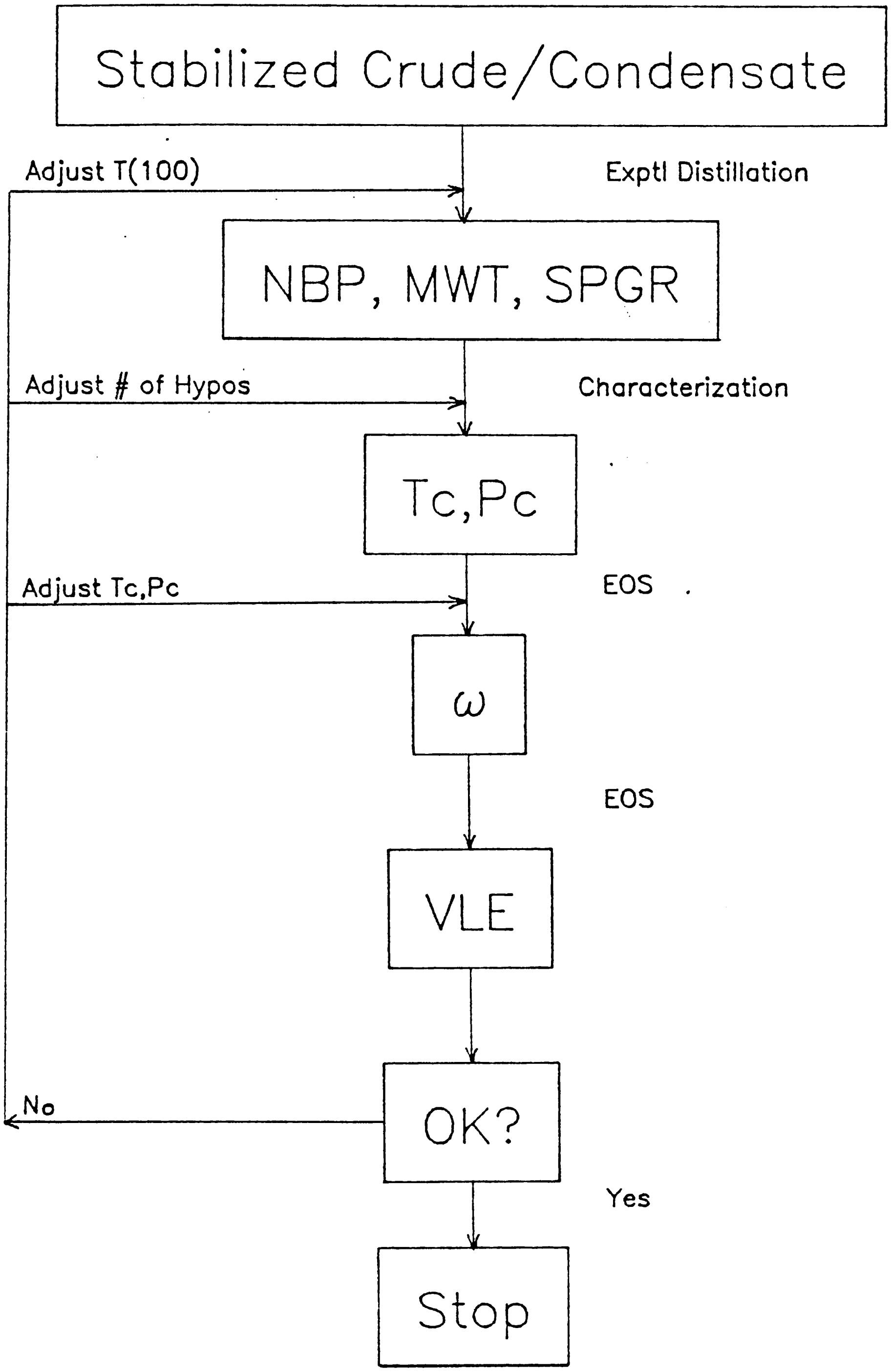

Figure 2. Adjustment Procedure Flowchart.

CHAPTER V

RESULTS AND DISCUSSION

Synthetic Fluids

The predicted dew points/bubble points at four locations on the phase envelope were compared to the experimental points for the two synthetic mixtures using ten hypothetical components. The four points were one bubble point and three dew points, including both the cricondenbar and the cricondentherm. The comparisons were repeated for each of the available critical property prediction methods and also after advanced characterization was carried out. The critical property prediction method by Riazi and Daubert gave the best optimum fit to the experimental data prior to any adjustment of the critical properties for the hypothetical components. However, the same fit to the experimental data could be obtained independently of the critical prediction method when advanced characterization was carried out. Figure 3 is a pictorial comparison of the predicted phase behavior for the five different critical property correlations using synthetic mixture 2. Appendix B includes a table of selected P,T points predicted from the five different critical property correlations and the correlated values for Tc and Pc used in the EOS. A comparison of the four predicted points using the Riazi and Daubert correlation for Tc and Pc for both synthetic mixtures with the "experimental" PVT data are listed in Tables II and III. Comparisons after critical property adjustments were performed are

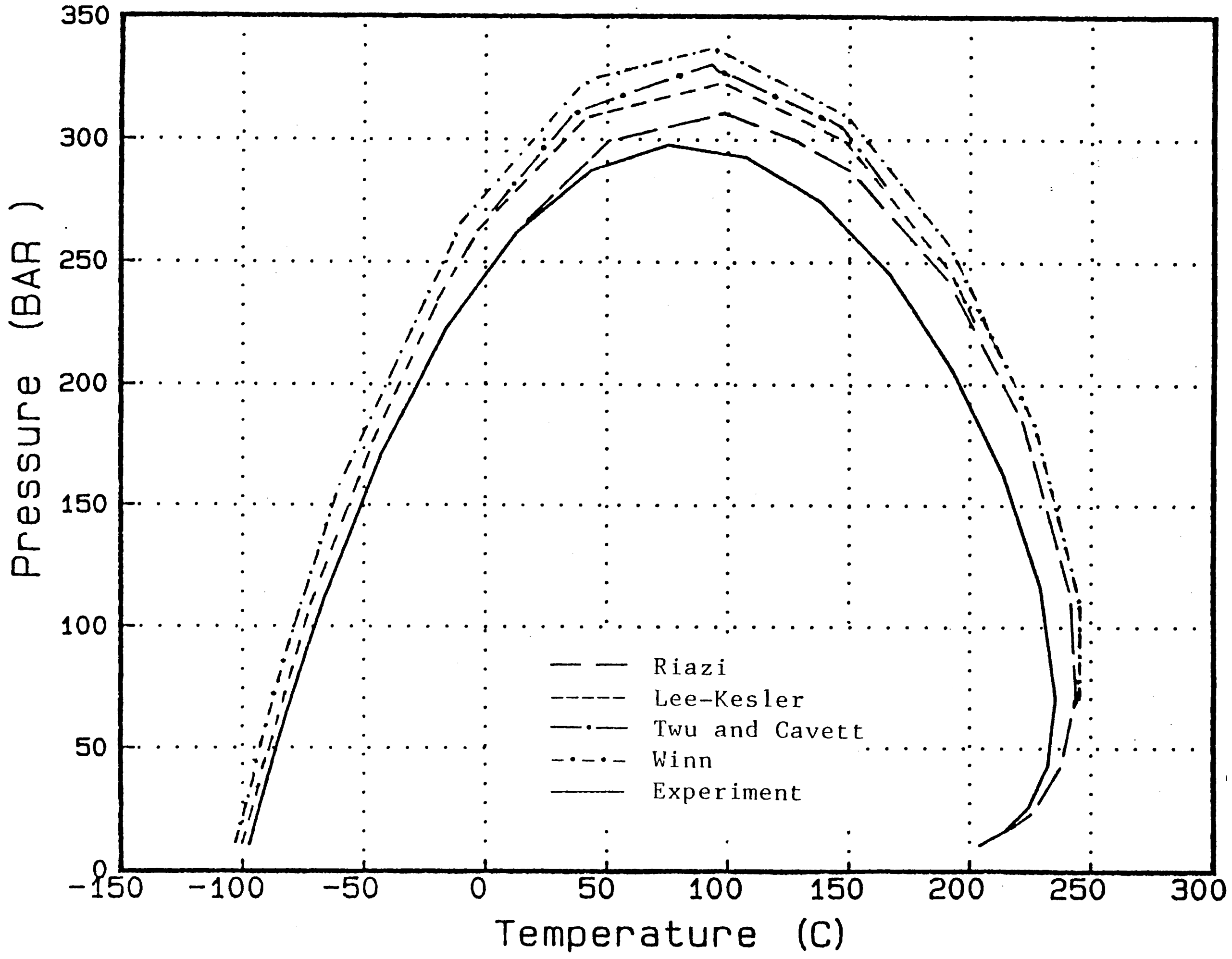

Figure 3. Synthetic Mixture 2. Comparison of Phase Behavior Predictions Using Different Correlations for Critical Properties.

TABLE II

PHASE BEHAVIOR SYNTHETIC MIXTURE 1
COMPARISON OF EXPERIMENTAL
AND PREDICTED DATA

	"Experiment"		Case 1				Case 2			
					Abs. Error				Abs. Error	
Phase	P[bar]	t[°C]	P[bar]	t[°C]	P[bar]	t[°C]	P[bar]	t[°C]	P[bar]	t[°C]
B. pt.	40.0	-84.5	40.0	-84.7	-	0.2	40.0	-84.1	-	0.4
D. pt.*	260.9	64.4	273.8	64.4	12.9	-	259.0	64.4	1.9	-
D. pt.	200.0	149.0	200.0	168.9	-	19.9	200.0	164.0	-	15.0
D. pt.**	66.6	193.0	66.6	203.6	-	10.6	66.6	202.4	-	9.4

*Cricondenbar
**Cricondentherm

Case 1: Tc and Pc from the Riazi and Daubert correlations.
Case 2: Pc from the Riazi and Daubert correlation, Tc adjusted to achieve a best possible match to the "experimental" phase behavior.

TABLE III

PHASE BEHAVIOR SYNTHETIC MIXTURE 2 COMPARISON OF EXPERIMENTAL AND PREDICTED DATA

	"Experiment"		Case 1				Case 2			
					Abs. Error				Abs. Error	
Phase	P[bar]	t[°C]	P[bar]	t[°C]	P[bar]	t[°C]	P[bar]	t[°C]	P[bar]	t[°C]
B. pt.	150.0	-51.0	150.0	-50.0	-	1.0	150.0	-45.5	-	5.5
D. pt.*	298.0	80.0	310.4	80.0	12.4	-	298.2	80.0	.2	-
D. pt.	200.0	196.0	200.0	214.0	-	18.0	200.0	209.6	-	13.6
D. pt.**	70.0	235.4	70.0	244.6	-	9.2	70.0	242.8	-	7.4

*Cricondenbar
**Cricondentherm

Case 1: Tc and Pc from the Riazi and Daubert Correlation
Case 2: Tc and Pc adjusted to achieve a best possible match to the "experimental" phase behavior.

also included. Due to the narrow boiling synthetic mixtures, the range of adjustments was limited. The tabulated result was the best overall fit that could be achieved using advanced characterization.

In addition to ten hypothetical components, five and ten hypothetical components were tried, but increasing or decreasing the number of components did not change the predicted phase boundary for these fluids. This result was to be expected due to the narrow boiling range of the C6+ fraction. Since the entire boiling point curve was known in this case, the T(100) was fixed and further adjustments could not be carried out. (The synthetic fluids have one degree of freedom less than the real fluids.)

Real Fluids

Gasmix1

The sensitivity in dew point to the number of hypothetical components is shown in Figure 4. The sensitivity in dew point to changes in T(100) is shown in Figure 5. Decreasing T(100) decreased the predicted dew point pressure around the cricondenbar and decreased the predicted dew point temperature around the cricondentherm. The same behavior was found by decreasing number of hypothetical components.

The change in dew point pressure as a function of the number of hypothetical components and T(100) is tabulated in Table IV for the one experimental dew point. As shown, the change in T(100) had no effect on the dew point when five or fewer hypothetical components were used to represent the whole C6+ fraction. Using 12 hypothetical components increased the dew point 19 bar. This means that as the slope of the upper end of the boiling curve increases more hypothetical components

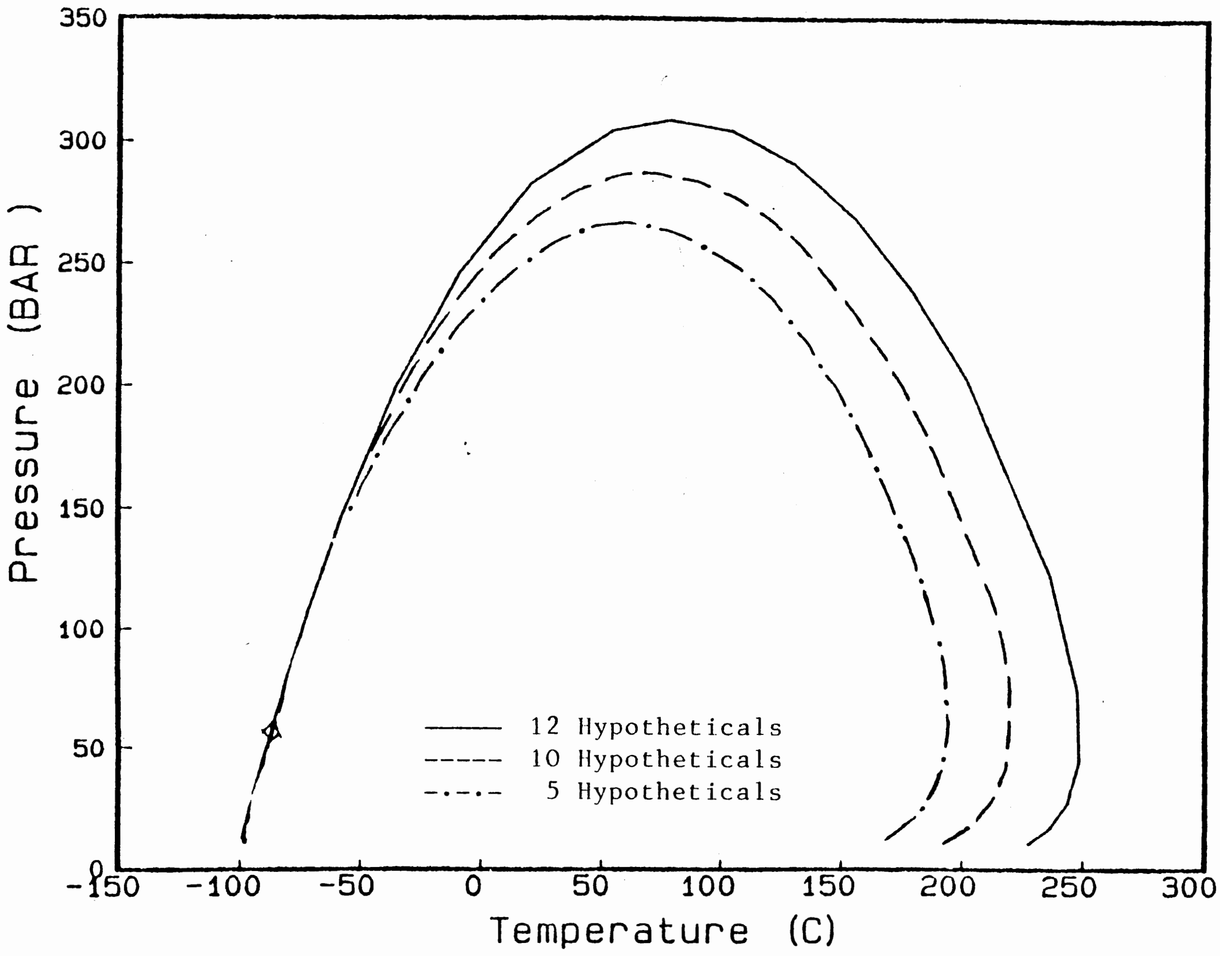

Figure 4. Phase Behavior of Gasmix1. The Sensitivity to Changes in the Number of Hypothetical Components.

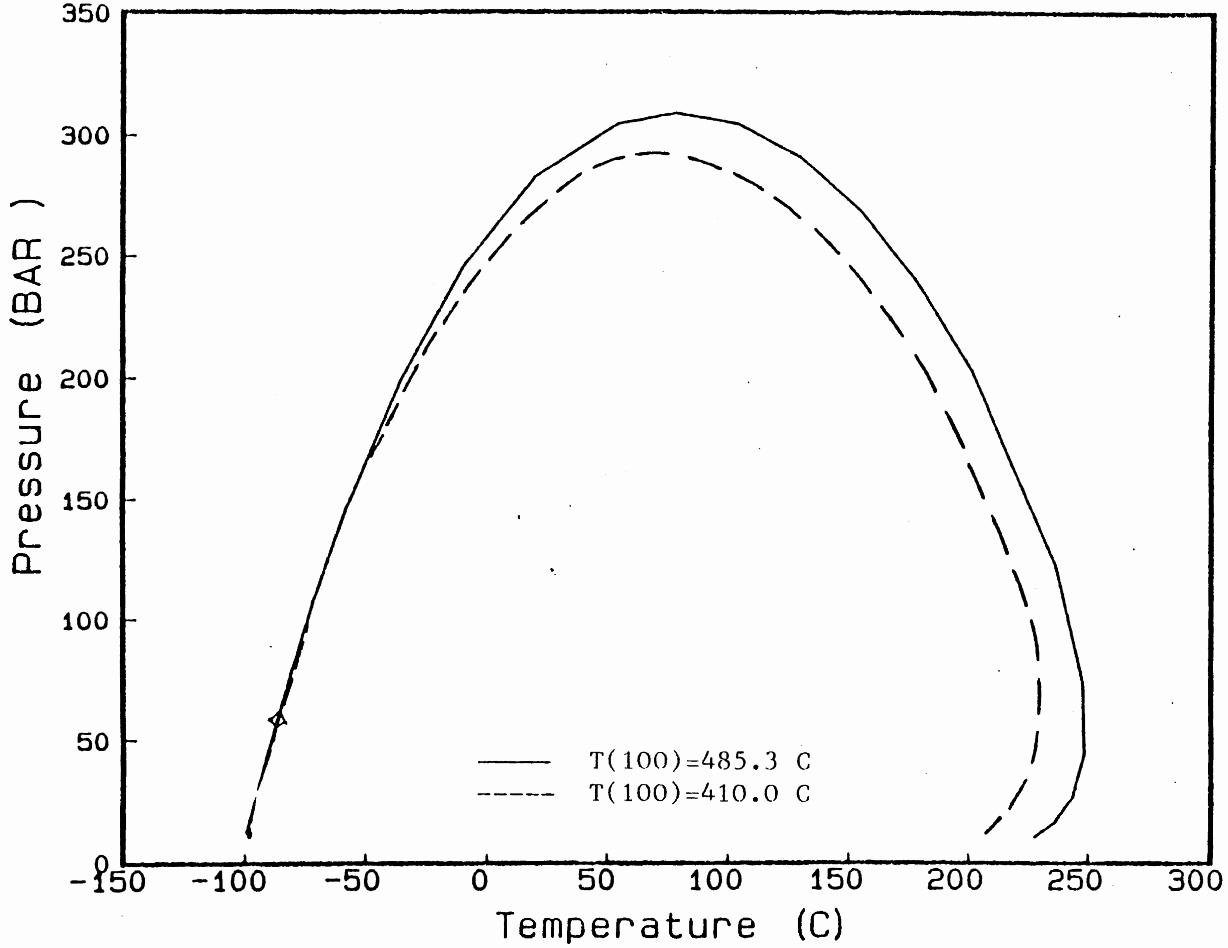

Figure 5. Phase Behavior of Gasmix1. The Sensitivity to Changes in T(100).

TABLE IV

DEW POINT OF GASMIX1 AS A FUNCTION OF NUMBER OF HYPOTHETICAL COMPONENTS AND T(100)

	Predicted Dew Point Pressure at 91.2°C P[bar]	
No. of Hypos.	T[100] = 485.3°C	T[100] = 410°C
1	221	221
5	261	261
10	283	-
12	308	287
Exptl.	259	259

are necessary to successfully describe this part of the curve. The experimental dew point was accurately matched using five hypothetical components (no adjustments of Tc and/or Pc were necessary); increasing the number of hypothetical components gave a dew point that was too high. This result indicates that the initial prediction of T(100) was too high. The match to the experimental dew point was significantly improved by shifting the T(100) of the boiling curve down when using more than five fractions.

The change in phase behavior as Tc is adjusted up to match the experimental dew point, and as Pc is adjusted down to match the same experimental dew point is shown in Figure 6. The respective change in Pc and Tc are shown in Figure 7 and 8. As seen, the whole phase envelope changes, but the area from cricondenbar to cricondentherm is the most sensitive. Changing Tc seem to alter the phase boundary around cricondentherm more than when Pc is used as adjustable parameter.

The effects of critical property adjustments on liquid drop out as a percentage of the dew point volume are shown in Figure 9. The observed decrease in liquid drop out as a percentage of the dew point volume after Tc was increased to match the one experimental dew point (or Pc was decreased to match the same point) is due to changes in both the predicted vapor volume and the predicted liquid volume. As mentioned, the liquid volumes predicted by COSTALD will increase with increasing Tc and/or decreasing Pc. Thus, one might expect the liquid dew point to increase with increasing Tc. However, the gas volume predicted from the EOS will also increase with increasing Tc and/or decreasing Pc. The change in the predicted gas volume was larger than the change in the predicted liquid volume, and the overall effect was a

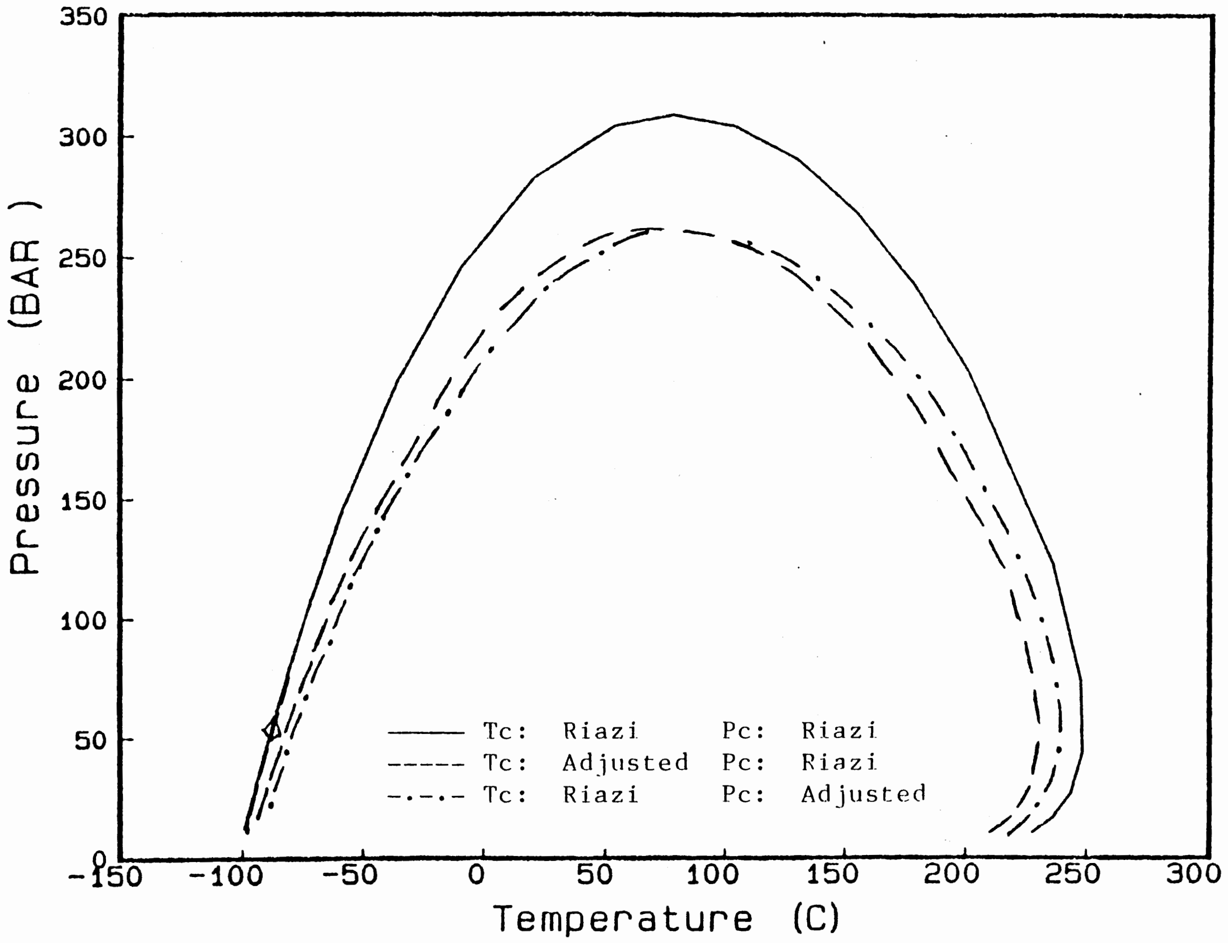

Figure 6. Phase Behavior of Gasmix1. Effect of Changing Tc or Pc to Match One Experimental Dew Point.

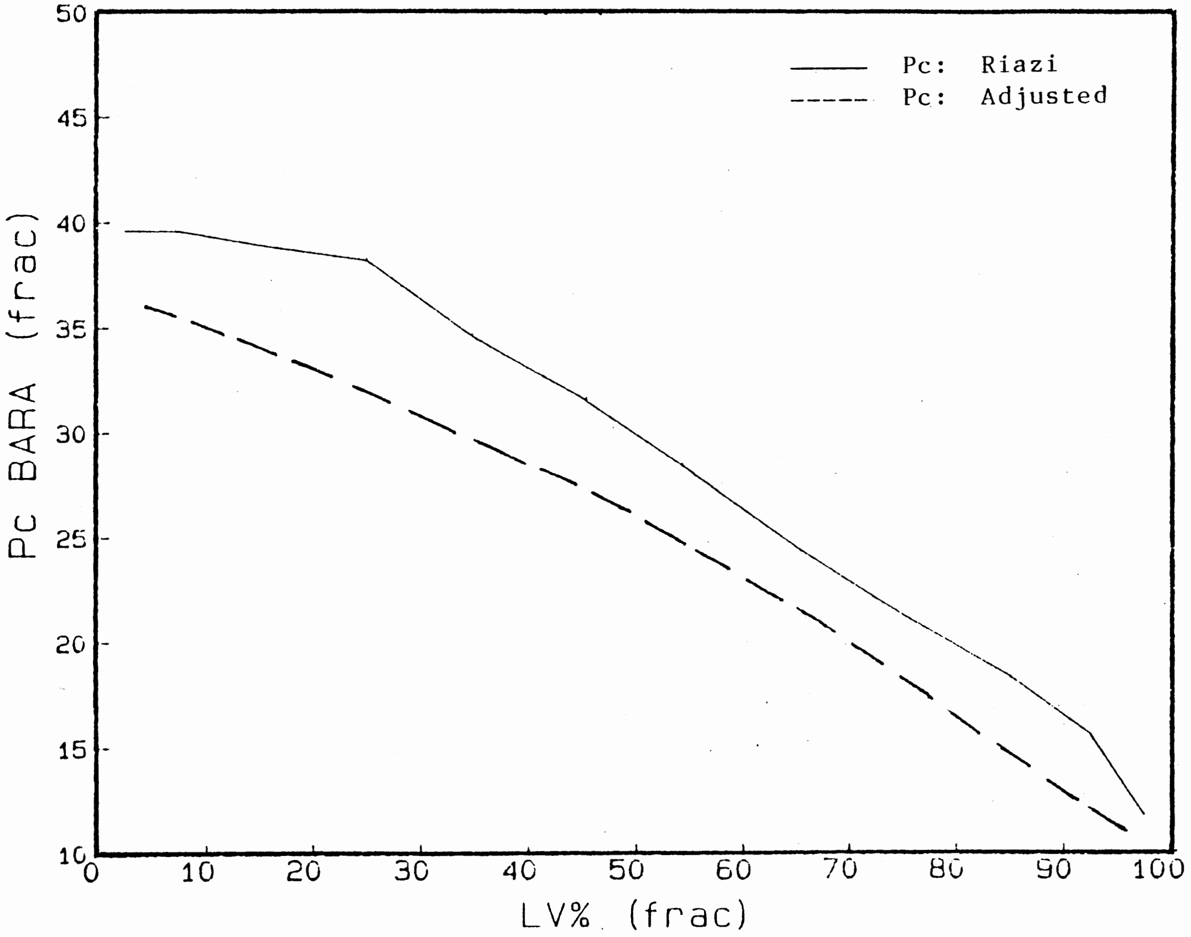

Figure 7. The Critical Pressures of the Hypothetical Components of Gasmix1 Before and After Adjustment to Match One Experimental Dew Point.

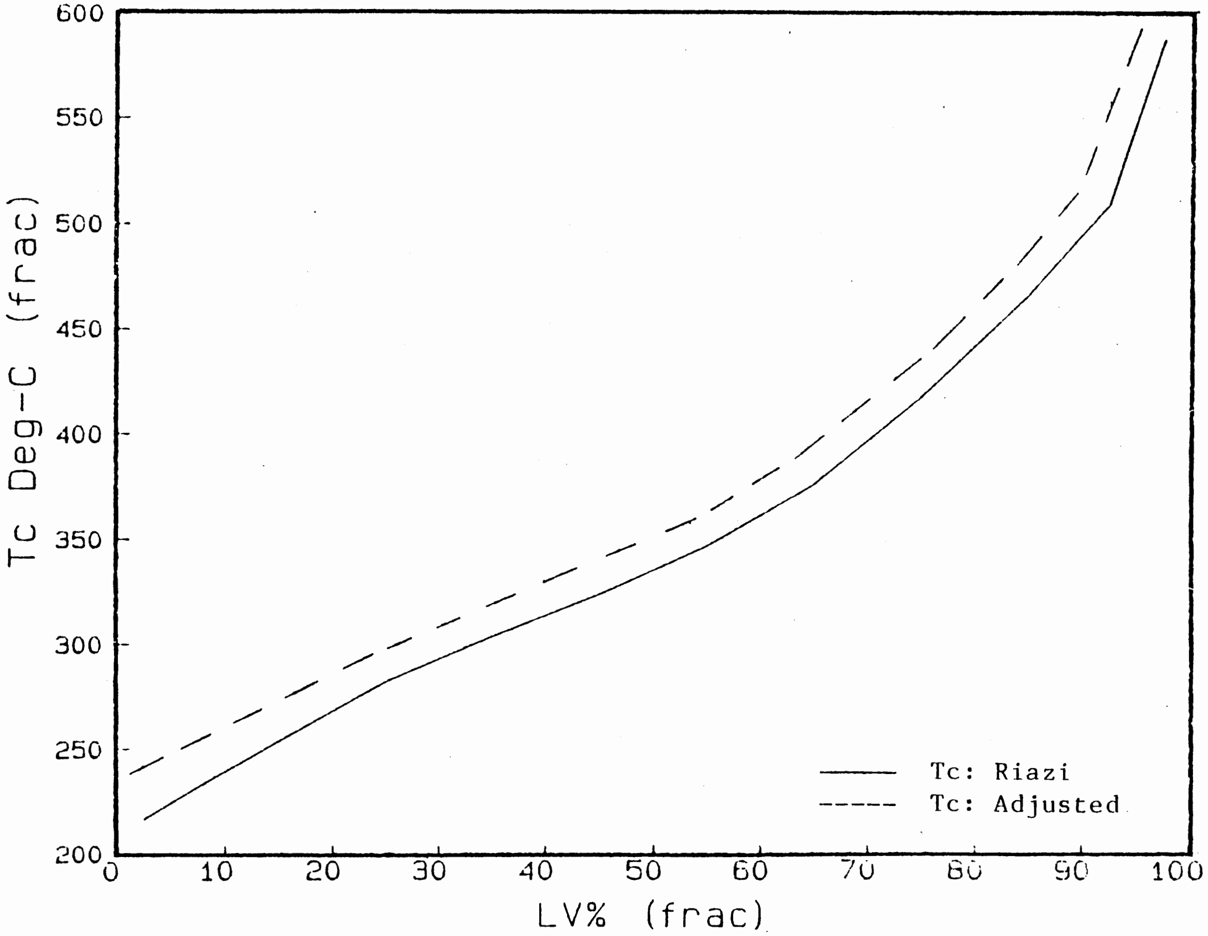

Figure 8. The Critical Temperatures of the Hypothetical Components of Gasmix1 Before and After Adjustment to Match One Experimental Dew Point.

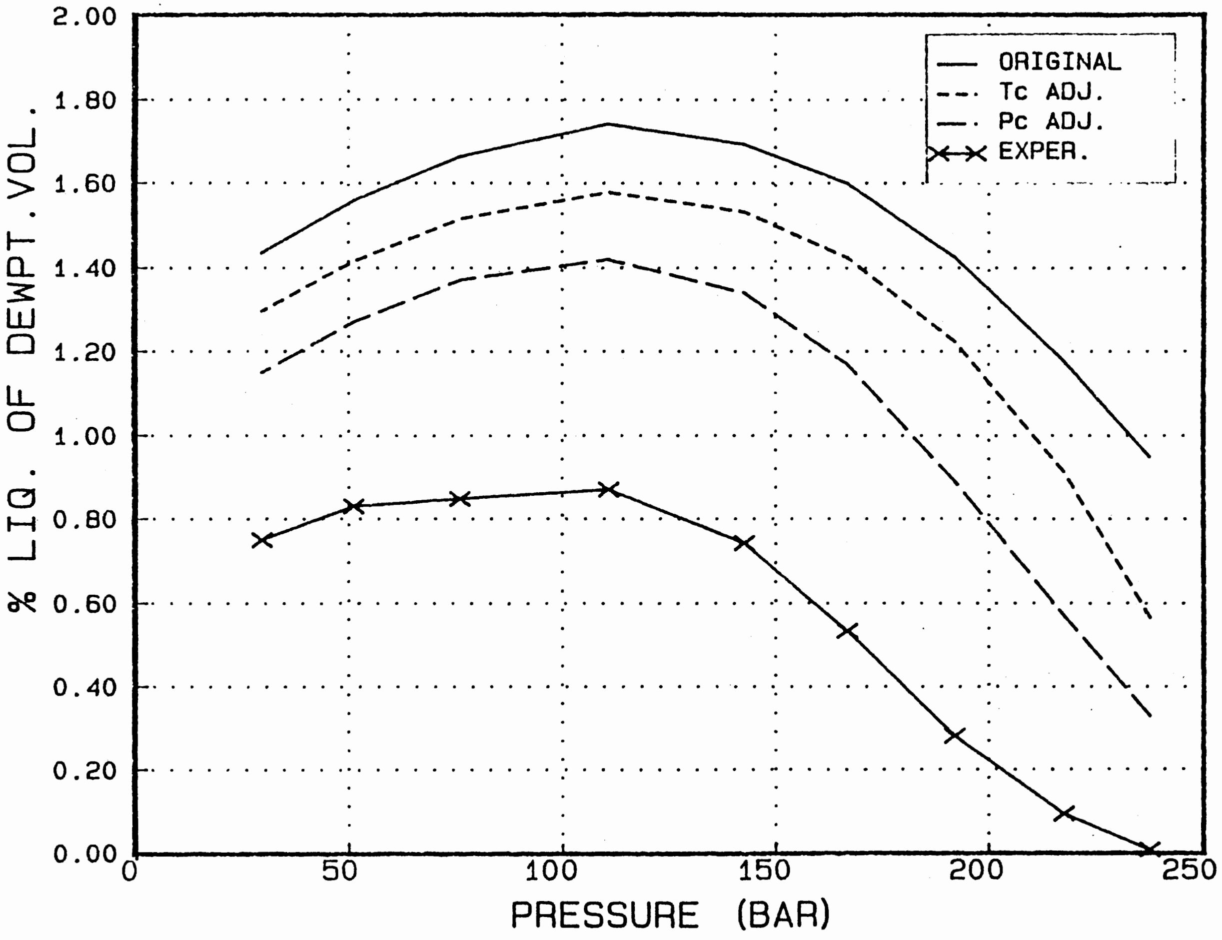

Figure 9. Gasmix1. Liquid Drop Out as Tc or Pc is Adjusted to Match One Experimental Dewpoint.

decrease in the liquid volume as a percentage of the gas volume. When Pc was adjusted to match the experimental dew point, a better fit to the experimental liquid drop out was obtained than when Tc was adjusted to achieve the same match to the experimental dew point. Even when Pc was adjusted, the prediction of liquid drop out was far from the experimental liquid drop out. A better agreement to the experimental liquid drop out could have been achieved by further adjustments of the critical properties, but this would also have given a discrepancy in the phase behavior, which was undesirable.

Figure 10 presents the liquid drop out as a function of the number of hypothetical components, and Figure 11 shows the effect of changing T(100).

The change in liquid drop out both with the number of hypothetical components and with T(100) was small. An increased liquid drop out was noted as the number of hypothetical components were decreased, and also as T(100) was shifted down.

Oilmix1

The change in the bubble point pressure with the number of hypothetical components is presented in Table V. The bubble point pressure increased with increasing number of hypothetical components used to define the C6+ fraction. Changing the number of hypothetical components from one to five increased the bubble point pressure as much as 16 bar, while further increasing the number of hypothetical components from five to twelve only increased the bubble point pressure 4 bar. These results indicate that five to ten hypothetical components

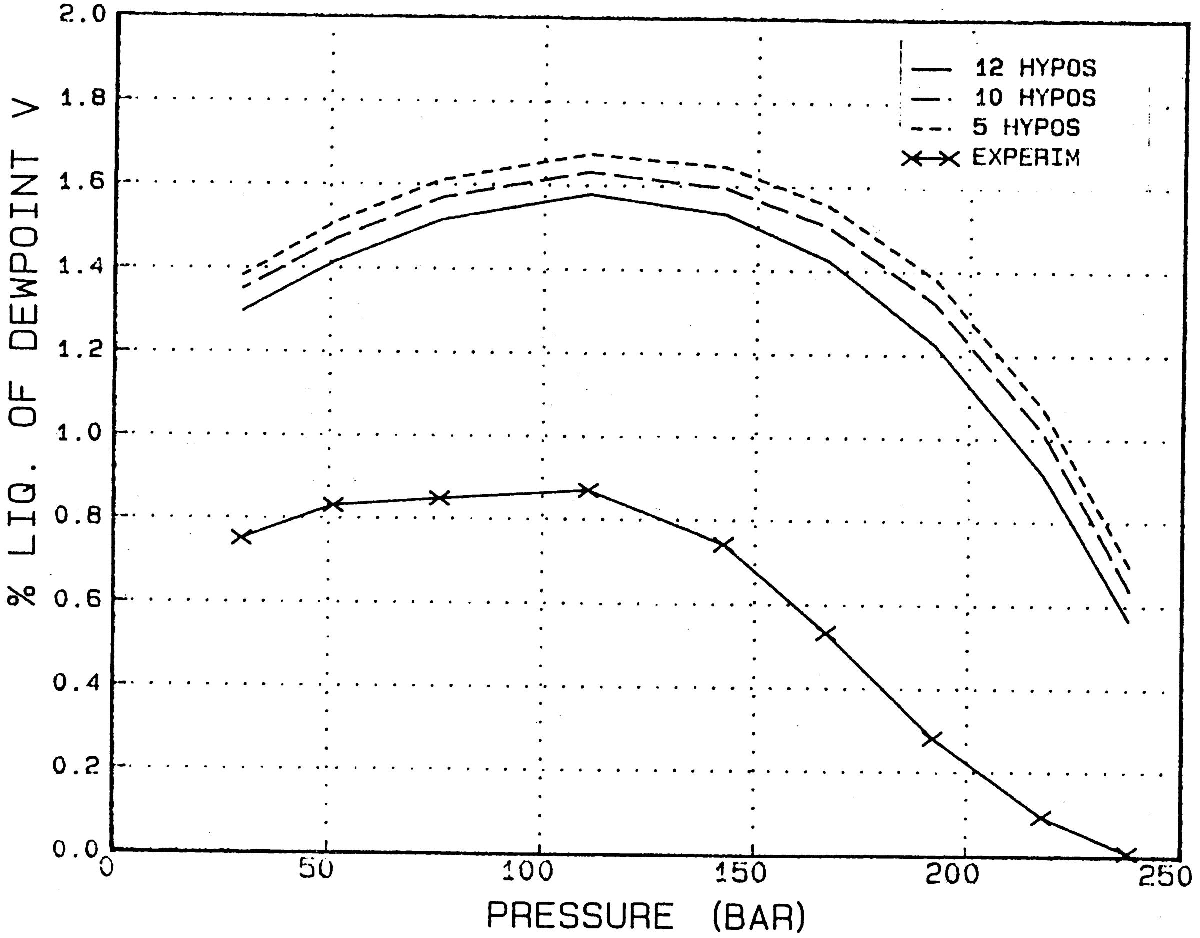

Figure 10. Gasmix1. Liquid Drop Out as the Number of Hypothetical Components is Changed.

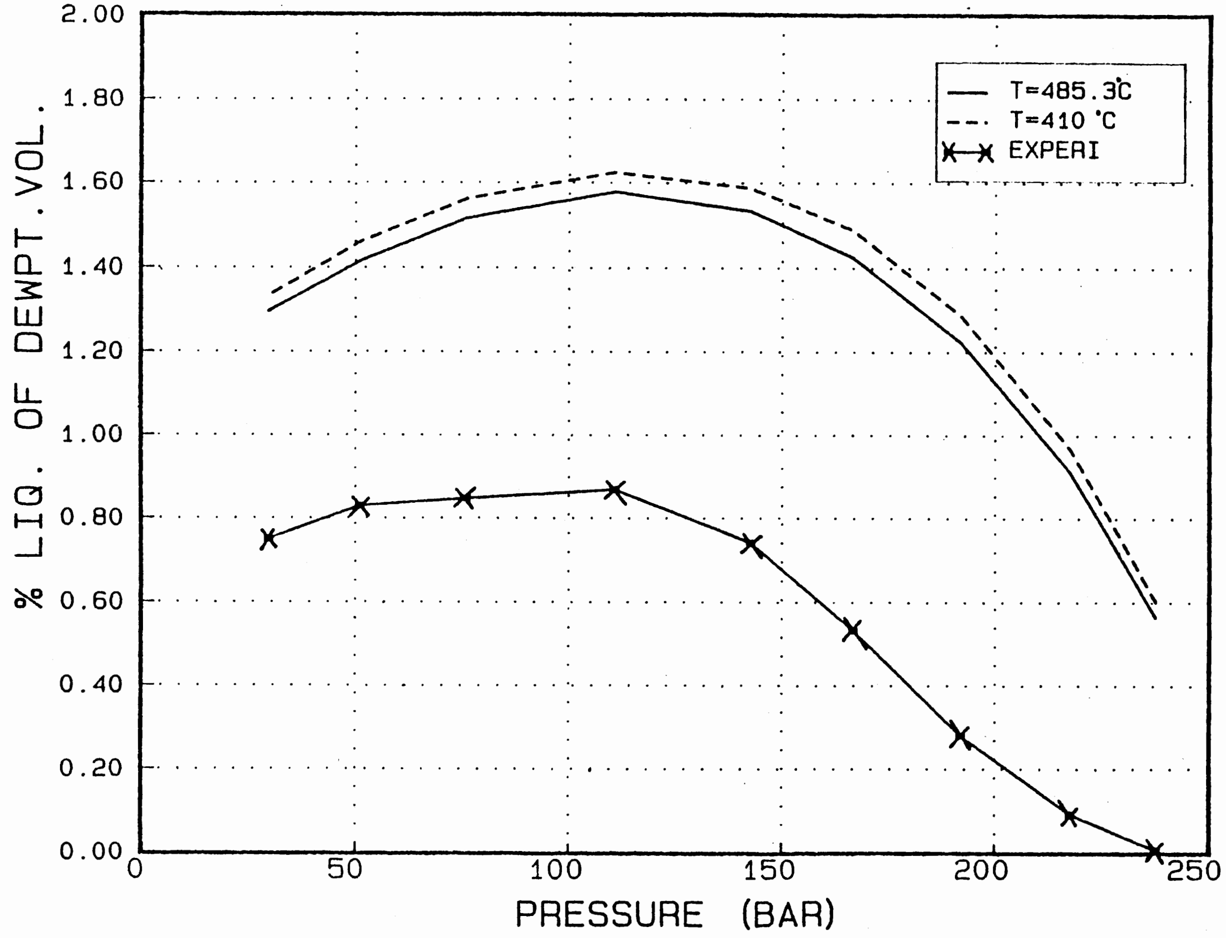

Figure 11. Gasmix1. Liquid Drop Out as T(100) is Changed.

TABLE V

BUBBLE POINT OF OILMIX1 AS A FUNCTION OF NUMBER OF HYPOTHETICAL COMPONENTS

No. of Hypos.	P[bar]
1	140.8
5	157.0
10	160.2
12	160.9
Exptl.	178.5

Predicted bubble point pressure at the reservoir temperature.

should be used in order to retain all the information from the experimental boiling curve.

The changes in bubble point pressure with T(100) are shown in Table VI. The bubble point pressure increased with increasing T(100), but not as drastically as was observed for gasmix1.

The change in the phase behavior for the whole phase envelope as Tc is adjusted down to match one experimental bubble point is shown in Figure 12.

The respective changes in Tc for the hypothetical components to match the one experimental bubble point are shown in Figure 13.

The phase boundary around the cricondentherm is not affected by the change in Tc while the cricondenbar is moved by 20 bar.

The solution GOR is compared to the experimental data before and after advanced characterization was performed. Figure 14 shows that the predicted GOR approaches the experimental GOR when the critical properties are adjusted to better match the experimental phase behavior. The observed decrease in GOR after Tc was decreased to match the one experimental bubble point is again due to changes in both the predicted vapor volume and the predicted liquid volume. The liquid volume predicted by COSTALD decreases with decreasing Tc. The gas volume predicted from the EOS also decreases with decreasing Tc. The dissolved gas volume decreased more than the liquid volume, and the overall effect was a decrease in the predicted solution GOR.

The Adjustment Procedure

A consistent way to change the initial characterization to provide a better representation of the phase boundary has been summarized.

TABLE VI

BUBBLE POINT OF OILMIX1 AS A FUNCTION OF T(100)

T(100)[°C]	P[bar]
720	160.2
770	164.9
850	166.7
Exptl.	178.5

Predicted bubble point pressure at the reservoir temperature

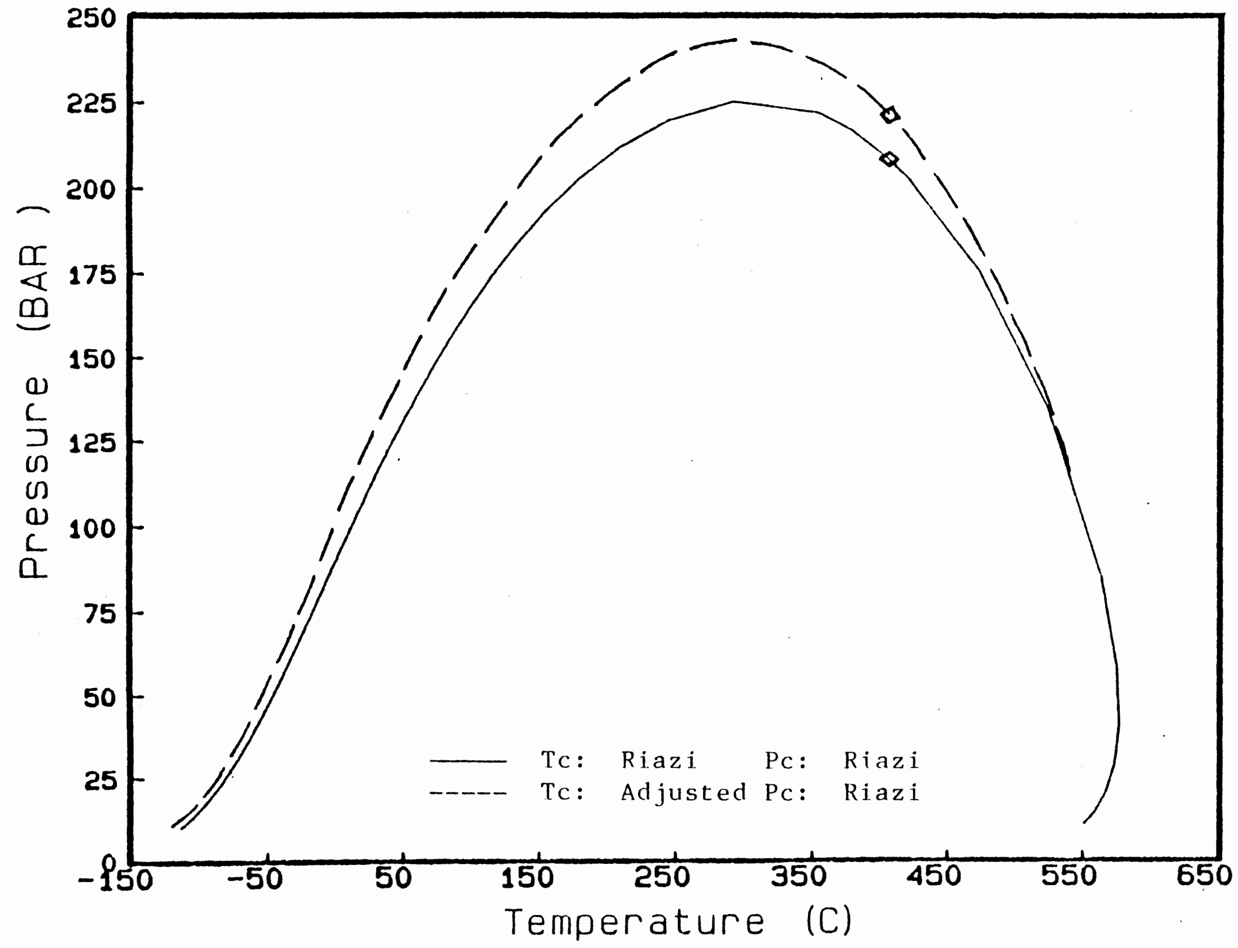

Figure 12. Phase Behavior of Oilmix1. The Effect of Changing Tc to Match One Experimental Bubble Point.

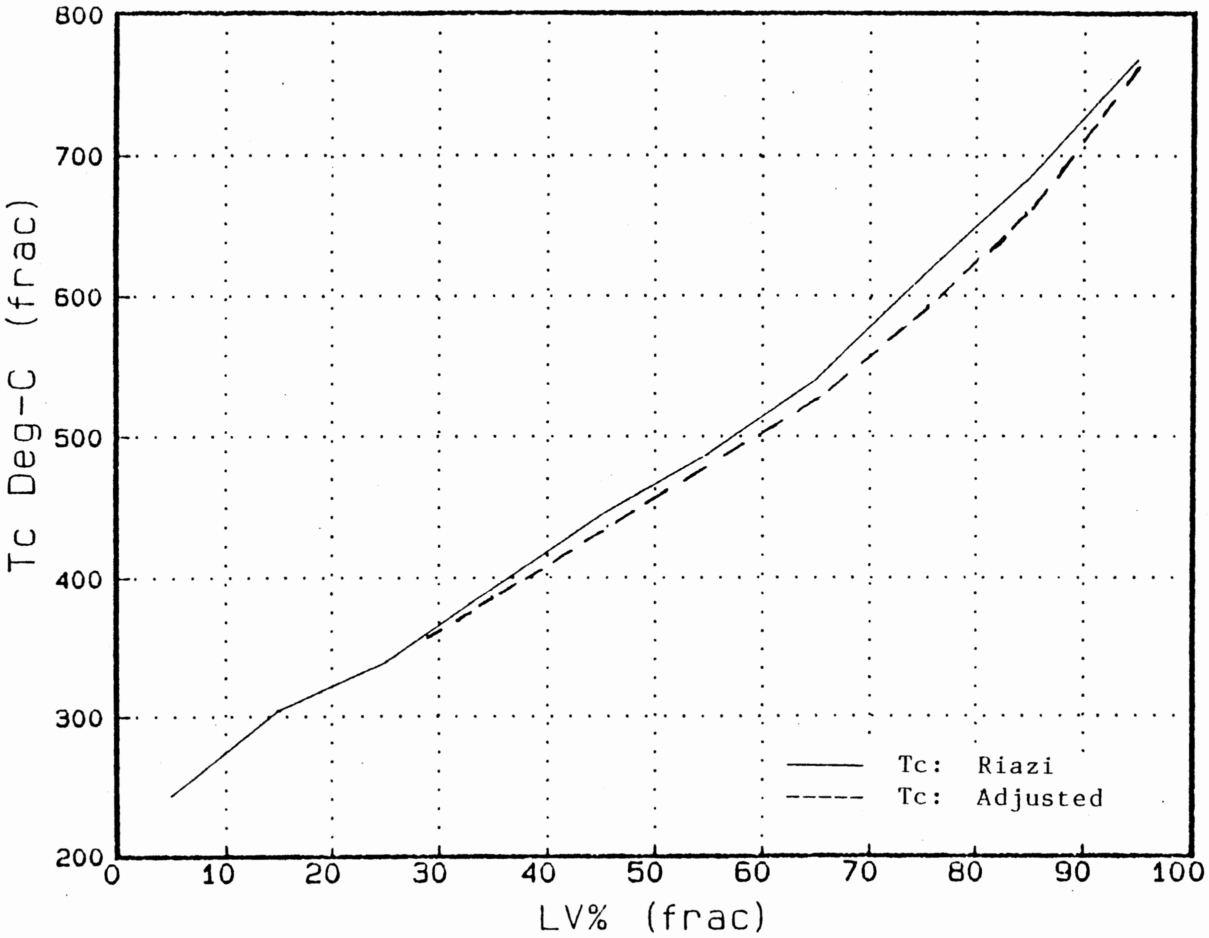

Figure 13. The Critical Temperatures of the Hypothetical Components of Oilmix1 Before and After Adjustment to Match One Experimental Bubble Point.

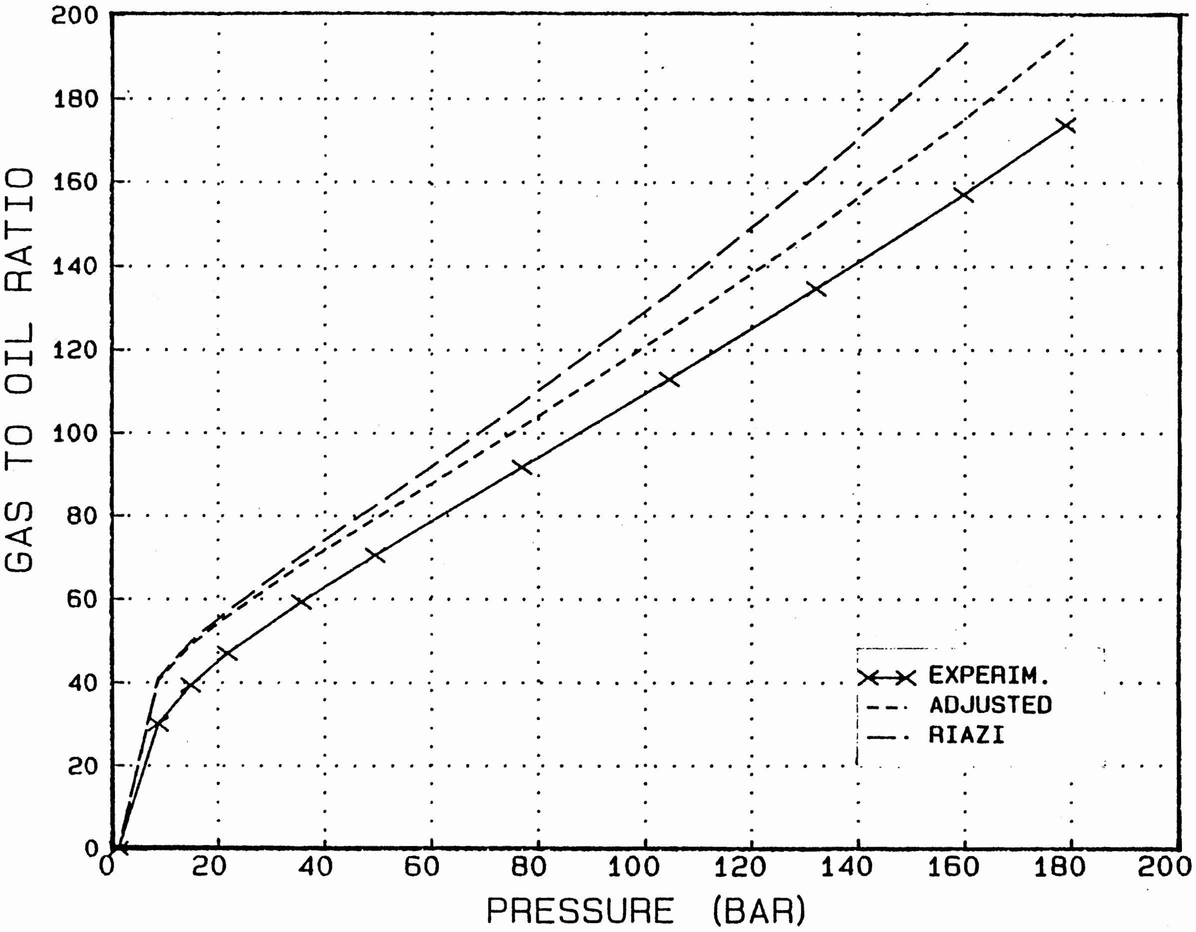

Figure 14. Oilmix1. The Solution Gas to Oil Ratio.

Advanced Characterization

Tc and/or Pc should be changed first, either one at a time starting with the heaviest hypothetical component and continuing through to the lighter hypothetical components, or all at one time. The advanced characterization can be carried out by adjusting only Tc, only Pc, or both Tc and Pc. The phase behavior around the cricondenbar is more sensitive to changes in Tc and/or Pc than the rest of the envelope. Decreasing Tc and/or increasing Pc will therefore make the phase envelope more egg shaped. The procedure for modifying Tc and Pc should be carried out following the guidelines given in Chapter 3.

Number of hypothetical Components

The number of hypothetical components used to represent the heavy fraction influences the phase boundary. Changes should be made if the characterization does not provide phase behavior predictions which match the experimental measurements. As the boiling point curve becomes more nonlinear, more hypothetical components are necessary to successfully represent the whole fraction. Also as the number of hypothetical components increases, the last component becomes very sensitive to the upper end of the boiling curve.

Increasing the number of hypothetical components will increase the predicted dew point or bubble point pressure around the cricondenbar, and increase the predicted dew point temperature around the cricondentherm, i.e. make the phase envelope more rounded. Decreasing the number of hypothetical components will give the opposite effect.

The Boiling Point Curve

The end of the boiling point curve represents a degree of freedom in the characterization work. Often as much as 30 volume percent liquid remains as bottom product in the still. The upper end of the boiling curve must therefore be correlated or manually extrapolated based on experience. Shifting this part of the curve up or down drastically changes the phase boundary, and this adjustment should always be considered when advanced characterization does not yield the desired phase behavior. Shifting T(100) up will increase the predicted dew point temperature at and around the cricondentherm and will increase the predicted dew point or bubble point pressure at and around the cricondenbar, i.e. make the phase envelope more rounded. Shifting T(100) down will give the opposite effect.

CHAPTER VI

SUMMARY

The sensitivity of the predicted phase boundary to changes in Tc, Pc, T(100) and the number of hypothetical components has been studied for four hydrocarbon fluids containing a C6+ fraction. Changes in selected volumetric properties were also noted. The C6+ fraction was initially characterized with hypothetical components given thermophysical properties as the real components. The critical properties Tc and Pc were then allowed to be adjustable, as were the number of hypothetical components. In addition the T(100) of the experimental boiling point curve was adjusted.

The predictions were compared to the available experimental data. The sensitivity on the phase envelope to changes in Tc, Pc, T(100) and the number of hypothetical components is summarized as follows:

1) Adjust Tc and/or Pc. The whole phase envelope will be affected, but the area around the cricondenbar will change most. Adjusting Tc down and/or Pc up will give a more eggshaped phase envelope, i.e., increase the predicted dew point or bubble point around the cricondenbar more than the changes for the rest of the envelope. Adjusting Tc up and/or Pc down will give a more rounded phase envelope, i.e. decrease the predicted dew point or bubble point around the cricondenbar more than the changes for the rest of the envelope.

2) Vary the number of hypothetical components to check that enough fractions are used to represent the entire boiling point curve. Increasing the number of hypothetical components will increase the predicted dew point or bubble point around the cricondenbar and increase the predicted dew point around the cricondentherm. This results in a more round phase envelope. Decreasing the number of hypothetical components have the opposite effect.

3) Adjust T(100). Increasing T(100) will increase the predicted dew point or bubble point pressure at and around the cricondenbar, and increase the prediction of dew point temperature around the cricondentherm. As for changing number of hypothetical components this gives a more rounded phase envelope.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

The conclusions from this study are:

1) Modifications of the initial C6+ characterization of a hydrocarbon fluid are often necessary to obtain the optimum predictions of the phase behavior.

2) The adjustments of Tc and/or Pc are important, but the experimental distillation curve should also be monitored carefully throughout the characterization work, since shifting T(100) of the boiling point curve up or down alters the phase envelope significantly. Also the number of hypthetical components must be chosen so that they represent all information in the experimental boiling point curve.

3) The critical property prediction method by Riazi and Daubert was found to give better or equally good predictions of the phase behavior than the other correlations tried. An equally good match to the experimental PVT data could be achieved independently of critical property correlation once advanced characterization was performed.

4) The adjustments carried out to improve the phase behavior predictions were found to also improve the volumetric properties predictions. The predictions of the volumetric properties were still poor, since the major concern was to tune the phase behavior. To

achieve better volumetric predictions the density correlation should be curve fitted to heavy petroleum fractions.

Only one point on the phase envelope was measured experimentally for the real fluids used in this work, but several experimental points should be requested to achieve a better curve fit to the whole phase envelope.

A Possible expansion beyond scope of this work is a study allowing the binary interaction parameters to be adjustable while the critical properties are kept constant at the initially predicted values. This could determine whether one method is to be preferred over the other.

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APPENDIX A

CRITICAL PROPERTY PREDICTION METHOD BY RIAZI AND DAUBERT

The correlations suggested by Riazi and Daubert is fairly simple, and has the form:

$$Tc = 24.278(Tb^{.58848})(SG^{.3596})$$

$$Pc = 3.12281(10^{9})(Tb^{-2.3125})(SG^{2.3201})$$

where:

Tb is the normal boiling point in Rankine.

Tc is the critical temperature in Rankine.

SG is the specific gravity.

Pc is the critical pressure in psia.

The critical properties are correlated for each PNA group, and then the value for the hypothetical component is computed as a weighted sum:

$$T_c = (X_P \cdot T_c)_P + (T_N \cdot T_c)_N + (X_A \cdot T_c)_N$$

$$P_c = (X_P \cdot P_c)_P + (X_N \cdot T_c)_N + (X_A \cdot T_c)_A$$

where:

X_P is the molefraction of paraffins

X_N is the molefraction of naphtenes

X_A is the molefraction of aromatics

For pure components the critical and pseudocritical (molar average) properties are identical, but since every hypothetical component actually is a mixture of many real components within a narrow boiling range, the correlated Tc and Pc for the hypothetical components will always be the pseudo critical properties. The Riazi and Daubert correlation is reported to stay within 1.3 percent of the data used in the curve fit, but experience with North Sea oil and gas has demonstrated the necessity of letting Tc and Pc for the hypothetical components be adjustable parameters to obtain an optimum fit to the experimental phase behavior data.

APPENDIX B

EFFECT OF CRITICAL PROPERTY PREDICTION METHOD ON THE PHASE BEHAVIOR

Tables VII and VIII show the predicted data for both synthetic mixtures at four selected points on the phase envelope as compared to the "experimental" data. The C6+ fractions were characterized using five different critical property prediction methods: Riazi and Daubert (1980), Lee and Kesler (1976), Cavett (1962), Twu (1984), and Winn (1957). Tables IX and X show the estimated critical properties using the five different correlations.

The two extreme points, the cricondenbar and the cricondentherm, and the phase boundary between them, represent the area on the phase boundary where the largest discrepancies between experimental and predicted data normally are found.

The relatively large disagreements between predicted and experimental bubble points for Synthetic Mixture 2 is due to convergence problems near the critical point.

As can be seen, the Riazi and Daubert correlation produced the closest match to the experimental phase envelope for the two synthetic mixtures. Similar results were obtained for Gasmix1 but the Cavett and the Riazi and Daubert methods led to approximately equal predictions of the one experimental dew point.

TABLE VII

PHASE BEHAVIOR SYNTHETIC MIXTURE 1. COMPARISON OF EXPERIMENTAL AND PREDICTED DATA FOR DIFFERENT CRITICAL PROPERTY PREDICTION METHODS

Phase	Exp. P[bar]	Exp. T[°C]	Prediction Method	P[bar]	T[°C]	Abs. Error P[bar]	Abs. Error T[°C]
B.pt.	40.0	-84.5	Riazi and Daubert	40.0	-84.7	-	.2
			Lee and Kesler	40.0	-85.2	-	.7
			Cavett	40.0	-85.4	-	.9
			Twu	40.0	-85.1	-	.6
			Winn	40.0	-85.5	-	1.0
D.pt.*	260.9	64.4	Riazi and Daubert	273.8	64.4	12.9	-
			Lee and Kesler	286.8	64.4	25.9	-
			Cavett	294.7	64.4	33.8	-
			Twu	289.2	64.4	28.3	-
			Winn	295.0	64.4	34.1	-
D.pt.	200.0	149.0	Riazi and Daubert	200.0	168.9	-	19.9
			Lee and Kesler	200.0	172.2	-	23.2
			Cavett	200.0	174.6	-	25.6
			Twu	200.0	174.4	-	25.4
			Winn	200.0	174.5	-	25.5

TABLE VII (Continued)

						Abs. Error	
Phase	Exp. P[bar]	Exp. T[°C]	Prediction Method	P[bar]	T[°C]	P[bar]	T[°C]
D.pt.**	66.6	193.0	Riazi and Daubert	66.6	203.6	-	10.6
			Lee and Kesler	66.6	204.2	-	11.2
			Cavett	66.6	204.5	-	11.5
			Twu	66.6	205.1	-	12.1
			Winn	66.6	204.9	-	11.9

*Cricondenbar
**Cricondentherm

TABLE VIII

PHASE BEHAVIOR SYNTHETIC MIXTURE 2. COMPARISON OF EXPERIMENTAL AND PREDICTED DATA FOR DIFFERENT CRITICAL PROPERTY PREDICTION METHODS

Phase	Exp. P[bar]	Exp. T[°C]	Prediction Method	P[bar]	T[°C]	Abs. Error	
						P[Bar]	T[°C]
B.Pt	150.0	-51.0	Riazi and Daubert	150.0	-50.0	-	1.0
			Lee and Kesler	150.0	-56.6	-	5.6
			Cavett	150.0	-59.1	-	8.1
			Twu	150.0	-58.1	-	7.1
			Winn	150.0	-63.2	-	12.2
D.Pt*	298.0	80.0	Riazi and Daubert	310.4	80.0	12.4	-
			Lee and Kesler	322.5	80.0	24.5	-
			Cavett	327.1	80.0	29.1	-
			Twu	328.1	80.0	30.1	-
			Winn	336.8	80.0	38.1	-
D.Pt	200.0	196.0	Riazi and Daubert	200.0	214.0	-	18.0
			Lee and Kesler	200.0	215.6	-	19.6
			Cavett	200.0	216.9	-	20.9
			Twu	200.0	218.3	-	22.3
			Winn	200.0	219.2	-	23.3

TABLE VIII (Continued)

Phase	Exp. P[bar]	Exp. T[°C]	Prediction Method	P[bar]	T[°C]	Abs. Error	
						P[Bar]	T[°C]
D.Pt**	70.0	235.4	Riazi and Daubert	70.0	244.6	-	9.3
			Lee and Kesler	70.0	244.9	-	9.5
			Cavett	70.0	244.6	-	9.2
			Twu	70.0	245.7	-	10.3
			Winn	70.0	246.1	-	10.7

*Cricondenbar
**Cricondentherm

TABLE IX

CRITICAL TEMPERATURE OF SYNTHETIC MIXTURE 2

	Tc[°C]				
Hypo. No.	R. and D.	Lee and Kesler	Cavett	Twu	Winn
1	321.24	318.22	317.61	320.65	315.00
2	344.07	340.73	341.37	344.24	337.46
3	360.01	356.48	358.19	360.61	353.38
4	375.01	371.24	374.05	375.92	368.47
5	390.09	385.98	389.98	391.23	383.72
6	405.20	400.67	405.88	406.48	399.03
7	419.57	414.57	420.97	420.91	413.65
8	433.14	427.64	435.26	434.45	427.57
9	447.43	441.26	450.46	448.61	442.41
10	468.41	461.14	472.94	469.31	464.32

R. and D.: Riazi and Daubert

TABLE X

CRITICAL PRESSURE OF SYNTHETIC MIXTURE 2

Hypo. No.	Pc[bar] R. and D.	Lee and Kesler	Cavett	Twu	Winn
1	23.93	24.45	25.24	25.17	24.56
2	22.46	23.13	24.03	23.60	23.12
3	21.04	21.70	22.65	22.19	21.68
4	19.69	20.28	21.25	20.84	20.31
5	18.42	18.90	19.85	19.52	19.02
6	17.30	17.65	18.56	18.31	17.88
7	16.32	16.53	17.38	17.22	16.88
8	15.34	15.38	16.19	16.14	15.88
9	14.18	13.96	14.74	14.86	14.68
10	12.66	12.04	12.83	13.14	13.10

R. and D.: Riazi and Daubert

)

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