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STEAM DISTILLATION EFFECT AND OIL QUALITY CHANGE DURING STEAM INJECTION

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January 1992

Performed Under Contract No. FG22-90BC14600

Stanford University
Petroleum Research Institute
Stanford, California

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ABSTRACT

Steam distillation is an important mechanism which reduces residual oil saturation during steam injection. It may be the main recovery mechanism in steamflooding of light oil reservoirs. As light components are distilled from the residual (initial) oil, the residuum becomes heavier. Mixing of the distilled components with the initial oil results in a lighter produced oil.

A general method has been developed to compute steam distillation yield and to quantify oil quality changes during steam injection. The quantitative results are specific because the California crude data bank was used. But general principles were followed and calculations were based on information extracted from the DOE crude oil assay data bank.

It was found that steam distillation data from the literature can be correlated with the steam distillation yield obtained from the DOE crude oil assays. The common basis for comparison was the equivalent normal boiling point.

Blending of distilled components with the initial oil results in API gravity changes similar to those observed in several laboratory and field operations.

1. INTRODUCTION

In a steamflood, four zones may be recognized. A steam zone precedes a condensed hot water and hydrocarbon zone, which in turn precedes a cold water front and reservoir fluids. In essence, a cold waterflood and then hot waterflood occurs ahead of the steam zone.

Willman et al. (1961) studied the contributions of various oil recovery mechanisms associated with steam injection. They concluded that the principal mechanisms responsible for additional oil recovery are thermal expansion of oil, viscosity reduction and steam distillation. Studies by Duerksen and Hsieh (1983) concluded that steam distillation yields can be significant, even for heavy crudes.

Steam distillation is the main mechanism which reduces the residual oil saturation behind the hot water front during a steamflood. Willman et al. (1961) also concluded that the steam zone residual oil saturation is independent of the initial oil saturation. At a given steam injection pressure or temperature, the residual oil saturation is essentially composition dependent.

In reservoirs containing light oil, steam distillation is the major mechanism contributing towards improved recovery. The recognition of steam distillation drive as an important enhanced recovery method has been discussed by Blevins et al. (1984).

If the residual oil changes in composition, the produced oil will also change. If the residual becomes heavier, the displaced oil must become lighter. This fact has been observed in field test results. It is also apparent in laboratory in-situ combustion tube run experiments. An increase of 2 to 4° API in the gravity of produced oil has been observed both during laboratory experiments (Willman et al., 1961) and field tests (Konopnicki et al., 1979, Valleroy et al., 1967, Volek and Pryor, 1972). The residual oil in the steam zone has a high content of heavy components. Similar observations have been made during in-situ combustion field tests (Gates and Ramey, 1958).

To our knowledge, this sort of information has not been used in interpretation of results or for operational control. A major objective of this study is to investigate changes in quality of produced oil compared to the initial oil. Existing laboratory and field data will be interpreted in the light of the findings. The primary source of information for this study will be the Department of Energy (DOE) crude oil analysis data bank. It contains crude oil analyses of all major U.S. oil fields by the Bureau of Mines routine method distillation.

Information on crude oil quality changes during steamflooding are useful. Assuming that the amount and quality of initial and produced oil are known, the amount and API gravity of the residual oil can be calculated from a material balance.

Information on residual oil saturation can be related to fuel concentration for in-situ combustion. Wu and Fulton (1971) have shown that during an in-situ combustion process, the mechanisms ahead of the combustion front resemble those of a steamflooding process. Knowledge of fuel concentration and composition would enable computation of air injection requirements during an in-situ combustion process.

2. STATEMENT OF THE PROBLEM

Quantification of oil quality changes during steam injection requires understanding of the major phenomena associated with the process. Steam distills lighter components, leaving behind heavier residuum. Blending of the lighter distilled components with the initial oil results in produced oil with higher °API gravity.

The main objective is to quantify these phenomena. For a given steam distillation condition, questions which should be answered are:

- What is the steam distillation yield?
- What is the quality or API gravity of the distilled portion?
- How much heavier does the residuum become?
- What API gravity change can be expected when the distilled components are mixed with the initial oil?

The DOE crude oil analysis data bank will serve as the main source of information. A basis of correlating the DOE data with steam distillation data will be established. Information derived from the DOE data will be used to answer the questions posed. The results will be verified by comparison with experimental data published in the literature.

3. LITERATURE REVIEW

One of the earliest and most comprehensive studies on oil recovery mechanisms associated with steam injection was reported by Willman et al. (1961). Crude oils, Napoleum (100% distillable at experimental conditions) and Primol (non-distillable at experimental conditions) were used in core flood experiments. They concluded that the principal oil recovery mechanisms are thermal expansion, viscosity reduction and steam distillation. Oil recovery by steam injection is higher for light oils than heavy oils because lighter oils contain high fractions of steam distillable components. Willman et al. also concluded that for a given oil and rock residual oil saturation in the steam zone is independent of the initial oil saturation.

Sukkar (1966) proposed a method of calculating oil distilled during steamflooding of light oil. The method used relative velocities of steam, condensing steam front and velocities which described the rate at which particular oil components were being distilled. The solution was influenced by reservoir properties and oil composition. Results of other investigators have indicated that steam distillation yield is independent of reservoir properties (for example Wu and Brown, 1975).

Johnson et al (1971) presented a method to calculate oil vaporization during steamflooding. Three quantities were calculated sequentially:

1. the volume of steam condensed at the steam front,
2. the volume of immobile oil left behind the hot-water zone, and
3. percentage of oil vaporized as a function of volume of steam and volume of immobile oil left behind the hot-water zone.

The oil vaporization involved a series of flash calculations for which an appropriate set of equilibrium ratios (K-values) was required. Oil composition corresponding to Bureau of Mines routine method distillation fractions were used in the calculations. The results were in essence dictated by the selected K-values. Comparisons with experimental data showed that the method overestimated the amount of oil vaporized.

Wu and Brown (1975) studied the steam distillation yield of crude oil in porous media. Six crude oils ranging from 9° to 36° API were used. Cumulative yields ranged from 7 to 68 volume percent. They concluded that yields were independent of the porous medium used, steam injection rate and initial oil volume. They also observed that superheating the steam significantly increased the yield for some crude oils.

Konopnicki et al. (1979) conducted several steam distillation experiments during the design of the Shiells Canyon field steam-distillation drive pilot project. They observed that 57 volume percent of a 35.15° API oil was steam distillable at 456° F. Density of the residual oil was estimated by material balance to be 25.6° API at 76° F.

Rhee and Doscher (1980) presented a semianalytical method for calculating oil recovery by steam flooding. The method accounted for effects of steam distillation and gravity override of steam. They divided the crude oil into twelve components on the basis of Bureau of Mines routine method distillation cuts. Fraction 12 and higher were treated as nonvolatile. Regression on experimental data (in this case a 36° API oil) was used to obtain appropriate coefficients relating cumulative yield to the logarithm of molecular weights. Although the matches between calculated and experimental yields were good, the method is essentially curve fitting of experimental data. Both crude oil composition and experimental steam distillation yield must be known to apply this approach.

Duerksen and Hsieh (1983) performed steam distillation tests on ten crude oils ranging in gravity from 9.4° to 37° API. In each test, the crude was steam distilled sequentially at about 220, 300, 400 and 500° F. They found that the cumulative steam distillation yields at 400° F ranged from 20 to 55 volume percent. This result indicated that crude oil steam distillation yields are significant, even for heavy oils. Steam distillation yields also showed a high correlation with crude oil API gravity and wax content. Cumulative yield increased for crude oils with increasing API gravity, but decreased with increasing wax content. For the low wax content crudes used in their experiment, the cumulative yield at 400° F was related to crude oil gravity by

$$\text{Volume \% yield} = 2\ (^\circ\text{API}) \tag{3.1}$$

Wu and Elder (1983) correlated crude oil steam distillation yields with basic crude oil properties such as API gravity, oil viscosity at 100° F, simulated distillation temperature at 20 percent yield and simulated distillation yield. The correlations were based on steam distillation tests performed on 16 crude oils from various parts of the United States. Oil gravities varied from 12° to 40° API. Steam distillations were performed at saturated steam pressure of 220 psia. The corresponding saturated steam temperature is 390° F. At steam distillation ratio --- volume of steam per volume of initial oil --- of 20 the distillation yields ranged from 13 percent to 57 percent of the initial oil volume. For most crude oils, 80 percent of the ultimate yield during steamflood occurred within a steam distillation ratio of 5, and at even lower ratios for high API gravity crudes.

Blevins et al. (1984) discussed the extension of the steamflood process to the recovery of light oil (higher than 20° API) and the state of the art of this emerging technology. Various aspects of the process were reviewed. One important point made was that distillation should dominate if steam is injected into light oil reservoirs.

Langhoff and Wu (1986) used simulated distillation data to calculate crude-oil / water / vapor separations at 387° and 456° F. The method required characterization of crude oils into twelve pseudocomponents based on simulated distillation data obtained by gas chromatography. Comparisons with experimental data showed an average error of 12 percent in the computed distillation yields.

3.1 STEAMFLOODING CASE HISTORIES

Literature on case histories of steamflooding are abundant, but there are few instances in which observation of changes in produced oil gravities have been considered or reported. This section cites case histories which have recorded increasing produced oil API gravity.

Valleroy et al. (1967) reported the results of a steam drive pilot in a shallow, low oil-saturation formation near Deerfield, Missouri. The pilot was conducted in a 160 ft deep sandstone formation. It contained an 18° API oil with 1000 cp viscosity at the original reservoir temperature of 60° F. It was observed that API gravity of produced oil increased to 21° compared to 18° for the initial oil.

Volek and Pryor (1972) reported the results of steam distillation drive in Brea field, California. The objective was to test the feasibility of driving a relatively light (24° API), low-viscosity (6 cp), volatile oil from updip injectors to downstructure producers. The crude oil contained 55 percent by weight of components C_{18} or lighter. The produced oil API gravity increased from 23° to about 27° for an updip producer, and a downdip producer had oil gravity changes from 23.5° to 25.9° API.

3.2 IN-SITU COMBUSTION

Observations of producing oil lighter than the initial oil are not limited to the steamflood literature. Gates and Ramey (1958) reported this phenomenon during the in-situ combustion project in the South Belridge field. For example, API gravity of oil produced from one of the producers increased to 18° API, compared to 12.9° API for the initial oil.

3.3 SUMMARY

Despite the many references cited, few gave much attention to oil gravity change during steam injection. Fewer references mentioned the nature of the residual oil.

4. STEAM DISTILLATION DATA

The importance of steam distillation has been studied by many authors. The general observation is that steam distillation can be significant, even for heavy crudes.

Attempts have been made to correlate steam distillation yields with API gravity, viscosity, simulated distillation yields and other factors. Wu and Brown (1975) and Wu and Elder (1983) observed that there is a linear relationship between steam distillation yield and oil gravity, °API. For a steam distillation factor ($V_w \ / \ V_{oi}$) of 15, Wu and Elder obtained an empirical relationship for steam distillation at 220 psi:

$$\text{Volume \% Yield} = -3.2 + 1.5 \times (°\text{API}) \qquad (4.1)$$

Duerksen and Hsieh (1984) gave the following steam distillation yield for crude oils with low wax content distilled with 400° F steam:

$$\text{Volume \% Yield} = 2 \times (°\text{API}) \qquad (4.2)$$

They also concluded that high wax content could cause deviation from the linear correlation.

Some of the steam distillation data found in the literature are graphed in Fig. 4.1. Each set of data displays some form of linear relationship between yield and oil °API. Each set of data may have a different terminal distillation condition (temperature, water-oil ratio). Increasing the distillation temperature or water-oil ratio will increase the cumulative yield, although the increase may not be significant in certain cases.

The oil yield correlations may be unique to the experimental conditions. Oil yield correlations may not be compared directly, unless there is a common basis. A method of comparing these correlations is proposed in the following. Oil yield may be compared to the Bureau of Mines routine method of distillation data. The basis of comparison is the equivalent normal boiling point (ENBP) of each set of experimental conditions. Only data obtained at similar equivalent normal boiling points can provide meaningful comparisons.

4.1 BUREAU OF MINES DISTILLATION DATA

The Department of Energy crude oil analysis data bank contains crude oil assays for all major reservoirs in the United States (Bartlesville Project Office, 1987). These crude oil analyses were obtained by the Bureau of Mines routine method distillation. Atmospheric distillation yields up to 527° F, and yields at 40 mmHg and temperatures to 527° F were reported. Useful information can be retrieved from this database without resorting to laboratory experiments. A method will be described to correlate the Bureau of Mines data with the steam distillation data obtained from the literature.

In the Bureau of Mines method, atmospheric pressure distillations are carried out to 527° F, and then continued as vacuum distillations to prevent cracking of hydrocarbon components. Reducing the total pressure has an effect similar to distilling to higher boiling points.

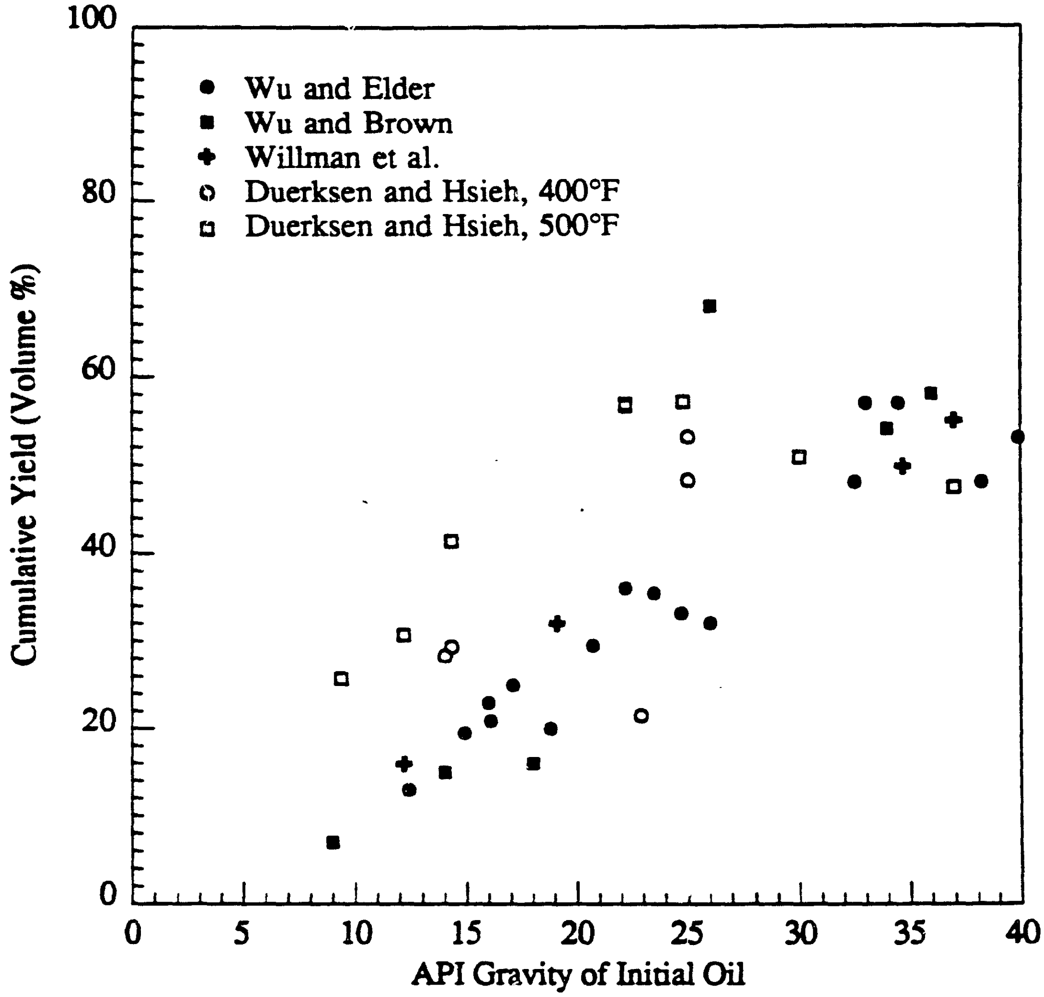

Figure 4.1 Cumulative oil yield vs. API gravity of initial oil

Equivalent atmospheric distillation temperatures for vacuum distillation conditions were determined using vapor pressure calculations. Vapor pressure charts of Lee and Kesler (1980) were used. With known pressure and temperature, the ENBP of the hydrocarbon can be determined. This ENBP represents the equivalent atmospheric distillation temperature. The assumption was made that at a given cut condition, vapor pressure is contributed solely by the residuum as a single hydrocarbon component. The calculated ENBP's of Bureau of Mines distillation cuts are shown in Table 4.1. Each increment in cut number represents an increase of approximately 50° F in the ENBP.

Table 4.1: Bureau of Mines routine method distillation cuts and equivalent normal boiling points.

Cut Number	Temperature (° F)	Pressure (mmHg)	ENBP (° F)
10	527	760	527
11	392	40	585
12	437	40	635
13	482	40	685
14	526	40	730
15	572	40	780

In this study, data from 454 California crude oil samples were analyzed. These data were extracted from the DOE Crude Oil Analysis data bank (1987). Appendix C contains the computer programs used for processing the crude oil analyses.

Figure 4.2 shows the cumulative distillation yield as a function of API gravity for cut number 12. This is the equivalent gas-oil cut at a distillation temperature of 437° F and a pressure of 40 mmHg. The equivalent normal boiling point is 635° F. A linear relation was found to fit the data:

$$\text{Volume \% Yield} = 1.75 \times (°\text{API}) \tag{4.3}$$

Cumulative yields for various cut temperatures are shown in Fig. 4.3. The equivalent normal boiling points are listed on the figures.

From Fig. 4.3, the cumulative yield is temperature dependent. Higher ENBP results in progressively higher yields. A series of parallel lines can be drawn, each representing a given ENBP. A 50° F increment in temperature results in a 5% increase in the cumulative volume distilled.

4.2 LITERATURE AND BUREAU OF MINES DATA

A question that naturally comes to mind is whether steam distillation data may be compared to the Bureau of Mines distillation data obtained in the absence of steam as the distilling agent. The equivalent atmospheric distillation temperature for various steam distillation conditions can be calculated. This enables comparison of steam distillation yields and Bureau of Mines data.

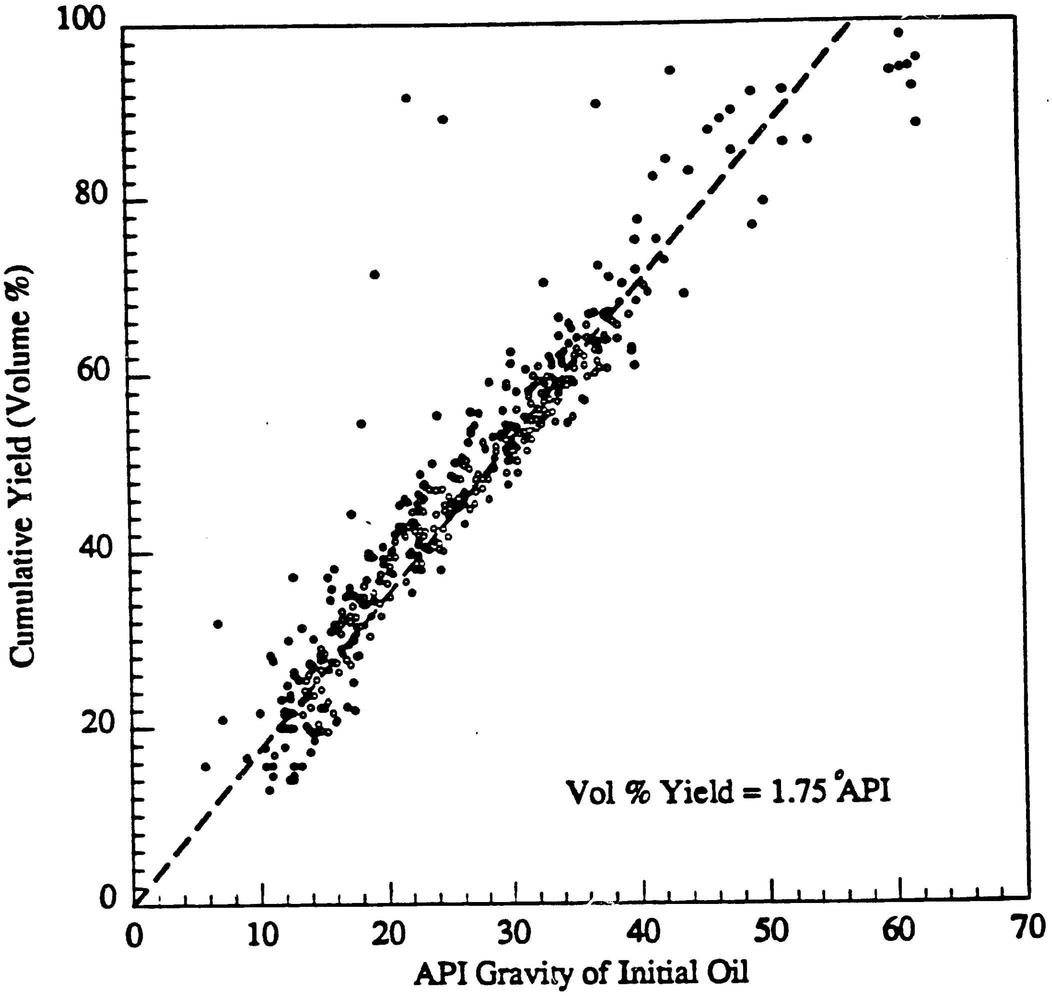

Figure 4.2 Distillation yield vs. API gravity of initial oil, for Cut 12, with EN'3P = 635°F

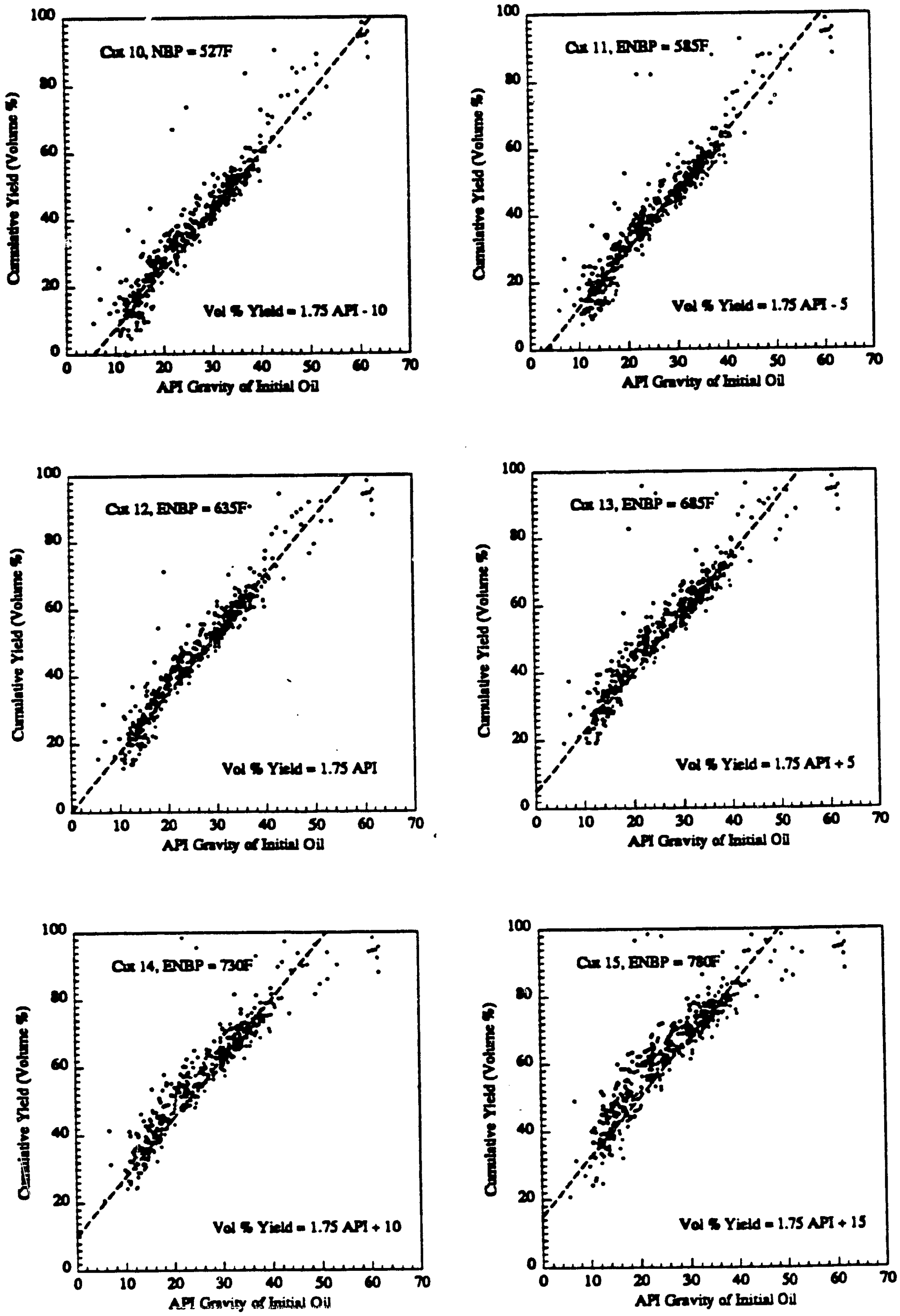

Figure 4.3 Distillation yield vs. API gravity of initial oil, for various cut temperatures

During steam distillation, partial pressures of steam and hydrocarbon make up the total pressure. At a given temperature:

Total pressure = partial pressure of steam
+ partial pressure of hydrocarbon

The terminal water-oil (or condensed steam-oil) ratio of a steam distillation experiment is required to determine the contributions of steam and hydrocarbon to the total pressure. A 500:1 molar water-oil ratio has been used. The rationale behind the selection of this number will be discussed in Section 6.

Assuming ideal mixing, the partial pressures of steam and hydrocarbon components in the system are proportional to the number of moles of each component. This assumption is acceptable as the partial pressure of the hydrocarbon component is very low at a 500:1 molar ratio. The vapor pressure of saturated steam at a given temperature can be determined from physical data handbooks. The vapor pressure of the hydrocarbon component is the difference between the total pressure and vapor pressure of saturated steam. Knowing the vapor pressure and temperature, the equivalent normal boiling point of the hydrocarbon can be determined. A vapor pressure equation, or chart (Lee and Kesler, 1980) can be used. The normal boiling point is the same as the equivalent atmospheric pressure distillation temperature. In this way, steam distillation yields at similar equivalent atmospheric pressure distillation temperatures can be compared directly.

The experimental data of Willman et al. (1961) were used to verify this procedure. For experiments performed at 84 psig, a 500:1 water-oil molar ratio gives a hydrocarbon partial pressure of 0.197 psia. Saturated steam temperature at 84 psig is 327° F. The normal boiling point of the hydrocarbon component at these conditions is 584° F. Figure 4.4 shows Willman et al. data for 84 psig distillation. Bureau of Mines distillation yield for cut number 11, ENBP = 585° F is superimposed as the solid line. A good match is apparent.

As a second example, a similar procedure was used to investigate the Willman et al. data for the 800 psig experiment. The partial pressure of hydrocarbon at a 500:1 molar water-oil ratio is 1.6 psia. The saturated steam temperature at 800 psig is 520° F. The equivalent normal boiling point of the hydrocarbon component was estimated to be 683° F. Figure 4.5 shows the Willman et al. data compared with the Bureau of Mines distillation yield for cut number 13, ENBP = 685° F. The match is reasonably close.

The two examples illustrate the point that if the ENBP of a steam distillation experiment can be determined, the Bureau of Mines distillation yields at the same ENBP can be used to compute cumulative yields for that ENBP. This procedure requires the partial pressure of the hydrocarbon component, which can either be obtained from experiments, or estimated as shown before. A 500:1 molar water-oil ratio gives a reasonably good estimate.

We will now consider changes in oil quality caused by distillation of residual oil.

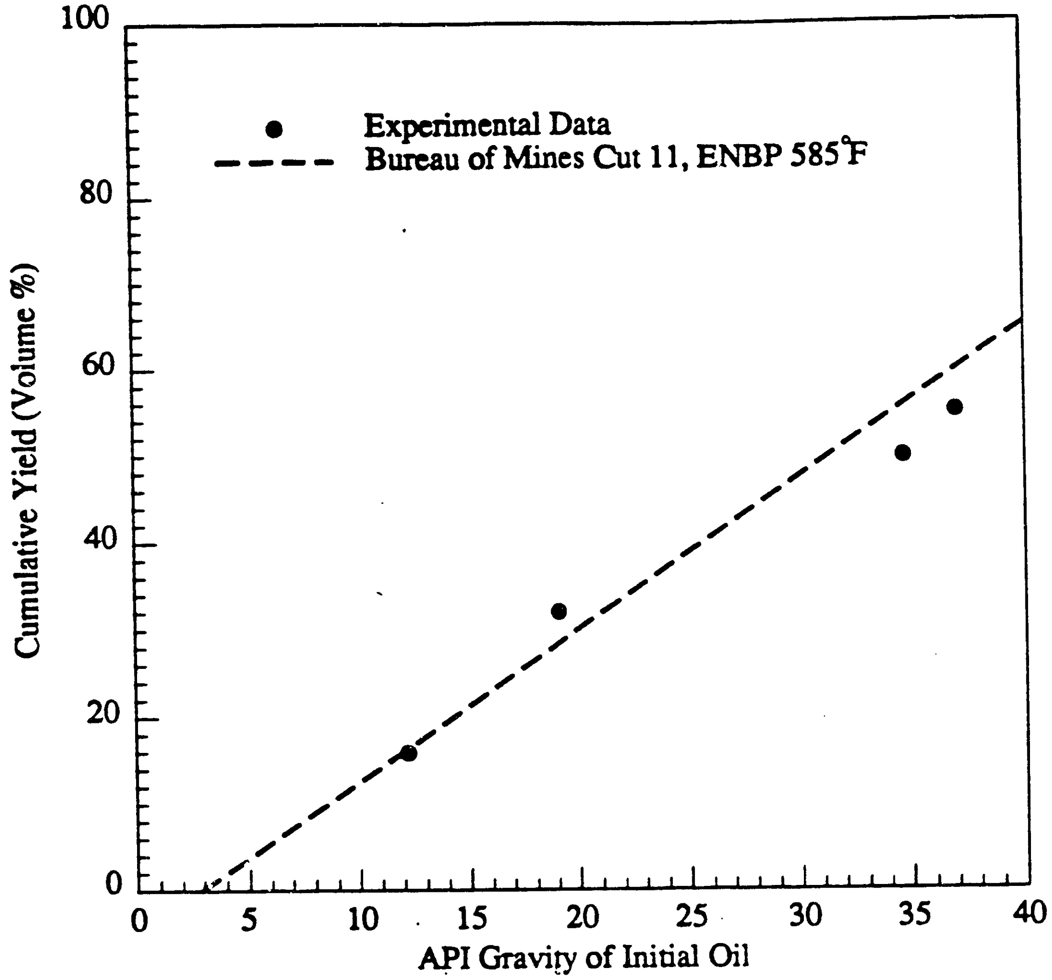

Figure 4.4 Bureau of Mines distillation yield for Cut 11, and Willman et al. data for steam injection at 84 psig. The ENBP for the experimental is 584° F

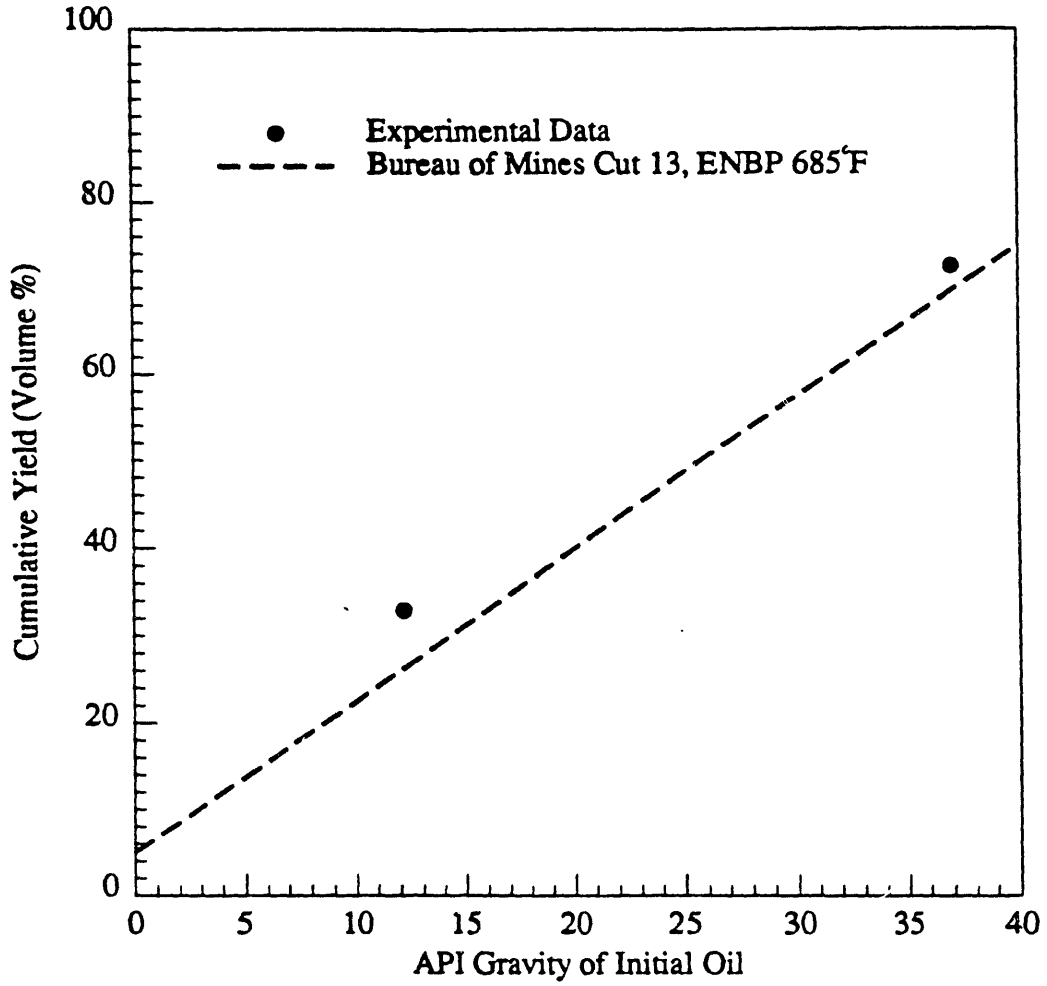

Figure 4.5 Bureau of Mines distillation yield for Cut 13, and Willman et al. data

5. OIL QUALITY CHANGES

Steam distillation extracts light components of the initial oil. The residuum, therefore, must become heavier than the initial oil. Blending of the distilled components with the initial oil results in lighter produced oil. This phenomenon has been observed in steam injection projects. A similar observation has also been made in in-situ combustion projects.

A change in API gravity can be calculated by a material balance. Consider the oil as a two-component system. One component is distillable, and the other is not at a given condition. If the API gravities of both the distilled component and residuum can be computed, a material balance can be accomplished. See Fig. 5.1.

Fig. 5.2 shows the distillate and residuum API gravities for California crudes for Bureau of Mines distillation cut number 12. The ENBP is 635° F. The distilled portion is substantially lighter than the initial oil. For example the distilled component of a 15° API oil is about 36° API. This is more than twice the initial oil API gravity number. The reduction in API gravity of the residuum is less dramatic. An oil initially of 15° API will have residuum of 11° API.

When the distilled component is mixed with the initial oil, a change in the produced oil should be evident. For steam to distill one volume of oil in the reservoir, one volume of initial oil must have been displaced. Fig. 5.3 shows the effect of mixing light components distilled from one volume of initial oil with an equal volume of initial oil. The data from Fig. 5.2 was used for this calculation. The calculations were performed by processing of the Bureau of Mines crude oil assays as shown in Appendix C.

The changes indicated in Fig. 5.3 are consistent with laboratory and field observations. For example, the change for the Brea steam injection project was from 23° API to 27° API, a change from 18° API to 21° API was observed in the Deerfield steam drive pilot, and a change from 12.9° API to 18° API was observed in the South Belridge in-situ combustion project.

Fig. 5.3 also illustrates another important result. No oil gravity change would be expected for either 0° or 60° API oil. This makes sense physically. The 0° API oil cannot be distilled at 635°F ENBP and therefore no change would be expected. On the other hand, practically all components of a 60° API oil would be distillable and blending with the initial oil would not cause a change. A maximum increase of 4.4° API is indicated for a 30° API oil.

Graphs similar to Fig. 5.3 were also made for other distillation cuts, or ENBP. However, the results indicated that the changes were not sensitive to the distillation temperature. Higher ENBP results in higher cumulative distillation volume, but progressively heavier components distilled. The heavier distilled components offset the higher volume distilled. The net result is similar to that shown in Fig. 5.3.

The preceding results are a general approach that can be used to estimate the API gravity of produced oil from steam injection oil recovery.

We will consider a quantitative evaluation of steam injection in the next section.

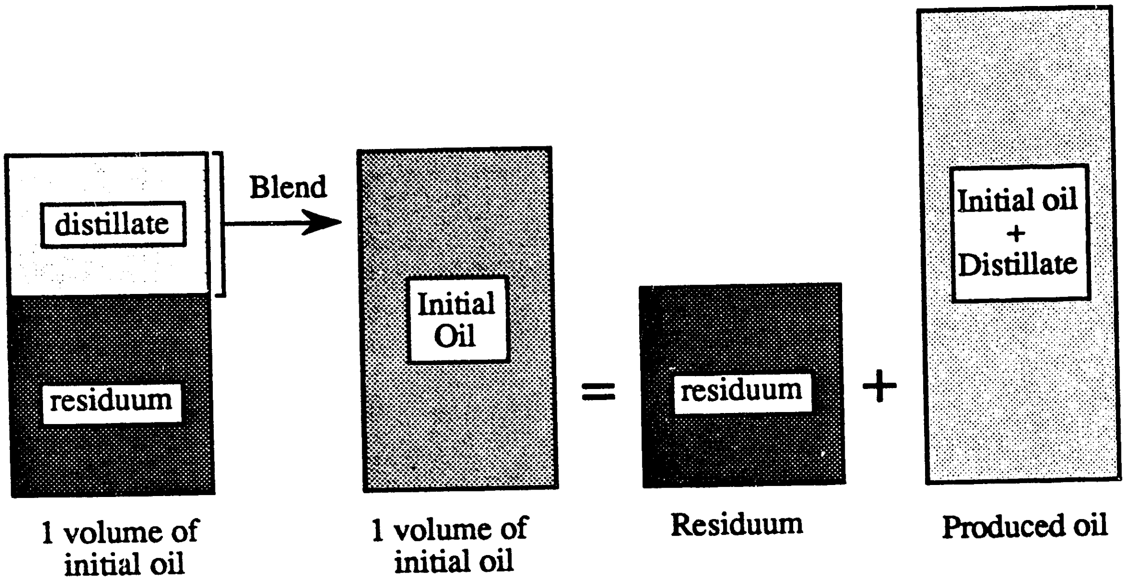

Figure 5.1 Schematic illustrating calculation of oil quality change

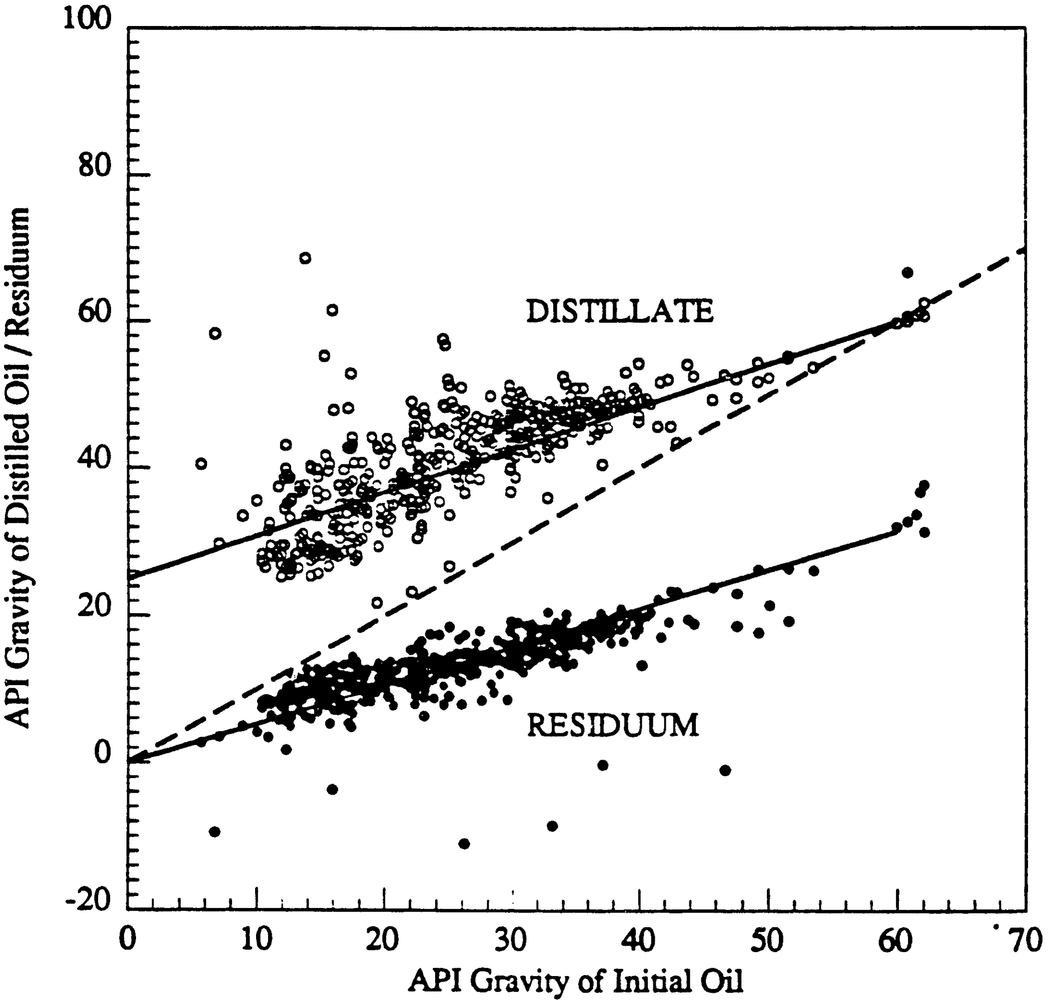

Figure 5.2 API gravities of distilled component and residuum for Cut 12, ENBP = 635°F

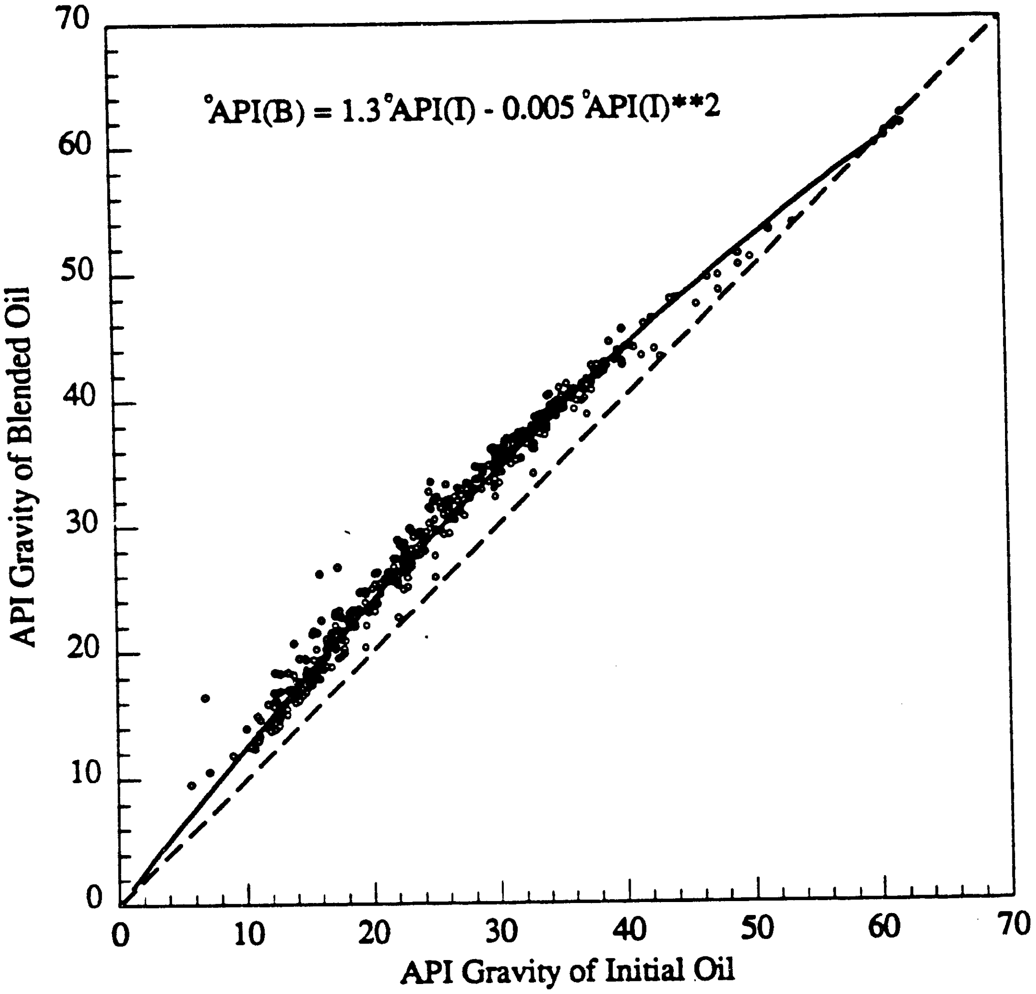

Figure 5.3 Gravity change Cut 12, ENBP = 635°F

6. STEAM DISTILLATION CALCULATION

Assume that steam distillation separates the oil into two components — the distilled component and the residuum, as indicated in Fig. 5.2. The residuum is not volatile at the given steam distillation condition. The partial pressures of each component in a phase can be related to the number of moles of the component. This ideal mixing assumption is reasonable because the partial pressure of the volatile oil component in the vapor phase is small at high steam-oil ratios. The same assumption is generally applicable to mixing of liquid components.

The number of moles of the volatile component remaining in the liquid phase at any time, n_{v2}, can be related to the system pressure, partial pressures of steam and nonvolatile component, the initial oil volume, and the cumulative water-oil ratio:

$$\frac{F_{wo}\ V_{oi}}{0.289} = \left[\frac{p}{p_{bv}} - 1 \right] (n_{v1} - n_{v2}) + \left[\frac{p\ n_n}{p_{bv}} \right] ln \left[\frac{n_{v1}}{n_{v2}} \right] \tag{6.1}$$

The cumulative fraction of initial oil distilled is:

$$f = \frac{\dfrac{M_v}{\rho_v} (n_{v1} - n_{v2})}{V_{oi}} \tag{6.2}$$

where:

F_{wo} = cumulative steam volume per volume initial oil, cu-ft water/cu-ft oil

M_v = molecular weight of volatile component

n_{v1} = total number of moles of volatile component in hydrocarbon mixture at start

n_{v2} = total number of moles of volatile component in hydrocarbon mixture at any time

n_n = total number of moles of nonvolatile component, constant

p_{bv} = vapor pressure of component v at distillation temperature, psia

p = total pressure of the system, psia, and

V_{oi} = initial oil volume, cu-ft

ρ_v = density of volatile component at standard conditions, lb/cu-ft

Derivation of Eqs. 6.1 and 6.2 is shown in detail in Appendix A. Equation 6.1 can be solved iteratively for n_{v2}. The iterative procedure is necessary as n_{v2} appears in both the algebraic and logarithmic terms. A computer program to solve this problem is presented in Appendix B. The calculated distillation yield can be graphed against either volumetric or molar water-oil ratios.

As an example, a run was made for a 19° API crude distilled with 84 psig steam. This is one of the samples presented in the Willman et al. (1961) study. The results of these calculations are shown in Figs. 6.1 through 6.3.

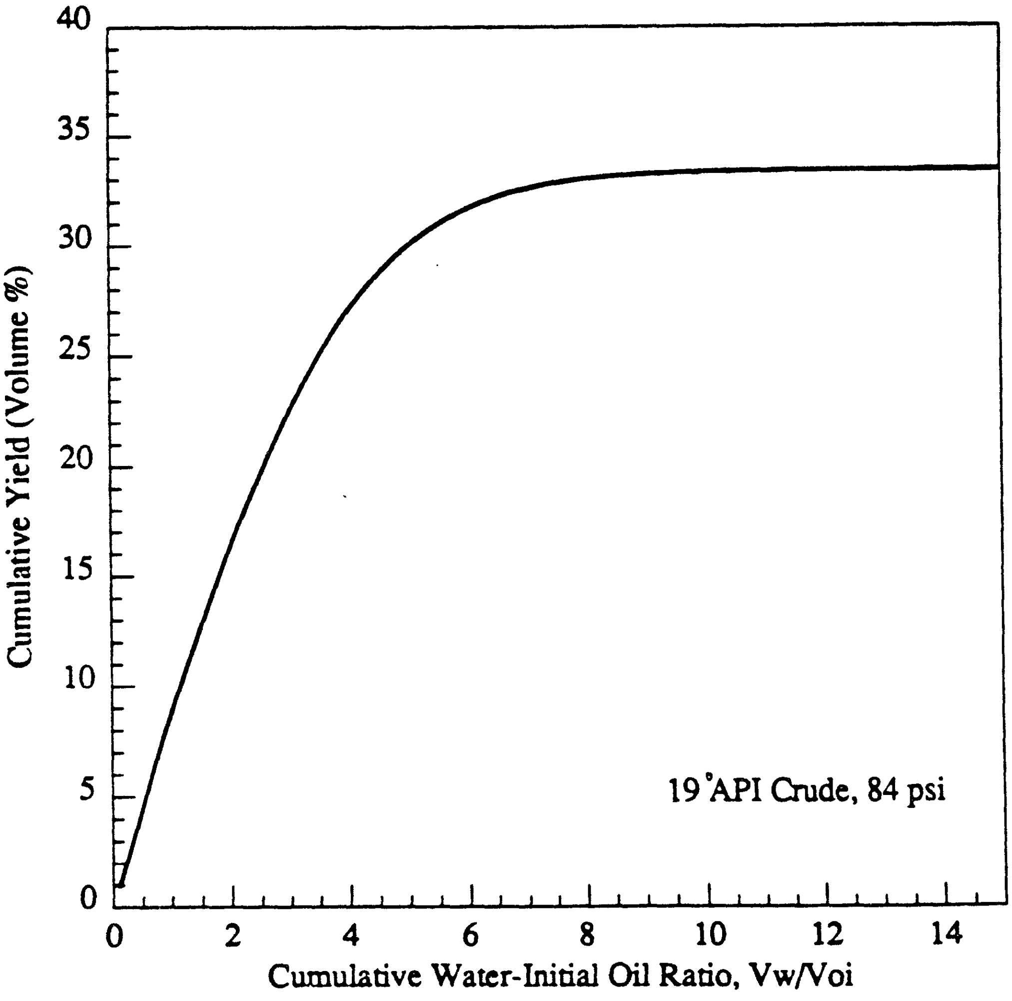

Figure 6.1 Calculated steam distillation yield as a function of cumulative water-oil ratio

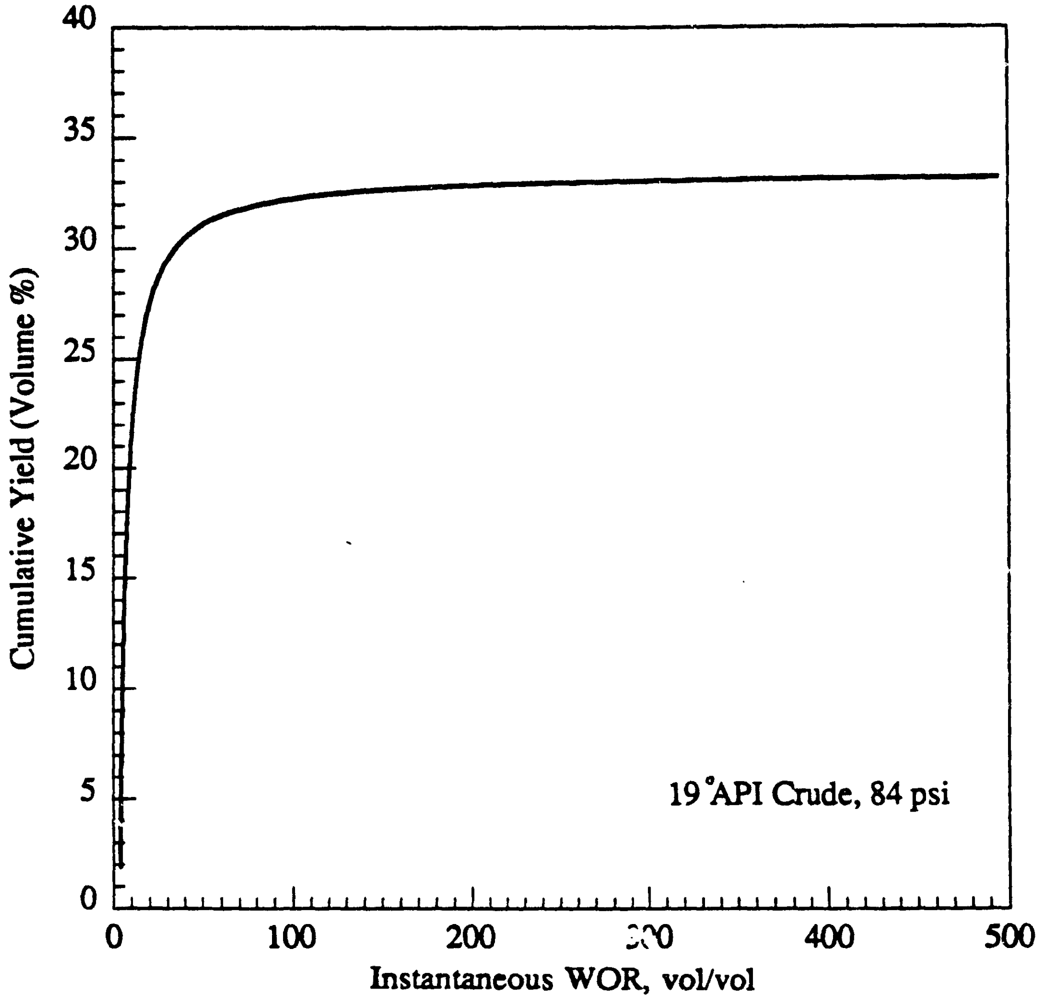

Figure 6.2 Calculated steam distillation yield as a function of instantaneous volumetric water-oil ratio

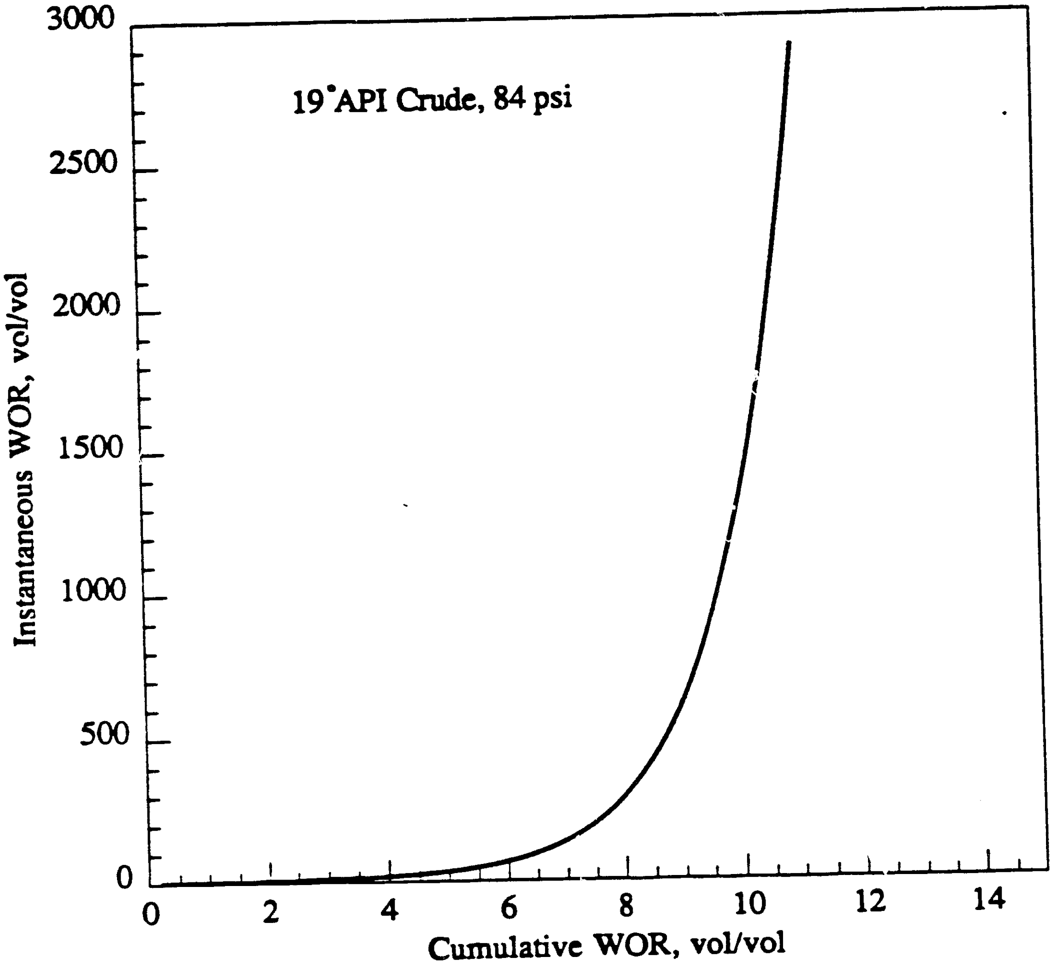

Figure 6.3 Instantaneous water-oil ratio vs. cumulative water-oil ratio

Figure 6.1 shows the calculated cumulative distillation yield graphed against cumulative water-initial oil ratio, or what is called steam distillation factor by Wu and Brown (1975). The result is consistent with experiment results presented in the literature. Most distillation occurs at cumulative water-initial oil ratios of 5 or less.

The cumulative yield is plotted against instantaneous water-oil ratio in Fig. 6.2. For this case most distillation occurs at water-oil ratios of 100 or less. The instantaneous water-oil ratio may be a useful measure in field operations. Cumulative water-initial oil ratio may not be a good choice when the amount of oil in-place prior to steam injection cannot be estimated. The relationship between the volumetric and molar water-oil ratios is shown in Fig. 6.3. The instantaneous water-oil ratio rises rapidly when most of the volatile components have been distilled.

Figure 6.4 shows the relation between cumulative distillation yield and instantaneous molar water-oil ratio. This information is useful for equilibrium and partial pressure calculations. For this case, more than 90% of distillation yield occurred at a molar water-oil ratio of 500:1 or less. This shows that the 500:1 molar ratio used to correlate the Willman et al. data with Bureau of Mines distillation data in Section 4.2 has a sound basis. A ratio higher than 500:1 results in changes in the partial pressure calculations, but little cumulative oil distillation results.

Comparisons were also made with the Wu and Elder (1983) data to verify the calculation procedure. Data for two California crudes were compared. Figure 6.5 shows the calculated and experiment oil yield for Brea crude. A similar graph for South Belridge crude is shown in Fig. 6.6. Results on these figures indicate that the two-component calculation provides a fairly reasonable representation of the steam distillation behavior. A better match was obtained for the heavier crude, as shown on Fig. 6.6. The differences observed in Fig. 6.5, especially at small water-oil ratios, is probably caused by the two-component assumption. The lighter crude oil contains a larger amount of light components which are distilled at a lower boiling point. The light components distill at lower temperature than the lumped volatile component used in the two-component calculation. Obviously, more than two components are required to represent light oil distillation behavior adequately, especially at the start of distillation.

Inspection of Figs. 6.5 and 6.6 shows that reasonably good results, particularly a calculation of the ultimate yield, can be obtained by the two-component approach. This method is based on generalized correlations for a crude type, in this case for California crudes. A good indication of steam distillation behavior was computed without resorting to laboratory experiments.

The binary crude oil approximation may be used to study other factors in thermal oil recovery. Examples are fuel concentration in in-situ combustion and residual oil saturation in steam injection. The next section presents a brief discussion of further applications.

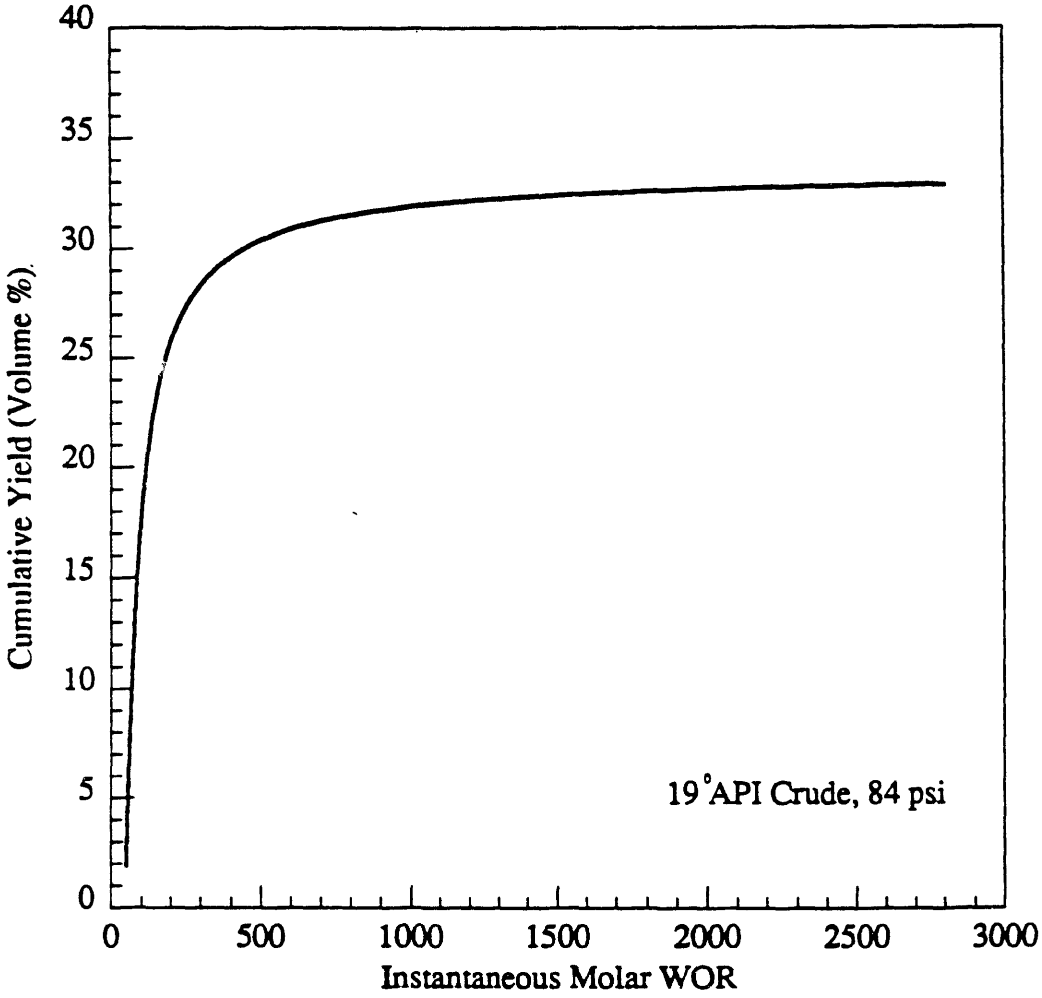

Figure 6.4 Calculated steam distillation yield as a function of instantaneous molar water-oil ratio

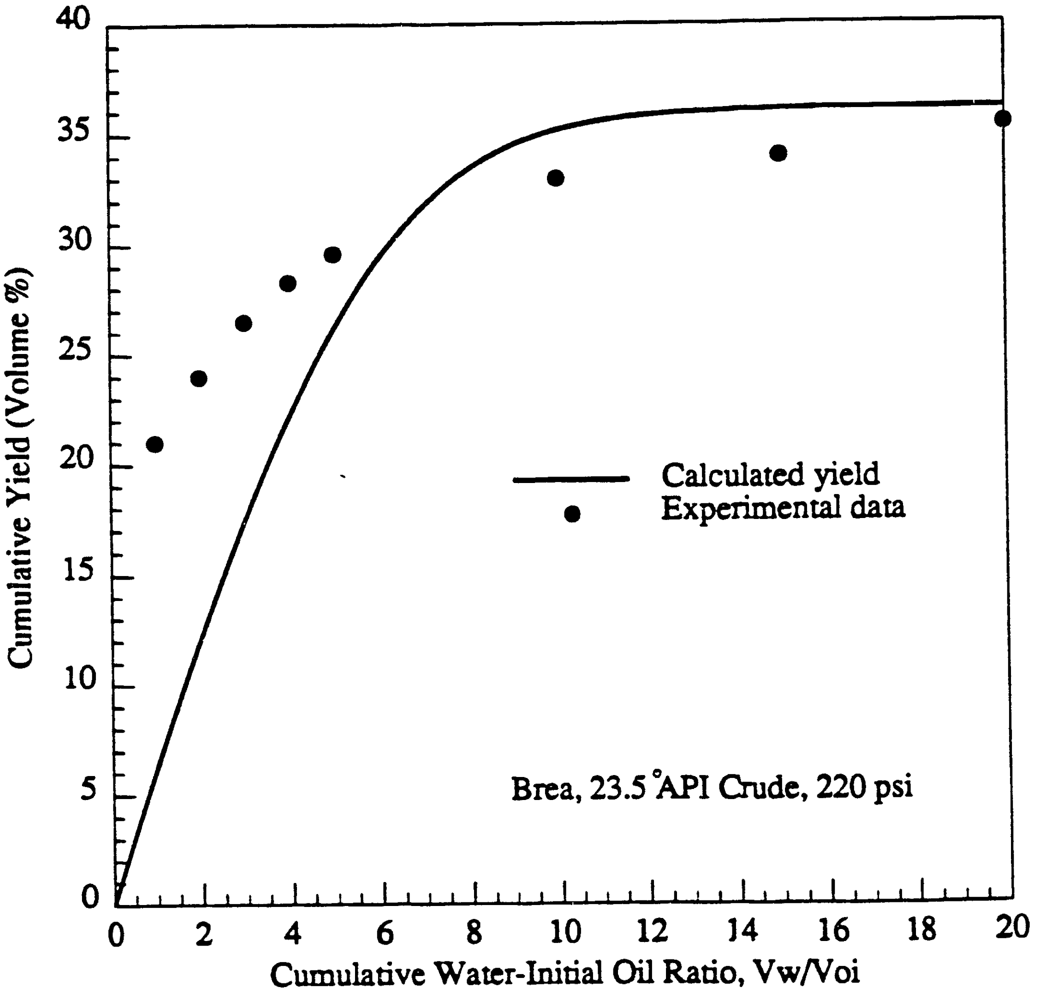

Figure 6.5 Calculated yield and experimental data of Wu and Elder for Brea crude

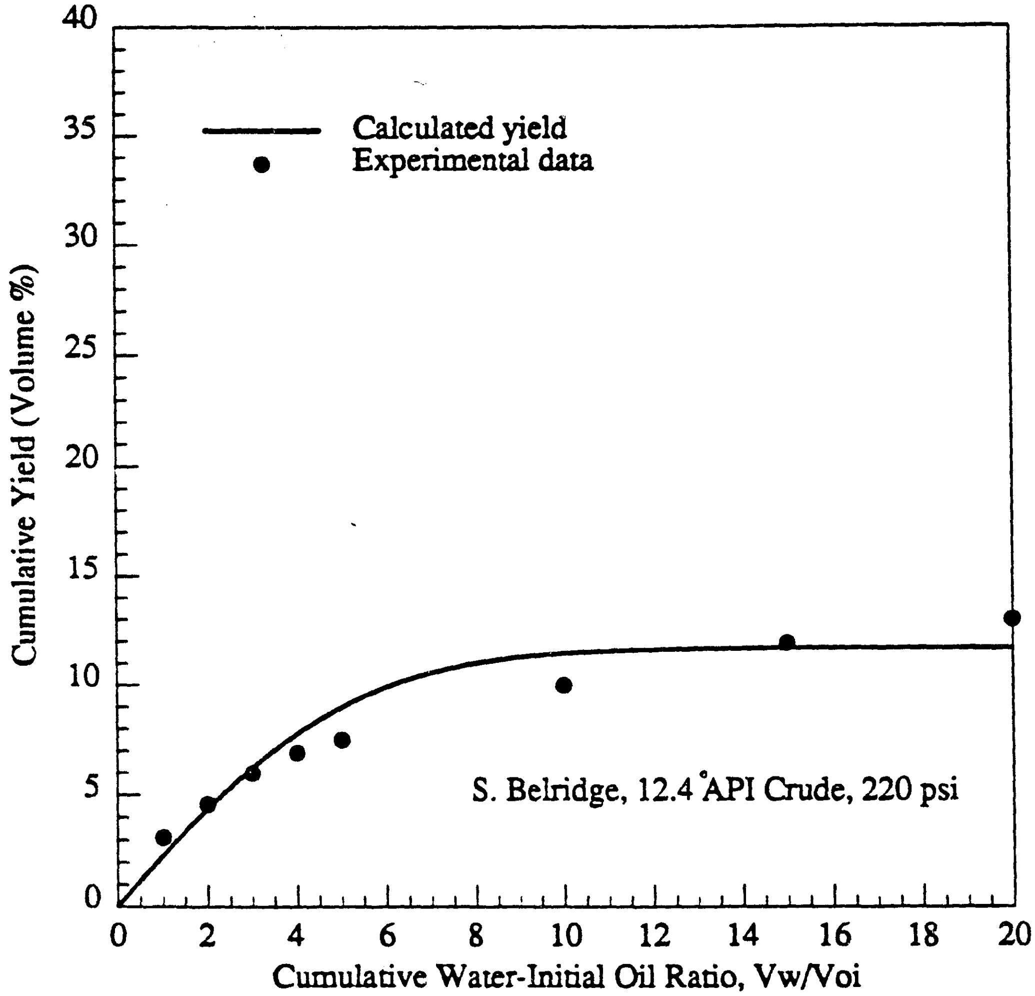

Figure 6.6 Calculated yield and experimental data of Wu and Elder for South Belridge crude

7. FURTHER APPLICATIONS

Information presented in the preceding sections led to our conclusions that the amounts and qualities of both distillable components and residuum during steam injection can be estimated in a logical manner. In the absence of a crude oil assay, the DOE data bank or correlations presented in this study can be used. This information has wider applications potentially than computing just the oil quality change. Some potential applications are described in the following.

7.1 RESIDUAL OIL SATURATION COMPUTATION

If both the amount and API gravity of oil present before steam injection and the amount produced are known, residual oil saturation can be calculated from a material balance. Similarly, the quality of the residual oil can be computed. The importance of knowing the quality, or °API gravity of the residual oil is explained in the following.

7.2 FUEL CONCENTRATION FOR IN-SITU COMBUSTION

During an in-situ combustion process, the mechanisms ahead of the combustion front are closely related to those for steam injection (Wu and Fulton, 1971). Steam distillation is the main mechanism for oil movement in the steam plateau. Residual oil saturation after steamflooding is essentially equal to the fuel concentration available for in-situ combustion. Fuel concentration for in-situ combustion can be computed from residual oil saturation and gravity. Prats (1986) pointed out that crude oil properties and rock properties can affect the fuel concentration for in-situ combustion.

Another subject of interest is the atomic hydrogen-to-carbon ratio, H/C, of the fuel in combustion. The H/C ratio is a measure of fuel composition. The Universal-Oil-Product (UOP) K-factor should be a useful correlating parameter. Hougen et al. (1954) presented a chart which relates the UOP K-factor and hydrocarbon cut boiling point to °API gravity and viscosity at 122° F (50° C). Figure 7.1 is a chart relating UOP K-factor, atomic H/C ratio and oil gravity °API. This is a modification of a chart presented by Hougen et al. Knowledge of the API gravity of residual oil after steamflooding should permit estimation of the atomic H/C ratio of the fuel for in-situ combustion.

Fuel concentration and the atomic H/C ratio are important information for operational control of an in-situ combustion process, such as determining whether high-temperature burning or low-temperature oxidation is happening.

7.3 NUMERICAL SIMULATION

The steam distillation yield correlations can be applied to numerical simulation models to represent steam distillation behavior. In this case, a correlation specific to the crude type should be used. The correlation can be obtained by the method described in Section 3 for crude oils from a specific geographic area.

We now consider observations and conclusions resulting from this study to date.

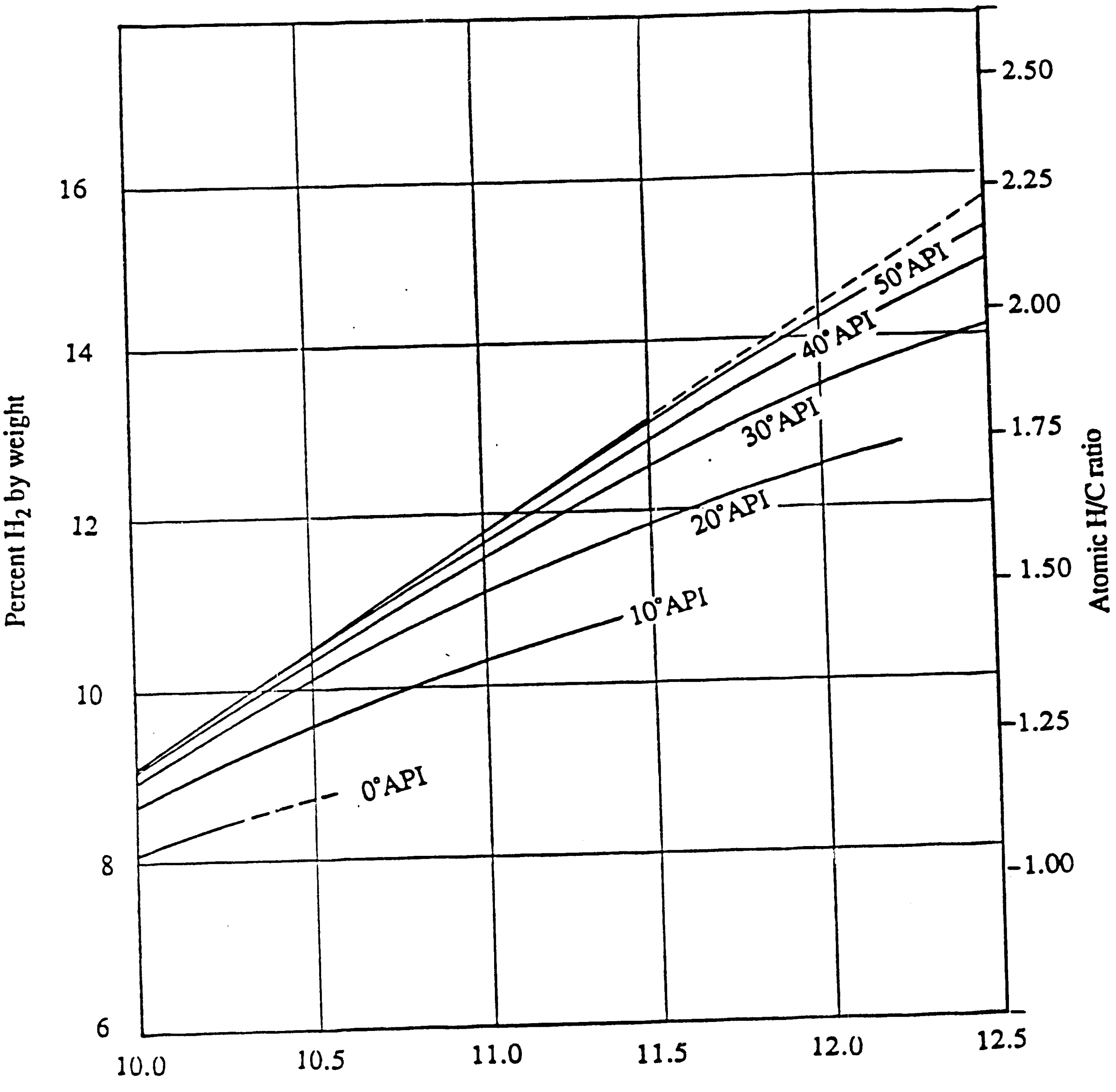

Figure 7.1 Relationship between UOP K-factor, °API and H/C ratio (after Hougen et al.)

8. CONCLUSIONS

The following conclusions have been reached from this study to date.

1. Distillation data from the DOE crude oil analysis data bank can be used to estimate steam distillation yield by calculating the equivalent normal boiling point of a steam distillation. A 500:1 molar water-oil ratio provides a reasonably good estimate.

2. The steam distillation yield can be significant, even for heavy crude oils. The steam distillation yield, in volume percent, for California crude oil is approximately 1.75 times the initial API gravity of the oil.

3. A general approach to quantify crude oil quality changes during steam injection has been developed and tested against laboratory experimental data.

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APPENDIX A. STEAM DISTILLATION CALCULATIONS

Consider crude oil as a binary mixture of a volatile and a nonvolatile component. The volatile component is vaporized by the injected steam as shown in Fig. A.1.

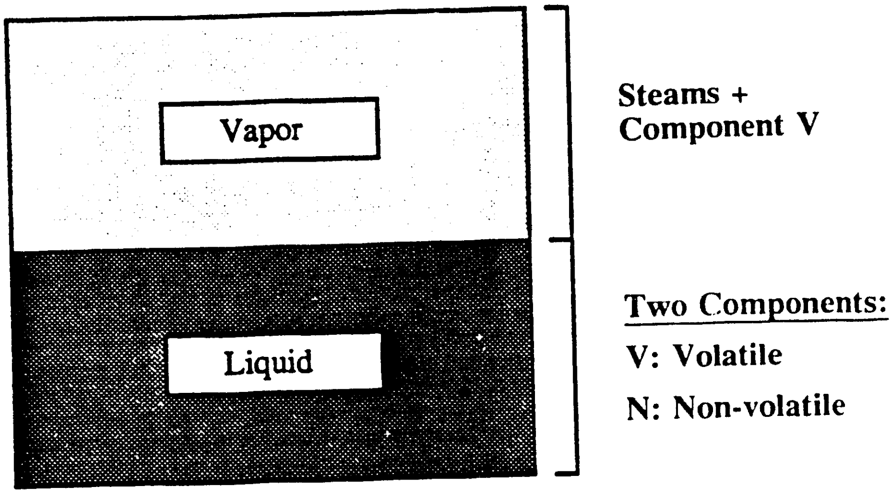

Figure A.1 Schematic of a two-component oil distilled by steam

Assume that a bubble of steam dn_s moles leaves a hot crude oil mixture carrying a small amount of the volatile oil component, $-dn_v$ moles. By Dalton's Law of partial pressures, the molar ratio of steam and volatile component in the bubble is proportional to the partial pressures of steam and volatile component:

$$\frac{dn_s}{-dn_v} = \frac{p_s}{p_v} = \frac{p - p_v}{p_v} = \frac{p}{p_v} - 1 \tag{A.1}$$

where:

n_s = total number of moles of open/saturated steam
n_v = total number of moles of volatile component in hydrocarbon mixture at any time
n_n = total number of moles of nonvolatile component, constant
p_{b_v} = vapor pressure of component v at distillation temperature, psia
p_v = partial pressure of component v in vapor phase, psia
p_s = partial pressure of steam in vapor phase, psia,
p = total pressure of the system, psia, and
x_v = mole fraction of component v in the liquid hydrocarbon mixture at any time.

The minus sign in front of the dn_v term indicates that the number of moles of the volatile component in the liquid oil phase decreases as the volatile component vaporizes. We assume that the vapor bubble leaves the system immediately. By Raoult's Law, the partial pressure of the volatile component is equal to the product of the mole fraction and vapor pressure of the volatile component in the liquid oil:

$$p_v = p_{bv}\, x_v = p_{bv} \left[\frac{n_v}{n_v + n_n} \right] \tag{A.2}$$

Substitution of Eq. A.2 in A.1 yields:

$$\frac{-dn_s}{dn_v} = \frac{p}{p_{bv} \left[\dfrac{n_v}{n_v + n_n} \right]} - 1$$

$$= \frac{p}{p_{bv}} - 1 + \frac{p n_n}{p_{bv}\, n_v} \tag{A.3}$$

Equation A.3 can be rearranged and integrated from the initial to the final condition:

$$\int_0^{n_s} d\, n_s = - \int_{n_{v1}}^{n_{v2}} \left[\left[\frac{p}{p_{b_v}} - 1 \right] + \left[\frac{p\, n_n}{p_{b_v}\, n_v} \right] \right] d\, n_v \tag{A.4}$$

where:

n_{v1} = number of moles of volatile component at time zero

n_{v2} = number of moles of volatile component remaining in the liquid phase at any time t.

$$n_s = \left[\frac{p}{p_{b_v}} - 1 \right] (n_{v1} - n_{v2}) + \frac{p\, n_n}{p_{b_v}}\, ln \left[\frac{n_{v1}}{n_{v2}} \right] \tag{A.5}$$

Eq. A.5 may be used to calculate the amount of volatile component left in the liquid phase after a total of n_s moles of steam is injected into the oil. The difference between the initial quantity of the volatile component and the quantity at any time t is the cumulative volatile component distilled.

Some modifications can be made to Eq. A.5 to express the result of distillation in terms of volumetric and molar water-oil ratios. The molar ratio of cumulative water (condensed steam) to initial oil is:

$$F_{wo}^{m} = \frac{n_s}{n_n + n_{v1}} \tag{A.6}$$

To express Eq. A.5 in terms of volume ratios, the molecular weight and density of each component are required.

Volume of steam condensate (water) is:

$$V_w = \frac{M_w\ n_s}{\rho_w} = \frac{18\ n_s}{62.36} = 0.289\ n_s \text{ cu-ft} \qquad \text{(A.7)}$$

Initial oil volume based on the ideal solution assumption is:

$$V_{oi} = \left[\frac{M_v\ n_{v1}}{\rho_v} \right] + \left[\frac{M_n\ n_n}{\rho_n} \right] \qquad \text{(A.8)}$$

where:

M_w = molecular weight of water
M_v = molecular weight of volatile component
M_n = molecular weight of nonvolatile component
ρ_w = density of water at standard conditions, lb/cu-ft
ρ_v = density of volatile component at standard conditions, lb/cu-ft
ρ_n = density of nonvolatile component at standard conditions, lb/cu-ft

For a given cumulative water-initial oil volume ratio, F_{wo}, Eqs. A.7 and A.8 can be combined:

$$F_{wo} = \frac{0.289\ n_s}{V_{oi}} \qquad \text{(A.9)}$$

or

$$n_s = \frac{F_{wo}\ V_{oi}}{0.289} \qquad \text{(A.10)}$$

Equating Eqs. A.5 and A.10 yields:

$$\frac{F_{wo}\ V_{oi}}{0.289} = \left[\frac{p}{Pb_v} - 1 \right] (n_{v1} - n_{v2}) + \left[\frac{p\ n_n}{Pb_v} \right] ln \left[\frac{n_{v1}}{n_{v2}} \right] \qquad \text{(A.11)}$$

Eq. A.11 can be solved iteratively for n_{v2}, the number of moles of the volatile oil component. The cumulative fraction of initial oil distilled is:

$$f = \frac{\frac{M_v}{\rho_v} (n_{v1} - n_{v2})}{V_{oi}} \qquad \text{(A.12)}$$

The instantaneous, volumetric water-oil ratio may be calculated using Eq. A.3.

APPENDIX B: STEAM DISTILLATION CALCULATION PROGRAM

```
c
c     Calculation of Steam Distillation Effect
c              Using two component assumption
c
c     Purpose: To generate:
c        (1) Cumulative yield vs cumulative water(cond. steam) to
c             initial oil ratio
c        (2) Cumulative yield vs instantaneous WOR
c
c     Primary input: API gravity of initial oil
c
c     Steam distillation effect based on BuMines data correlation
c     for Cut #12 (ENBP = 635 F):
c
c     Vol % yield    = 1.75 ( API of initial oil)
c     API(residue)   = 0.525 API(initial oil)
c     API(distill)   = API(initial) + 25*(60-API(initial))/60
c                      (or by material balance)
c
```

APPENDIX B. STEAM DISTILLATION CALCULATION PROGRAM

```
c
c     Basis of calculation: 100 cu ft of initial crude
c
      open(unit=1,file='yield1')
      open(unit=2,file='yield2')
      open(unit=3,file='yield3')
      open(unit=4,file='yield4')
      open(unit=8,file='yield5')
c
      write(*,*)'Input API gravity of Initial Crude'
      read(*,*)apii
      write(*,*)'Input Temperature, F'
      read(*,*)temp
      write(*,*)'Input Saturation Pressure of Steam at T, psia'
      read(*,*)psteam
      write(*,*)'Equivalent BuMines cut number? e.g. 10, 11, 12, 13'
      read(*,*)key
c
      yield = 1.75*apii + 5. * (key - 12)
      apir  = 0.525*apii
      asgi  = 141.5 / (131.5 + apii)
      asgr  = 141.5 / (131.5 + apir)
c
c     get API gravity of distilled oil from material balance
c
      rhoi = asgi * 62.4
      wti  = 100. * rhoi
c
      rhor = asgr * 62.4
      wtr  = (100. - yield) * rhor
c
```

APPENDIX B. STEAM DISTILLATION CALCULATION PROGRAM

```
      wtd  = wti - wtr
      rhod = wtd / yield
      asgd = rhod / 62.4
      apid = 141.5 / asgd - 131.5
c
      amwr  = 0.23154 * 10**(3.5633*asgr)
      amwd  = 0.23154 * 10**(3.5633*asgd)
c
      xres  = wtr / amwr
      xdis1 = wtd / amwd
c
c     calculate volume of initial oil
c
      voi = xres*amwr/rhor + xdis1*amwd/rhod
c
      write(1,1)xres,xdis1,amwr,amwd,rhor,rhod,voi,apid
1     format(7f10.4,1x,f5.1)
c
c     Need to get vapor pressures of steam and distillable component
c     from vapor pressure correlations
c
      tb = 2411.3 - 6649.4 * asgd + 5278.4 * asgd**2
      call vapor(temp,tb,pvapor)
c
      write(1,5)tb,pvapor
    5 format(1x,'Calc Tb, Psat = ',2f15.5)
c
c     use as initial guess x dis2 = xdis1
c
   10 ptotal = psteam + pvapor
      xdis2 = xdis1
```

```
      cumwor = 0.1
      steam = 0.
   20 iter = 0
      steam0 = steam
      xold = xdis2
c
c     use bisection method iteration
c
      x1 = 0.
      x2 = xdis1
   30 fun1 = cumwor/0.289 * (amwd*xdis1/rhod + amwr*xres/rhor)
     &       - (ptotal/pvapor -1)*(xdis1 - x0)
     &       - (ptotal*xres/pvapor)*log(xdis1/x0)
      fun2 = cumwor/0.289 * (amwd*xdis1/rhod + amwr*xres/rhor)
     &       - (ptotal/pvapor -1)*(xdis1 - x1)
     &       - (ptotal*xres/pvapor)*log(xdis1/x1)
      half = (x1+x2)/2.
      fun3 = cumwor/0.289 * (amwd*xdis1/rhod + amwr*xres/rhor)
     &       - (ptotal/pvapor -1)*(xdis1 - half)
     &       - (ptotal*xres/pvapor)*log(xdis1/half)
        if(fun1*fun3 .ge. 0) x1=half
        if(fun1*fun3 .lt. 0) x2=half
      if(abs(x2-x1) .lt. 0.001)goto 50
      iter = iter + 1
      if(iter .gt. 500)goto 99
      goto 30
c
c     convergence achieved
c     calculate cumulative yield, volume and molar ratio
c
   50 xdis2 = half
```

APPENDIX B. STEAM DISTILLATION CALCULATION PROGRAM

```
      steam = (ptotal/pvapor -1) + (ptotal*xres)*log(xdis1/xdis2)
      deltas = steam - steam0
      deltad = xdis2 - xold
      ratiom = -deltas / deltad
c
      vwater = deltas*18./62.36
      vdis   = deltad*amwd/rhod
      if(deltad .eq. 0) then
        wor = 0.
      else
        wor    = - vwater/vdis
      endif
c
c     cumulative yield in volume %
c
      distil = 100.*amwd*(xdis1-xdis2)/rhod/voi
c
      write(1,61)cumwor,distil,xdis2
      write(2,62)wor,distil
      write(3,62)cumwor,wor
      write(4,62)ratiom,distil
      write(8,62)wor,ratiom
   61 format(f8.3,10x,f8.4,10x,f8.4)
   62 format(f15.5,10x,f15.5)
c
      cumwor = cumwor + 0.1
      if(cumwor .gt. 20.1)goto 999
      goto 20
c
   99 write(*,*)'No convergence after 500 iterations at cum. WOR='
      write(*,*)cumwor
```

APPENDIX B. STEAM DISTILLATION CALCULATION PROGRAM

```
  999 stop
      end
c
c     -----------------------------------------------------------
c
      subroutine vapor(temp,tb,pvapor)
c
c     estimating vapor pressure by Lee-Kesler method
c     Input: boiling point
c
      temp =5./9. *(temp + 460.)
      tbn = 341.9
      tstar = 3870.
c
      c = (tb/tbn -1)*(10.15 - 0.1285*tb)
      b1 = 1./(tstar + c) - tbn/tstar/(tb+c)
      b2 = 1. - tbn/tstar
      b = b1/b2
      te = tb * (1/(tb+c) -b) / (1/(temp+c) -b)
      plog = te*(0.1047 + 259.8/(te+55)) - 6.074*te**0.5 - 140.65
      pvapor = exp(plog)
      pvapor = pvapor / 6896.55
      return
      end
```

APPENDIX C: PROGRAMS TO PROCESS DOE CRUDE OIL ANALYSES

```
c
c     Program to extract crude oil distillation data for a given
c     location from the DOE Crudeoil distillation databank
c     (example: NL=4 for California, see locname.dat for listing)
c
c        The following is a list of files from the DOE data bank:
c          1. readme.1st
c          2. locname.dat
c          3. counties.dat
c          4. crudeoil.dat
c          5. timestrat.dat
c        See user guide for more information.
c
c     The following information will be extracted
c     Field name, API gravity, Saybolt U. viscosity
c     at 77, 100, 130 & 180 F, volume percent & specific gravity
c     for each of the 15 fractions
c
```

APPENDIX C. PROGRAMS TO PROCESS DOE CRUDE ANALYSES

```
c     All original data are contained in the file crudeoil.dat
c
c     The following are the FORTRAN write format statements used
c     to create the crudeoil.dat file. See readme.1st for
c     description of variable names
c
c   WRITE(2,480)LAB,ID,NL,PRA,PRPT,SUA100,SU100,DEEP,
c    1                NCNTY,SUA77,SU77,SUA130,SU130,SUA180,
c    1                SU180,(CLA(I),CL(I),I=5,15)
c 480     FORMAT(1X,A1,I5,I3,A1,I3,A1,2I6,I3,14(A1,I6),4X)
c         WRITE(2,485)(RID(I),I=1,15)
c 485     FORMAT(1X,15F7.5,26X)
c         WRITE(2,485)(RIG(I),I=1,15)
c         WRITE(2,490)(SGR(I),I=1,15),(SUA(I),SU(I),I=5,12)
c 490     FORMAT(1X,15F5.3,8(A1,I6))
c         WRITE(2,492)(SUA(I),SU(I),I=13,15),(VOL(I),I=1,15),
c                     DEEP2,IATMPR,IFDROP,IVFRAC,STAG1D,STAG2D,
c                     CRR,CRC,GOVOL,SL,SCR
c 492     FORMAT(1X,3(A1,I6),15F4.1,I6,2I3,I2,2I3,3F4.1,A1,
c    1             F5.2,12X)
c         WRITE(2,494)APIG,SPGC,SRES,SVOL,TGNVOL,VLD,VOLKD,
c    1                VOLR,XCRN,XMLD,XNLD,XNRES,AVED,DGN,DKD,SGRR
c 494     FORMAT(1X,F5.1,F5.3,F5.2,5F5.1,F5.3,2F5.1,5F5.3,51X)
c         WRITE(2,496)AAPGMN,AAPGMD,FIELD,AAPGNO,AGE,
c    1                COLOR,FORM,FORMMD,FORTYP
c 496     FORMAT(1X,A4,A1,A33,A3,A3,A2,A23,A1,A2,59X)
c
      Dimension sg(16),vol(16),cumvol(16)
      character*1 sua77,sua100,sua130,sua180
      character*33 field
      Open (5,file='crudeoil.dat',status='old')
```

APPENDIX C. PROGRAMS TO PROCESS DOE CRUDE ANALYSES

```
      Open (6,file='calif.sum')
c
c     choose nloc = nl = 4 for Californiua
c
      nloc = 4
      kount = 0
   10 read(5,100,end=999)id,nl,sua100,isu100,sua77,isu77,
     &                    sua130,isu130,sua180,isu180
  100 format(2x,i5,i3,4x,a1,i6,9x,3(a1,i6))
      if(nl .eq. nloc)then
         kount = kount + 1
         read(5,110)(sg(i),i=1,15)
  110    format(//,1x,15f5.3)
         read(5,120)(vol(i),i=1,15)
  120    format(22x,15f4.1)
         read(5,130)api,volr,sgrr
  130    format(1x,f5.1,30x,f5.1,35x,f5.3)
         read(5,140)field
  140    format(6x,a33)
c
         write(6,150)id,field,api,sua100,isu100,sua77,isu77,
     &                 sua130,isu130,sua180,isu180
  150    format(/,1x,'ID # ',i5,5x,a33,'       API: ',f5.1,/,
     &   1x,'Viscosity, S.U.@77, 100, 130 & 180F: ',
     &   4(1x,a1,i6),' secs')
         do 15 i=1,15
   15    cumvol(i) = 0.
         cum = 0.
         do 20 i=1,15
         cum = cum + vol(i)
         cumvol(i) = cum
```

```
   20      continue
           cumvol(16) = cumvol(15) + volr
           write(6,160)(vol(i),i=1,15),volr
  160      format(1x,'Vol%',16(1x,f5.1))
           write(6,170)(cumvol(i),i=1,16)
  170      format(1x,'Cum%',16(1x,f5.1))
           write(6,180)(sg(i),i=1,15),sgrr
  180      format(1x,'S.G.',16(1x,f5.3))
        else
           read(5,200)field
  200      format(/////,6x,a33)
        endif
c
c       if(kount .eq. 10)goto 999
        goto 10
c
  999 stop
      end
```

APPENDIX C. PROGRAMS TO PROCESS DOE CRUDE ANALYSES

```
c
c     This program extracts distillation information from the
c     summary file and creats output files by cut number
c
c     Output information:
c        API gravity of initial oil
c        volume distilled
c        API gravity of distilled component
c        API gravity of residuum
c        API gravity of mixed/produced oil for a given mix ratio
c
      Dimension sg(16),vol(16),cumvol(16)
      character*4 word
      Open (5,file='calif.sum',status='old')
      Open (10,file='f10.dat')
      Open (11,file='f11.dat')
      Open (12,file='f12.dat')
      Open (13,file='f13.dat')
      Open (14,file='f14.dat')
      Open (15,file='f15.dat')
   10 read(5,100,end=999)word
  100 format(1x,a4)
      if(word .eq. '    ')then
         kount = kount + 1
         read(5,110)id,api
  110    format(6x,i5,50x,f5.1,/)
         read(5,120)(vol(i),i=1,16)
  120    format(5x,16(1x,f5.1))
         read(5,120)(cumvol(i),i=1,16)
         read(5,130)(sg(i),i=1,16)
  130    format(5x,16(1x,f5.3))
```

```
c
c     API gravity of distilled
c
         do 50 iunit=10,15
         cumdis = 0.
         weight = 0.
         do 20 i=1,iunit
            cumdis = cumdis + vol(i)
            weight = weight + vol(i)*sg(i)
   20    continue
         if(cumdis .eq. 0)then
            asg1 = 0.
            apidis = 0.
         else
            asg1   = weight/cumdis
            apidis = 141.5/asg1 - 131.5
         endif
c
c    API gravity of residue
c
         asg0 = 141.5/(api+131.5)
c
         if(sg(16) .ne. 0 .and. cumdis .ne. 0)then
            index=1
            cumres = 0.
            weight = 0.
            do 30 i=iunit+1,16
               cumres = cumres + vol(i)
               weight = weight + vol(i)*sg(i)
   30       continue
            asg2   = weight/cumres
```

```
        apires = 141.5/asg2 - 131.5
      else
        index=2
        if(cumvol(16) .eq. cumdis)then
          apires = 0.
        else
          asg2 = (cumvol(16)*asg0-cumdis*asg1)
   &               /(cumvol(16)-cumdis)
          apires = 141.5/asg2 - 131.5
        endif
      endif
c
c     calcualte api gravity of mix, use ratio vmix:1
c     volume distilled from vmix (volume) of initial oil mixing
c     with 1 volume of initial oil
c
      vmix = 1.0
      if(asg1 .eq. 0)then
        apimix = 0.
      else
        asgmix = (asg0 + vmix*asg1*cumdis/100.) /
   &              (1. + vmix*cumdis/100.)
        apimix = 141.5/asgmix - 131.5
      endif
c
      write(iunit,150)id,api,cumvol(iunit),apidis,apires,apimix,
   &             index,asg0,asg1,asg2
c 150 format(1x,i5,5(' ',f5.1),' ',i2)
  150 format(1x,i5,5(1x,f5.1),1x,i2,3(1x,f5.3))
   50 continue
    endif
```

```
c
      goto 10
c
  999 stop
      end
```

APPENDIX C. PROGRAMS TO PROCESS DOE CRUDE ANALYSES

```
c
c     Program to rearrange summary tables into x-y data sets
c     for gps plotting (on Pangea)
c
      Open  (5,file='f12.dat')
      Open (10,file='f12.vol')
      Open (11,file='f12.dis')
      Open (12,file='f12.res')
      Open (13,file='f12.mix')
      Open (14,file='f12.sgdis')
      Open (15,file='f12.sgres')
c
   10 read(5,100,end=999)id,api,cumvol,apidis,apires,apimix,index,
     &                     asg0,asg1,asg2
c 100    format(1x,i5,5(' ',f5.1),' ',i2)
  100    format(1x,i5,5(1x,f5.1),' ',i2,3(1x,f5.3))
      write(10,110)api,cumvol
      write(11,110)api,apidis
      write(12,110)api,apires
      write(13,110)api,apimix
      write(14,111)asg0,asg1
      write(15,111)asg0,asg2
  110 format(1x,f5.1,10x,f5.1)
  111 format(1x,f5.3,10x,f5.3)
      goto 10
c
  999 stop
      end
```

END

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