# The presence of impurities in the crude oil

## 1. Sulfur

Difficulties with oils that contain sulfur compounds arise in only three main ways: corrosion, odor and poor explosion characteristics of gasoline fuels.

a) Corrosion: corrosion by finished products presents little difficulty because most products are used at low temperatures. The main bulk of the corrosive sulfur compounds can by removed by treatment with alkalis or the sweetening treatments. In presence of air and moisture the sulfur gases produced during the burning of oil may cause corrosion, as in steel stacks, ducts, and engine exhaust pipes and mufflers.

Real difficulties arise when high sulfur oils are heated to temperature 300 $^{0}$F or higher for copper, or 400 0F for steels.

b) Odor : Odor is most obnoxious with low boiling or gaseous sulfur compounds, as $H_2S$ or $SO_2$ in flue gases, mercaptans up to even six carbons atoms (B.P. of about 400 $^{0}$F), sulfides up to 8 carbons atoms (about 350 $^{0}$F), and among disulfides only methyl disulfide (B.P. 243 $^{0}$F) . This odor is not obnoxious in sweetened products except in certain extremely high- sulfur gasoline.

Percentage of S in crude oil ranges from nearly 0.1 for high API- gravity crude oils as high 5 percentage in a few very heavy crude oils.

Generally crude with greater than **0.5%** S require more extensive processing than those with lower sulfur content.

## 2. Salt

Salt carried into the plant in brine associated with crude oils is a major cause of the plugging of exchangers and coking of pipe still tubes.

If salt content expressed as NaCl , is greater than 10 lb/1000 bbl, it is generally necessary to desalt the crude before processing.

## 3.Carbon Residue :

The less the value of carbon residue the more valuable the crude.

## 4. Nitrogen Compounds:

The nitrogen compounds in petroleum are not of major importance, but they do tend to cause a reduction in the activity of the catalysts used in catalytic cracking and they may assist in the formation of so- called "gum" in distillated or diesel fuel oil.

Crude containing in amount above 0.25 % by weight require special processing to remove the nitrogen.

## 5. Hydrocarbons Gaseous

The amount of gaseous hydrocarbons dissolved in crude oil is almost totally a function of the degree of weathering that the oil has undergone or the pressure at which it is collected. The percentage of involved when the dissolved gases are lost cannot be stated with accuracy but it is about

$$\text{Liquid vol. \% loss} = \frac{\text{Reid V. P} - 1}{6}$$

If the gas have M.W= 40, the gas amount to about 16.1 ft$^3$ per 1% loss of liquid.

## **6.** Metallic Content (Ni, V, Cu)

The metal content in crude oil can vary from a few ppm to more than 1000 ppm, disadvantages affect activities of catalyst, corrosion, deterioration of refractory furnace lining and stacks. Can be reduced by solvent extraction with $C_3$.

# Analysis of Crude Petroleum

**1) Distillation Curves :** When a refining company evaluate its own crude oils to determine the most desirable processing sequence to obtain the required products, its own laboratories will provide data concerning the distillation and processing of the oil and its fractions. The first step in refinery is distillation in which the crude oil separated into fractions according to its boiling point.

There are at least four types of distillation curves or ways of relating vapor temperature and percentage vaporized

**a) True-boiling-point (T.B.P)**: (Fractional, run only on crude oil, batch) .

Distillation characteristics of a crude are assessed performing a preliminary distillation called "True Boiling Point" analysis (TBP). This test enlightens the refiners with all possible information regarding the percentage quantum of fractions, base of crude oil and the possible difficulties beset during treatment operation etc.

True boiling point (TBP) and gravity-mid percent curves can be developed from U.S Bureau of mines crude petroleum analysis data sheet Fig. (1) which is reported in two portions: The first is the portion of the distillation at atmospheric pressure and up to 527 $^0$F (275 $^0$C) end point, the second at 40 mm Hg total pressure to 572 $^0$F (300 $^0$C) end point. The portion of distillation at reduced pressure is necessary to prevent excessive pot temperature which cracking of the crude oil. The distillation temperatures reported in the analysis be corrected to 760 mm Hg pressure. Generally, those reported in the atmospheric distillation section need to be corrected. The distillation temperature at 40 mm Hg can by converted to 760 mm Hg by use of chart Fig. (2) shows the relationships between boiling temperatures at 40 mm Hg and 760 mm Hg pressure. The gravity mid- percent curve is plotted on the same chart with TBP. The gravity should be plotted on the average volume percent of the fraction, as the gravity is the average of the gravities from the first to the last drops in the fractions. For narrow cuts, a straight line relationship can be assumed and the gravity used as that of the mid-percent of the fraction. Smooth curves are drawn for both TBP and gravity mid- percent curves. Fig. (3) illustrated these curves for the crude oil.

**b) Equilibrium or Flash Vaporization (EFV).** The feed material is heated as it flows continuously through a heating coil. As vapor is formed it kept cohesively with liquid at some temperature and a sudden release of pressure quickly flashes or separates the vapor from the mixture without any rectification. By successive flash evaporation like this the stock can be progressively distilled at different increasing temperatures. a curve of percentage vaporized vs. temperature may be plotted.
travels along in the tube with remaining liquid until separation is permitted in a vapor separator or vaporizer. By conducting the operation at a series of outlet temperature, a curve of percentage vaporized vs. temperature may be plotted.

**c) ASTM or no fractionating distillation:** (no fractional , run on fractions) .

It is supposed to be like EFV, a non fractionating distillation system, distinguishing itself as differential distillation. It is a simple distillation carried out with standard ASTM flasks 100,200,500 ml flasks. The data obtained is similar to TBP data

**d) Hempel:** (Semi fractional).

It is considered as a semi-fractionating type of distillation like Saybolt 's, Where TBP data is insufficient , this can be used.

## CRUDE PETROLEUM ANALYSIS

Bureau of Mines Bartlesville Laboratory
Sample 53016

### IDENTIFICATION

Hastings Field

Texas
Brazoria County

### GENERAL CHARACTERISTICS

Gravity, specific, 0.867 Gravity, ° API, 31.7 Pour point, ° F., below 5
Sulfur, percent, 0.15 Color, brownish green
Viscosity, Saybolt Universal at 100° Nitrogen, percent,

### DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 751 mm. Hg
First drop, 84 ° F.

| Fraction No. | Cut temp. ° F. | Percent | Sum, percent | Sp. gr., 60/60° F. | ° API, 60° F. | C. I. | Refractive index, $n_D$ at 20° C. | Specific dispersion | S. U. visc., 100° F. | Cloud test, ° F. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 122 | 0.8 | 0.8 | 0.673 | 78.8 | | | | | |
| 2 | 167 | 1.0 | 1.8 | .685 | 75.1 | 15 | | | | |
| 3 | 212 | 3.0 | 4.8 | .725 | 63.7 | 24 | 1.39574 | 127.7 | | |
| 4 | 257 | 3.4 | 8.2 | .755 | 55.9 | 29 | 1.41756 | 128.6 | | |
| 5 | 302 | 3.1 | 11.3 | .777 | 50.6 | 32 | 1.42985 | 135.4 | | |
| 6 | 347 | 3.9 | 15.2 | .798 | 45.8 | 35 | 1.44192 | 137.8 | | |
| 7 | 392 | 4.9 | 20.1 | .817 | 41.7 | 38 | 1.45217 | 139.9 | | |
| 8 | 437 | 6.8 | 26.9 | .833 | 38.4 | 40 | 1.46057 | 140.3 | | |
| 9 | 482 | 8.0 | 34.9 | .848 | 35.4 | 41 | 1.46875 | 148.0 | | |
| 10 | 527 | 10.9 | 45.8 | .864 | 32.3 | 44 | 1.47679 | 149.8 | | |
| STAGE 2—Distillation continued at 40 mm. Hg | | | | | | | | | | |
| 11 | 392 | 7.3 | 53.1 | 0.873 | 30.6 | 45 | 1.48274 | 155.2 | 42 | Below 5 |
| 12 | 437 | 7.8 | 60.9 | .879 | 29.5 | 44 | 1.48474 | 156.2 | 50 | do |
| 13 | 482 | 6.2 | 67.1 | .889 | 27.7 | 45 | 1.49058 | 152.7 | 71 | do |
| 14 | 527 | 5.7 | 72.8 | .901 | 25.6 | 48 | | | 125 | 10 |
| 15 | 572 | 6.9 | 79.7 | .916 | 28.0 | 52 | | | 280 | 20 |
| Residuum | | 20.3 | 100.0 | .945 | 18.2 | | | | | |

Carbon residue, Conradson: Residuum, 4.7 percent; crude, 1.0 percent.

### APPROXIMATE SUMMARY

| | Percent | Sp. gr. | ° API | Viscosity |
|---|---|---|---|---|
| Light gasoline | 4.8 | 0.708 | 68.4 | |
| Total gasoline and naphtha | 20.1 | 0.771 | 52.0 | |
| Kerosine distillate | -- | -- | -- | |
| Gas oil | 36.9 | 0.858 | 33.4 | |
| Nonviscous lubricating distillate | 10.2 | .879-.895 | 29.5-26.6 | 50-100 |
| Medium lubricating distillate | 5.8 | .895-.908 | 26.6-24.3 | 100-200 |
| Viscous lubricating distillate | 6.7 | .908-.924 | 24.3-21.6 | Above 200 |
| Residuum | 20.3 | 0.945 | 18.2 | |
| Distillation loss | 0 | | | |

Figure (1) U.S Bureau of Mines crude petroleum analysis (From Gary and Handwerk, 2001)

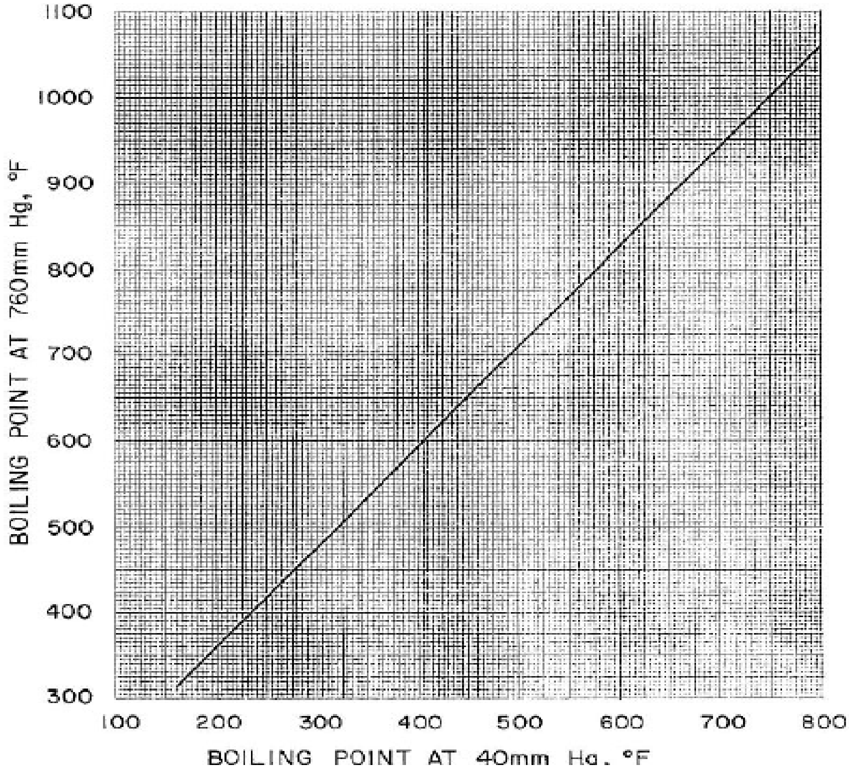


Figure (2) Boling point at 760 mmHg versus boiling point at 40mmHg (From Gary and Handwerk, 2001)

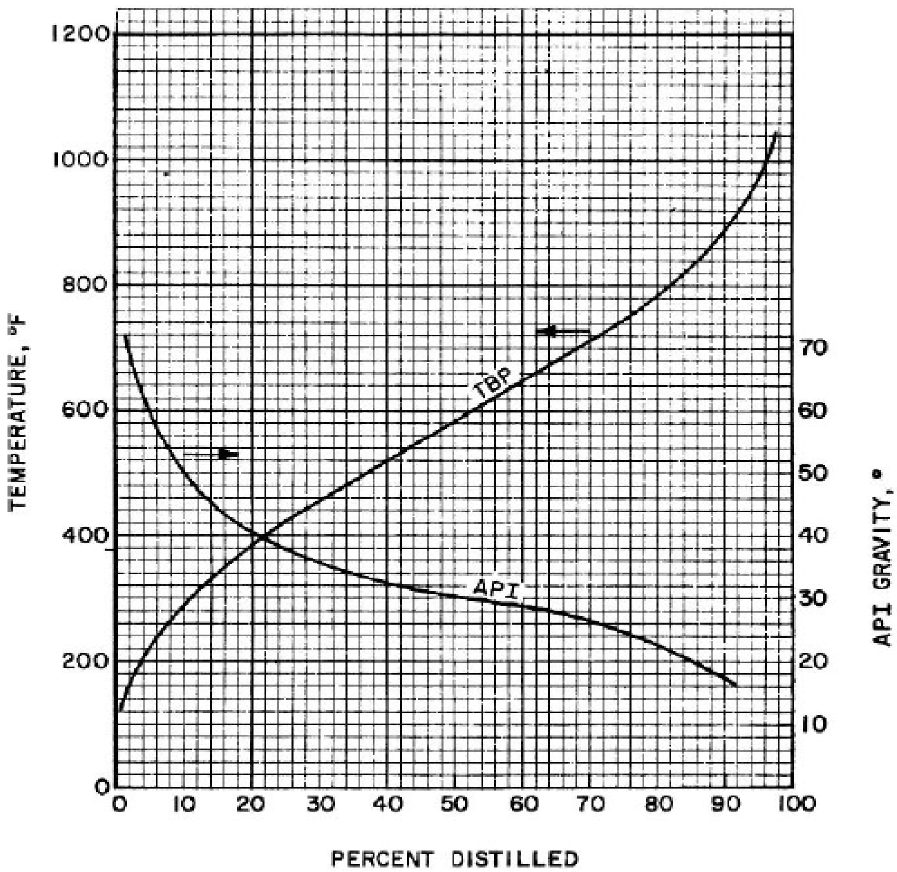


Figure (3): TBP and gravity- mid percent curves. Hasting Field, Texas crude: gravity 31.7 $^{o}$API; sulfur, 0.15 wt%.(From Gary and Handwerk, 2001)

## 2) <u>Mid Percent Curves</u>:

The physical properties of an oil found to vary gradually throughout the range of compounds that constitute the oil. Distillation is a means of arranging of compounds these chemical compounds in order of their boiling points. The properties such as color, specific gravity, and viscosity are found to be different for each drop or fraction of the material distilled. The rate at which these properties change from drop to drop may plot as mid per cent curves.

In reality, <u>the specific gravity or viscosity</u> of a fraction is an average of the properties of the many drops that constitute the fraction. If each drop is equally different from the last drop and from the succeeding one, then the drop that distills at exactly half of the fraction has the same property as the average of all the drops. This would be the condition for a mid per cent that is a straight line, but they are substantially straight through any short range of percentage. For a short range of percentage the average property is equal to the property at the mid-point of the fraction. The arithmetical average of the properties of these small fractions is the property of the total or large fraction, or even the entire sample.

Integral- averaging by adding together the properties of a series of short fractions and dividing by number of fractions can not be used on properties that are not additive. Specific gravity (not API gravity) is an example of an additive property, e. g. 10 volumes of an oil of specific gravity 0.8 when mixed with an equal volume of 0.9 specific gravity oil yields a mixture that has a specific gravity 0.85.

| **Additive Properties** | **Non additive Properties** |
|---|---|
| Boiling Point (T.B.P) | API Gravity |
| Vapor Pressure | Viscosity |
| Specific Gravity | Color |
| Aniline Point | Flash Point |
| Sulfur Content | |
| Hydrogen/Carbon ratio | |

## 3) <u>Yield Curves</u>:

If a property is not additive, the property of various ranges of fractions can be determined experimentally by blending and plotting the property value as obtained as a function of yield or amount of blended material.

## <u>Crude Suitable for Asphalt Manufacture</u>

If a crude oil residue (750 $^0$**F mean average boiling point**) having a Watson **characterization factor < 11.8** and **gravity < 35 $^0$API** , it is usually suitable for asphalt manufacture.
If however, the difference between the K values for the **750 $^0$F** and **550 $^0$F** fraction is grater than **0.15**, the residue may contain too much wax to meet most asphalt specification.

## <u>Calculation of (K) (Characterization Factor) for The Whole Crude</u>

1. Calculate the TVABP using 20, 50, and 80 volume % TBP temperature.
2. Calculate the 10 to 70% slope of the whole curve.
3. Using a proper correction factor, convert TVABP to TMABP. (or some time given ): (TMABP=TVABP-ΔT)
4. Constract a spg mid percent curve and evaluate the spg for the whole crude.
5. K is found as a function of TMABP and spg.

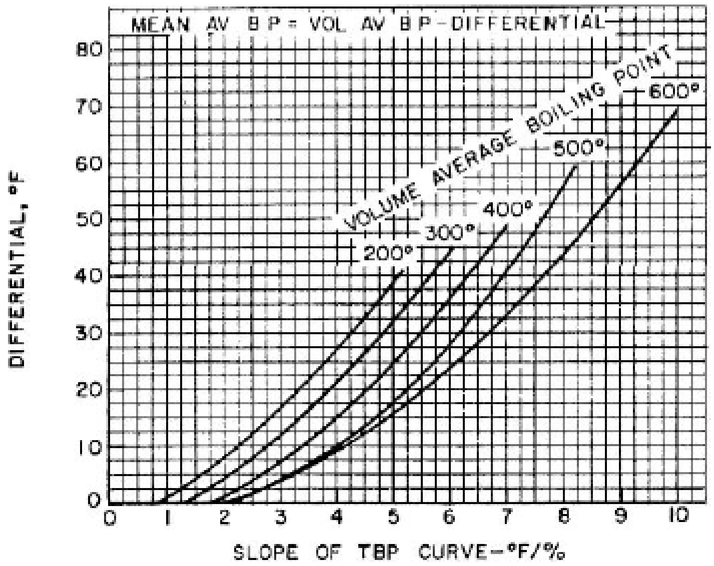


Figure (4): Mean average boiling point of petroleum fractions. (From Gary and Handwerk, 2001)

## Estimation of EFV Distillation Curve

### A- Estimation of the straight line EFV curve:

1. Estimate of t 50% of ASTM/ TBP using:
2. Estimate the 10 to 70% slope of ASTM/TBP using

$$Slope(ASTM/TBP) = \frac{t_{70} - t_{10}}{60}$$

3. Use Fig. (5) to convert slope (ASTM/TBP) to slope of EFV

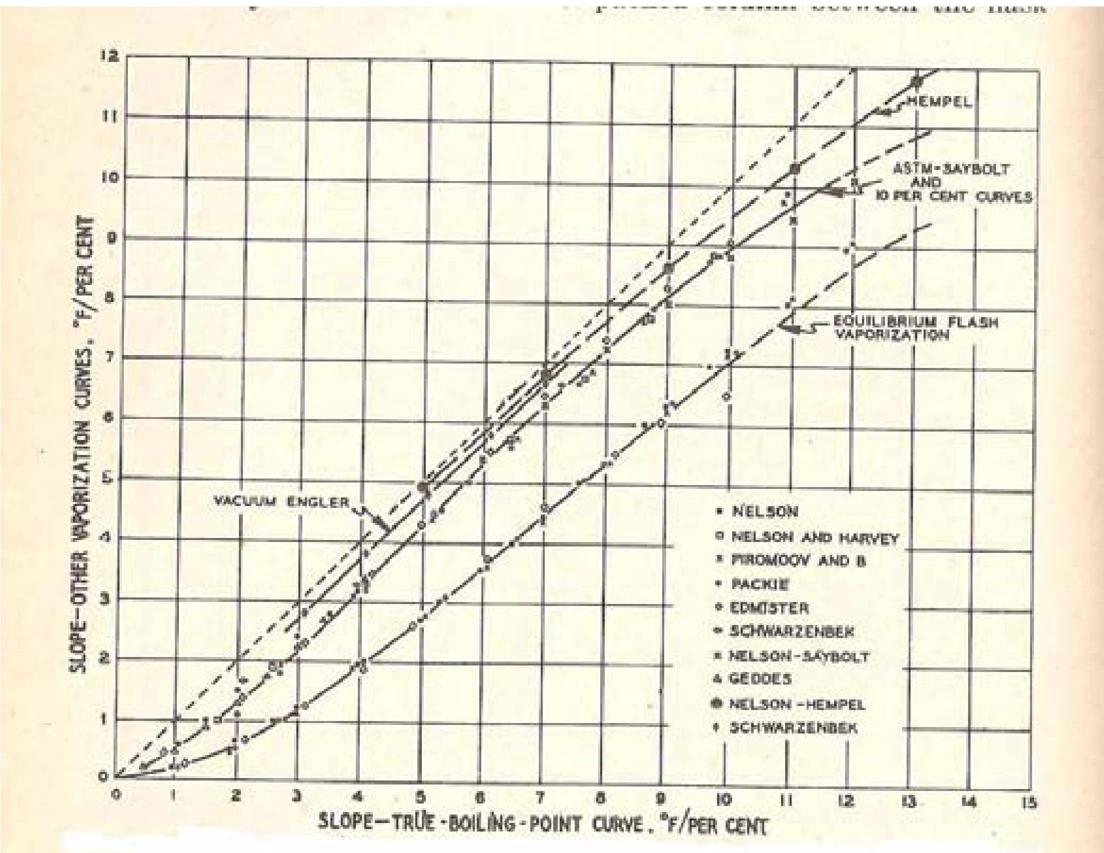


Fig (5): Relationships between the slopes (degrees/ per cent) of various distillation or vaporization curves. (From, Nelson, W. L, 1985)

4. Estimate t 50% of EFV from Fig. ( 6 )

$$t_{50\%\,EFV} = t_{50\%\,EFV/TBP} - \Delta T$$

5. Draw a straight line through $t_{50\%}$ EFV with slop of EFV.

6. $t_{0\%\,EFV}$ ( bubble point ) $= t_{50\%\,EFV}$ - slope*(50)

7. $t_{100\%\,EFV}$ (dew point) $= t_{50\%\,EFV}$ + slope*(50)

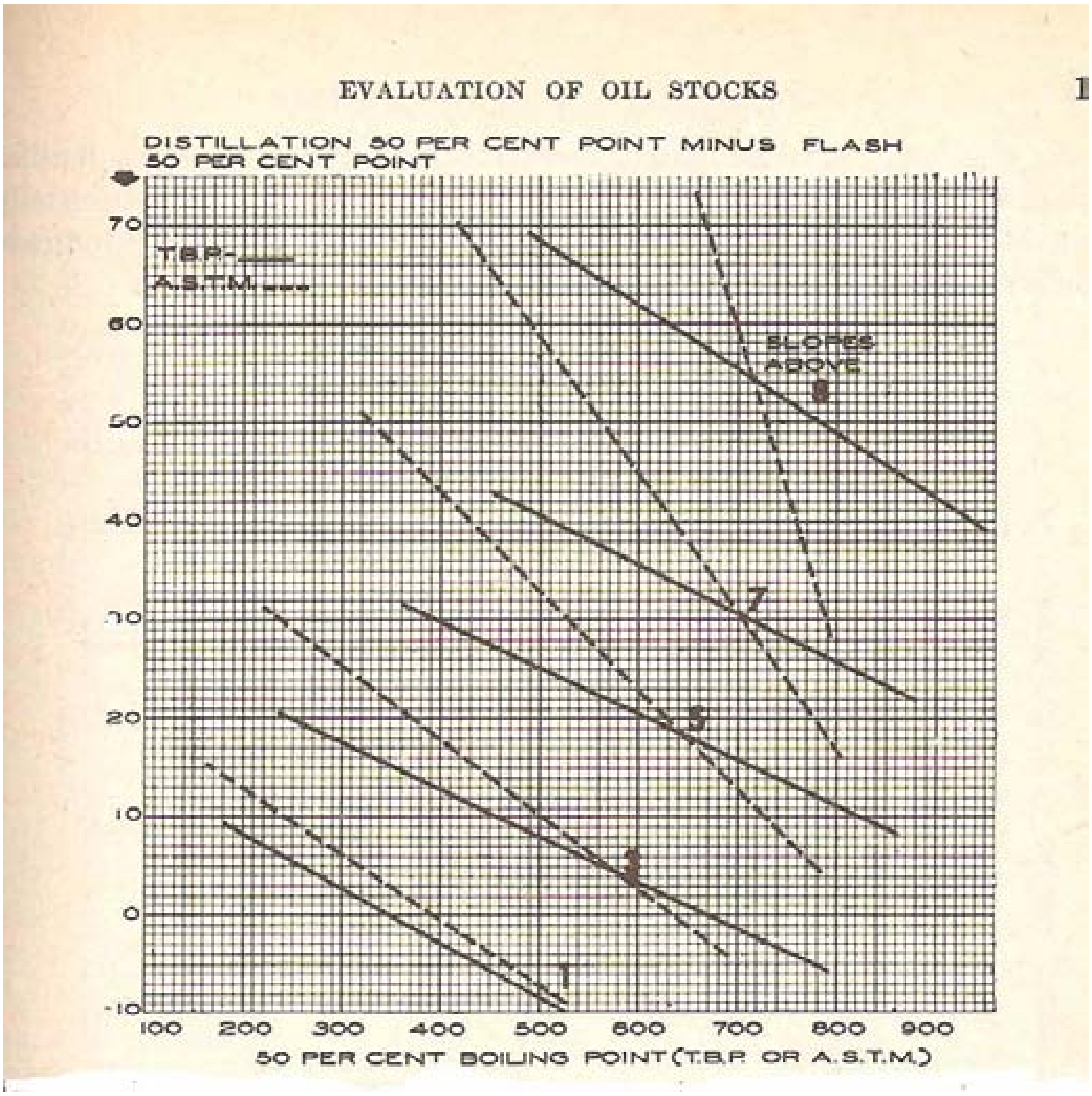


Fig (6): Relationship between distillation temperatures at 50 per cent vaporized and the flash (E. F.V.) temperatures at 50 per cent. (From, Nelson, W. L, 1985)