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.

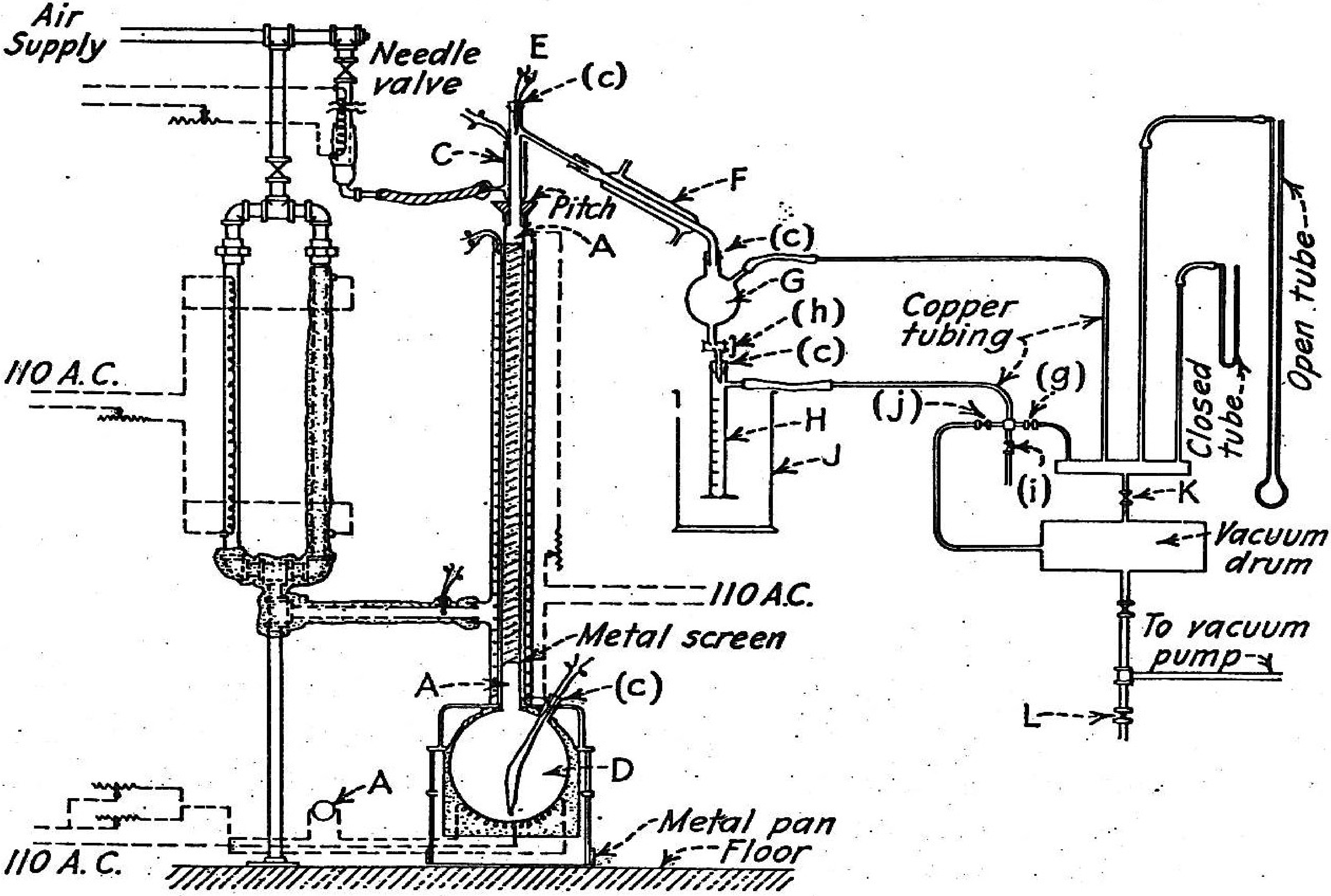

FIG. 4-7. Diagram of a true-boiling-point apparatus.

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

Fractionation column like (IP24 or D86).

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			

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

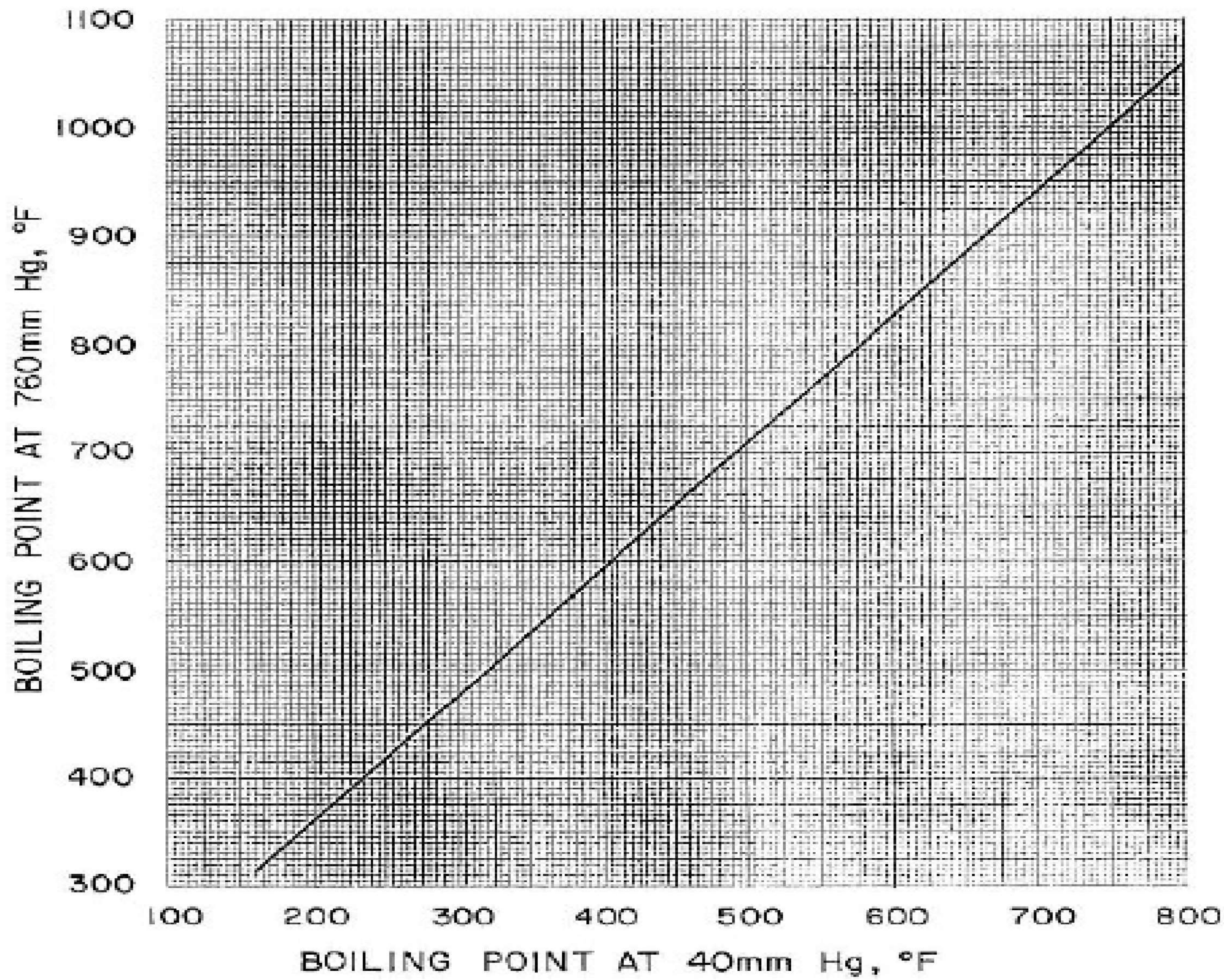


Figure (2) Boling point at 760 mmHg versus boiling point at 40mmHg (From Gary and Handwerk, 2001)

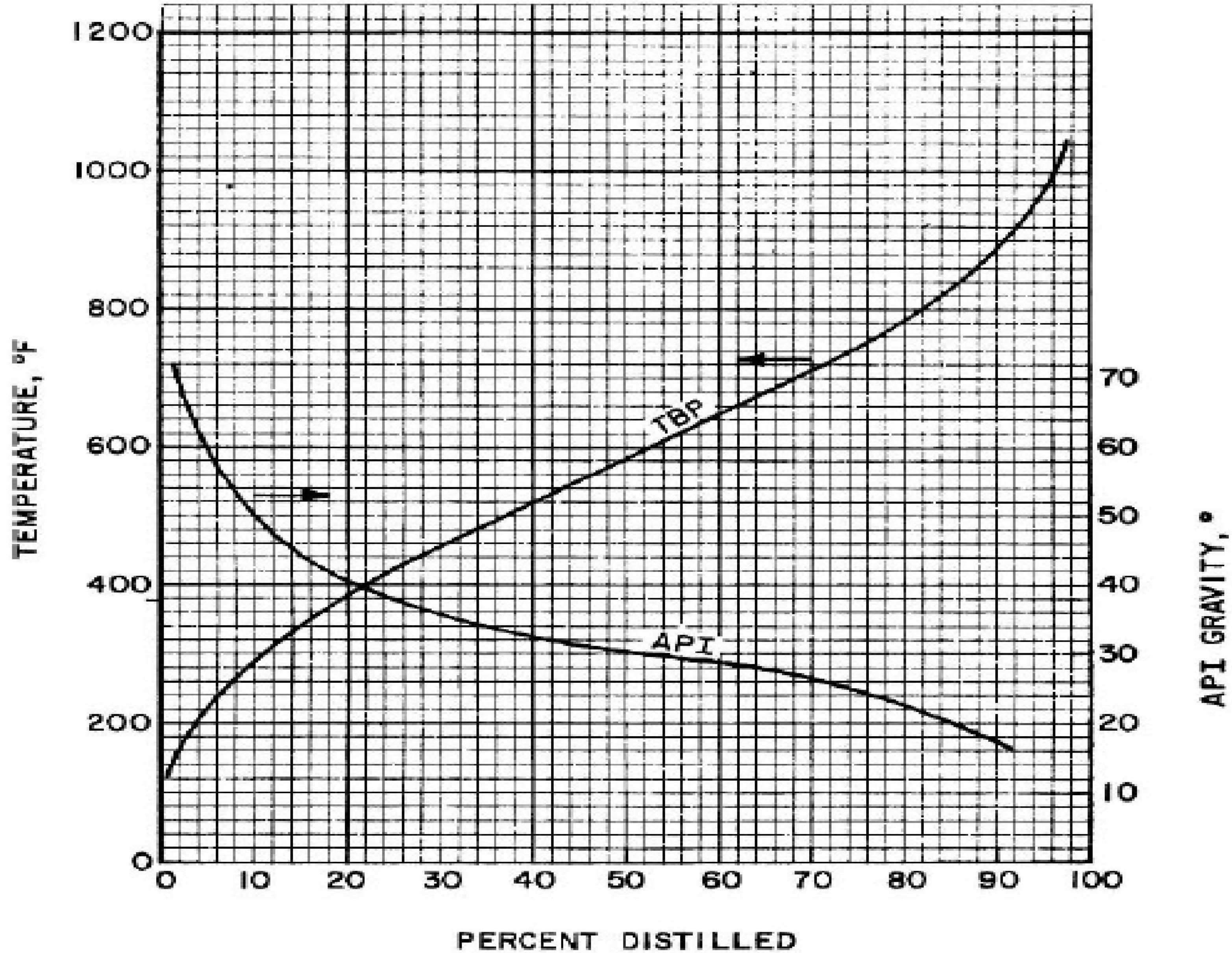


Figure (3): TBP and gravity- mid percent curves. Hasting Field, Texas crude: gravity 31.7 °API; sulfur, 0.15 wt%.(From Gary and Handwerk, 2001)

2) Mid Percent Curves:

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, the specific gravity or viscosity 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) Yield Curves:

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.

Crude Suitable for Asphalt Manufacture

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.

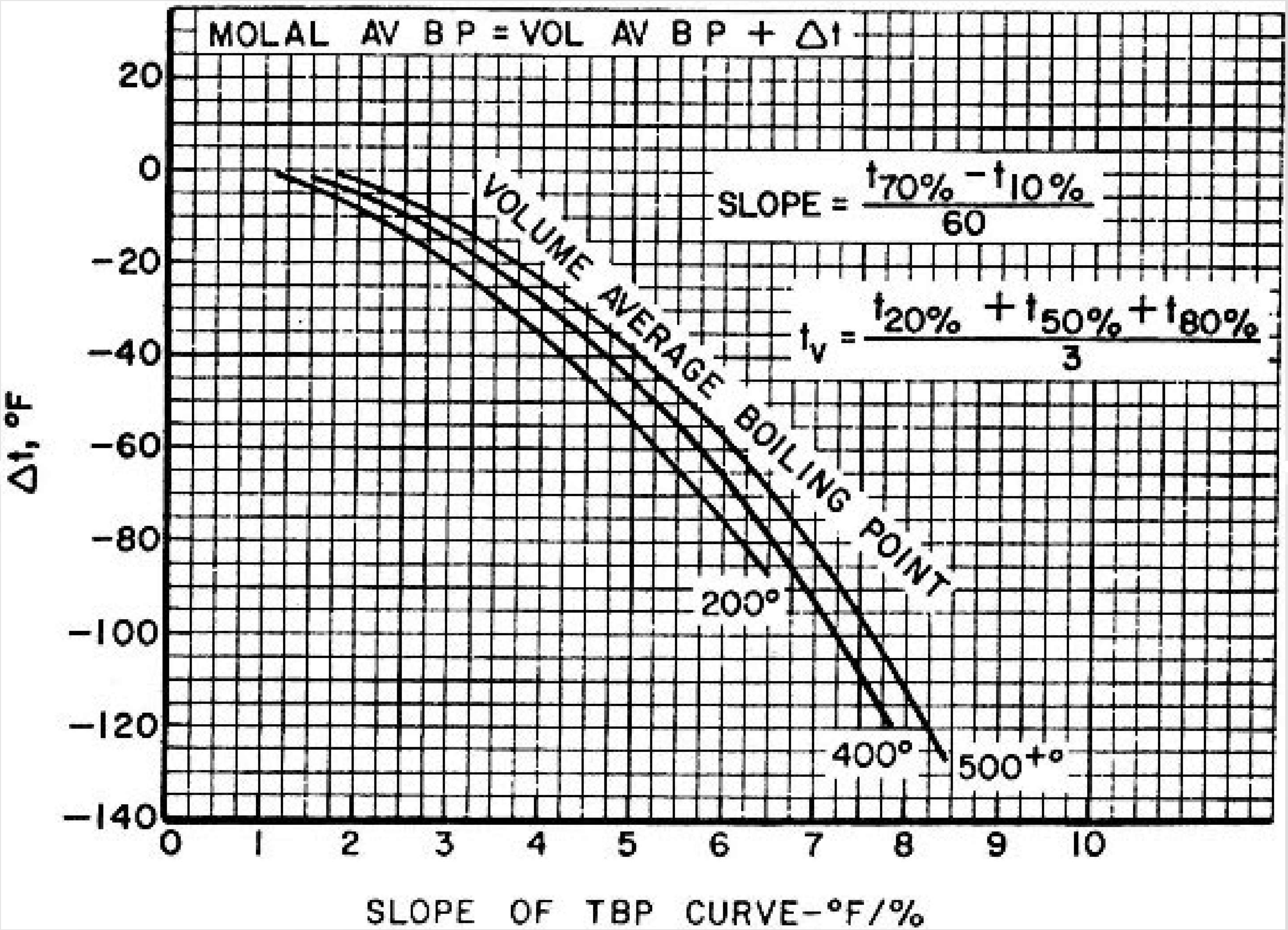
If however, the difference between the K values for the **750 ^{0}F** and 550 ^{0}**F** fraction is grater than **0.15**, the residue may contain too much wax to meet most asphalt specification.

Calculation of (K) (Characterization Factor) for The Whole Crude

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.



Fig(4) Molal 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 Fig. (8)
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

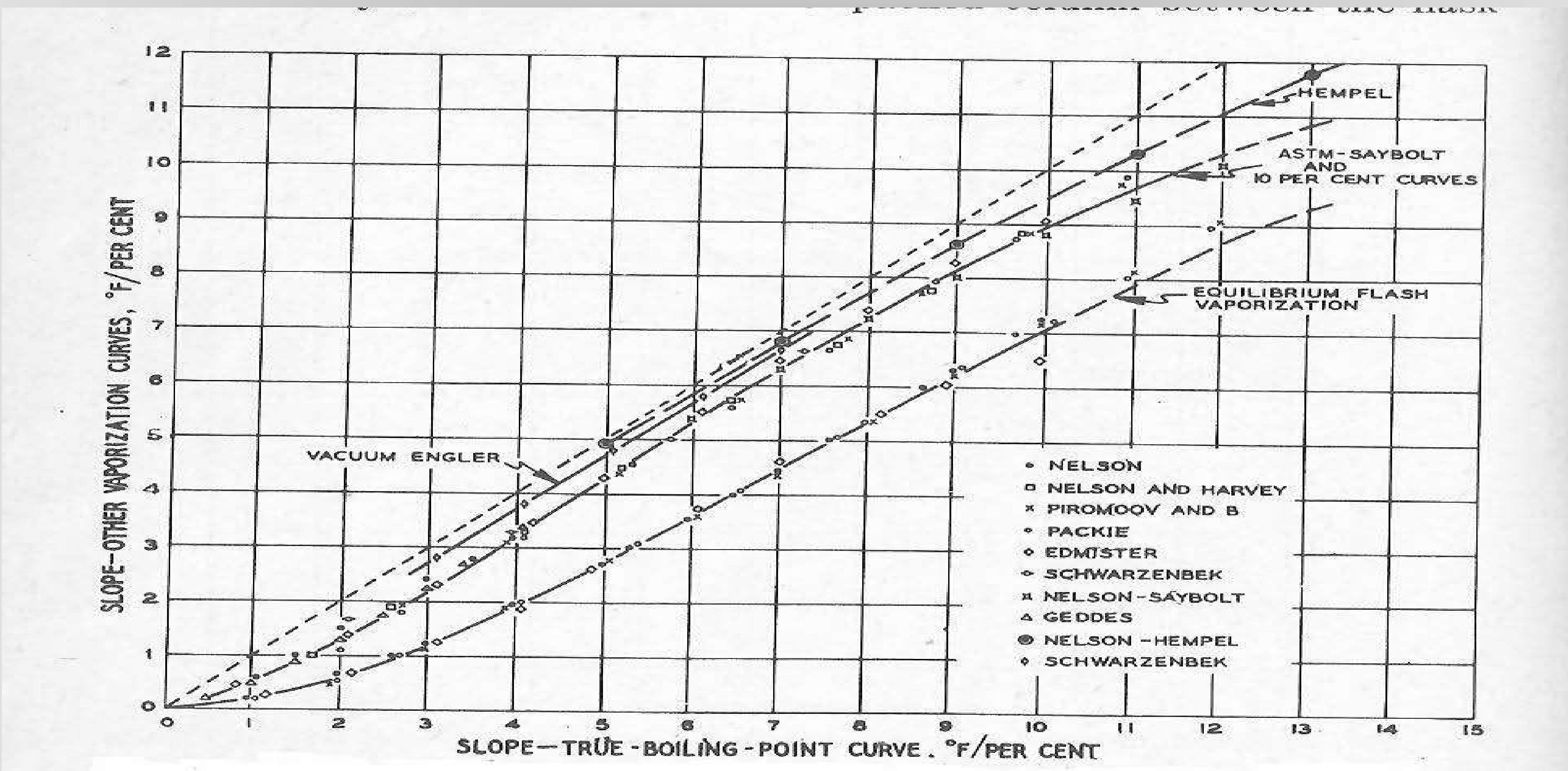


Fig (5): Relationships between the slopes (degrees/ per cent) of various distillation or vaporization curves. (From, Nelson, W. L, 1985)

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

$$\underset{\text{EFV}}{t_{50\%}} = \underset{\text{ASTM/TBP}}{t_{50\%}} - \Delta T$$

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

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

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

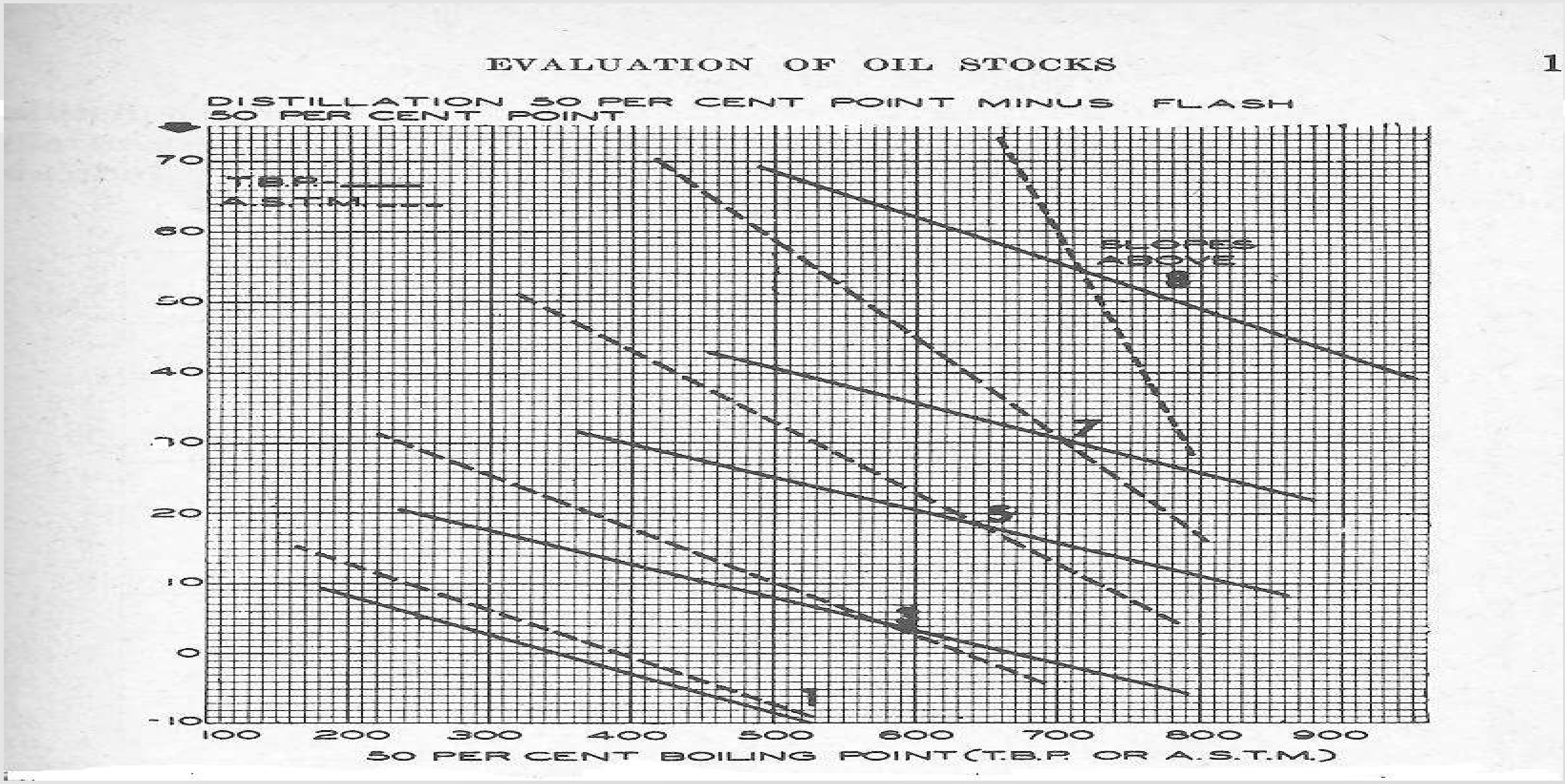


Fig (6): Relationship between distillation temperatures at 50 per cent vaporized and the flash (E. F.V.) temperatures at 50 per cent. (From, Nelson, W. L, 1985)

B. Estimation of EFV Curvature

1. Estimate $t_{50\%}$ (ASTM/TBP)

The proper 50% temperature is intermediate between the temperature on the distillation curve and the temperature on a straight line connecting the 10 and 70 percent points, and usually about halfway between.

2. Convert to $t_{50\%}$ EFV using Fig (6)
3. Estimate the (ASTM/TBP) 10-70 % slope
4. Estimate the EFV slope from Fig (5)
5. Estimate $t_{100\%}$ on flash curve = $t_{50\%}$ + slope *(50)

   $t_{0\%}$ on flash curve= $t_{50\%}$ - slope *(50)
6. Ratio of 10-70 slopes = R
7. Starting at the 10 % and compute the 5 %

$t_{10\%} = t_{50\%} - 40 *$ (slope)

EFV

8. Slope of (ASTM/TBP) through 5-10 % = r
9. Slope of EFV through 5-10 % = r / R
10. Temperature at 5 % on EFV = $t_{10\%}$- slope * (5)

$$R = \frac{\text{Slope of dist. Curve (10 -70)}}{\text{Slope of flash. Curve (10 -70)}} = \frac{\text{Slope of dist. Curve through short range (r)}}{\text{Slope of EFV through short range}}$$

<u>Average Boiling point</u>

1) Volume Average Boiling Point (TVABP)

$$TVABP = \frac{t_{10\%} + t_{20\%} + - - - - - - - - - - - + t_{90\%}}{9}$$

If such data is not available then it may be defined as

$$TVABP = \frac{t_{30\%} + t_{50\%} + t_{80\%}}{3}$$

Where all % are in volumes

2) Weight Average Boiling Point (TWABP)

$$TWABP = \frac{t_{10\%} + t_{20\%} + - - - - - - - - - - - - + t_{90\%}}{9}$$

Where % are based on weight

3) Molar Average Boiling Point (TMABP)

$$TWABP = \frac{t_{x1} + t_{x2} + t_{x3}}{x_1 + x_2 + x_3}$$

where x_1,x_2,x_3 are mole fractions
t_{x1}, t_{x2}, t_{x3} are corresponding boiling points.
All these boiling point are interconvertable.

Interconvertability of boiling points can be worked out by knowing the slope of distillation curve of a fraction. The method of finding out the slope for ASTM/TBP/EFV is the same

TBP slope is given as $\frac{t_{70} - t_{10}}{60}$ i.e. ^{0}t/ percent; where
70% and 10% are volumetric boiling points on vaporization curve.
The conversion of TBP slope to ASTM or EFV slope can be done with Fig (5)

<u>Example (1)</u> :(Use of Gravity Mid percent Curve) (Nelson p/106)

Compute the spg of a 41.4 API (0.8183 spg) mixed base crude oil from the spg mid percent

Fraction No.	Range of %	spg	Fraction No.	Range of %	spg
١	0 - 5	٠.٦٥٠٦	١١	50-55	٠.8280
٢	٥-١٠	.6939٠	١٢	٥٥-٦٠	٠.8388
٣	١٠-١٥	.7227٠	١٣	٦٠-٦٥	٠.8498
٤	١٥-٢٠	.7420٠	١٤	٦٥-٧٠	٠.8602
٥	٢٠-٢٥	.7583٠	١٥	٧٠-٧٥	٠.8713
٦	٢٥-٣٠	.7720٠	١٦	٧٥-٨٠	٠.8827
٧	٣٠-٣٥	.7844٠	١٧	٨٠-٨٥	٠.8939
٨	٣٥-٤٠	.7958٠	١٨	٨٥-٩٠	٠.9065
٩	٤٠-٤٥	.8067٠	١٩	٩٠-١٠٠	٠.9340
١٠	٤٥-٥٠	.8170٠			

$$\textbf{Spg of c.o} = \frac{5(0.65+0.69+0.72+0.74+0.76+0.77+0.78+0.79+0.81+0.815+0.82+0.83+0.85+0.86+0.87+0.88+0.89+0.91)+10(0.93)}{100}$$

Computed Sp.gr = 0, 8171, Actual Sp.gr = 0.8183 reasonable check (good for most engineer design work), See fig (7).

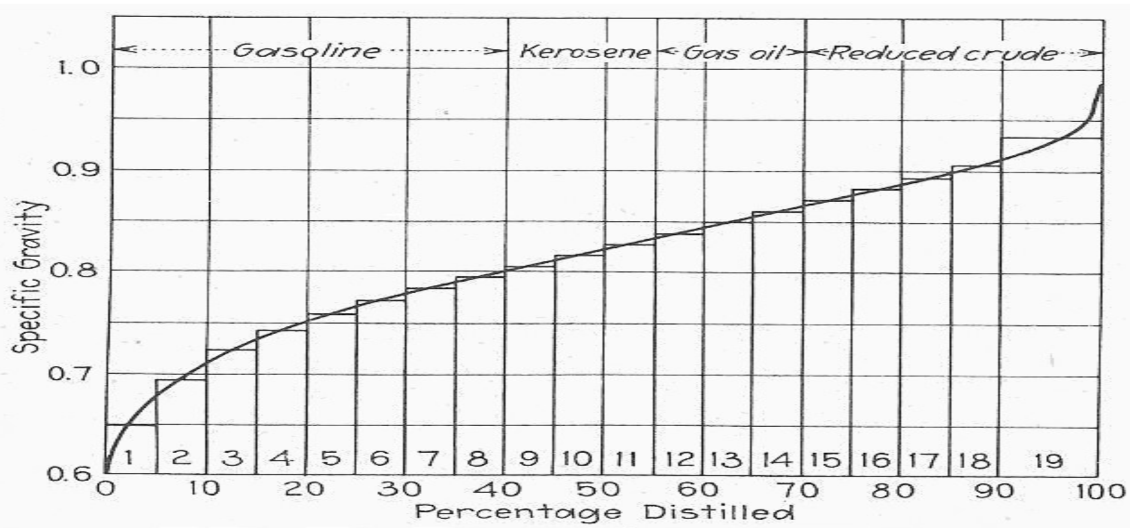


Fig (7): Gravity mid per cent curve. (From, Nelson, W. L, 1985)

Example (2): **(Estimate of Flash Vaporization Curve) p/113 Nelson**

1) The TBP curve of Fig (8) has a slope (degree/percent) between 10 and 70 percent point of;

$$\frac{t_{70} - t_{10}}{60} = \frac{775 - 210}{60} = 9.4$$ Deg/percent

3) From Fig (8), 50 % percent temperature of TBP curve =576 ^{0}F

4) From Fig (6), the50 % percent temperature of flash curve will be about 64 ^{0}F below of 50 percent temperature of the TBP curve

576- 64 =512 ^{0}F

6) A straight line flash curve can be drawn through 512 ^{0f} with slope of 6.5

Thus at zero percent the temperature=512-50*6.5=187 ^{0}F

At 100 percent the temperature =512+50*6.5= 837 ^{0}F

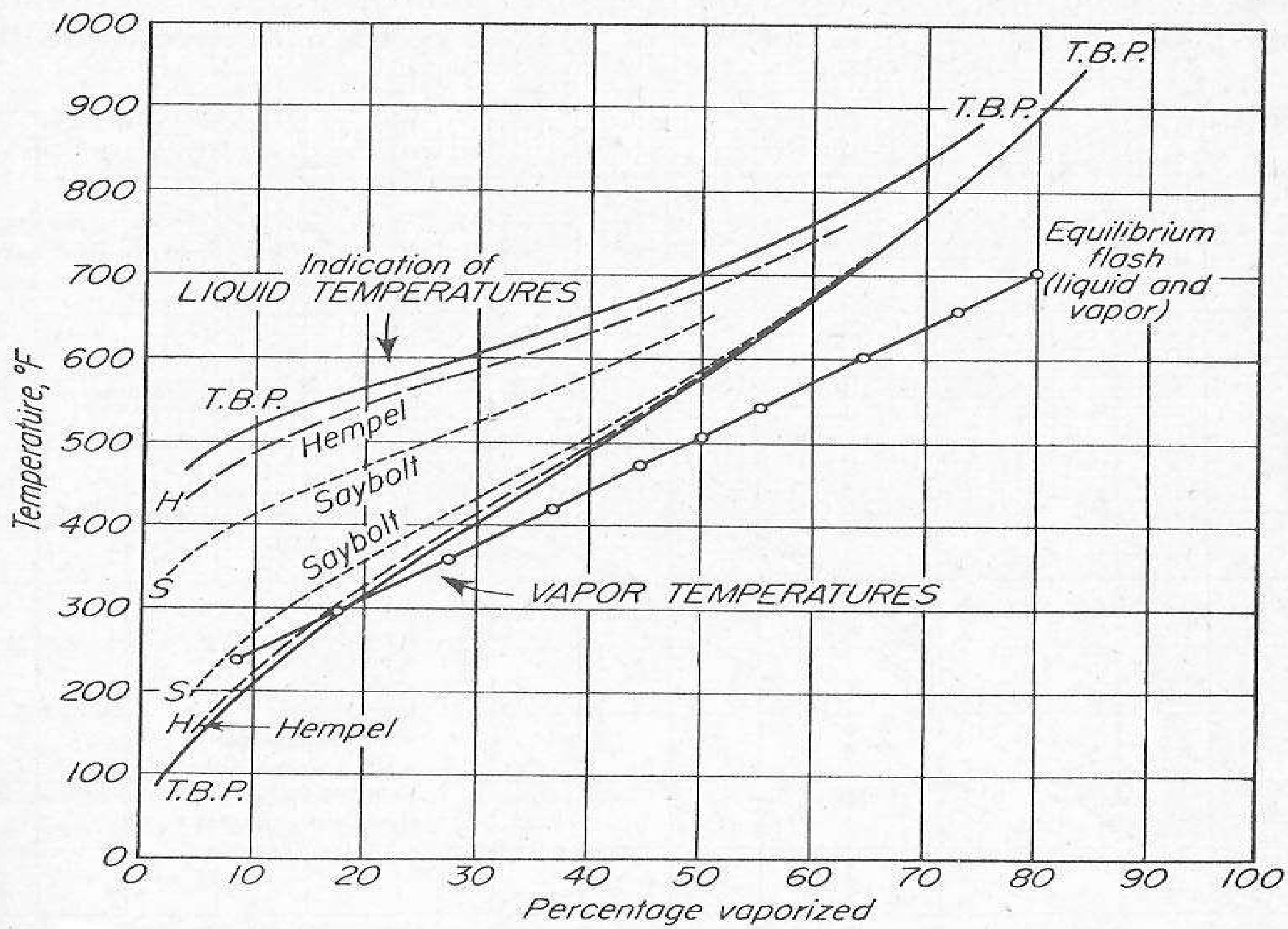


Fig (8) typical liquid and vapor temperature distillation of a 35 API crude oil

(From, Nelson, W. L, 1985)

$$\frac{170-125}{5}=9.0$$

8) Slope of flash curve between 5 and 10 %

$$R=\frac{\text{Slope of dist. Curve(10 -70)}}{\text{Slope of flash. Curve(10 -70)}}=\frac{\text{Slope of dist. Curve through short range (r)}}{\text{Slope of EFV through short range}}$$

$$=\frac{4.34}{2.8}=\frac{9}{\text{Slope of flash through short range}}$$

Temperature at 5 % on flash curve = 205-5.8*5 = 176 ^{0}F

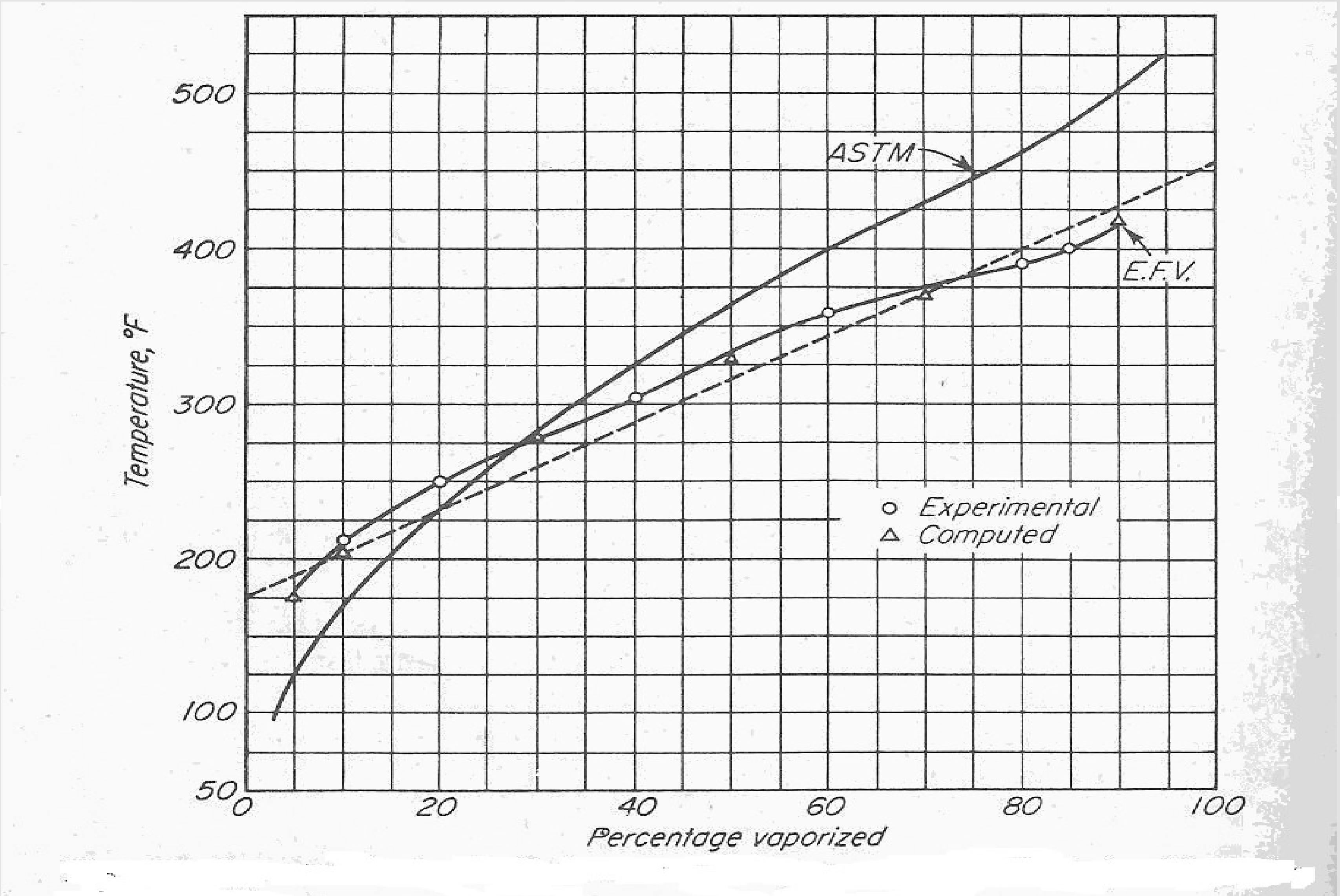


Fig (9): Curvature in the distillation curves of a pressure still distillate.

(From, Nelson, W. L, 1985)

Conversion between ASTM and TBP Distillation

The following equation suggested by Riazi and Daubert

$$\mathrm{TBP} = a(\mathrm{ASTM\ D86})^{b}$$

where a and b are constants varying with percent of liquid sample distilled as given in Table 3

TBP is true boiling point temperatures at 0, 10, 30, 50, 70, 90, and 95 volume percent distilled, in degrees Rankin.

ASTM D86 isthe observed ASTM D86 temperatures at corresponding volume percent distilled, in degrees Rankin.

Table 3

Volume % distilled	*a*	*b*
0	0.9167	1.0019
10	0.5277	1.0900
30	0.7429	1.0425
50	0.8920	1.0176
70	0.8705	1.0226
90	0.9490	1.0110
95	0.8008	1.0355

Example

A petroleum cut has the following ASTM D86 Distillation data:

Volume % distilled	0	10	30	50	70	90	95
Temperature (°C)	36.5	54	77	101.5	131	171	186.5

Convert these data to TBP data using the API method of Riazi and Daubert and Daubert's method. Plot the results and compare.

Solution

Application of the API method is straightforward using equation (3) and the constants in Table 3

Volume % distilled	D86 T (°C)	TBP (°C) API method equation (3.3)
0	36.5	14.1
10	54	33.4
30	77	69.0
50	101.5	101.6
70	131	135.2
90	171	180.5
95	186.5	194.1

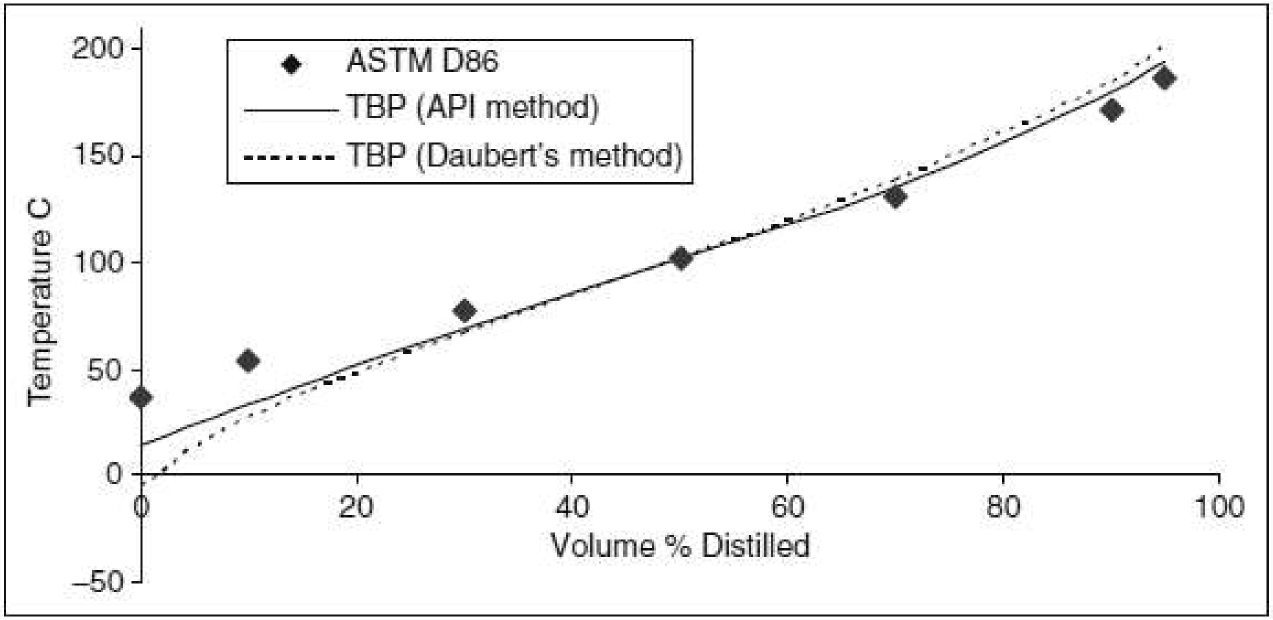
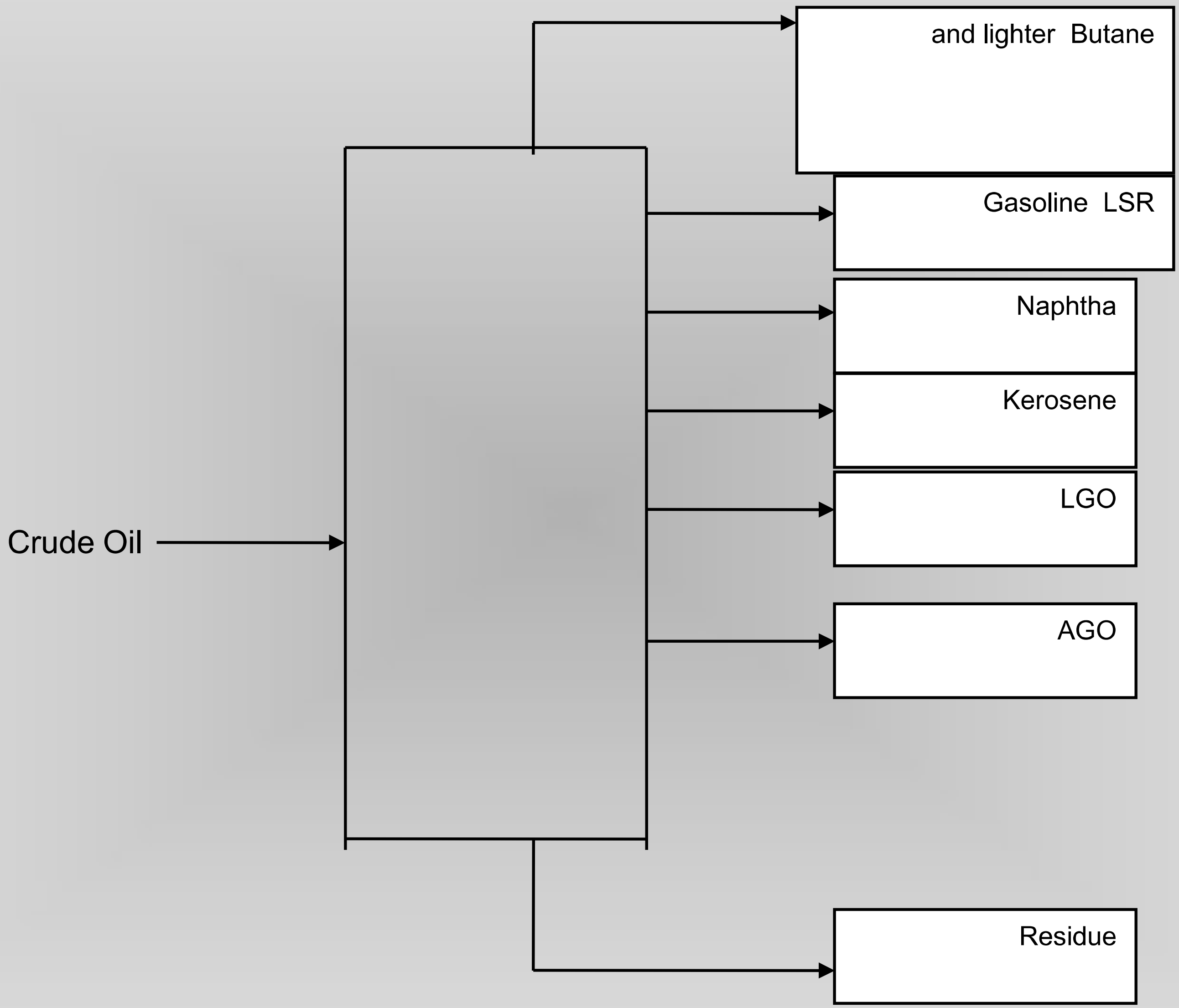


Figure E3.1 Conversion of ASTM D86 into TBP

As can be seen from Figure E3.1, the TBP distillation curve is below the ASTM curve at volume distilled below 50% and above it for volume distilled above 50%.

Distillation Fractions: All the components that boil between the two specified temperature which called the cut point



Distillation Fractions: All the components that boil between the two specified temperature which called the cut point

Fractions	Cut points	Cut points
C4 and ltr	< 32 ^{0}C	< 90 ^{o}F
Light Straight Run (LSR) Gasoline	32-105 ^{0}C	90-220 ^{o}F
Naphtha HSR	105-150 ^{0}C	220-300 ^{o}F
Kerosene	150-282 ^{0}C	300-540 ^{o}F
Gas oil	282-425 ^{0}C	540-800 ^{o}F
Residue	425^{+} ^{0}C	800^{+} ^{o}F

Cut Point

Each fraction has an **IBP** and **EP** on **ASTM** curve because of un efficient fractionation the **IBP** of heavier fraction is interrelated with the **EP** of lighter fraction.

H.W (4.1): The ASTM data for a pressure distillation are as given. Estimate the EFV curve.

% volume dist.	ASTM (temp.)	% volume dist	ASTM (temp.)
5	125	50	365
10	175	55	380
15	200	60	400
20	230	65	420
25	255	70	425
30	280	75	450
35	300	80	460
40	325	85	480
45	350	90	500

H.W (4.2): Evaluate the crude oil whose ^{0}API= 35, MABP=600, sulfur%= 0.52%.

H.W (4.3): 4000 BPD of (35 ^{0} API) crude oil having the given TBP data is available.

TBP ^{0}F	% vol. Distilled	^{0}API	% Sulfur
٨٥	١	١١٠	-
١٨٠	١٣	٦٣	-
٣٨٥	٣٠	٤٩	0.1
٥١٠	٥٠	٣٨	0.3
٦٢٠	٦٣	٢٣	0.5
٧٥٠	٧٣	٢٠	0.8
١٠٠٠	٨٤	١٧	1.5
١٠٠٠+	١٠٠	١١	2.3

a) Draw an assay curve.

b) Evaluate the given crude ; TMABP=TVABP- 120 (^{0} F)

c) Select TBP cut temperature for the products to be obtained from distilling this crude and estimate their yields.

H.W (4.4) : For the given crude oil ;

a) Evaluate the given oil.

b) Select TBP cut points for the products to be obtained from processing this crude in an atmospheric distillation unit and estimate the %yield for each cut.

% vol. Distilled	TBP (^oF)	API	% S
0	40	---	---
20	200	40	0.1
40	280	35	0.18
60	330	30	0.25
80	410	26	0.42
90	500	25	0.68
95	520	20	0.8

H.W (4.5) : For the given crude oil (31.7 0 API),sulfur percent 0.15 ;
a) Evaluate the given oil.
b) Select TBP cut points for the products to be obtained from processing this crude in an atmospheric distillation unit and estimate the %yield for each cut.

Stage 1- Distillation at atmospheric pressure 751 mm Hg

Fraction No.	Cut Temp. °F	Percent Distilled	Sum. Percent	Sp. gr. 60/60 °F	⁰ API 60 °F
1	122	0.8	0.8	0.673	78.8
2	167	1.0	1.8	0.685	75.1
3	212	3	4.8	0.725	63.7
4	257	3.4	8.2	0.755	55.9
5	302	3.1	11.3	0.777	50.6
6	347	3.9	15.2	0.798	45.8
7	392	4.9	20.1	0.817	41.7
8	437	6.8	26.9	0.833	38.4
9	482	8.0	34.9	0.848	35.4
10	527	10.9	45.8	0.864	32.3

Stage 2- Distillation at atmospheric pressure 40 mm Hg

Fraction No.	Cut Temp. ^{o}F	Percent Distilled	Sum. Percent	Sp. gr. 60/60 ^{o}F	^{0} API 60 ^{o}F
11	392	7.3	53.1	0.873	30.6
12	437	7.8	60.9	0.879	29.5
13	482	6.2	67.1	0.889	27.7
14	527	5.7	72.8	0.901	25.6
15	572	6.9	79.7	0.916	22.94
16	-------	20.3	100.0	0.945	18.2