ANILINE POINT BLENDING

The aniline point is of a gas oil indicative of the aromatic content of the gas oil. The aromatic hydrocarbon exhibits the lowest and paraffins the highest values. Aniline point (AP) blending is not linear, and therefore blending indices are used.

The following function converts aniline point to the aniline index:

$$\text{ANLIND} = 1.25^{*}\text{AP} + 0.0025^{*}(\text{AP})^2$$

where ANLIND is the aniline index and AP is the aniline point.

The aniline index can be converted back into the aniline point by the following function:

$$\text{AP} = 200 \times (\text{SQRT}\left(1.5625 + \frac{\text{ANLIND}}{100}\right) - 1.25)$$

EXAMPLE 11-9

Determine the aniline point and diesel index of the following gas oils blend:

BLEND COMPONENTS	VOL%	SPECIFIC GRAVITY	ANILINE POINT, °F
LIGHT DIESEL	0.5000	0.844	159.8
KEROSENE	0.2000	0.787	141.3
L. CYCLE GAS OIL	0.3000	0.852	98.3
BLEND	1.0000	0.835	138.57

The aniline point of the blend is determined by first estimating the aniline blend index of each component, then blending them volumetrically. The diesel index is determined as function of aniline point and API gravity:

BLEND COMPONENTS	VOL%	SPECIFIC GRAVITY	ANILINE POINT, °F	A. P. INDEX	VOL*API
LIGHT DIESEL	0.5000	0.844	159.8	263.59	131.795
KEROSENE	0.2000	0.787	141.3	226.54	45.307
L. CYCLE GAS OIL	0.3000	0.852	98.3	147.03	44.109
BLEND	1.0000	0.835	138.57		221.215

$$
\begin{aligned}
\text{Diesel Index} &= (\text{API GRAVITY} \times \text{ANILINE POINT})/100 \\
&= 37.96 \times 138.57/100 \\
&= 52.60
\end{aligned}
$$

CRUDE OIL ASSAYS

A frequent problem encountered in process studies is the determination of the yield and properties of crude oil cuts. The usual crude assay data provide information on limited number of cuts, and in general, the desired information on specific cuts has to be obtained by some form of interpolation or approximation. Also, the property of a wide cut may not be the same as the combined properties of two adjacent narrow cuts spanning the same cut points as the wide cut. The same criticism applies to most nomographs (property vs. start and end of cut and also property vs. mid-volume percent or middle boiling point) presented in many crude assays; that is, they are not property conservative.

Typically, the crude TBP between 100°F and vacuum resid end point is cut into narrow cuts, each spanning 20°F. The entire boiling range of crude oil, excluding light ends, is therefore cut into 56 narrow cuts, which are defined by standard TBP boiling ranges. These are called *pseudocomponents*, since their boiling ranges are narrow, and for all intents and purposes, they act like pure components.

The properties of the narrow cuts are generated in such a way that, when reconstituted into the wide cuts, given as input data in the assay, the errors in the back-calculated properties are minimized in a least square sense. This procedure has the advantage of being property conservative; that is, the property of the wide cut is consistent with the properties of any combination of narrower cuts of the same composition. The whole crude is the widest possible cut and therefore any breakdown of it conserves mass, sulfur, and other extensive properties. Intensive properties such as viscosity and pour point, which in general do not blend linearly, are handled using linear blending indices, which are also conserved.

CRUDE CUTTING SCHEME

The first seven crude cuts are pure components. The crude assay light ends analysis provides the vol% of these constituent in the crude: (1) H_2S, (2) H_2, (3) C_1, (4) C_2, (5) C_3, (6) iC_4, (7) nC_4. The $(iC_5 + nC_5)$ are, together, treated as the eighth cut, with a TBP end point of 100°F. The sum of light ends through nC_5 should be equal to the lights vol% distilled at 100°F. If the two numbers do not agree, the light ends yields are assumed to be correct and the TBP yields between 100 and 200°F are adjusted to provide a smooth transition between light ends and the reminder TBP curve.

The ninth cut has a TBP cut point of (100–120°F). Each successive cut has a TBP end point 20°F higher than the preceding component. The 63rd component has end point of 1200°F. The TBP end point of a crude is difficult to establish with any degree of certainty in the laboratory and therefore always is assumed to be 1292°F. The 64th (last) cut is assumed to have a TBP cut range of (1200–1292°F). Table 11-19 shows the TBP cuts of all pseudocomponents in the crude. This cutting scheme is not unique; any other convenient cutting scheme can be used, provided the cuts are narrow.

DETERMINATION OF NARROW CUT (PSEUDOCOMPONENT) PROPERTIES

The vol% of each narrow cut or pseudocomponent is known from TBP curve of the crude, once the cut points of pseudocomponents are defined. If their properties can be determined, these can be combined to determine the yield and properties of any other wide cut of that crude not available in the crude assay data. Also, narrow cut properties from different crudes can be combined to predict the wide cut yields and the properties from mixed crudes.

Narrow cut properties are determined from the wide cut properties data in the crude assay. Every crude assay provides data on the properties of different wide cuts (naphthas, kerosenes, diesels, vacuum gas oils, vacuum resides, etc.). The crude assay also provides data on the proper-

Table 11-19
Pseudocomponents Narrow Cut Points

CUT INDEX	CUT NAME	TBP TEMPERATURE END, °F
1	H_2S	−76.5
2	H_2	−422.9
3	C_1	−258.7
4	C_2	−127.5
5	C_3	−43.7
6	IC_4	10.9
7	NC_4	31.1
8	CUT NC4–100°F	100
9	CUT 100–120	120
10	CUT 120–140	140
11	CUT 140–160	160
12	CUT 160–180	180
13	CUT 180–200	200
14	CUT 200–220	220
15	CUT 220–240	240
16	CUT 240–260	260
17	CUT 260–280	280
18	CUT 280–300	300
19	CUT 300–320	320
20	CUT 320–340	340
21	CUT 340–360	360
22	CUT 360–380	380
23	CUT 380–400	400
24	CUT 400–420	420
25	CUT 420–440	440
26	CUT 440–460	460
27	CUT 460–480	480
28	CUT 480–500	500
29	CUT 500–520	520
30	CUT 520–540	540
31	CUT 540–560	560
32	CUT 560–580	580
33	CUT 580–600	600
34	CUT 600–620	620
35	CUT 620–640	640
36	CUT 640–660	660
37	CUT 660–680	680
38	CUT 680–700	700
39	CUT 700–720	720
40	CUT 720–740	740
41	CUT 740–760	760

Table 11-19
Continued

CUT INDEX	CUT NAME	TBP TEMPERATURE END, °F
42	CUT 760–780	780
43	CUT 780–800	800
44	CUT 800–820	820
45	CUT 820–840	840
46	CUT 840–860	860
47	CUT 860–880	880
48	CUT 880–900	900
49	CUT 900–920	920
50	CUT 920–940	940
51	CUT 940–960	960
52	CUT 960–980	980
53	CUT 980–1000	1000
54	CUT 1000–1020	1020
55	CUT 1020–1040	1040
56	CUT 1040–1060	1060
57	CUT 1060–1080	1080
58	CUT 1080–1100	1100
59	CUT 1100–1120	1120
60	CUT 1120–1140	1140
61	CUT 1140–1160	1160
62	CUT 1160–1180	1180
63	CUT 1180–1200	1200
64	CUT 1200–1292	1292

ties of whole crude (specific gravity, sulfur, RVP, salt content, etc.), and this is, in fact, the largest wide cut, spanning the 0–100% TBP distillation range. With the input of each wide cut from the crude assay, the properties are processed to make them blend volumetrically (i.e., sulfur is multiplied with specific gravity, viscosity is converted into viscosity blending index, and so forth). The composition of each wide cut is expressed in terms of volume of pseudocomponents such that the sum of volume fractions of the pseudocomponents in the wide cut add to 1.

Then, for each property, it is postulated that there is a set of property values for all pseudocomponents, so that adding the appropriate volume of pseudocomponent times its respective property value equals the property of each wide cut.

Thus, for each wide cut,

$$p_1 \times v_1 + p_2 \times v_2 + p_3 \times v_3 \ldots p_j \times v_j = P(k) + E(k) \qquad (11\text{-}5)$$

here

$v_1, v_2, v_3, \ldots, v_j$ = the volumetric fraction of the pseudocomponents $1, 2, 3, \ldots, j$ contained in the wide cut. The sum of these, for each wide cut, is 1.

$p_1, p_2, p_3, \ldots, p_j$ = the property of pseudocomponents $1, 2, 3, \ldots, j$, respectively. For example, p_1, p_2, and p_3 could be the specific gravity, RON, or any other linearly blendable property. These are unknown and to be determined.

$P(k)$ = the property of wide cut k (known).

$E(k)$ = the error in calculation of wide cut property from assumed pseudocomponent property.

The property of both the wide cut and the pseudocomponents or narrow cuts must be in volumetric linear blending units. For example, the wide cut viscosity must be converted into corresponding viscosity blending index to determine the viscosity blending index of the pseudocomponents spanning the wide cut.

If there are *m* wide cuts, for which the property in question is known, it is possible to write *m* simultaneous equations such as the preceding.

In general, *m* is less than *n*, the number of pseudocomponents, so that the system of equations cannot be solved. Some additional constraints are needed. These are provided by the following:

1. The $p_1, p_2, \ldots, p_j$ set of values (pseudocomponent properties) must be smooth and continuous as a function of volume.
2. The sum of square of errors should be minimum.

The solution is carried out with an iterative procedure. This will be demonstrated later with an example.

The $p(i)$ values are initialized to an arbitrary starting point for the first iteration. A constant value, equivalent to the average of the properties of the wide cut data supplied, is used:

$$p(1) = p(2) = p(3) = \cdots = p(n) = \frac{(\text{sum from } k = 1 \text{ to } k = m \text{ of } P(k))}{m}$$

On subsequent iterations, of course, the latest values of $p(i)$ are used.

Equation (11-5) is solved for the error $E(k)$ in prediction of each wide cut property, using the assumed data of previous step:

$$E(k) = (\text{sum from } i = 1 \text{ to } j, p(i)^* v(i) - P(k))$$

The values of $v(i)$, the volume fraction of each pseudocomponent in the wide cut k has already been established by a TBP curve.

The set of $p(i)$ values are then adjusted by a composite set of correction terms in the direction opposite to error, in each equation, to bring the estimated wide cut property closer to the actual.

A volumetric average of all applicable error terms is used to correct the old property value of the pseudocomponent. In the averaging calculations, the volumetric weight of the pseudocomponent in a wide cut is calculated and multiplied with the wide cut error to arrive at the correction for that wide cut. Each wide cut error introduces a correction term to the pseudocomponent property.

After the first iteration, the set of $p(i)$ values (pseudocomponent properties) is discontinuous, with several groups of adjacent $p(i)$ having the same values and with discontinuities occurring at the boundaries of the wide cuts. The set of $p(i)$ values is passed through a smoothing procedure, and the smoothed set of $p(i)$ values is used to start the next iteration.

Each iteration introduces some irregularity in the set of $p(i)$ values while improving the overall fit. After each iteration, the smoothing procedure restores continuity with some loss of goodness of fit.

After each iteration, the standard deviation of the wide cut property error is computed:

$$\sigma = \sqrt{\frac{(E_{\mathrm{WCUT1}})^2 + (E_{\mathrm{WCUT2}})^2 + (E_{\mathrm{WCUT3}})^2 + \cdots + (E_{\mathrm{WCUT}m})^2}{m - 1}}$$

where

σ = standard deviation;
m = number of wide cuts in the input;
$E_{\mathrm{WCUT}j}$ = error (input – calculated) of a property for the jth cut.

The standard deviation is generally seen to improve dramatically at first, approaching a final value asymptotically. The standard deviation is computed before smoothing. The later iterations, which apply very small corrections to the set of $p(i)$ values, have little effect on the smoothness of continuity of $p(i)$ values.

The whole procedure terminates when either the standard deviation increases by less than 1% between successive iterations or a preset number of iterations (usually 20) has been reached.

Smoothing Procedure

A problem with the method discussed so far is that, although the pseudocomponents blend back to the original wide cut input data better after the first iteration than with the first estimate values, many of the adjacent pseudocomponents still have identical values and there are sharp discontinuities where wide cut boundaries occur. The next step helps smooth out these sharp discontinuities.

For most pseudocomponents, four components are required to determine a new smoothed property for each pseudocomponent:

1. The pseudocomponent's unsmoothed property (already determined).
2. The linear interpolated property of the immediately adjacent pseudocomponents (to be determined).
3. The linear interpolated property of the adjacent but once removed pseudocomponents (to be determined).
4. The smoothed value is computed as equal to (40% of (1)+ 40% of (2) + 20% of (3)).

As an example consider the data in the following table after the first iteration and after the first smoothing.

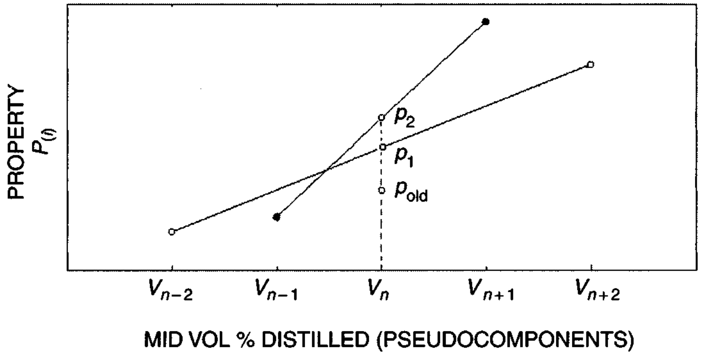
PSEUDO-COMPONENT,°F	FIRST ITERATION	SMOOTHED VALUE
n	a	a
$n+1$	b	$0.5 \times b + 0.5 \times (a+c)/2$
$n+2$	c	$0.4 \times c + 0.4 \times (b+d)/2 + 0.2 \times (a+e)/2$
$n+3$	d	$0.4 \times d + 0.4 \times (c+e)/2 + 0.2 \times (b+f)/2$
$n+4$	e	$0.5 \times e + 0.5(d+f)/2$
$n+5$	f	f

We see that

1. The n and $n + 5$ pseudocomponents properties are not smoothed, having adjacent components only on one side.
2. The $n + 1$ and $n + 4$ pseudocomponents are smoothed using 50% of (1) and 50% of (2). The unsmoothed specific gravities and middle vol% are used for interpolation calculation.
3. The $n + 2$ and $n + 3$ pseudocomponents properties are smoothed by adding 40% of the unsmoothed value, 40% of the adjacent value average, and 20% of adjacent but once removed value.

The smoothing procedure is also shown in Figure 11-2.

The process of cutting the crude oil into narrow cuts is best illustrated with an example. Suppose the following crude oil data were supplied. (For simplicity, only one property and a short range of TBP are used for this illustration. Actual crude oil cutting into narrow cuts requires the TBP distillation of whole crude.)



p_{old} = value of property nth cut (unsmoothed value)

p_1 = linear interpolation between V_{n-2} and V_{n+2}

p_2 = linear interpolation between V_{n-1} and V_{n+1}

p_{new} = value of property nth cut (smoothed value)

$$p_{new} = 0.4 \times p_{old} + 0.4 \times p_2 + 0.4 \times p_1$$

Figure 11-2. Smoothing procedure.

The given TBP distillation data are as follows:

TBP CUT, °F	VOL%
400–420	1.7400
420–440	1.8450
440–460	1.3050
460–480	2.6300
480–500	1.9150
500–520	1.9850
520–540	2.1200
540–560	2.0200
560–580	2.0250
580–600	2.0775

And, the given wide cut data are

TBP CUT POINTS, °F	SPECIFIC GRAVITY
400–500	0.8244
500–600	0.8562
400–600	0.8410

We need to determine the specific gravities of the pseudocomponents consistent with the wide cut specific gravities available from the assay data.

The first step is to assume an initial set of specific gravities for each of the pseudocomponents. These are the average specific gravities of the wide cuts input. In this case,

$$\text{Initial value} = (0.8244 + 0.8562 + 0.8410)/3 = 0.8405$$

Therefore, to begin with, all the pseudocomponents have a specific gravity of 0.8405.

The next step is to calculate the vol% of each pseudocomponent in the wide cut; for this example, these are

PSEUDO-COMPONENTS, °F	CRUDE	WIDE CUT, VOL.%		
		400–500°F	500–600°F	400–600°F
400–420	1.7400	18.44		8.85
420–440	1.8450	19.55		9.38
440–460	1.3050	13.83		6.64
460–480	2.6300	27.87		13.38
480–500	1.9150	20.30		9.74
500–520	1.9850		19.41	10.10
520–540	2.1200		20.73	10.78
540–560	2.0200		19.75	10.27
560–580	2.0250		19.80	10.30
580–600	2.0775		20.31	10.57
TOTAL	19.6625	100.00	100.00	100.00

Next the pseudocomponents are blended to calculate the specific gravities of each wide cut. This is easy for the first iteration. For the 400–500°F cut, this equals the initial assumption for each pseudocomponent's specific gravity (SG):

$$\begin{aligned}\mathrm{SG}_{400-500} &= 18.44/100 \times 0.8405 + 19.55/100 \times 0.8405\\ &\quad + 13.83/100 \times 0.8405 + 27.87/100 \times 0.8405\\ &\quad + 20.30/100 \times 0.8405\\ &= 0.8405\end{aligned}$$

Since all the pseudocomponents have the same specific gravity in this initial iteration, the specific gravities of other wide cuts are calculated to be 0.8405 as well.

Next, an error term is calculated for each wide cut:

$$\text{Error} = \text{estimated SG} - \text{input SG}$$

Therefore,

$$\begin{aligned}\text{Error}_{400-500} &= 0.8405 - 0.8244\\ &= 0.0161\\ \text{Error}_{500-600} &= 0.8405 - 0.8562\\ &= -0.0157\\ \text{Error}_{400-600} &= 0.8405 - 0.8410\\ &= 0.0004\end{aligned}$$

Next, a volumetric average of all applicable error terms is used to correct the old specific gravity (0.8405) of all pseudocomponents.

For the 400–420°F pseudocomponent, only the 400–500°F and 400–600°F error terms apply, since the 400–420°F pseudocomponent is not a part of the wide cut 500–600°F. In the averaging calculations, the weight of the 400–500°F error terms is

$$\begin{aligned}\text{Weighted error}_{400-500} &= 18.44/(18.44+8.85)\\ &= 0.6757\end{aligned}$$

Similarly, the weight of the 400–600°F error terms is

$$\begin{aligned}\text{Weighted error}_{400-600} &= 8.85/(18.44+8.85)\\ &= 0.3243\end{aligned}$$

The new specific gravity value of the 400–420°F pseudocomponent is

$$\begin{aligned}\text{New SG} = \text{old SG} &- \text{weighted error } 400 - 500^\circ\text{F cut}\\ &- \text{weighted error } 400 - 600^\circ\text{F cut}\end{aligned}$$

Therefore,

$$\begin{aligned}\text{New SG} &= 0.8405 - 0.6757\times(0.0161) - 0.3243\times(-0.0004)\\ &= 0.8298\end{aligned}$$

The same procedure is carried out for all other pseudocomponents.

PSEUDOCOMPONENT, °F	INITIAL ESTIMATE	FIRST ITERATION
400–420	0.8405	0.8298
420–440	0.8405	0.8298
440–460	0.8405	0.8298
460–480	0.8405	0.8298
480–500	0.8405	0.8298
500–520	0.8405	0.8510
520–540	0.8405	0.8510
540–560	0.8405	0.8510
560–580	0.8405	0.8510
580–600	0.8405	0.8510

After each iteration, the property of the wide cut is recalculated and the standard deviation of the wide cut property error is computed:

WIDE CUT, °F	INPUT SG	CALCULATED SG	ERROR
WIDE CUT 400–500	0.8244	0.8298	−0.0054
WIDE CUT 500–600	0.8562	0.8510	0.0052
WIDE CUT 400–600	0.8410	0.8408	0.0001

The standard deviation is 0.0053.

The smoothing procedure is carried out next, on the pseudocomponent properties computed after each iteration by the procedure described earlier:

PSEUDOCOMPONENT, °F	FIRST ITERATION	FIRST SMOOTHING
400–420	0.8298	0.8298
420–440	0.8298	0.8298
440–460	0.8298	0.8298
460–480	0.8298	0.8319
480–500	0.8298	0.8361
500–520	0.8510	0.8446
520–540	0.8510	0.8489
540–560	0.8510	0.8510
560–580	0.8510	0.8510
580–600	0.8510	0.8510

The second iteration is now started with smoothed property (SG) data of the first iteration:

TBP CUT, °F	VOL%	SG (SMOOTHED VALUES, FIRST ITERATION)
400–420	1.7400	0.8298
420–440	1.8450	0.8298
440–460	1.3050	0.8298
460–480	2.6300	0.8319
480–500	1.9150	0.8361
500–520	1.9850	0.8446
520–540	2.1200	0.8489
540–560	2.0200	0.8510
560–580	2.0250	0.8510
580–600	2.0775	0.8510

Wide cut SGs are calculated on the basis of this data; and the error, for each wide cut, is calculated:

WIDE CUT	ESTIMATED SG	INPUT SG	ERROR (SG)
WIDE CUT 400–500	0.8316	0.8244	0.0072
WIDE CUT 500–600	0.8493	0.8562	−0.0069
WIDE CUT 400–600	0.8408	0.8410	−0.0002

Wide cut errors are again distributed to pseudocomponents by the same procedure as in the first iteration. After second iteration, the data are again smoothed by the procedure described earlier. The results of second iteration and second smoothing are as follows:

PSEUDOCOMPONENT, °F	SECOND ITERATION	SECOND SMOOTHING
400–420	0.8249	0.8249
420–440	0.8249	0.8249
440–460	0.8249	0.8260
460–480	0.8270	0.8295
480–500	0.8313	0.8356
500–520	0.8492	0.8449
520–540	0.8535	0.8510
540–560	0.8556	0.8545
560–580	0.8556	0.8556
580–600	0.8556	0.8556

This procedure is continued until the standard deviation of the error terms, calculated after each iteration, ceases to get significantly smaller. The process is repeated for all properties of the wide cuts in the crude assay data. The following properties are generally determined for each of the narrow cuts from wide cut data:

Specific gravity.
Sulfur, wt %.
Mercaptan sulfur, ppmw.
RON clear.

MON clear.
Aromatics.
Naphthenes.
Refractive index.
Cetane index.
Pour point .
Cloud point.
Freeze point.
Aniline point.
Conradson carbon.
Nitrogen content, ppm.
Vanadium, ppm.
Nickel, ppm.
Iron, ppm.
Viscosity (blending index), at 122°F, in cst.
Viscosity (blending index), at 210°F, in cst.

In the preceding explanation, it is assumed that all the pseudocomponents are computed. This is rarely the case. Either some of the lighter components do not exist or the property is not applicable over the whole boiling range. When the latter happens, the procedure is identical but only the *p*(*i*) within the range are computed, with the others set to 0. This ensures that the property values are not extrapolated beyond the range but only interpolated.

Wide cut input data must be in linearly blendable units. For example,

- Sulfur, mercaptants, nitrogen, vanadium, nickel, iron, and the like (in weight units) must be multiplied by their specific gravities.
- All viscosities, pour points, and cloud points must be converted to corresponding blend indices.

The cutting of crude TBP into narrow cuts, as just shown, is best done with a computer program. Software from many vendors is available. There may be differences in the TBP cutting scheme or smoothing procedure, but the basic logic of these programs is broadly similar (Figure 11-3).

Crude assay data are cut into narrow cuts and the narrow cut data are stored in the form of a crude library. Such data can readily be used for diverse purposes, such as estimating the properties of user-specified wide cuts from single or mixed crudes, spiking crude with light ends, or blending crude with condensate.

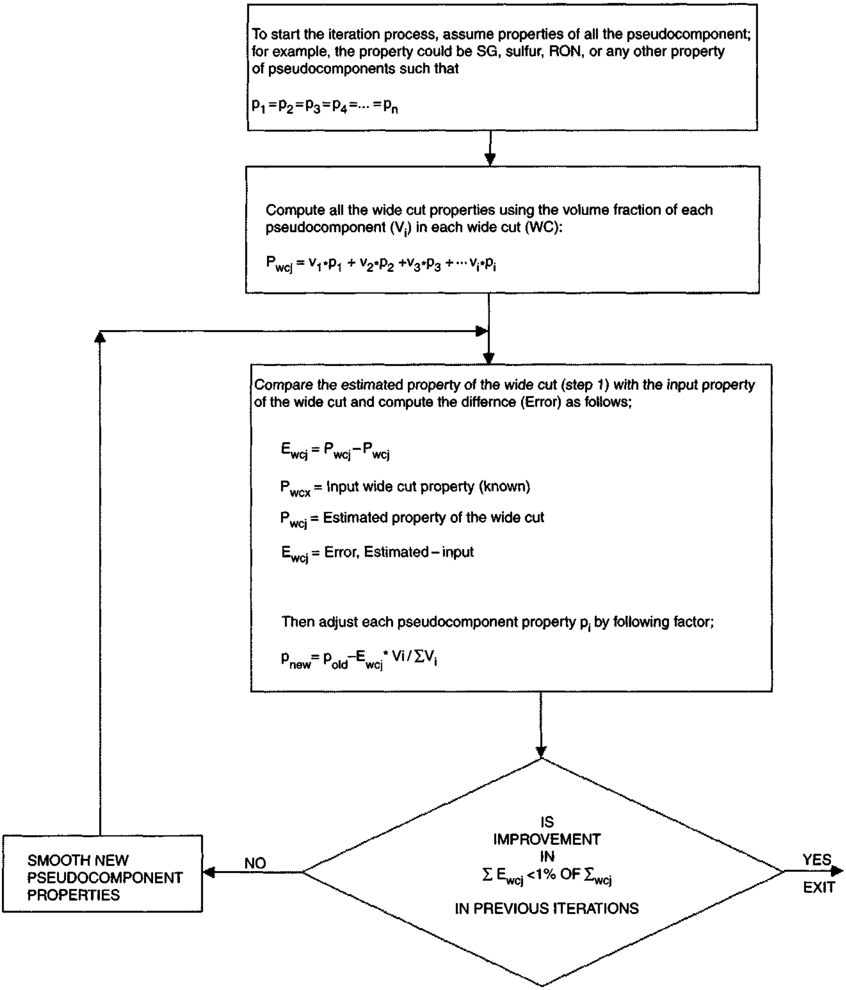


Figure 11-3. Crude cutting algorithm.

A successful run of the procedure calculates a good fit of narrow cut properties, which blend with little error back to original wide cuts properties entered. Generally, the more wide cuts entered with data, the better is the prediction of narrow cut properties. When only a small number of wide cut data points are available, the prediction of the original or different wide cut properties is much poorer.

Problems with procedure occur when

- The assay has too few wide cuts (usually less than six).
- A large stretch of the crude's TBP is described by only one wide cut (for example, an atmospheric residuum cut as opposed to one or two vacuum gas oil cuts and a vacuum residuum cut).
- A property is given for less than three adjacent or overlapping cuts. The smoothing algorithm may distort a property if too few data points are given, one or two data points are for very wide cuts, or there is a major change in the value of a property between adjacent cuts. This can occur, for example, for nitrogen content or metals (ppm), which may change by two orders of magnitude between adjacent cuts. Because of smoothing algorithm, the narrow cuts may show no orderly increase with respect to increasing TBP. Instead, they may oscillate and even go negative while maintaining average wide cut input data. In this case, pseudocomponent properties showing negative values could be manually changed to zeros at the risk of compromising the fit of pseudocomponent properties with respect to wide cuts input data.
- If the properties of different cuts with overlapping TBPs are given, there may be conflicting data, since the data values for each property would be average for respective wide cut and not the instantaneous values.

PROPERTIES OF THE WIDE CUTS

The yield and properties required of a wide cut is simply the volumetric linear blend of the appropriate narrow cuts. In other words, the yield on the crude of a wide cut is the sum of yields on the crude of the narrow cuts that constitute the wide cut. The properties of the wide cut are the volumetric weighted average properties of the same narrow cuts. If the TBPs at the start and end of the cut do not coincide with the narrow cuts, portions of narrow cuts at the start and end are used. These portions are calculated basis a simple ratio of the narrow cut TBP that is part of the wide cut to the whole TBP of the narrow cut.

EXAMPLE 11-10

Calculate the specific gravity and sulfur of diesel cut 500–650°F TBP from the following pseudocomponent data:

PSEUDOCOMPONENT, °F	CRUDE, vol%	SG	SULFUR, w%
500–520	1.9850	0.8448	1.3090
520–540	2.1200	0.8503	1.4540
540–560	2.0200	0.8561	1.5780
560–580	2.0250	0.8618	1.6820
580–600	2.0780	0.8679	1.7720
600–620	2.0680	0.8745	1.8510
620–640	1.9650	0.8806	1.9200
640–660	1.9650	0.8863	1.9780

As the required end point of diesel is 650°F, the properties of the 640–650°F pseudocomponent are estimated from the 640–660°F pseudocomponent as follows:

$$\text{Boiling range } 640-650^\circ\text{F pseudocomponent} = 10^\circ\text{F}$$
$$\text{Boiling range } 640-660^\circ\text{F pseudocomponent} = 20^\circ\text{F}$$
$$\text{Ratio of } (640-650) \text{ cut to } (640-660) \text{ cut} = 0.5$$
$$\text{Vol\% } (640-650) \text{ cut} = 0.5 \times 1.965 = 0.9825$$

By linear interpolation,

$$\text{Specific gravity of } (640-650) \text{ cut} = 0.8806 + 0.5 \times (0.8863 - 0.0.8806) = 0.8835$$
$$\text{Sulfur (wt \%)} = 1.9200 + 0.5 \times (1.9780 - 1.9200) = 1.949$$

PSEUDO-COMPONENT, °F	CRUDE, VOL%	SG	SULFUR, Wt %	VOL× SG	SG× SULFUR	(SG×SULFUR) ×VOLUME
500–520	1.9850	0.8448	1.3090	1.6769	1.1058	2.1951
520–540	2.1200	0.8503	1.4540	1.8026	1.2363	2.6210
540–560	2.0200	0.8561	1.5780	1.7293	1.3509	2.7289
560–580	2.0250	0.8618	1.6820	1.7451	1.4495	2.9353
580–600	2.0780	0.8679	1.7720	1.8034	1.5379	3.1958
600–620	2.0680	0.8745	1.8510	1.8084	1.6187	3.3475
620–640	1.9650	0.8806	1.9200	1.7303	1.6908	3.3223
640–650	0.9825	0.8835	1.9490	0.8680	1.7218	1.6917
TOTAL	15.2435			13.1644		22.0376

$$\begin{aligned}\text{SG of wide cut} &= \Sigma(\text{SG} \times \text{VOL})/\text{VOL}\\ &= 13.1644/15.2435\\ &= 0.8636\\ \text{SG} \times \text{sulfur of wide cut} &= \Sigma(\text{SG} \times \text{SULFUR} \times \text{VOL})/\Sigma\text{VOL}\\ &= 22.0376/15.2435\\ &= 1.4457\\ \text{Sulfur (wt\%)} &= \text{SG} \times \text{sulfur}/\text{SG}\\ &= 1.4457/0.8636\\ &= 1.6740\end{aligned}$$

Many other properties of the wide cuts are estimated from already determined properties, using correlations, as follows.

API gravity is thus determined:

$$°\text{API} = 141.5/\text{SG} - 131.5$$

where SG is specific gravity.

ASTM DISTILLATION FROM TBP DISTILLATION

ASTM distillation of the wide cut is obtained by conversion of the TBP to ASTM (D-86) by the method used in the API data book.[5] As the TBP of the wide cut is known from input data, the ASTM distillation of the wide cut can be determined.

ASTM Specification D-86 Distillation 50 and 99% Temperatures from TBP Temperatures (°F)

Calculate factors *A* and *B* as follows:

$$A = \text{TBP}_{50} - \text{TBP}_{10}$$

$$B = \text{TBP}_{90} - \text{TBP}_{50}$$

Calculate the 50% ASTM boiling point as follows:

1. Calculate delta (D):

$$D = 0 \text{ (if A.LT. 50)}$$

$$D = 0.735 \times A - 3.765 \text{ (if 50 GE A BUT LT 220)}$$

$$D = 0.027 \times A + 6.555 \text{ (if A.GE. 220)}$$

2. Calculate the uncorrected D-86 50% boiling point:

$$\text{ASTM}_{50\%} = \text{TBP}_{50\%} - D$$

Calculate the 99% ASTM boiling point as follows:

1. Calculate delta (D):

$$D = 0.00398 \times B^2 - 0.556 \times B \text{ (if B.LT. 90)}$$

$$D = -74.914 + 12.672 \times \ln(B) \text{ (if B.GE. 90)}$$

2. Calculate the uncorrected D-86

$$\text{ASTM}_{99\%} = \text{TBP}_{99\%} - D$$

Now correct the D-86 points using stem correction, if temperature greater than 274°F. (Note the iterative calculation, since stem correction is based on corrected D-86 points.)

$$T_{50\%\text{corrected}} = T_{50\%\text{uncorrected}} - \text{stem correction}_{50\%}$$

$$T_{99\%\text{corrected}} = T_{99\%\text{uncorrected}} - \text{stem correction}_{99\%}$$

$$\text{Stem correction}_{50\%} = 5.04 + 0.00006751 \times T_{50\%\text{corrected}}$$

$$\text{Stem correction}_{99\%} = 5.04 + 0.00006751 \times T_{99\%\text{corrected}}$$

"K" WATSON AND MOLECULAR WEIGHT FROM THE ASTM DISTILLATION TEMPERATURE

1. From the ASTM distillation temperature, calculate the (uncorrected) average boiling point (V) of the petroleum fraction:

$$V = (T_{10\%} + T_{30\%} + T_{50\%} + T_{70\%} + T_{90\%})/5$$

2. Calculate the slope (S) of the 10–90% ASTM distillation curve:

$$S = (T_{90\%} - T_{10\%})/(\mathrm{VOL}_{90\%} - \mathrm{VOL}_{10\%})$$

3. Correct the average boiling point by the following correction factor (C):

$$\begin{aligned} C = & -2.34813 - 5.52467 \times S + 0.01239 \times V - 0.87567 \times S \\ & \times S - 1.33817\mathrm{E}{-05} \times \mathrm{V} \times \mathrm{V} + 4.39032\mathrm{E}{-03} \times \mathrm{V} \\ & \times S - 3.29273\mathrm{E}{-02} \times S \times S \times S + 3.553\mathrm{E}{-07} \times S \\ & \times S \times V \times V \end{aligned}$$

4. Add the correction factor to the boiling point in (1) and convert the temperatures in °F to temperature in °R (Rankine).

$$T = V + C + 460$$

5. Then calculate the Watson K as follows;

$$\mathrm{K} = T^{(\frac{1}{3})}/\mathrm{density}$$

6. Molecular weight (MW):

$$\mathrm{MW} = 100\exp(0.001 \times A \times T + C)$$

where

$A = 2.386 - 0.710 \times D$
$C = 0.546 - 0.460 \times D$
D = density of the cut.
T = average boiling point in °F, calculated from the ASTM boiling point.

EXAMPLE 11-11

ASTM distillation of a heavy straight-run (HSR) naphtha with an API gravity of 61.33 follow. Calculate the Watson K and molecular weight of the naphtha.

VOL%	TEMPERATURE, °F
IBP	209
10	214
30	230
50	250
70	269
90	288
END POINT	297

Referring to this procedure,

$$\begin{aligned} V &= 250.2 \\ S &= (288 - 214)/(80) \\ &= 0.925 \\ C &= -4.93637 \\ T &= 245.26^\circ\mathrm{F} \\ &= 705.26^\circ\mathrm{R} \\ \mathrm{API} &= 61.33 \\ \mathrm{Density} &= 0.7338 \\ \mathrm{K} &= (705.26)^{(\frac{1}{3})}/0.7338 \\ &= 12.13 \end{aligned}$$

Calculate the molecular weight:

$$\begin{aligned} &A = 1.864997 \\ &C = 0.208449 \\ &\text{Molecular weight} = 114.6 \end{aligned}$$

CHARACTERIZATION FACTOR FROM API GRAVITY AND KINEMATIC VISCOSITY AT 210°F (FOR VISCOSITIES GREATER THAN 3.639 CST AT 210°F)

Calculate factor 1 (FCTR1), a function of viscosity:

$$\text{FCTR1} = B^2 - 4 \times \text{C} \times [\text{A} - \ln(\text{viscosity})]$$

where

$$A = 384.5815;$$

$$B = -74.2124;$$

$$C = 3.592245;$$

$$S = 0.082;$$

$$\text{FCTR2} = ((\text{FCTR1})^{0.5} - B)/2 \times C;$$

$$\text{Watson K} = (\text{FCTR2}) + S \times (\text{API} - 10).$$

EXAMPLE 11-12

Calculate the Watson K for an atmospheric resid with a viscosity of 26.44 cst at 210°F and an API gravity of 16.23.

Using the constants just described,

$$\text{FCTR1} = 26.49309$$

$$\text{FCTR1} = 11.0725$$

$$\text{Watson K} = 11.5833$$

MOLECULAR WEIGHT OF NARROW CUTS WITH TEMPERATURES GREATER THAN 500°F

Molecular weight is calculated as a function of API gravity and the Watson K by the following correlation:[6]

$$\begin{aligned} MW = {} & 51.38 \times API - 1017^{*}WK + 0.2845 \times (API)^2 + 55.73 \\ & \times (WK)^2 - 0.001039 \times (API)^3 - 3357 \times \exp(-WK/15) \\ & - 6.606 \times (WK) \times (API) + 6633.855 \end{aligned}$$

where

MW = molecular weight;
API = API (specific gravity);
WK = Watson K.

EXAMPLE 11-13

Calculate the molecular weight of the atmospheric resid in the preceding example. The API gravity of the resid is 16.23.

The Watson K was computed earlier at 11.583. The molecular weight is estimated by the previous correlation at 442.69

DETERMINATION OF THE (LOWER) HEATING VALUE OF PETROLEUM FRACTIONS

1. If the API gravity of distillate is above 42°, the net heat (*H*) of combustion in Btu/lb can be estimated by following correlation:[7]

$$\begin{aligned} H = {} & 8505.4 + 846.81 \times (K) + 114.92 \times (API) + 0.12186 \\ & \times (API)^2 - 9.951 \times (K) \times (API) \end{aligned}$$

2. If the API gravity of distillate or residua is below 42°, the net heat (*H*) of combustion in Btu/lb can be estimated by following correlation:[8]

$$H = 17213 + 5.22 \times API - 0.5058 \times (API)^2$$

3. Correct the preceding heating values for sulfur content of the distillate or residua:

$$\text{Heat} = H \times (1 - 0.01 \times S) + 43.7 \times S$$

where

Heat = lower heating value (Btu/lb);
K = Watson K;
API = API gravity;
S = Sulfur content (wt%).

VAPOR PRESSURE OF NARROW HYDROCARBON CUTS

Vapor pressure of narrow hydrocarbon cuts can be estimated from their boiling point and temperature by correlation of Van Kranen and Van Ness, as follows.

Determine factor x:

$$I = 6.07918 - 3.19837 \times \frac{(232.0 + B)}{(232 + T)} \times \left[\frac{(1120 - T)}{(1120 - B)}\right]$$

$$\mathrm{VP}_{\mathrm{mmHg}} = 10^{x}$$

$$\mathrm{VP}_{\mathrm{psi}} = 10^{x} \times 0.01932$$

where

B = average boiling point, °C.
T = temperature, °C
$\mathrm{VP}_{\mathrm{mmHg}}$ = vapor pressure, mmHg;
$\mathrm{VP}_{\mathrm{psi}}$ = vapor pressure, psi.

DETERMINATION OF RAMSBOTTOM CARBON RESIDUE[9] FROM CONRADSON CARBON[10]

The carbon residue value of burner fuel oil serves as a rough approximation of the tendency of the fuel to form deposits in vaporizing pot-type and sleeve-type burners. Provided additives are absent, the carbon residue of diesel fuel correlates approximately with combustion chamber deposits. Ramsbottom carbon can be estimated from Conradson carbon[11] by the following correlation:

$$\mathrm{RAMSBTM} = \mathrm{EXP}\left(\left(\frac{(((0.1314{*}\mathrm{LN(CONCARBON)} + 0.8757)^2) - 0.76685)}{0.2628}\right) - 0.2141\right)$$

PENSKEY MARTIN FLASH[12] AS A FUNCTION OF IBP (TBP) AND CUT LENGTH (NOT FOR COMMERCIALLY FRACTIONATED CUTS)

Estimate the cut length (CUTL) as follows:

$$\mathrm{CUTL} = T_{\mathrm{end}} - T_{\mathrm{start}}$$

where

T_{start} = initial boiling point (IBP), °F;
T_{end} = final boiling point (FBP), °F.

Calculate a factor X as follows:

$$X = 0.7129 \times (\mathrm{IBP}) - 122.227$$

$$\text{Penesky Martin Flash (PMFL)} = X + (2.571 \times \mathrm{CUTL} - 225.825)^{0.5}$$

FLASH POINT, °F (ABEL), AS A FUNCTION OF AVERAGE BOILING POINT

The correlation is applicable up to 1050°F:

$$\text{Flash} = 0.537 \times T - 93 \text{ if } (T \leqslant 174°\text{F})$$
$$\text{Flash} = 0.67 \times T - 116 \text{ if } (174 \leqslant T < 303)$$
$$\text{Flash} = 0.7506 \times T - 140.3 \text{ if } (303 \leqslant T < 577)$$
$$\text{Flash} = 0.674 \times T - 94.5 \text{ if } (577 \leqslant T < 1050)$$

where T is the average boiling temperature, °F.

SMOKE POINT OF KEROSENES

The smoke point (S) of a kerosene can be estimated by the following correlation with the aromatic content of the stream.

$$S = \left(53.7/\mathrm{arom}^{0.5}\right) + 0.03401 \times \mathrm{API}^{1.5} + 1.0806$$

where

$$S = \text{Smoke point, mm;}$$
$$\text{arom} = \text{aromatics content, LV\%;}$$
$$\text{API} = \text{API gravity of the cut.}$$

LUMINOMETER NUMBER

The luminometer number is qualitatively related to the potential radiant heat transfer from the combustion products of aviation turbine fuels. It provides an indication of the relative radiation emitted by combustion products of gas turbine fuels.

The luminometer number (L_n) is related to the smoke point by following correlation (ASTM specification D-1740):

$$L_n = -12.03 + 3.009 \times \text{SP} - 0.0104 \times \text{SP}^2$$
$$\text{SP} = 4.16 + 0.331 \times L_n + 0.000648 \times {L_n}^2$$

where L_n is the luminometer number and SP is the smoke point.

LUMINOMETER NUMBER BLENDING

Luminometer numbers do not blend linearly. Therefore, blending indices are employed that blend linearly by weight. The procedure is to first determine component Luminometer blending indices, blend component indices on weight basis to obtain blended index, next calculate stream Luminometer number from following relations.

The blending index is

$$L_i = \exp(\exp[(139.5 - L_n)/128.448])$$

where

$$L_i = \text{luminometer number blending index;}$$
$$L_n = \text{luminometer number;}$$
$$L_n = 139.35 - 128.448 \times \log_e(\log_e L_i)$$

CETANE INDEX

The cetane index (CI) is estimated from the API gravity and 50% ASTM distillation temperature in °F of the diesel, by the following correlation.[13]

$$\begin{aligned}\mathrm{CI} = &-420.34 + 0.016 \times (\mathrm{API})^2 + 0.192 \times (\mathrm{API}) \times \log(M)\\ &+ 65.01(\log M)^2 - 0.0001809 \times M^2\end{aligned}$$

or

$$\begin{aligned}\mathrm{CI} = &\,454.74 - 1641.416 \times D + 774.74 \times D^2 - 0.554 \times B\\ &+ 97.803 \times (\log B)^2\end{aligned}$$

where

API = API gravity;
M = mid-boiling temperature, °F;
D = density at 15°C;
B = mid-boiling temperature, °C.

DIESEL INDEX

The diesel index (DI) is correlated with the aniline point of diesel by the following relationship:

$$\mathrm{DI} = \text{aniline point} \times \text{API gravity}/100$$

The diesel index can be approximately related to cetane index of diesel by following relation:

$$\mathrm{DI} = (\mathrm{CI} - 21.3)/0.566$$

(U.S.) BUREAU OF MINES CORRELATION INDEX (BMCI)

$$\mathrm{BMCI} = 87{,}552/(\mathrm{VAPB}) + 473.7 \times (\mathrm{SG}) - 456.8$$

where VABP is the volume average boiling point, °Rankine, and SG is the specific gravity. The BMCI has been correlated with many characteristics of a feed, such as crackability, in-steam cracking, and the paraffinic nature of a petroleum fraction. Paraffinic compounds have low BMCIs and aromatics high BMCIs.

AROMATICITY FACTOR

The aromaticity factor is related to the boiling point, specific gravity, aniline point, and sulfur as follows:

$$\begin{aligned}\mathrm{AF} = {} & 0.2514 + 0.00065 \times \mathrm{VABP} + 0.0086 \times \mathrm{S} + 0.00605 \\ & \times \mathrm{AP} + 0.00257 \times (\mathrm{AP}/\mathrm{SG})\end{aligned}$$

where

AF = aromaticity factor;
VAPB = volume average boiling point, °F;
S = sulfur, wt%;
AP = aniline point, °F;
SG = specific gravity.

FLUIDITY OF RESIDUAL FUEL OILS

The low temperature flow properties of a waxy fuel oil[14] depend on its handling and storage conditions. These properties may not be truly indicated by the pour point. The pour point of residual fuel oils are influenced by the previous thermal history of the oil. A loosely knit wax structure built up on cooling of oil can normally be broken by the application of relatively little pressure. The usefulness of pour point test in relation to residual fuel oils is open to question, and the tendency to regard pour point as the limiting temperature at which a fuel oil will flow can be misleading.

In addition, the pour point test does not indicate what happens when an oil has a considerable head of pressure behind it, such as when gravitating from a storage tank or being pumped from a pipeline. Failure to flow at the pour point is normally attributed to a separation of wax from the fuel. However, it can also be due to viscosity in case of very viscous fuel oils.

Fluidity Test

The problem of accurately specifying the handling behavior of fuel oils is important. Because of technical limitation of the pour point test, various pumpability tests[15] have been devised. However, most of these test methods tend to be time consuming. A method that is relatively quick and easy to perform has found limited acceptance, as the "go/no go" method is based on an appendix to the former ASTM specification D-1659-65. This method covers the determination of fluidity of a residual fuel oil at a specified temperature in an "as-received" condition.

Summary of the Test Method

A sample of fuel oil in its as-received condition is cooled at the specified temperature for 30 min in a standard U-tube and tested for movement under prescribed pressure conditions.

The sample is considered fluid at the temperature of the test if it will flow 2 mm under a maximum pressure of 152 mmHg. The U-tube for the test is 12.5 mm in diameter.

This method may be used as a go/no go procedure for operational situations where it is necessary to ascertain the fluidity of a residual oil under prescribed conditions in an as-received condition.

The conditions of the method simulate those of a pumping situation, where oil is expected to flow through a 12 mm pipe under slight pressure at specified temperature.

Fluidity, like the pour point of specification D-97, is used to define cold flow properties. It differs from D-97 in that

1. It is restricted to fuel oils.
2. A prescribed pressure is applied to the sample. This represents an attempt to overcome the technical limitation of pour point method, where gravity-induced flow is the criterion.

The pumpability test (ASTM specification D-3245) represents another method for predicting field performance in cold-flow conditions. The pumpability test, however, has limitations and may not be suitable for very waxy fuel oils, which solidify so rapidly in the chilling bath that no reading can be obtained under conditions of the test. It is also time consuming and therefore not suitable for routine control testing.

Fluidity Blending

Fluidity, like pour points, do not blend linearly. Blending indices are therefore used for blending the fluidity of two fuel oils. The blending indices used are the same as those used for distillate fuels (Table 11-14).

EXAMPLE 11-14

Determine the fluidity of a blend of two fuel oil grades. The blend contains 30 vol% grade 964 and 70 vol% grade 965. As per fluidity tests, grade 964 is fluid at 32°F and grade 965 is fluid at 59°F.

The fluidity of the blend is determined by first determining the fluidity index of the two grades and blending linearly. The fluidity index is then converted into a fluidity temperature, as follows. The fluidity index can be read directly from Table 11-14 or determined from the following correlations:

$$\text{Fluidity index} = 3162000 \times [(\text{fluidity}, {}^\circ\text{R})/1000]^{12.5}$$

$$\text{Fluidity } ({}^\circ\text{R}) = 1000 \times [(\text{fluidity index})/3162000]^{0.08}$$

GRADE	VOL%	FLUIDITY TEMPERATURE, °R	FLUIDITY INDEX	BLEND
964	30.0	492	446.20	133.86
965	70.0	519	870.07	609.07
BLEND				742.91

The corresponding fluidity of the blend is 512.5°R or 52.5°F.

CONVERSION OF KINEMATIC VISCOSITY TO SAYBOLT UNIVERSAL VISCOSITY OR SAYBOLT FUROL VISCOSITY

Saybolt universal viscosity is the efflux time in seconds for a 60-cm^3 sample to flow through a standard orifice in the bottom of a tube. The orifice and tube geometry are specified in the ASTM standards. Saybolt furol viscosity is determined in the same manner as Saybolt universal viscosity except that a larger orifice is used.

Conversion to Saybolt Universal Viscosity

Kinematic viscosity in centistokes (mm^2/sec) can be converted to Saybolt universal viscosity in Saybolt universal seconds (SUS) units at the same temperature by API databook[16] procedure or using ASTM conversion tables:[17]

$$\mathrm{SUS} = 4.6324 \times (\mathrm{cst}) + \frac{[1.0 + 0.03264 \times (\mathrm{cst})]}{[3930.2 + 262.7 \times (\mathrm{cst}) + 23.97 \times (\mathrm{cst})^2 + 1.646 \times (\mathrm{cst})^3] \times 10^{-5}} \tag{11-6}$$

where

SUS = Saybolt universal viscosity in Saybolt universal seconds units at 37.8°C;

cst = kinematic viscosity, centistokes $\left(\mathrm{mm}^2/\mathrm{sec}\right)$.

SUS viscosity at 37.8°C can be converted to SUS viscosity at another temperature by following relationship:

$$\mathrm{SUS}_t = [1 + 0.000110 \times (t - 37.8)] \times \mathrm{SUS} \tag{11-7}$$

where

SUS = SUS viscosity at 37.8°C;

SUS_t = SUS viscosity at the required temperature;

t = temperature at which SUS viscosity is required, °C.

EXAMPLE 11-15

An oil has a kinematic viscosity of 60 centistokes at 37.8°C. Calculate the corresponding Saybolt universal viscosity at 37.8 and 98.9°C.

Using equation (11-6), the Saybolt universal viscosity at 37.8°C is calculated at 278.59 sec.

The viscosity at 98.9°C is calculated, by equation (11-7), at 280.45 sec.

Conversion to Saybolt Furol Viscosity

Kinematic viscosity in centistokes (mm^2/sec) at 50 and 98.9°C can be converted to Saybolt furol viscosity in Saybolt furol seconds (SFS) units at the same temperature by API databook[18] procedure:

$$SFS_{50} = 0.4717 \times VIS_{50} + \frac{13.924}{(VIS_{50})^2 - 72.59 \times VIS_{50} + 6.816} \tag{11-8}$$

$$SFS_{98.9} = 0.4792 \times VIS_{98.9} + \frac{5.610}{(VIS_{98.9})^2 + 2.130} \tag{11-9}$$

where

SFS_{50} = Saybolt furol viscosity at 50°C, Saybolt furol seconds;
VIS_{50} = kinematic viscosity at 50°C, centistokes (mm^2/sec);
$SFS_{98.9}$ = Saybolt furol viscosity at 98.9°C, Saybolt furol seconds;
$VIS_{98.9}$ = kinematic viscosity at 98.9°C, centistokes (mm^2/sec).

EXAMPLE 11-16

1. Estimate the Saybolt furol viscosity of an oil at 50°C, if the kinematic viscosity at 50°C is 3000 centistokes. Saybolt furol viscosity at 50°C is estimated from kinematic viscosity by equation (11-8) at 1415.1 sec.
2. Estimate the Saybolt furol viscosity of an oil at 98.9°C, if the kinematic viscosity at 98.9°C is 120 centistokes.

   Saybolt furol viscosity at 98.9°C is estimated from kinematic viscosity by equation (11-9) above at 57.50 sec.

REFRACTIVE INDEX OF PETROLEUM FRACTIONS

The refractive index of a petroleum fraction can be predicted from its mean average boiling point, molecular weight, and relative density using the API databook procedure.[19]

The method may be used to predict refractive index for a petroleum fraction with normal boiling point up to 1100 Kelvins.

$$n = \left(\frac{1 + 2 \times I}{1 - I}\right)^{\frac{1}{2}} \tag{11-10}$$

$$I = 3.587 \times 10^{-3} \times T_b^{1.0848} \times \left(\frac{M}{d}\right)^{-0.4439} \tag{11-11}$$

where

n = refractive index at 20°C;
I = characterization factor of Huang[20] at 20°C;
T_b = mean average boiling point, Kelvins;
M = molecular weight of petroleum fraction;
d = liquid density at 20°C and 101.3 kPa, in kilogram per cubic decimeter (kg/dm^3).

EXAMPLE 11-17

Calculate the refractive index of a petroleum fraction with a liquid density of 0.7893 kg/dm^3, molecular weight of 163.47, and mean average boiling point of 471.2 K.

Here,

$d = 0.7893$;
$M = 163.47$;
$T_b = 471.2\,\text{K}$.

First calculate Huang characterization factor by equation (11-11):

$$I = 3.587 \times 10^{-3} \times (471.2)^{1.0848} \times (163.47/0.7893)^{-0.4439}$$
$$= 0.2670$$

Next calculate the refractive index by equation (11-10):

$$n = [(1 + 2 \times 0.2670)/(1 - 0.2670)]^{0.5}$$
$$= 1.4466$$

DETERMINATION OF MOLECULAR-TYPE COMPOSITION

An estimate of fractional composition of paraffins, naphthenes, and aromatics contained in light and heavy petroleum fractions can be done if the data on viscosity, relative density, and refractive index of the desired fraction are available. The algorithm is based on a procedure of API databook.[21]

$$X_p = a + b \times (R_i) + c \times (\text{VG}) \tag{11-12}$$

$$X_n = d + e \times (R_i) + f \times (\text{VG}) \tag{11-13}$$

$$X_a = g + h \times (R_i) + I \times (\text{VG}) \tag{11-14}$$

where

X_p = mole fraction of paraffins;

X_n = mole fraction of naphthenes;

X_a = mole fraction of aromatics;

R_i = refractivity intercept as given by equation (11-15);

a, b, c, d, e, f, g, h, and i = constants varying with molecular weight range as given later;

VG = viscosity gravity function VGC, as given by equations (11-16) and (11-17) for heavy fractions, or viscosity gravity function VGF, as given by equations (11-18) and (11-19) for light fractions.

$$R_i = n - d/2 \tag{11-15}$$

where n is the refractive index at 20°C and 101.3 kPa and d is the liquid density at 20°C and 101.3 kPa in kg/dm^3.

The constants used in equations (11-12) to (11-14) are as follows:

CONSTANT	LIGHT FRACTION (MW = 80–200)	HEAVY FRACTION (MW = 200–500)
a	−23.940	−9.000
b	24.210	12.530
c	−1.092	−4.228
d	41.140	18.660
e	−39.430	−19.900
f	0.627	2.973
g	−16.200	8.660
h	15.220	7.370
i	0.465	1.255

For heavy fractions (molecular weight 200–500), the viscosity gravity constant is determined by following equations:

$$\mathrm{VGC} = \frac{10 \times d - 1.0752 \times \log(V_{311} - 38)}{10 - \log(V_{311} - 38)} \tag{11-16}$$

or

$$\mathrm{VCG} = \frac{d - 0.24 - 0.022 \times \log(V_{372} - 35.5)}{0.755} \tag{11-17}$$

where d is the relative density at 15°C and 101.3 kPa and V is the Saybolt universal viscosity at 311 or 372 K in Saybolt universal seconds.

For light fractions (molecular weight 80–200), the viscosity gravity constant is determined by following equations:

$$\mathrm{VGF} = -1.816 + 3.484 \times d - 0.1156 \times \ln(\nu_{311}) \tag{11-18}$$

or

$$\mathrm{VGF} = -1.948 + 3.535 \times d - 0.1613 \times \ln(\nu_{372}) \tag{11-19}$$

where ν is the kinematic viscosity at 311 or 372 K, in mm^2/sec.

The viscosity-gravity (VG) constant[22] is a useful function for approximate characterization of viscous fractions of petroleum. It is relatively insensitive to molecular weight and related to the composition of the fraction. Values of VG near 0.8 indicate samples of paraffinic character, while those close to 1.0 indicate a preponderance of aromatic molecules. The VG, however, should not be applied to residual oils or asphaltic materials.

EXAMPLE 11-18

Calculate the molecular type distribution of a petroleum fraction of relative density 0.9433, refractive index 1.5231, normal boiling point 748 K, and a viscosity of 695 Saybolt universal seconds at 311 K.

First, determine the molecular weight of the fraction as a function of the mean average boiling point and relative density at 15°C by API databook procedure.[23]

$$\begin{aligned} \mathrm{MW} &= 2.1905 \times 10^2 \times \exp(0.003924 \times T) \times \exp(-3.07 \times d) \\ &\quad \times (T)^{0.118} \times (d)^{1.88} \end{aligned}$$

where MW is the molecular weight, d is the relative density at 15°C, and T is the mean average boiling point in K. Therefore,

$$\begin{aligned} \mathrm{MW} &= 2.1905 \times 10^2 \times \exp(0.003924 \times 748) \\ &\quad \times \exp(-3.07 \times 0.9433) \times (748)^{0.118} \times (0.9433)^{1.88.} \\ &= 446 \end{aligned}$$

As the molecular weight is greater than 200, the fraction is termed *heavy*. Viscosity gravity constant VGC is determined as per equation (11-16):

$$\begin{aligned} \mathrm{VGC} &= \frac{10 \times 0.9433 - 1.0752\ \log(695 - 38)}{[10 - \log(695 - 38)]} \\ &= 0.8916 \end{aligned}$$

Next, calculate the refractivity index as per equation (11-15):

$$\begin{aligned} R_i &= 1.5231 - 0.9433/2 \\ &= 1.0514 \end{aligned}$$

The mole fraction of paraffins, naphthenes, and aromatics are next determined using equations (11-12) to (11-14) and constants for heavy fractions:

$$\begin{aligned}X_p &= -9.00 + 12.53 \times 1.0514 - 4.228 \times 0.8916\\ &= 0.4051\\ X_n &= 18.66 - 19.90 \times 1.0514 + 2.973 \times 0.8916\\ &= 0.3869\\ X_a &= -8.66 + 7.37 \times 1.0514 + 1.225 \times 0.8916\\ &= 0.2080\end{aligned}$$

EXAMPLE 11-19

Calculate the molecular-type distribution of a petroleum fraction of relative density 0.8055, refractive index 1.4550, normal boiling point 476 K, and a viscosity of 1.291 mm^2/sec at 311 K.

First, determine the molecular weight of the fraction as a function of the mean average boiling point and relative density at 15°C:

$$\begin{aligned}\text{MW} &= 2.1905 \times 10^2 \times \exp(0.003924 \times 476)\\ &\quad \times \exp(-3.07 \times 0.8055) \times (476)^{0.118} \times (0.8055)^{1.88}\\ &= 164.73\end{aligned}$$

As the molecular weight is less than 200, the fraction is termed *light*. Viscosity gravity constant VGF is determined as per equation (11-18) or (11-19):

$$\begin{aligned}\text{VGF} &= -1.816 + 3.484 \times 0.8055 - 0.1156 \times \ln(1.291)\\ &= 0.9608\end{aligned}$$

Next, calculate the refractivity index as per equation (11-15):

$$\begin{aligned}R_i &= 1.4550 - 0.8055/2\\ &= 1.0522\end{aligned}$$

The mole fraction of paraffins, naphthenes, and aromatics are next determined using equations (11-12) to (11-14) and constants for light fractions:

$$\begin{aligned}
X_p &= -23.94 + 24.21 \times 1.0522 - 1.092 \times 0.9608 \\
&= 0.4858 \\
X_n &= 41.14 - 39.43 \times 1.0522 + 0.627 \times 0.9608 \\
&= 0.2521 \\
X_a &= -16.2 + 15.22 \times 1.0522 + 0.465 \times 0.9608 \\
&= 0.2621
\end{aligned}$$

DETERMINATION OF VISCOSITY FROM VISCOSITY/ TEMPERATURE DATA AT TWO POINTS

Kinematic viscosity/temperature charts[24] are a convenient way to determine the viscosity of a petroleum oil or liquid hydrocarbon at any temperature within a limited range, provided viscosities at two temperatures are known. The procedure is to plot two known kinematic viscosity/ temperature points on the chart and draw a straight line through them. A point on this line within the range defined shows the kinematic viscosity at the corresponding desired temperature and vice versa.

The kinematic viscosity of a petroleum fraction can also be expressed as a linear function of temperature by following equations. These equations agree closely with the chart scales. They are necessary when calculations involve viscosities smaller than 2 cst:

$$\log \log Z = A - B \log T \tag{11-20}$$

$$Z = \nu + 0.7 + \exp(-1.47 - 1.84 \times \nu - 0.51 \times \nu^2) \tag{11-21}$$

$$\begin{aligned}
\nu = {} & (Z - 0.7) - \exp[-0.7487 - 3.295 \times (Z - 0.7) \\
& + 0.6119 \times (Z - 0.7)^2 - 0.3193 \times (Z - 0.7)^3]
\end{aligned} \tag{11-22}$$

where

ν = kinematic viscosity, cst $(\mathrm{mm}^2/\mathrm{sec})$;
T = Temperature, K or °R;
A and B = constants.

Constants A and B for a petroleum fraction can be calculated when the temperature and corresponding viscosity are available for two points, as follows. Writing equation (11-20) for the two temperature/viscosity pairs gives the following:

$$\log\log Z_1 = A - B\log T_1 \tag{11-23}$$

$$\log\log Z_2 = A - B\log T_2 \tag{11-24}$$

where

$$Z_1 = v_1 + 0.7 + \exp(-1.47 - 1.84 \times v_1 - 0.51 \times v_1^2) \tag{11-25}$$

$$Z_2 = v_2 + 0.7 + \exp(-1.47 - 1.84 \times v_2 - 0.51 \times v_2^2) \tag{11-26}$$

v_1 and v_2 are the kinematic viscosities at temperatures t_1 and t_2, in K or °R, respectively.

Let

$$k_1 = \exp(-1.47 - 1.84 \times v_1 - 0.51v_1^2) \tag{11-27}$$

$$k_2 = \exp(-1.47 - 1.84 \times v_2 - 0.51v_2^2) \tag{11-28}$$

$$y_1 = \log Z_1 = \log(v_1 + 0.7 + k_1) \tag{11-29}$$

$$y_2 = \log Z_2 = \log(v_2 + 0.7 + k_2) \tag{11-30}$$

Thus equations (11-23) and (11-24) can be rewritten as follows:

$$\log y_1 = A - B\log T_1 \tag{11-31}$$

$$\log y_2 = A - B\log T_2 \tag{11-32}$$

Substituting the value of A from (11-31) in equation (11-32) yields

$$B = \frac{\log\left(\dfrac{Z_1}{Z_2}\right)}{\log\left(\dfrac{T_2}{T_1}\right)} \tag{11-33}$$

$$A = \log(Z_1) + B + \log(T_1) \tag{11-34}$$

With the values of A and B known, viscosity at any other temperature in K or °R can be determined from equations (11-20), (11-21), and (11-22).

EXAMPLE 11-20

A kerosene stream of Dubai crude has a kinematic viscosity of 1.12 cst at 323 K and a viscosity of 0.70 cst at 371.9 K. Determine the kinematic viscosity of the stream at 311 K. Here,

$$\nu_1 = 1.12\,\text{cst}$$
$$\nu_2 = 0.70\,\text{cst}$$

First, calculate factors k_1 and k_2:

$$\begin{aligned} k_1 &= \exp[-1.47 - 1.84 \times (1.12) - 0.51 \times (1.12)^2] \\ &= 0.0154 \\ k_2 &= \exp[-1.47 - 1.84 \times (0.70) - 0.51 \times (0.70)^2] \\ &= 0.0494 \end{aligned}$$

Next, calculate Z_1 and Z_2:

$$\begin{aligned} Z_1 &= \log(1.17 + 0.7 + 0.0154) \\ &= 0.2637 \\ Z_2 &= \log(0.7 + 0.7 + 0.0494) \\ &= 0.1612 \end{aligned}$$

Calculate constants A and B for the petroleum fraction:

$$\begin{aligned} B &= \frac{\log\left(\dfrac{0.2637}{0.1612}\right)}{\log\left(\dfrac{371.9}{323}\right)} \\ &= 3.4942 \\ A &= \log(0.2637) + 3.4942 \times \log(323) \\ &= 8.1889 \end{aligned}$$

The viscosity at 311 K can now be determined as follows:

$$\begin{aligned} \log\log Z_{311} &= 8.1889 - 3.4942 \times \log(311) \\ &= -0.5214 \\ Z_{311} &= 2.0001 \end{aligned}$$

The corresponding viscosity at 311 K can be determined by equation (11-22):

$$\begin{aligned} v_{311} &= (2.001 - 0.7) - \exp[-0.7478 - 3.295 \times (2.001 - 0.7) \\ &\quad + 0.6119 \times (2.001 - 0.7)^2 - 0.3193 \times (2.001 - 0.7)^3] \\ &= 1.2910\,\text{cst} \end{aligned}$$

NOTES

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6. Ibid.
7. Ibid.
8. ASTM equation.
9. ASTM specification D-524.
10. ASTM specification D-189.
11. ASTM specification D-524, under nonmandatory information, presents a graph of Ramsbottom carbon as a function of Conradson carbon.
12. ASTM specification D-93.
13. ASTM test method specification D-976–80.
14. ASTM specification D-97 (supplement; nonmandatory information).
15. ASTM specification D-3245.
16. API databook procedure 11A1.1.
17. ASTM specification D-2161.
18. API databook procedure 11A1.4.
19. API databook procedure 2B5.1.
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21. API databook procedure 2B4.1. See also, M. R. Raizi and T. E. Daubert. "Prediction of Composition of Petroleum Fractions." *Industrial Engineering and Chemistry, Process Design and Development* 16 (1980), p. 289.
22. ASTM specification D-2501.
23. API databook procedure 2B2.1.
24. ASTM specification D-341.