Refinery Processing of Asphalt Cement

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ABSTRACT

Crude petroleum varies in its makeup of distillable fractions as well as in its bitumen content. Initially, it is separated by distillation with the major volume of asphalt cement manufactured today prepared by straight reduction to grade. Other processing methods, such as solvent deasphalting, supercritical extraction, blending, and continuous air-blowing, supply fractions that are usable in asphalt cement within the limitations of specification compliance. Crude oils may be arbitrarily classified according to their API (American Petroleum Institute) gravity, which is shown to relate to composition, physical properties, and the viscosity-penetration relationship of the asphalt cement therefrom. It is also related to distillation cut-points and how that crude might best be processed. The viscosity-penetration relationship is shown to correlate with temperature susceptibility and may be used directly in determining specification compliance. The viscosity graded (Table 2) specifications as used in the United States are more rational than the penetration-softening point control systems used in Europe and Eastern countries.

It is generally believed that asphalt cement specification quality is closely dependent on the crude oil being processed as well as on the refinery processes applied. It is not as well-known how these two variables are controlled in meeting product standards.

The inherent differences found in crude petroleum are first discussed followed by a discussion of the reason it is initially processed by distillation. The other refinery processes and methods that may be applied and how they may be worked into the scheme of manufacture are described. An arbitrary classification of crudes is suggested and shown to be related to product test characteristics as well as to the processing method applied. The viscosity-penetration relationship is suggested as a means for controlling the effect of the crude as well as adapting it to the processing route used. The difference between the viscosity graded system used in the United States is compared with that used in European and Eastern countries.

CRUDE PETROLEUM VARIES

The compositional makeup of crude petroleum varies appreciably, especially with respect to its content of distillable fractions as well as its content of residual bitumen. This is illustrated by the three examples in Figure 1 showing typical volume percentages of those fractions that are distillable compared with the bitumen content shown by the shaded areas. Low American Petroleum Institute (API) (1) gravity crudes contain relatively low percentages of distillable overhead fractions with a high percentage of bitumen, whereas the high API gravity crudes contain a relatively high percentage of overhead fraction with a low percentage of bitumen. The low gravity crudes are generally referred to as heavy crudes or as sour crudes if their sulfur content is high. Conversely, the high gravity crudes are known as light crudes, or sweet crudes if their sulfur content is low. The fractional makeup of a crude thus becomes an important consideration to the refiner because he must balance his product yield with sales movement. For reference purposes, each crude is always identified by name or source along with its API gravity.

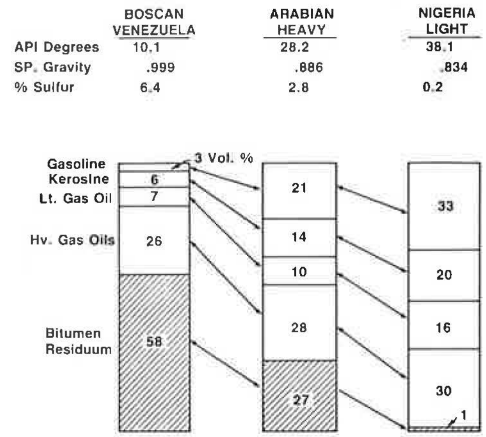

FIGURE 1 Make-up of crude petroleum.

DISTILLATION IS FIRST STEP

Straight reduction by distillation is a necessary first step in the processing of all crude petroleum (2). As shown in Figure 2, the distillation principle is used to separate the lower boiling points, or boiling ranges of the hydrocarbons contained in the crude petroleum. Because bitumen or asphalt is

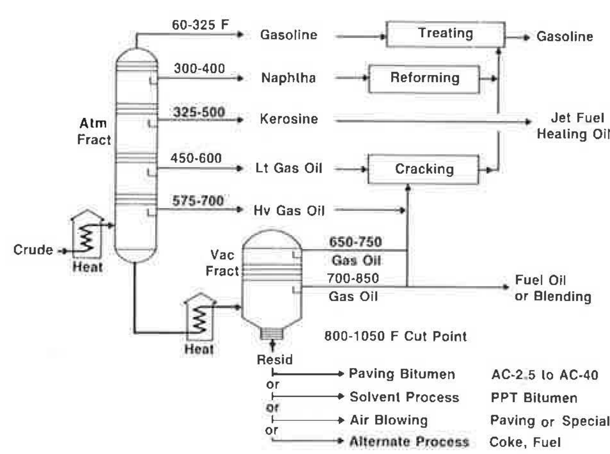

FIGURE 2 Crudes initially separated by distillation.

primarily made up of the highest boiling fractions, it becomes the residuum from the atmospheric fractionator. Usually a second stage of distillation, under vacuum, is needed to yield a residuum of suitable consistency for use as an asphalt cement. All of this is done by a continuous flow operation.

A typical range in distillation temperature is shown for the different overhead fractions, noting that the asphalt residuum from the vacuum fractionator is identified by a cut-point, which is the atmospheric equivalent vapor temperature needed to fractionate the residuum from the overhead fractions above it. Most refineries are designed to yield high percentages of fuel type products. Treating, reforming, cracking, and solvent processing are thus part of the overall scheme, although they have little bearing on the asphalt manufactured. Where the characteristics of the crude feed permit, asphalt cements are commonly prepared by straight reduction to grade, as indicated by the bold lines in this figure.

SOLVENT DEASPHALTING

Solvent deasphalting (SDA) is sometimes applied to a vacuum residua in order to extract additional quantities of high boiling fractions (deasphalted oil) for either lube manufacture or as a feed for catalytic cracking (3). Propane and butane are usually used as the extracting solvent in a flow process such as that shown in Figure 3. Vacuum residuum is fed into an extracting (EXT) tower where it is contacted at 100 to 150°F with the solvent in a countercurrent fashion. This process yields a high softening point bitumen (precipitated asphalt) that may be used as a blending component for asphalt cements. As discussed later, the use of precipitated bitumen is often limited because it often downgrades temperature susceptibility. It does represent a source of bitumen, which at times can be used in minor proportions in asphalt cement.

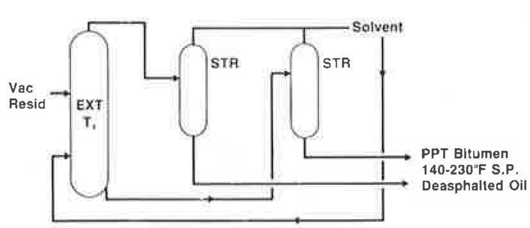

FIGURE 3 Solvent deasphalting (SDA).

SOLVENT EXTRACTION

The Residuum Oil Supercritical Extraction (ROSE) is a newer process (4,5), which provides a wider flexibility in resid fraction characteristics. Figure 4 shows the processing scheme that is initiated by admixing a resid feed with any one of a variety of low-boiling hydrocarbon solvents, for example, normal pentane. This mixture is then fed into a separator (SEP) at a predetermined controlled temperature (T_1) and pressure, which causes the separation of an asphaltene concentrate, subsequently recovered by stripping (STR) off the solvent. The extract portion from above is then taken to a second separator where at a controlled higher temperature (T_2) and pressure, a decrease in solubility is effected, causing the precipitation of a second fraction (resins). Similarly, a third fraction (oils) is separated and recovered. The ROSE process thus offers either the asphaltene or the resin fraction as a blending com-

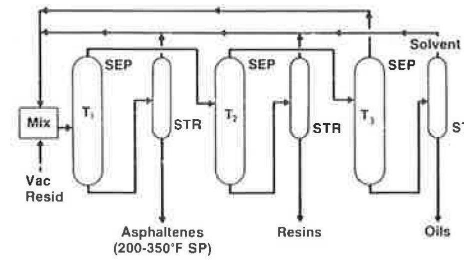

FIGURE 4 Supercritical extraction (ROSE).

ponent for asphalt cements, subject to specification compliance, as will be explained later.

CONTINUOUS AIR-BLOWING

This process is used only when vacuum resids must be increased in viscosity or are in need of improved temperature susceptibility (6). As shown in Figure 5, this process involves the continuous pumping of a vacuum resid (flux) through an oxidation tower held within the temperature range of 450 to 525°F, while air is passed through the hot flux. This causes a chemical conversion (7) within the flux, yielding a product of higher viscosity and softening point and improved temperature susceptibility. Batch air-blowing is a common process in the manufacture of roofing asphalts, whereas continuous air-blowing involves a lesser degree of conversion and thus is more applicable for asphalt cement manufacture. Continuous air-blowing is sometimes used in Europe and in Eastern countries, whereas it is infrequently used in the Americas.

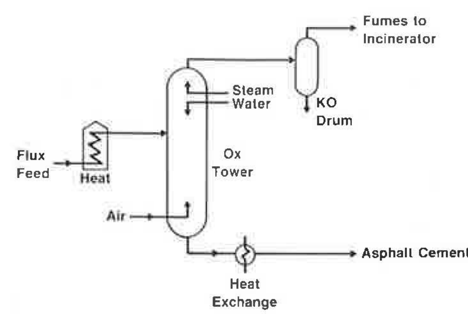

FIGURE 5 Continuous air-blowing.

CRUDES CLASSIFIED

After first arbitrarily classifying crudes according to their API gravity, it will be shown how the crude type correlates with the specification quality of the asphalt cement derived from the crude. Table 1 lists examples of the arbitrary type classification and some of the sources that are typical of those types.

Also related to crude types is its cut-point at a given viscosity level of asphalt residua. The cut-point is the atmospheric equivalent vapor temperature (AEVT) required to separate overhead fractions from a residuum as shown in Figure 6. To the refiner, this is an important consideration because it indicates the temperature equivalence that must be attained if asphalt cement is manufactured by straight reduction to grade. For example, to yield an AC-20 from crude type A, a cut-point temperature of about 1,190°F must be reached, whereas for crude

TABLE 1 Arbitrary Crude Types and Typical Sources

TYPE	°API	SOURCE
A	34	ARABIAN LT.,SA
	32	KUWAIT, KU
B	28	HAWKINS, US
	26	TIAJUANA, VN
C	19	GALAN, CO
	18	CYRUS, IR
D	16	LLOYDMIN STER,CA
	15	OBEJA, VN
E	12	PANUCO, MX
	10	BOSCAN, VN

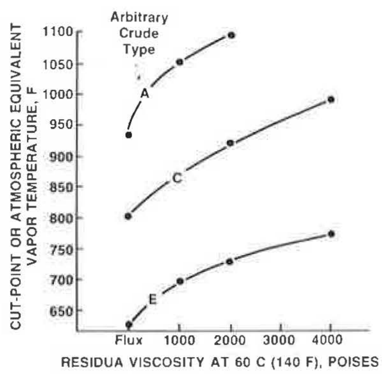

FIGURE 6 Distillation cut-point relates to crude type.

type E, a temperature equivalence of about 730°F is needed. The use of vacuum in the second stage of distillation aids in attaining the equivalent of these high temperatures.

Crude Type is Relevant

It has been shown (8) that crude type relates both to composition and to the physical properties of the asphalt cement. This is shown in Figure 7 where crude type A asphalt is found to be relatively high in saturates and naphthene-aromatics and low in polar-aromatics and asphaltenes (9). It will also be noted that type E asphalt typically displays the reverse of that, namely, low saturates and naphthene-aromatics and high polar-aromatics and asphaltenes. The physical properties of mid-range AC-20 from each of these types also show a pattern of differences. Asphalt from type A crude has a relatively low penetration, low viscosity at 275°F, low penetration ratio, and low viscosity after thin film oven testing. Asphalts from type E crude are relatively high for the same test characteristics with type C intermediate. The average molecular weights of the numbers (measured with a Mechrolab vapor pres- sure osmometer with benzene) for each of the four fractions show high values for type A fractions and low values for type E. This is directionally con- sistent with the data shown in Figure 6 relating cut-points to crude type. That is, high cut-points mean higher hydrocarbon boiling points and higher molecular weights, and low cut-points have the op- posite effect. There are, of course, exceptions to any arbitrary classification and its correlations, but for the most part, these relationships hold true.

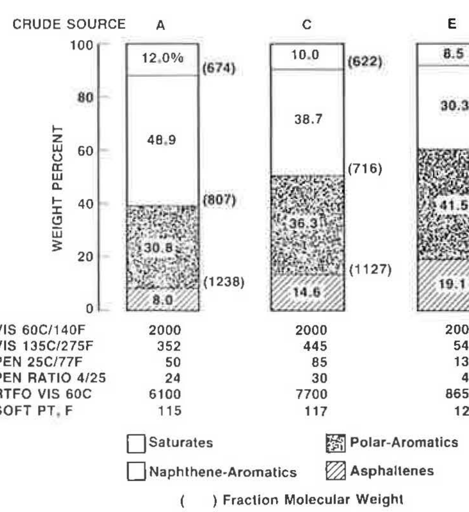

FIGURE 7 Crude type versus composition.

SEVERAL MANUFACTURING ROUTES

Asphalt cements may be prepared by any one of several routes depending on the crude type being used. If the crude feed permits, straight reduction to grade is the most direct and most commonly practiced route. Figure 8 shows the different routes that may be selected. Blending or mixing the crude feed is one route often selected. If two or more crudes were processed separately with one yielding a low viscosity residuum and the other yielding a high viscosity residuum, the resids could be blended. If only a low viscosity resid was made, it could be blended with a precipitated bitumen or air-blown. If only a high viscosity type resid was made, it could be regulated to asphalt cement during distillation, or it could be blended back with a gas oil or a similar fraction. Thus, the refiner has several choices, but his choice is largely dictated by the crude type or crude mix being used.

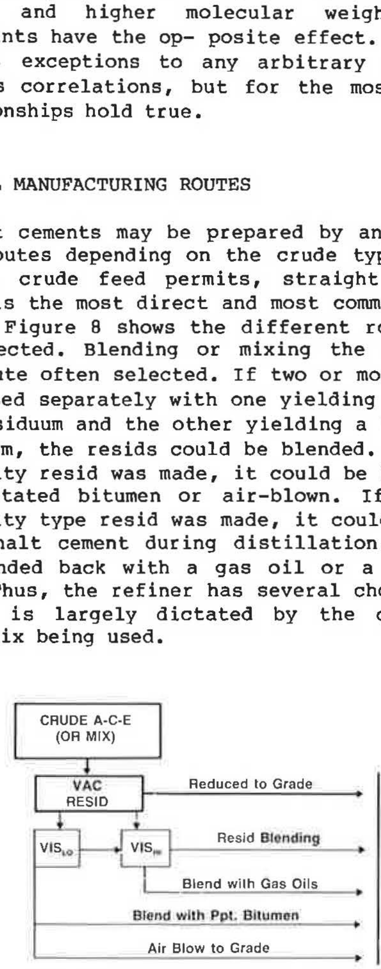

FIGURE 8 Asphalt cement prepared by several routes.

VISCOSITY PENETRATION RELATIONSHIPS

The relationship between viscosity at 140°F in poises and penetration at 77°F is an important and useful characteristic when considering the manufacture of asphalt cement. This is related to crude type as based on the finding (10) that straight reduced asphalts, including those made by blending, may be represented by a straight line when plotting viscosity at 140°F in poises against penetration at 77°F on a log-log chart. Figure 9 shows that this results in a nesting of lines varying slightly in slope but differing considerably in level between a maximum and minimum, based on a survey of free world sources of crudes. At a viscosity level of 2,000 poises, asphalt cements from crude A have a penetra-

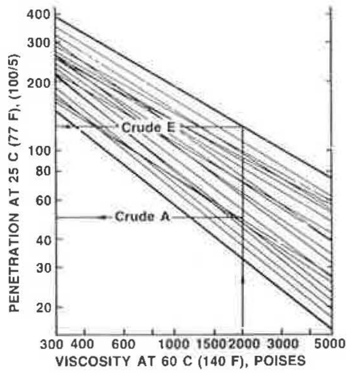

FIGURE 9 Viscosity-penetration relationship.

tion of 50 and a penetration of 130 for asphalt from crude E. Viscosity levels could also be related for a common penetration of 90, which would be about 500 poises for asphalt from crude A and about 3,600 poises for asphalt from crude E. Thus asphalts from crude A would be termed low viscosity asphalts and those from crude E would be termed high viscosity asphalts.

Viscosity Penetration Guides

The selection of crudes as well as the fitting into specifications is dependent on the viscosity-penetration relationship. For example, Figure 10 shows that asphalts from crude type A have little chance of meeting either an AC-10 or AC-20 specification under AASHTO (11) or ASTM (12) (Table 2). Asphalts from crude type C, D, or E will easily comply, however. Generally if the asphalt meets grade AC-20 specifications, the higher and lower viscosity grades from that crude will also meet specifications.

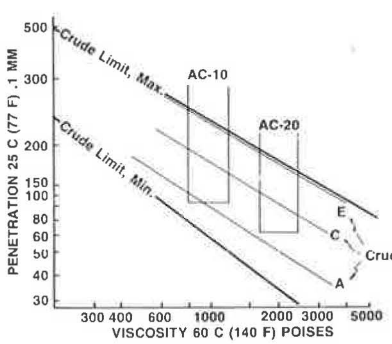

FIGURE 10 Viscosity-penetration relationship guides.

TABLE 2 AASHTO, Table 2, Specifications

	AC-20	PURPOSE
Vis 140 F, Poises	1600-2400	Grade Control
Pen 77 F, .1 mm	60 +	Temp. Susceptibility
Vis 275 F, cSt	300+	Hot-Mix Guide
Flash, F	450+	Contamination
Solubility, TCE	99+	Purity
TFO, Loss	0.5-	Optional
TFO, Vis Ratio	4-	Hardening Quality
TFO, Duct Res	50+	Crude Suitability

Viscosity Penetration Indicates Temperature Susceptibility

If the often-used penetration index (13,14) can be accepted as a measure of temperature susceptibility, it can be shown that the viscosity-penetration relationship does the same. If the penetration at a given viscosity level (i.e., 2,000 poises) is plotted against penetration index (pen/pen 45-77°F) (15), a good correlation can be found (see Figure 11). To support this, refer to the high temperature viscosity (275°F) and the penetration ratios shown in Figure 7. Low viscosity at high temperatures and low penetration ratios relate to type A asphalts and the opposite effect to type E asphalts.

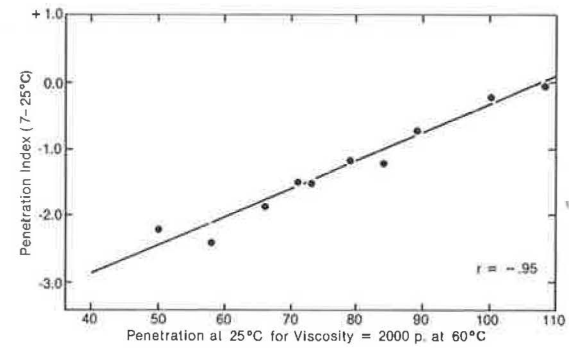

FIGURE 11 Viscosity-penetration relationship relates to temperature susceptibility.

SPECIFICATIONS GOVERN

Under AASHTO and ASTM specifications, a minimum penetration is required for each grade, which is simply another way of stating the viscosity-penetration relationship previously described. Knowing this relationship for the specific crude or crude mix, the refiner can quickly determine compliance by using the log-log plot shown in Figure 12. If the viscosity-penetration requirements pass, the other test requirements will normally conform. This, of

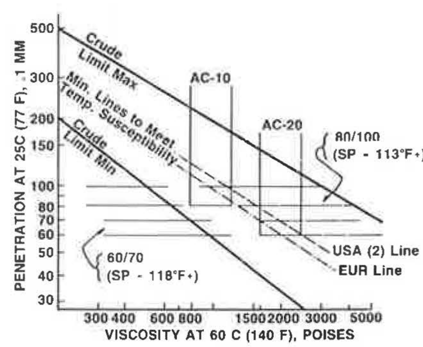

FIGURE 12 USA system is more rational.

course, is subject to laboratory verification for the specific crude or mix involved. In Table 2 the viscosity grade and the penetration at 77°F are underlined to emphasize their prime consideration in specification compliance.

If the viscosity-penetration requirements are a problem, the refiner will ordinarily take steps to effect a change in the asphalt cement product. As previously indicated, he may blend crudes, blend mately eight different authors in this paper's reference list who have used this same or a very similar correlation in their study of asphalt cement. Furthermore, it has a very practical value in refinery planning as well as in meeting current specifications.

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Refinery Economics

K. W. HOLBROOK

ABSTRACT

The following aspects of refinery economics are covered: relation to asphalt-cement production; the outlook for crude-oil supply and demand; refinery data and the statistics of refining operations; past, current, and future changes in the economics; the effect of those changes on asphalt-cement supply, price, and availability; and a review of the general outlook for asphalt production.

Refinery economics is a subject about which there are many questions. Some assumptions can be made as to what we think is going to happen in the refining industry, but the economics changes rapidly. The subject of this paper is not just refinery economics but also how refinery economics relates to asphalt-cement production. The paper will cover the outlook for crude-oil supply and demand; refinery data and the statistics of refining operations; past, current, and future changes in the economics; the effect of those changes on asphalt-cement supply, price, and availability; and a review of the general outlook for asphalt production.

It can be seen from the data in Table 1 on world oil consumption that the 1960s was the decade of

TABLE 1 World Oil Consumption

Time Period	Percentage of Growth	Characteristics
1960s	6/year	Expanding world economies
1970s	3/year	Slowing growth and energy conservation
1980-1985	0/year	Flat world economies and greater energy conservation
1985-1990	1-2/year	Improved economic conditions