Bitumen quality and manufacturing processes—Past and present technological status

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Bitumens for road paving applications are derived from refining of crude oils. Their quality depends upon the nature and origin of crude and processing scheme. Bitumen manufacture since the late eighties has undergone significant changes, basically due to better understanding of chemistry of hydrocarbons constituting the feedstocks, processing chemistry and final bitumen through the use of advanced analytical techniques and understanding of the mechanism of aggregate interaction. In view of this, there are fast developments in the technology of bitumen making, some of which are: (i) detailed characterisation of feedstocks and fluxes, (ii) better understanding of the role of different types of constituting hydrocarbons on performance properties, (iii) upgradation of process technology, based on reaction kinetics, (iv) multigrading concept to have bitumen with low temperature susceptibility and acceptable performance level in extreme climatic conditions, and (v) use of unconventional (non-bitumen bearing) crudes in making bitumen. The present review examines some of the above on going developments for their application in improving quality and technology of bitumen making.

Historically bitumen/asphalt was the first petroleum product used by human being as an adhesive and water proofing material by the civilizations along the Euphrates river as early as 3800 B.C. It is further believed that soft bitumen was used extensively in the preservation of Egyptian mummies as well. Many theories have been advanced concerning origin and formation of petroleum and native bitumen. Red Wood’s suggested that bitumens are of inorganic origin. Lucas and Maberry however believed in an organic origin of bitumen as later confirmed by Peckham who showed that bitumen was a product of distillation. Modern theories are also in favour of the organic origin.

The use of bitumen for walls and pavement surfaces in ancient days has been well authenticated by excavations and inscriptions on vases and tablets of different periods. Considerable research has been carried out to determine whether bitumen was used in any way on old roads so that one can bridge the enormous gap in time between its use in ancient days and the present. Little information has come to light, although one reference of considerable interest and importance is worth recording. Abraham has elaborated on this aspect using road construction history of Peru.

Bitumen and Highways - Prehistoric

In order to form some idea of the reasons why a bituminous material was ever used on a road it is desirable to very briefly review highway conditions prevailing before and after the coming of the automobile. The roads/highways of preautomobile period (around the turn of present century) were mainly of stone or gravel, or of such other materials as would compact and support the loads transported. Those were demanded by farmers, the postal service, and the people living outside cities as improved means for travel. The birth of automobile thereafter is considered more responsible for the development of use of bitumen than any other agency.

Bitumen base crude oils were plentiful in many southern sections of California, USA and its use soon spread to all parts of the west and, as its beneficial effect became known, to the eastern part of the country. No specifications were then in existence. The cutback bitumen had not been developed, and the methods of application were indeed crude. Engineers therefore, experimented...
with other types of construction using this promising material. Many references to its successful use can be found in reports of State Highway Departments of USA. In addition to the use of liquid bitumens for dust elimination, numerous experiments were conducted, in many states, using mixes of stone and heated bitumen as binders. The processing and placing of road mixes of sand, gravel, or stone were all done by manually, a method inefficient and costly (A practice followed in our country even today). Highway engineers felt need of mechanised system to mix bitumen with aggregate, spread and consolidate the mixture to the proper grade and camber.

The introduction of cut back bitumen in the early 1930's was largely responsible for the development of road machines to incorporate bitumen with the aggregates. The self operated spreading machine come into general use in the early 1930's replacing all hand spreading on major projects. Further developments of hot mix plants are probably responsible for the excellent performance of sheet bitumen and bituminous concrete pavements than any other mechanical device. The importance of the machinery required and the proper handling of the mix therefore assumes great significance as the very success of a pavement is largely dependent on the machinery used. The percentage of bitumen in the mix as a binder usually varies from 3 to 10% as compared to 90% and above of aggregate depending upon the requirement of traffic and specifications.

**Bitumen Quality Aspects**

In view of huge expenditure involved in the construction of new roads and maintenance of the existing road network, the quality considerations of bitumen have become a subject of interest. The bitumen quality varies with the variation in crude oil source and refining process, which often cause considerable distress to road pavement. Bitumen obtained from refineries, though meet the existing specifications but do not give required inservice performance under the prevailing heavy traffic and environmental conditions thus indicating deficiencies in the specifications itself. It is desirable that the specifications should enable the engineers to select a bitumen on the basis of performance required under the current and also under the projected traffic and environmental conditions. The daily and seasonal variations in temperature and traffic loadings besides changes in original properties during construction and inservice aging makes the task of designer more difficult to select an appropriate binding material.

The quality of bitumen is judged by: (i) its flow properties at different temperatures, (ii) chemical composition, (iii) resistance to change in flow properties during inservice aging and climatic variations. The compositional changes during aging and corresponding effect on flow can help explain serviceability of bituminous roads. Hence, quality of a bitumen to achieve performance levels required by present and projected traffic loadings and environmental exposures prevailing in practically world over can be controlled by a set of specifications based on valid relationship between its properties, mix properties and field performance. Hence, as a result of increased traffic loading conditions, variations in nature of crudes and developed quality consciousness among highway engineers, recent trends all over the world are to move from a simple to performance based specifications. Since an approach allows field engineers to match materials to desired levels of pavement serviceability and to tailor the choice of bituminous binder and bitumen - aggregate mixtures to alleviate or minimize specific road distress associated with bitumen characteristics. Besides taking care of key performance factors, the specifications should also enable the control of (i) constructability and (ii) safety aspect involved in bituminous road construction.

A performance based specification may be defined as “the limits and requirements developed from an extensive data base related to performance based tests by means of well established performance prediction models, which have been validated by correlation within place field performance data”. In the 4th Eurobitume Conference held at Madrid, Spain, Shell Research Laboratories Amsterdam presented Qualagon concept for performance based specifications. This concept consist of 9 tests that includes 6 tests on bitumen and 3 tests on bituminous mixtures which cover the following three key performance elements:
Cohesion - Low temperature ductility
Adhesion - Retain Marshall stability
Durability - Rolling thin film oven test

The background philosophy of quality polygon for performance emanates from the fact that by proper choice of feedstock and processing conditions, the bitumen may be produced with right balance in properties, i.e.,

- A balance in molecular weight distribution.
- A balance in chemical composition.
- A balance in physical properties.

In case the properties of the bitumen prepared from any crude/feedstock does not fall within the preferred limits of qualagon they are brought within the area by altering the process conditions. These limits are however not used as pass/fail criteria.

According to Strategic Highway Research Programme (SHRP) concept of specifications, it should be based on a set of validated relationship between, bitumen properties, mixture properties and pavement performance factors that establish acceptable response to changes during construction and inservice aging. SHRP specifications are presented in Table 1. It is reported that moisture sensitivity and adhesion can be controlled by specifying limits of strength of the bitumen aggregate bond in blister test. Fatigue cracking can be controlled by specifying limits in repeated bending beam test. Details of both the tests are given under SHRP specifications.

Summary of specifications representing American viewpoint is as follows:
- Average 7 days maximum pavement temperature.
- Minimum pavement design temperature.
- Flash point.
- Maximum viscosity at 135°C.
- Dynamic shear ($G' \sin \delta$)
- Physical hardening index.
- Rolling thin film oven test residue
- Mass loss
- Dynamic shear ($G' \sin \delta$).

A tripartite group of IIP, IOC R&D Centre and CRRI has also worked into the prevailing BIS bitumen specifications in our country. The group has evolved an elaborate approach/set of specifications to be followed at refineries during manufacturing of bitumen and later for performance during application.

Relationship between bitumen composition/constitution and performance—Bitumens are visco-elastic materials and their behaviour varies from purely viscous to elastic, depending upon time of loading and temperature. Viscosity of paving bitumen therefore plays an important role during bituminous road construction and subsequent performance. During mixing, compaction of bituminous mixes at high service temperatures their properties can be expressed through a stiffness modules. The field performance of bitumen is further linked with their chemical compositions in terms of concentration of asphaltenes and wax present.

Cerrone studied the influence of asphaltenes in controlling the properties of paving grade bitumen. With increase in percentage of asphaltenes, there is a substantial change in the bitumen’s colloidal structure which tend to assume more and more the configuration of a “Gel” type. At the same time important properties of bitumen are altered in a manner more favourable to their use. The altered properties are thermal susceptibility and rheological characteristics in general and the mechanical and elastic properties in particular. Asphaltenes therefore constitute an important element in estimating the commercial value of bitumen. It is possible that a bitumen of specified origin containing small quantity of asphaltene may posses a structure and characteristics which are more favourable than those of bitumen of another type containing a higher percentage of asphaltene constituents. Asphalt Institute, USA opined that chemically asphaltenes are most complex fraction of bitumen, they contain largest tendency to interact and associate. Indonesian specification stipulate a range of 15-25% asphaltenes as more appropriate.

In petroleum industry paraffins (wax) is the collective name given to a crystalline material with melting point above 45°C that is present in oil products including bitumen. The melting point of the paraffin increases with the increase in carbon number of the paraffin chain and decreases when
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structural variations are present. The structure (crystallinity and hardness) of paraffin wax, its molecular weight, and its concentration all affect bitumen performance in two ways: At low road temperature (below 15°C) paraffin crystallizes and bitumen surfacings show sign of distress in the form of fine hair cracks. At high road temperature (above 60°C) paraffin melts, act as a flux and the bituminous surfacings start bleeding. The presence of high paraffin content reduces the net bitumen content in the surfacings and thus affects its durability. Also presence of high paraffin content in bitumen poses adhesive problems and affects setting characteristics. Wax decreases the penetration viscosity number (PVN) making bitumen more susceptible to temperature changes.

The bitumen produced from indigenous crudes particularly for special application in Assam region at Digboi Refinery contain paraffin wax as high as ~8% while bitumen derived from imported crude the quantity of paraffin is below 4.5% at par with the international standards.

It has also been shown that the rheological properties of bitumen depend strongly on the asphaltene content. At constant temperature the viscosity of the bitumen increases as the concentration of the asphaltenes blended into the parent malthenes is increased. The increase in viscosity, however, is substantially higher than would be expected if the asphaltenes were spherical, non-solvated entities. This suggests that the asphaltenes can interact with each other and/or the solvating medium. Even in a dilute toluene solution the viscosity increase observed when increasing the asphaltene content corresponds to a concentration of non-solvated sphere, some five times higher than the amount of asphaltene used. Bitumen asphaltenes are believed to be stacks of plate-like sheets formed of aromatic/naphthenic ring structures. The viscosity of a solution, in particular a dilute solution, depends on the shape of the asphaltene particles. Size is important only if shape changes significantly as size increases. At high temperatures the hydrogen bonds holding the sheets/stacks together are broken, resulting in a change in both the size and shape of the asphaltenes. Dissociation of the asphaltene entities continues until the limiting moiety, the unit sheet of condensed aromatic and naphthenic rings, is reached. Consequently, viscosity falls as temperature increases. However, as a hot bitumen cools, associations between asphaltene occur to produce extended sheets. These, in turn, interact with other chemical types present (aromatics and resins) as well as stacking together to form discrete asphaltene particles. Thus property relationship of late has become extremely important with the introduction of multigrade concept in paving bitumen as well.

Physico-chemical Methods for the Separation of Bitumens

Developments in the past two decades in the field of separation science and advances in analytical techniques have provided better understanding of the compositional aspects of the bitumens.

Fractionation using solvents—The fractionation of bitumens by selective solvents dates back to 1916. This is based on the pioneering work of Marcusson relating to the differentiation between
native and petroleum bitumens. In the succeeding forty years a number of investigators have followed methods reported by Abraham. In 1944 Hoiberg and Garris described a procedure for the separation of bitumen into five fractions. Hexane was used to precipitate asphaltenes. This method was found applicable to bitumens varying in consistency from road oils to highly air blown products. Chelton and Traxler fractionated asphaltenes precipitated by n-pentane by treatment with increasing amounts of methanol in benzene. Traxler and Schweyer developed a procedure which gave a three component analysis that proved useful in classifying bitumens on the basis of their colloidal, rheological and physical properties.

Hewett and Faid modified the procedure (as mentioned by Traxler and Schweyer) by first precipitating the asphaltenes with n-pentane from roofing bitumens and then fractionating the pentane soluble material with acetone at -23.3°C (11.2°F). It is noteworthy to mention here that throughout the history of studies related to petroleum composition, there has been considerable attention paid to the asphaltic constituents, i.e., the asphaltenes and resins due to their being responsible for high yields of thermal coke and also for shortened catalyst life in refinery operations. Although the early studies were primarily focussed on the compositional behaviour of bitumen, the techniques developed for those investigations have provided an excellent means of studying heavy petroleum feed stocks.

Adsorption chromatography—In 1932 Poll developed a method for separation of bitumens into several fractions by first removing the asphaltene with light petroleum naphtha then contacting the pentane soluble (maltenes) with fuller’s earth. Hubbard and Stanfield used adsorption on anhydrous alumina followed by washing with n-pentane and a methanol-benzene solution to obtain oils and resins, respectively. Grader used carbon tetrachloride, benzene, and trichloroethane as the agents for removing materials from the adsorbents. O’Donnell, in his elaborate study of the analysis of bitumen used adsorption on silica-gel followed by elution with iso-pentane and other solvents. The aromatics were dissolved in iso-pentane and separated into mono- and dicyclic hydrocarbon types over Alcoa grade F-20 alumina. Serguienko et al. fractionated three Russian asphaltic oils by first precipitating asphaltene with n-pentane. The pentane solution was percolated through silica to remove the resins. The mass was washed with petroleum ether to remove oils and resins displaced from the silica gel by carbon tetrachloride (fraction I), benzene (fraction II), and acetone (fraction III). The total (unfractionated) resins were determined in a separate experiment.

Kleinschmidt fractionated air blown bitumens by adsorbing the n-pentane soluble materials on fuller’s earth. White oils, dark oils, and asphaltic resins were then removed by washing with n-pentane, methylene chloride and methyl-ethyl ketone, successively. Fuchs and Netteseim and Middleton separated different bitumens by adsorption of silica gel followed by elution with solvents including benzene and aromatic ketones. The study based on 5 bitumens concludes that “Efficient fractionation in elution analysis is assured if the composition of the eluent is changed during the fractionation in a smooth, uniform manner towards a stronger eluent”. The principles of forming such gradients have been discussed by Bock and Ling. Chelton and Traxler analyzed three typical vacuum reduced residua and a 50 penetration air blown bitumen from each residuum by first precipitating the asphaltenes with n-pentane. The three residua represented the gel, sol-gel; and sol types bitumens respectively.

Corbett described a convenient method for determining bitumen composition based on fractionation into four generic components. This method follow chromatographic separations involving elution of each component from an absorbent with solvents of increasing polarity. The polar nature and adsorption tendency become the separation criteria. Based on Corbett method Mullin et al. developed mathematical equations relating generic components of bitumens obtained by the above procedure with essential properties.

Fractionation methods based on electrical deposition and urea/thiourea adduction of asphaltics from crude oil are also reported for the separation of long, straight chain hydrocarbons from branched molecules.
**Spectral methods**—The successful use of infrared and ultra violet spectrometry in the study of chemical compounds and mixtures such as lubricating oils suggests their applicability to bitumens and fractions thereof. The ACS Symposium of April 1959 on "Spectroscopy in the Petroleum Industry" at Ohio presented an excellent picture of the status and future possibilities of the various spectroscopic fields. Most of the investigations considering the vanadium and nickel porphyrins found in oils and bitumens have used infrared spectroscopy for analysis. Knotnerus used infrared analysis in his excellent studies of the oxygen containing functional groups in air blown bitumens. By this technique he obtained evidence that the saponifiable matter in the bitumen consists mainly of ester groups and that acid anhydrides and ketones were almost entirely absent. Beitchman reported infrared spectra of a number of bitumens in films 1.5 to 2.0 mm thick. He inferred that, in general, the less durable bitumens exhibited stronger hydroxyl absorption than the more durable ones. Stewart after fractionating weathered and unleathered roofing bitumens by selective adsorption obtained infrared absorption spectra of the fractions. His data indicated differences in the chemical composition of the bitumen from various sources as well changes in concentration produced by weathering.

Ultraviolet absorption has been used to follow the separation of aromatic compounds found in bitumen. An exploratory study of the absorption of the ultraviolet and infrared energy of several bitumens was made by Schweyer. He also investigated the applicability of Beer-Lambert Law to bitumens dissolved in a mixture of iso octane and butanol for ultraviolet absorption, and in carbon tetrachloride as thin films for infrared absorption. Infrared absorption data were obtained on 10 fractions separated by thermal diffusion from the petrolenes (maltenes) of a paving bitumen. From these and other values it was possible to make deductions concerning hypothetical structures of different bitumen fractions. Fischer and Schram used infrared absorption in conjunction with mild hydrogenation to obtain evidence concerning the structure and composition of asphaltens, resins and oils separated from bitumens.

Developments in mass spectrometry have also led to the application of this technique to the study of molecular structure of oils and heavier hydrocarbons obtained from bitumen by various procedures. Various authors from their studies concluded that the structural composition of such molecules are simpler than have been suggested by most authors. Swaminathan and Swami used a photoelectric absorbtiometer to analyze road building bitumens. On the assumption that extinction coefficient is constant for a given wavelength, the authors found that absorption characteristics bear no relationship to the usual physical properties of the bitumen and these can only be related to the chemical composition of the constituents of the bitumen. The changes in the structure of the bitumen as a result of weathering, over heating, etc., thus can be predicted by this approach.

Shanxiang based on the assumption of equal degree of substitution or equal number of substituents on an aromatic ring estimated the aromatic ring distribution of bitumen by proton NMR spectroscopy. He also estimated aromatic carbons in bitumens and developed an improved method for characterizing saturated carbons, including naphthenic internal carbons, methyl and alkyl substituted naphthenic carbons etc. Strausz detected new classes of compounds appearing as homologous series in bitumen using combination of instrumental and chemical methods like NMR, IR and potentiometric titration. Sadeghi characterized fractions of bitumen based on polarity by using elemental analysis and FTIR and $^1H$ NMR spectroscopy by the modified Brown-Ladner equations as well as the 5-regions method. Phillip also characterized corbett fractions of bitumen by FTIR and NMR spectroscopic methods. Very recently Shanxiang established a complete system for estimating concentrations of structural groups and parameters of bitumen from NMR spectra and paraffinic chain distribution obtained by selective oxidation of the protonated carbons in aromatics. Zho et al. analyzed paraffinic wax fraction in bitumen by Differential Scanning Calorimetry (DSC) methods. Qian and Hsu studied the use of on-line LC/MS-
combined with low voltage electron impact ionization (LV-EI) medium resolution mass spectrometry (MR-MS) and advanced analytical data handling system to provide in depth molecular level characterization of high boiling petroleum and synthetic fuel fractions. This approach is expected to be very useful in understanding the chemistry of bitumen in the coming years.

Smith and Patterson used gas chromatography to determine the Henry's Law constants and infinite dilution activity coefficients for hydrocarbons and other vapour phase solutes in two bitumens. They discussed its use for components with widely varying molar masses and of parameters (measuring solvent/solute interaction energies) as is used in polymer systems. Mitera reported a quantitative mass spectrometric determination of petroleum asphaltenes and lactum oligomers. Equations for calculating the average molecular weight of the compounds studied were presented. Sebor et al. characterized metalloporphyrins in bitumen and asphaltene fractions of a Russian crude oil by mass spectrometry. Brule determined the molecular size of bitumens, asphaltenes and maltenes using Gel permeation chromatography. He found that there was usually a linear relationship between the molecular size distribution coefficient and maximum molecular size. Selucky et al. used gel permeation and other chromatographic means to separate asphaltenes and resins from Athabasca bitumen. Kozlova et al. reported an absorption spectroscopic method for the rapid quantitative determination of petroleum bitumen group compounds in solution. The method is based on individual luminescence characteristics of light, middle, and heavy aromatic hydrocarbons, resins, and asphaltenes. Paukku and coworkers reported polar components of asphaltenes-resinous substances of petroleum with metals (Fe, Ti or V) of variable valence.

Khu1be et al. employed ESR (Electron Spin Resonance) to determine free radical concentration and their formation in Athabasca bitumens. Studies on the effect of solvents (CO₂, polar and non-polar solvents) and heating rates provided information on free radical formation. Interactions of bitumen with CO₂ are important in petroleum reservoir engineering. ESR was also used to study the possible mechanism of bitumen oxidation with oxygen or photoexcited oxygen. Charge-transfer complexes were presented as the reaction pathway for the oxidation of bitumens. The method elucidates the oxidative reaction chemistry of sulfur and nitrogen species. Also, the effect of the addition of charge-transfer deactivating chemicals was related to bitumen's physical properties. Smiljanic et al. reported aging studies on pave roads by characterization of asphalts, extracted from the wearing coarse of the Belgrade highway. Stefanova et al. predicted paving grade bitumen performance by a triangular diagram. They concluded that it is possible to judge the characteristics for producing paving grade bitumen of a given quality.

Manufacture of Bitumen

Bitumen production - early attempts

Production of bitumen from petroleum developed slowly during the years immediately preceding and following the advent of the twentieth century. In the beginning, heavy residues from the distillation of almost any crude oil were used to soften the relatively hard native bitumens. It soon became evident that residues from the paraffin oils were not suitable. Thus, when available, the heavy viscous bottoms from the distillation of asphaltic and semi-asphaltic oils were used. The refiners began to distill asphaltic oils to harder residues, some times obtaining good bitumens, some time inferior ones. Applications other than road building were found for the hard bitumens. Roofing and water proofing developed as outlets and demanded radical alterations in manufacturing procedures. Air blowing and compounding procedures were developed.

Assessment of crude oil for bitumen manufacture

The chemical nature of the crude source has a profound effect on the composition of bitumen. Usually bitumens are of two types, i.e., sol and gel type. In the presence of sufficient quantities of resins and aromatics of adequate solvating power the asphaltenes are fully peptised, and the resulting micelles have good mobility within the bitumen. These are known as 'sol' types bitumen. If the aromatic/resin fraction is not present in sufficient quantity to peptise the micelles, or has insufficient solvating power, the asphaltenes can associate...
further together. This can lead to an irregular open packed structure of linked micelles, in which the internal voids are filled with an intermicellar fluid of mixed constitution. These bitumens are known as ‘gel’ type bitumens. Some crude oils yield bitumen having essentially sol characteristics. Other may give bitumen with such pronounced gel properties that they are unsuitable for road building purposes, though useful for other applications. When evaluating any new asphaltic or semi asphaltic crude it is necessary to determine the amount of bitumen that can be obtained on a volume and weight basis. A laboratory run usually is made to determine the amount present of bitumen of an established consistency, e.g., 100 penetration at 25°C. If a reasonable amount of quality bitumen (around 10%) is available further work is carried out to establish the commercial feasibility including the use of other light products. In fact Institut of Francais Du Petrole (IFP) has proposed a procedure how to select crude for asphalt (bitumen) making - based on various physico-chemical characteristics. Stanfield has presented in detail a procedure for evaluating an asphaltic crude oil in the laboratory. Operating procedures for atmospheric and vacuum distillation, standard tests, and results on 12 different crudes are given in detail.

Indian Institute of Petroleum (IIP) has also done considerable work on this subject as technological support to industry. Over 30 imported and indigenous crudes have been evaluated for their bitumen yields and quality.

The refinery helps to manufacture bitumen from the particular crude. If a few grades of road building bitumen best fit the manufacturing and marketing facilities of the refinery, the problem is fairly simple. The required grades of bitumen are selected from the evaluation run and the properties are compared with the specifications established by the purchaser or qualifying organisations. If the manufacturing and sales departments are interested in the handling of roofing bitumens and wide range of speciality product, the evaluation becomes quite involved and expensive. For full scale evaluation, it may be necessary to start with one or two barrels of crude oil in order to that adequate residua of different viscosities may be obtained for use as blending and air blowing stocks. It is therefore, evident that the complete evaluation of crude oil as a suitable source for a wide variety of asphaltic material is a tedious and expensive procedure. It also require skill and experience for proper interpretation of the results obtained. Even, after a favourable evaluation is completed, an experimental plant run is sometimes advisable since difficulties not apparent in the small scale laboratory or pilot plant operations may appear in commercial manufacture.

**Bitumen manufacturing practices**

*Bitumen from vacuum distillation*—Various types of equipments have been used to fractionate asphaltic-base petroleums, but the vertical still is universally used today. The modern unit is a precise tool made up of integrated units plus their auxiliary service facilities. The crude oil is pumped, preferably after desalting (to control bituminous electrical properties and water absorbing tendency), through a furnace in which the oil is heated to about 315°C (600°F) and then injected into the atmospheric section of the still to flash off the lower boiling point products. The heavy oil at the bottom of the atmospheric tower goes to the vacuum section of the still, at a temperature of about 357-400°C (675-750°F), where a vacuum of 10 to 150 mm of mercury is maintained, depending on the type of crude being processed. Low pressure makes it possible to vapourize the heavier oils without over heating the residuum. The consistency of the asphaltic residuum at the bottom of the vacuum tower depends upon (a) the nature of the oil (b) rate at which it enters the distillation unit, (c) temperature at which it enters and progresses through the still, (d) pressure in the vacuum section, and (e) rate at which the residuum leaves the unit. Gagle has supplied a succinct review of the design and operation of an asphalt/bitumen plant. He gave flow sketches for atmospheric and vacuum distillation, high vacuum distillation, and propane deasphalting units. A modernized bitumen plant was described by Pruess.

*Air blowing operation (non-catalytic blowing)*—Some heavy crudes give vacuum residues which can be used directly in the manufacture of paving bitumen. In many refinery situations, however, this
is not an acceptable route as the use of such crudes could have an adverse effect on mainline refinery products. For instance, many of these crudes are waxy, or have high sulphur contents, or do not yield the required amounts of main refinery products using the existing refinery process plants. Other crudes, which are better suited for the production of main refinery products, give vacuum residues which are unsuitable for direct use in bitumen manufacture. For example, the viscosity of the vacuum residue could be too low for bitumen production. Air blowing of such feed stocks enables acceptable bitumens to be made from these crudes provided that care is taken to select the correct residue length (cut point). In some cases it is also possible to include surplus refinery components (fluxes) in the feed stock intended for air blowing as this can provide a valuable method of disposing off such stocks. Industrial grade bitumen, which have high softening points, can also be made using the bitumen blowing process. By selecting the appropriate feed stock for blowing it is possible to prepare a wide variety of industrial grade bitumens, with differing penetration values for a given softening point, to meet specific industrial uses.106

References to early experimental work on oxidation (air blowing) of asphaltic oils are well documented by Abraham.107 The continuous type of converter come into use during mid 30's.108 It usually comprises a series of two or more vertical vessels. Hot residuum enters and finished bitumen leaves the system at the same rate. The rate of flow regulates the time of contact between the air and hot oil. Longer type of contact and an increased air flow rate yields a bitumen possessing higher consistency. Continuous converters are flexible and economical in operation and require a minimum of time to reduce a ton of residuum to bitumen of the desired consistency. Mechanical agitation of liquid air mixture reduces the time required to air blow a bitumen to a particular consistency. Laboratory studies on mechanical mixing were reported by Rescorla et al.109 Pilot plant experiments have been conducted by others, and it appears that a high power input per barrel of bitumen is required to increase materially the rate of oxidation110. The air blowing is exothermic in nature. The amount of heat liberated varies with the chemical nature source of the stock, extent of the oxidation, and temperature at which the oxidation is conducted. Cramer111 proposed injecting water into the vapour space above the bitumen to control the temperature. The effects of temperature, air rate, pressure, and liquid level in the converter on the rate of reaction and properties of the air blown bitumens were determined in pilot plant studies by Chelton, Traxler and Romberg.112

A typical flow diagram of a conventional bitumen manufacturing process involving air blowing step is shown in Fig. 1. In the bitumen blowing process aromatic compounds present in the feed stock are oxidised with air under controlled conditions to produce hydrocarbons of higher molecular weight (of which those soluble in toluene and insoluble in n-heptane are called asphaltenes), with the simultaneous formation of water vapour. The main effect of this reaction is that it increases the viscosity of the blown product. For a given viscosity increase, however, the asphaltene content increases much more rapidly during air blowing than would be the case if the feed stock were vacuum distilled, hence the air blown product has different rheological properties. An air blown product is characterised by having a higher softening point than a bitumen of similar penetration value obtained from the same crude source by vacuum reduction. The air blowing thus correct the deficiency of certain crudes which have low asphaltene contents and can produce paving bitumens suitable for use on the road and or in industrial applications.

Lockwood113 and Patwardhan114 have published studies on kinetics of air blowing. They concluded that a first-order kinetic analysis describes the air blowing reaction except at high temperatures and low air rate. They mentioned that such an analysis "gives a middle-of-the-road basis for pilot plant design and control of operations". Many patents have been taken dealing with the oxidation kinetics of bitumens.

Catalytic air blowing—The aim of air blowing process is to generate asphaltenes. This phenomena is characterized by three basic reactions namely: reactions leading to the size increase of the molecules through the process of oxygen linkage,
formation of cyclic hydrocarbons by means of dehydrogenation and reactions during which the size of the molecules decrease due to dealkylation of side chains. The net effect of all the above reactions is change in colloid-chemical constitution and rheological properties of the bitumen. In early 50’s attempts were reported involving addition of external agents (catalysts) in air blowing step of bitumen making. This was done with a view to accelerate the blowing reactions (reduction in time cycle), produce bitumen of greater flexibility at low service temperature and to increase resistance to flow at high temperatures. Chlorine has also been investigated as an agent for the dehydrogenation and hardening of bitumen, but the process has not been used commercially. Bencowitz and Boe developed a procedure for incorporating finely powdered sulphur into bitumen without the generation of much hydrogen sulphide. Properties of the resulting mixtures were studied.

Catalytic air blowing process of bitumens most widely used today is the one patented and described by Hoiberg. P₂O₅ and FeCl₃ were tried as catalysts for accelerating the rate of oxidation. Later, Shearon and Hoiberg described in detail the use of P₂O₅ as a modifier in the air blowing process. Illman and Sommer patented the use of mono-, di-, or hexafluoro phosphoric acid as an aid in producing air blown bitumens possessing higher penetration indices. Fink et al. proposed heating of 80-98 parts asphaltic residuum with 2-20 parts petrolatum followed by air blowing in the presence of 0.2 to 2.0% by weight ferric chloride.

Modern Methods of Making Paving Bitumens
The conventional “blowing operation” however, has certain limitations with respect to efficient oxygen utilization, temperature control management, likely coking, leading to process interruption and processing of wide variety of current refinery feed stocks to yield quality bitumens. All this has resulted in the development of new generation processes with specified internals in reactor/convertor and catalytic route to make quality paving and industrial grade bitumens. The two most notable developments of the immediate past are the Biturox Process: Compositionally controlled chemical processing of bitumen making by PORNER and premium asphalt making process of Petro Canada.

The reactor is key component of Biturox process as it provides the reaction control to achieve the
chemically modified. The process is economical and represents a significant advance over simply increasing penetration index by processes which employ air rectification of short residues or fluxed feed stocks. Table 2 reports comparison of performance properties of conventional bitumen with that of multigrade product - Mobil bitumen.

The catalyst based production technology of Petro Canada for making premium asphalt is still a closely guarded secret. Basically it involves the following steps:

- Premium asphalt is produced by blending.
- A catalytic polymerization/air oxidation process is used.
- Hydrocarbon emissions are controlled by incineration.

The blended premium asphalt product is produced from a hard and soft asphalts, usually originating from the same crude source. The hard asphalt is produced in a catalytic asphalt modifier and is blended to specification grade product utilizing the soft asphalt as the cutter stock. The blending step is accomplished using a programmable in line blender yielding product to a shipping tank or routed directly to the loading rack (truck, rail, etc.). The premium asphalt technology has the potential to upgrade the residue derived from marginal crudes to the point where minimum asphalt specifications can often be met. This value-added potential has attracted keen attention from refiners looking for enhanced profitability from residuum. Table 3 reports comparison of performance properties of conventional bitumen with that of premium asphalt.

With the discovery of Bombay High crude in 1976 and earlier availability of Assam crude mix for the processing in Indian refineries, there has always been an attempt to establish the feasibility of using the crude for making asphalt. However, the technology has not been commercialized due to various reasons. The present paper discusses the feasibility of using these crudes for making asphalt.

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### Table 2 — Mobil Australia - Compositionally Controlled (Multigrade) Bitumen

<table>
<thead>
<tr>
<th>Properties</th>
<th>C170 MA*</th>
<th>80/100 CA**</th>
<th>C320 MA</th>
<th>50/70 CA</th>
<th>C600 MA</th>
<th>35/45 CA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (Pa s) at 60°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEN, 15°C (0.1 mm) 200 g, 60 s</td>
<td>170</td>
<td>160</td>
<td>334</td>
<td>297</td>
<td>635</td>
<td>520</td>
</tr>
<tr>
<td>Penetration Index</td>
<td>-0.7</td>
<td>-1.4</td>
<td>-0.5</td>
<td>-1.2</td>
<td>+0.2</td>
<td>-0.6</td>
</tr>
<tr>
<td>Durability (days)</td>
<td>13.1</td>
<td>9.0</td>
<td>8.5</td>
<td>8.0</td>
<td>6.7</td>
<td>4.0</td>
</tr>
<tr>
<td>RTFOT, % change in viscosity</td>
<td>200</td>
<td>250</td>
<td>195</td>
<td>250</td>
<td>255</td>
<td>283</td>
</tr>
<tr>
<td>Ductility, residue 15°C (mm)</td>
<td>&gt;700</td>
<td>600</td>
<td>450</td>
<td>-</td>
<td>300</td>
<td>-</td>
</tr>
</tbody>
</table>

* MA: Multigrade Asphalt  ** CA: Conventional Asphalt

### Table 3 — Petro Canada - Premium Asphalt (Comparison of Properties)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Conventional</th>
<th>Premium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutting Resistance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vis. at 60°C, Poise</td>
<td>1453</td>
<td>3092</td>
</tr>
<tr>
<td>TFOT, Vis. at 60°C, Poise</td>
<td>2999</td>
<td>13124</td>
</tr>
<tr>
<td>Low Temp. Flexibility</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEN 4°C, 200 g, 60 S</td>
<td>27</td>
<td>38</td>
</tr>
<tr>
<td>TFOT PEN 4°C, 200g, 60 S</td>
<td>20</td>
<td>29</td>
</tr>
<tr>
<td>Temperature Susceptibility</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TFOT PVN</td>
<td>-0.5</td>
<td>+0.5</td>
</tr>
<tr>
<td>TFOT PI</td>
<td>-0.9</td>
<td>+0.5</td>
</tr>
</tbody>
</table>

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of using these crudes in bitumen making in locations like AOD (IOC) refinery at Digboi and other coastal refineries receiving BH crude. The R&D efforts in this direction met with limited success due to techno-economic reasons, that required to eliminate or reduce waxes in feed stock and upgrade the asphaltene constituents. This situation still needs more R&D efforts to find a suitable solution. Similar examples also exist in USA as well, where procedures based on solvent deasphalting were found to overcome such problems. The most recent advance reported in this effort is the development of Paratox Process for making bitumen from waxy crude.

**High Performance Bitumens**

With the continuing increase in traffic, both in terms of vehicle numbers, axle weight (upto 22 tonnes in the case of heavy goods vehicles) and tyre pressures, there is a growing concern within the road industry regarding resistance to rutting (permanent deformation or mechanical stability) of asphalt mixes and the consequential cost of building and maintaining the road system. Due to visco-elastic behaviour of bitumen in asphalt mixes permanent deformation (Fig. 2) develops typically under heavy axle load and at high pavement service temperatures. In short the above features calls for pavement to be constructed with high stability of asphalt mixes in order to prevent excessive rutting. With the standard and convention materials the mix design options are limited: An increase of mechanical stability may lead to a trade off between the low temperature mix properties (resistance to cracking and fretting) or the mix durability (resistance to aging). For conventional asphalt mixes in most cases, an optimum choice has been made in terms of, for example, bitumen hardness and bitumen content, giving an adequate balance between pavement rutting and pavement cracking under normal loading conditions. With the move towards more closely specified performance from bituminous binders, conventional paving grade bitumen may be upgraded using bitumens obtained from modified/improved processes.

As stated earlier bitumen is a complex mixture of chemical compounds (hydrocarbons) in a complex equilibria, hence the proportion of each chemical species is critical to performance. This is shown in Fig. 3. Performance of bitumens (both paving and industrial) is related to their chemical composition. This in turn is determined by the crude source used and the processing scheme used. Mobil, Shell, Petro-Canada and other US companies have developed processes by which the chemical composition and rheology of bitumen may be controlled leading to development of high performance bitumen commonly designated as multigrade/premium asphalt/super pave products. The controlled chemical balance also ensure that properties such as durability and adhesion are optimized as well.

Basically the high performance bitumens are based on Penetration Index (PI), i.e., the higher the PI, lower is the dependence of rheology on temperature. These materials have therefore characteristics of a softer grade at low temperature and of harder grade at high temperature. They have a higher penetration at lower temperature and a higher viscosity at higher temperature than those of conventional bitumens.

Multigrade/premium and super pave bitumens are all proprietary engineered oil-based bitumen which exhibits superior rutting and low temperature cracking resistance, temperature susceptibility and fatigue resistance as compared to
conventional bitumen. All the products are 100% recyclable and no special handling and mixing operations are required for during pavement laydown, compared to conventional bitumen. Multigrade bitumens are produced by a technique of physical and chemical modification that alters the chemistry and balance of the bituminous components to a desired optimum. The process creates those components which have right chemical balance leading to acceptable road performance, from those available in the feed stocks being processed. Premium bitumen process technology involves the catalytic polymerization of straight run bitumen using liquid catalysts supplemented by air-blowing and special in-line blending techniques.

Polymer modified materials—The literature is full with suggestion for using small amount of non-petroleum compounds for improving the properties of bitumens. Materials to increase the adhesion of bitumen to solid surfaces (stone and aggregates) have received greatest attention. Next often mentioned are additives for improving rheological properties and, especially low temperature characteristics. Finally, a number of materials have been proposed for adjusting the colloidal characteristics in order to reduce syneresis and incompatibility.

Lewis and Welborn investigated the use of different kinds of powdered rubber (natural and synthetic) in different kinds of bitumen. They concluded that the properties of the blend depend on the kind and quality of rubber used, the nature of bitumen, and the manner in which the blend is processed. Addition of rubber was found to increase the viscosity and decrease temperature susceptibility and tendency to flow. Gregg and Alcoke studied the effect of rubber in road building bitumens. A flexure-fatigue test was used to evaluate the merits of the various blends. The influence of rubber on the brittleness and viscosity of bituminous material was studied by Mason et al. The blends were subjected to an imposed tensile strain at -17.8°C; stress and strain were measured throughout the test. The deformation characteristics of the bitumens, blends, and mixtures with sand were measured in a concrete cylinder viscometer.

Attempts at improvement of bitumens through blending with small amount of polymers particularly rubbers, have been the subject matter of attention and imagination of great many workers in both the bitumens and rubber/polymer fields. The main objective has been to obtain bituminous binder of improved service performance level (capable of meeting the developing needs). Beyond those when manufactured according to conventional processing step, i.e., vacuum distillation, air blowing or solvent deasphalting. Bahl et al. reviewed the bitumen properties modification using organic polymers. They concluded that addition of certain organic polymers to bitumen in small concentration improve their performance, enhances service life and ability to withstand extreme climatic conditions.

Naugautuck Chemical, a division of United States Rubber Company, is marketing a blend of rubber and bitumen under the trade name “Surfa-Sealz”. They have made extensive investigations of the rheological properties of the blends. They concluded from their field evaluations that the mixture prevent rutting and shoving, and stripping from the aggregate by water, and give increased resistance to skidding. The presence of the polymer in the bitumen also increases the elasticity of the pavement, reduces temperature susceptibility and decreases the rate of age hardening. Aromatic oils, resins, and pitches have been proposed as additive for improving the physical and rheological properties of bitumens. Usually several per cent of such materials are required to effect a useful change in colloidal properties of the bitumen.

Recent studies—characterisation of bitumens—Whiting et al. employed use of elemental and functional group analysis for monitoring compositional changes occurring on air blowing of a natural asphalts. The heteroatom content, degree of unsaturation and functional group composition were found to be related to asphalt durability. Subramanian et al. studied compositional studies of bitumen and bitumen derived product by gas chromatography. Borrego et al. reported NMR and FTIR spectroscopic studies of bitumen and shale oil from selected Spanish oil shales. Results related to composition
of bitumen and shale oil suggest that with increase in maturity the similarity of bitumens and Shale oils increase. Mojelsky et al.\textsuperscript{153} reported structural features of Alberta oil sand bitumen and heavy oil asphaltenes. Rafenomanantsoa et al.\textsuperscript{154} reported structural analysis by NMR and FIMS of the tar-sand of Bemolanga. Huang \textit{et al.}\textsuperscript{155} reported photo-oxidation of corbett fractions of asphalt by FTIR spectroscopy. Bukka \textit{et al.}\textsuperscript{156,157} reported the influence of carboxylic acid content on bitumen viscosity by FTIR characterization, fractionation and characterization of Utah tar-sand bitumens by NMR and IR spectroscopy. The results suggest that a discrete group of compounds present in polar fraction of bitumen may have a significant influence on viscosity and may be of equal, if not greater importance than the asphaltene content itself. Quddus \textit{et al.}\textsuperscript{158} studied the chemical composition of catalytic air blown asphalts. They reported chemical changes during air blowing of asphalts, in the presence of transition metal salt by adsorption-desorption chromatography. They proposed general transformation mechanism. Recently Huang and Bertholf\textsuperscript{159} studied the molecular weight distribution of bitumen fractions obtained by corbett method using Gel permeation chromatography. Laurent \textit{et al.}\textsuperscript{160} studied qualitative and quantitative functional determination in bitumen acidic fractions by $^{29}$Si NMR spectroscopy.

Conclusions

Based on the review presented current state of technology of feed stocks for making quality bitumen, process technology involved and relationship between compositional parameters and performance properties can be summarized as follows:

1. Bitumen making which was considered to be a "Black Art" till early 70's has now attained the status of an important refining process converting variety of feed stocks to quality paving and industrial grade bitumens.

2. Advances in 'separation science' and 'instrumental' techniques have enabled improved understanding of chemical/structural parameters of bitumen feed stocks, products, and their inter-relationship with performance properties.

3. Although majority of quality paving bitumen continues to be made from bitumen bearing curdes but slowly non-bitumen bearing curdes (having high wax and low in asphaltenes) are also being increasingly accepted as feed stock for bitumen making through new technological schemes and processes.

4. There has been deep understanding of science and chemical engineering principles involved in the air blowing process of bitumen making. This has led to the development of: (a) New generation reactor internals enabling more efficient utilization of oxygen and reduction in time duration and (b) Reaction kinetics involved in air blowing operation thus linking the feed stock/fluxing component compositions with operating parameters to obtain an acceptable balance of hydrocarbon type combinations, leading to required performance features.

The studies reported in the subsequent chapters makes an attempt to confirm some of the reported findings and presents new correlations for making use of non-bearing bitumen curdes as feed stock for paving bitumens and equations relating compositional parameter with performance properties.

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