

BITUMEN: CHEMICAL COMPOSITION AND RHEOLOGICAL BEHAVIOR

A thesis submitted towards the
partial fulfillment of the BS-MS Dual Degree Programme

by

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PUNE

Certificate

This is to certify that this dissertation entitled "Bitumen: Chemical Composition and Rheological Behavior" towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune, represents original research carried out by "Sandeep Gupta at Shell India Markets Private Limited", Bangalore, under the supervision of "Dr. B. Koenders, Portfolio Manager bitumen, Shell India Markets Private Limited", Bangalore and Dr. A. A. Natu, Visiting Faculty, IISER Pune, during the academic year 2011-2012.

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Declaration

I hereby declare that the matter embodied in the report entitled “Bitumen: Chemical Composition and Rheological Behavior” are the results of the investigations carried out by me at the Bitumen Department, Shell India Markets Private Limited, under the supervision of Dr. B. Koenders and Dr. A. A. Natsu, visiting faculty, Indian Institute of Science Education and Research and the same has not been submitted elsewhere for any other degree.

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Date:

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Abstract

Modern techniques are being employed to carry out testing and characterizing bitumen. Attempts have been made to correlate the conventional physical tests (penetration test, softening point test) to modern techniques in order to reduce the amount of time taken to characterize samples. Here, we have studied the relation of Dynamic Shear Rheometry and Near Infra Red Spectroscopy with the conventional tests such as penetration test, softening point test, viscosity test. In order to study how chemical composition affects the properties of the bitumen, 28 bitumen samples from various crudes and different methods of processing were selected

Good correlations for penetration and softening point values with the complex modulus as determined with the Dynamic Shear Rheometer were obtained with standard deviations close to the precision limits for the respective tests. It was also found that Near Infra Red Spectroscopy can be correlated with the conventional tests and that it has the ability to distinguish between fresh and the aged samples. SARA fractions and their ratios do not show a clear relation to the physical properties when considering all the samples, but show a trend when considering similar samples suggesting that properties are highly origin and processing dependent. These results can help in quicker screening of samples; for example, characterizing a bitumen sample takes one day but using these correlations we can potentially reduce the time to fifteen minutes.

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Introduction

Bitumen is defined as a mixture of hydrocarbons derived from petroleum naturally or by distillation [1]. It is a complex hydrocarbon material which contains components of many forms, most of them have high molecular weights, some of them are polycyclic aromatic compounds (PAC), which consists of a number of benzene rings fused together (3-7 rings). Elemental analysis of bitumen shows that most bitumens contain Carbon 82-88 %, Hydrogen 8-11 % and Sulphur 0-6 %. Other than that it also contains trace amounts of metals such as nickel, vanadium, iron magnesium and calcium which can occur in the form of organic salts, oxides or in porphyrine rings [2].

Bitumen has many uses [1]:

In agriculture- damp proofing and water proofing structures, disinfectants, tree paints.

Buildings- floors, roofing, acoustical blocks, cement water proofing compounds.

Hydraulics and erosion control – canal linings, sealants, dam linings, water barriers.

Industrial- insulating boards, friction elements, brake linings, paint compositions.

Paving- airport runways, taxiways, asphalt blocks, driveways, and drainage ditches.

Railways- ballast treatment, curve lubricant, rail fillers, sleeper impregnating.

Recreation- dance pavilions, gymnasiums, race tracks, skating rings.

The chemical composition of bitumen cannot be defined accurately, because it is a complex mixture of many different aliphatic, aromatic, polynuclear aromatic hydrocarbons. Usually, they are categorized into four groups depending on the solubility in selected solvents: Saturates, Aromatics, Resins and Asphaltenes (SARA) [1].

Saturates: They constitute 5-15 wt % of total bitumen, colorless or light color liquid at room temperature, H/C ratio is close to 2, with traces of hetero atoms [4]. They contain a few crystalline linear n-alkanes [5, 6]. Their number-average molecular weight is around 600 g/mol with very few polar atoms or rings present [2].

Aromatics: They constitute 40-60 wt % of total bitumen [4], form a yellow to red liquid at room temperature [5, 6]. They are somewhat more viscous than the saturates at the same temperature, because of a higher glass transition temperature around $-20\text{ }^{\circ}\text{C}$ [7, 30]. The structure has some linear chains with condensed rings having number average molecular weight in range of 300-1000 g/mol [2].

Resins: They constitute 30-45 wt % of total bitumen [4]. They are dark brown solids or semisolids which are polar in nature and are strongly adhesive [5, 6]. Its number average molecular weight ranges from 500-1500 g/mol [8, 9, 10]. In the colloidal model they are the stabilizing agents for the asphaltenes in bitumen.

Asphaltenes: These are the n-heptane insoluble black or brown compounds [4]. They contain some hetero atoms like nitrogen sulphur and oxygen [9]. Asphaltenes are generally considered to be highly polar complex aromatic materials of rather high molecular weight [9, 10, 12]. Different methods of determining molecular weight have led to different values ranging widely from 600 to 3500 [2] depending on the separation techniques employed, particle size of 5 to 30 nm [11], and hydrogen to carbon ratio of about 1.1 [12, 13]. With increasing asphaltenes content, bitumen becomes harder, more viscous, with low penetration, a high softening point and high viscosity. They constitute 5 to 25 % of total bitumen [16, 17].

Bitumen structure

The most well-known theory to describe bitumen is the colloidal model: a colloidal which consists of asphaltenes micelles dissolved in an oily medium (maltenes) [13, 14]. Resins are supposed to be stabilizing, solvating the micelles. The colloidal behavior of asphaltenes in bitumen results from aggregation [15, 17, 21]. Asphaltenes form micelles which are stabilized by resins dispersed in the saturates and aromatics medium [19]. There is a polarity gradient from the centre of micelles to less polar aromatic resins. If the aromatics/resins fraction is not present in sufficient quantities, then the asphaltenes will aggregate leading to a regular open packed structures of linked micelles forming voids filled with inter micellar fluid of mixed constitution [22]. The viscosity of saturates, aromatics, resins and asphaltenes depend upon their molecular weight distribution [27].

It is almost impossible to separate and identify all the different molecules of bitumen, because the number of molecules with different chemical structure is very high and the composition of the bitumen will vary depending upon the crude source and the processing conditions. It is a complex mixture of molecules with different molar mass and polarity with an arrangement in an organized micellar system whose structure is built on rather weak bonds and depends on the chemical-physical interactions between all the constituents [27, 28]. The rheological behavior, which directly reflects changes in internal structure, therefore strongly depends on temperature and imposed strain or stress applied to the material [2].

It is important to characterize and understand the compositional and micro structural changes. Typically, rheology test methods have been used to characterize bitumen. Various crudes and different refinery processes lead to different amounts and types of molecules in the SARA fractions [32]. From literature we know that the stability and microstructure of the bitumen is related to the blend of molecules with different solubility levels. There are quite a large number of tests and evaluations to be carried out to determine the effect of blending various streams or study the evolution over time.

Such characterizations and evaluations are time-consuming, laborious in terms of manpower effort in sample preparation and require large sample size for all the different tests. Besides, this cannot be done in real-time and will require multiple samples, leading to more variables in the evaluations.

2. Objective

Evaluating bitumen samples from different crudes and different processing routes in combination with rheological and compositional information requires a large effort. A quicker approach is of considerable interest in order to reduce this effort and cost. An approach is desired that offers the potential of establishing possible changes in composition in relation with the rheological behavior (stiffness, elasticity) at reduced amount of material required and effort compared to the conventional, separate and time consuming tests.

As an example of the testing efforts and time required for typical conventional tests is as follows:

- I. 2 hours to prepare the bitumen sample, pour samples into penetration cups, softening point rings, RTFOT bottles and viscometer tubes (left for conditioning).
- II. Conditioning time: 90 minutes for penetration, 45 minutes for softening point, 85 minutes for RTFOT and same amount will be required to condition penetration and softening point samples from RTFOT residues.
- III. In total about 1 day of work for one sample, requires attention of one person.

To have a higher throughput for testing, several tests can be carried out in parallel, requiring good organization skills of the experimenter.

The aim is to come up with correlations between conventional tests (penetration test, softening point test) and advanced techniques like Dynamic Shear Rheometry and Near Infra Red spectroscopy. This would enable us to:

- I. Use smaller sample sizes.
- II. Reduce the amount of waste.
- III. Quicker screening of samples.
- IV. Quicker determination of properties.

As an example, the smaller sample sizes will help in determining the changes in the properties with depth in the asphalt pavement layer using a limited number of cores from the road.

This work will provide the opportunity of using single equipment with the ability of carrying out several tests without destroying the internal equilibrium of the sample. Interpretation of the data will also lead to more information and useful correlations. This could then lead to quicker screening to understand the properties than the classical approach. This can then be used, subsequently, to propose modifications to influence the properties.

3. Experimentation

3.1 Materials

A set of 28 samples (EE1-EE28) was used. They were from various crudes, different processing types, ranging from very soft to very hard. The idea was to cover a large range of bitumens. These samples were aged and the same set of experiments was carried out with the aged samples. 30 % of the samples (both fresh and aged) were repeated to determine the repeatability.

3.2 Testing Methods

3.2.1 Penetration Test (ASTM D5)

This test consists in measuring the depth (expressed in tenth of millimeters) at which a standard needle penetrates after 5 s loading time and with a 100 g load usually at 25 °C. Under these conditions, typical values for paving grade bitumen range between 15 and 200 dmm [30]. For a penetration less than 30 dmm, the bitumen is said to be hard [30]. Penetration values higher than 100 dmm correspond to soft bitumens. Figure 3.2.1 a shows the dimensions of a standard needle and figure 3.2.1 b shows the Petrotest penetrometer.

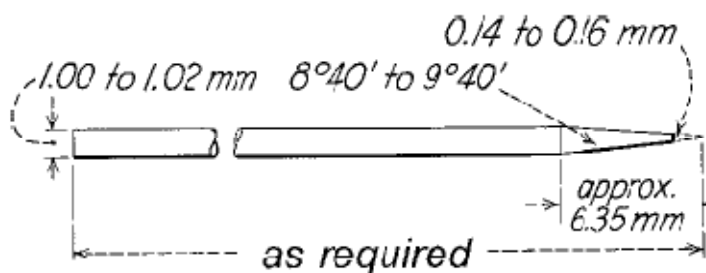


Figure 3.2.1 a: dimensions of a standard needle and Figure 3.2.1.b: Petrotest PNR-12 Penetrometer

The precision is given in table below:

Penetration, dmm	0-49	50-149	150-249	250 above
Maximum Difference between highest and lowest penetration (dmm)	2	4	12	20

3.2.2 Softening Point Test (ASTM D36)

Another consistency test is the Ring & Ball test to determine softening point temperature ($T_{R\&B}$). The experimental set-up consists in preparing an 8mm thick bitumen film inside a metal ring (average diameter close to 16 mm). The sample of bitumen poured in the ring is then put inside a water bath at an initial temperature of 5 °C and a normalized 3.5 g steel ball (9.5 mm diameter) is placed onto the bitumen film. The heating rate is 5 °C/min. The softening temperature is defined as the temperature at which the steel ball deforms the bitumen film to such an extent that it contacts the bottom of the vessel 25 mm below. Under these conditions, typical values for paving grade bitumen range between 35 and 65 °C. Figure 3.2.2 a shows the apparatus used and figure 3.2.2 b shows the details of the experiment. A hard bitumen has a softening temperature close to 60 °C while a softer grade will typically have a softening temperature around 40 °C. Multi-laboratory precision-results of two properly conducted tests on the same sample of bitumen from two laboratories should not differ by more than 2.0 °C.



Figure 3.2.2 b: Infracast 20-2200 Ring and Ball apparatus

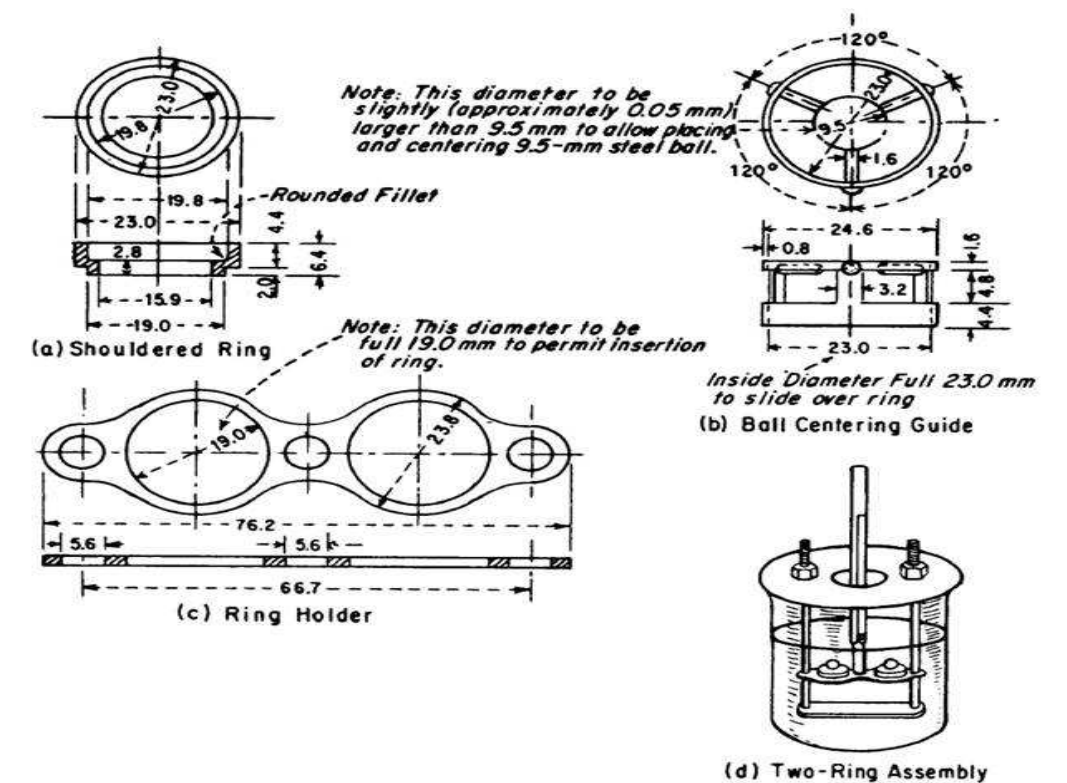


Figure 3.2.2 b: Ring and ball instrumentation and dimensions

3.2.3 Ductility Test (ASTM D113)

This test method describes the procedure for determining the ductility of a bituminous material measured by the distance to which it will elongate before breaking when two ends of a briquette specimen of the material, of the form shown in figure 3.2.3, are pulled apart at a specified speed and at a specified temperature [39]. For this test, the temperature used was 10 °C and the speed was 5 cm/min [39]. This test method provides one measure of tensile properties of bituminous materials and is used to measure ductility for specification requirements [39].

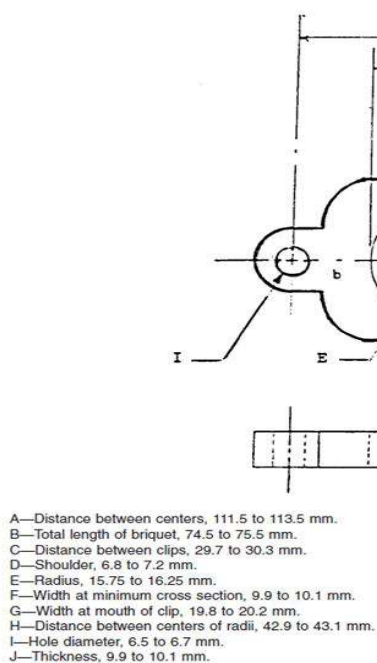


Figure 3.2.3: dimension of mould for ductility



Figure 3.2.3 a: Ductility experiment.

3.2.4 Viscosity Test (ASTM D 4402)

A Brookfield rotational viscometer is used to measure the dynamic viscosity of bitumen at elevated temperatures. The torque on the apparatus-measuring geometry, rotating in a thermostatically controlled sample holder containing a sample of bitumen, is used to measure the relative resistance to rotation [38]. The viscosity of the bitumen is determined by the torque and speed and the unit is in Pascal seconds, millipascal seconds, or centipoises [38]. This test method is used to measure the dynamic viscosity of bitumen at handling, mixing or application temperatures [38]. Repeatability (expressed as a percent of their mean) - the difference should not exceed 3.5 % and reproducibility (expressed as a percent of their mean) - results should not differ by more than 14.5 %. Figure 3.2.4 shows the instrument used [38].



Figure 3.2.4: Brookfield RVDV-11+P Rotational Viscometer

3.2.5 Rolling Thin-Film Oven Test (RTFOT) (ASTM D2872)

This test method is intended to measure the effect of heat and air on a moving film of semi-solid bituminous materials. The effects of this treatment are determined from measurements of the selected properties of the bitumen before and after the test [40]. This test method indicates approximate change in properties of bitumen during conventional hot-mixing in the asphalt plant at about (150 °C) as indicated by viscosity and other rheological parameters [40]. The yielded residue gives information about the

bitumen condition as incorporated in the pavement [40]. The test method also can be used to determine mass changes, which is a measure of bitumen volatility [40]. Figure 3.2.5 a shows the instrument used and figure 3.2.5 b shows the schematics of the instrument.



Figure 3.2.5 a: Koehler K88001P RTFOT instrument

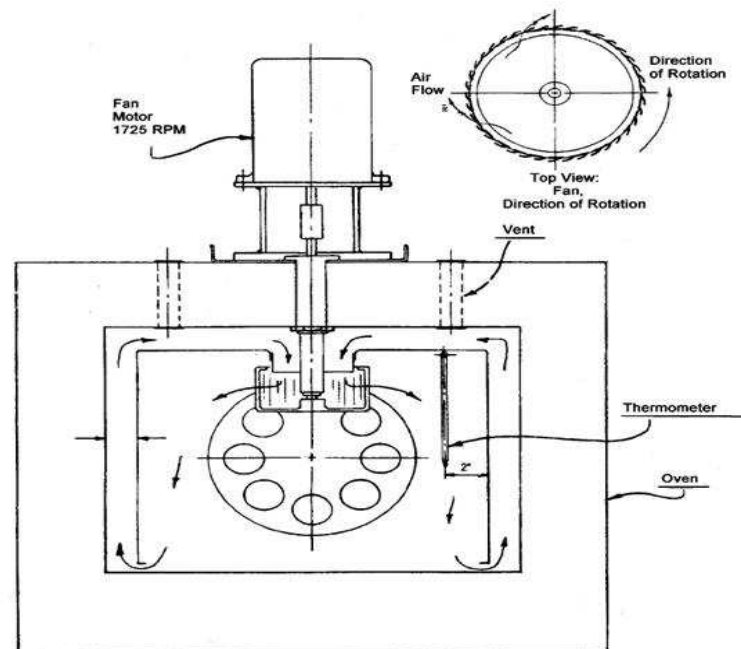


Figure 3.2.5 b: schematics for RTFOT

3.2.6 Dynamic Shear Rheometry (DSR)

3.2.6.1 Complex Modulus Test

Theory: The Storage Modulus (G') value in Pa is a measure of deformation energy stored in a sample during the shear process in the rheometer. Once the load is removed, this energy acts as a driving force for the reformation which partially or completely compensates the previous deformation [33]. Energy storing materials display reversible deformation behavior if they remain in an unchanged form after the load cycle, thus, G' represents the elastic behavior of the sample [33].

The Loss Modulus (G'') value (Pa) is the measure of the deformation energy used up in the sample during the shear process. This energy is either depleted during the process of changing the sample's structure or dissipated into the encompassing surroundings in form of heat [33]. Energy losing materials display irreversible deformation behavior if they occur in a changed form after the load cycle. Thus G'' represent the viscous behavior of a sample [33].

The viscoelastic behavior of every real material consists of a viscous and an elastic portion. The sum can be illustrated using a vector diagram (figure 3.2.6.1). G' is plotted on X-axis and G'' on Y-axis [33]. The length of each vector represents the value of the corresponding parameters. The Complex Modulus (G^*) is the vector sum of both the components G' and G'' [33]. G^* therefore represents the complete viscoelastic behavior which consist of both viscous and elastic parameters [33]. $|G^*| = \sqrt{(G')^2 + (G'')^2}$ [33].

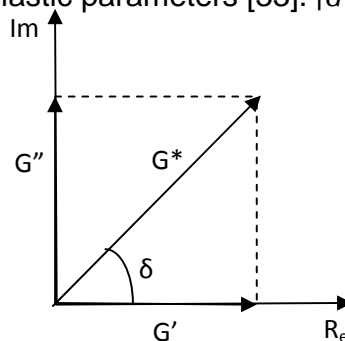


Figure 3.2.6.1: vector diagram with G' , G'' and the resulting vector G^*

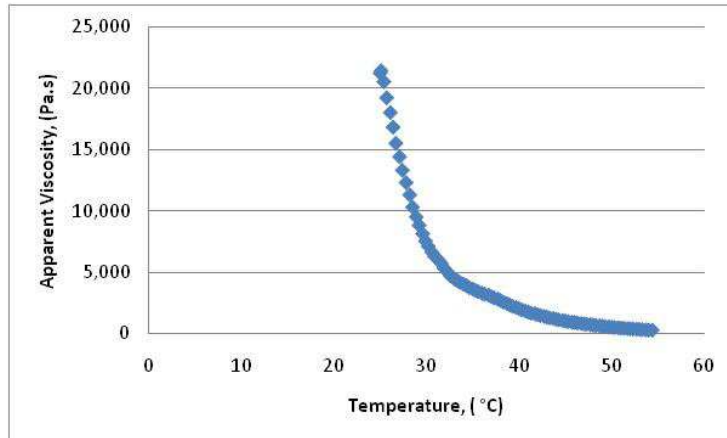
The complex shear modulus is an indicator of the stiffness or resistance of bitumen to deformation under load. This test method covers the determination of the dynamic shear modulus and phase angle of asphalt binders (bitumen) when tested in dynamic (oscillatory) shear using parallel plate geometry. The procedure involves determining the complex shear modulus and phase angle of the binders using a range of frequency tests and temperature tests which are carried out in oscillatory shear mode. Figure 3.2.6.2 shows the oscillation mode of parallel plate rheometer.



Figure 3.2.6.2: oscillation mode in DSR

The bottom plate is fixed and the top plate rotates in two directions in a sinusoidal movement. From this test the norm of the complex shear modulus (G^*) and its phase angle delta (δ) at given temperature and frequency can be measured. The measuring profile was oscillation mode with 20 measuring points, 1 % strain, 0.4 Hz frequency, temperature 25 °C.

3.2.6.2 Temperature Sweep: This test gives viscosity as a function of temperature, i.e. viscosities values at every temperature. The measuring profile was rotation mode with 120 measuring points, heating rate 5 °C per min, shear rate 0.4 Hz, temperature range 25 °C – 100 °C. A typical viscosity temperature graph is shown in figure 3.2.6.3.



3.2.6.3: Apparent Viscosity versus Temperature

3.2.7 SARA Analysis

The method used was an in house method based on ASTM D4124. The basis of the method is to initially precipitate asphaltenes by using n-heptane followed by chromatographic separation of the remaining material (called maltenes). First asphaltenes are separated from maltenes by precipitation of the product in a standard hot heptane and filtering under vacuum to determine the asphaltenes content. In a second step maltenes are separated into three distinct fractions (saturates, aromatics and resins) by elution with different solvents on two distinct HPLC columns.

3.2.8 Near Infra Red Spectroscopy (NIR)

The spectral range of NIR is $\lambda = 780 - 2500 \text{ nm}$ ($12500 - 4000 \text{ cm}^{-1}$). It detects combination and overtones of CH-, OH-, and NH- vibrations. In contrast to sharp absorption peaks in the Mid Infrared region, Near Infrared spectra show less intense and broad bands. Figure 3.2.8 shows a typical NIR spectrum.

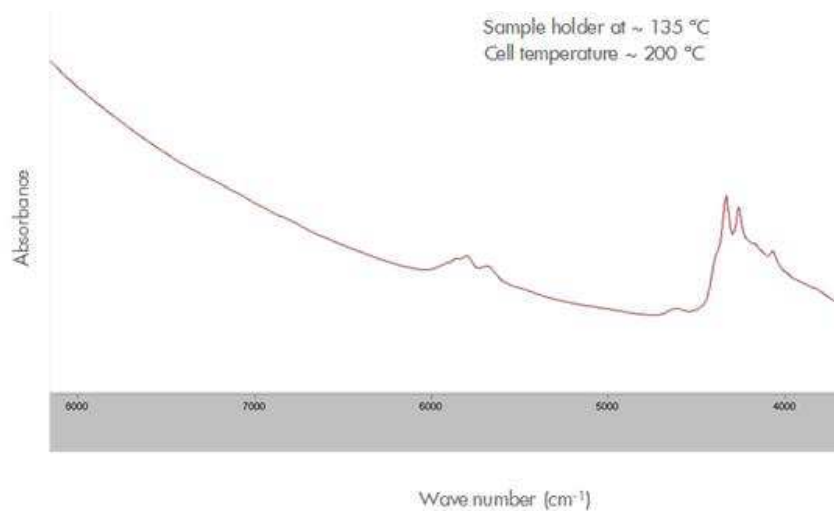


Figure 3.2.8: typical NIR spectrum of bitumen

3.2.8.1 Characteristics

- It is not possible to assign individual peaks.
- Reflection intensity in the NIR region is higher than in mid infrared. In NIR spectra single compounds influence not only individual regions, but often the whole spectrum.
- Visually analyzing the spectra is impossible.
- NIR spectra have no significant peaks, but they are unique “reproductions” of a substance or a mixture.
- Data have to be combined with multivariate mathematical methods.

3.2.8.2 Advantages

- Liquids, powders and even high-viscosity substances can be measured without sample preparation.
- Silica cuvettes can be used as transmittance material.
- Measurement period.
- One NIR spectra is a characteristic “reproductions” of an individual extract and covers all organic compounds.

3.2.8.3 Evaluation of spectra

Qualitative classification

- Sufficiently large sample set with a certain variety concerning to the expected determination range.
- Development of a qualitative model, e.g. principal component analysis.

Quantitative Analysis

- Reference data of all samples have to be determined.
- Spectral data and reference data are combined in a calibration, e.g. PLS.

3.2.8.4 NIR experimental set-up

A NIR set-up with a flow cell has been used for measuring NIR spectra of other hydrocarbons and hence it is a natural extension to apply the same system for bitumen. The set up is shown in Figure 3.2.8.4 a and 3.2.8.4 b. We were using this set up to measure NIR of bitumen. The sample holder is at 135 °C and the measurement cell is at 200 °C. The whole process of NIR spectra collection for a sample takes less than 30 minutes.



Figure 3.2.8.4 a: ABB NIR Instrument

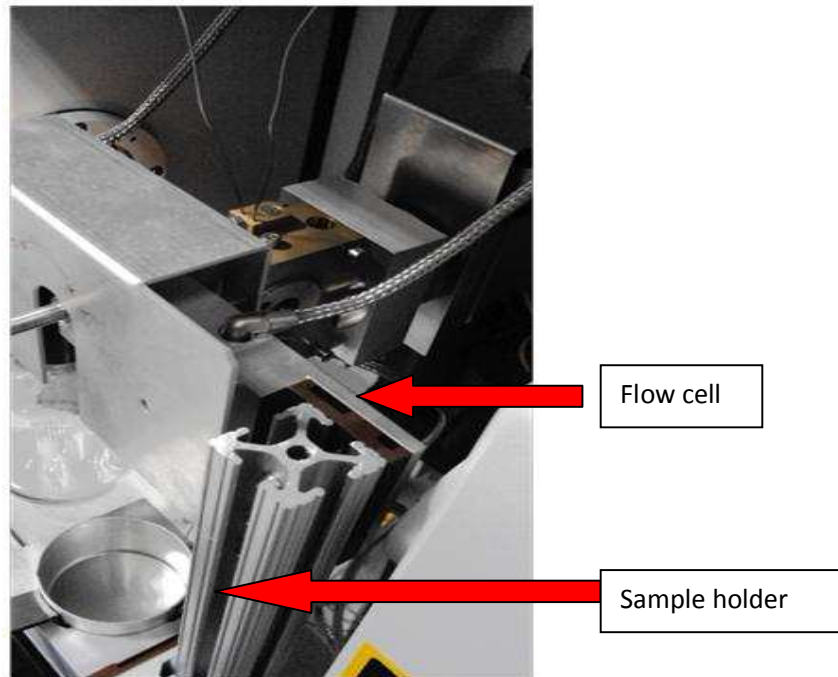


Figure 3.2.8.4 b: Detailed view of the NIR set up showing flow cell

3.2.8.5 Identification procedure

This procedure is explained with the help of an example. First the original spectrum for all the samples is recorded (Figure 3.2.8.5 a), which is then corrected by reference spectra. Then the first derivative (Figure 3.2.8.5 b) is taken, followed by the second derivative (Figure 3.2.8.5 c). Then two principal components (PC1, PC2) are selected and the samples are plotted against these two principal components (Figure 3.2.8.5 d). Based on this PC1 vs PC2 plot and using mathematical tools, a model is proposed correlating to the particular properties to be studied. Generally, a large sample set is required to come up with a significant correlation.

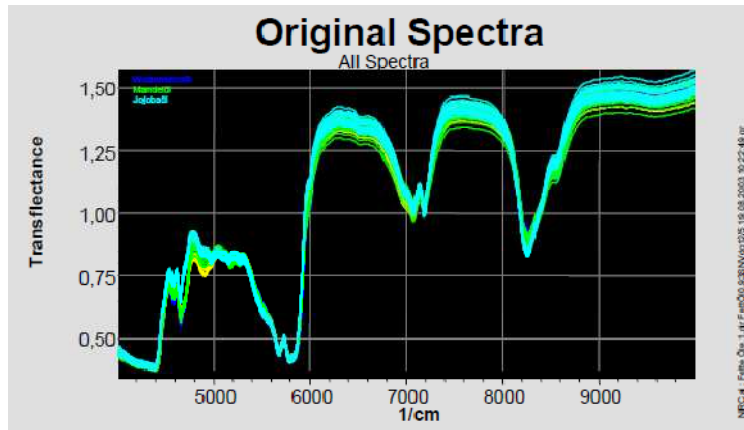


Figure 3.2.8.5 a: Original spectra

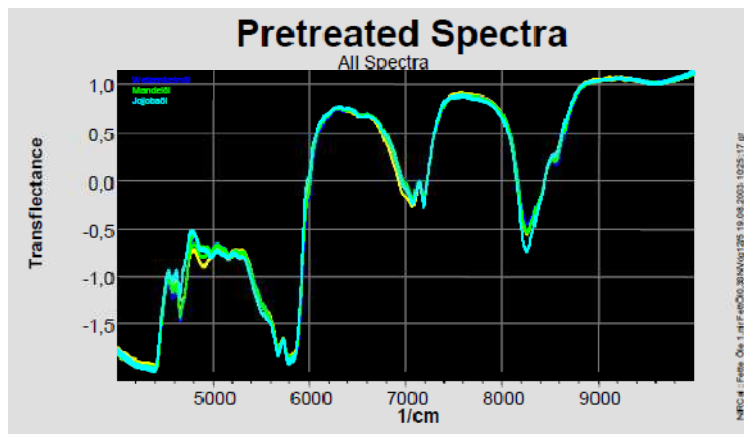


Figure 3.2.8.5 b: First derivative spectra

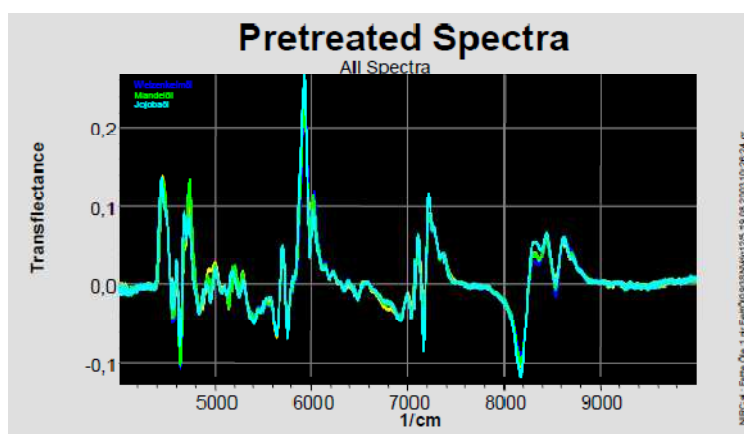


Figure 3.2.8.5 c: second derivative spectra

(archipelago or continental), size of the asphaltenes micelles and their effect on the bitumen properties. Therefore, if we take similar samples, i.e. samples with similar processing type and both fresh and aged, we get a better plot, as can be seen in figure 4.1.2 a, which shows that with an increase in asphaltenes concentration, the penetration decreases. This holds good even for the aged samples. This suggests that a correlation can be obtained for similar samples with sufficient number of samples. The same can be observed for softening point and asphaltenes concentration, see Figure 4.1.1 a.

Resins to asphaltenes ratio has also been studied in the past for its effect on bitumen properties [31]. Figure 4.1.5 and figure 4.1.6 show resins to asphaltenes ratio with penetration and softening point, respectively. Also in this case, considering all samples, there is a large spread in points. As we have taken samples from different crudes and different processing routes, this could be the reason for the spread. If again similar samples are selected, we observe a trend in properties with increase in resins to asphaltenes ratio. Figure 4.1.5 a shows the plot between penetration and the resins to asphaltenes ratio from similar samples and Figure 4.1.6 a shows a plot between softening point temperature and resins to asphaltenes ratio from the same set of samples.

Change in the resins to asphaltenes ratio after ageing was plotted against the change in the properties like penetration and softening point. No visible correlation or trend was observed. Figure 4.1.7 and 4.1.8 show the change in resins to asphaltenes with change in softening point and penetration values respectively.

Another idea explored was to correlate the change in properties and chemical composition after ageing. Ageing is an oxidation process and the chemical composition changes after ageing and the bitumen stiffness is increased. But no trend was observed in change of resin/asphaltenes ratio and the difference in Tr&b or retained penetration. This clearly shows that it is necessary to take into account the large classes of individual components (saturates, aromatics, resins and asphaltenes) that are present with different polarities in different bitumen.

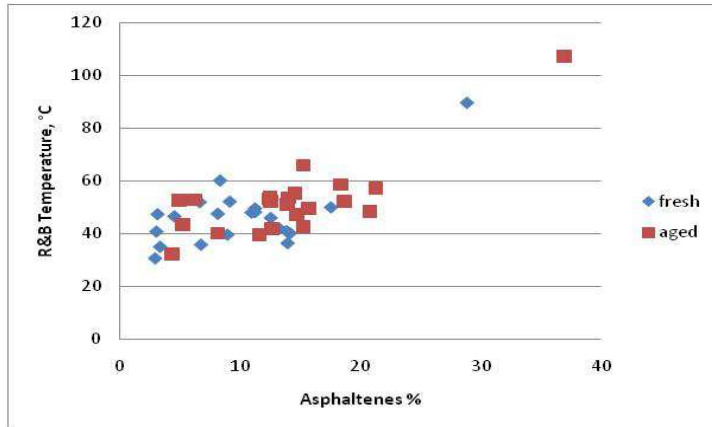


Figure 4.1.1: Asphaltenes versus Softening Point

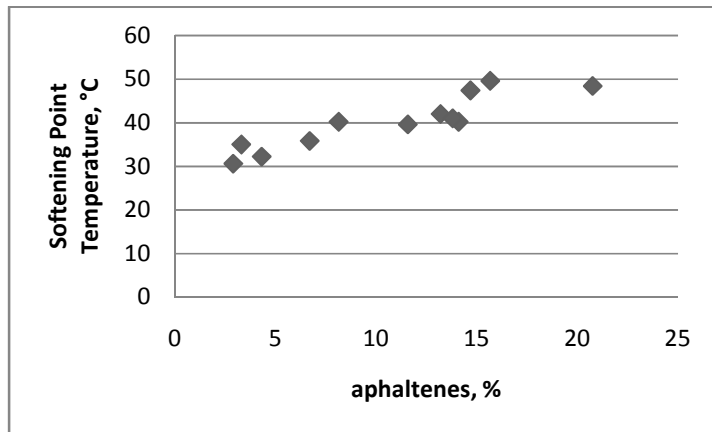


Figure 4.1.1 a: Softening Point Temperature versus asphaltene concentration for similar samples.

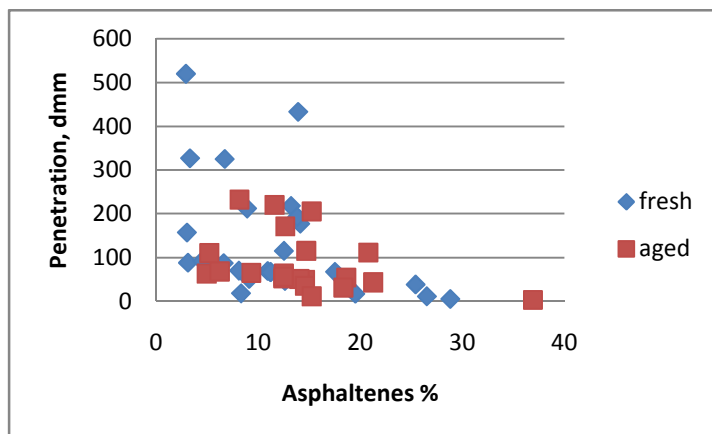


Figure 4.1.2: Asphaltenes versus penetration at 25 °C.

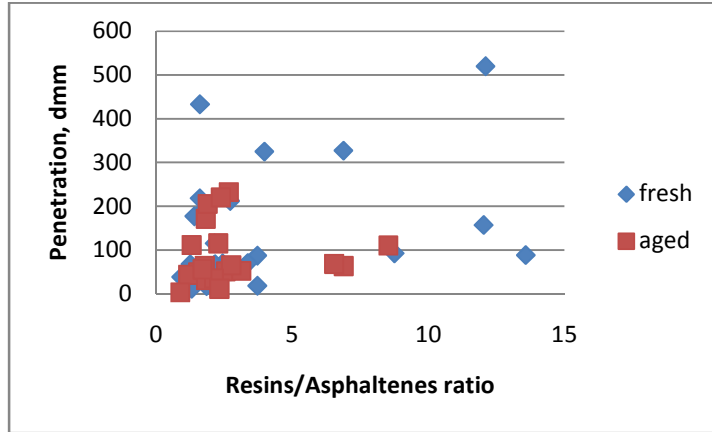


Figure 4.1.5: Penetration versus Resin / Asphaltenes ratio

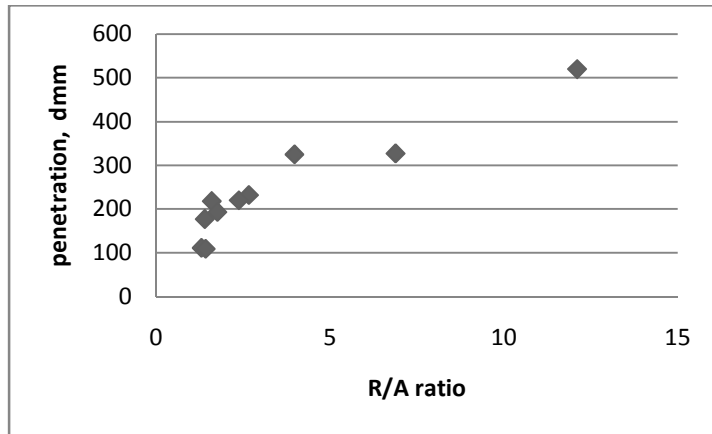


Figure 4.1.5 a: Penetration versus R/A ratio for bitumen samples that are similar.

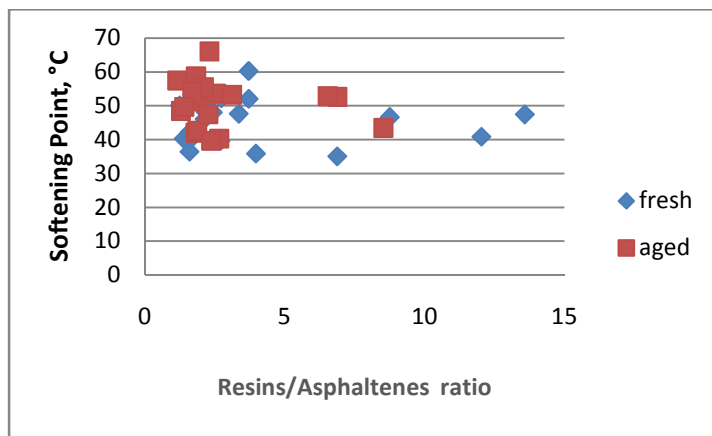


Figure 4.1.6: Softening Point versus Resin / Asphaltenes ratio

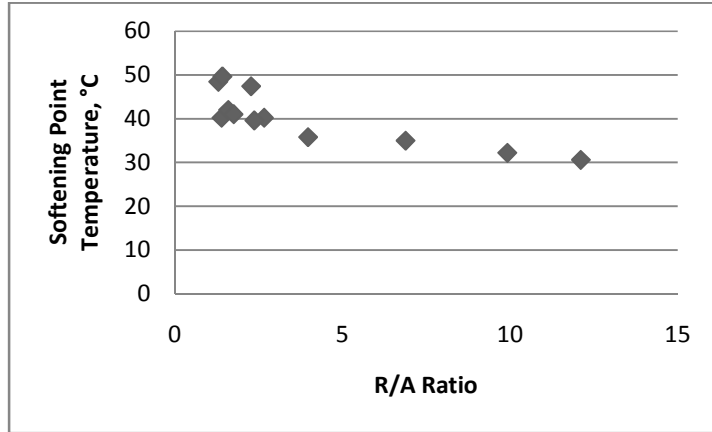


Figure 4.1.6 a: Softening Point versus R / A ratio for similar samples

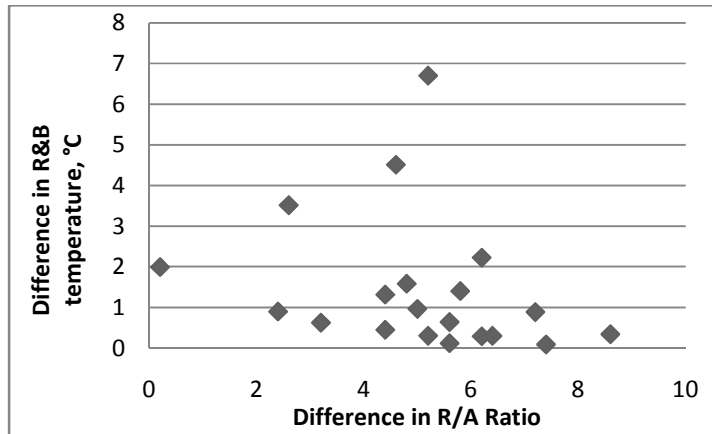


Figure 4.1.7: Change in softening point versus change in R / A ratio after ageing.

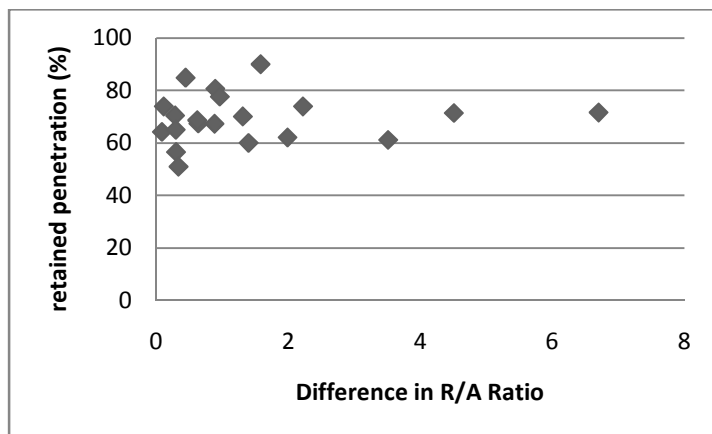


Figure 4.1.8: Change in penetration versus change in Resin / Asphaltenes ratio after

4.2 Penetration and complex modulus

Penetration test and complex modulus test both the tests use stress and loading time (frequency in case of DSR) as parameters for determining the properties. There has to be a correlation between the two properties. This correlation has been studied but for a smaller range of penetration value [30]. Our aim was to study this for a large range (5 – 520 dmm) to cover a broad range of bitumen penetration values. The choice of frequency (time of loading) was based on the fact that at 0.4 Hz the stiffness of bitumen is independent of Penetration Index [29].

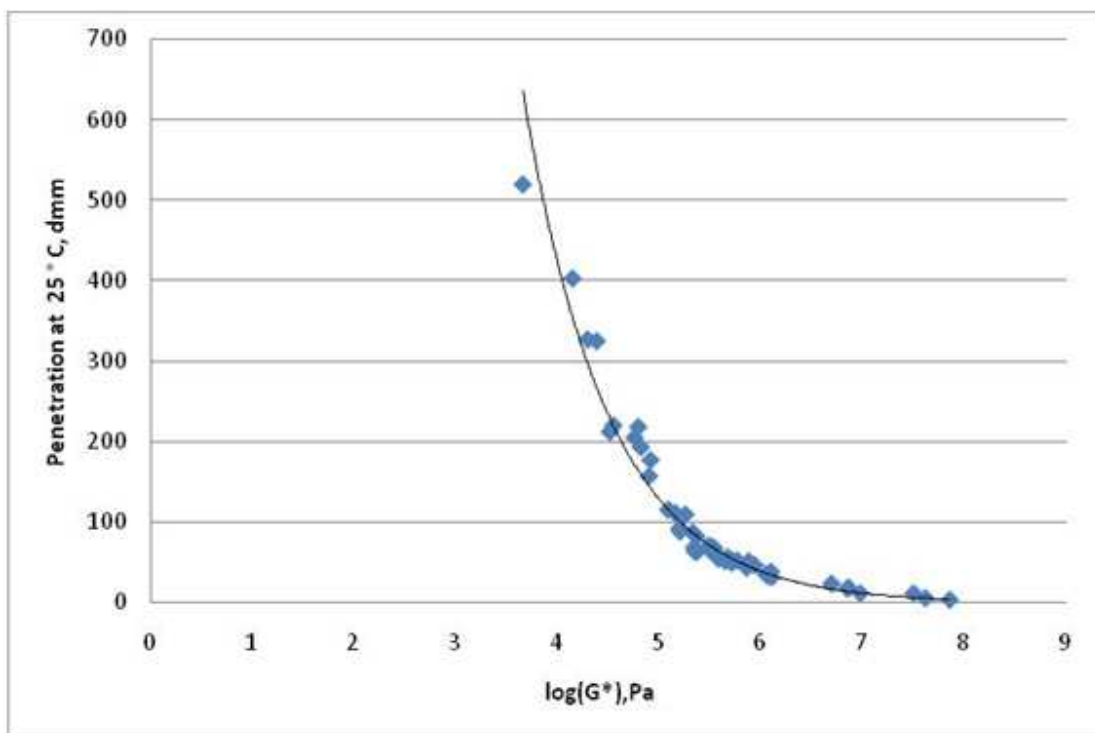


Figure 4.2: Penetration versus log (G*)

Figure 4.2 gives correlation between penetration (range 5 to 520 dmm) and log (G*) (By DSR) the equation is:-

$$P \text{ (dmm)} = 50434 * e^{(-1.194 * (\text{Log} (G^*(Pa))))}$$

$$R^2 = 0.9746$$

$$\text{Standard deviation} = 4.18$$

The testing temperature in the DSR was kept the same as that for the penetration test. The choice of frequency and strain percentage was based on previous work [29].

The standard deviation does not meet the multi laboratory precision. However, in the standard the precision is given for different penetration ranges (see section 3.2.1). Therefore, two different equations were derived: for below 150 pen and for above 150 pen.

(i) For 0-150 dmm range: $P \text{ (dmm)} = 32336 * e^{(-1.125 * (\text{Log}(G^*(Pa))))}$

This gave a standard deviation of 2.13 which is within the precision limits.

(ii) For 150 dmm above: $P \text{ (dmm)} = 29208 * e^{(-1.058 * (\text{Log}(G^*(Pa))))}$

This has a standard deviation of 13.39, which is very close to the precision limits.

4.3 Softening Point and DSR

It is known that the viscosities of all the bitumens vary from 800 to 3000 Pa.s with an average value of 1200 Pa.s at their respective softening point [30]. Hence, a temperature sweep was carried out and the temperature corresponding to 1200 Pa.s was plotted against softening point. The choice of frequency (time of loading) was based on the fact that at 0.4 Hz the stiffness of bitumen is independent of Penetration Index [29].

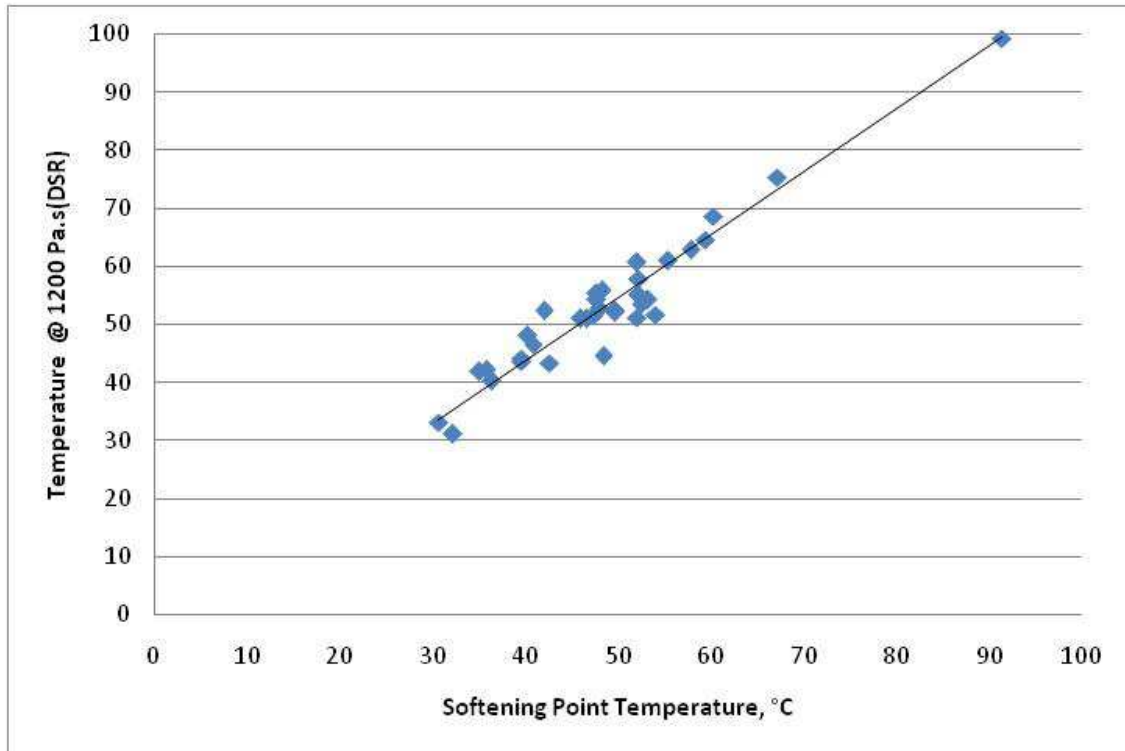


Figure 4.3: Softening point versus temperature@1200 Pa.s (DSR)

Figure 4.3 gives correlation between Softening point temperature and temperature at 1200 Pa.s viscosity calculated by DSR by doing a temperature sweep for every bitumen sample. The equation is:

$$T_{DSR} = 1.092 * T_{R\&B}$$

$$R^2 = 0.9485$$

$$\text{Standard deviation} = 3.30$$

This equation gives a standard deviation of 3.30 which is higher than that mentioned in standard. The large deviation can be explained on the basis that we have used the average viscosity value as mentioned above, hence, it leads to more deviation in results.

4.4 NIR Results

4.4.1 Correlation between NIR spectra and penetration

The procedure followed is mentioned in section 3.2.8.5. After generating the PC1 versus PC2 plot, a model based on the multivariate mathematical methods was developed and the values of penetration were predicted using this model, shown in figure 4.4.1.

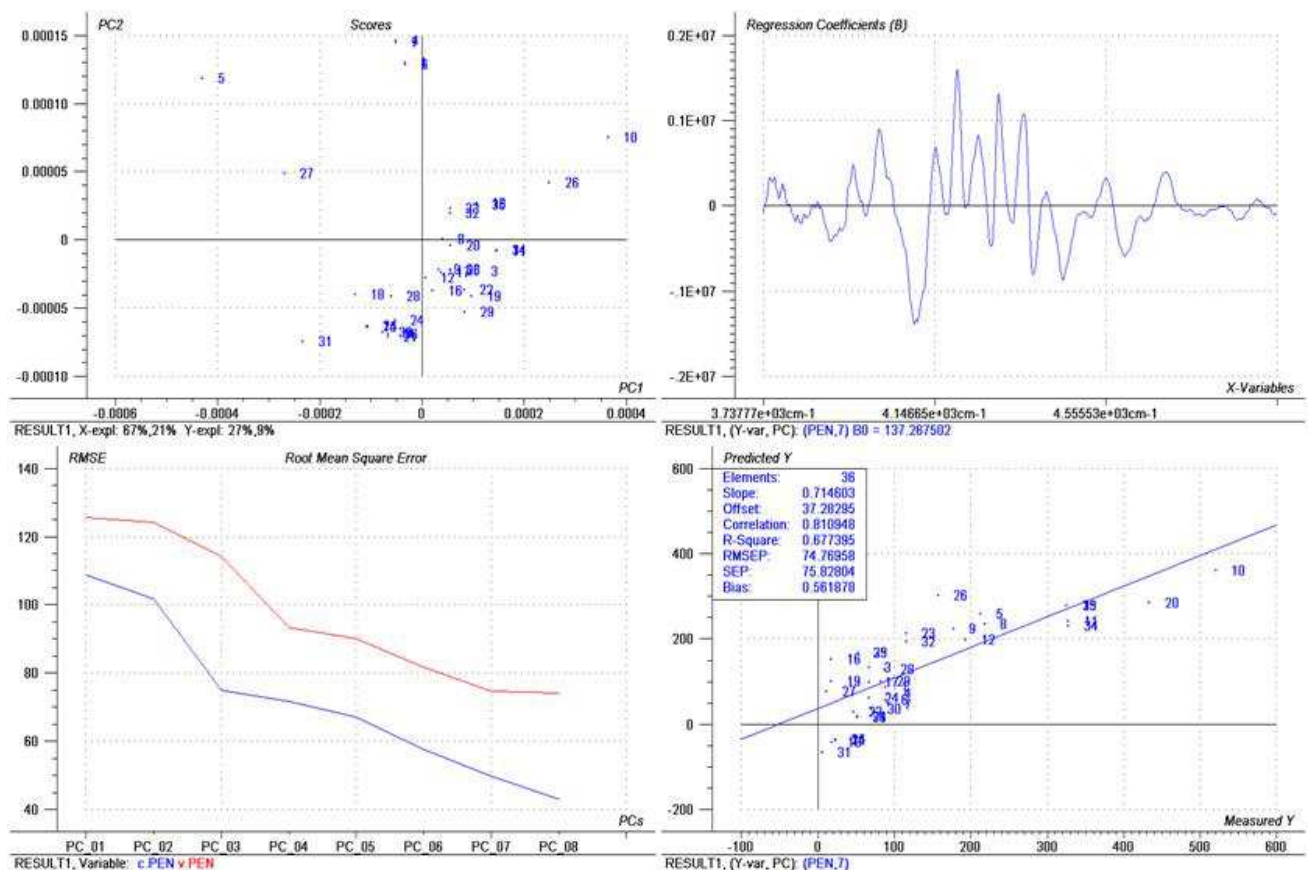


Figure 4.4.1: from top left clockwise a) PC1 versus PC2 plot b) Regression plot c) comparison between predicted and measured value d) RMSE plot.

Figure 4.4.1 clearly shows some relatively isolated samples like 5, 27 and a set of repeats like 4/7 and 1/6. The regression, however, seems to indicate some non linearity, although this is driven by only a few samples, so care needs to be taken to ensure this

is correct. RMSEP needs to be compared to the method reproducibility to evaluate if the achieved RMSEP is good enough or whether further investigation is needed.

The prediction is not good enough probably because the sample set is small (only 28 samples); a large sample set is required to come up with a better model. RMSEP for reproducibility shows the same trend but there is a deviation. This deviation is more than the reproducibility of the penetration test.

4.4.2 NIR spectra and softening point

Figure 4.4.2 shows that there is a better relation between NIR and softening point. Although 8 factors are suggested, this is a rather large number of factors as the regression gets very noisy and the gain is limited. Five factors seem adequate and show a much improved line compared to the first one using all samples.

RMSEP at 5 factors is 4.2 and needs to be compared with the method reproducibility (1.9 for multi lab) and user requirements. Current model precision is somewhat low compared to method R.

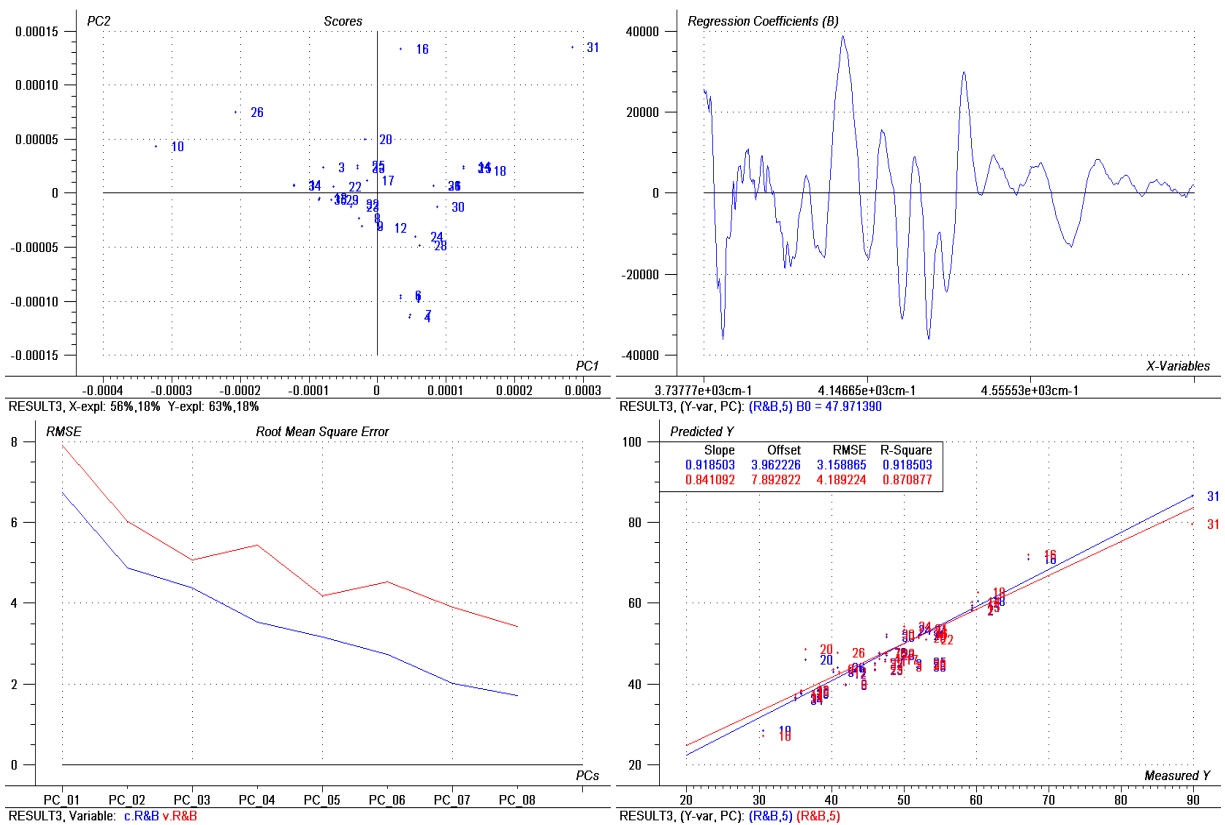


Figure 4.4.2: from top left clockwise a) PC1 versus PC2 plot b) Regression plot c) comparison between predicted and calculated value d) RMSE plot

Although the RMSEP is high as compared to the reproducibility for the softening point test, there seems to be a better correlation between NIR and softening point temperature. This model can be refined by using a larger sample set and the RMSE values can be lowered to match the reproducibility of the test.

4.4.3 NIR spectra and G^* (complex modulus)

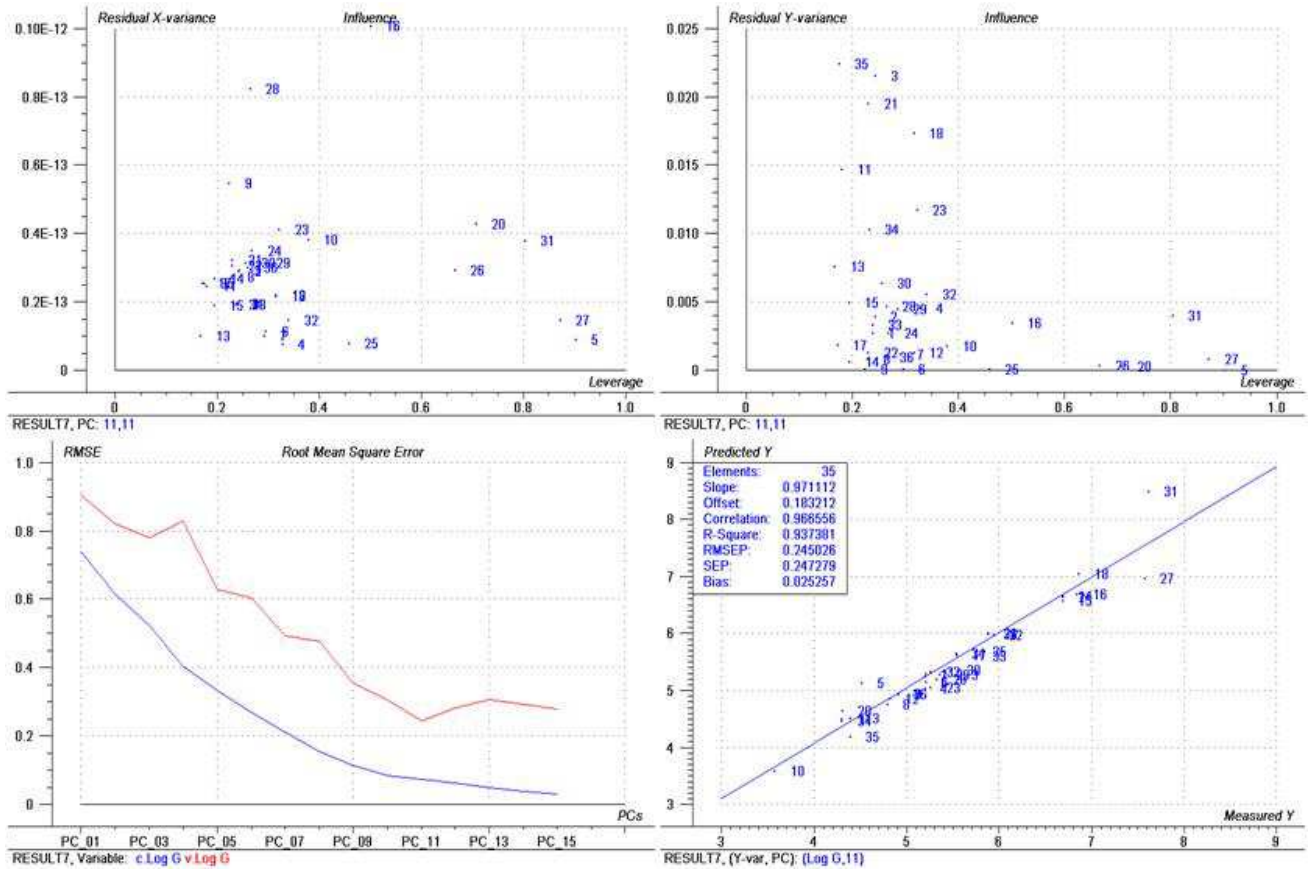


Figure 4.4.3: from top left clockwise a), b) variance plots c) Comparison between proposed and calculated value d) RMSE plot.

Although the model seems nice, converting the LOG results of the prediction to “normal” numbers it is very poor with prediction that vary between 25 % of the PTM value to as much as 750 % of the PTM value. This variation is too large to be of practical use. Taking the $\ln(G^*)$ predictions and converting them into “real” numbers it shows they vary between 60 and 350 percent of the PTM values. Hence, this does not give a good correlation.

4.4.4 Correlation between NIR and aged binders

A total of 76 spectra were taken and they were imported into Unscrambler (this is a software package that separates the noise from signal) and treated as per initial set. The database was also corrected using the MSC file (Reference files) as used for the models. The set was combined with the initial set and a PCA was done as before and projection of the aged samples on the original set is shown in figure 4.4.4.

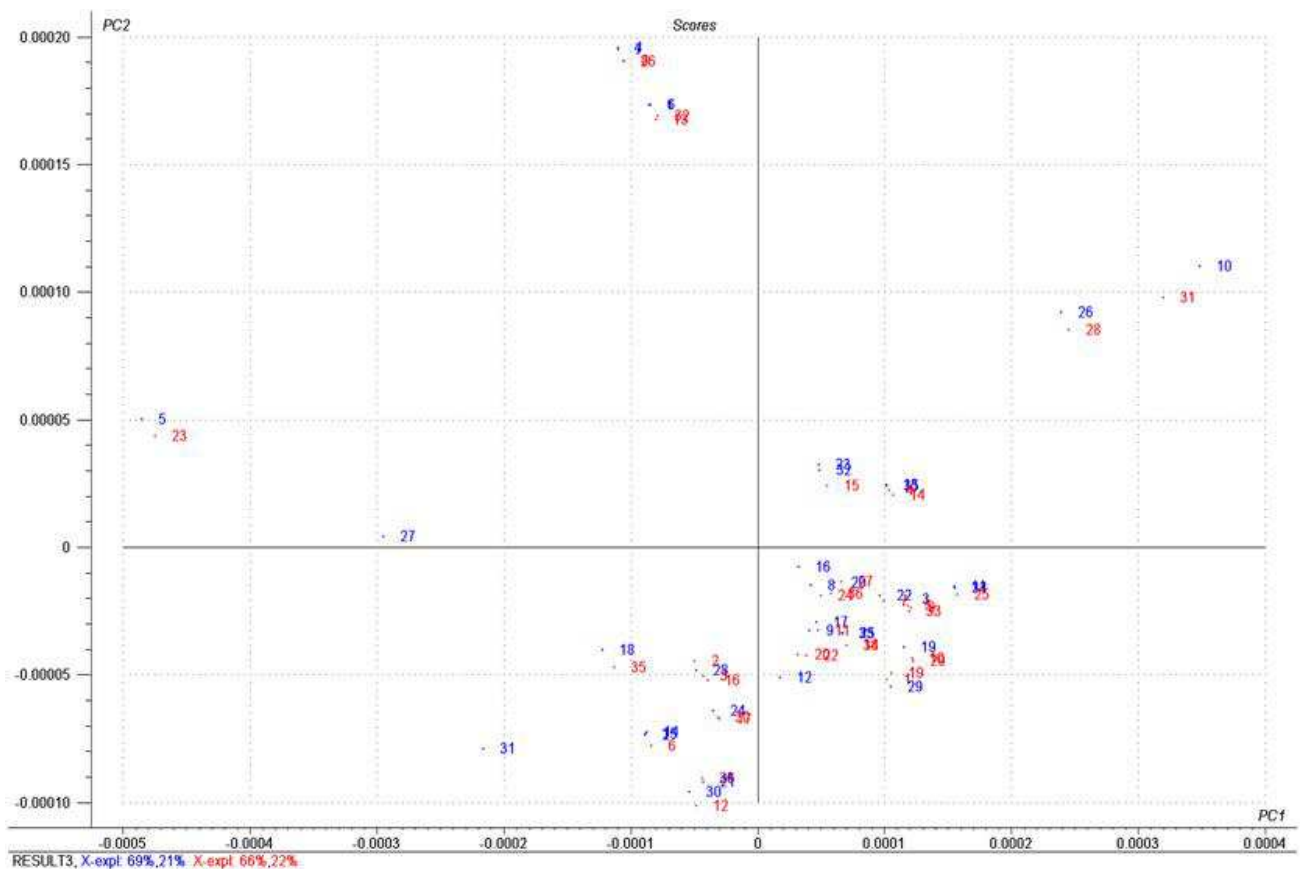


Figure 4.4.4: NIR distinguishing fresh (blue) and Aged (Red) bitumens.

The above also shows the (often tight) clustering of the duplicates (either in the blue (fresh) or red (aged)) samples and their differences in spectra features. It clearly seems to indicate the ability of the NIR to distinguish between the fresh spectra and the aged ones. No predictive models have been made as the initial models already indicated that the grade differences are such that models are problematic due a limited number of data points.

5. Conclusions and outlook for further work

The development of correlations as described in this report can help in quicker screening of samples and can save time and effort required to characterize samples. For example, with selected tests on the DSR, the softening point, penetration and viscosity can be derived, when coupled with the Bitumen Test Data Chart in less than 15 minutes which otherwise would have taken one whole day.

Since the SARA analysis did not show the detailed information required to interpret the difference or change in properties observed, more structural data is required to understand the morphology which influences the properties. A direct correlation between asphaltenes concentration and properties could not be made. However, when considering similar samples (both fresh and aged) we see the trend which suggests that the properties are highly origin and processing dependent. More samples from the same set are required to come up with concrete correlations. These correlations will be specific for that particular set and cannot be generalized for total range of bitumens. Correlation between nature of asphaltenes (archipelago or continental) and its concentration or aggregate size and properties could be studied in future. It is proposed that AFM and TEM can provide additional information.

NIR set up and protocol can be leveraged for studying bitumen and the data collected are repeatable and can differentiate various grades of bitumen. PCA analysis shows that we can develop correlations between softening point and penetration and NIR spectra. Correlation of NIR with complex modulus G^* is not satisfactory so far. NIR spectra are different for fresh and aged binders i.e. the RTFOT binder aging induces some changes at molecular level that leads to a different NIR spectrum. This feasibility study shows correlations can be developed between bitumen properties and NIR. However, the numbers of data points were not sufficient to develop quantitative predictive models.

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