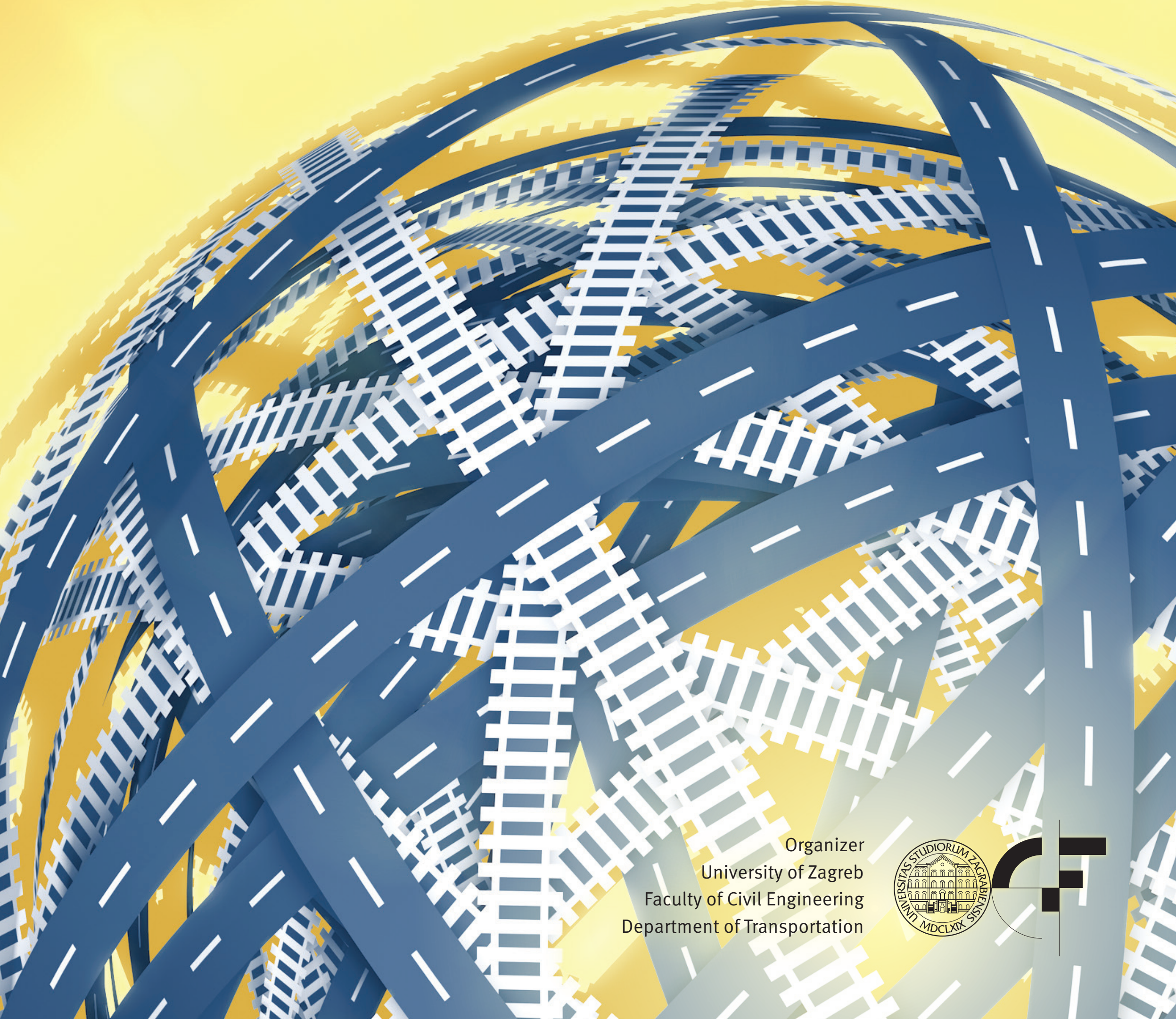
CETRA[2016]

4th International Conference on Road and Rail Infrastructure
23–25 May 2016, Šibenik, Croatia

Road and Rail Infrastructure IV

Stjepan Lakušić – EDITOR



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Road and Rail Infrastructure IV

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EVALUATION OF CHEMICAL FRACTIONS IN PAVING GRADE BITUMEN 50/70 AND EFFECTS ON RHEOLOGICAL PROPERTIES

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University of Kassel, Germany

Abstract

Generally, paving grade bitumen is characterized by mechanical properties at low, medium and high temperatures (breaking point Fraass, penetration and softening point R&B). However, the origin of the raw oil used for bitumen production has a significant effect on the chemical bitumen characteristics usually described by the asphaltene and maltene colloid model concept. Different chemical analysis methods were applied to differentiate the colloidal properties of the binders. In order to evaluate the potential effects on rheology, 14 bitumen 50/70 samples from different proveniences and producers were analyzed on physical, chemical and rheological properties. For the rheological characterization, complex shear modulus tests were conducted in a temperature range of 20 °C to 90 °C at different frequencies. The physical properties were determined by softening point ring and ball. Chemical groups of binders were characterized by thin layer chromatography (TLC/FID) to differentiate in asphaltenes, resins, aromatics and saturates (SARA-analysis) according to colloid model concept. Furthermore asphaltenes were separated into three fractions of different solubility by dissolution/precipitation procedure. This paper presents the differences between rheological, physical and chemical properties of several bitumen samples, which all represent the requirements on 50/70 according to European Standard EN 12591 and which are commonly applied in German asphalt industry. The paper discusses if the specification system based on conventional characteristics is sufficient for European road industry or if still significant differences in rheological and chemical properties are observed.

Keywords: paving grade bitumen, rheology, SARA-analysis, asphaltenes, FTIR

1 Introduction

Generally, paving grade bitumen is characterized by mechanical properties at low, medium and high temperatures (breaking point Fraass, penetration and softening point R&B) according to EN 12591 [1]. For evaluating the general applicability of additional/alternative properties for characterization, in Germany rheological properties are measured for experience since 2012 [2]. Softening point ring and ball and thermo-rheological characteristics of bituminous binders are directly associated with its chemical composition. They can simplistically be characterized with a colloidal model which is based on the theory that colloids with high polarity (asphaltenes) are peptized to micelles surrounded by a layer of resins in an oily phase with lower polarity, called maltenes [3]. At high temperatures, asphaltenes can be fully dispersed in the maltene phase which results in viscous behavior and can be interpreted as Newton fluent. The higher the asphaltene content, a higher temperature is required to reach this non-elastic fluid characteristics which can be observed by an increased softening point ring and ball. On the other hand at lower temperature, elastic behavior of bitumen is caused by interaction between asphaltene micelles when asphaltene colloids become more complex

[4]. Chemical methods for separating bitumen into maltenes, asphaltenes and further in low soluble asphatenes (lsA), medium soluble asphaltenes (msA) and high soluble asphaltenes (hsA) by dissolution/precipitation procedure as well as by SARA analysis for separating bitumen in asphaltenes, resins, aromatics and saturates are available test methods for evaluating the colloidal system [7, 12].

2 Experimental

2.1 Materials

In order to evaluate the relevance of chemical characteristics of the same type of paving grade bitumen, 14 bitumen 50/70 samples from different producers (as described by the first sample numbers 1 to 5) and production sites / raw oil source were analyzed.

2.2 Mechanical bitumen characteristics

The softening point ring and ball was measured according to the EN 1427 [5]. The rheological properties of bituminous binders were evaluated by Dynamic Shear Rheology (DSR), using plate-plate tests according to EN 14770 [6]. Cylindrical samples with a diameter of 25 mm and a height of 1 mm were tested. For temperatures between 30°C and 90 °C at frequency 1.59 Hz the shear moduli and phase angels were measured.

2.3 Chemical bitumen characteristics

The compositions of asphaltenes in terms of low, medium and high solubility are measured by a dissolution/precipitation procedure by Zenke [7] with three different solvent combinations of iso-octane and cyclohexane. The sum of these fractions results in total asphaltene content. The solvent defining asphaltenes in this test is Iso-Octane iC_8.
Four chemical fractions of different polarity were determined by thin layer chromatography (TLC/FID) according to IP 469 [12].For the analysis 0.1 g of the bitumen sample was dissolved in 5 ml of dichloromethane. Fractions of saturates are evaluated by chromatographically seperation in heptane, aromatics in toluoene/heptane (80:20), resins in dichloromethane/methanol (95:5) and asphaltenes are not eluated. In this study the maltene phases consist of saturates, aromatics and resins. Note, that the resulting asphaltenes content is here defined by solubility in dichloromethane which results in different proportions compared to evaluation with iC_8. The test procedures are described in more detail in [8]

3 Results

3.1 Mechanical bitumen characteristics

The measured softening points are given in Figure 1. All results are within the limits (46°C to 54°C) for binders with penetration grade 50/70 according to EN 12591. Highest temperatures are evaluated for binder B1.1, B3.5, B2.1 and B4.1.
The results of complex shear modulus and phase angle tests at the frequency 1.59 Hz are plotted versus the temperature in Figure 2. Generally the shear moduli of the tested samples are within a cmparatively small range for each tested temperature. However, at lower test temperatures < 60°C binder samples B1.1 and B3.4 indicate higherG* values . For the phase angles, which represents viscous and elastic propertiesin bituminous binders a higher differentiation between the samples can be observed. Binders 3.3, 3.4 and 3.5 show lowest phase angles which indicates higher elastic and lower viscous deformation properties compared to the other binders. Continuous high phase angles are observed for binder B5.1 and B3.1..

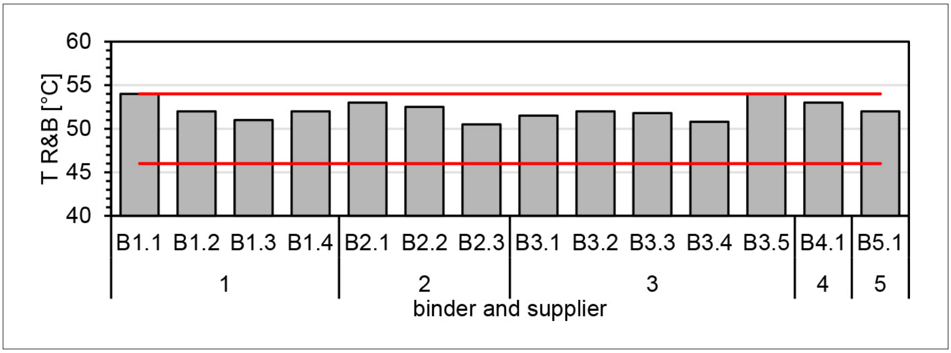

Figure 1 Results for $T_{R\&B}$ for all 50/70 penetration bitumen

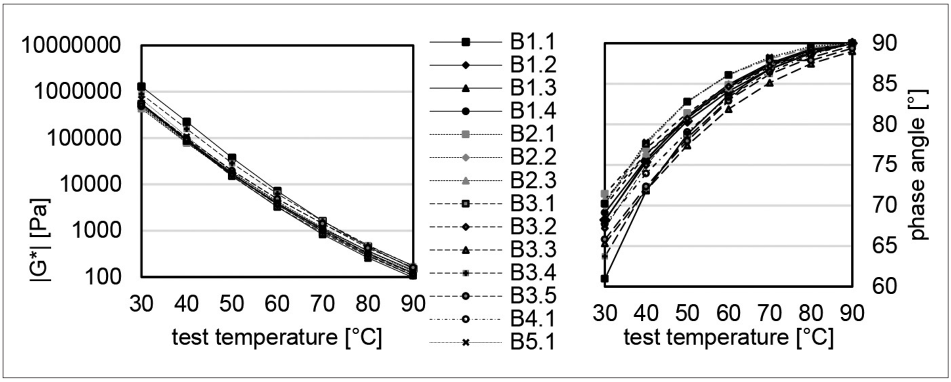

Figure 2 Complex modulus and phase angle versus temperature meausred at 1,59 Hz

3.2 Chemical bitumen characteristics

Results of the precipitation experiments by Zenke are presented in Figure 3, showing the maltene content (as defined by soluble compounds in iC_8) and the three asphaltene proportions.

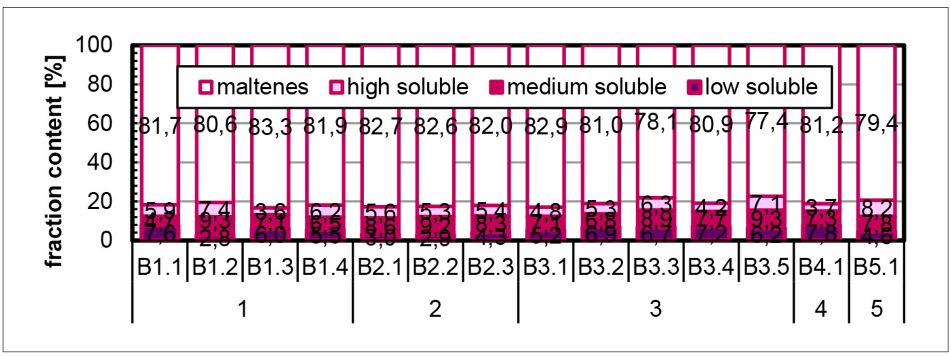

Figure 3 Content of low, medium, high soluble asphaltenes, total asphaltenes

To the resulting total asphaltene content vary between 16.7% (B1.3) and 22.6% (B3.5). Highest asphaltene contents of › 20% can be observed for B3.3, B3.4 and B5.1. The majority of samples indicate total asphaltene contents of between 17% to 19%. In most cases medium soluble asphaltenes could be evaluated as highest fraction of the three types of asphaltenes. Exceptions are B1.1, B3.2 and B4.1 with highest low soluble asphaltene content and B5.1 with highest content of high soluble asphaltenes and lowest content of low soluble asphaltenes. The proportions of the bitumen SARA fractions obtained from TLC/FID tests are plotted in Figure 4.

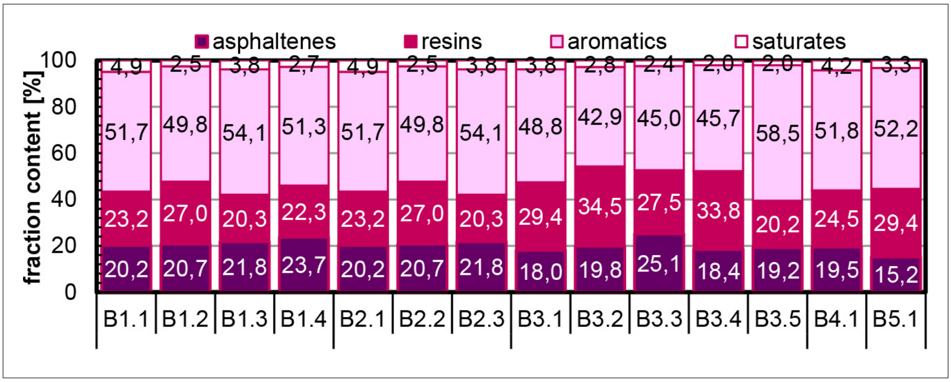

Figure 4 SARA components of binders 50/70

Saturates are the fraction with lowest and aromatics the fractions with highest content in all 50/70. The asphaltene content varies between 15.2% (B5.1) to 25.1% (B3.3). In most cases resin contents in bitumen sample are higher than asphaltene content.

4 Discussion

For discussing the effects of chemical characteristics on physical and rheological properties, linear correlation analysis is conducted. For assessment of an existing link between two compared properties, these are plotted one versus the other and the coefficient of determination (R^2) is calculated. The nearer R^2 increases the value 1, the better is the correlation between the two properties.
In the following sections some found correlations for selected pairs of parameters are discussed. Further, it was found, that the properties of binder sample 1.1 doesn't meet the found correlations. This binder 50/70 was especially specified as binder for preparing foamed bitumen. Therefore, the results of this binder sample are not included in the following evaluation. Based on the previous rheological results better coefficient of determination could be determined without binder 1.1 with special foam bitumen characteristics.
Surprisingly, no correlation between the two asphaltene contents evaluated by the TLC/FID and dissolution/precipitation method could be identified, see Figure 5 (left). For example, binder 5.1 shows the lowest asphaltene content in SARA analyse (dichloromethane) while it has one of the highest asphaltene contents in the other method, where asphaltenes are defined by Iso-Octane. This result shows the importance of clear defining chemical characteristics and careful evaluation of chemical bitumen compounds.
However, a feasible correlation is found for total asphaltene content (iC_8) and resins content by SARA analyse ($R^2 = 0.66$). With increasing resins content, total asphaltene content by Zenke rises, see Figure 5 (left).
Table 2 shows the coefficients of determination for selected chemical fractions and the results of DSR tests (shear modulus and phase angle). As an example the correlation between phase angle and content of asphaltenes and resins is shown in Figure 5 (right).

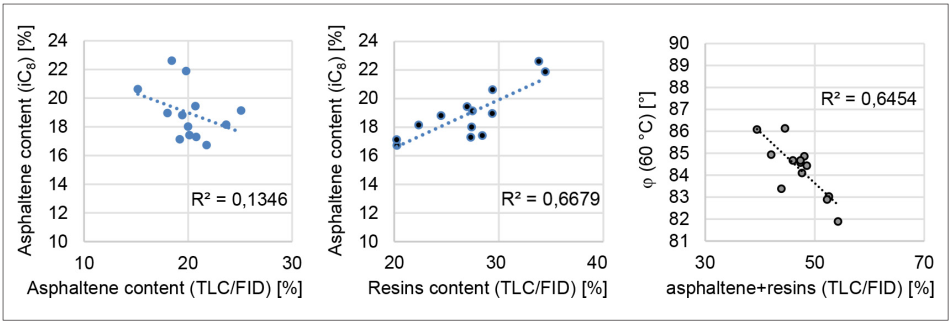

Figure 5 Examples for correlation between chemical and rheological parameters: left: iC_8-asphaltene content by dissolution versus TLC test; middle: iC_8-asphaltene content by dissolution versus resins content by TLC test; right: Phase angle (DSR) versus content of asphaltenes and resins by TLC test

Table 1 Selected results for coefficient of determination

Rheolog. Property @ 1,59 Hz	Temperature [°C]	asphaltene contents by dissolution test		contenst of SARA compounds by TLC/FID test	
		total asphaltenes	low and medium soluble asphaltenes	aromatics	Aspaltenes and Resins
Complex shear modulus G*	30	0,06	0,07	0,03	0,07
	40	0,10	0,18	0,15	0,21
	50	0,16	0,28	0,36	0,44
	60	0,28	0,37	0,54	0,64
	70	0,43	0,43	0,65	0,77
	80	0,45	0,40	0,68	0,80
	90	0,54	0,41	0,67	0,80
Phase angle ϕ [°]	30	0,33	0,72	0,28	0,37
	40	0,39	0,81	0,46	0,53
	50	0,37	0,73	0,56	0,61
	60	0,34	0,64	0,61	0,65
	70	0,30	0,60	0,58	0,62
	80	0,49	0,70	0,60	0,67
	90	0,59	0,57	0,45	0,55
$T_{R\&B}$		0,16	0,04	0,05	0,04

Complex shear modulus is mostly influenced by asphaltenes and combination of low soluble and medium soluble asphaltene content as identified in dissolution test especially at higher test temperatures. For SARA analyse feasible correlation for content of aromatics and the combination of asphaltenes and resins could be determined. With increasing temperature coefficient of determination increase for all results, too.
Phase angle is also influenced by same chemical fractions as complex shear modulus. Phase angle is continuous influenced by the combination of the content of low and medium soluble asphaltenes as well as contents of aromatics and combination of asphaltenes and resins at all test temperatures. For the softening point ring and ball only low coefficients of correlations are identified. This can be explained by the small range of softening points identified in the binder samples of 51 °C to 54 °C.

5 Interpretation

In this study no relationship between the asphaltene contents evaluated by the two different test procedures could be determined. The general magnitude of asphaltene contents identified by the two test procedure are similar (dissolution test: 17% to 22.5%; TLC/FID tests: 15% to 25%). It is not possible to differentiate a high asphaltene content by Zenke to a high asphaltene content by SARA analyse. Reasons for the non-existing correlation can be explained by the different evaluation technique as well as the diverting solvent used [9, 10]. The identified relationship between the total asphaltene content in dissolution test and the resins content as identified in TLC/FID tests however shows that comparable results can be obtained.
Besides the identification of the binder optimised for foamed bitumen additional anomalies could be found for binder sample B5.1 with regard to highest phase angle which results in lowest elastic properties compared to the other 50/70. In [11] elastic rheological properties are determined by asphaltene content. In this case B5.1 is a binder with one of the highest asphaltene content (dissolution experiment) by Zenke. On the hand B5.1 show one of lowest asphaltene content by SARA analyse. It seems that SARA analyse is more suitable to describe rheological properties in a chemical way. By combining the single asphaltene fractions by Zenke, another chemical profile for bituminous binders is given. Figure 6 shows one of lowest results for the combination of low and medium soluble asphaltene (lsA+msA) content for binder B5.1. These good correlation can be seen as well as in coefficient of determination.

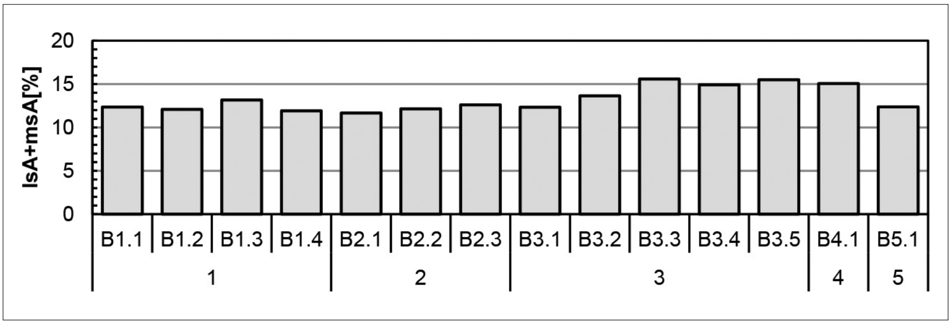

Figure 6 Content of low and medium solvable asphaltenes (dissolution test)

Despite the low variation of rheological properties between the binder samples of the same type 50/70 clear correlations could be identified to individual chemical properties. Based on colloid model of micelles built of asphaltenes and surrounding resins as described in [4]. By increasing temperature the correlation of the four selected fractions to complex shear modulus increases, especially for results of TLC/FID tests. At low temperatures, asphaltenes are covered by agglomerated resins and therefore, the pure asphaltene content doesn't affect the rheological properties. However with increasing temperatures resins (and high-soluble asphaltenes) will melt and be form a part of the maltene phase. In this state, the content of the still solid asphaltenes affects the rheological properties significantly by stiffening the maltene phase showing increased shear modulus and reduced phase angles. The shear modulus increases if the content of asphaltenes and resins increase and content of aromatics decrease.
Results of correlation according to asphaltene dissolution/precipitation tests show that high soluble asphaltene are not important to explain rheological properties of 50/70 but the sum of low and medium asphaltenes. This is an indication that the high soluble asphaltenes will shift to maltene phase with increasing temperature. The general concept idea of micelle structure based on SARA compounds [4] can therefore be adopted for the concept of asphaltene separation according different solubility, compare Figure 7.

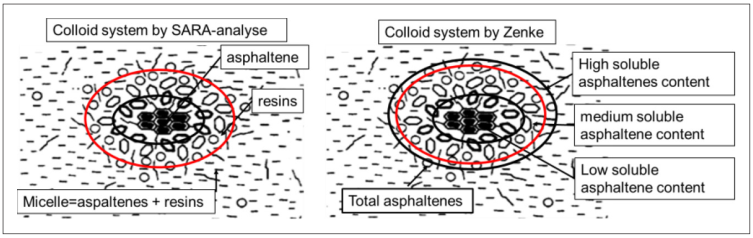

Figure 7 Colloid model according to SARA fractions [4] and interpretation of effect of asphaltenes as identified by dissolution/precipitation tests

6 Conclusion

The following conclusions can be drawn from the results of the presented investigation:
- Chemical properties depends on their methods to determine the chemical fractions.
- Even straight bitumen of the same kind (here: 50/70) shows variations in chemical structures which can be explained by individual refinery process and raw oil provenience.
- These variations affects the rheological properties of the bitumens despite the same range of conventional characteristics.
- Rheological characteristic could not be described by single chemical fraction but significantly by combinations of bitumen fractions.

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