Bituminous emulsions

Bitumen and emulsion properties: an innovative shared approach

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Abstract

Some viscosity variations of the bituminous emulsions are sometimes observed in the emulsion plants, depending on the bitumen deliveries. So, this study deals with the understanding of the bitumen characteristics that may impact the viscosity variations of the emulsions. 49 samples of bitumen 160/220 were collected in different refineries for 18 months. Several physicochemical properties of the bitumens were measured as SARA content, salt content, interfacial tension… Emulsions were produced with the different bitumen samples and in order to maximize the viscosity variations, the bitumen contents in the emulsions were chosen as 69% and 71%. So, 98 emulsions were produced in the laboratory and characterized. So, in total, more than 2500 data were generated and analyzed by statistical approach. The statistical analysis of the data highlights differences of physicochemical characteristics between the bitumens depending on their resource point. No strong viscosity variations were observed on the emulsions at laboratory scale. Trends were observed between the bitumen composition and some emulsions characteristics. However, no bitumen parameter explains in itself the viscosity variations of the emulsions.

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1. INTRODUCTION

Emulsions producers may encounter variations in the emulsions characteristics during their manufacture, mainly related to the viscosity parameter. In addition to the discrepancies or non-conformities regarding the emulsions quality, these fluctuations may cause problems during the emulsions laying and may lead to pavement premature degradations. Although some chemicophysical parameters inherent to the emulsion have a well-known influence on its viscosity (water content, particle size and type of surfactant) [1], they are not sufficient to explain alone the variations in viscosity from one emulsion to another. In a previous work, we have shown that asphaltenes are also active at the bitumen−water interface [2].

The fluctuations origin is not sufficiently well identified, although the bitumen used seems to play a significant role. Indeed, these variations may be visible:

- between two bitumen origins (when an emulsion plant changes refinery for its bitumen supply).
- between two deliveries from the same refinery even if the bitumen batch produced at the refinery is the same.
- during the year for the same resource point (essentially April-May and October), with sometimes unexpected changes.
- especially for emulsions containing 69% of bitumen.
- and mainly with 160/220 bitumen penetration grade.

COLAS, as road company and emulsion producer, and TOTAL, as bitumen supplier, have worked together to identify the bitumen chemicophysical characteristics that influence the viscosity fluctuations of emulsions. With this in mind, bitumens were sampled in different refineries and entirely analyzed. Emulsions were manufactured in the laboratory with all the sampled bitumens and then were characterized. More than 2500 data were collected and a statistical approach has been undertaken to investigate possible correlations between the bitumen properties and the emulsion characteristics, especially the viscosity.

2. EXPERIMENTAL

2.1. Bitumens

49 bitumens, 160/220 penetration grade (bitumens for emulsions), were sampled in 8 refineries between 2014 and 2016. The bitumen references and their respective sampling date (when available), are listed in Table 1. The bitumens A2 and A4 are acidified binders. The bitumens from the refinery H are known to be “difficult to emulsify”
The bitumens were analyzed according to different tests:

- Penetration 25°C – NF EN 1426
- Ring and ball softening point – NF EN 1427
- Viscosity at 135°C – NF EN 13702
- Density at 90°C – NF EN ISO 15326
- TOTAL acid number – NF T 66-066
- TOTAL Basic Number – ASTM D2896
- Chloride content (salinity) – NFM 07-023
- Chlorine content by fluorescence X – TOTAL method MA0124
- Elements contents (Cl, Al, Ca, Fe, K, Li, Mg, Na, Ni, P, Si, V, Zn) – IP 501 and TOTAL method MA ETS 000600.
- Heptane asphaltenes content - NFT 60-115
- SARA fractions by HPTLC – TOTAL Method 1065/13
- Interfacial tension and surface elasticity – TOTAL method CAB-0720-MO using a droplet tensiometer equipment - The test is done at 90°C in a cell under pressure. The bitumen droplet is in contact with D_2O (heavy water) at pH equal to 2.7. The interfacial tension and the surface elasticity are measured at t0 and after 19500 seconds (contact time between the bitumen and the heavy water). The measurements at t0 and at t = 19500 seconds respectively evaluate the ability of the bitumen to emulsify and the emulsion storage stability.

Table 1. Bitumen references (160/220 penetration grade)

Refinery	Bitumen reference	Sampling date	Refinery	Bitumen reference	Sampling date
A	A1	07/07/2014	E	E1	11/07/2014
	A2	07/07/2014		E2	28/07/2014
	A3	11/07/2014		E3	12/08/2014
	A4	19/08/2014		E4	27/08/2014
	A5	19/08/2014		E5	11/09/2014
	A6	02/10/2014		E6	26/09/2014
B	B1	04/07/2014		E7	10/10/2014
	B2	31/07/2014		E8	10/11/2014
	B3	18/08/2014		E9	27/10/2014
	B4	10/09/2014		E10	25/11/2014
	B5	15/09/2014		E11	21/10/2015
	B6	29/09/2014		E12	09/11/2015
	B7	13/10/2014		E13	27/11/2015
	B8	28/10/2014		E14	14/12/2015
	B9	12/11/2014		E15	23/12/2015
	B10	27/11/2014		E16	07/01/2016
C	C1	Unknown	F	F1	09/11/2016
	C2	Unknown	G	G1	02/07/2014
D	D1	Unknown		G2	23/07/2014
	D2	Unknown		G3	07/10/2014
	D3	Unknown		G4	16/01/2015
				G5	26/01/2015
			H	H1	Unknown
				H2	Unknown
				H3	Unknown
				H4	Unknown
				H5	Unknown
				H6	Unknown

2.2. Emulsions

Preliminary tests have been carried out in order to get an optimized emulsion formula and to decrease as far as possible the scatter of emulsion properties and results.
All the emulsions have been manufactured with the same colloidal mill (Emulbitume) at a high shear speed in the range 8500 to 9000 rd/min. The bituminous phase is heated at 145°C and the aqueous phase temperature is 45°C. Aqueous phase batches have been prepared in advance and used for a series of emulsions. The target for the final composition was:

Binder	69 %
Dinoram S ®	1.3 kg/T
Hydrochloric acid	1.3 kg/T

The bituminous emulsions were analyzed according to the following tests:

- Water content — EN 1428
- Residue on sieves — EN 1429
- pH — EN 12850
- Efflux time 40°C - ∅ 4 mm — EN 12846
- Dynamic viscosity @ 40°C — EN 13302
- Breaking value — EN 13075
- Storage stability (settling tendency) — EN 12847
- Granulometry — COLAS method

3. RESULT AND DISCUSSION

More than 2500 data were collected, on the bitumens and on the emulsions. So, a statistical analysis has been done to use the data and to look for possible correlations between the bitumens characteristics and the emulsions properties. In particular, the impact on the emulsions viscosity of the bitumens characteristics and other parameters, such as the experimental conditions of the emulsions manufacture, has been looked at.
In a preliminary step, the statistical analysis has been done on the bitumen data and then on the emulsions data to check for the presence of outliers that would require special treatment and to highlight atypical bitumens and/or emulsions.

3.1. Bitumens descriptive analysis

Figure 1 displays the penetration, ring and ball softening points and viscosities at 135°C values of the 49 bitumens. Even if there are few samples coming from some refineries, it can be seen that the penetrations and ring and ball softening points values are more or less scattered depending on the bitumen resource point. The penetrations values of the bitumens from the refinery D are low and even out of the specifications of the 160/220 penetration grade (Figure 1). Nevertheless, these values have not been discarded, considering the repeatability/reproducibility of the penetration test. Figure 1 shows that the viscosities at 135°C of the bitumens from the refinery A are significantly higher than those of other bitumen resource points (values circled in red). No viscosity differences between the acidified and the non-acidified bitumens of the refinery A were observed.

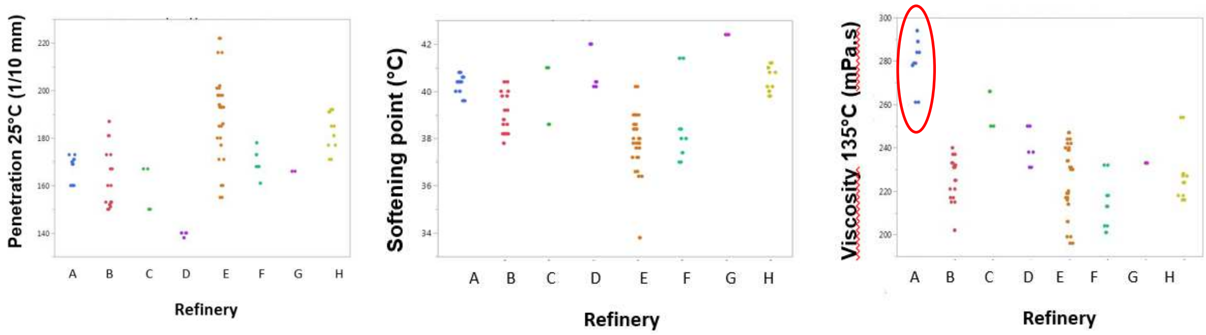


Figure 1: Penetration at 25°C, ring and ball softening point and viscosity at 135°C of the bitumens

Figure 2 displays the asphaltenes content and the relationship between the aromatics content versus the resins content for the 49 bitumens. On the left graph, the bitumens from the refinery H, known to be difficult to be emulsified, display the highest asphaltenes content (Figure 2, values circled in red on the left graph). On the contrary, bitumens from the refinery B are lower in asphaltenes (Figure 2, values circled in red on the left graph). Regarding the asphaltenes content, the bitumens from the refinery E are splitted into 2 groups: the lower asphaltenes contents correspond to the bitumen sampled in 2014 and the higher to the ones sampled in 2015.
The right graph of Figure 2 displays the relationship found between the aromatics and the resins content. The majority of the bitumens are on or close to the linear regression line except the bitumens from the refinery C (values circled in green on the right graph of the Figure 2). Once again, the bitumens from the refinery A appear to be different as they are low in aromatics and rich in resins, compared to the other bitumen (Figure 2, values circled in black on the right graph).

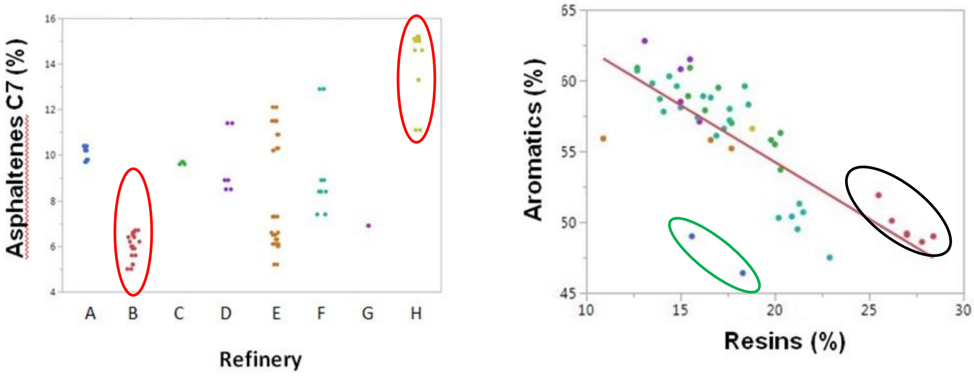


Figure 2: Asphaltenes C7 content and relationship aromatics vs resins of the bitumens

Table 2 presents, for 9 elements, the correlation coefficients between these element contents. The highest coefficients are highlighted in green in Table 2. It can be noted some tendencies between the Ca-Mg, Ca-V, Mg-Ni and Mg-V contents. The highest correlation has been observed between Nickel and Vanadium contents.

Table 2. Correlation coefficients of the elements contents analysis

	Ca	Fe	K	Mg	Na	Ni	Si	V	Zn
Ca	1,0000	0,1011	0,1283	0,8257	0,1342	0,6607	0,1154	0,7132	-0,5103
Fe	0,1011	1,0000	0,1117	0,0167	0,1893	0,3260	-0,0337	0,0998	-0,2359
K	0,1283	0,1117	1,0000	0,3262	0,2474	0,3230	0,0319	0,1886	-0,1124
Mg	0,8257	0,0167	0,3262	1,0000	0,3858	0,7637	-0,0374	0,8127	-0,5227
Na	0,1342	0,1893	0,2474	0,3858	1,0000	0,5794	0,1821	0,5418	-0,3323
Ni	0,6607	0,3260	0,3230	0,7637	0,5794	1,0000	0,1721	0,9135	-0,5311
Si	0,1154	0,0337	0,0319	-0,0374	0,1821	0,1721	1,0000	0,1614	0,0877
V	0,7132	0,0998	0,1886	0,8127	0,5418	0,9135	0,1614	1,0000	-0,4974
Zn	-0,5103	-0,2359	-0,1124	-0,5227	-0,3323	-0,5311	0,0877	-0,4974	1,0000

The Cl, Al, Li, and P contents have not been taken into account in the analysis because the values are roughly constant. The chloride content is also not considered because the values are low and more or less the same (< 20 ppm) for all the samples. Only 2 samples from refinery H display salt content higher than 50 ppm.
In the same way, the TAN values have not been taken into account; all the samples display a TAN lower than 0.5 mg KOH/g and very often a TAN equal to 0,1 mg KOH/g except the samples C1 and C2 which the TAN are higher than 2,5 mg KOH/g. The TBN value can be predicted from 4 variables: the K, Zn and resins contents and the density at 90°C ($R^2 = 0.82$).

Some studies mentioned that the bitumen composition impacts its interfacial tension, its surface elasticity and the emulsions characteristics [2] [3] [4] [5] [6]. We have looked for possible correlations between the bitumen bulk and the bitumen interfacial characteristics.
Figure 3 shows significant differences in interfacial tension at t = 0 s and t = 19500 s across bitumen resource points.

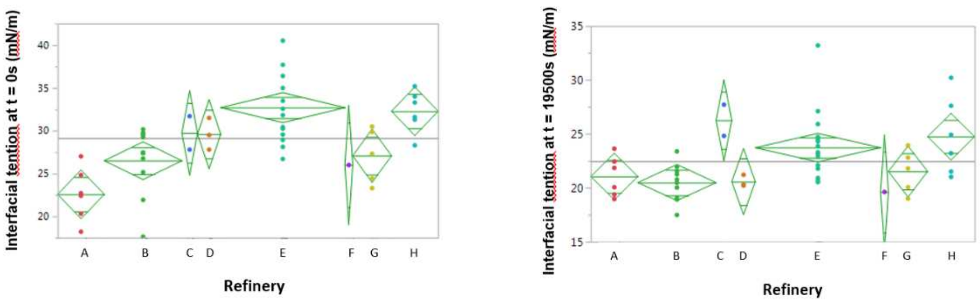


Figure 3: Interfacial tensions of the bitumens

On Figure 4, the surface elasticity of the bitumens is represented as a function of their resins and calcium contents. The blue zones correspond to low surface elasticity. Dark blue areas correspond to the lowest surface elasticity. On the opposite, the red zones correspond to high surface elasticity. And the bright red zones correspond to the highest surface elasticity.
So, it can be noted that the bitumens, from the refineries E and F, with low resins and calcium contents display higher surface elasticity. We can differentiate, for example, the bitumens from refinery A. Their surface elasticity is quite low compared to that of other bitumens. Bitumens from refinery H show intermediate values of surface elasticity.

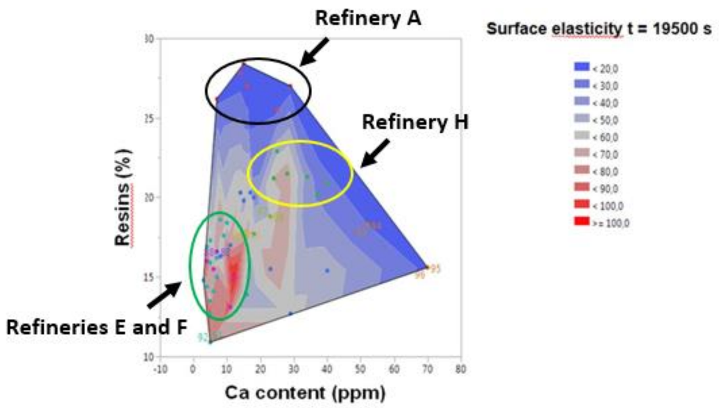


Figure 4: Surface elasticity (t = 19500 s) of the bitumens versus the resins and the Ca contents

In conclusion, the analysis highlights differences between the bitumens, depending on the resource point. In the next paragraphs, we will investigate the relationship between bitumens physico-chemical properties and emulsions mechanical characteristics.

3.2. Emulsions characteristics analysis

As the viscosity of bituminous emulsions is very sensitive to the binder content, most of the bitumen samples have also been used for producing emulsions with 71% of binder (target value). To minimize the effect of the binder content, the viscosities were recalculated at exactly 69% and 71% of binder content, thanks to the interpolation of the results obtained from 69% (target value) and 71% (target value) emulsions.

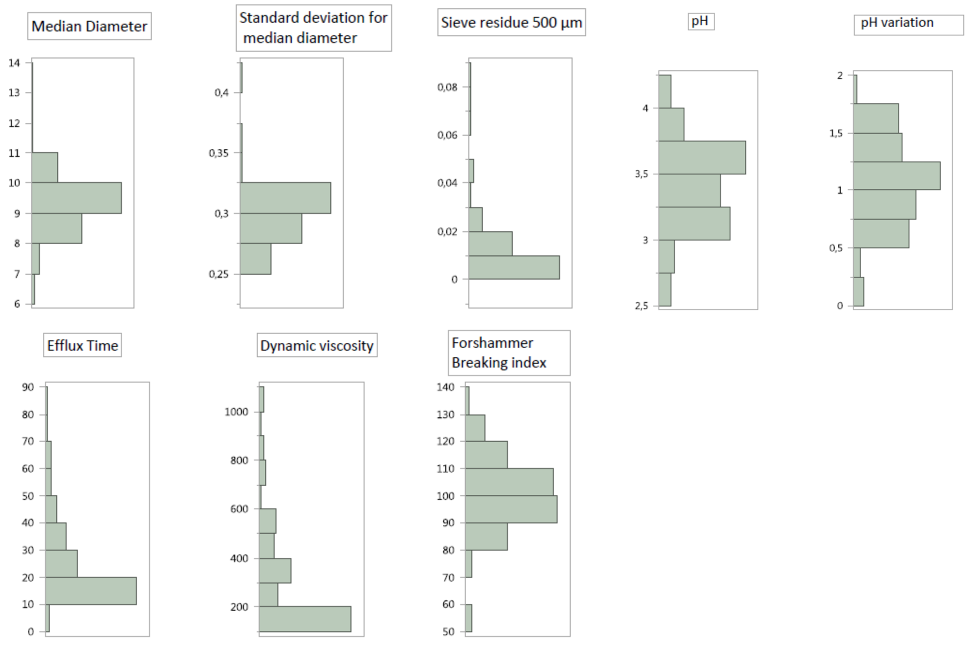


Figure 5: Granulometry, pH, residue on sieves, viscosity and breaking value of emulsions

Figure 5 displays the median diameter, the pH, the pH variation, the residue on sieves, the efflux time, the dynamic viscosity and the Forshammer breaking index for the 69% emulsions.

The efflux times are not very high since only a few values are over 40 s. This viscosity level is relatively low compared to the variability observed among industrial emulsions.

The pH, the pH variation, the efflux time and the dynamic viscosity could be described according to a normal distribution law. By contrast, the other characteristics such as the median diameter and the residues on sieves do not comply with a normal distribution law.

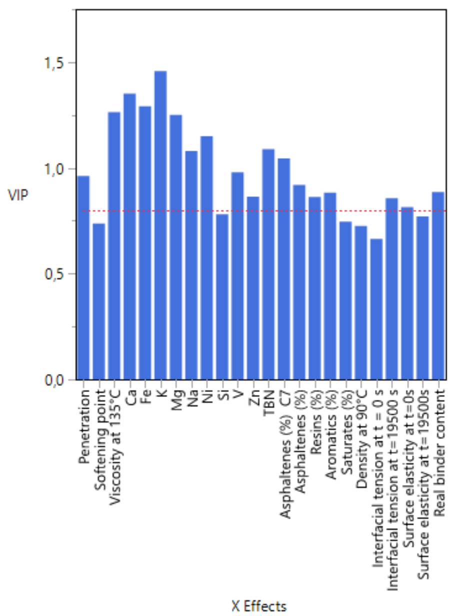
A detailed analysis of emulsions characteristics shows quite good correlations between the pH and the pH increase, the efflux time and the dynamic viscosity and also between the median diameter and the standard deviation. Similar conclusions could be drawn from the 71% emulsions results. Therefore, in the next steps, emulsion description could be limited to 3 parameters such as dynamic viscosity, pH and median diameter.

3.3. Correlations between the bitumen properties and the emulsions characteristics

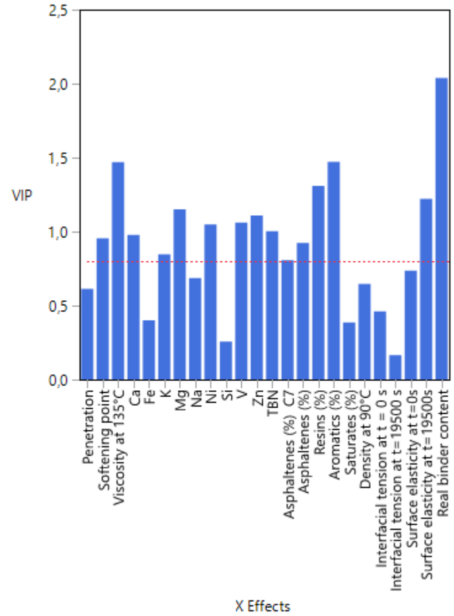
The objective is to establish relationships between the bitumen and the emulsions characteristics. First, we focus on 4 representative emulsions characteristics, as seen in paragraph 3.2: the median diameter, the pH, the dynamic viscosity and the storage stability. One of the standard techniques used to rank input variables according to their influence on a given output variable is linear regression. In the present work, the correlation search has been done using a particular version of regression called the method of the Partial Least Squares Regression (PLS method) [7], which is particularly suited when the number of input variables is large compared with the number of data points, and when they are correlated).

No correlation has been observed between the bitumen characteristics and the emulsion stability (measured from the deposit on sieves).

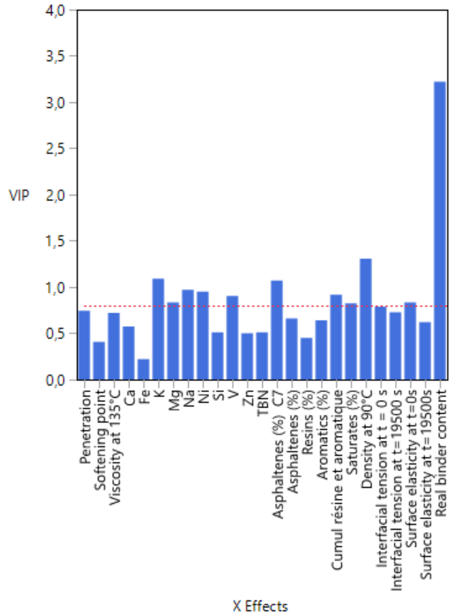
Figure 6 displays the importance of bitumen variables in the models for pH, median diameter, and equivalent dynamic viscosity. A bitumen variable can be considered as statistically important if the blue bar exceeds the red dotted line, it is statistical evidence of a link between that bitumen variable and the considered emulsion characteristics. The higher the bar, the greater the importance of the bitumen variable on the characteristic of the emulsion.



pH



Median diameter



Equivalent dynamic viscosity

Figure 6: Important bitumens characteristics regarding some emulsions characteristics
VIP = Very Important Parameter

Regarding, the pH value, 71% of its variability is mainly explained by the bitumens elements contents (Ca, Fe, K, Mg, Na, Ni, V and Zn), the TBN, the SARA fractions, the penetration and the bitumen viscosity at 135°C (Figure 6). The other 29% of the pH variability are linked to other factors, such as the experimental conditions of the emulsion production.
In the case of the median diameter, 68% of its variability is explained by some bitumens characteristics (Figure 6): the viscosity at 135°C, the resins and the aromatics content, some chemical elements (Mg, Ni, V, Zn), the TBN and the surface elasticity at 19500 s. But the main parameter is the bitumen content in the emulsion: the higher the bitumen content, the higher the median diameter.
Now, if we look at the equivalent dynamic viscosity, 78% of its variability is linked to some bitumen characteristics and mainly to the bitumen content in the emulsion (Figure 6). The other 22 percents are explained by other factors, such as the experimental conditions of the emulsion manufacture again.

A variety of PLS, called PLS2, has been used to find a global model, considering all the emulsions characteristics and all the bitumens charactristics (Figure 7). The quality of the obtained model is poor because it explains only 54% of the variability of the emulsion characteristics. The other 46% are explained by other parameters, once again the production conditions. Nevertheless, the Figure 7 gives the information that among all the bitumen characteristics, the bitumen content of the emulsion is far away the most important parameter. The influence of the other bitumens characteristics is lower.

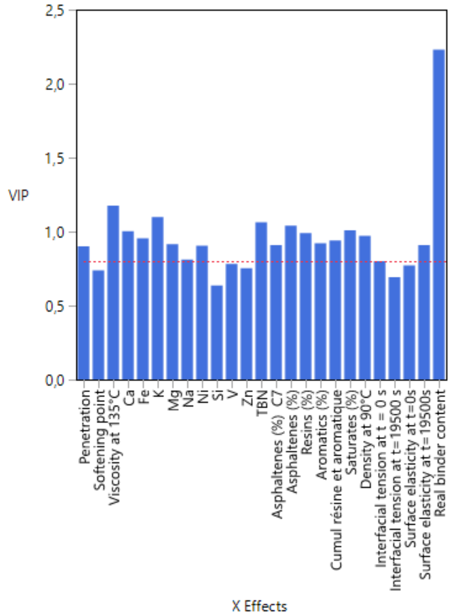


Figure 7: Emulsions characteristics vs bitumen characteristics (PLS2 method)
VIP = Very Important Parameter

4. CONCLUSION

49 bitumens and 98 emulsions have been completely characterized to study the impact of the bitumen on the emulsion characteristics, especially the viscosity. More than 2500 data have been collected and PLS method has been used to search correlations between the bitumen and the emulsions characteristics.
The bitumens analysis show that there are differences in properties and composition between them, depending on their ressource point.
Emulsions analysis shows that viscosity is not as high and versatile as it could be noticed with industrial production from emulsions plants. The emulsions are well described by focusing on pH, viscosity and granulometry (median diameter).
The correlation research between the bitumens charateristics and the emulsions properties show that the bitumen variability can explain only a part of the emulsion variability. Among all the characteristics, the bitumen content is emphasized as the main factor to explain the emulsions properties variability. Other parameters, such as the experimental conditions of the emulsions production, have also an impact on the emulsions properties. And yet, in this study, all the emulsion have been manufactured in the laboratory where all the production parameters can be more easily managed. We can assume that the production parameter is even more critical at the plant.

5. ACKNOWLEDGEMENTS

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