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Understanding Asphaltenes Stability in Marine Fuel Oil Through Separability Number

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Abstract: Near Infra-red (NIR) Spectroscopy method was used to analyze NIR light transmittance through Marine Fuel Oil (MFO) samples. This method uses Separability Number as a measure of asphaltene stability in MFO. The separability number as given by the Near Infrared Optical Scanning Machine (NIR-OSM) directly indicates the stability reserve in the MFO. In this study, an in-depth analysis of separability number to understand its science and meaning as a method for determining asphaltenes stability in MFO is presented. An analysis of rates of asphaltene flocculation, aggregation and settlement for six Intermediate Fuel Oil (IFO 180) samples is also presented. It was realized that separability number is a fast and reliable method for asphaltene stability analysis in MFO. The gradient of the graph of line of best fit for average percentage NIR transmittance can also be used to predict the stability reserve in the MFO. The smaller the gradient value; the more stable is the fuel oil. It was also established that there are three regions of NIR transmittance; low transmittance region, acceleration region and high transmittance region. The dominance of any of the three regions directly influences Separability Number obtained for a sample.

Key words: Asphaltenes stability, separability number, near infrared (nir) spectroscopy, marine fuel oil

INTRODUCTION

Asphaltenes are the heavy, polar, aromatic component of fuel oil or crude oil which is insoluble in n-alkanes (pentane, heptane) but soluble in toluene, xylene and naphtha (Trejo *et al*., 2009; ASTM D7061-06, 2006). They are generally characterized by fused ring small aliphatic side chains, aromatic and polar hetero-atoms that contain functional groups (carboxyl acids, carbonyl, phenol, pyrolles and pyridines) capable of intra and inter-molecularly donating or accepting protons (Gawrys and Kilpatrick, 2004). Asphaltenes are believed to exist as colloidal dispersions in the bulk fluid medium of saturates, aromatics and resins. While asphaltenes will tend to remain as colloidal suspension in the fluid medium, factors such as oil composition, nature of asphaltenes, temperature and pressure can cause asphaltenes to flocculate (Maijoni, 2011). If unstable, asphaltenes will aggregate or colloidally disperse into visible large masses that may settle or remain suspended in the fluid medium (Gharfeh *et al*., 2004). This flocculation poses a threat to fuel oil handling equipment, fuel injectors and fuel combustion characteristics (Shimizu *et al*., 1998).

Therefore, it is important that the stability of fuel oil is predicted well in advance to curb the costly problems that can arise during use.

Yen *et al*. (2001) discussed several asphaltene stability analysis methods and experimentally compared their effectiveness. The methods can broadly be classified as Spot Test Techniques, Stability Indices Techniques and Solvent Titration Techniques. NIR Spectroscopy falls under the latter technique but uses NIR is to scan through a sample of fuel oil under n-alkanes induced phase separation. The rate of phase separation is then reported as Separabiity Number which acts as oil Stability Reserve Indicator (ASTM D 7061-06, 2006).

Near Infrared Spectroscopy has been used for sample analysis for quite some time. Infrared energy is the electromagnetic energy of molecular vibration (Workman Jr, 2001). The energy band spans the wave length range from 780nm to 2500nm. NIR spectroscopy can quickly and accurately be used in the non-destructive analysis of samples. In the asphaltene stability analysis, the decrease or increase in radiation intensity (transmittance) is measured. As asphaltenes flocculate, the change in transmittance is recorded and analyzed for stability reserve via the separability number. In this experiment, a NIR probe of 850nm was used. The sample was prepared according to ASTM D 7061. Other variables like temperature and pressure were well controlled.

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EXPERIMENTAL SECTION

The reagents used included toluene and n-heptane. The test samples were IFO 180 from China Marine Bunker Supply Company Ltd obtained from six different users. They were numbered as (1) Ningbo sample, (2) Shanghai ZR Sample Shenran7, (3) Shanghai ZR Sample Hailian 62, (4) Shanghai ZRC sample 1, (5) Shanghai ZR sample Ludingtan and (6) Shanghai ZR sample Tongyin.

During the experiment, an appropriate mass of fuel oil was measured (5 g) by electric balance with 0.001 g precision. The fuel oil was then diluted with toluene, in a weight ratio of 1:9 then put in a bottle with cap and shaken. The oil-toluene solution was then stirred by a magnetic stirrer for about 1 h. The Optical Scanning Machine (OSM) was then turned on and set for scanning. 23 mL of n-heptane was transferred into a glass bottle. Using a pipette 2 mL of the oil/toluene mixture was added to the heptane and the mixture shaken for about 6 sec. Using a pipette, 7 mL of the oil-toluene-heptane mixture was immediately transferred into the cylindrical clear glass vial and the cap screwed tightly. The machine was then turned on for measurement of NIR transmittance though the sample. After the measurement was finished, the glass vial was removed from the OSM and cleaned with toluene.

Table 1 shows the average percentage NIR transmittance for the six oil samples used in the experiment. The table further displays the separability numbers of the samples calculated as the standard deviation of the average transmittance of each of the samples. Figure 1-6 shows the percentage transmittance of NIR from the different oil samples. From the graphs, we can clearly understand the onset and rate of the progress of flocculation from the different oil samples. Figure 1 is for sample Ningbo without additives. This gives the highest separability number as seen from Table 1.

Table 1: Average percentage of transmittance for the six oil samples and their separability numbers

	Samples					
	1	2	3	4	5	6
Average transmittance (%)	5.90	4.97	6.64	6.06	5.18	5.66
	5.93	5.11	7.07	6.02	5.23	5.59
	6.03	5.38	8.02	6.01	5.38	5.54
	6.21	5.69	9.86	6.00	5.55	5.51
	6.55	6.20	12.43	6.00	5.79	5.49
	7.02	7.04	14.90	6.01	6.10	5.49
	7.91	8.33	16.93	6.01	6.51	5.48
	9.57	10.02	18.29	6.04	7.01	5.48
	11.93	11.89	19.60	6.02	7.56	5.50
	14.79	13.74	20.45	6.04	8.05	5.49
	17.51	15.26	21.22	6.11	8.56	5.50
	19.79	16.47	21.95	6.16	9.01	5.52
	21.55	17.42	22.57	6.24	9.40	5.58
	22.98	18.43	23.21	6.36	9.82	5.67
	24.06	19.25	23.79	6.49	10.15	5.79
	25.06	20.02	24.26	6.73	10.42	5.98
Separability No.	7.392	5.624	6.293	0.212	1.884	0.134

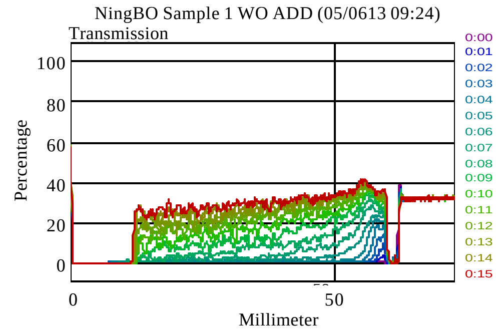

Fig. 1: The percentage of NIR transmittance for sample 1

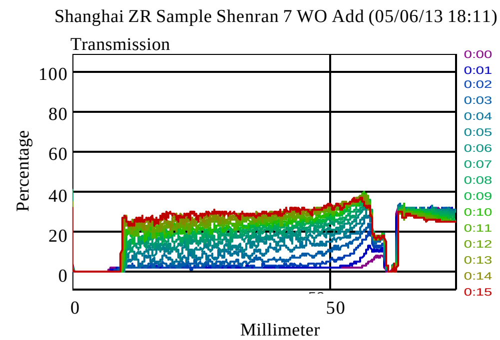

Fig. 2: The percentage of NIR transmittance for sample 2

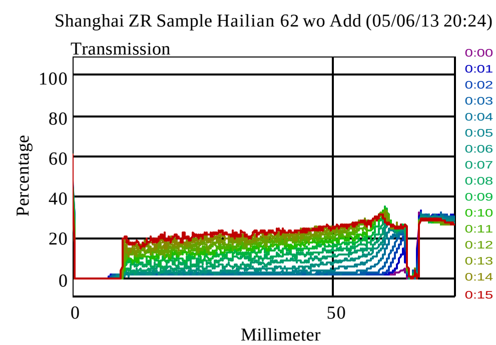

Fig. 3: The percentage of NIR transmittance for sample 3

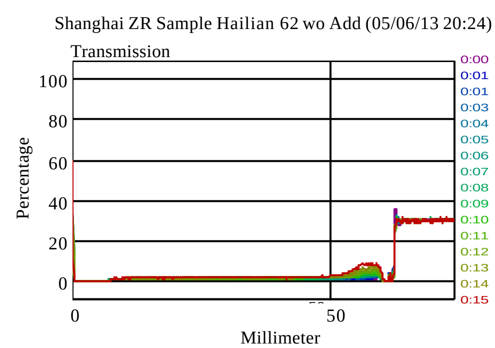

Fig. 4: The percentage of NIR transmittance for sample 4

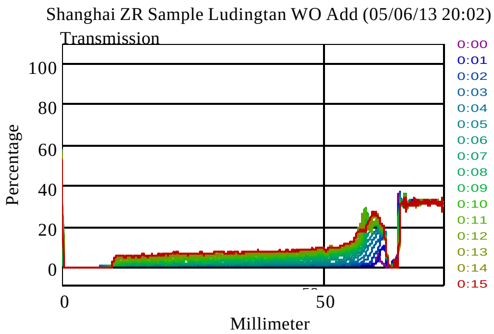

Fig. 5: The percentage of NIR transmittance for sample 5

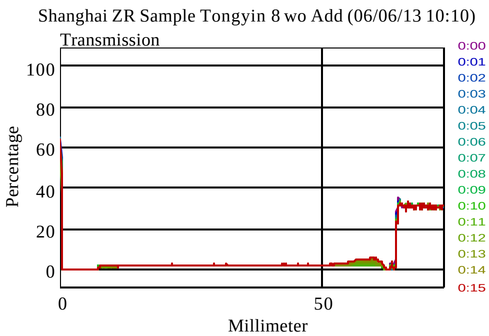

Fig. 6: The percentage of NIR transmittance for sample 6

Sample 6 (Shanghai ZR sample Tongyin) and sample 4 (Shanghai ZRC) gives the lowest separability numbers as can also be seen from Table 1.

DISCUSSION

Separability number is a rate-related factor that measures how easy or difficult a fuel oil phase-separates on addition of n-alkanes. From the experiments, it was observed that NIR transmittance varies greatly for a less stable fuel oil than for a more stable one. The transmittance along the glass vial increase with time as asphaltenes agglomerate out of solution and fall to the bottom of the test glass vial. The faster the asphaltenes flocculate and settle; the higher is the separability number. Sample 4 and 5 portrays a stable fuel oil since the variance in NIR transmittance is very low. The separability number is a measure of the standard deviation from the average transmittance. As can be seen from Ttable1, the samples have separability numbers decreasing in the order from No. 1, 3, 2, 5, 4 and 6. Sample 1 has the highest separability number hence the lowest stability reserve. From ASTM D 7061, the oils with 0-5 separability numbers are considered to have high stability reserve and are most highly unlikely to flocculate. Fuel oils with separability

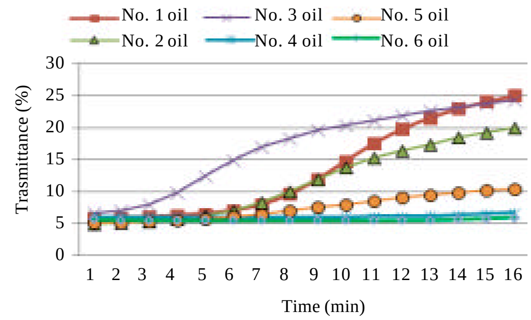

Fig. 7: The percentage of NIR transmittance for the six oil samples against time

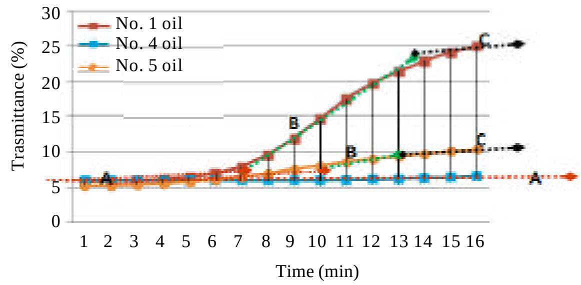

Fig. 8: The percentage of transmittance for samples 1, 4 and 5 showing the stability regions

numbers of between 5-10 are moderately stable and are not likely to flocculate under normal circumstances unless exposed to worse operation and storage conditions. If the separability number of the fuel oil is above 10, stability reserve is very low and the asphaltenes in the fuel oil will easily flocculate or have already started to flocculate. From the above analysis, samples 1 and 3 are moderately stable. Samples 2, 4, 5 and 6 are stable with samples 4 and 6 leading the stability ranking. The gradient of the line of best fit also indicates how fast or slow the transmittance increases. Samples 4 and 6 are stable as can be seen from Fig.7 since the gradient of the line of best fit for the average transmittances are very small i.e., 0.0004 and 0.0001, respectively. The gradient of the line of best fit for oil No. 1 is the biggest followed by oil No. 3, 2 and then No. 5 with gradients of 0.0149, 0.0128, 0.0116 and 0.0039, respectively. By just looking at the gradients, we can comparatively determine the stability of an oil sample relative to the others. The rate of NIR transmittance falls into three major stability regions.

Low transmittance region: This region is characterized by low transmittance since most of the asphaltenes have not yet phase separated from the solution. As denoted by letter A in Fig. 7 and 8, the region exhibits low but almost

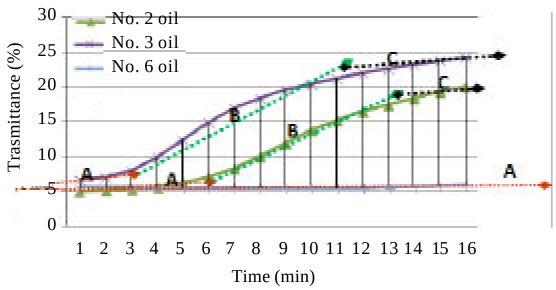

Fig. 9: The percentage of transmittance for samples 2, 3 and 6 showing the stability region

constant transmittance increasing slowly as the oil phase separates allowing asphaltenes to agglomerate and fall to the bottom of the test vial. The longer the region; the more stable is the asphaltenes in the oil. Sample 4 and 6 consists of almost entirely this region. Others follow in the order of samples 5, 2, 1 and 3 in decreasing dominance.

Acceleration region: This region is characterized by increasing transmittance. If the transmittance increases faster and continues for a long time, then it implies that asphaltenes in the sample are very unstable. The region is denoted by letter B in Fig. 8 and 9. The region has a significant effect on both the gradient of the line of best fit and the separability number. Sample 1, 3 and 2 have higher separability numbers hence steeper and/or longer region B.

High transmittance region: The region exhibits high percentage transmittance as compared to region A. The transmittance is almost constant; just increasing slowly. This region influences the stability positively. If region B for a given sample is short while region C is relatively long, we expect the sample to exhibit comparatively low separability number unlike if the region was short with a longer region B.

CONCLUSION

Separability number is a powerful, fast and reliable way for determining asphaltene stability of a given oil sample. The higher the separability number; the more unstable an oil sample is. Further, the gradient of the line of best fit of the percentage of transmittance data can also be used as an indicator of stability. The smaller the gradient; the higher is the stability reserve. It was also found that transmittance through oil samples falls into three major regions indicated by A, B and C. Regions A and C have positive influence on asphaltene stability analysis results while region B influences stability negatively.

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