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INVESTIGATION ON VISBREAKING-RESIDUE AND FINISHED FUEL OIL PRODUCT CLOSED CUP FLASH POINT

Dicho Stratiev

Research Department, Lukoil Neftochim Bourgas, 8104 Bourgas, Bulgaria, e-mail: stratiev.dicho@neftochim.bg

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Abstract

Investigation on the closed cup flash point of visbreaking residue and finished fuel oil was carried out in the Lukoil Neftochim Bourgas, Bulgaria (LNB). It was found that depending on preliminary sample treatment flash point in closed cup of the fuel oil and visbreaker residue can be differed by 26^{0}C. This difference is much higher than the specified in EN ISO 2719 repeatability – 5^{0}C and reproducibility - 10^{0}C and was observed in three laboratories: LNB Research laboratory, Saybolt and SGS. A possible explanation of the observed difference in the flash point of the fuel oil is the fact that the residual fuel oil is a colloidal dispersion system and the different treatment of a sample results in different stability of the colloidal dispersion system which eventually affect the measured value of flash point in closed cup.

Key words: fuel oil; visbreaker residue; flash point; colloidal dispersion system.

1. Introduction

Residue fuel oil at present is used mainly as marine fuel oil IFO-380. The present specification requirement of product flash point determination is to be carried out by closed cup method and not to exceed 60^{o}C. Up to the beginning of the last year Lukoil Nephtochim Bourgas (LNB) produces residue fuel oil which specification has required its flash point to be determined by open cup method and not to exceed 110^{o}C. It may be seen from data included in Table I that there is no correlation between LNB fuel oil component flash points determined by open and closed cup methods. While the specification requirement for flash point not lower than 110^{o}C obtained by open cup method has not been serious problem for residue fuel oil production at LNB the implementation of the new specification requirement for flash point not lower than 60 ^{o}C by closed cup method is difficult to be met at the residue fuel oil production. One example for this data presented in Table 1.

Table 1 The LNB residue fuel oil components flash points determined by open and closed cup test methods

No	Sample	Flash point (CP cup), ^{o}C EN ISO 2719	Flash point (OC), ^{o}C Ст на СИВ 1496-79
1.	Fuel oil (FO) from Thermal cracking (TC)	68	115
2.	Fuel oil for own needs (Tank farm 31)	125	149
3.	FCC heavy catalytic gas oil	124	128
4.	FCC slurry	80	148
5.	ADU(atmospheric Distillation Unit) -4 Atmospheric gas oil (AGO)	142	163
6.	Heavy pyrolysis resin from Ethylene unit	72	-
7.	FO – Tank farm *	58	102
8.	FO **	61	126

**- FO (fuel oil from tank farm) produced by the following formula: 86% Visbreaker residue; 7,6 % FCC HCO; 3,8 % FCC Slurry and 2,6% Atmospheric gas oil from crude distillation unit.*
*** - Fuel oil (FO) laboratory sample prepared by the formula of fuel oil from tank farm shown above.*

It is obvious from this data that all components for fuel oil production have closed cup flash point over 68°C. The closed cup flash point of the end product obtained by blending of Visbreaking - residue (86 %), FCC slurry (7,6 %), FCC HVGO (3,8 %) and atmospheric gas oil (2.6 %) is 61°C and is lower than this of all components. An investigation of the fuel oil flash point problem has been carried out. The purpose of this work is to discuss the results of this investigation.

2. Results and discussion

The commercial test at which outlet temperature at "Visbreaker" unit furnaces was increased from 436°C up to 455°C at rate of 215 m^3/h (175 t/h) on September 2008 was carried out. It has was established within this investigation that as furnaces outlet temperature increases the conversion increases also and this is accompanied by vacuum residue Visbreaking unit main fractionator's pressure increase and Visbreaking residue closed cup flash point reduces (Fig. 1). It was established after the coke removal from the column bottom at the beginning of 2009 and the test carried out in March 2009 that at one and the same conversion the main fractionator's bottom pressure was lower and this resulted to higher value of vacuum-residue closed cup flash point (Fig. 2). On the base of these data we reached to the conclusion that the main fractionator's bottom pressure is parameter controlling closed cup flash point property of the vacuum residue. However, detection of Visbreaking residue closed cup flush point low values at low "Visbreaker" init rates and as a result main fractionator's pressure low values made us to carry out series of experiments for determination of flash point by closed cup method as of Visbreaking residue so also of the finished fuel oil product. The first experiment was carried out on 28.08.2009. Unit rate according to feed was 134 t/h (160 m^3/h). Only one furnace was on operation and furnace outlet temperature was 447 °C. Vacuum residue conversion up to 360°C was 16 % and main fractionator's bottom pressure was 2.8 kg/cm^2. According to the data presented on Fig. 1 and 2 Visbreaking residues closed cup flash point should have been not lower than 70°C. Samples of 1 liter volume in 5 bottles were sampled on that day. Sampling was realized at connected water cooler to the sampler in order to reduce sample temperature up to 40 – 50°C.

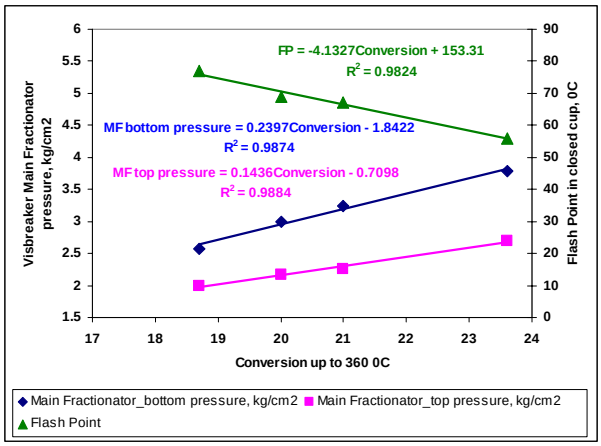

Fig. 1 Dependence of Visbreaking residue closed cup flash point on bottom and top Visbreaker Main fractionator pressure

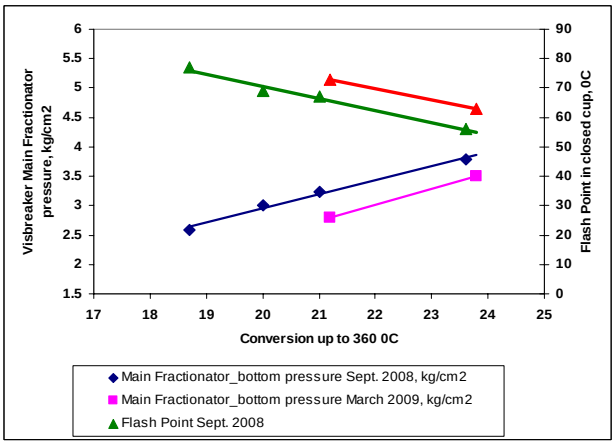

Fig. 2 Dependence of Visbreaking residue closed cup flash temperature on Visbreaker Main fractionator bottom pressure before (Sept. 08) and after cleaning of column bottom from coke (March 09)

The first bottle was tempered at 40°C in thermostat within ½ hour and then a specimen was sample from it in order closed cup flash point at LNB Research Laboratory to be determined. It was detected 61°C flash point. The second bottle was submitted to Saybolt laboratory to determine closed cup flash point property. At first Saybolt operators checked sample temperature that was 36°C and then they loaded the apparatus for determination of closed cup flash point. As the sample was poured out its temperature reduces to 33°C after which it started to increase by rate determined by the standard for closed cup flash point according to EN ISO 2719. The detected sample closed cup flash point was 36°C. At such difference of Visbreaking residue closed cup flash point values doubt arose that due to sample tempering up to 40°C at the Research laboratory it was impossible to detect value lower than 40°C of flash point. That is why, the

third bottle with Visbreaking residue was used for second determination of closed cup flash point at the Research laboratory. The sample temperature was 36°C. When the sample was loaded for closed cup flash point determination sample temperature reduced to 34°C and then started to increase. The detected flash temperature at this determination was 36°C i.e. it was equal to the closed cup flash point value determined by Saybolt Laboratory. After 2 hours the fourth bottle of the same sample was submitted to SGS Laboratory for determination of closed cup flash point property. This sample temperature was 30°C. The detected flash point by SGS was 63°C. These results represented an illustration for how the preliminary treatment of sample to be analyzed effects closed cup flash point property value of Visbreaking residue product. In the standard EN ISO 2719 for determination of closed cup flash point is written the following:

„9.1.4 Samples that are semi-solid or solid at ambient temperature"

Sample in the container is heated up to 30°C ± 5°C in bath or in drying-oven (6.4) for 30 min or up to temperature not exceeding 28°C below the expected flash point depending on which of both temperatures is higher. If after 30 min the sample is not completely liquefied heating continues on 30 min periods as it is described. The sample should not to be overheated since this may result to volatile substances loss. After careful agitation it is continued according to the procedure described in point 10"

The visbreaking residue pour point determined was 21°C (Table 2) because of that it may be consider to belong to this sample class that are semi solid or solid at ambient temperature.

Table 2 Physical-chemical properties of Visbreaking residue and Visbreaker unit diesel fraction

Date	7.9.09	7.9.09	8.9.09	8.9.09	7.9.09
Visbreaker unit furnace outlet temperature, °C	445	450	450	455	Visbreaker diesel
Properties	Visbreaker Residue 12h	Visbreaker Residue 16h 30min	Visbreaker Residue 10h	Visbreaker Residue 15h	
		Hot filtration sediments, %			
Prior aging	0.024	0.038	0.045	>0.5	
After aging	0.028	0.039	0.053	Unstable Visbreaking residue	
Pour point, °C		21			
Closed cup flash point, °C	60	32	42	61	below 1,5°C
Density, d4/20, g/cm^3					0,8406
		ASTM D-1160 distillation			
IBP	211	229	210	228	IBP-154
5%	311	337	322	330	5%-194
7%	360				10%-204
8%		360	360	360	20%-218
10%	392	214	396	388	30%-230
20%	454	464	452	438	40%-242
29%		512			50%-254
30%	506		512	496	60%-270
31%	512				70%-288
33%				512	80%-307
					90%-330
					95%-354
					EBP-355
					Recovery-97.5%

The fifth bottle of the same sample Visbreaking residue sampled on 28.08.2009 was tempered for ½ hour at 30°C. Then, specimen of it was sampled for closed cup flash point determination at the Research Laboratory. The detected value was 62°C. In other words for one and the same Visbreaking residue sample we received for closed cup flash point values between 36 and 62°C. This value is beyond the limitation for repeatability (5°C) and reproducibility (10°C). The

most probable reason for this difference is due to the fact that Visbreaking residue is colloid-disperse system consisting of over molecular structures (micelles) with composition including asphaltenes and high molecular paraffin as micelle nucleus and lower molecular hydrocarbons that build up the solvate micelle cover (complex structural unit)[1-6]. It is typical for these colloid-disperse systems to be polydisperse one and it is observed abnormal behavior at definite conditions. The same sample of Visbreaking residue was mixed at 50°C with FCC HCO and slurry, and CDU diesel fraction in the same ratio as used for production of finished fuel oil product. Then, the obtained mixture was tempered at 30°C for ½ hour and loaded for closed cup flash point determination. The detected temperature was 36°C. The same mixture was obtained by components mixing at 30°C, tempered for ½ hour at 30°C and loaded in apparatus for closed cup flash point determination. The detected flash point was 58°C. The most likely mixing at different temperatures affected intermolecular forces interaction in complex structural units of the fuel oil composition. Complex structural units of different stability resulted. Where stability was higher, the complex structural units were destructed more difficultly and low molecular hydrocarbons build up solvate cover released at higher temperature and as a result it was detected higher closed cup flash point. The finished fuel oil pour point was determined to be 6°C. The next experiment was mixing of Visbreaking residue sample with FCC HCO and slurry at 50°C in the same ratio as the one of the previous two samples; mixture was tempered at 20°C for ½ hour and loaded to apparatus for closed cup flash point determination. In this case the detected flash point was 66°C. On the base of these studies was assumed that Visbreaking residue sample should be tempered at 30°C for ½ or an 1 hour and after that to be loaded in apparatus for closed cup flash point determination and end fuel oil product samples should be tempered at 20°C for 1/2 or an 1 hour and then to determine property closed cup flash point. The next experiments included increase of the LNB Visbreaker unit furnace outlet temperature from 443 up to 455°C and sampling visbreaking residue and finished fuel oil product samples for closed cup flash point determination. In Tables 2 and 3 it is presented products distribution at different operation modes of Visbreaker unit and visbreaking residue and visbreaker unit diesel fraction physical-chemical properties.

Table 3 Visbreaker unit products distribution at different furnace outlet temperature and different feed rate

Date	7.9.09	8.9.09	8.9.09	9.9.09
Rate, t/h	175	179	167	155
Furnace outlet temperature, ^{0}C	443	450	455	450
Visbreaker unit material balance, %				
Hydrocarbon gas	3.0	3.3	3.9	3.8
Naphtha	2.4	2.4	3.7	3.3
Diesel fraction	6.5	8.0	9.0	7.4
Visbreaking residue	87.6	86.1	83.4	85.3
Total	99.33	99.63	99.75	99.57
Vacuum residue conversion up to 360^{0}C, %	18.0	19.7	22.4	20.4
Computed conversion of first order kinetics of vacuum residue Visbreaking process, %	18.0	19.6	22.0	21.8

It is obvious from these data that as the furnaces outlet temperature was increased and unit rate decreased the conversion increased regularly. The data as well show that as difference of the other experiments. (Figures 1 and 2) closed cup flash point does not correlate with conversion. This temperature does correlate also neither with initial boiling point nor with $T_{5\%}$ point of the Visbreaking-residue distillation. All flash points were obtained as primary Visbreaking-residue samples were tempered at 30 °C for ½ hour. These data show that temperature and conversion increase does not result to the production of visbreaking-residue with lower closed cup flash point. For example, visbreaking-residue samples sampled at 445 and 455°C had one and the same closed cup flash point and the difference in vacuum residue conversion between the two modes was 22.4 -18.0 = 4.4 %. Closed cup flash point values of the fuel oil end product produced by blending of visbreaking-residue (main component) with FCC HCO and slurry and heavy straight run diesel fraction are shown in Table 4.

Table 4 Finished fuel oil closed cup flash points

Sample/Date	Finished fuel oil header/ 08.09.		
Preliminary treatment of the sample	Tempered 30 min at 30°C	Tempered 30min at 20°C	Tempered 120 min at 20°C
Closed cup flash point, °C.	61	47	59

It is seen from these data that the preliminary preparation of the sample for analysis of closed cup flash point has influence on the end result. Value differences of the various measurements are beyond allowable limits for repeatability (5°C) and reproducibility (10°C). Again, explanation of the observed phenomenon may be found in fuel oil colloid-disperse nature The formation of over molecular structure for heavy petroleum products is proved [7] and their size and composition depend on inter molecular force interaction between nuclear and solvate cover of the micelle. The different thermal effect, adding of fractions that have different surface active substances have influence on aggregation stability on complex structural units. Unfortunately, in present study we do not have available any equipment to measure complex structural units size and respectively to determine the conditions at which the colloid-disperse system is stable in order to obtain results about closed cup flash point of one and the same samples that to be within the range of repeatability and reproducibility of the test method EN ISO 2719.

3. Conclusions

The carried out study on closed cup flash point of visbreaking-residue and the finished fuel oil product allows drawing the following conclusions:

1. The correlation between petroleum product closed and open cup flash points does not exist.
2. It is not proved that there is correlation between visbreaking-residue closed cup flash point and vacuum residue conversion.
3. The visbreaking-residue and the fuel oil end product are colloid-dispersion systems and their closed cup flash point depends on the preliminary sample treatment.
4. At different preliminary treatment of one and the same sample of visbreaking-residue or residue fuel oil may be obtained values for closed cup flash point that differ by 26°C, significantly higher difference than specified in standard EN ISO 2719, 5°C – repeatability and 10°C reproducibility.
5. Additional studies are required by equipment that should detect complex structural unit's size in order to provide stable condition of colloid-disperse system – fuel oil, thus to secure repeatability and reproducibility identical to those specified in EN ISO 2719.

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