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Challenges in Meeting Aluminum and Silicon Content Requirements During the Production of Modern Marine Fuels Based on H-Oil Hydrocracking Vacuum Residue

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Abstract

Production of modern marine fuel is a challenging task for the refineries not only for their attempt to respond to IMO sulfur cap of 0,5 % but also for the fulfillment of all other requirements of ISO 8217. Variation in aluminum (Al) and silicon (Si) content in this heavy fuel should be subjected to strict monitoring, and high value should not be permitted because they are highly abrasive towards engine parts. The above elements in the form of catalysis fines enter heavy marine fuels mainly with slurry oil (SLO), produced in the fluid catalytic cracking unit in a refinery. Their quantity rose with the worsening status of FCC hardware – an increase of catalysis lost. Other FCC gas oils, light cycle oil, and heavy cycle oil are considered more appropriate diluents and liquids for co-processing in vacuum residue hydrocracking for the absence or negligible quantities in them of the two elements. Fractionation of the residue hydrocracking vacuum bottom product shows that Al and Si are concentrated in the heaviest cut of this product when FCC SLO is co-processed in the residue hydro-cracking unit. Thus allow low boiling fraction, bellow 470^{0}C, of ebullated bed hydrocracking residue, to be used for marine fuel production. Quantitative relations between FCC SLO Al and Si content and total mechanical impurities content are derived in this study.

Keywords: *Aluminum and silicon; marine fuels; slurry oil from FCC; hydrocracking; residue.*

1. Introduction

The heavy fuel oil (HFO), also known as residual fuel oil (RFO), is the part of crude oil that remains when all of the useful short chain hydrocarbons have been boiled off and condensed in the refinery column [1]. Typically, the heavy fuel oil produced in an oil refinery is traded as a marine fuel after dilution with appropriate cutter stocks enhancing fuel sulfur content, CCR content, density, viscosity and simultaneously do not deteriorate colloidal fuel stability [2].

In order to be sold as a marine fuel, the heavy fuel oil must meet the specification laid down in ISO 8217 international standard: Specifications of marine fuels [3]. The specifications in the standard ISO 8217, amongst other properties, define the limit for Al+Si. The most commonly used revision of the specification, ISO 8217:2005, lists a maximum limit of 80 mg/kg Al+Si for the thicker heavy fuel grades, whereas the latest revisions, ISO 8217:2010, 2012 and 2017, have the stricter requirement of a maximum 60 mg/kg Al+Si for the thicker grades, and thinner grades are limited to 25, 40 or 50 ppm Al+Si [4]. Specification restrictions for Al+Si are related to undesirable catalytic fines (cat fines), incorporated into heavy fuels via diluents, originate from FCC processes in the refineries. Most catalysts being used in FCC commercial units processes are based on aluminum-and silicon oxides [5], which ends up in FCC heavy products. The presence of these abrasive particles entering the combustion chamber with marine fuel will cause engine wear [4]. Nevertheless, FCC products disadvantages related to cat fines content, light cycle oil (LCO), heavy cycle oil (HCO), and slurry oil/decant oil/FCC (Fluidized Catalytic Cracker) bottoms (SLO), all obtained from the fluid catalytic cracking unit (FCC) in a refinery, are the most appropriate, for their high aromaticity and relatively low in sulfur levels diluents amongst refinery streams. Generally, due to their overwhelmingly aromatic nature, these complex mixtures can be used only as viscosity cutter and cannot be used as automotive fuels [6-7]. Furthermore, cat fines in modern, advanced marine fuels are expected to rise in conjunction with IMO adopted lower sulfur emissions at 0,5 % sulfur equivalent [8] as low in sulfur cat fines containing FCC products will be an important part of the marine fuel pool.

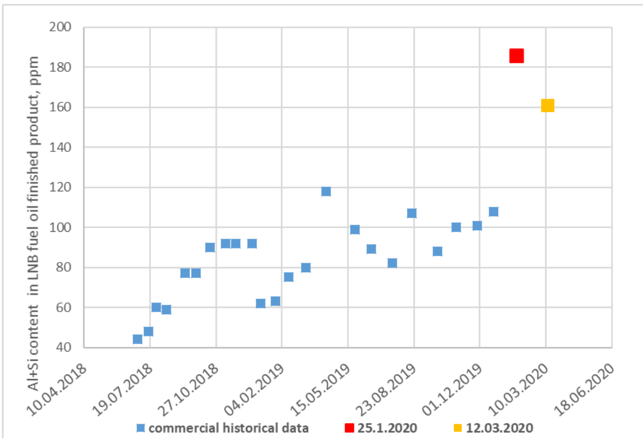

Figure 1. Al+Si content in the finished heavy fuel oil produced in the LNB refinery for the period June 2018-March 2020

LUKOIL Neftohim Burgas (LNB) refinery produces heavy fuel oil that consists of H-Oil unconverted hydrocracked vacuum residual oil (UHCVRO) or so-called vacuum tower bottom (VTB) and mainly FCC HCO as a diluent. The FCC SLO is processed along with the VRO as a feedstock for the H-Oil hydrocracker, as described in our recent study [9]. Lately, a trend of increasing Al+Si content in the finished fuel oil is registered, as shown in Figure 1. Further, a step change related to a sudden increase in the finished fuel oil Al+Si content is registered. For that reason, a study dedicated to the identification of the reasons for this sudden increase of the Al+Si content in the heavy fuel oil is carried out. The Al+Si content in all FCC streams and H-Oil products is studied. The aim of this paper is to discuss the obtained results.

2. Material and methods

The Al+Si content in the studied oils is performed in accordance with ASTM D 5184. Density is measured in accordance with ASTM D 4052. High temperature simulated distillation of the samples is carried out in accordance with ASTM D 7169. Fractionation of the FCC SLO is performed in a laboratory vacuum distillation column in accordance with ASTM D 5236 method. The advantage of the last method for distillation is the ability to derive hydrocarbon cuts with the desired interval of boiling width – 10^0C to 40^0C, as is the case with FCC SLO under study. Thus, the obtained cuts are sufficient for subsequent testing. ASTM D 4294 method is employed to measure the sulfur content in the studied oils.

Total mechanical impurities content in slurry oils is determined according to the internal procedure as follows: The sample of 20 g slurry is blended with 200 mL of toluene and stirred until completely dissolved. The blend is transferred to a filter and then washed until a drop of the filtrate leaves no oil stain on filter paper. The washed filter is placed in the weighing glass in which it is prepared and dried for 45 minutes at a temperature of 105^0C Total mechanical impurities content is calculated as a subtraction of the weight of the filter without precipitate from the weight of the filter with precipitate, divided to the weight of the sample. After total mechanical impurities content is determined, the filters with precipitate are placed in the preheated quartz cups. Then burned in an oven at 800^0C for 1 hour, temper for 1 hour, and weigh. Catalyst content is calculated as a subtraction of the weight of the quartz cups from the weight of quartz cups with the residue after heating up, divided by the weight of the sample.

3. Results and discussion

As evident from the data in Figure 1, since the beginning of 2020, the content of aluminum and silicon in the finished fuel oil produced in the LNB refinery has shown a step raised of 70 % - from about 100 ppm to about 170 ppm. While, for the period June 2018 – December 2019, the increase of the content of aluminum and silicon in the finished fuel oil follows the trend of increasing the catalyst losses from the fluid catalytic cracking (FCC) unit - Figure 2. Moreover, together with increased catalyst losses, Figure 2 shows the rise of the SLO/VTB ratio. This ratio reveals that after increasing the conversion of vacuum residue in hydrocracking unit during this period from 72 to 92 % due to several technological innovations (implementing HCAT® technology, low LHSV, co-processing FCC SLO; selecting more aromatic crudes), the quantity of residue for residual fuel oil production decreases [10] and therefore slurry oil share in fuel oil increases. Trends in Figure 2 reveals that FCC SLO cat fines increase with increased catalyst losses from FCC unit and thus deposit in VTB to a greater extend. Already enriched VTB with FCC cat fines containing Al and Si is the contributor of the last two elements in finished fuel oil. In order to find the reason for this increase, the feedstock for the H-Oil VRO hydrocracker before and after the addition of FCC SLO and the products of the H-Oil were analyzed. Additionally, samples from FCC SLO taken from the FCC unit and from the storage tank for FCC SLO where some separation of the FCC catalyst fines is expected to happen were analyzed. Summary from the results of the analyses mentioned above is presented in Table 1.

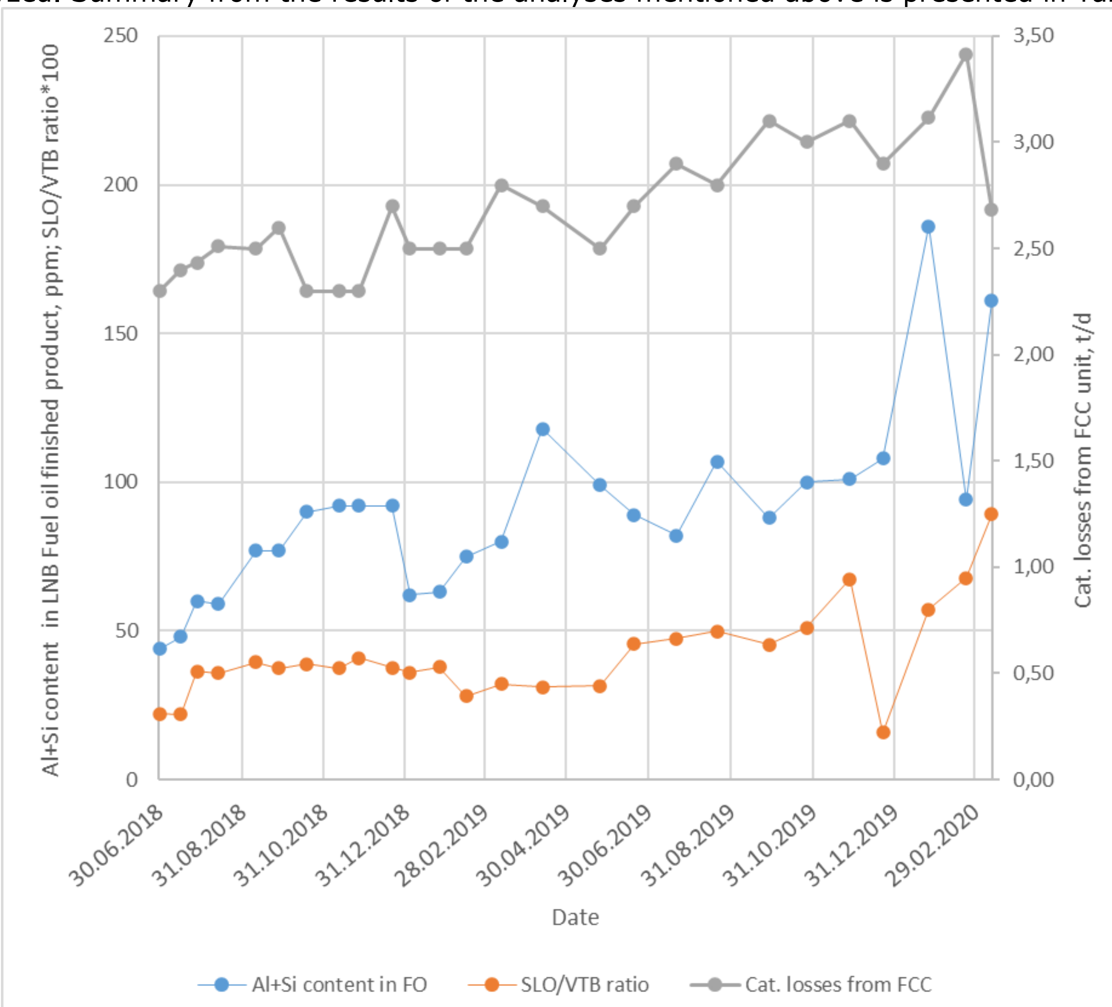

Figure 2. Fluid catalytic cracking catalyst loss and SLO content in hydrocracking feed effect over Al+Si content in the finished heavy fuel oil produced in the LNB refinery

It is evident from the data in Table 1 and Figure 2 that the FCC SLO is the stream with the highest content of Al+Si and thus is the main contributor of Al+Si in the H-Oil feed and products. LNB commercial data presents a quantitative relationship between total mechanical impurities content of FCC SLOs and their aluminum (Figure 3) and silicon content (Figure 4).

Total mechanical impurities of FCC SLOs are mainly catalyst from the unit. This statement is confirmed by LNB commercial data shown in Figure 5.

Table 1. Properties of the studied oils

	SR Vacuum Residue	H-Oil Feed (Combined)	H-Oil ATB	H-Oil VTB	PBFO	H-Oil Diesel	H-Oil HAGO	H-Oil LVGO	H-Oil HVGO	H-Oil Slurry	FCC Slurry	FCC Slurry	FCC HCO	FCC HCO	FCC LCO
Date	15.1.2020	21.1.2020	21.1.2020	21.1.2020	21.1.2020	21.1.2020	21.1.2020	21.1.2020	21.1.2020	21.1.2020	21.1.2020	22.1.2020	22.1.2020	13.5.2019	22.1.2020
Density at 15 ^{0}C, g/cm^3	1.0268	1.0336	0.9861	1.0349	1.0187	0.8634	0.9442	0.9604	0.9652	1.086	1.0957	1.0939	1.0052		0.92249
Sulfur, wt.%	4.42	3.69	0.741	1.215	1.097	0.134	0.404	0.378	0.614	0.949	0.934	0.763	0.409		0.172
Evaporate, %	^{0}C														
IBP 0,5	457	235	313	354	240	140	267	270	355	205	200	210	219		136
5	522	373	365	498	272	164	327	324	395	318	317	319	257		178
10	546	423	390	523	291	179	347	341	413	340	339	340	267		192
20	574	526	424	548	325	207	369	364	435	364	361	363	281		202
30	596	566	453	566	372	232	381	380	451	379	378	378	293		215
40	615	592	480	581	524	252	392	393	465	394	393	393	306		223
50	632	614	507	597	557	274	401	406	478	409	407	407	316		227
60	648	635	535	614	580	294	412	418	491	423	421	421	327		242
70	664	654	564	635	604	314	423	432	504	441	439	437	338		246
80	686	678	597	658	633	333	439	451	518	462	459	456	351		256
90	711	707	643	692	671	354	463	480	536	498	493	483	370		269
95	743	734	676	714	699	367	485	505	551	549	540	511	383		279
FBP 99,5	852	848	744	833	806	390	540	557	580	643	636	581	419		313
FCC catalyst fines content,%										0.07	0.17				
Aluminium, ppm	3	20	67	155	95		< 5 (1.6 ppm)	< 5 (1.5 ppm)	< 5 (2 ppm)	176	352	210	4	< 1	
Silicon, ppm	6	24	65	154	94		< 10 (2.2 ppm)	< 10 (2.0 ppm)	< 10 (2 ppm)	187	370	197	8	< 1	

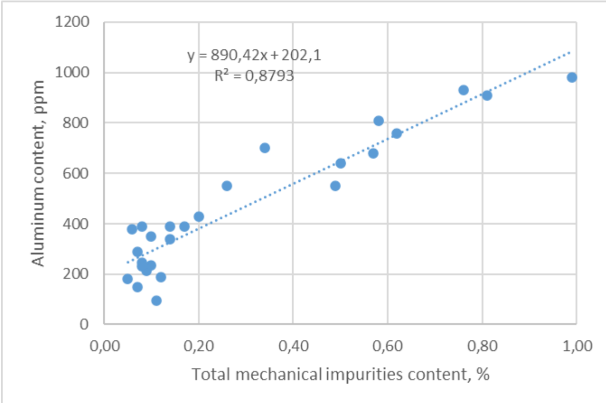

Figure 3. Dependence of FCC SLO aluminum content from total mechanical impurities content

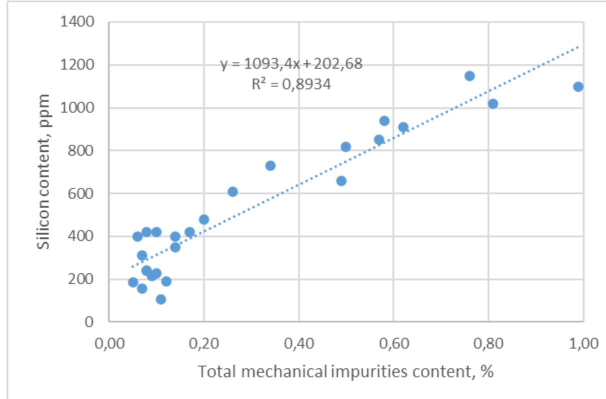

Figure 4. Dependence of FCC SLO silicon content from total mechanical impurities content

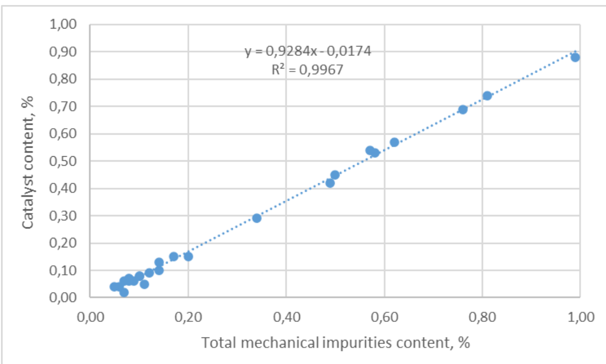

Figure 5. Relationship between catalyst content and total mechanical impurities content

The FCC gas oils LCO and HCO, as apparent from the data in Table 1, do not contain FCC catalyst fines. Detailed analysis of FCC HCO's, Table 1 second and third right hand columns, presents that during periods with increased FCC catalyst losses (2.5 t/d at 05.2019 to 3.4 t/d at 02.2020 – gray line in Figure 2) is possible a small content at about several ppm of Al+Si to entrain FCC HCO. Nevertheless, the addition of FCC HCO to the H-Oil VTB in the process of production of the finished fuel oil could not contribute to the increase of Al+Si in the fuel oil.

The content of FCC SLO in the H-Oil feed on 21.01.2020 was 12.1 %. This 12.1 % of FCC SLO in the H-Oil feed is responsible for the increase of H-Oil feed density from 1.0268 to 1.0336 g/cm^3 and for the augmentation of the Al+Si content from 9 to 44 ppm. The content of Al+Si in the H-Oil atmospheric tower bottom (ATB) product increases threefold from 44 to 132 ppm, suggesting that the FCC catalyst fines are concentrated in the heavy oil H-Oil products. The content of Al+Si in the H-Oil vacuum tower bottom (VTB) product increases by a factor of 2,3 from 132 to 309 ppm, suggesting that the FCC catalyst fines are concentrated in the H-Oil VTB product. The content of Al+Si in the H-Oil gas oils (HAGO, LVGO, and HVGO) is below the lower limit of detection of the method used in this work to determine the Al+Si in the H-Oil gas oils.

It is difficult to judge from the data in Table 1 whether some separation of the catalyst fines from the FCC SLO occurs in the FCC SLO storage tank. If we compare the Al+Si content in the FCC SLO storage tank (H-Oil slurry sample in Table 1) and in the FCC SLO from the FCC unit (FCC slurry samples in Table 1) on the date 21.01.2020, we could conclude that some separation occurs because the FCC SLO sample from the FCCU has a twice as high content of AL+Si as that of the FCC SLO storage tank. However, if a comparison is made between the Al+Si content in the FCC SLO storage tank from 21.01.2020 and the FCC SLO from the FCC unit on the date 22.01.2020, the difference is only 12%. Therefore, the efficiency of the separation of the FCC catalyst fines from the FCC SLO during storage as a result of settling is difficult to assess as significant. Moreover, some accumulation of FCC catalyst fines in the storage tank can take place, and entrainment of the FCC catalyst fines with the FCC SLO may occur. This could be the reason for the sudden increase of the Al+Si content in the finished fuel oil product as from January 2020.

It is worth knowing that the content of Al and Si change in FCC SLO to H-Oil VTB and commodity fuel oil. Figure 6 reveals this transformation as Si is 15 % more than Al in slurry oil. There are literature [11-12] conformation for the prevailed content of SiO_2 to Al_2O_3 in the modern FCC catalyst - reduced aluminum zeolites, also called ultra-stabilized Y-zeolites. Chemical dealumination (increased SiO_2/Al_2O_3 ratio), during the production step of catalyst, is responsible for enhanced development of mesopores that facilitate the diffusion of larger molecules and for higher thermal and hydrothermal stability.

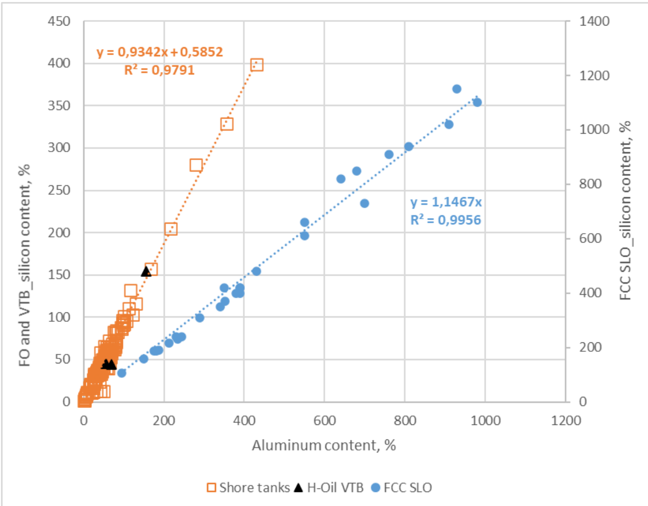

Figure 6. Si to Al content alternation from FCC SLO through H-Oil VTB to fuel oil final product

LNB commercial data shows that SiO_2/Al_2O_3 ratio for the e-cat from the refinery FCC unit is average 1.17, which is pretty close to the slope of the line describing Si and Al relation in FCC SLO. SiO_2 content in the equilibrium catalyst is at the level of 52 %. No doubt that these two elements fall in the slurry with the catalyst fines from the process. Unlike, LNB commercial catalyst for residue ebullated bed hydrocracking contains small quantities of Si. Analytical results show only an average of 0.6 % in the burnt spent catalyst samples. Therefore, it is expected that some hydrocracking catalyst quantity presents in VTB and decreases SiO_2/Al_2O_3 ratio in it and also in fuel oil. Thus, different Si content in the two catalyst types (for FCC and residue hydrocracking) may be the cause for the declined ratio of Si to Al in the fuel oil. Another reason can be the sedimentation of catalyst fines in the equipment.

In order to establish the distribution of the Al+Si in the FCC SLO, a sample taken from the LNB FCCU on 18.02.2020 is fractionated in a vacuum distillation laboratory unit operating according to the requirements of the ASTM D5236 standard. Properties of the FCC SLO fractions and the distillation characteristics of the whole FCC SLO measured by the use of high temperature simulated distillation (HTSD) according to ASTM D7169 are summarized in Table 2.

Table 2. Properties of FCC SLO and its fractions obtained by physical vacuum distillation (ASTM D5236)

Whole FCC SLO properties (18.02.2020)		Density at 15°C = 1,0993 g/cm³		Sulfur = 1.32 %	Al = 275 ppm		Si = 285 ppm
ASTM D5236 vacuum distillation							
Fractions		IBP- 360 °C	360- 380 °C	380-390 °C	390-430 °C	430-470 °C	> 470 °C
Fraction yield, %		3.17	4.85	3.90	30.92	24.64	31.79
accumulated %		3.17	8.02	11.92	42.84	67.48	99.27
Sulfur, wt.%		1.04	1.51	1.52	1.35	1.37	1.31
Density at 15°C, g /cm³		1.0032	1.0355	1.0433	1.0565	1.0788	1.1437*
Softening point, °C		-	-	-	-	-	61.6
Al, ppm		-	-	<5 (0.8)	<5 (1.0)	<5 (1.2)	826
Si, ppm		-	-	<10 (2.3)	<10 (2.6)	<10 (5.5)	800
HTSD ASTM D7169, °C							
IBP	219	171	243	266	298	341	393
5%	320	220	284	304	332	369	420
10%	345	239	296	315	344	376	431
20%	371	259	315	333	359	389	448
30%	388	275	326	342	371	398	460
50%	418	304	346	361	387	414	483
60%	433	316	356	371	395	422	496
70%	451	331	365	379	404	430	513
90%	507	370	393	405	428	455	606
95%	567	387	406	417	440	467	642
FBP	673	431	438	445	466	496	711

Concerning the Al+Si content distribution in the FCC SLO fractions, it is evident from the data in Table 2 that the Al+Si content in all fractions except the fraction > 470°C is below the detection limit of the method employed. It seems that almost all of the FCC catalyst fines are concentrated in the bottom fraction of the FCC SLO. When the share of FCC SLO against vacuum residue feed to hydrocracker increase (orange line in Figure 2), more quantity of Al + Si is delayed in VTB and fuel oil, respectively (blue line in Figure 2).

Figure 7 depicts graphs of the boiling point distribution versus the evaporated quantity according to the physical vacuum distillation method ASTM D5236 and to the HTSD method ASTM D7169. The data in Figure 6 indicates that the boiling points of the evaporated according to physical vacuum distillation method ASTM D5236 are higher than those obtained by the use of the HTSD method ASTM D7169. The physical vacuum distillation method studied in several articles [13-16] is considered to better represent the real vacuum distillation occurring in the commercial vacuum towers. Unfortunately, its performance is costly and more time consuming than HTSD. Based on the data for the HTSD of the studied FCC SLO (18.02.2020), one may conclude that 15% of that material boils below 360°C. At the same time, the data from the physical vacuum distillation ASTM D5236 shows that the material boiling below 360°C represents only 3% of the whole FCC SLO. Therefore, one may conclude that from this FCC SLO, no diesel could be extracted during the fractionation of the reaction mixture of the H-Oil VRO hydrocracking processing a blend of 88% VRO and 12% FCC SLO. Moreover, it has been reported that during H-Oil hydrocracking of blends of VRO and FCC SLO, no conversion of the FCC SLO takes place [17]. Some hydrogenation of the FCC SLO may occur, as was shown in our earlier research [9].

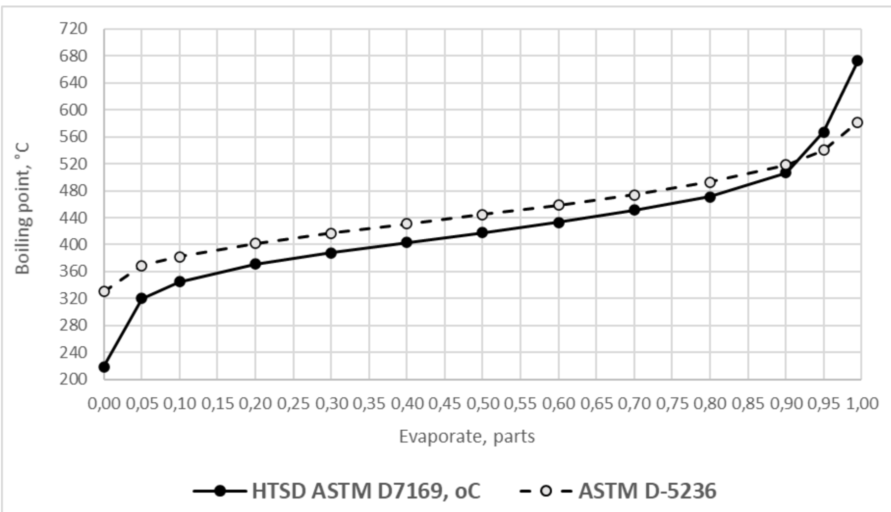

Figure 7. Distillation data for FCC SLO from 18.02.2020 according to the HTSD (ASTM D7169) and the physical vacuum distillation ASTM D5236

4. Conclusions

The main contributor for Al+Si content in fuel oil is FCC SLO diluent. Almost all of the measured total mechanical impurities content in this stream is catalyst fines from the FCC unit and is strictly related to its Al+Si content. An increase in Al+Si content can be twofold - either increase the share of FCC SLO diluent in its blends with residual fractions or/and increase of catalyst losses from the FCC unit. Al+Si content is concentrated in the heaviest fraction of FCC SLO, boiling above 470^{0}C. In order to respond to residual marine fuel specifications concerning Al+Si content, SLO can be fractionated, and only the lower boiling fraction can be used for the production of modern marine fuel. Other more appropriate diluents are FCC LCO and HCO, which do not contain FCC catalyst fines, are lower in sulfur, CCR, viscosity, and density. A sign is noticed for the contribution of hydrocracking catalyst, left in VTB, for the increased content of metals in fuel oil.

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