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IMO 2020 stability and compatibility headaches

The year 2020 will be a mess from the fuel oil stability and compatibility points of view. The year will be price-driven, so the temptation to "cut corners" is great—meaning that a highly variable number of blend components to manufacture the fuel oil will open a "Pandora's box" of complex and questionable fuel formulations.

Blending issues. Exhaustive studies of the relationship between asphaltene content and aromaticity have shown that the order in which the fuel oil blends are created is critical to obtaining compatible and stable fuels.[1,2,3]

The order of blending is one of the concerning issues[1] (**FIG. 1**). Two fuel oil blend components, A and B, each perfectly stable on their own, exhibit a puzzling behavior: When blending fuel A into B, the blended fuel is perfectly stable and compatible. On the other hand, blending fuel component B into A leads to immediate sludging. Why is that?

By now, most people know that asphaltenes micelles in fuel oil are kept in a colloidal solution by "high" aromaticity of the colloidal "soup" of maltenes. The question is, what signifies high aromaticity? Some answers can be found in various studies[3] and patents.[2]

Asphaltene content and aromaticity. An extreme case analysis of expected 2020 fuel oil blend categorizes them into paraffinic, aromatic and hybrid. Before considering the characteristics of these blends, typical properties of residual materials and cutters must be examined.

TABLE 1[3] illustrates some of the properties of vacuum residue—i.e., vacuum tower bottoms and visbreaker tar bottom. These residues have high aromaticity of between 50% and 60%.

TABLE 2[3] illustrates properties of typical cutters in two categories: aromatic cutters and paraffinic cutters. Aromatic cutters are typically from FCC units and include light cycle oil (LCO), heavy cycle oil (HCO) and slurries or clarified oils (CLO). These cutters are highly aromatic liquids, at 80% or higher. Paraffinic cutters are typically from atmospheric and vacuum distillation units, such as atmospheric gasoil (AGO), light and heavy AGO and vacuum gasoil (VGO).These cutters have low aromaticity of around 30% to 50%.

2020 fuel oil blends. The types of 2020-compliant fuel oil blends fall into three categories: paraffinic blends, aromatic blends and hybrid blends.

Paraffinic blends typically use vacuum tower bottoms and the cheapest cutter [e.g. light atmospheric gasoil (LAGO), heavy atmospheric gasoil (HAGO) or more expensive ultra-low-sulfur diesel (ULSD)]. The problem is that while vacuum tower bottoms have approximately 80% aromatics, gasoils typically have 30%–40% aromatics, and the resulting blend aromaticity could drop below 40% depending on the blend ratio and the order of blending. The vacuum tower bottoms/gasoil blend becomes a candidate for sludging, depending on the order of blend: GO dropped in vacuum tower bottoms is acceptable because it keeps the aromaticity of the blend above 50% constantly; the reverse is not true.

Aromatic blends typically use "cracked" blend components, such as visbreaker tar bottoms, and highly aromatic cutters, such as LCO and HCO. The aromaticity of visbreaker tar bottoms are in the range of 47% to 56%; the aromaticity of cycle oils is in excess of 80%. Any aromatic blend will always have an excess of aromaticity (more than 50%) and be stable.

Hybrid blends typically use paraffinic blend components such as atmospheric tower bottoms, vacuum tower bottoms and mixtures of both paraffinic cutters, such as AGO, LAGO and HAGO; and aromatic cutters, such as LCO and HCO. The aromaticity of atmospheric tower bottoms and vacuum tower bottoms are in the 50%–60% range; the gasoils are 30%–40% aromatics, and the cycle oils are in excess of 80%. Depending on the blend recipe, a hybrid blend is not guaranteed to always have an excess of aromaticity (more than 50%) and be stable.

Typical recipes using components readily available on the US Gulf Coast are found in literature.[4] For example, a hybrid blend recipe might have 70% vacuum tower bottoms, 10% LCO, 16% AGO and 4% slurry.

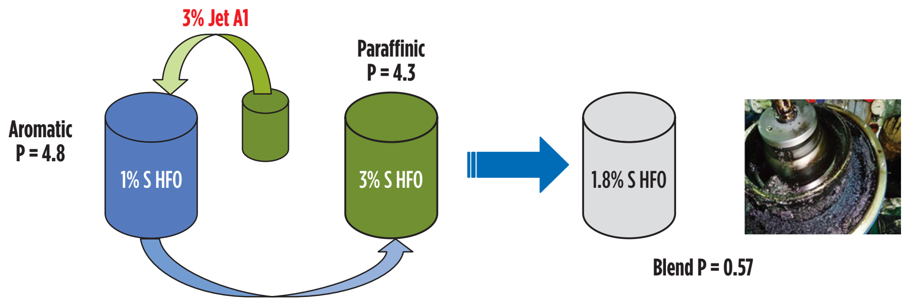

FIG. 1. Blending aromatic fuel oil into paraffinic fuel oil equals sludge. Image credit: G. Ivey and PetroJam.

Order of blending. If an aromatic cutter is poured into a paraffinic tank, then the initial small volume of aromatics in a paraffinic medium will just disturb the low aromaticity of the paraffinic "base," thereby increasing the probability of asphaltene sludging.

In the opposite situation, where paraffinic blendstock (either cutter or heavy fuel oil) is poured into an aromatic medium (above 70%–80% aromaticity), the aromaticity at the interface of the two liquids will be predominated by the aromatics and will always keep asphaltenes in the solution.

Shipowners vs. blenders. Stability and compatibility have different meanings for shipowners and blenders. Shipowners do not have the time to calculate fuel stability and compatibility using lengthy lab titration methods, such as toluene equivalent and asphaltenes content, to predict stability and compatibility. However, having a superficial and incomplete lab certificate of analysis is not a guarantee of stability.

For fast, efficient testing, shipowners frequently use two ASTM test methods—the "spot" test method and total sediment potential. These tests are available as inexpensive, onboard, manual test kits with step-by-step instructions. Shipowners must follow instructions, such as heating the components to 100°C, blending the components in desired ratios and then putting a drop of the desired finished product on a filter paper to compare what is observed with reference charts and photos. This allows for a quick determination of whether or not the fuel is stable and should be purchased.

Blenders must ensure (and sometimes guarantee) that their blended products are stable and compatible. To do this, blenders must analyze stability and compatibility issues in more detail by calculating the asphaltene solubility of their blends. Lab analysis of the aromaticity of blends can be done, using well-established test methods such as toluene equivalent (the ExxonMobil method, or Exxon 79-004), xylene equivalent (the BP method) and asphaltenes content with ASTM D6560 or IP-143.

The abovenamed methods use heptane to precipitate the asphaltenes and toluene, or xylene to keep the asphaltenes in solution. Then nonlinear equations are used to calculate the final blend stability and compatibility factor, as shown in Eq. 1:

TABLE 1. Resid properties[a]

Properties	Virgin Vacuum residue (VVR)	Blend of 60% VVR, 30% HVGO, 10% LVGO	VBR Sample 1	VBR Sample 2	VBR Sample 3	Sample
Specific gravity, d_4^{20}	0.9969	0.9598	1.011	1.003	1.004	1.01
Kinematic viscosity at 80°C, mm^2/s	1194	136	260	260	228	270
Conradson carbon, %	15.3	9.2	22.4	20.08	23.1	22.4
Sulfur, %	2.48	2.13	2.43	2.44	2.29	2.28
Metals, mg/kg						
Sodium	59.1	62.5	76	64.8	56	
Aluminum			4	6	4	4
Silicon	9	14	9	8		
Nickel	71.2		50.9	79.8	58.5	71.1
Vanadium	207		212.7	229.2	209.4	228
Distillation D-1180, °C						
350, vol%	0	7	10.4	10	10	10.7
360, vol%	0	10	12	12	13	13
400, vol%	0.1	20	19	20.5	21	20
440, vol%	0.7	30	25.9	28	27	26.5
480, vol%	5	41.4	33	35.5	36	35
510, vol%	19	51.5	40	43	47.8	43
Group hydrocarbon composition						
Saturates, wt%	24	38.7	22.8	26.5	27.1	30
Total aromatics, wt%	62.7	52.9	55.8	52.4	51.4	47.6
Mononuclear aromatics, wt%	13	12.2	7.7	7	6.1	5.3
Polynuclear aromatics, wt%	49.7	40.7	48.1	45.4	45.3	42.3
Resins, wt%	10.2	6.5	11.1	13	11.8	10.1
Asphalthenes, wt%	3.2	1.9	10.3	8.1	9.8	12.4
Sediments, wt.%, ISO 10307-1	0	0	0.07	0.09	0.18	0.37
Sediments measured after sample treatment with hexadecane at 100°C for 1 hr, wt%						
ISO 10307-2	0	0	0.08	> 0.5	> 0.5	> 0.5
Stability factor after Kuo[7]	0.198	0.167	0.131	0.123	0.107	0.083

[a] Adapted from D. Stratiev[3]

$$k = \text{BMCI} \div \text{TE} \quad (2)$$

where BMCI = Bureau of Mines Correlation Index, an indicator of aromaticity of the blend; and TE = the measured toluene equivalent value.

Compatibility calculation. Compatibility and stability issues have been thoroughly investigated for more than 30 yr. A well-known method to measure the propensity of bunker fuel to become incompatible/unstable is to measure the aromatics solvent power of asphaltenes in bunker fuel, in the form of toluene or xylene equivalence (TE or XE). This refers to the percentage of aromatics (toluene or xylene) required to keep asphaltenes in the bunker fuel oil colloidal solution without precipitation. Most oil companies have filed patents based on these fundamental principles.[2,5,6]

Following the ExxonMobil patent US9,803,152,[2] the TE is directly proportional to the asphaltene content of bunker fuel, as shown in Eq. 2:

$$\text{TE} = \Sigma TE_i \times A_i \times y_i \div \Sigma A_i \times y_i \quad (1)$$

where A_i = asphaltene content and y_i = mass fraction of component in blend.

Compatibility/stability is defined by bunker fuel oil asphaltene "solubility reserve," *K*, as the ratio of BMCI divided by TE or XE, as shown in Eq. 3:

$$K = (\text{BMCI} \div \text{TE}) = > 1.5 \quad (3)$$

$$\text{Or, } K = (\text{BMCI} - \text{TE}) = >15$$

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The higher the *K* ratio of available aromaticity (BMCI) to required aromaticity (TE), the greater the "solubility reserve," and, therefore, the more compatible and stable the bunker fuel.

Modern tools, like a bunker fuel oil blend optimizer (**FIG. 2**) allow users to predict compatibility and stability with one click. The optimizer allows users to understand if a finished product (for example, IFO-380, 0.5% sulfur) is compatible or not. The optimizer has already incorporated all the equations for stability and compatibility, plus all the nonlinear equations, to predict viscosity, pour point, flashpoint, etc.

Blenders and shipowners could use such a standalone tool to estimate the compatibility of a desired fuel, or to check if blending components can be mixed without creating sludge and damaging the engine.

Desirable additions to ISO 8217-2017. To minimize uncertainty and risk

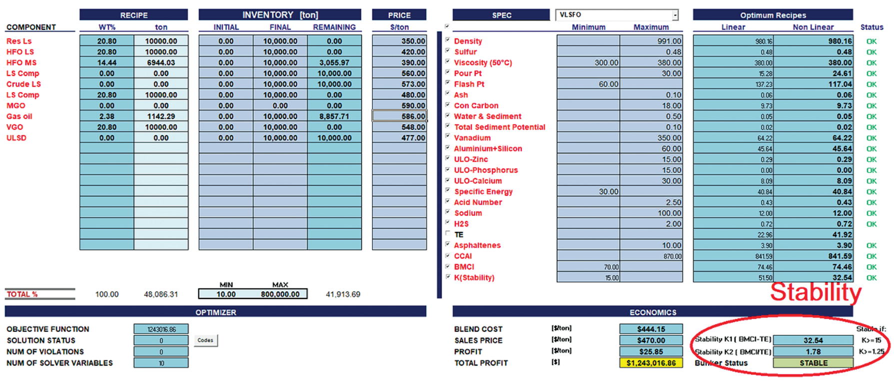

FIG. 2. Bunker blend optimizer automatic calculation of stability and compatibility.

TABLE 2. Cutter properties[a]

Properties	FCC slurry	FCC HCO	FCC LCO	HSRGO	AGO	HVGO	VBGOb	VBHGOb
Specific gravity, d_4^{20}	1.054	0.9888	0.9196	0.8506	0.8737	0.904	0.874	0.9361
Kinematic viscosity at 40°C, mm^2/s	40.4	5.8	1.7	4.4	10.6	4.6		
Kinematic viscosity at 80°C, mm^2/s						14.7		18
Distillation, vol%	**ASTM D1160**	**ASTM D86**	**ASTM D86**	**ASTM D86**	**ASTM D86**	**ASTM D1160**	**ASTM D86**	**ASTM D1160**
IBP	199	235	180	163	257	239	194	207
10	292	280	210	269	314	369	221	373
30	334	295	229	290	343	403	257	427
50	372	310	240	302	357	430	289	462
70	409	326	252	315	366	459	299	481
90	475	350	270	335	381	497	330	512
FBP	518	369	295	353	398	515	347	524
Recovery	95	98	98.5	96		95	98	95
Group hydrocarbon composition								
Saturates, wt%	14.39	19.2	19	70	62.7	59.1	53	38.1
Total aromatics, wt%	81.57	80.8	81	30	37.3	39.5	47	58
Mononuclear aromatics, wt%	0.75	27.8	30	12	15.1	8.3	23	17.2
Polynuclear aromatics, wt%	80.82	53	51	18	22.2	31.2	24	40.8
Resins, wt%	3.25					1.4		3.9
Asphalthenes, wt%	0.79							
Conradson carbon, wt%	6.18					0.2		

[a] Adapted from D. Stratiev[3]
[b] VBGO and HVBGO have been distilled from VBR Sample 2

on the part of bunker buyers, the ISO should consider including the following changes and additions to ISO 8217 RM-grade residual fuels:

- Asphaltene content, because compatibility is a function of asphaltene content
- Compatibility test using ASTM D4740 spot test, a simple and an approximate indication of compatibility and stability.

Adding these desired specifications could give blenders, shipowners and other parties the possibility to estimate the fuel compatibility quickly, thereby avoiding expensive surprises.

Recommendations. The asphaltene content and aromaticity of fuel oil is critical to its fitness for use. With the new IMO 2020 low-sulfur regulation, most bunker suppliers and buyers will need to use low-sulfur blend components to be compliant. As described here, this increases the chance of creating sludge and/or damaging ship engines because of the wide-ranging blending outcomes of aromatic and paraffinic components.

Blenders and shipowners can avoid the sludge issue by calculating the fuel's compatibility and stability. Blenders and shipowners have different way of calculating it, but the use of an optimizer makes these calculations easier.

Although the addition of these parameters (asphaltene and aromaticity) to ISO 8217 specifications has been pointed out to ISO and other bunker industry organizations in written proposals, they have not been adopted so far. The authors believe that these organizations have done a great disservice to the bunker community by refusing to adopt these additions. Bunker users will pay the price in buying ISO 8217-compliant bunkers that may not be fit for use. HP

LITERATURE CITED

[1] Ivey, G. *et al.,* "Heavy fuel oil separation at power plants," PetroJam presentation, May 29, 2014.

[2] Kar *et al.,* US Patent 9,803,152 B2, assignee: ExxonMobil, "Modifications of fuel oils for compatibility," October 31, 2017.

Complete Literature Cited available online at www.HydrocarbonProcessing.com

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ARA BARSAMIAN is the President and CEO of Refinery Automation Institute LLC (RAI) and has more than 49 yr of experience in bunker, gasoline, diesel and biofuels blending operations and technology. Early in his career, he was a Group Head and Section Head with Exxon Research & Engineering Co., President of 3X Corp. and VP of ABB Simcon, all in the area of fuels blending. Among his first experiences at Exxon was computerized bunker blending in the Aruba refinery. Lately, he has been involved in the IMO 2020 bunker blends, recipes and ISO 8217 specs. Mr. Barsamian is a member of AIChE, ASTM, IBIA, ISA and ILTA. He holds BS and MS degrees in electrical engineering from City University of New York.