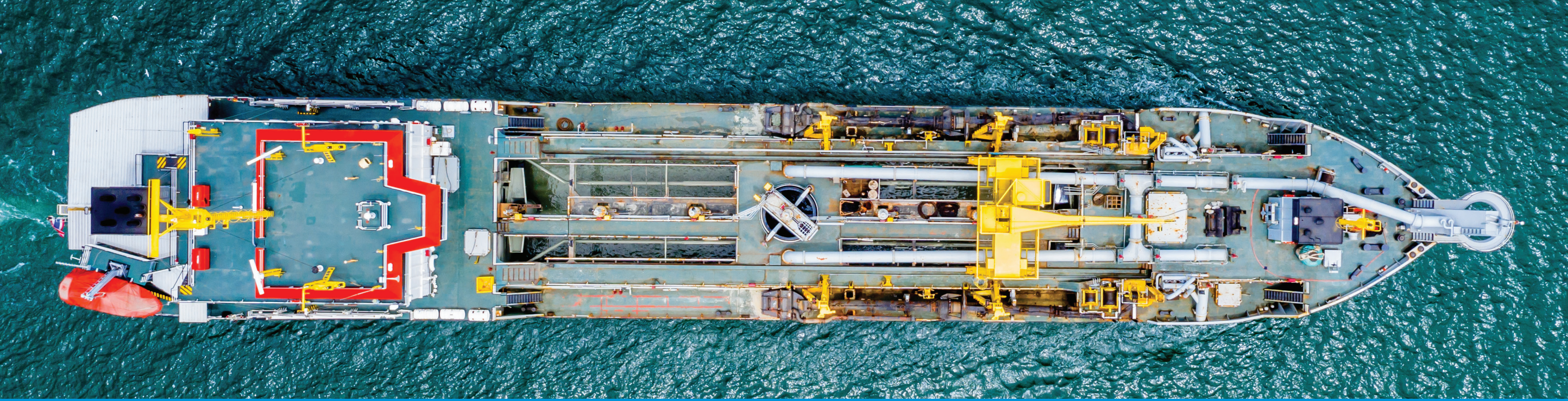


AN ANALYTICAL APPROACH TO MARINE FUEL STANDARDS

Marine transportation is a growing method to ship cargo across the world's oceans. For the first time in a single year, ships transported over 10 billion tons of cargo in 2016. Marine shipping is such a popular method for the transportation of goods since it is the most environmentally sustainable way to transport cargo globally. When considering the amount of mass of cargo that a ship can hold and per distance travelled, studies have shown that the most energy efficient transportation method is with marine ships.

With a rise in seaborne trade, further specifications and regulations may be needed to ensure the fuels that are consumed during a ship's voyage are as safe and efficient as possible, and create minimal harm to the environment. With the marine transportation sector burning around 3.8 million barrels of fuel oil per day in 2017 – which accounted for about half of the global world fuel oil demand – there are elevated concerns surrounding the effects from pollution due to the emissions of these fuels.

To oversee the safety and security of marine transportation, the International Maritime Organization (IMO), an agency within the United Nations, regulates and mandates the specifications of marine fuels. Most notably, IMO is responsible for the sulfur emissions limits placed on marine fuels across the world. At the International Convention for the Prevention of Pollution from Ships, or MARPOL Convention, in 2005, sulfur emission regulations for these fuels began. In recent years, these sulfur limitations have tightened and in 2020, IMO further cut the allowed sulfur content of marine fuel oil to 0.5%, where it was previously limited to 3.5%. The IMO 2020 sulfur regulations are the most drastic reduction in sulfur content of any transportation fuel taken in one step.

The only exception from this new specification is fuels burned in Sulfur Emission Control Area regions. High sulfur content fuels are permitted on ships that have exhaust gas cleaning systems (scrubbers), which removes sulfur oxides and lowers sulfur emission. In normal times, total global demand for fuel oil is roughly 7 million barrels per day, with the marine industry accounting for half of residual fuel oil demand. Therefore, this new regulation will have a drastic effect on availability and the cost of low-sulfur fuels.

A matter of concern arising from this new regulation is the compatibility and stability of sulfur compliant fuels. According to the specification of marine fuels (ISO 8217), fuels are required to have a "homogeneous blend of hydrocarbons derived from petroleum refining" which is an indication of stability [1]. The stability of a residual fuel is associated with the ability of the asphaltenes to remain in a suspended state, otherwise leading to precipitation of the asphaltenes and an unstable state of the fuel. The stability depends on the nature of the hydrocarbons in the fuel, which are the asphaltenes in the case of residual fuels. Ideally, bunker residual fuels should be segregated to prevent agglomeration of the asphaltene contents. During the blending of fuel oils, the uniform dispersion of asphaltenes in the residual fuel can be thrown out of equilibrium, causing an unstable dispersion of asphaltenes. Asphaltene separation, also referred to as sludge, can be harmful to ship engines and should be avoided for optimal performance. However, during the storage of various fuel oils in bunkers, it is not always possible to separate the fuels and, consequently, commingling can occur. New fuel formulations are also being made using different fuels with varying sulfur contents to adhere to the new sulfur specification. Therefore, the compatibility of commingled fuels is a requirement and knowledge of these new sulfur compliant fuels is a necessity.

Table 1. Fuel Sample Distribution

Number of samples	9 ULSFO	27 VLSFO	5 LSFO	11 HSFO
Samples from traders and shipping companies	5	0	3	10
Samples from fuel suppliers	4	27	2	1
Number of suppliers	unknown	9	1	unknown
Off-specification samples	0	3 TSP	2 - TSP - TSP, CCAI density, Al+Si	0
ISO 8217 fuel category	7 DMA 1 RMA10 1 RMG180	1 DMA 1 RMA10 3 RMB30 7 RMD80 7 RMG180 5 RMG380 2 RMG500 1 RMK380	1 RMD80 2 RMG380 1 RMK380 1 RMK700	1 RMG180 5 RMG380 1 RMG500 4 RMK500

Source: Concawe

Further marine fuel requirements are defined in the ISO 8217 specification for marine fuels. This specification labels marine fuels into seven different categories of distillate fuels and six different categories of residual fuels. For each category of fuel, the specification considers the safety, storage and handling, combustion, and the environment. ISO 8217 sets limits on many properties of these fuels, including the viscosity, flash point, density and others. These properties are measured through various ASTM methods and other standardized methods. Some of these methods are discussed below regarding their significance for the seven categories distillate fuels.

1) Sulfur Content
(ASTM D4294 – Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry)

ASTM D4294 uses energy dispersive x-ray fluorescence (EDXRF) to determine the total sulfur content in marine fuels. This method can detect sulfur in marine fuels to a ppm level, and can effectively be used to determine if a fuel meets the 0.5% sulfur content limit as per ISO 2020.

2) Kinematic Viscosity at 40°C
(ASTM D445 – Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids)

When considering the performance and handling conditions of marine fuels, viscosity is an important property. If a fuel is too viscous or not viscous enough, issues may arise as the fuel is delivered through the engine. Viscosity will decrease with increasing temperatures, so the temperature is specified at 40°C in ISO 8217. The specification also sets the kinematic viscosity to be between 1.4 cSt and 11.00 cSt at this temperature, depending on the category of distillate marine fuel.

3) Density at 15°C
(ASTM D4052 – Standard Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter)

Density is another fundamental physical property that is used to characterize marine fuels. ISO 8217 sets the density of marine fuels to be between 35 and 900.0 kg/m^3, depending on category of fuel. If the fuel's density is greater than that of water or similar to that of water (around 1000 kg/m3), water contaminants can disrupt fuel performance and storage, and any spillage into the ocean can harmfully distress the environment.

Table 2. Test results of fuel samples with TSP > 0.10% m/m

Final sample numbers			2018009	2018015	2018016	2018017	2018027
			VLSFO	LSFO	LSFO	VLSFO	VLSFO
Residues from crude atmospheric distillation				X			
Residues from thermal cracking units							X
Residues from Fluid Catalytic Cracker				X	X		X
Residues subject to sulphur reduction via hydrogenation			X			X	
Waxy residual stream from hydrocracker unit				X	X	X	
Distillate fractions from crude atmospheric distillation							X
Distillate fractions from Fluid Catalytic Cracker							X
Distillate fractions from hydrocracker unit				X			
Distillate fractions from hydrotreating unit						X	X
Kinematic Viscosity@50°C	ISO3104	mm^2/s	102.9	65.15	92,36	337,9	40,63
Density@15°C	ISO3675/12185	kg/m^3	921,1	957,6	1018,7	935,1	956,0
Sulphur	ISO8754/14596	mass %	0,29	0,60	0,80	0,49	0,52
Existent Total Sediment	ISO10307-1	mass %	0,02	0,03	0,02	0,33	0,14
Potential Total Sediment	ISO10307-2A	mass %	0,12	0,17	0,67	0,40	0,16
Accelerated Total Sediment	ISO10307-2B	mass %	0,06	0,08	0,53	0,34	0,28
Asphaltenes	IP 143	mass %	0,57	0,81	1,70	1,90	3,96
spot test	ASTM D4740	-	2	3	2	4	1
S-Value parameters Rofa Analyzer	ASTM D7157	S	no flocculation in test range	3,03	1,53	2,07	1,25
		So		0,79	0,76	0,71	0,70
		Sa		0,74	0,50	0,65	0,44
P-value parameters Porla Analyzer	ASTM D7112	P	2,34	unstable	unstable	2,12	1,06
		Po	0,66			0,82	0,65
		Pa	0,72			0,61	0,39
P-ratio parameters Zematra Analyzer	ASTM D7060	Po	asphaltenes <1%	93	direct flocculation	25	74
		Fr_{max}		89		42	71
		P-ratio		1,04		0,60	1,04

Source: Concawe

4) Flash Point
(ASTM D93 Standard Test Method for Flash Point by Pensky-Martens Closed Cup Tester)

The flash point temperature is considered when assessing the flammability of a marine fuel. Flash point is an essential property when defining shipping and safety regulations. Fuels with a low flash point could potentially produce dangerously flammable vapors in the headspace of the fuel tank. The specification sets the minimum flash point at 43.0°C for DMX marine distillate fuels, and at 60.0°C for the other six categories of marine distillate fuels.

5) Lubricity, corrected wear scar diameter (WSD) at 60°C (ASTM D6079 – Standard Test Method for Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig (HFRR))

Lubricity is a qualitative term to describe the ability of a fluid to affect friction between, and wear to, surfaces in relative motion under a load. Marine fuels with poor lubricity can damage fuel injection equipment. Lubricity is particularly important when discussing low sulfur marine fuels – for example, when ULSD ultra low sulfur diesel fuels became the common type of diesel used in automotive diesel engines in the mid-2000s, a decrease in lubricity quality was noticed. It has yet to be determined if similar problems will arise for marine fuels as the IMO 2020 sulfur regulations have only just begun this year. Lubricity is determined by measuring the wear scar diameter, which is set to have a maximum value of 520 µm for all seven types of distillate marine fuels as per ISO 8217.

A study was performed to evaluate the effectiveness of ASTM test methods D4740, D7157, D7112, and D7060 in predicting the stability and compatibility of compliant marine fuels. The fuels used for this study were: ultra-low sulfur fuel oil (ULSFO), very low sulfur fuel oil (VLSFO), low-sulfur fuel oil (LSFO) and high-sulfur fuel oil (HSFO). By testing the stability of a fuel sample mixture, an indication can be obtained regarding the potential compatibility between the two fuels used in the mixture at a specific ratio. However, even if two individual residual fuels are found to be stable, the compatibility of the two fuels is still inconclusive. The study predicted that approximately 60% of all possible fuel combinations were able to produce a stable blend using ASTM D7157 and D7112, and approximately 50% of all possible fuel combinations were able to as well, when considering all three test methods together, regardless of mixture ratio under all conditions.

The fuel samples consisted of 9 ULSFO (0.10% max sulfur), 27 VLSFO (0.50% max sulfur), 5 LSFO (1.00% max sulfur) and 11 HSFO (3.50% max sulfur). Some of the VLSFO samples are prototype fuels since the study was done before the new regulation was imposed and only a few VLSFO samples were available. Table 1 shows a detailed distribution of the samples and the associated fuel category.

The parameters used in ASTM D7157, D7112, and D7060 are s-value, p-value, p-ratio, So, Po, Sa, Pa, and FR_{max}. The s-value is used to quantify the intrinsic stability of a fuel oil by observing the state of peptization of the asphaltene. The p-value is used to quantify the stability of a fuel oil through titration and optical detection of asphaltene sludge. The p-ratio is a quantification used to evaluate the stability of a fuel oil in terms of "maximum flocculation ratio of the asphaltenes in the oil and the peptizing power of the oil medium" [12]. The fuel is stable when the s-value, p-value, and p-ratio is above 1. A higher value, or ratio, is associated with less flocculation of asphaltenes and higher stability. So, or Po, is defined as the solvency, or the peptization power which is the ability of the asphaltenes to remain in a suspended state in the fuel oil. So, or Po, is directly proportional to the capability of the asphaltenes staying uniformly distributed in the oil medium. Sa, Pa, or FR_{max} is the ability of the asphaltene to peptize. This term used to determine the amount of asphaltene allowed to remain in a dispersed state. The parameters So, Po, Sa, Pa and FR_{max} are used to evaluate the stability reserve of a fuel. The standard accepted values for stable marine fuels of s/p-values, p-ratio, Sa (or Pa), and So (or Po) are 1.5, 1.1, 0.45, and 0.8, respectively.

According to ISO 8217, standard test method ISO 10307-2 is used to determine stability of a fuel. In this test method, "TSP is the total sediment after ageing a sample of residual fuel for 24h at 100°C under prescribed conditions i.e. the amount of sediment after stressing the fuel through heating" [2]. A TSP value below 0.10 mass % is considered for stable fuel. The study focused on five samples in particular with TSP values greater than 0.10 mass %, which is considered unstable. The test results are shown in Table 2.

Observing VLSFO sample 2018009, it was found that the s-value and p-ratio could not be obtained due to low asphaltene content. The p-value and Pa-value was measured to be 2.34 and 0.72, respectively, indicating stability. This result does not agree with the TSP value obtained from ISO 10307-2.

Samples 2018015, 2018016, and 2018017 "contain a waxy residual stream from a hydrocracker unit of combination with a residue containing asphaltenes" [8]. These three samples have an unstable TSP value but the reasoning for this instability is unclear as other fuel blends with the same waxy residual stream do not exhibit instability. All three samples were found to have a stable s/p-value. The p-ratio of sample 2018015 was found to be borderline stable and the p-ratio of sample 2018017 was found to be unstable. The data deviates away from the measured TSP value except the p-ratio of sample 2018017.

"Sample 2018027 contains a residue from a thermal cracking unit" [8]. All the parameters derived from the three test methods confirm that this fuel sample is unstable with respect to the TSP value. There were several other fuel samples that contain the same residue as 2018027 but do not exhibit the same instability. Rather, the asphaltenes in these samples were found to have a greater stability as shown with a higher Sa/Pa value. The importance of this discrepancy is that the stability of the fuel sample could have been affected by the extent of the thermal cracking unit.

This study indicated that the stability of a marine fuel does not directly correlate with the identity of the streams at which the fuel originates from. Rather, it is the parameters that describe the nature between the asphaltenes stability and the aromaticity of fuel that affects compatibility of marine fuels. Aromatic molecules have the ability to keep asphaltenes in suspension through its solvency power.

In this study, ASTM D7112, D7157, and D7060 were used to assess the compatibility of fuel blends. The compatibility model is based on two factors: solubility blending number (SBN) and insolubility number (IN). These parameters are produced from ASTM D7112 as an output or are calculated using the parameters obtained from ASTM D7157, as shown in Equations 1 and 2. The compatibility parameters of ASTM D7060 are Po and FR_{max}. Po/FR_{max} is equivalent to the p-ratio.

$$IN = 100 * (1\text{-}Sa) \quad \textbf{(Eqn. 1)}$$

$$SBN = IN * (1+(\text{s-value} - 1) * d_{15}/1000) \quad \textbf{(Eqn. 2)}$$

The solubility blend number measures the degree of solubility of the asphaltene. The insolubility number measures the degree of insolubility of the asphaltene. Theoretically, the fuel combination is stable if $SBN_{mix} > IN_{max}$, where SBN_{mix} "is the volumetric average of the SBN of the individual fuels" and IN_{max} is the highest IN out of all the fuels in the mixture. A margin for error of 1.4 was considered in the evaluations of the parameters, except for ASTM D7060, where a margin for error was not required. Considering the margin for error, the compatibility of a fuel blend is determined by the following guideline

Stable area: $SBN_{mix} > 1.4 * IN_{max}$ (fuel 1, fuel 2)
Critical area: $IN_{max} < SBN_{mix} < 1.4 * IN_{max}$
Unstable area: $SBN_{mix} < IN_{max}$

Figure 1. Stability Guideline

Source: Concawe

Samples 2018012 and 2018020 were predicted to be stable at any mixing ratio in all three methods because $SBN_{mix} > 1.4IN_{max}$, or p-ratio > 1, at every volume percent of sample 2018020. Samples 2018025 and 2018020 were predicted to be stable when the volume of sample 2018020 was above 28% (D7157), 10% (D7112), and 50% (D7060). Samples 2018025 and 2018022 were predicted to be unstable when the volume of sample 2018022 was below 23% (D7157) and 15% (D7112). This sample subset was discussed to show a case in each area.

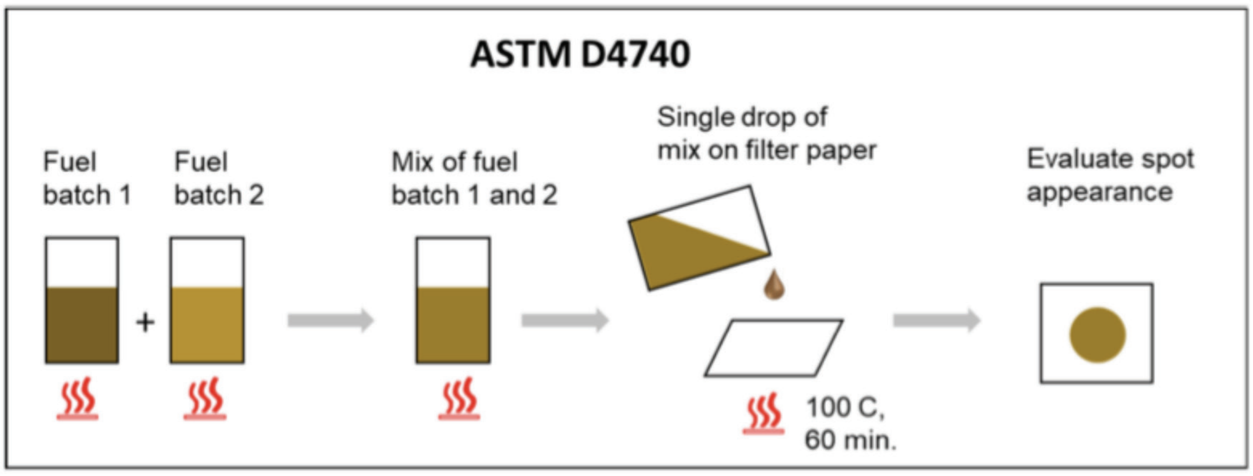
The overall comparison of the performance of ASTM D7157, D7112, and D7060 with ISO 10307-2 Total Sediment Potential is shown in Table 3. The green-shaded areas, orange-shaded areas, and red-shaded areas represent "good", "poor", and "bad" predictions. These predictions are used as an indication of the quality and accuracy of the prediction methodology.

Table 3. Predicted stability vs. actual stability

ASTM D7157 (Rofa) prediction		Actual blend stability based on TSP and TSA		
		Stable	Borderline	Unstable
Predicted classification	Stable	16	2	1
	Borderline	10	0	3
	Unstable	2	0	1
ASTM D7112 (Porla) Prediction		**Actual blend stability based on TSP and TSA**		
		Stable	Borderline	Unstable
Predicted classification	Stable	13	1	1
	Borderline	14	1	2
	Unstable	1	0	2
ASTM D7060 (Zematra) prediction		**Actual blend stability based on TSP and TSA**		
		Stable	Borderline	Unstable
Predicted classification	Stable	18	2	0
	Unstable	6	0	4

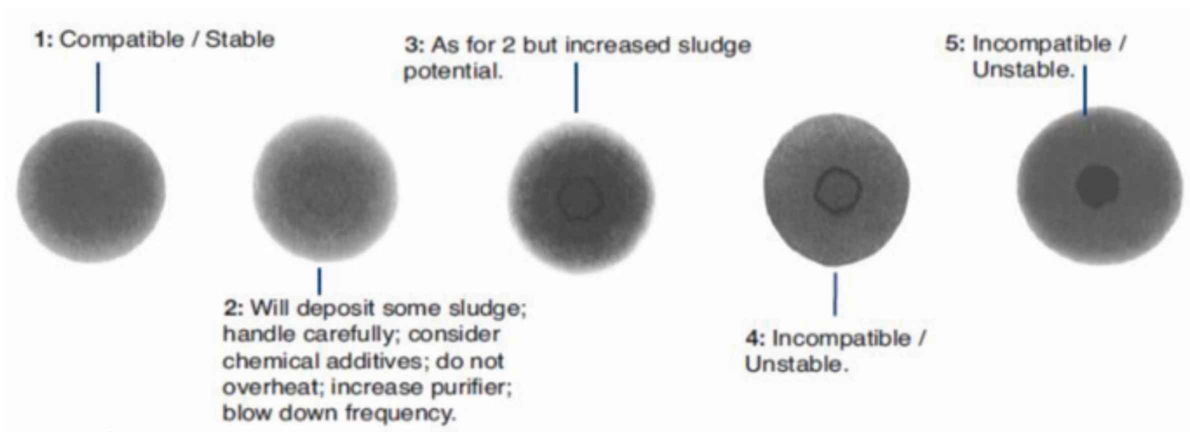
Source: Concawe

Figure 2. ASTM D4740 Spot Test



Source: MAN Energy Solutions

Figure 3. ASTM D4740 reference spots



Source: ASTM D4740

For ASTM D7157 and D7112, predictions agree with TSP evaluation when $SBN_{mix} > 1.4IN_{max}$. However, when the predictions are in the critical or unstable area, verification with TSP is recommended. Predictions from ASTM D7060 agree with TSP evaluation when the p-ratio is greater than 1. Incompatible fuels evaluated from D7060 should be verified with TSP.

Consider fuels with s/p-value > 1.5 and p-ratio < 1, 86% of all fuels were compatible using D7157, 95% using D7112, and 70% using D7060. Inconsistencies have occurred in the comparison, but the three ASTM test methods can still be useful in preventing the possibility of incompatible fuels.

Another common test for fuel compatibility is ASTM D4740 Spot Test. ASTM D4740 is specifically intended for residual fuels with considerable asphaltene content. Highly paraffinic or distillate fuel blends are avoided in this test because the results can come out as false positive. In this test, two fuel samples are mixed together and heated to produce a homogenous mixture. Subsequently, a drop of the fuel blend is placed on a test paper and heated to 100°C for one hour. Graphical representation of the procedure is shown in Figure 2. After the time completion, the spot on the paper is examined and rated according to D4740 reference spots, shown in Figure 3.

The test is performed at different mixture ratios because some fuel blends may be stable at a certain ratio but unstable at a different ratio. The content of aromatic molecules has an effect on the solubility of asphaltenes; and, therefore, the stability of the fuel. A benefit of the spot test is that it could be performed on-board if the test kit is available.

After the IMO ruled in favor of the sulfur reduction of marine fuels, a new variety of fuel formulation was required. With the addition of new compliant fuels, compatibility and stability of fuel blends are now an issue. Incompatible fuels are known to lead to asphaltene precipitation, which is detrimental to ship engine performance. The test methods discussed above are meant to inform the audience of the possible test methods available for predicting the stability/compatibility of blends.

The ASTM methods discussed above are only a portion of the methods included in the ISO 8217 marine fuel specification. As further regulations are imposed on marine fuels used around the world, these specifications may change to ensure the safety of the environment, equipment, and operators and to certify these fuels will perform efficiently.

Since the implementation of the IMO 2020 sulfur reductions only occurring a couple months ago, the global impact of these regulations has yet to be fully seen. As international agencies demand more stringent marine fuel emissions regulations, standards will play an unprecedented role in ensuring that these fuels can meet and exceed the performance specifications. ASTM International's committee on petroleum products, liquid fuels, and lubricants (D02) will be acclimating these fuel standards for a marine fuel market that is growing in size while reducing its negative effects on the environment.

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