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STABILIZING HEAVY FUEL OIL

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This invention relates to a method of improving heavy fuel oil, particularly cracking coil tar. It is concerned with stabilizing such fuels against sediment formation by a heat digesting treatment carried out under controlled conditions for a proper period, the temperature being held within determined limits related to the time of treatment.

The residua from pressure still or petroleum cracking units of various types, including those in which petroleum cracked stocks are heated in coils, are known as "pressure still tars" or "cracking coil tars." They are ordinarily sufficiently fluid for flowing through pipes; they generally have suitably high flash points and high B. t. u. values, but they frequently contain appreciable percentages of coke-like and asphaltic materials, which are considered colloidally suspended, and which on standing tend to form undesirable sediments that make the oils containing them ill adapted for use as a fuel. This is particularly true when the cracking is intense and maximum yields of light products are desired. The sediment formed in the fuel may be to various extents soluble or insoluble in light oils, such as benzene, naphtha, kerosene or gas oil, but it is very likely to precipitate out during storage or handling, owing to the behavior of carbonaceous bodies often referred to as "free carbon," which have a tendency to flock out.

The sediment in a heavy fuel oil gives rise to great difficulties in plugging fuel lines, burners, sticking of valves, etc. thus, making the fuel difficult to employ and unmarketable. Hence, a number of attempts have been made to counteract the formation of sediment in the heavy fuel oils, for example, removal of the sediment by filtration or centrifuging, by addition of a substance, e. g., rosin, purported to stabilize the colloidal sediment, or by the addition of lighter oils to solubilize part of the sediment but by which the heating value and flash point of the fuel are lowered. It is apparent, however, that such proposed methods alter the character of the fuel oil and are not economically feasible.

The object of the present invention is to provide a simple, economical, and efficient method for making a satisfactory reduction in the sediment forming tendency of heavy fuel oils. A more specific object is to stabilize the heavy fuel oils, not only against precipitation of soluble sediment, but, also, against formation of insoluble sediment; and to accomplish this primarily without having to blend the fuel oil with large amounts of a more expensive light petroleum distillate, which also alters the high heating value characteristics of heavy fuel oil. The light distillates, moreover, cannot be employed without certain precautions in blending and selecting them because, in general, they usually tend to precipitate sludges from the pressure distillate tars at ordinary and moderately elevated temperatures, and unless they have a sufficiently high flash point entail the further expense of distilling the blend to obtain the proper flash point.

The foregoing objects and advantages have been attained in accordance with the present invention, which is based on my discovery, that when a heavy fuel oil, such as derived from a cracking operation on reduced crudes or gas oils under severe cracking conditions, is heated in a closed container, e. g. a closed bomb, autoclave, or pressure vessel, over certain periods of time at definite temperatures within the range of 450° F. to 750° F., then cooled to below 450° F. an excellent decrease in sediment formation, both of soluble and insoluble kinds, was obtained. In the bomb the fuel oil was heated in the absence of air without substantial distillation.

In no case was more than a trace of coke formed in the bomb at the end of a run, therefore the sediment reduction could not be attributed to settling therein. At temperatures below 650° F. no coke at all was found. The optimum conditions are somewhat difficult to define, because in all runs made for periods of ¼ hour to 2 hours at temperatures below 650° F. the sediment reduction was of the same order of magnitude, but the more striking results were obtained in the range of 550° F. to 650° F. with the heating period varying inversely with the temperature and being about 2 hours to ½ hour.

Another indication of the maximum severity of conditions in the heating treatment stabilization, beside that of coking in the bomb and the analytical results of sediment reduction, is that of the constancy in gravity and viscosity of the treated material. It was found that at the proper temperatures of treatment, the sediment reduction was effected with no substantial change in gravity, the variation being at the most only about 0.1° A. P. I. to 0.2° A. P. I., mainly not more than 0.1° A. P. I.; and the viscosity in Saybolt furol seconds at 122° F. only varied about 0.1 second to about 5 seconds. In effect, these small changes confirm that no substantial cracking nor viscosity breaking occurs in the stabilization treatment.

By the present method of heavy fuel oil sta-

bilization, cracking coil tar, or even bottoms of reduced crude tars, having low A. P. I. gravities and containing too much sediment and sludge after a short period of standing to be used as liquid fuels, are greatly improved in lowering of their insoluble solid impurities as shown by the A. S. T. M, tests using the centrifuging (B. S. and W.) and filtration (Insol. Sed.) methods, wherein the fuel is treated with a light oil that extracts much of the sediment. Furthermore, using a more advanced test which detects by filtration, sediment in the viscous oil per se, i. e. undiluted with light oils, which under practical conditions would not be present since they impair the flash point of the fuel, the total reduction of insoluble sediment which is actually made can be shown to be obtained by the present process to a high degree. In this test, known as the hot filtration sediment test, the straight heavy fuel oil, undiluted, is filtered at about 212° F. through a weighed Gooch filter bearing an asbestos mat, and the total amount of sediment is weighed and determined in percentage of the oil filtered. To demonstrate the resulting improvement from various pressure still tars stabilized by the treatment illustrated in this invention, the test data is shown in the following table:

Temperature, °F.	450				550			
Time of run, hrs.	¼		2		¼		2	
Stock	Feed	Prod.	Feed	Prod.	Feed	Prod.	Feed	Prod.
Grav., °A. P. I.	13.1	13.1	12.9	13.0	13.1	13.2	13.0	13.0
SSF, vis. at 122° F.	42.4	42.5	42.0	42.8	41.8	41.7	42.0	42.7
B. S. and W., percent	1.2	0.6	1.4	0.6	1.2	0.4	1.2	0.4
Insol. sed., do.	0.191	0.089	0.192	0.117	0.18	0.101	0.247	0.074
Red. in insol. sed., do.		0.102		0.075		0.079		0.173
Sed. by hot filtr., do.	0.264	0.106	0.275	0.129	0.253	0.079	0.311	0.056

Temperature, °F.	600				650			
Time of run, hrs.	¼		2		¼		2	
Stock	Feed	Prod.	Feed	Prod.	Feed	Prod.	Feed	Prod.
Grav., °A. P. I.	13.0	13.0	13.0	12.9	12.9	12.8	13.0	13.1
SSF, vis. at 122° F.	45.4	43.0	42.0	42.5	45.2	41.5	43.0	38.1
B. S. and W., percent	1.2	0.3	1.2	0.3	1.0	0.4	1.4	0.6
Insol. sed., do.	0.204	0.087	0.189	0.065	0.214	0.111	0.172	0.136
Red. in insol. sed., do.		0.117		0.124		0.103		0.036
Sed. by hot filtr., do.	0.273	0.081	0.245	0.130	0.270	0.140	0.290	0.280

Temperature, °F.	700–740		750					
Time of run, hrs.	1		¼		½		2	
Stock	Feed	Prod.	Feed	Prod.	Feed	Prod.	Feed	Prod.
Grav., °A. P. I.	13.4	13.0	13.0	12.9	13.0	12.7	13.0	12.6
SSF, vis. at 122° F.	56.7	57.0	43.0	38.0	43.0	41.0	43.0	43.4
B. S. and W., percent	0.3	1.4	1.3	0.6	1.3	1.5	1.3	2.5
Insol. sed., do.	0.109	[1] 0.169	0.181	0.148	0.202	[1] 0.256	0.160	[1] 0.854
Red. in insol. sed., do.		[1] −0.060		0.033		[1] −0.054		[1] −0.694
Sed. by hot filtr., do.	0.126	[1] 0.395	0.26	[1] 0.27	0.23	[1] 0.57	0.26	[1] 1.65

[1] Increases in sediment denoted.

The data clearly shows the beneficial effect of the heat stabilization treatment and illustrates that no substantial cracking accompanied the reduction in sediment, in that no substantial change in viscosity or gravity was made, while the total sediment content was substantially and permanently reduced. In the runs made at above 700° F., as the time of treatment exceeded ¼ hour, the sediment forming tendency was increased as denoted.

At above 650° F., and more particularly at from 700° F. to 750° F., the sediment begins to increase just as cracking begins, hence, the maximum temperature is about 750° F., although it is preferred to restrict the maximum temperature to below 700° F., and particularly to 650° F. At the minimum temperatures of about 450° F. the time should be at least ¼ hour and may go as high as 3 hours without detrimental cracking effects, but, as stated before, the optimum conditions are 500° F. to 650° F. for a period of ¼ hour to 2 hours.

It has been observed that heat treatments of pressure still tars under incipient cracking conditions, as for example, by laboratory methods used in determining the effect of cracking conditions on sediment formation, are not useful for stabilizing cracking still tars, because by these methods, the still is held at 650° F. to 800° F. for a period of 4 hours to 6 hours, and this treatment tends to concentrate the bottoms and produce more sediment forming bodies. Similarly, a pressure still tar passed directly to tar receptacles, where they undergo substantial flashing or reduction by vaporization and in which time and temperature are not properly controlled, give rise to an increase in sediment forming bodies.

Hence, it is to be understood that in the heat stabilization treatment it is desirable to maintain the heavy fuel oil under sufficient pressure to avoid substantial vaporization, and more particularly under the autogenous pressure created by vapors of the oil or tar in a closed vessel without vapor withdrawal. Any partial pressure added by the presence of an inert or reducing gas is permissible, but, of course, it is desirable to avoid the presence of oxidizing gases.

The initial pressure still tar, or heavy fuel oil,

to be stabilized can be treated just after recovery in a cracking unit, or at some time thereafter. The initial material may be procured from the conventional types of cracking apparatus, as for example, directly from a separator drum receiving conversion products discharged from a cracking coil, from a flash zone that is connected to a separator drum, or intermediate withdrawal from the separator drum and flashing. The tar may be subjected to the stabilization treatment in a tar pot connected with the cracking unit, or in a drum capable of withstanding pressure, like the autoclaves or closed bombs which were used experimentally. The heat stabilization vessel may be heated internally or externally, or may be in the form of a heating coil which finally passes through a heat exchanger for cooling the stream of heavy oil conducted through the coil. The initial tar may have an A. P. I. gravity below 10°, e. g. as low as 3° A. P. I., and as high as 15° A. P. I., and may have Saybolt furol viscosities from 25 to 400 seconds at 122° F. to be made into marketable stabilized bunker fuel oil. Frequently, and more advisably for many uses, the tar should have a gravity of 8° A. P. I. to 14° A. P. I.

After the heat stabilization treatment, the stabilized fuel oil may be filtered or centrifuged, or may be doped with various colloidal fixing agents, if desired, but these additional steps, which are costly, are unnecessary for obtaining satisfactory products with the present process. Also, the fuel oil may be blended with any lighter or heavier oil to obtain any specified viscosity or gravity, for, as pointed out, the material treated in accordance with the present invention is not altered substantially with respect to viscosity and gravity. The blending oil may be added as a quenching medium at the end of the stabilization heat treatment, and is preferably an oil of sufficiently high flash point to avoid forming a low flash point blend.

Since a yield advantage exists in running oils to a low A. P. I. gravity tar with increased intensity of cracking, but which also increases insoluble sediment in the tar, the present treatment is of particular interest for recovering larger yields of higher quality fuel oils from the tarry products made by these processes. By the treatment of the present process, the pressure still tar is given a reduction in total sediment even without being blended with a light distillate oil which further lowers the sediment at least partly by dilution or solution.

The exact mechanism of the stabilization treatment is not understood, but in accordance with the colloidal theory, it appears that the controlled digestion of the tarry oil causes protective asphaltic compounds therein to envelop and disperse the sediment-forming carbonaceous bodies and, therefore, prevents their flocculation.

My invention is not to be limited by any theory or mechanism, nor to any specific example given for the purposes of illustration.

I claim:

1. A method for producing a stabilized heavy fuel oil from a pressure still tar of petroleum of substantially the same gravity having a tendency to precipitate excessive quantities of sediment, which comprises heating the initial pressure still tar without addition of lighter petroleum distillate oil to a temperature between about 450° F. and 750° F. for a period insufficient to cause cracking, ranging from ¼ hour to 3 hours, while maintaining said tar under pressure.

2. The process of producing a stabilized heavy fuel oil which comprises heating a sediment-forming cracking coil tar of petroleum having an A. P. I. gravity in the range of 8° to 14°, at a temperature in the range of 450° F. to 650° F. for a period of ¼ hour to about 2 hours, under the autogenous pressure developed by vapors of said tar undiluted by a lighter petroleum distillate oil.

3. The process of producing a stabilized heavy fuel oil which comprises heating a reduced cracking coil tar of petroleum containing less than 10% of hydrocarbons boiling below 500° F. at a temperature in the range of 450° F. to 650° F. for a period of ¼ hour to about 2 hours without substantial separation of vapors and without addition of a lighter distillate oil, then immediately thereafter cooling said heated tar to below 450° F.

4. A method for stabilizing a sediment forming heavy fuel oil which comprises heating a sediment forming cracked residuum of petroleum, containing less than 10% hydrocarbons boiling below 500° F., at a temperature in the range of 450° F. to 750° F., under a pressure of vapors generated by heating said residuum unblended with a lighter distillate oil for a period sufficient to substantially reduce the sediment forming content of the residuum, but insufficient to change the gravity of the residuum by more than 0.2° A. P. I.

5. A method as described in claim 3, in which the stabilized heavy fuel oil formed by the heat treatment is blended with a lighter oil to form a blend of higher A. P. I. gravity.

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