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DESULFURIZATION OF DISTILLATE FUELS

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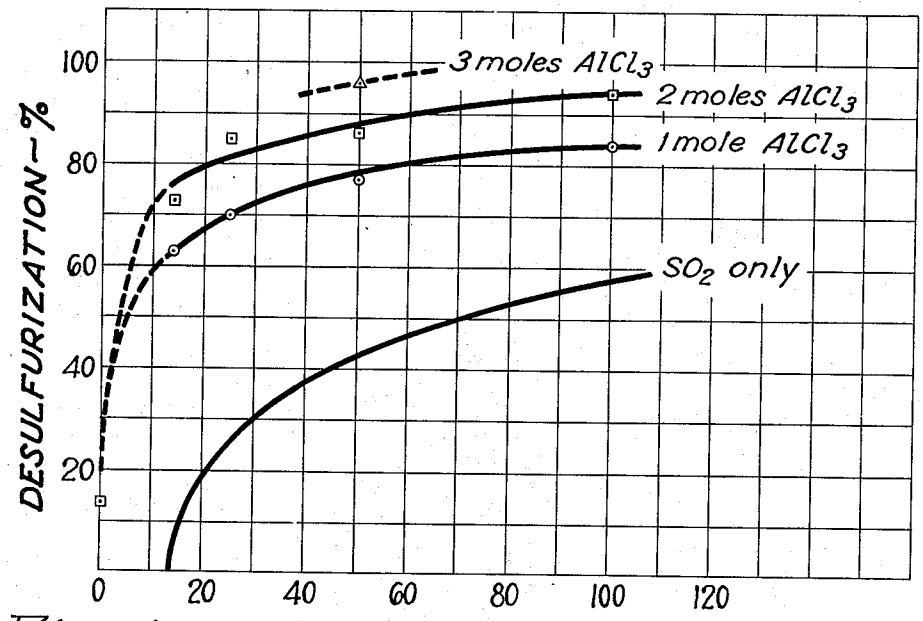


Fig. 1

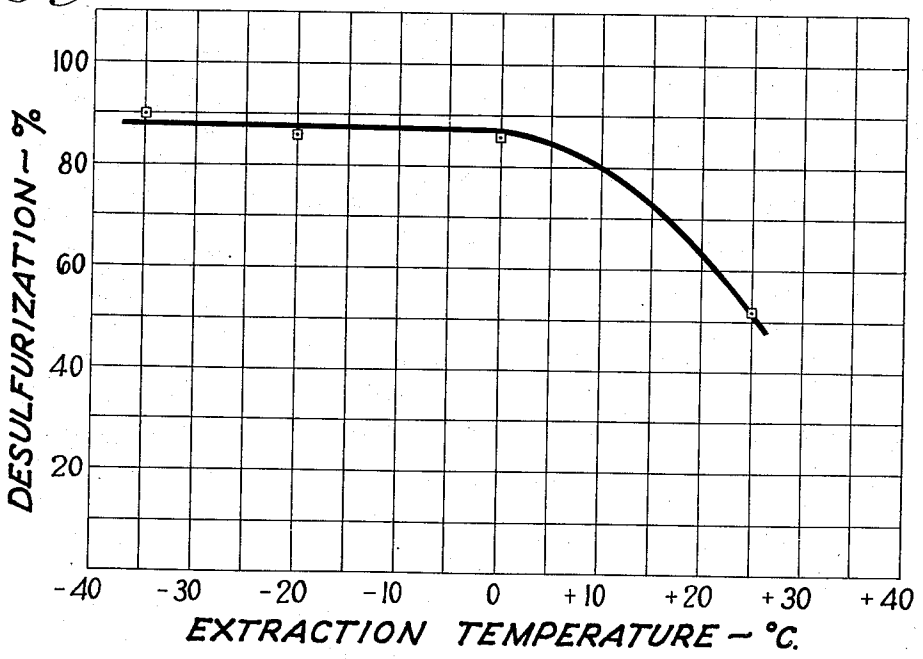


Fig. 2

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DESULFURIZATION OF DISTILLATE FUELS

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Desulfurization of distillate fuels

This invention relates to the treatment of hydrocarbon oils containing organic sulfur compounds for the purpose of reducing sulfur content. More particularly, the invention is directed to the treatment of high sulfur petroleum oils; the invention is of especial interest for the treatment of distillate fuels, i. e. oils boiling in the range of 300° F. (150° C.) to 650° F. (343° C.), such as heavy naphtha, kerosene, diesel oil, furnace oil and heater oil. Still more particularly, the invention is directed to the treatment of distillate fuels intended for use in domestic heating installations, to improve the burning qualities by reducing the sulfur and aromatic content thereof.

The presence of sulfur in gasoline, diesel fuel and in distillate fuels intended for use in domestic type heating units is believed to be undesirable. It is thought that gasoline should contain less than about 0.15 weight per cent of sulfur in the form of organic sulfur compounds and most strict specifications require less than 0.10 weight per cent. It is believed that the distillate fuels for domestic use either in space heaters or furnaces should contain less than about .5% and preferably less than about .3% sulfur. In raw petroleum distillate fuels, a sulfur content of 0.6% is common and some oils contain as much as 1.5%.

Carbon deposition is a serious problem in domestic heating plants. Aromatic hydrocarbons are particularly susceptible to carbon deposition difficulties and, therefore, excessive amounts of these hydrocarbons are undesirable in distillate fuels. Those aromatics removable with small amounts of liquid sulfur dioxide appear to be especially harmful in this respect.

It is known to treat sulfur bearing and aromatic bearing distillate fuels with sulfuric acid; but this process has the drawback of degrading a large proportion of the distillate into virtually valueless sludge. In some cases, this method is uneconomic because of the large amount of acid that must be used in order to produce a satisfactory distillate fuel. The use of sulfur dioxide to reduce the aromatic content also reduces the sulfur content of the raffinate oil. However, sulfur dioxide extraction is not a satisfactory method of desulfurizing a distillate fuel containing large amounts of sulfur because of the large volumes of sulfur dioxide needed and the very large loss of distillate to the extract oil.

An object of this invention is to produce a distillate fuel suitable for use in diesel motors and in domestic heating units from a hydrocarbon oil containing objectionable amounts of organic sulfur compounds and aromatic hydrocarbons. Another object is to produce a low sulfur distillate fuel of good color and good burning quality. Still another object is to provide a process for making good quality distillate fuels from petroleum distillates containing objectionable amounts of sulfur and aromatics by treating these distillates with liquid sulfur dioxide and substantially anhydrous aluminum chloride under such conditions that maximum yields of usable oils are obtained.

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We obtain a low sulfur oil of good burning quality by treating a high sulfur raw oil with liquid sulfur dioxide along with aluminum chloride. For a low sulfur product, the minimum amount of liquid sulfur dioxide needed is about that amount soluble in the oil in the absence of aluminum chloride at the treating temperature. For example, at about —35° C. about 10 volume per cent of liquid sulfur dioxide is soluble in heater oil. However, some desulfurization is obtainable using smaller amounts of liquid sulfur dioxide since a sulfur dioxide-rich phase appears when the aluminum chloride is added to the oil-sulfur dioxide solution. At a fixed aluminum chloride usage, the extent of desulfurization increases markedly with the increase in liquid sulfur dioxide usage up to about 25 volume per cent based on oil of liquid sulfur dioxide usage; above this point, the gain in desulfurization per unit of sulfur dioxide usage is small and about 100 volume per cent appears to be about the maximum desired. An effective amount of desulfurization can be obtained by using as little as 0.5 gram mol of aluminum chloride per gram atom of sulfur present in the raw oil and virtually complete desulfurization is obtainable by using 3 or more mols of aluminum chloride. Normally, a sufficiently low sulfur product oil is obtainable by using from about 1 to about 2 gram mols of aluminum chloride per gram atom of sulfur present in the raw oil. In some cases, sufficient desulfurization can be obtained by treating at a temperature as high as +20° C., but preferably the treating temperature should be less than about 0° C. Where the color of the product oil is of importance and the burning quality must be maximized, the treating should be about —20° C. or lower.

The figures illustrate the results obtainable with our process.

Figure 1 shows the per cent desulfurization obtainable with aluminum chloride addition to liquid sulfur dioxide in the treatment, at —20° C., of a heater oil distillate containing 0.7 weight per cent sulfur.

Figure 2 shows the effect of temperature of treatment on the desulfurization attainable.

Our typical experimental procedure consisted of placing 250 ml. of oil in a separatory funnel, adding the desired amount of liquid sulfur dioxide thereto and immersing the funnel in a constant temperature bath. The aluminum chloride was added to the mixture in the separatory funnel and the contents were agitated for about two minutes, while being maintained at the desired temperature. This time was more than enough to reach equilibrium under the conditions of the particular run. In some cases, the aluminum chloride was dissolved in liquid sulfur dioxide and the mixture added to the oil; no significant difference was noticed by varying the method of introducing the aluminum chloride. The extract and raffinate phases were separated. The raffinate was stripped of sulfur dioxide and its properties determined. The extract phase was allowed to stand until the sulfur dioxide had evaporated whereupon the extract separated into two layers: a highly aromatic oily layer which constituted about 50% of the extract and an aluminum chloride sludge which yielded, upon hydrolysis, a high sulfur viscous tarry liquid with drying oil properties.

In one specific example of our procedure 125 ml. of liquid sulfur dioxide were added to 250 ml. of a West Texas heater oil, described below, and the mixture was chilled to —20° C. in a Dry Ice acetone bath. Aluminum chloride to the extent of one gram mol per atom of sulfur in the heater oil, i. e. 6.2 grams, was added to the funnel and the mixture was vigorously shaken for about two minutes. The mixture was allowed to settle and the two phases separately withdrawn. A yield of 90% of raffinate oil containing 0.17 weight per cent sulfur and a 28 Saybolt color was obtained. The aromatic oil in the extract contained about 2% sulfur and the tarry liquid from the hydrolysis of the sludge contained about 6% sulfur.

The expression "mols" of aluminum chloride will be hereinafter employed to mean gram mols of $AlCl_3$ per gram atom of sulfur in the raw oil to be treated.

The data shown in Table I were obtained by treating, according to the above procedure, a heater oil from a West Texas crude, which heater oil had the following properties:

API gravity	40.3
Sulfur, weight per cent	0.73
Saybolt color	+19
Refractive index (N_D^{20})	1.4585
ASTM distillation:	
IBP	330° F. (166° C.)
10%	390° F. (199° C.)
50%	445° F. (230° C.)
90%	500° F. (260° C.)
Max.	544° F. (284° C.)

The data shown in Table II were obtained by treating, according to the above procedure, a distillate fuel derived from fluid catalytic cracking of a West Texas virgin gas oil. This distillate had an API gravity 30, a sulfur content 1.2 weight per cent, and a refractive index (N_D^{20}) 1.4962.

TABLE I

Temp., ° C.	SO_2, Vol. Percent	$AlCl_3$ Added [1]	Raffinate				
			Sulfur, Wt. Percent	Percent Desulfurization	Yield, Vol. Percent	Color, Saybolt	N_D^{20}
—20	14	1	.27	63	96	20	1.4540
—20	14	[2] 2	.16	73	92	17	1.4524
—20	None	2	.63	14	96	30	1.4572
—20	25	None	.55	25	96		1.4533
—20	25	1	.22	70	92	26	1.4513
—20	25	2	.11	85	91	28	1.4499
—20	50	None	.42	43	91		1.4501
—20	50	1	.17	77	90	28	1.4502
—20	50	2	.10	86	89	27	1.4485
—20	50	3	.03	96	85	30	1.4462
—20	100	None	.31	58	86		1.4470
—20	100	1	.12	84	84	28	1.4464
—20	100	2	.04	94	82	28	1.4454
—35	50	2	.07	90	90	30	1.4474
0	50	2	.10	86	87	17	1.4492
+25	50	2	.35	52	85	17	1.4521

[1] Mols of $AlCl_3$ per gram atom of sulfur in distillate.
[2] All $AlCl_3$ did not dissolve in SO_2.

TABLE II

Temp., ° C.	SO_2, Vol. Percent	$AlCl_3$ Added [1]	Raffinate				
			Sulfur, Wt. Percent	Percent Desulfurization	Yield, Vol. Percent	Color, Saybolt	N_D^{20}
—20	50	None	.57	53	65	—2	1.4696
—20	50	2	.18	85	65	21	1.4656

Using the data presented in Table I, the desulfurization obtained with liquid sulfur dioxide alone and with various amounts of liquid sulfur dioxide with aluminum chloride at a treating temperature of —20° C. was plotted in graphical form in Fig. 1. At this temperature, —20° C., about 14 volume per cent of liquid sulfur dioxide is soluble in this West Texas heater oil. It has been noticed that the addition of aluminum chloride to an oil-sulfur dioxide solution results in the immediate separation of a sulfur dioxide-rich extract phase. At about —20° C., 14 volumes of liquid sulfur dioxide per 100 volumes of oil will just dissolve the amount of aluminum chloride equivalent to one gram mol per gram atom of sulfur present in this particular oil. However, it is possible to obtain good results using more aluminum chloride than is soluble in the liquid sulfur dioxide as is seen when 2 mols of aluminum

chloride were added to 14 volume per cent of liquid sulfur dioxide. In fact, some desulfurization is obtained when no liquid sulfur dioxide is present. For example, the use of 2 mols aluminum chloride alone gave 14% desulfurization of this particular oil. At 50 volume per cent of liquid sulfur dioxide, usage of 3 mols of aluminum chloride resulted in 96% desulfurization of this oil or virtually complete desulfurization.

The effectiveness of aluminum chloride in promoting sulfur removal by liquid sulfur dioxide is startling in the low region of liquid sulfur dioxide usage. The "percentage-point" difference in desulfurization between 10 and 25 volume per cent of sulfur dioxide use is about the same as the difference between 25 and 100 volume per cent of sulfur dioxide use.

It is indicated that for a high sulfur content virgin distillate fuel, normally 1.5 weight per cent sulfur but sometimes even higher, a satisfactory oil of about 0.3 weight per cent sulfur or less can be obtained by using a maximum of about 80 volume per cent of liquid sulfur dioxide along with about one gram mol of aluminum chloride per gram atom of sulfur in the raw oil.

Fig. 2 shows the effect of temperature of extraction on desulfurization at 50 volume per cent of liquid sulfur dioxide and 2 mols of aluminum chloride. The effectiveness appears to be substantially independent of temperature below about 0° C.; above about 0° C., the effectiveness drops rapidly and is less than about 60% at about +20° C.

Another remarkable feature of this process is the very slight decrease in raffinate yield with a very large increase in desulfurization, over the use of liquid sulfur dioxide alone. At —20° C. with 25 volume per cent of sulfur dioxide and 1 mol of $AlCl_3$, the raffinate yield is decreased only 4 per cent below the yield of raffinate obtained by sulfur dioxide alone, while the sulfur reduction amounts to 45 percentage points (about 180% increase). Using 2 mols of $AlCl_3$, the raffinate yield is reduced only about another 1% while the sulfur reduction increases by about 33%.

Still another remarkable result of this process is the fact that the selectivity of the sulfur dioxide for aromatics appears to be enhanced by the $AlCl_3$. The decrease in refractive index of the raffinate with increased amounts of $AlCl_3$ at constant sulfur dioxide usage shows this very desirable improvement. A very great improvement in burning quality of the finished distillate fuel is realized by accepting this very slight decrease in raffinate yield.

The data in Table I show that the effectiveness of the sulfur dioxide-aluminum chloride in color improvement decreases with temperature rise. Thus, the oils treated below —20° C. had an excellent color of about 28 Saybolt (water-white), whereas at 0° C. and above the treated oils were silghtly poorer than the raw heater oil itself. Even though the yield of raffinate decreases with increasing temperature of extraction, the refractive index of the raffinate shows an increase in the aromatic content. Thus, while satisfactory desulfurization can be obtained at between 0° to +20° C., considerations of raffinate yield, quality and color indicate that the extraction temperature should be below 0° C. and preferably about —20° C.

This process has the added advantage over sulfuric acid treating in that all the extract phase is not degraded to virtually valueless sludge. Over sulfur dioxide treating alone, our process has an advantage in that about one-half of the extract phase is essentially aromatic in nature and the remainder of the extract is a material that can be used as a commercial fuel, or the tarry liquid can be further refined for use as a drying oil. The aromatic oil can be used as a solvent "as is" when sulfur content is of no importance. The aromatic oil from our process has a lower sulfur content, a better odor, and a better color than the aromatic oils obtained by other extractive processes.

In general, our invention can be carried out in conventional Edeleanu process equipment, with the addition of a mixer for dissolving the aluminum chloride in the liquid sulfur dioxide; a vessel for separating the aromatic oil extracted from the tarry sludge containing the spent $AlCl_3$, and means for hydrolyzing the tarry sludge. The temperature can be varied between —40° C. and +20° C., with —20° C. preferred. In all cases pressure sufficient to maintain the sulfur dioxide in the liquid state must be used.

We claim:

1. A process for refining a high-sulfur virgin petroleum distillate fuel, which process comprises contacting said distillate, at a temperature of between about —20° and about —40° C., with between about 0.5 and 3 gram mols of substantially anhydrous aluminum chloride per gram atom of sulfur in said distillate in the presence of at least sufficient liquid sulfur dioxide to form distinct raffinate and extract phases, separating said phases and recovering from said raffinate phase a product oil characterized by a sulfur content lower than that of said distillate, a Saybolt color not more than about that of said distillate, and improved burning quality.

2. The process of claim 1 wherein said distillate is a straight-run heater oil distillate boiling between about 165° and 285° C. and having a sulfur content of between about 0.6 and 1.5 weight percent.

3. A process for refining a high-sulfur, straight-run petroleum distillate boiling between about 150° and 343° C., which process comprises the steps of introducing into a contacting zone, said distillate, liquid sulfur dioxide in an amount between about 25 and about 50 volume percent based on said distillate, and substantially anhydrous aluminum chloride, in an amount between about 1 and 2 gram mols per gram atom of sulfur in said distillate, maintaining said zone at a temperature between about —20° and about —40° C. for a time sufficient to attain substantially equilibrium desulfurization, separating a raffinate phase consisting essentially of refined oil and SO_2 from an extract phase consisting essentially of liquid SO_2, $AlCl_3$ and dissolved hydrocarbons and organic-sulfur compounds, and recovering from said raffinate phase a refined oil characterized by a sulfur content of not more than 40% of the sulfur content of said distillate, a Saybolt color better than that of said distillate and good burning quality.

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