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DESULPHURIZING GASOLINE

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Fig. 1.

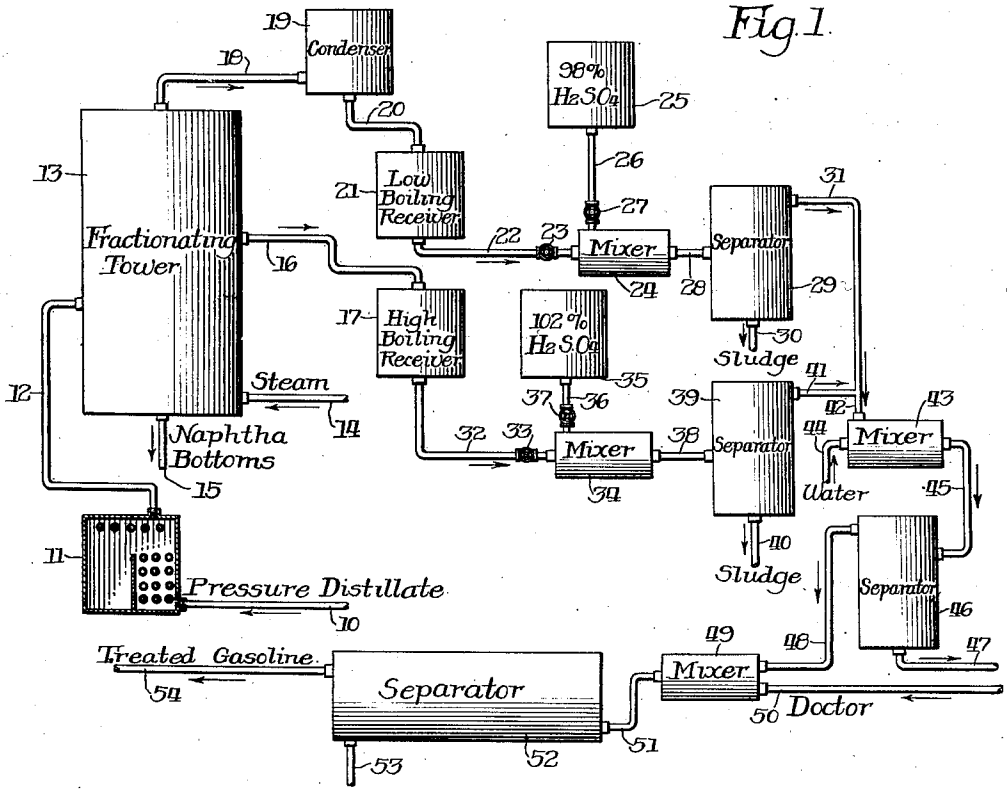
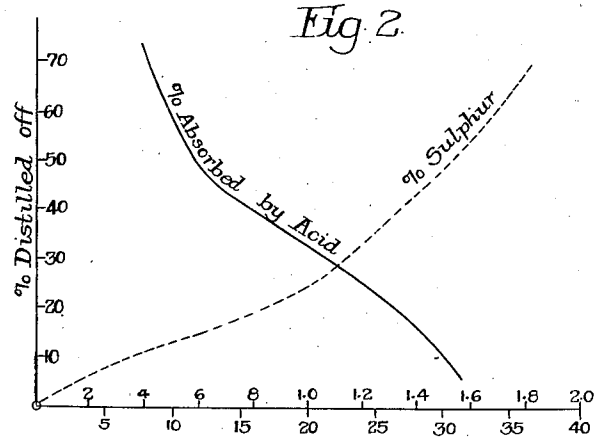


Fig. 2.



% Sulphur ----------

% Aborbed by Acid ———

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DESULPHURIZING GASOLINE

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10 Claims. (Cl. 196—31)

This invention relates to a process of desulphurizing gasoline and it pertains more particularly to an improved method of desulphurizing cracked gasoline of high sulphur content.

The object of our invention is to provide a process for removing sulphur from high sulphur cracked gasoline which will increase the yield of treated gasoline and minimize the absorption of gasoline in the treating acid (minimize the amount of sludge formed).

A further object is to reduce the amount of acid required for removing sulphur from a given quantity of gasoline.

A further object is to obtain a maximum yield of stable cracked gasoline which will be substantially free from sulphur. Other objects will be apparent as the detailed description of our invention proceeds.

After extensive research on cracked gasoline (pressure still distillate) prepared from different crudes, we discovered that the sulphur compounds are not uniformly distributed according to boiling point but are more concentrated in the higher boiling fractions than in the lower boiling fractions. We also discovered that the unsaturated hydrocarbons tend to be concentrated in the lower boiling fractions and that the bulk of treating losses therefore occur in these lighter fractions. We have provided an improved treating process wherein we make practical use of these discoveries by separating the gasoline into two or more fractions of successively higher boiling range, treating the lower boiling fraction (which is low in sulphur and high in unsaturated hydrocarbons) with a small amount of acid, treating the higher boiling fraction (which is high in sulphur content and low in unsaturated hydrocarbons) with a larger amount of strong sulphuric acid, and finally mixing the fractions to obtain the desired properties for the final treated gasoline.

The invention will be more clearly understood from the detailed description which follows and from the accompanying drawing, wherein—

Figure 1 is a flow diagram of our improved process.

Figure 2 is a characteristic graph showing the percentages of sulphur and percentage of gasoline absorbed by acid plotted against the percent of cracked gasoline distilled.

Referring to Fig. 1, pressure still distillate is introduced by pipe 10 through pipe still 11 and pipe 12 to a mid-point of fractionating tower 13. The fractionating tower may be of any conventional type and is preferably provided with bubble trays and baffle plates. This tower, per se, forms no part of the present invention and will not be described in detail.

Stripping steam is introduced by pipe 14 to remove all low boiling point hydrocarbons from the naphtha bottoms, which are withdrawn through pipe 15. A high boiling fraction is withdrawn from the tower at a point above the discharge of pipe 12 by a pipe 16 which conveys this fraction to receiver 17.

The reflux vapors are conducted from the top of tower 13 by conduit 18 which leads to a condenser 19, wherein said vapors are liquefied. These low-boiling hydrocarbons are conveyed by pipe 20 to low boiling receiver 21.

The low-boiling distillate is conveyed through pipe 22 in amounts regulated by valve 23 to mixer 24, which is preferably an orifice or "knot-hole" mixer. Sulphuric acid of a concentration between 89 and 100%, preferably about 98%, is supplied from storage tank 25 through pipe 26 in amounts regulated by valve 27 to said mixer 24. For a light cut containing 0.2% sulphur, about 8 pounds of acid are mixed with 50 gallons of oil, for a light fraction containing .39% sulphur about 20 pounds of acid are used to treat 50 gallons of oil, and for a light cut containing .96% sulphur about 44 pounds acid are used to treat 50 gallons of oil, 98% acid being used in each of the above examples.

The mixture of the acid and oil is conducted from mixer 24 by pipe 28 to separator 29, wherein the sludge settles out and is withdrawn by pipe 30, the treated gasoline being discharged through pipe 31.

The heavy fraction is conducted from the high boiling receiver 17 through pipe 32 in amounts regulated by valve 33 to mixer 34. Sulphuric acid of a concentration of from 93 to 104½%, for example 98%, is introduced from storage tank 35 through pipe 36 in the amounts regulated by valve 37 to said mixer. When the heavy cut contains .46% sulphur about 20 pounds of 98% acid are used per 50 gallons of oil, when the fraction contains .81% sulphur 43 pounds of 98% acid are used to treat 50 gallons of oil, and when the fraction contains 1.48% sulphur about 60 pounds of 98% acid are used per 50 gallons of oil.

The mixture of oil and acid is conveyed from mixer 34 by pipe 38 to separator 39 wherein the sludge is settled out and withdrawn by pipe 40 and the treated gasoline is withdrawn through pipe 41.

The treated gasoline from pipe 41 is mixed

with the treated gasoline from pipe 31 in pipe 42, which discharges into a mixer 43, wherein the treated gasoline is mixed with water introduced through pipe 44. From mixer 43, the gasoline and water are conveyed through pipe 45 to separator 46, impurities being withdrawn from the bottom of the separator by pipe 47 and the washed gasoline being withdrawn by pipe 48 which conveys it to mixer 49, where it is treated with doctor solution introduced through pipe 50.

The doctor solution is a conventional sodium plumbite which is made up by dissolving lead oxide in sodium hydroxide. This step, per se, is well known and forms no part of the present invention. The doctor treatment sweetens the gasoline by removing mercaptans and other sulphur compounds.

The gasoline-doctor mixture is conveyed from mixer 49 by pipe 51 to separator 52, from which the sludge is removed by pipe 53, and the treated gasoline by pipe 54.

The treatment with sulphuric acid often leaves in the gasoline certain resin-forming or gum-forming compounds which should be removed if stability of a long period of time is desired. These resin-forming bodies are preferably removed by a second distillation, the treated gasoline being introduced by pipe 54 into a still (not shown) for final distillation.

The fundamental principles on which our invention is based will be understood from the diagram in Fig. 2 and from the following tables. Pressure still distillate from three separate crudes were fractionally distilled and determinations were made to show (1) the percentage of sulphur in each fraction and (2) the percentage of pressure distillate absorbed by sulphuric acid. The results are as follows:

Crude No. I

Percent distilled off	Percent Sulphur	Percent Absorbed
10	.1	29
20	.2	25
30	.3	17
40	.4	8
50	.5	6
60	.6	5
70	.75	5

Crude No. II

Percent distilled off	Percent Sulphur	Percent Absorbed
10	.18	28
20	.37	22
30	.55	18
40	.72	10
50	.89	7
60	1.06	5
70	1.20	5

Crude No. III

Percent distilled off	Percent Sulphur	Percent Absorbed
10	.38	25
20	.90	19
30	1.25	15
40	1.41	11
50	1.56	9
60	1.70	8
70	1.85	7

From Fig. 2 and from the above tables will be seen that the sulphur compounds are not uniformly distributed according to boiling point but these tend to be concentrated into the higher boiling fractions. It is also shown that the unsaturated higher hydrocarbons are more concentrated in the lower boiling fractions. Therefore, by treating these fractions separately less acid can be used for lower boiling fractions. This will in turn result in a decreased gasoline absorption and as a result we will be able to increase the yield of gasoline and decrease the amount of acid required by the simple expedient of separately treating the fractions and subsequently uniting them.

The cracked gasoline, represented by Crude No. I in the above table, was fractionated into a light cut having a .2% sulphur content and the heavy cut having a .46% sulphur content. Using 8 pounds of 98% acid for the light cut and 20 pounds of 98% acid for the heavy cut per 50 gallons of oil, a total of 14 pounds of acid was used per 50 gallons and a total treating loss of 5.7% resulted. When this gasoline was treated in one batch, 20 pounds of 98% acid were required per 50 gallons of oil and the treating loss was 9.10%. It will be seen that 6 pounds of acid was saved for every 50 gallons of gasoline treated and that the loss was reduced from 9.10% to 5.7%, the difference being 3.40% of the gasoline treated which is equivalent to 37.7% of the losses by the old method of treating all of the gasoline in one batch.

Similar tests on cracked gasoline from crude stock No. II showed an acid saving of 12½% and a treating loss decrease of 4.38% of gasoline treated (which was equivalent to 25.3% of the loss by the old method of treating all of the gasoline in one batch).

Similar tests on cracked gasoline from crude stock No. III showed an acid saving of 7.1% and a treating loss decrease of 10.15% of the gasoline treated (which was equivalent to 38.5% of the losses by the old method of treating all of the gasoline in one batch). Examples might be multiplied indefinitely to show the saving effected by our improved process.

While we have disclosed a prefered embodiment of our invention, we are not limited to the details therein set forth. We contemplate the separate treatment of a plurality of fractions, the amount of acid used being increased with increasing boiling points. Various modifications of apparatus will be apparent to those skilled in the art.

We claim:

1. The process for removing sulphur from cracked gasoline which comprises separating a quantity of cracked gasoline into a high boiling fraction and a low boiling fraction, the volume of the low-boiling fraction being less than the volume of the high boiling fraction, treating the low boiling fraction with 89 to 98% sulphuric acid in the proportion of about eight pounds of acid for each fifty gallons of the fraction, treating the high boiling fraction with 93 to 104½% sulphuric acid in proportions of about twenty pounds of acid for each fifty gallons of said fraction, and reuniting the treated fractions to form gasoline.

2. The process for removing sulphur from cracked gasoline and at the same time preserving a substantial proportion of the compounds that normally react with strong sulphuric acid, which comprises separating the cracked gasoline into a high boiling fraction and a low boiling fraction of about equal volumes, treating the low boiling fraction with 89 to 98% sulphuric acid in the proportions of about eight pounds of acid for

about fifty gallons of said fraction, treating the high boiling fraction with 93 to 104½% sulphuric acid in the proportion of about twenty pounds of acid for fifty gallons of oil, and reuniting said treated fractions to form the cracked gasoline.

3. The process of desulphurizing cracked gasoline and at the same time preserving a substantial proportion of the components therein that normally react with 93–98% sulphuric acid, which comprises separating the cracked gasoline into a low boiling fraction and a high boiling fraction of about equal volumes, treating the high boiling fraction with 93 to 104% sulphuric acid in proportions of about twenty pounds of acid for fifty gallons of said fraction, treating the low boiling fraction with 89 to 98% sulphuric acid in the proportion of about eight pounds of acid for about fifty gallons of said fraction, and reuniting said treated fractions to form the cracked gasoline.

4. The process of removing sulphur from cracked gasoline which comprises separating the cracked gasoline into a high boiling fraction and a low boiling fraction, the volume of the high boiling fraction being not more than 30% greater than the volume of the low boiling fraction, treating the low boiling fraction with 89 to 98% sulphuric acid in the proportions of about eight pounds of the acid for about each 0.2% of sulphur per fifty gallons of the low boiling fraction, treating the high boiling fraction with 93 to 104½% sulphuric acid in the proportions of about 20 pounds of the acid for about each 0.46% of sulphur per fifty gallons of the high boiling fraction, removing the sludge formed during the treating of the respective fractions, and reuniting the treated fractions to form gasoline.

5. The process of removing sulphur from cracked gasoline which comprises separating a quantity of the gasoline into a low boiling fraction and a high boiling fraction, the volume of the low boiling fraction being less than 10% of the volume of the high boiling fraction, treating the low boiling fraction with 89 to 98% sulphuric acid in the proportions of about eight pounds of the acid for about 0.2% sulphur per fifty gallons of the low boiling fraction, treating the high boiling fraction with 93 to 104½% of sulphuric acid in the proportions of about 20 pounds of the acid for about each 0.4% of sulphur per fifty gallons of the high boiling fraction, removing the sludge formed during the treating of the respective fractions, and reuniting the treated fractions to form gasoline substantially free from objectionable sulphur compounds and containing a large quantity of hydrocarbons that normally react with concentrated sulphuric acid.

6. The process of removing sulphur from cracked gasoline and at the same time preserving a substantial proportion of the compounds that normally react with strong sulphuric acid, which comprises separating the cracked gasoline into a high boiling fraction and a low boiling fraction in the proportions of about forty percent of the high boiling fraction and sixty percent of the low boiling fraction, treating the low boiling fraction with 89 to 98% sulphuric acid in the proportions of about eight pounds of the acid for about each 0.2% of sulphur per fifty gallons of the low boiling fraction, treating the high boiling fraction with 93 to 104% sulphuric acid in the proportions of about twenty pounds of the acid for about each 0.46% of sulphur per fifty gallons of the high boiling fraction, and reuniting said treated fractions to form a cracked gasoline.

7. The process of desulphurizing cracked gasoline and at the same time preserving a substantial portion of the hydrocarbons in said cracked gasoline which normally react with strong sulphuric acid, which comprises separating the cracked gasoline into a high boiling fraction and low boiling fraction, the volume of the high boiling fraction being equal to or not more than 10% greater than the volume of the low boiling fraction, treating the low boiling fraction with 89 to 98% sulphuric acid in proportions of about 8 pounds of acid for each 50 gallons of said fraction, treating the high boiling fraction with 93 to 104% sulphuric acid in proportions of about 20 pounds of acid for each 50 gallons of said fraction, and reuniting the treated fractions to form cracked gasoline which is substantially free from sulphur and which contains a large quantity of hydrocarbons that normally react with strong sulphuric acid.

8. The process of desulphurizing cracked gasoline which comprises separating the gasoline into a low boiling fraction and a high boiling fraction, said low boiling fraction containing a small amount of sulphur-bearing compounds and a large proportion of hydrocarbons that are reactive with sulphuric acid, said high boiling fraction containing a large proportion of sulphur-bearing compounds, treating the low boiling fraction with 89 to 98% sulphuric acid in the proportions of about 8 pounds of acid for each 0.2% of sulphur per 50 gallons of the low boiling fraction, treating the high boiling fraction with 93 to 104½% sulphuric acid in the proportions of about 20 pounds of acid for each 0.46% of sulphur per 50 gallons of the high boiling fraction, and reuniting the treated fractions to form a cracked gasoline.

9. The process of desulphurizing cracked gasoline and at the same time preserving a substantial portion of the unsaturated compounds in said cracked gasoline, which comprises separating the gasoline into a low boiling fraction and a high boiling fraction, the volume of the low boiling fraction being from one-third to one-fourth the volume of the high boiling fraction, treating the low boiling fraction with 89 to 98% sulphuric acid in the proportions of about 8 pounds of acid for each 0.2% of sulphur per 50 gallons of the low boiling fraction, treating the high boiling fraction with 93 to 104½% sulphuric acid in the proportions of about 20 lbs. of acid for each 0.46% of sulphur per 50 gallons of high boiling fraction, and reuniting the treated fraction to form a cracked gasoline.

10. The process of desulphurizing cracked naphtha which comprises separating the naphtha into a low boiling fraction and a high boiling fraction, the volume of the low boiling fraction being less than the volume of the high boiling fraction, treating the low boiling fraction with 89 to 98% sulphuric acid in the proportions of about 20 lbs. of the acid for about each 0.39% of sulphur per 50 gallons of the low boiling fraction, treating the high boiling fraction with 93 to 104½% sulphuric acid in the proportions of about 60 lbs. of acid for about each 1.48% of sulphur per 50 gallons of the high boiling fraction, removing the sludge formed during the treating of the respective fractions and reuniting the fractions to form gasoline substantially free from objectionable sulphur compounds.

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