METHOD OF REDUCING SULFUR CONTENT OF RESIDUAL PRODUCTS

Filed June 1, 1960 2 Sheets-Sheet 1

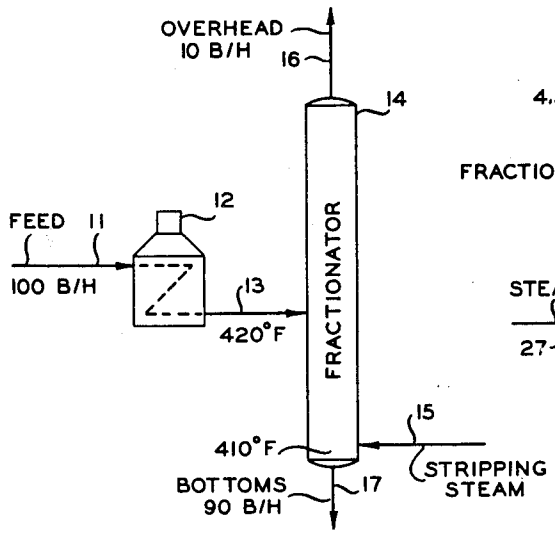


FIG. 1
PRIOR ART

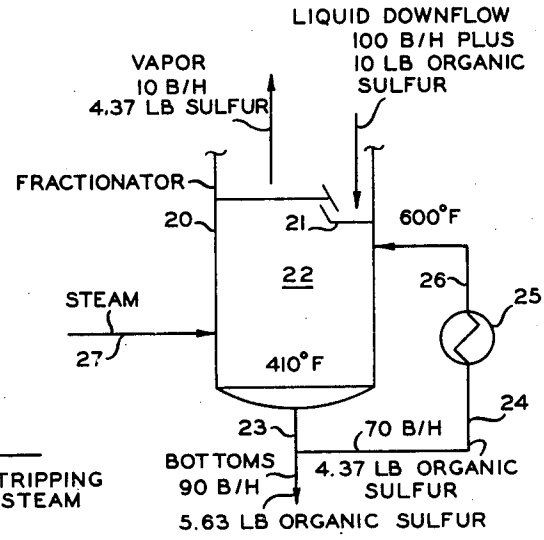


FIG. 2
PRIOR ART

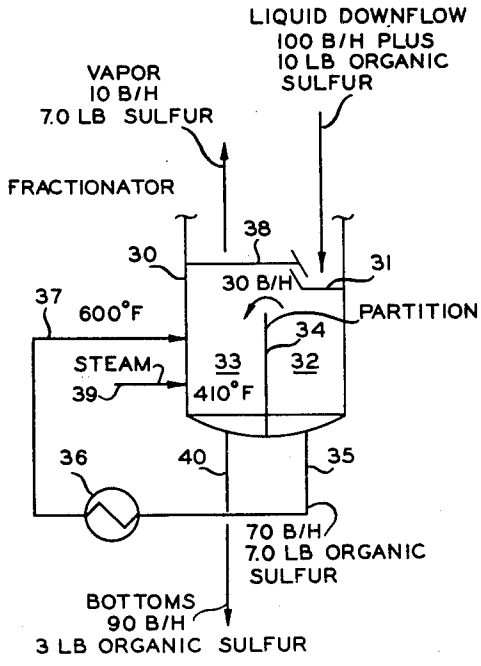


FIG. 3

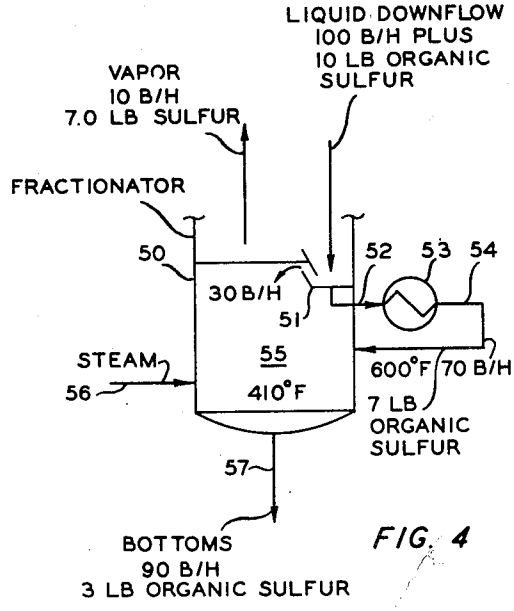


FIG. 4

INVENTOR.
J. T. CABBAGE

BY
Anderson & Young
ATTORNEYS

Jan. 28, 1964 J. T. CABBAGE 3,119,764

METHOD OF REDUCING SULFUR CONTENT OF RESIDUAL PRODUCTS

Filed June 1, 1960 2 Sheets-Sheet 2

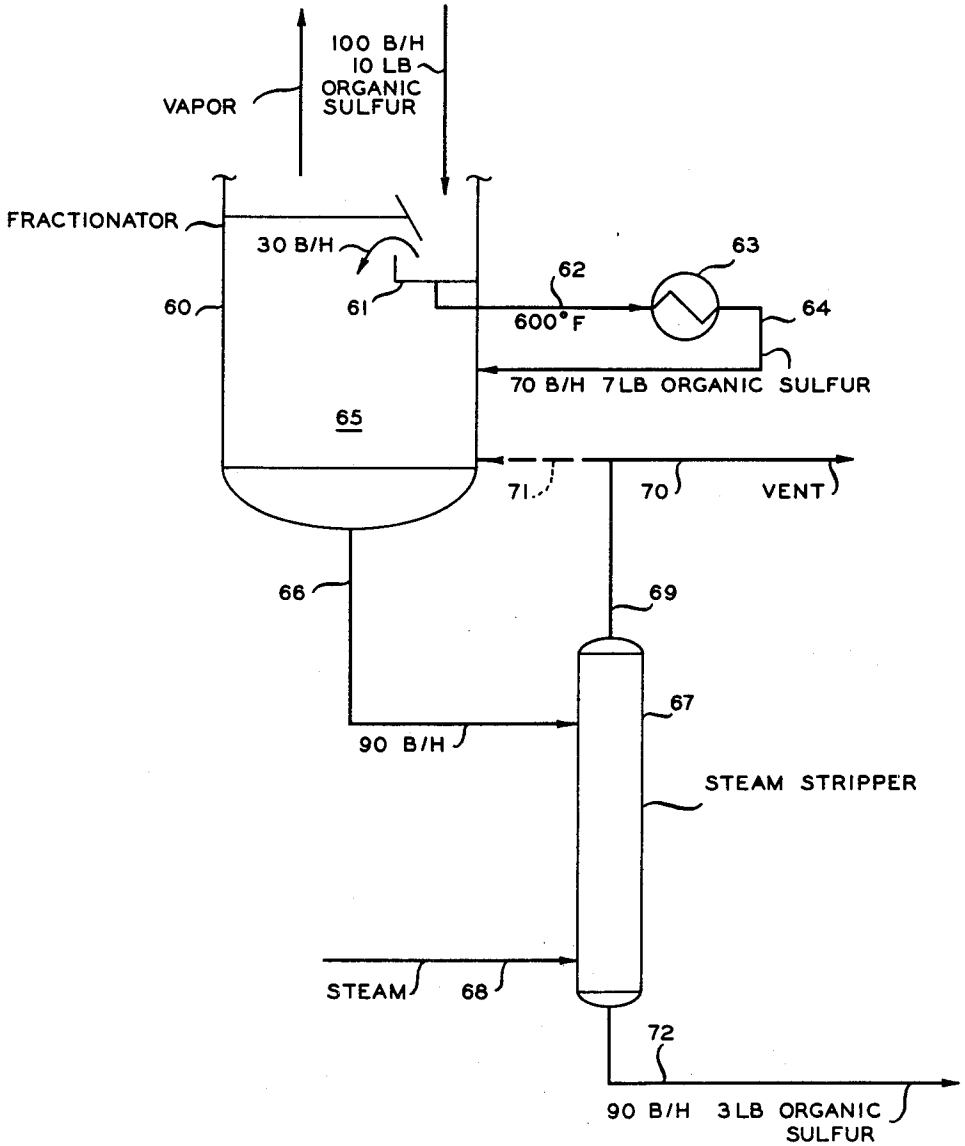


FIG. 5

INVENTOR.
J. T. CABBAGE

BY

ATTORNEYS

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3,119,764

METHOD OF REDUCING SULFUR CONTENT OF RESIDUAL PRODUCTS

John T. Cabbage, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

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5 Claims. (Cl. 208—208)

This invention relates to the reduction of the sulfur content of an oil. In one aspect, the invention relates to the heat treating of a sulfur compound containing oil. In another apect, the invention relates to the reduction of the sulfur content of a product of a distillation column. In another aspect, the invention relates to the reduction of the sulfur content of a product of a fractionator. In still another aspect, the invention relates to thermal desulfurization of the bottoms yield of a fractionator. In another aspect, the invention relates to the reduction of the content of sulfur compounds in residual products by reboiling the bottoms of the fractionator and introducing stripping steam. In a further aspect, the invention relates to the fractionation of crude oil wherein the residual product is subjected to an elevated temperature to reduce the sulfur content of the product. In another aspect, the invention relates to the control of the feed to the reboiler by withdrawing the feed directly from the bottom tray downcomer of the fractionator. In another aspect, the invention relates to the control of the feed to the reboiler by utilizing a partitioned bottom in a fractionator. In still another aspect, the invention relates to the reduction of the sulfur content of the product of a distillation column by controlling the feed to the reboiler in such a manner that the heat treated material cannot be recycled back through the reboiler.

Reduction of the sulfur content of a residual oil is definitely required when the oil is used as is, or is blended into fuel oil if, without sulfur reduction, the fuel oil cannot meet the sulfur specification. Further, where residual oil, such as topped crude, is to be processed in a vacuum unit, the heat treatment in the distillation operation will break out a major portion of the reactive sulfur and thereby reduce the load on the vacuum jets in the vacuum flasher (resulting in a saving of investment cost and operating expenses of a vacuum operation).

Sulfur compounds in crude oil are usually made up of a number of different organic sulfur compounds which vary in thermal stability. For example, a portion of the sulfur compounds will decompose rapidly at 400° F., and other portions can react very slowly. If the reaction temperature is raised to 500° F. then an additional fraction can react rapidly, while the remainder of the sulfur compounds are relatively stable at this temperature. When the reaction temperature is raised to 600° F., a further additional fraction can react rapidly, leaving a substantially smaller amount, if any, of stable sulfur compounds.

In the distillation of oils, a product can be desulfurized by subjecting the oil to an elevated temperature to crack or destroy at least a portion of the sulfur compounds therein. The heat treatment of the oil produces hydrogen sulfide in vapor form which can be removed from the oil by steam stripping. I have found that a substantial gain in the effectiveness of utilizing a heat treatment to desulfurize the oil can be made by maintaining the portion of the treating zone from which the sulfur compound containing oil is withdrawn for heating, substantially free from any returned oil which has been heat treated to decompose sulfur compounds contained therein, which does not vaporize in said treating zone. I have further found that a substantial gain in the effectiveness of utilizing a heat treatment to desulfurize the residue from a fractionator can be made by withdrawing

a portion of the oil from a first section of the fractionator, heating the removed oil to a temperature at which sulfur compounds therein will decompose, thus decomposing sulfur compounds therein, returning the thus treated oil to a second section of said fractionator separate from said first section and withdrawing from said second section directly and from the operation as a product thereof oil in said second section, as contrasted with withdrawing a portion of the product stream, heat treating said product stream portion and introducing said product stream portion back into the bottom of the fractionator. The latter operation allows a part of the treated portion to be recycled again through the heat treating means thus reducing the amount of fresh material which can be heat treated.

Accordingly, an object of this invention is to desulfurize an oil. Another object of this invention is to desulfurize a product from a distillation column. Still another object of this invention is to desulfurize a product from a fractionator. Still another object of this invention is to desulfurize the residual product of a fractionator. Another object of this invention is to provide a method for increasing the destruction of organic sulfur compounds in a bottoms product from a fractionator. Another object of this invention is to provide a method and/or an apparatus for more complete removal of organic sulfur compounds from the topped crude. A further object of this invention is to provide a method of and means for desulfurization of topped crude which will result in material savings in the investment cost and maintenance expenses of the equipment for processing topped crude in a vacuum flasher operation. Another object of this invention is to reduce the load on the vacuum jets in a vacuum flasher by providing an improved method of desulfurizing the residual oil prior to its treatment in a vacuum flasher. Another object of this invention is to reduce the sulfur content of fuel oil.

Other aspects, objects, and the several advantages of the invention are apparent from a study of the disclosure, the drawing, and the appended claims.

According to this invention, there are provided a method and means for treating a sulfur compound containing oil wherein the oil is removed from a treating zone in which vaporization can occur and heated to cause decomposition of said sulfur compound and returned to said treating zone for further treatment therein, and the portion of the treating zone from which the sulfur compound containing oil is withdrawn for heating is maintained substantially free from any returned oil which has been heat treated to decompose sulfur compounds therein, which does not vaporize in said treating zone.

In the drawing, FIGURE 1 is a diagrammatic view of one conventional method of fractionating crude oil by supplying heat to fractionation as preheat. FIGURE 2 is a diagrammatic view of another conventional method wherein the heat is supplied by reboiling. FIGURE 3 is a diagrammatic view of a flow arrangement for carrying out the present invention. FIGURE 4 is a diagrammatic view of another flow arrangement for carrying out the present invention. FIGURE 5 is a diagrammatic view as still another flow arrangement for carrying out the present invention.

In FIGURE 1, crude oil is fed to pipe **11** to a preheater **12** and then through pipe **13** to fractionator **14**. Stripping steam is introduced into fractionator **14** by pipe **15**. Overhead vapors are removed through pipe **16** while the bottoms product is removed through pipe **17**. The temperature of the oil in pipe **11** may be 300° F., the temperature of the oil in pipe **13** may be 420° F., and the bottoms product may be approximately 410° F.

In FIGURE 2, the downflowing fluid in the fractionator **20** collects in a bottom trap-out tray **21** and then over-

flows into the bottom compartment **22** of the fractionator. The bottoms product is removed from fractionator **20** by pipe **23**. A portion of the bottoms product is taken from pipe **23** through pipe **24** to reboiler **25** where the temperature of the bottoms product is raised from approximately 410° F. to approximately 600° F. and then returned to bottom compartment **22** of fractionator **20** by pipe **26**. Stripping steam is injected into compartment **22** by pipe **27**. This is a conventional arrangement whereby heat for the organic sulfur destruction is supplied by reboiling. This operation results in greater organic sulfur destruction than the method of FIGURE 1, due to the higher oil temperature (410 to 600° F. in FIGURE 2 as contrasted with 300 to 420° F. of FIGURE 1). The arrangement of FIGURE 2 allows much of the organic sulfur to bypass the reboiler, thus decreasing the effectiveness of this arrangement for desulfurizing a residual oil. It should be noted that a large part of the material which is cycled through reboiler **25** and returned to fractionator **20** and then removed through pipe **23** may again return to reboiler **25**. This continual recycling of a portion of the fluid decreases the amount of fresh fluid which may be treated in the reboiler, thus decreasing the effectiveness of the reboiler for desulfurizing the residual product.

My invention, illustrated in FIGURES 3, 4, and 5, rearranges the reboiler suction locus to maximize the organic sulfur going to the reboiler, which increases the organic sulfur destruction.

In FIGURE 3, the downflowing fluid in fractionator **30** collects in the bottom trap-out tray **31** and then overflows into compartment **32**. The bottom of fractionator **30** is separated into two compartments, **32** and **33**, by the vertical partition **34**. A portion of the bottoms product is removed from compartment **32** by pipe **35** and transmitted to reboiler **36** where the temperature of said portion of bottoms product is increased from approximately 410° F. to approximately 600° F. Said portion of the bottoms product is passed from reboiler **36** to compartment **33** by pipe **37**. The partition **34** is spaced from the lower most plate **38** of fractionator **30** to permit the excess fluid in compartment **32** to flow over partition **34** into compartment **33**. Stripping steam is injected into compartment **33** through pipe **39**. A final bottoms product is removed from compartment **33** by pipe **40**.

In FIGURE 4, the downflowing fluid in fractionator **50** collects in the bottom trap-out tray **51**. A portion of the downflowing fluid is removed from tray **51** by pipe **52** and is transmitted to and through reboiler **53**, where the temperature of said portion is raised from approximately 410° F. to approximately 600° F. and then said portion is returned by pipe **54** to bottom compartment **55** of fractionator **50**. Stripping steam is injected into compartment **55** through pipe **56**. The bottoms product is removed from compartment **55** by pipe **57**.

In FIGURE 5, the downflowing fluid in fractionator **60** collects in the bottom trap-out tray **61**. A portion of the downflowing fluid is removed from tray **61** through pipe **62** and transmitted to and through reboiler **63** where the temperature of said portion is raised from approximately 410° F. to approximately 600° F. and then said portion is returned by pipe **64** to bottom compartment **65** of fractionator **60**. The bottoms product is removed from fractionator **60** through pipe **66** and injected into steam stripper **67**. Stripping steam is fed into steam stripper **67** by pipe **68**. The vapors are removed from stripper **67** by pipe **69** and then either vented through pipe **70** or returned to bottom compartment **65** by pipe **71**. This may be accomplished by venting all of the vapors or transmitting all of the vapors to fractionator **60**, or by venting part of the vapors and transmitting the remainder of the vapors to fractionator **60**. The residue from the steam stripping operation is removed from stripper **67** through pipe **72**.

For purposes of illustration and not in limitation of the invention, it can be seen that when ten pounds of organic sulfur per 100 barrels of material enters the bottom of the tower as downflow, and the organic sulfides are destroyed at reboiler temperatures, that in FIGURE 2, the ten pounds of organic sulfur entering with the 100 barrels mixes with 60 barrels of liquid returned from the reboiler resulting in 160 barrels containing ten pounds of organic sulfur. This results in 0.0625 pound of organic sulfur per barrel. Organic sulfur charged to the reboiler is 70×0.0625 or 4.37 pounds. Assuming for comparison that no destruction occurs in the bottom of the tower, the remainder, 5.63 pounds, yields unconverted with the bottoms product.

In FIGURE 3, the 70 barrels of reboiler charge is drawn directly from the downcomer which contains 0.1 pound organic sulfur per barrel. Thus, 7 pounds of organic sulfur are charged to the reboiler, leaving but 3 pounds yielded with the bottoms.

It is to be understood that the arrangement in FIGURE 4 gives the same results as FIGURE 3 except that FIGURE 4 permits more reaction time in the bottom of the tower (wherein additional destruction can occur).

It is also to be understood that the arrangement in FIGURE 5 can be used to give adequate stripping of hydrogen sulfide formed from the bottoms product. This stripping can be done in two towers as shown or in a single tower where the reboiler charge is withdrawn a few trays up from the bottom.

The use of a pump to charge the reboiler and a back pressure control valve to increase time and temperature in the coil at the same heat to the tower is known in the prior art.

The temperatures given in the description of the drawing are for purposes of illustration. The particular temperature of the lower section of a fractionator is determined by the composition of the feed to the fractionator and the desired fractionating conditions, such as the desired composition of the overhead products.

As noted above, the drawing is merely diagrammatic and is not intended to fully show all component parts of equipment which one skilled in the art will routinely design for the operation. Indeed, the showing of an element or piece of equipment does not mean that all such or similar pieces of equipment which may or can be designed by one skilled in the art in possession of this disclosure cannot be utilized in substitution therefor,

Tabulation

Figure and Stream	B./h. Liquid	"B./h." Vapor	#/hr. Organic Sulfur	#/bbl. Organic Sulfur	#/hr. Decomp. of S. Compounds
Figure 2:					
Downflow to 21	100		10.0	0.1	
To Reboil 24	70		4.37	0.0625	
From Reboil 26	60	10			4.37
Liquid	60				
Vapor		10			[1] 4.37
Bottoms Yield	90		5.63	0.0625	
Figure 3:					
Downflow to 31	100		10.0	0.1	
To Reboil 36	70		7.0	0.1	
From Reboil 37	60	10			7.00
Liquid	60				
Vapor		10			[1] 7.00
Bottoms Yield	90		3.0	0.033	
Figure 4:					
Downflow to 51	100		10.0	0.1	
To Reboil 52	70		7.0	0.1	
From Reboil 54	60	10			7.00
Liquid	60				
Vapor		10			[1] 7.00
Bottoms Yield	90		3.0	0.033	
Figure 5:					
Downflow to 61	100		10.0	0.1	
To Reboil 62	70		7.0	0.1	
From Reboil 64	60	10			7.00
Liquid	60				
Vapor		10			[1] 7.00
Bottoms Yield	90		3.0	0.033	

[1] H_2S reported as sulfur, and returning all vapors via 71 in Figure 5.

likewise the omission of an element which one skilled in the art may include in an actual unit does not mean that such a piece of equipment is intended to be omitted simply because it does not appear in the drawing. Suffice to say, the drawing is for illustrative purposes as is the description thereof.

All data are based on 100 b./h. topped crude charge (Western Kansas crude) containing 0.1 #/barrel organic sulfur compounds (measured as sulfur). All fractionations are operated under like conditions including bottom tower temperature of 410° F., and reboiler effluent of 600° F. with 100 percent destruction of organic sulfur compounds. Each example yields vapor from the bottom zone equivalent to 10 liquid b./h. The same quantities of stripping steam are used in all examples. Each example yields 90 b./h. of bottoms product. It is seen that when operating in accordance with my invention, as compared to prior art practice, the bottoms products from my processing contain only 53 percent as much organic sulfur as the bototms produced conventionally.

Reasonable variation and modification are possible within the scope of the foregoing disclosure, the drawing, and the appended claims to the invention the essence of which is that a sulfur compound containing feed from a distilling or other treating zone to a heating zone is taken from a section of said distilling or treating zone which is maintained substantially free from any returned oil which has been heat treated to decompose sulfur compounds contained therein which does not vaporize in said distilling or treating zone.

I claim:

1. A method of reducing the sulfur content in a bottoms product from a fractionation column, said fractionation column having a first section and a second section with vapor phase communication therebetween, comprising the steps of withdrawing a portion of liquid therein contained from said first section and from said fractionation column, heating the thus withdrawn portion to a temperature at which sulfur compounds therein will decompose, thus decomposing sulfur compounds contained therein; passing the thus heated portion into said second section, maintaining said first section substantially free of any of said portion which has been heat treated to decompose sulfur compounds contained therein and which did not vaporize during the step of heating, withdrawing at least a portion of the thus decomposed sulfur compounds from the top of said fractionation column, and withdrawing from the bottom of said fractionation column a bottoms product having a substantial reduction in the concentration of sulfur compounds contained therein.

2. A method of reducing the sulfur content in a bottoms product from a fractionation column, said fractionation column having an upper section, a bottom section and a trap-out tray positioned within said fractionation column and between said bottom section and said upper section, said bottom section being in vapor phase communication with said upper section, comprising the steps of withdrawing a portion of downflowing fluid therein contained from said trap-out tray and from said fractionation column; heating the thus withdrawn portion to a temperature at which sulfur compounds therein will decompose, thus decomposing sulfur compounds contained therein; passing the thus heated portion into said bottom section; withdrawing a bottoms product from said bottom section and from said fractionation column, and withdrawing at least a portion of the thus decomposed sulfur compounds from said upper section.

3. A method of reducing the sulfur content in a bottoms product from a fractionation column, said fractionation column having an upper section, a bottom section and a trap-out tray positioned within said fractionation column and between said bottom section and said upper section, said bottom section and said upper section being in vapor phase communication, comprising the steps of withdrawing a portion of downflowing fluid therein contained from said trap-out tray and from said fractionation column; heating the thus withdrawn portion to a temperature at which sulfur compounds therein will decompose, thus decomposing sulfur compounds contained therein; passing the thus heated portion into said bottom section; injecting stripping steam into the liquid in said bottom section; withdrawing a bottoms product from said bottom section and from said fractionation column, and withdrawing at least a portion of the thus decomposed sulfur compounds from said upper section and from said fractionation column.

4. A method of reducing the sulfur content in a bottoms product from a fractionation column, said fractionation column having an upper section, a bottom section and a trap-out tray positioned within said fractionation column and between said bottom section and said upper section, said bottom section and said upper section being in vapor phase communication, comprising the steps of withdrawing a portion of downflowing fluid therein contained from said trap-out tray and from said fractionation column; heating the thus withdrawn portion to a temperature at which sulfur compounds therein will decompose, thus decomposing sulfur compounds contained therein; passing the thus heated portion into said bottom section; withdrawing a bottoms product from said bottoms section and from said fractionation column, steam stripping the thus withdrawn bottoms product, and withdrawing an overhead product from said upper section and from said fractionation column, said overhead product containing at least a portion of the thus decomposed sulfur compounds.

5. A method of reducing the sulfur content in a bottoms product from a fractionation column, said fractionation column having a bottom section, a partition positioned in said bottom section and dividing said bottom section into a first compartment and a second compartment, and a trap-out tray positioned within said fractionation column and above said bottom section so that downflowing liquid overflows from said trap-out tray into said first compartment, said second compartment being in vapor phase communication with the upper portion of said fractionation column, comprising the steps of withdrawing a portion of liquid therein contained from said first compartment, heating the thus withdrawn portion to a temperature at which sulfur compounds therein will decompose, thus decomposing sulfur compounds contained therein; passing the thus heated portion into said second compartment; injecting steam into the liquid in said second compartment, withdrawing a bottoms product from said second compartment and from said fractionation column, and withdrawing from the top of said fractionation column an overhead stream containing at least a portion of the thus decomposed sulfur compounds.

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