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PROCESS FOR REMOVING METALS FROM CRUDE OILS AND THEN HYDRODESULFURIZING THE CRUDE OILS

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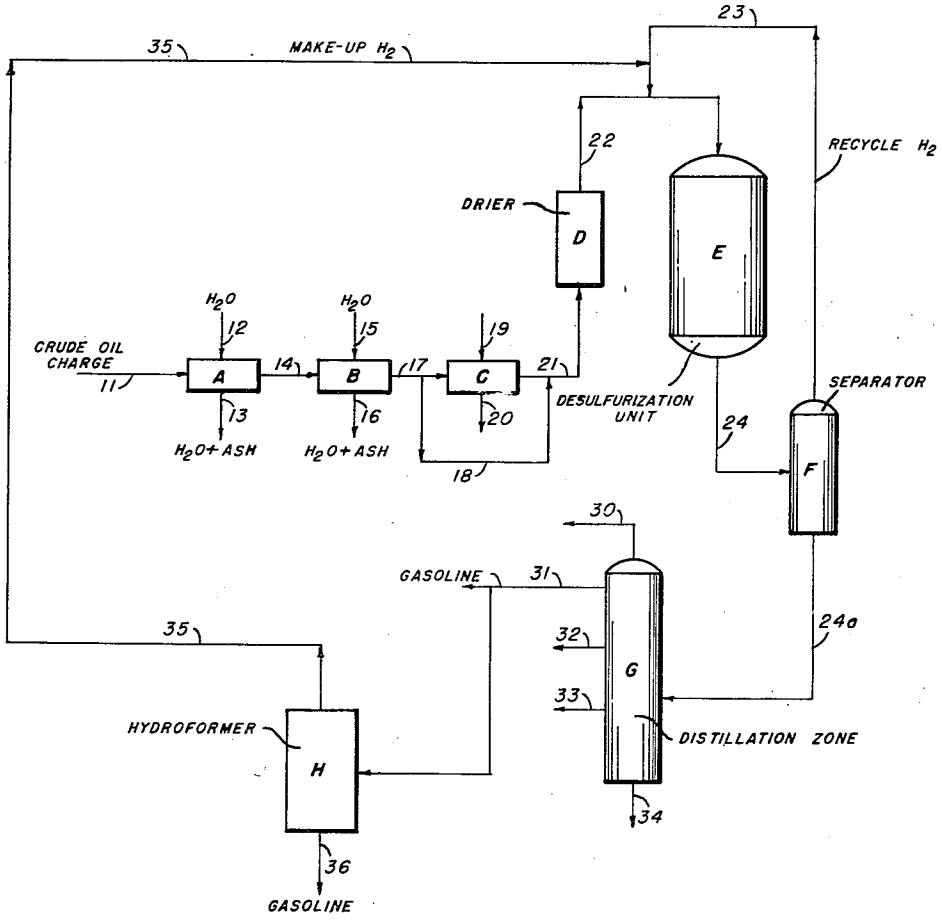

INVENTOR.
Wilson D. Seyfried,
BY
ATTORNEY.

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2,772,212

PROCESS FOR REMOVING METALS FROM CRUDE OILS AND THEN HYDRODESULFURIZING THE CRUDE OILS

Wilson D. Seyfried, Baytown, Tex., assignor, by mesne assignments, to Esso Research and Engineering Company, Elizabeth, N. J., a corporation of Delaware

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2 Claims. (Cl. 196—28)

This invention is directed to a method for removing sulfur from crude oil and crude oil fractions having a high ash content.

The present invention is particularly adapted for the treatment of a crude oil containing materials which deposit as solids upon catalytic surfaces when the hot feed stock is brought into contact with said catalytic surfaces. The nature of these materials in the crude petroleum and in the crude petroleum fractions is not completely understood. These materials may be porphyrins, porphyrin-metal complexes including nickel, iron, copper, vanadium porphyrins as well as other organometallic compounds. These also may in part consist of high boiling hydrocarbon residues. Hereafter for convenience in the specification these materials will be referred to as solids residues although it is to be understood that actually in the feed stocks these materials may not be solids but may be in the liquefied form and may form the solids only when the feed stock is vaporized at a high temperature and brought into contact with a catalytic surface.

Specific examples of crude petroleum oils and fractions of crude petroleum oils are West Texas crudes, Hawkins crudes, Middle East crudes, and the like.

The present invention is directed to a method for hydrodesulfurizing petroleum feed stocks which are selected from the class of high ash content, high sulfur content, petroleum crude oils and petroleum crude oil fractions.

In accordance with the present invention, the feed stock to be desulfurized is water washed in a plurality of stages to remove the metallic constituents. The washed crude oil, if it contains naphthenic acids or naphthenic acid salts, may optionally be treated with an aqueous solution of sodium naphthanates, sodium salts of sulfonic acids, sodium sulfate and sodium hydroxide. This treating step removes the acidic constituents. It is desirable to remove the naphthenic acids at this stage of the process, for if they are not removed, additional pickup of metals such as iron will result from reaction with pipes and vessels with which the feed stock may come in contact. As the next step, the feed stock is desulfurized by passing it in vaporized form in admixture with hydrogen into contact with a sulf-active catalyst to reduce its sulfur content. The product from the desulfurization step may be distilled to separate a gasoline fraction which may be hydroformed simultaneously to up-grade the octane number and produce hydrogen which is used in the desulfurizing step.

The method for practicing the present invention will now be described in greater detail in conjunction with the drawing in which the sole figure is in the form of a diagrammatic flow sheet.

Turning now specifically to the drawing a feed stock which may be a total crude petroleum oil or crude oil fraction is introduced through line **11** into a first water washing zone A. Fresh water is introduced into zone A through inlet line **12** and water containing ash is withdrawn through line **13**. The feed stock from the first stage is passed through line **14** to a second water washing stage B where it is washed with fresh water introduced

through line **15** and withdrawn with dissolved ash constituents through outlet line **16**. The feed stock from the second washing stage is passed through line **17**. If this material contains appreciable amounts of naphthenic acids it is then passed to treating stage C but alternatively if the material does not contain appreciable amounts of naphthenic acids stage C may be bypassed with the material bypassing through line **18**. In treating stage C, a fresh treating mixture is introduced through line **19** and is withdrawn through line **20**. The material introduced through line **19** is a mixture made up of components in ranges as follows:

	Percent
Alkali metal hydroxide	.5–5
Alkali metal salt of sulfonic acid	10–15
Alkali metal salt of inorganic acid	5–7.5
Water	72.5–84.5

This solution of treating reagent should have a specific gravity no less than 1.1. By way of specific example, a solution having the following composition may be used:

	Weight percent
Sodium sulfonates	30
Sodium sulfate	10
Free sodium hydroxide	1
Water	59

A more detailed description of the washing step is described and claimed in copending U. S. Patent application Serial No. 255,464 entitled "Treatment of Acidic Oils," filed November 8, 1951, in the name of Linnie P. Hodges.

The treated oil from step **17** or alternatively the oil from bypass line **18** is discharged into line **21** and passes to drier D where entrained water is removed therefrom. The dried feed stock passes through line **22** and is admixed in hydrogen discharged into line **22** from line **23** the mixture of feed stock and hydrogen then passing to desulfurization unit E.

Desulfurization unit E contains a sulf-active catalyst. Sulf-active hydrogenation catalysts suitable for use are known to the art. Examples of suitable catalysts selected from this class are the oxides and sulfides of V, Cr, Mn, Fe, Co, Ni, Mo, W. These may be used either alone or in admixture or may, if desired, be used with other materials such as alumina, magnesia silica, zinc oxide. Specific examples of suitable sulf-active catalysts are cobalt molybdate, nickel tungsten sulfide, cobalt sulfide, molybdenum oxide, nickel sulfide and tin sulfide. It is preferred that sufficient hydrogen be admixed with the feed stock to maintain a ratio of hydrogen to oil within the range of 2 to 40 moles of hydrogen per mol of said stock. The following conditions should be maintained within reactor E: A temperature within the range of 700–850° F., a pressure in the range of 0 to 500 pounds per square inch gauge and a feed rate in the range of 0.2 to 10 volumes of liquid feed per volume of catalyst per hour. The mixture of hydrogen and treated feed stock is withdrawn from vessel E through line **24** and passed to a separator F where hydrogen is separated from the desulfurized feed stock and the hydrogen recycled to vessel E through line **23**. The treated feed stock is withdrawn from separator F through line **24***a* and passed to a distillation zone G where it is separated into a gas fraction withdrawn through line **30**, a gasoline fraction withdrawn through line **31**, a gas oil fraction withdrawn through line **32**, a lubricating distillate withdrawn through line **33** and a residual oil withdrawn through line **34**.

The gasoline fraction passes from line **31** to a hydroformer unit H.

Hydroforming operations are well known to the art. For a description see, for example, Oil and Gas Journal,

March 27, 1941, page 86 and the Journal of Petroleum Technology, January 1944, pages 3 and 4. In general, hydroforming operations may be characterized as those chemical reactions which take place when hydrocarbon oils, particularly hydrocarbons boiling in the gasoline range, are reacted at a temperature in excess of 500° F. in the presence of hydrogen and a reforming catalyst. These reactions involve a net effect of taking hydrogen away from the hydrocarbon molecules. The chemical reactions involved are complex and are generally considered to consist of dehydrogenation and cyclization. Other reactions such as cracking, hydrogenation, and desulfurization may also occur.

By way of specific example, it is preferred that the reaction in hydroformer unit H take place within the range of 900 to 950° F. While any reforming catalyst in general may be employed, a preferred group may be the same type of sulf-active catalyst as used in desulfurization unit E and in order to simplify the description these specific catalysts will not be again enumerated. In hydroformer unit H there is an over-all net production of hydrogen and this hydrogen is withdrawn through line 35 and is added as make-up hydrogen to the recycle hydrogen in line 23, the mixtures of make-up hydrogen and recycle hydrogen being admixed with the oil charged to desulfurizing unit E.

Hydroformed gasoline of improved octane number is withdrawn from hydroformer unit H through line 36. Thus, it will be seen that the hydroforming of the gasoline fraction in hydroforming unit H serves a dual purpose. The gasoline fraction produced by desulfurization unit E is particularly suitable for upgrading in hydroformer unit H so that in unit H the quality of the gasoline fraction is substantially improved and at the same time hydrogen is produced for the desulfurization unit E.

Having fully described and illustrated the invention of the present application, what I desire to claim is:

1. In a method for treating a petroleum feed stock to be hydrodesulfurized in a hydrodesulfurization zone in contact with a sulf-active catalyst, said feed stock being selected from the group consisting of crude oils and crude oil fractions containing an appreciable amount of ash forming constituents and acid constituents, including acid constituents selected from the group consisting of naphthenic acids and naphthenic acid salts, the improvement which comprises the steps of water washing said feed stock in sequence in a plurality of water washing zones with fresh water in each of said zones to remove ash forming constituents therefrom, and contacting said water washed feed stock with an aqueous solution containing an alkali metal hydroxide, an alkali metal salt of sulfonic acid and an alkali metal salt of an inorganic acid to remove acid constituents therefrom.

2. A process as in claim 1 wherein the said aqueous solution contains about 30 weight percent of sodium sulfonates, about 10 weight percent of sodium sulfate, about 1 weight percent of sodium hydroxide and about 59 weight percent of water.

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