

1

2,920,936

RECOVERY OF HEAVY METALS FROM
HYDROCARBONS

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4 Claims. (Cl. 23—50)

This invention relates to a method for the recovery of metal values from hydrocarbons comprising naturally-occurring heavy metal constituents. Liquid and semi-solid hydrocarbons may be treated in accordance with the method of this invention for the recovery of valuable metal constituents therefrom.

Petroleum, particularly heavy crude oils, bitumens, and asphalt, commonly contains small quantities of naturally-occurring heavy metal compounds. The most common heavy metals contained in petroleum are vanadium, nickel, iron, chromium and molybdenum. The exact chemical compositions of the naturally-occurring heavy metal compounds are somewhat in doubt. It is generally agreed that the metals are present, at least in part, in the form of oil-soluble metallo-organic compounds. The present invention provides a method for recovery of metal values contained in these naturally-occurring metallo-organic compounds. Petroleum containing naturally-occurring heavy metal compounds is referred to herein as "ash-forming" hydrocarbons.

Ash-forming hydrocarbons, particularly crude oil, crude residua, and heavy distillates from crude oils, have been found unsatisfactory as fuels for many purposes because of the corrosive nature of the resulting ash. The corrosive ash is due primarily to normally solid oxidation products of metals contained in these oils.

A copending application of du Bois Eastman, Serial No. 702,661, filed December 13, 1957, discloses that when a hydrocarbon oil containing metal constituents is subjected to partial combustion at a temperature above 2000° F. with oxygen under conditions such that carbon contained in said hydrocarbon is liberated as free carbon in an amount at least equal to 50 times the combined weights of the vanadium and nickel contained in the hydrocarbon, metal constituents of the hydrocarbon combine with the carbon without damage to the refractory walls of the reaction vessel.

The present invention permits recovery of heavy metals of their compounds from carbon containing ash resulting from incomplete combustion or partial oxidation of the ash-forming hydrocarbon. The method of this invention involves converting insoluble ash containing metal constituents from the hydrocarbons to soluble form by roasting the carbon containing the ash in an oxidizing atmosphere and leaching the metal compounds from the carbon. Carbon, containing heavy metal constituents, is released from the hydrocarbon by combustion of a major portion of the hydrocarbon using insufficient free oxygen for complete consumption of carbon contained in the hydrocarbon. Valuable gaseous products are produced and, at the same time, at least part of the metals content of the hydrocarbon is recovered. The gaseous products are useful as fuel gas or as a source of hydrogen-rich feed gas for synthesis reactions.

Heavy metals occur in petroleum in varying amounts ranging from a trace to as much as about 2000 parts per million by weight based upon the weight of the metal, per se. Many heavy oils contain heavy metals in con-

2

centrations on the order of 200 parts per million. A Venezuelan crude contains as much as 1200 p.p.m. vanadium. In general, hydrocarbons containing in excess of 50 p.p.m. vanadium are not generally satisfactory as fuels because of the corrosive, or erosive, nature of the ash both to high temperature refractories and to metal alloys. In contrast, petroleum hydrocarbons containing higher concentrations of heavier metals are preferred as charge stock for the process of this invention. Heavy metal constituents of petroleum may be concentrated by distillation, the heavy metal constituents largely remaining in the distillation residues. The process of this invention is particularly applicable to the recovery of the metals from such distillation residues, which are of limited value as fuel. The residue from propane de-asphalting and solvent refining operations often comprises heavy metal rich residues suitable as charge stock for the present process.

Carbon obtained by partial oxidation of a hydrocarbon containing naturally-occurring heavy metal compounds is roasted by heating in an oxidizing atmosphere, suitably in air, to a temperature of at least 220° F., but below ignition temperature, and subsequently leached with water. Roasting of the carbon which contains adsorbed metal compounds resulting from the partial oxidation of hydrocarbons to carbon monoxide and hydrogen converts metal compounds contained therein from water-insoluble form largely to water-soluble form. Subsequent leaching with water results in nearly complete extraction of resulting water-soluble metal salts from the carbon. A minor portion of the heavy metal compounds, e.g. 5 to 10 percent, is not removed by leaching with water. Generally it is not necessary to further treat the carbon for removal of heavy metal compounds. Substantially complete extraction of the heavy metal compounds may be effected by leaching of the roasted carbon with a dilute aqueous solution, e.g. 0.1 to 0.5 N solutions, of a strong mineral acid, i.e. hydrochloric, nitric, or sulfuric acid. When substantially complete extraction of the metal compounds is required, it is often advantageous to leach the roasted carbon with water, followed by leaching with a dilute solution of a strong mineral acid, and finally a water wash to remove the acid. Metal values may be recovered from aqueous solutions by precipitation, e.g. by the addition of phosphoric acid to the solution to precipitate the metals as the phosphates. The recovered metals, e.g. phosphates, are industrially useful, e.g. as additives in the manufacture of steel.

In addition to the recovery of valuable metal from the hydrocarbon, the properties of the carbon are improved as evidenced by increased oil absorption and decreased volatile content.

When carbon from synthesis gas generation runs was water washed without preliminary heating, no significant reduction in ash or increase in oil absorption value was obtained. Upon heating the carbon in an oven to 220° F. for a period of 20 minutes to 1 hour and then water washing, or leaching, the ash content of the carbon was substantially reduced.

As a specific example of the present process, water wet carbon from synthesis gas generation containing 13.8 weight percent ash is dried at 220° F. in an oven in an atmosphere of air and water extracted. The ash content of the resulting carbon is 1.0 percent. A separate sample of the carbon as recovered from the same operation showed no reduction in ash content when washed with water. Extraction of the roasted carbon with dilute hydrochloric acid reduced the ash content to 0.3 weight percent. Water extraction of the dried carbon reduced the volatile matter from 22.5 weight percent to 4.9 weight percent, whereas extraction with hydrochloric acid reduced the volatile content to 8.7 weight percent. Oil

3

absorption increased from 28.5 to 35.0 gallons per 100 pounds on water washing. The hydrochloric acid extracted comparison had an oil absorption value of 42.0 gallons per hundred pounds.

Oil absorption represents the amount of oil required to form a stiff paste with the carbon. Volatile matter represents the weight loss of a sample heated at 1750° F. for 7 minutes in a closed crucible.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for the recovery of metal values from hydrocarbon oils containing naturally-occurring metal constituents which comprises subjecting said hydrocarbon to partial combustion with an oxygen-containing gas in relative proportions such that at least 0.5 percent of the carbon contained in said hydrocarbon is liberated as free carbon together with metal constituents from said hydrocarbon, separating said free carbon containing metal constituents from gaseous products of reaction, heating the

4

recovered carbon containing said metal constituents to a temperature of at least 220° F. but below ignition temperature in an oxidizing atmosphere effecting conversion of said constituents to water-soluble form compounds of said metals, and subjecting the resulting carbon containing said water-soluble metal compound to aqueous leaching in order to separate said water-soluble metal compounds from said carbon.

2. A process as defined in claim 1 wherein said aqueous leaching is effected with water.

3. A process as defined in claim 1 wherein said aqueous leaching is effected with water followed by leaching with a dilute aqueous solution of a strong mineral acid.

4. A process as defined in claim 1 wherein said oxidizing atmosphere is air.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,920,936

January 12, 1960

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 52, for "of their compounds" read ~~---~~ or their compounds ~~---~~; column 4, line 4, strike out "form".

Signed and sealed this 7th day of June 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents