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SYNTHESIS GAS GENERATION WITH RECOVERY OF NATURALLY-OCCURRING METAL VALUES

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This invention relates to a method for the gasification of heavy hydrocarbons. In one of its more specific aspects, it relates to the recovery of metal values from hydrocarbons containing naturally-occurring heavy metal constituents. Both liquid and semi-solid heavy hydrocarbons containing heavy metal constituents can be gasified in accordance with the method of this invention.

The non-catalytic partial oxidation of hydrocarbons by reaction with free oxygen and steam at elevated temperature to produce carbon monoxide and hydrogen is of considerable commercial importance. Both liquid and semi-solid hydrocarbons may be gasified by reaction of the hydrocarbon at an autogenously maintained temperature above about 2,000° F. with steam and an oxygen-containing gas to produce a gas mixture comprising carbon monoxide and hydrogen. Generally, it is desirable to carry out the gasification reaction with steam and substantially pure oxygen, i.e. oxygen of at least 95 volume percent purity. If nitrogen is desirable in the product gas, for example, for ammonia synthesis, or is relatively innocuous, as in fuel gas or reducing gas, air or oxygen-enriched air may be used for the gasification reaction. Carbon monoxide produced in the reaction may be subjected to reaction with steam in a separate water gas shift reaction step to produce an equivalent quantity of hydrogen.

Petroleum, particularly heavy crude oils, bitumins, and asphalt commonly contain small quantities of naturally-occurring heavy metal compounds. Heavy crude oils and crude residua from refinery operations often have relatively high contents of metals in the form of their compounds. The most common heavy metals contained in petroleum are vanadium, nickel, iron, chromium, and molybdenum. The exact chemical compositions of the compounds comprising the naturally-occurring heavy metals are somewhat in doubt. It is generally agreed, however, that the metals are present, at least in part, in the form of oil-soluble metallo-organic compounds. Petroleum fuels containing naturally-occurring heavy metal compounds are referred to herein as ash-forming hydrocarbons. Ash-forming hydrocarbons, particularly crude oil, crude residua, and heavy distillates from crude oils, are unsatisfactory as fuels for many purposes because of the corrosive nature of their ash. The corrosiveness of the ash is due primarily to oxidation products of the naturally-occurring metal compounds. The ash from such heavy hydrocarbons has been found to be particularly detrimental to oxidic refractory materials available for high temperature service, e.g. 2,000 to 3500° F., as required for a successful direct partial oxidation of hydrocarbons to carbon monoxide and hydrogen. The present invention provides a method for protection of gas generation and simultaneous recovery of metal values contained in the ash-forming hydrocarbons.

Heavy metals occur in petroleum in varying amounts ranging from a trace to as much as 2,000 parts per million by weight based upon the weight of the metal, per se. Many of the heavy hydrocarbon crude oils contain heavy metals in concentration on the order of 200 parts per million. A Venezuelan crude contains as much as 1200 p.p.m. vanadium. Hydrocarbons containing in excess of

50 p.p.m. vanadium are generally not satisfactory as fuels because of the corrosive, or erosive, nature of the ash both to high temperature refractory and to metal alloys. In contrast, petroleum hydrocarbons containing higher concentrations of heavier metals are preferred as charge for the process of this invention. Heavy metal constituents of petroleum may be concentrated by distillation, the heavy metal compounds largely remaining in the distillation residues. The process of this invention is particularly applicable to recovery of the metals from such distillation residues which are of limited value as fuel. The residue from propane deasphalting and solvent refinery operations often comprise heavy metal-rich residues suitable as charge stock for the present process.

High temperature refractories may be protected from attack by heavy metal compounds of petroleum as is disclosed in United States patent by Du Bois Eastman, 2,976,135. This application discloses a process in which hydrocarbon oil containing metal constituents is subjected to partial combustion with oxygen and steam at a temperature above 2,000° F. under conditions such that carbon contained in said hydrocarbon is liberated as free carbon in an amount at least equal to fifty times the combined weights of the vanadium and nickel metals contained in the hydrocarbon so that metallic constituents of the hydrocarbon combine with the carbon without damage to the refractory walls of the reaction vessel. Carbon containing the heavy metal compounds is separated from the product gas by washing the gas stream with water.

The present invention provides a method of gasifying petroleum fuels containing naturally-occurring heavy metal compounds in which complete utilization of the carbon content of the fuel is accomplished while at the same time protecting the refractory walls of the reaction vessel from attack by oxidation products of metals contained in the fuel. The present invention also permits recovery of heavy metals or their compounds in concentrated form, substantially free from carbon. The concentrate so obtained is a valuable by-product of the gasification process which may be used in steel manufacture.

It has now been found that hydrocarbons containing heavy metals can be gasified with no net production of carbon while still protecting the refractory materials of the reaction chamber from attack by heavy metal compounds. This is accomplished by carrying out the partial oxidation of the carbonaceous fuel with an insufficient quantity of free oxygen for complete conversion of carbon contained in the fuel carbon compounds so that carbon in an amount within the range of 1 to 5 percent of the carbon contained in said hydrocarbon, preferably 2 to 3 percent, is liberated as free carbon. Apparently the freshly formed carbon occludes ash resulting from the partial oxidation of the ash-forming hydrocarbon. This carbon, containing said ash, is returned to the partial oxidation reaction zone wherein the carbon is consumed to form additional carbon monoxide while the metal content of said carbon, comprising heavy metal compounds, is liberated from the carbon. It has been found, unexpectedly, that when the heavy metals or their compounds are so liberated from the carbon they do not attack the refractory materials of the generator. The liberated heavy metal compounds are removed from the gas stream and from the free carbon combined with heavy metal compounds contained in the gas stream by means of water as described hereinafter.

In the process of this invention, the liberated carbon containing naturally-occurring heavy metal compounds is recycled to the synthesis gas generator wherein the carbon is converted to carbon monoxide and hydrogen by reaction with steam and oxygen while the metals, mostly in the form of water-insoluble sulfides, are lib-

erated in liquid or solid form and discharged from the gas generation zone with the gas stream. Gas generated in the synthesis gas generation zone is quench-cooled by direct contact with water in a quench zone. The metal compounds contained in the gas stream are accumulated in the form of small granular particles in the quench zone. These particles are retained in the water in the quench zone. The solid particles settle to the bottom of the quench water which also contains carbon separated from the gas stream. The heavy metal compounds are readily separated from the carbon-containing quench water by settling. The liberated heavy metals or heavy metal compounds are heavier than the carbon and have a higher settling rate than the settling rate of the carbon. Carbon remains suspended in the quench water due to the agitation of the water by the hot gas from the generator whereas the heavier metal compounds settle to the bottom of the quench vessel and may be withdrawn therefrom with a small amount of water.

Carbon removed from the synthesis gas stream in the quenching and scrubbing operation is separately recovered from the quench water and recycled to the gas generator. This carbon, as previously explained, contains some of the heavy metal compounds. It may be admixed with the liquid hydrocarbon feed to the gas generator, for example by the method described in U.S. Patent 2,665,980 to Charles R. Carkeek or recycled in other suitable manner. It has been found, contrary to expectations, that so long as sufficient carbon is produced from the hydrocarbon liquid to sequester the metal originally present in the hydrocarbon, i.e. to produce free carbon in an amount at least equal in weight to 50 times the combined weight of the vanadium and nickel contained in the hydrocarbon, expressed as pure metals, the refractory lining of the gasification reaction vessel is protected from attack by the ash or slag from the hydrocarbon. This is entirely unexpected since the recycled carbon contains a fairly high percentage of the heavy metal compounds. All of the carbon can be returned to the gasification zone and completely consumed so that there is no net production of carbon in the process.

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 claim.

We claim:

A process for the generation of synthesis gas and simultaneous recovery of metal values from heavy hydrocarbon fuels containing naturally-occurring metal constituents comprising vanadium and nickel which comprises subjecting said fuel to partial oxidation in a reaction zone at a temperature in the range of 2000 to 3500° F. by reaction with steam and a free oxygen-containing gas in relative proportions such that from about 1 to about 5 percent of the carbon contained in said hydrocarbon is liberated as free carbon together with reaction products of metal constituents comprising vanadium and nickel from said hydrocarbon fuel, separating said liberated free carbon containing said reaction products from gaseous products of reaction, returning said separated free carbon containing said reaction products to said partial oxidation reaction into admixture with said hydrocarbon fuel whereby said carbon is ultimately substantially completely consumed thereby releasing normally solid reaction products of said metal constituents, discharging gaseous products of reaction together with released solid reaction products and said liberated carbon from said reaction zone, quench cooling said gaseous products of reaction containing said released solid reaction products of said metal constituent and said liberated carbon by direct contact with liquid water in excess of the amount vaporizable by the heat contained in said products of reaction effecting removal of liberated carbon from gaseous products and the formation of dense granular particles of said released solid reaction products comprising vanadium and nickel substantially free from carbon, and recovering said granular particles of released solid reaction products from said water and carbon by sedimentation.

References Cited in the file of this patent

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2,920,936	Dille et al.	Jan. 12, 1960
2,976,135	Eastman	Mar. 21, 1961