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Dugan et al.

[11] **3,852,188**

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[54] **HYDROCARBON CRACKING IN A REGENERABLE MOLTEN MEDIA**

[75] Inventors: **John J. Dugan; James P. Higgins,** both of Sarnia, Ontario, Canada

[73] Assignee: **Exxon Research and Engineering Company,** Linden, N.J.

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 186,776, Oct. 5, 1971, abandoned.

[52] **U.S. Cl.** ..... **208/114,** 48/202, 208/235, 208/249, 260/683 R, 423/563

[51] **Int. Cl.** **C10g 11/02**

[58] **Field of Search** ..... 208/106, 114, 125; 260/683 R; 48/202

[56] **References Cited**

UNITED STATES PATENTS

3,081,256	3/1963	Hendal et al.	208/125
3,553,279	1/1971	Bawa	260/683
3,647,358	3/1972	Greenberg	23/2 R
3,745,109	7/1973	Heredy et al.	208/106

FOREIGN PATENTS OR APPLICATIONS

386,669	1/1933	Great Britain

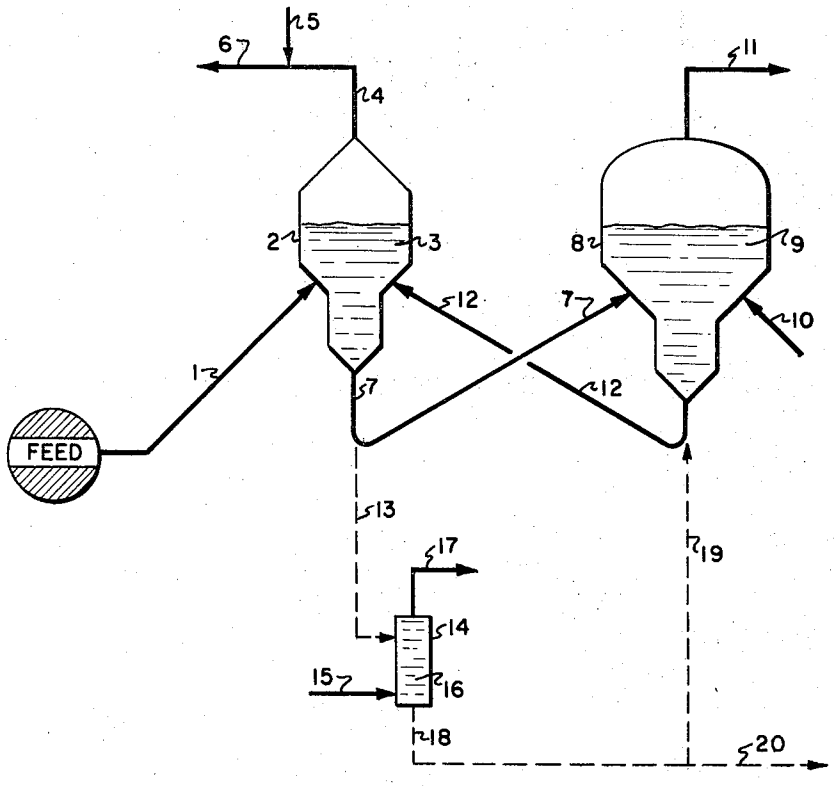
Primary Examiner—Delbert E. Gantz
Assistant Examiner—S. Berger
Attorney, Agent, or Firm—Donald C. Caulfield

[57] **ABSTRACT**

Hydrocarbon feedstocks are cracked at elevated temperatures in a regenerable molten media comprising an oxide of phosphorus, such as phosphorus pentoxide, in combination with a critically defined amount of an alkali or alkaline earth metal oxide or hydroxide including mixtures thereof, to produce high yeilds of light olefins, which olefins such as ethylene are useful in the synthesis of polymers and other valuable chemicals. The carbonaceous materials, such as coke, which are formed and suspended in the molten media during the cracking operation are gasified by contacting said carbonaceous materials with a gaseous stream containing oxygen, such as air, steam or carbon dioxide at temperatures of from about above the melting point of said medium to about 3,000°F. in order to regenerate the melt. When the mole ratio of the alkali and alakline earth metal oxide or hydroxide expressed as the oxide thereof to the glass-forming oxide in the melt is maintained in the range of at least about 1, and preferably in the range of from about 1 to about 3, the gasification rate of the carbonaceous materials which are suspended in the molten media is significantly increased while at the same time suppressing the evolution of sulfur oxides from the gasification zone when the hydrocarbon feedstock contains sulfur and when a gaseous stream containing oxygen is employed as the gasifying reagent.

17 Claims, 1 Drawing Figure

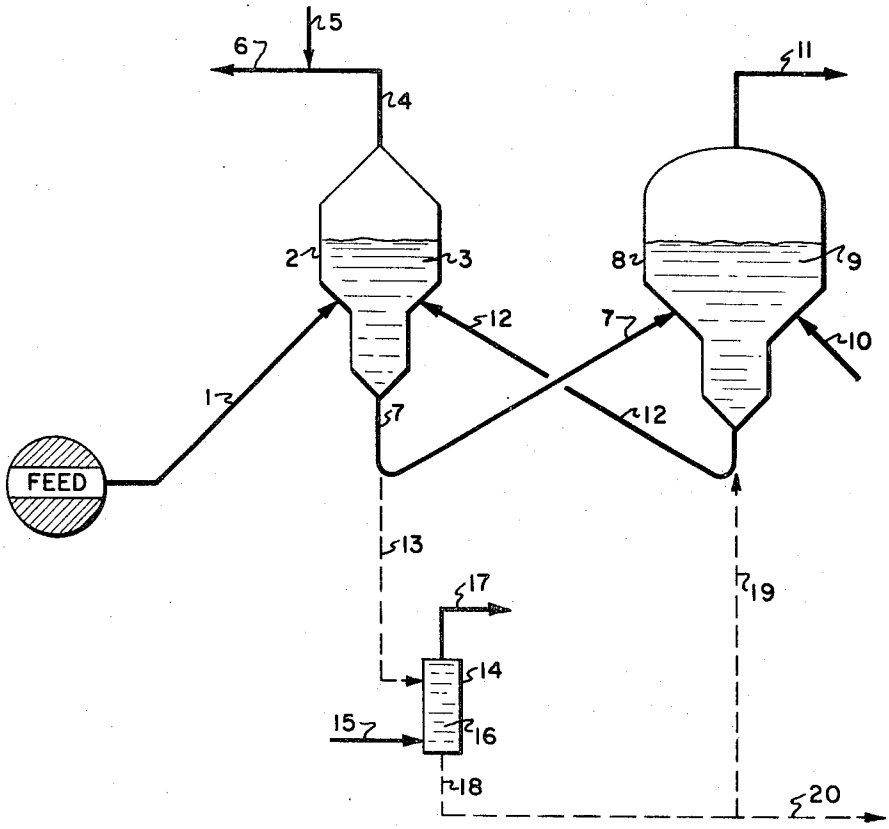
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HYDROCARBON CRACKING IN A REGENERABLE MOLTEN MEDIA

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of U.S. Ser. No. 186,776, filed Oct. 5, 1971 and now abandoned.

FIELD OF THE INVENTION

This invention relates to the preparation of unsaturated organic compounds such as ethylene from hydrocarbon feedstocks. More particularly, this invention relates to cracking a hydrocarbon feedstock at elevated temperatures in a regenerable molten media. Still more particularly, this invention relates to the cracking of a heavy hydrocarbon feedstock, e.g., hydrocarbons such as gas oils, crude oils, atmospheric or vacuum residua, in a regenerable molten media containing an oxide of phosphorus such as phosphorus pentoxide in combination with a critically defined amount of an alkali or alkaline earth metal oxide or hydroxide including mixtures thereof to produce cracked hydrocarbon products such as ethylene and carbonaceous materials. The carbonaceous materials such as coke which are formed during the cracking process are gasified by contacting said carbonaceous materials in the molten media with a gaseous stream containing an oxygen, i.e., air; water, i.e., steam; or carbon dioxide reagent at elevated temperatures in order to regenerate the melt. The cracked hydrocarbon products find use in the synthesis of polymers and other valuable chemicals.

DESCRIPTION OF THE PRIOR ART

The thermal cracking of hydrocarbons at elevated temperatures to produce olefinic compounds such as ethylene by employing a molten salt such as eutectic mixtures of lithium and potassium-chloride as the heat transfer medium is well-known to the art. The cracking of hydrocarbon feedstocks in molten heat transfer media such as lead to produce ethylene has likewise been disclosed.

However, the molten media which have heretofore been employed to crack hydrocarbons have suffered from one or more disadvantages which has resulted in limited industrial application of these processes. The difficulty primarily encountered in the prior art processes such as molten lead was the fact that the carbonaceous particles produced during the cracking operation were not suspended in the melt, but formed a separate phase which contaminated the liquid and gaseous products. Further, with molten media that partially suspended the coke, such as lithium-potassium chloride eutectics, the buildup of such carbonaceous material in or above the molten medium necessitated additional steps such as to physically remove the carbonaceous particles from the melt. In addition, numerous contacting media have been proposed in the literature including metals, alloys, slags, basalt and glass (see Czechoslovakian Pat. No. 109,952) in order to effectuate the thermal cleavage of hydrocarbon feedstocks.

Recently it has been suggested that hydrocarbon feedstocks can be cracked in a molten salt of either alkali metal carbonate, alkali metal hydroxide, or a mixture thereof, to form hydrocarbon products containing ethylene and thereafter regenerating the molten salt by intimate contact with oxygen or steam (see U.S. Pat. No. 3,553,279 and U.S. Pat. No. 3,252,774). Such a molten medium, however, suffers from the disadvantage of undergoing decomposition at operating conditions normally employed for cracking hydrocarbon feedstocks, i.e., temperatures in the range of from about 1,200° to 1,650°F. Accordingly, the art is in need of an alternate molten medium which, in addition to providing the heat transfer medium for the cracking of the hydrocarbon feedstock, will permit the rapid regeneration of the melt.

In a copending application, U.S. Ser. No. 280,183, filed Aug. 14, 1972, there is described a regenerable molten medium system comprising an oxide of phosphorus in combination with an alkali or alkaline earth metal oxide(s) or hydroxide(s) which molten medium, in addition to providing the heat transfer media for the cracking of the hydrocarbon feedstock, permits the rapid regeneration of the melt by contacting the carbonaceous material present in the melt with a gasification reagent such as air. It has now been discovered that when the mole ratio of the alkali and/or alkaline earth metal oxide and/or hydroxide component(s) expressed as the oxide thereof to the oxide of phosphorus component(s) in the melt is maintained within a critically defined range there occurs an unexpected increase in the gasification rate of the carbonaceous materials present in the melt so as to accelerate the regeneration of the molten medium, while at the same time suppressing the evolution of sulfur oxide during the gasification of the carbonaceous material with a reagent containing oxygen.

SUMMARY OF THE INVENTION

It has now been discovered that hydrocarbon feedstocks are converted to produce high yields of light olefins such as ethylene by a process which comprises contacting the hydrocarbon feedstock with a regenerable molten medium, as hereinafter defined, at a temperature in the range of from about above the melting point of the medium to about 2,500°F. for a time sufficient to form cracked hydrocarbon products and carbonaceous materials. Thereafter, the carbonaceous materials formed and suspended in the molten medium during the cracking operation are contacted wit a gaseous stream containing as a reagent oxygen, e.g., air, steam or carbon dioxide, including mixtures thereof, at a temperature in the range of from about the melting point of said medium to about 3,000°F. for a period of time in order to regenerate the molten media. The regenerable molten media of the instant invention comprises an oxide of phosphorus such as phosphorus pentoxide (P_2O_5), phosphorus tetroxide (P_2O_4), phosphorus trioxide (P_2O_3), and the like including mixtures thereof in combination with one or more alkali or alkaline earth metal oxide(s) or hydroxide(s) including mixtures thereof.

The oxide(s) of phosphorus are employed in combination with an alkali or alkaline earth metal oxide or hydroxide, including mixtures thereof, to comprise the molten media which is initially charged to the cracking zone. The preferred alkali metal oxides or hydroxides include sodium, potassium, lithium, cesium and mixtures thereof. The preferred alkaline earth metals which are introduced into the cracking zone in either their corresponding oxide or hydroxide form include barium, strontium, calcium, and magnesium. While the alkali earth metal oxides or hydroxides may be emmployed alone in combination with a glass-forming ox-

ide, it is preferred that when employing an alkaline earth metal oxide or hydroxide in the molten media system of this invention that alkali metal oxides or hydroxides be present in order to lower the melting point of the molten media to that temperature range which is preferred for conducting the cracking or gasification of a hydrocarbon feedstock.

The mole ratio of the alkali metal compound, that is the mole ratio of the alkali metal(s) and/or alkaline earth metal(s) oxide and/or hydroxide to the oxide(s) of phosphorus is an important feature of the instant invention. It has been surprisingly discovered that when the mole ratio of the alkali and/or alkaline earth metal oxide(s) and/or hydroxide(s) expressed as the oxide thereof to the oxide(s) of phosphorus is at least 1, and more preferably from about 1 to about 3, and still more preferably from about 1.2 to about 2.5, there occurs an unexpected increase in the gasification rate of the carbonaceous materials present in the molten media when the carbonaceous materials are contacted with a gasifying reagent, such as air, in order to burn off the carbonaceous materials and thus regenerate the melt. In addition, by maintaining the mole ratio within this range, it has been discovered further that the sulfur emissions in the flue gas during gasification of the carbonaceous materials with a gaseous stream containing oxygen, i.e., air, are significantly reduced. Furthermore, maintaining the mole ratio below about 3.0, and preferably below about 2.5, minimizes carbon dioxide emissions from the cracking zone.

As mentioned above, the mole ratio of the alkali metal compound is defined in terms of the oxide(s) of the alkali or alkaline earth metal(s) that is employed in combination with the oxide of phosphorus. The basis for defining the mole ratio of the alkali metal compound in terms of its oxide form, i.e., "expressed as the oxide(s) thereof," is the fact that the alkali metal constituent of the alkali metal oxide(s), e.g., lithium oxide (Li_2O), alkaline earth metal oxide(s), e.g., barium oxide (BaO) and alkaline earth metal hydroxide, e.g., barium hydroxide ($Ba(OH)_2$) all possess a total number of equivalents of alkali metal or alkaline earth metal of two. The total number of equivalents of alkali metal in an alkali metal hydroxide, e.g., lithium hydroxide (LiOH), however, is one. Accordingly, it has been discovered that when an alkali metal hydroxide is employed as an alkali metal compound in combination with an oxide of phosphorus to comprise the molten media of the instant invention, it is necessary to employ two moles of alkali metal hydroxide(s) for each mole of the oxide of phosphorus in order to achieve the same advantages exhibited by a molten media containing an oxide of phosphorus in combination with one mole of either an alkali metal oxide, alkaline earth metal oxide or alkaline earth metal hydroxide. Therefore, it is evident that it is necessary to employ twice as many moles of an alkali metal hydroxide as compared to alkali metal oxides or alkaline earth metal oxide(s) or hydroxide(s) in order to achieve the identical mole ratio of alkali metal compound to the oxide of phosphorus. Hence, when the mole ratio of the alkali metal compound is expressed as the oxide of the particular alkali or alkaline earth metal employed, the singular effect is that the number of moles of alkali metal hydroxides that are employed in the molten media must be divided by two and the combined with the total number of moles of alkali metal oxides and alkaline earth metal oxides and hydroxides in order to determine the total number of moles of alkali metal compound expressed as oxide that are employed in a particular molten media. Thereafter, the total number of moles of the alkali metal compound is divided by the total number of moles of the oxide(s) of phosphorus that is present in the molten media in order to determine the mole ratio of the alkali metal compound to the oxide(s) of phosphorus component in the melt.

The advantage of cracking a hydrocarbon feedstock in the above-mentioned molten medium resides in the ability of the molten media of this invention to: (a) suspend the carconaceous materials formed in situ during the cracking operation uniformly throughout the melt, and (b) thereafter, upon contact with a gaseous stream containing oxygen or steam at elevated temperature, to promote the rapid gasification of said carbonaceous materials. Accordingly, the instant invention permits the thermal cracking or a heavy hydrocarbon feedstock such as atmospheric or vacuum residuum, the cracking of which feedstocks have heretofore not been feasible due to excessive coking in tubular reactors. In addition, in view of the fact that heavy hydrocarbon feedstocks, as hereinafter defined, such as crude oils and residua normally contain sulfur, e.g., thiols thiophenes and sulfides, the molten medium of the instant invention offers the additional advantages of significantly lowering the emission of pollutants into the atmosphere by absorbing the sulfur compounds produced during the burning of the carbonaceous materials with a gasifying reagent containing oxygen. Further, sulfur impurities initially present in the hydrocarbon feedstock are retained by the molten media of the instant invention in view of the fact that a major portion of the hydrogen sulfide formed during the cracking operation is retained by the melt, particularly when the cracking step is conducted in the essential absence of steam. Also, a portion of the sulfur impurities that are present in the carbonaceous materials are believed to be leached out of the carbonaceous materials by the molten media of the instant invention, thereby effectuating a further removal of sulfur from the carbonaceous materials. Furthermore, the molten media of the instant invention: (a) have a sufficiently low melting point and possess a suitably wide liquid range to permit a wide range of operating temperatures to be employed; (b) possess good thermal conductivity to allow efficient heat transfer, and (c) possess high stability such as to undergo essentially no decomposition to volatile products under high severity cracking and/or gasification conditions. Thus, it is evident that these advantageous properties exhibited by the stable molten medium of the instant invention offer significant advantages in the thermal cracking of hydrocarbon feedstocks.

Individual, regenerable, stable molten systems that are preferred consist of phosphorus pentoxide employed in combination with an alkali metal oxide(s) or hydroxide(s), including mixtures thereof, wherein the mole ratio of the alkali or alkaline earth metal oxide or hydroxide component expressed as the oxide thereof to phosphorus pentoxide is in the range of from at least 1 to about 3. The most preferred melt systems of the instant invention comprise phosphorus pentoxide as the phosphorus oxide component in combination with either sodium oxide, potassium oxide, or lithium oxide and mixtures thereof, as the alkali metal oxide component wherein the mole ratio of the alkali metal compo-

nent expressed as the oxide thereof to phosphorus pentoxide is at least 1, and preferably from 1.5 to about 3.

It is to be understood that it is clearly within the scope of this invention to employ and define the molten phosphate melts of this invention with respect to the salt formed when an oxide of phosphorus is heated to the molten state in combination with an alkali or alkaline earth metal oxide or hydroxide. For example, a molten medium consisting of sodium oxide as the alkali metal oxide and phosphorus pentoxide as the oxide of phosphorus can also be expressed in the molten state as a phosphate, specifically sodium metaphosphate, on the basis of the following reaction:

$$Na_2O + P_2O_5 \rightarrow 2NaPO_3$$

Accordingly, it is to be noted that any of the molten phosphate melts of this invention may be prepared by fusing any combinations of raw materials which, upon heating, form a molten ten medium containing an oxide of phosphorus in combination with an alkali metal oxide wherein the mole ratio of the alkali or alkaline earth metal oxide or hydroxide to phosphorus oxide is within the above-defined critical limits.

In the process of this invention, a wide variety of feedstocks may be converted to produce high yields of light olefins such as ethylene. Generally, cracking can be conducted in the above-described molten metals with any hydrocarbon feedstock such as low boiling hydrocarbons, e.g., ethane, propane, butane, as well as high boiling hydrocarbons such as naphthas, gas oils and the like. Preferably, the hydrocarbon feedstocks of this invention are heavy hydrocarbon feedstocks such as crude oils, heavy residua, atmospheric and vacuum residua, crude bottoms, pitch, asphalt, other heavy hydrocarbon pitch-forming residua, coal, coal tar or distillate, natural tars including mixtures thereof. Preferably, the hydrocarbon feedstock which is cracked in the stable molten media of the instant invention comprises a hydrocarbon feedstock which contains material boiling above about 400°F. at atmospheric pressure. The preferred hydrocarbon feedstocks which can be employed in the practice of the instant invention are crude oils, aromatic tars, and atmospheric or vacuum residua containing material boiling above about 650°F. at atmospheric pressure. Aromatic tar, atmospheric or vacuum residua or particularly preferred.

While not essential to the reaction, an inert diluent can be employed in order to regulate the hydrocarbon partial pressure in the molten media cracking zone. The inert diluent should normally be employed in a molar ratio of from about 1 to about 50 moles of diluent per mole of hydrocarbon feed, and more preferably 1 to 10. Illustrative of the diluents that may be employed are helium, carbon dioxide, nitrogen, steam, methane and the like.

This invention will be further understood by reference to the accompanying drawing which is a schematic flow diagram for thermally cracking a heavy hydrocarbon feedstock in the molten media of the instant invention.

A heavy hydrocarbon residua fraction having a boiling point at atmospheric pressure of above 650°F. and Conradson carbon content of **12** is passed by way of line **1** into the cracking zone **2.** Within the cracking zone **2** is maintained a molten bed containing phosphorus pentoxide as the oxide of phosphorus in combination with lithium and potassium oxide wherein the mole ratio of lithium oxide to potassium oxide is 60 to 40 and the mole ratio of lithium and potassium oxide to boron oxide is about 1.2. The liquid hydrocarbon feedstock passing by way of line **1** is introduced into the cracking zone **2** by bubbling the feedstock through the molten media **3.** Alternatively, the molten media may be sprayed into the reactor or trickled down the reactor walls as the hydrocarbon feedstock passes through the reactor. The molten media may flow either cocurrently or countercurrently to the flow of the hydrocarbon feedstock.

The temperature of the molten media **3** is maintained in the range of from about 1,200° to about 2,000°F., and more preferably from about 1,300° to about 1,700°F. in order to form cracked hydrocarbon products and carbonaceous materials. The temperature of the molten media is maintained within the above-mentioned range due to the exothermic gasification reaction of the carbonaceous materials formed during the cracking reaction, as will be hereinafter described, such that the molten media provides the heat for the cracking operation. Depending upon the temperature and the specific type of hydrocarbon feedstock, the rate at which the feedstock is passed via line **1** into cracking zone **2** is in the range of from about 0.1 to about 100 w./w./hr. (weight of feed/weight of melt/-hour), and more preferably from about 0.1 to about 20 w./w./hr. Pressures are not a critical feature of the instant invention such that the reaction may be conducted at a pressure ranging from subatmospheric, e.g., 0.1 atmosphere to about 50 atmospheres, preferably from about 1 to about 10 atmospheres. The reaction time, as expressed in the amount of time the feedstock is in contact with the melt **3,** i.e., residence time, is in the range of from about 0.01 to about 20 seconds, and more preferably from about 0.3 to about 5.0 seconds.

After the hydrocarbon feedstock has been cracked in the molten media at the desired temperature and pressure, the gaseous effluent emanating from the molten media **3** passes overhead from the cracking zone **2** and is recovered by way of line **4.** The cracked products passing by way of line **4** are cooled by being subjected to a quenching medium introduced by way of line **5.** Thereafter, the cracked products are further cooled to condense and separate liquid products from the gaseous products containing light olefins by passing the quenched products by way of line **6** to a fractionation zone, not shown. Most of the hydrogen sulfide formed during the cracking operation is absorbed by the melt, particularly when the cracking operation is conducted in the absence of significant amounts of steam. The product distribution obtained by cracking a hydrocarbon feedstock in the manner described above is substantially identical to the product distribution obtained by subjecting the same feedstock, under identical conditions, to the well-known steam cracking process.

The significant advantage of employing the molten media of the instant invention is that the carbonaceous materials which are formed during the above-described cracking process become uniformly suspended throughout the melt and can be gasified, i.e., burned to gaseous products, when contacted with a gasifying reagent such as an oxidizing gas, i.e., air, steam or carbon dioxide at elevated temperatures in order to rapidly regenerate the molten media. Accordingly, the molten

media containing suspended carbonaceous material is withdrawn from the cracking zone **2** by way of line **7** and is passed by way of line **7** into a gasification zone **8.** The rate at which the molten media is withdrawn from the cracking zone depends on the type of hydrocarbon feedstock being pyrolyzed and the rate at which the feedstock is being introduced into the cracking zone **2.** Preferably, a vapor lift is employed in order to circulate the molten media by way of line **7** from the cracking zone **2** to the gasification zone **8.**

The carbonaceous materials which are formed during the thermal cracking reaction may be generally described as solid particle-like materials having a high carbon content such as those materials formed during high temperature pyrolysis of organic compounds and normally referred to as coke. While the carbonaceous material heretofore discussed has been produced in situ during the cracking of a hydrocarbon feedstock, as described above, it should be emphasized that it is clearly within the scope of the instant invention to gasify carbonaceous materials which may be added, in conjunction with or independently of a thermal cracking reaction, to the molten media of the instant invention in the form of coal of various grades, polygnite, lignite coal, coke of various types such as coal coke and petroleum coke, peat, graphite, charcoal and the like. Accordingly, the term gasification as used herein describes the contacting of such carbonaceous materials in the molten media of the instant invention with a gasifying reagent comprising a gaseous stream containing oxygen, steam, carbon dioxide and mixtures thereof. The gasification reaction is carried out by contacting the carbonaceous material in the molten media **9** with the gasifying reagent introduced into the gasification zone **8** by way of line **10.** The gasification reaction is carried out at temperatures in the range of from about the melting point of the molten media to 3,000°F. or higher and at a pressure in the range of from subatmospheric to about 100 atmospheres. Preferably, the temperature at which the gasification reaction is carried out is in the range of from about 1,200° to about 2,000°F., and more preferably from about 1,400° to about 1,800°F. It is preferred to maintain the pressure in the gasification zone in the range of from 1 to about 10 atmospheres.

When a gaseous stream containing oxygen is employed as the gasifying reagent in order to regenerate the molten media, the amount of oxygen which must be present in the gaseous stream is in the range of from about 1 to about 100 weight percent oxygen, and more preferably in the range of from about 10 to about 25 weight percent oxygen. Normally, the gaseous stream containing oxygen is passed through the molten media **9** at a rate of less than about 0.01 w./w./hr. (weight of oxygen/weight of molten media/hour) to about 50 w./w./hr., and more preferably from about 0.1 w./w./hr. to about 10 w./w./hr. Most preferably, air is introduced by way of line **10** at a temperature in the range of from about 100° to about 1,000°F. in order to effect a rapid regeneration of the molten media.

Alternatively, a gaseous stream containing steam or carbon dioxide may also be introduced as the gasifying reagent by way of line **10** into the gasification zone **8** in order to regenerate the molten media. When steam is employed as the gasifying reagent, the amount of steam which must be present in the gaseous stream is in the range of from about 10 to 100 weight percent, and more preferably from about 50 to about 100 weight percent. The steam is normally introduced by way of line **10** at a temperature in the range of from about 300° to about 1,000°F., and at a pressure in the range of from about 100 to about 500 psig in order to regenerate the molten media. In the event a gaseous stream containing carbon dioxide is employed as the gasifying reagent, the amount of carbon dioxide that must be present in the gaseous stream is in the range of from about 10 to about 100 weight percent. Preferably, the temperature and pressure at which carbon dioxide is introduced into the gasification zone **8** is in the range of from about 100° to about 1,000°F. and 100 to about 1,000 psig, respectively.

The specific gasification rate of the carbonaceous materials in individual stable, regenerable molten media, as defined by the amount of carbonaceous material which is gasified per hour per cubic foot of melt, is dependent upon the temperature at which the gasification process is carried out, as well as the residence time of the oxygen containing gas or steam in the melt, the concentration of carbonaceous material in the melt, and feed rate of oxygen containing gas into the media. As a general rule, the carbon gasification rate increases as the temperatuare of the melt, concentration of carbonaceous materials and feed rate of the oxygen containing gas increase. Preferably, the concentration of carbonaceous materials in the molten medium is maintained in the range of from 0.1 to about 60 weight percent, and more preferably from about 1.0 to about 20 weight percent, in order to effect a rapid gasification thereof.

The gaseous products produced by contacting the carbonaceous materials in the molten glass media with either an oxidizing gas, steam or CO_2 are recovered from the gasification zone by way of line **11.** When steam is employed as the gasifying reagent, a hydrogen-rich gaseous effluent is produced and recovered by way of line **11.** The contacting of the carbonaceous materials with steam under the preferred conditions of temperature and pressure for regenerating the molten media of the instant invention, normally 1,500°F. and atmospheric pressure, respectively, result in a gaseous effluent containing about 75 mole percent hydrogen and about 24 mole percent carbon oxides.

As opposed to the production of either a hydrogen or methane-rich steam when steam is employed as the gasifying reagent, the use of an oxygen-containing gas such as air as the gasifying reagent results in the formation of a nitrogen-rich gaseous effluent. As mentioned above, when air is employed as the gasifying reagent, it has surprisingly been discovered that the mole ratio of the alkali component to the oxide of phosphorus significantly affects the amount of sulfur oxides that are present in the gaseous effluent recovered from the gasification zone. Accordingly, when the mole ratio of the alkali or alkaline earth component to the oxide(s) of phosphorus is at least 1, as defined above, it has been discovered that the emissions of sulfur oxides, predominantly in the form of sulfur dioxide in the flue gas, i.e., gaseous effluent, from the gasification zone is drastically reduced.

Thus, it is evident that the practice of the process of the instant invention offers the further advantage of removing objectionable contaminants such as sulfur impurities which are inherently formed during the processing of heavy hydrocarbon feedstocks. During the

gasification of the carbonaceous materials with an oxidizing gas such as air, it is believed that the sulfur impurities present in the carbonaceous material are oxidized to sulfur oxides and are abosorbed by the molten media of the instant invention. In addition, the process of the instant invention further serves to remove other contaminants present in a heavy hydrocarbon feedstock such as ash forming impurities which include trace metals such as vanadium, iron and nickel that are normally present to a greater or lesser degree depending on the specific type of hydrocarbon feedstock being cracked and/or gasified.

The melt which has been regenerated as described above in gasification zone **8** is withdrawn by way of line **12** and reintroduced back into the cracking zone **2.** Normally, the amount of carbonaceous material that is gasified in the gasification zone **8** is substantially equivalent to the amount of carbonaceous material being formed during the cracking operation in the cracking zone **2,** such that an overall balance of carbonaceous material is maintained throughout the system. A further advantage of employing a gaseous stream containing oxygen as the gasifying reagent is the fact that the gasification, i.e., burning of carbonaceous materials with oxygen, is an exothermic reaction. Thus, when an oxidizing gas such as air is employed to gasify the carbonaceous materials in gasification zone **8,** a sufficient amount of heat is liberated in order to provide an overall heat balance for both the gasification and cracking processes. Accordingly, in addition to regenerating the melt, the gasification of the carbonaceous materials with an oxidizing gas maintains the temperature of the melt such that the melt being passed by way of line **12** into the cracking zone **2** provides the heat required for the thermal cracking of the hydrocarbon feedstock.

As can be appreciated, while the molten media of the instant invention effectuates the removal of sulfur and ash-forming impurities from the carbonaceous materials by absorbing these impurities during the gasification of the carbonaceous materials with an oxygen containing gasifying reagent, the continual buildup of these impurities in the melt requires that a slip-stream be withdrawn from the integrated cracking and gasification processes described above in order to restore the level of these impurities present in the melt to an acceptable level. While the slip-stream may be withdrawn from either the cracking or gasification zone or from any of the transfer lines wherein the molten media is being passed to either the cracking or gasification zone, i.e., lines **7** and **12,** respectively, it is preferred to withdraw a stream of the molten media from transfer line **7.** The basis for this preference of removing a portion of the contaminated molten media from the cracking zone resides in the fact that the cracking zone contains a greater amount of carbonaceous material, which carbonaceous material effects the reduction of alkali or alkaline earth metal sulfur oxides to metal sulfides, thereby facilitating the subsequent removal of the sulfur from the molten media, as will be hereinafter described.

The sulfur impurities present in the carbonaceous material as mentioned above are retained by the molten media during gasification with an oxidizing gas stream as well as being leached from the coke by the melt at elevated temperatures. When steam is employed as the gasifying reagent, however, the sulfur impurities are not converted to sulfur oxides and are not absorbed by the melt but rather the sulfur in carbonaceous material is primarily converted to hydrogen sulfide and is recovered in the effluent from the gasification zone. Thus, when an oxidizing gas stream is employed as the gasifying reagent, the sulfur impurities are absorbed by the melt in the form of metal sulfites or sulfates. The presence of carbonaceous materials in the molten media serves to reduce the metal sulfites or sulfates, predominantly alkali or alkaline earth metal sulfites, to their sulfide form. The metal sulfides are thereafter contacted with a carbon dioxide and water in order to recover the sulfur impurities as hydrogen sulfide. Accordingly, a slip-stream **13** is withdrawn from line **7** and is passed to a sulfur recovery zone **14,** wherein carbon dioxide and steam is introduced by way of line **15** and passed through the melt **16** at a temperature in the range of from about 800° to about 1,800°F. Alternatively, the molten media containing the sulfur impurity as a metal sulfide is passed into a sulfur recovery zone and is contacted with water in order to dissolve the melt and recover precipitated metals and ash and thereafter carbon dioxide is bubbled through the solution in order to recover the sulfur impurity as a hydrogen sulfide rich stream. In either embodiment, it is essential that the sulfur impurities be present in the sulfide form before being contacted with water or steam and carbon dioxide. In the event that a sufficient amount of carbonaceous material is not present in the system described above, and specifically in the cracking zone **2** in order to reduce the metal sulfate and sulfite to their sulfide form, it may be necessary to employ a reducing zone prior to passing the molten media into the sulfur recovery zone **16.** If a reducing zone is required, it is evident that the slip-stream may be withdrawn from any point in the system and thereafter passed to the reducing zone wherein such reducing agents as carbon, hydrogen, carbon monoxide, methane, ethane or the like may be employed in order to reduce the metal sulfite or sulfates to their sulfide form. If such a reducing zone is required, it is preferred to have a holding zone below the cracking zone wherein the addition of further amounts of carbon may or may not be necessary, depending on the specific type of hydrocarbon feedstock, to effectuate the reduction of substantially all of the metal sulfate or sulfites to their sulfide form.

The hydrogen sulfide rich stream is recovered from the sulfur recovery zone by the way of line **17** and may be ultimately passed to a Claus plant for sulfur recovery. The molten media with a reduced sulfur content is withdrawn from the sulfur recovery zone by way of line **18,** wherein this molten media containing a reduced sulfur level is returned to the gasification zone by way of line **19.**

It will, likewise, be necessary to treat the molten media in order to remove trace metals and ash which have accumulated in the melt. Accordingly, a stream of the melt with a reduced sulfur content is withdrawn by way of line **20** from line **18** and is passed to an ash recovery zone, not shown, wherein the ash is separated from the melt by dissolution in water.

While the initial charge of the molten media to the cracking zone may consist solely of an alkali or alkaline earth metal oxide or hydroxide in combination with an oxide of phosphorus as described above, it is to be understood that the cracking and gasification of a heavy hydrocarbon feedstock in such a molten media in ac-

cordance with the processing scheme disclosed above will necessarily result over a prolonged period of time in varying the overall composition of the melt. For example, during the gasification when an oxygen containing gas is employed to gasify the carbonaceous materials present in the melt, a portion of the carbon dioxide that is formed during combustion, i.e., the gasification reaction, is absorbed by the melt. A fraction of this portion of carbon dioxide that is absorbed by the melt forms a carbonate in the melt, and predominantly an alkali or alkaline earth metal carbonate depending upon the specific alkali or alkaline earth metal oxide or hydroxide that is employed as the alkali or alkaline earth metal component of the molten media of the instant invention. The extent of the absorption of carbon dioxide by the molten glass media and thus the amount of carbonate that is formed in the melt of the instant invention is a function of the mole ratio of the alkali metal component to the glassforming component, the specific alkali metal component employed, as well as the temperature of the melt and the carbon dioxide partial pressure existing over the bed of the molten media. As mentioned above, after a prolonged period of conducting the gasification process in the molten media of the instant invention such as will occur in a commercial unit, an equilibrium carbonate concentration will exist in the melt. The equilibrium carbonate concentration in any glass-forming melt will generally increase as the mole ratio of alkali metal oxide or hydroxide to the glass-forming oxide increases, as the molecular weight of the cation increases, i.e., a melt containing potassium will absorb more carbon dioxide than a melt containing sodium, and a melt containing sodium will absorb more carbon dioxide than a melt containing lithium. The carbonate concentration predominantly in the form of alkali or alkaline earth metal carbonates in molten media of the instant invention is preferably kept to a minimum and, depending on the factors indicated above, will comprise below about 30 weight percent of the melt, preferably below about 20, and more preferably below about 15 weight percent of the melt.

In addition, the continuous melt cracking and gasification process of this invention will result in the composition of the molten media being effected by the presence of alkali or alkaline earth metal sulfates, sulfites and sulfides, as mentioned above, as well as with ash components, including that amount of residual carbonaceous material that may be tolerated in the melt. Accordingly, the steady state composition of the molten media will normally contain, in addition to the alkali and alkaline earth metal carbonates referred to above, from about 10 to about 20 weight percent sulfates, 0 to about 10 weight percent metal sulfites, **0** to about **10** weight % metal sulfides, from 3 to about 5 weight percent carbonaceous materials and from about 2 to about 10 weight percent ash. As will be appreciated, the melt composition will vary from the gasification zone to the cracking zone as well as in the reducing and sulfur recovery zones. For example, while the metal sulfate may be present in the melt in the gasification zone in an amount in the range of from 10 to 20 weight percent, the amount of metal sulfate in the cracking, reducing and sulfur recovery zones will normally vary from about 0 to about 10 weight percent. Likewise, whereas the amount of metal sulfide in the cracking, reducing and sulfur recovery zones is in the range of from about 5 to about 20 weight percent, the amount of metal sulfide in the melt in the gasification zone is normally in the range of from about 0 to about 10 weight percent. Thus, after continuous practice of the cracking and gasification process described herein, the amount of alkali and alkaline earth phosphorus compound such as alkali metal phosphate that is present in the melt will normally constitute from about 15 to about 85 weight percent of the melt, preferably at least about 30 weight percent, and more preferably at least about 50 weight percent of the molten media. It is to be understood, however, that the only requirement of the molten media of this invention is that said molten media contain a sufficient amount of an alkali or alkaline earth metal oxide or hydroxide, including mixtures thereof in combination with an oxide of phosphorus, to be regenerable, that is both suspend the carbonaceous materials formed during the cracking reaction uniformly throughout the melt and thereafter promote the rapid gasification of such carbonaceous materials upon contact with a gasifying reagent such as air or steam at elevated temperatures.

It should be noted that the presence of such alkali and alkaline earth metal sulfides, sulfates, sulfites, carbonates as well as ash components in the molten media of the instant invention will effectively alter, to a slight degree, the mole ratio of the alkali or alkaline earth metal oxide or hydroxide compound to the oxide of phosphorus component from the initial mole ratio of the molten media that was initially charged to the cracking zone. For example, the existence of an equilibrium carbonate concentration in the molten media as well as the presence of metal sulfates and sulfides will effectively lower, to a slight degree, the initial mole ratio of alkali or alkaline earth metal oxide component to the oxide of phosphorus component which was charged to the cracking zone. Accordingly, the critical mole ratios disclosed and claimed herein define that mole ratio(s) of the alkali and alkaline earth metal oxide or hydroxide to the glass-forming oxide that must be maintained in the molten media in the cracking and gasification zones, in the presence of the above-mentioned carbonate and sulfur compounds, ash components, and the like, in order to obtain the advantages of the instant invention. By this is meant that after continuous cracking and gasification operation wherein a buildup of contaminants such as sulfur compounds, coke, ash and the like occurs in the melt, the mole ratio of alkali metal compound to oxide of phosphorus component does not include that amount of alkali metal compound that is present in these contaminants. Accordingly, due to the buildup of these contaminants in the melt and the loss, to a slight degree, of a small amount of alkali metal compound and thus a slight reduction in the mole ratio of the alkali metal compound to the oxide of phosphorus compound, it may be necessary to add additional amounts of alkali metal compound to the melt in order to maintain a specific mole ratio of the alkali metal compound to the oxide of phosphorus in the melt.

This invention will be further understood by reference to the following examples.

EXAMPLE 1

A heavy residua hydrocarbon feedstock containing materials boiling above 650°F. was introduced by means of a pump at a rate of about 2 grams per minute

through a ¼ inch inlet tube into a reactor containing a molten medium consisting of equimolar amounts of phosphorus pentoxide and sodium oxide. The cracking zone was 2 inches in diameter and 12 inches in length, and was placed in a Lindberg furnace. The melt temperature was measured by a thermocouple inserted into a thermowell positioned in the center of the molten media connected to a portable pyrometer. The effluent gases were passed directly to a gas chromatograph for analysis. The quantity of C_5^+ liquid products and carbonaceous material, namely coke, produced was also measured.

TABLE I

RESID CRACKING IN MOLTEN MEDIA

Melt	$NaPO_3$
Temperature, °F.	1350
Feed (g)	220
Product Yield, Wt. % on Feed	
Hydrogen	0.3
Methane	9.5
Ethylene	16.4
Ethane	5.0
Propane	1.3
Propylene	15.0
C_3^- Conversion	47.5
Butanes	0.3
i-Butylene	2.3
n-Butylenes	4.3
Butadiene	4.6
Total C_4	11.5
Total C_5^+ Liquid	41.6
Coke	4.9
Wt. Balance	105.5

As can be seen from the results as shown in Table I, the cracking of a heavy hydrocarbon feedstock in a molten sodium metaphosphate melt results in a high conversion to C_3^- products.

As discussed above, the carbonaceous particles which are formed during this cracking reaction become dispersed in the molten phosphate media. The specific operating conditions employed and the results obtained in gasifying these carbonaceous materials which become dispersed in the melt with air and steam as the gasifying reagent are set forth in the following Table II.

TABLE II

COKE GASIFICATION

Melt	$NaPO_3$	
Temperature, °F.	1670	1700
Air Flow Rate (1/min.)	2	—
Steam Rate (g/min)	—	0.25
Effluent Gas Composition, Mole %		
H_2	0.0	83.5
N_2	77.4	0.0
O_2	19.7	0.0
CO	0.1	8.1
CH_4	0.0	0.7
CO_2	2.8	7.2
H_2S	0.0	0.5
Sulfur in Effluent (Nanograms/cc.)	250–450	2100
H_2O Conversion, %	—	6.6
O_2 Conversion, %	8.3	—
% Coke Gasified	75	42
% Coke Carried out of Reactor	25	58

As can be seen from the results as shown in Table II, the gasification of the carbonaceous material with steam results in a hydrogen-rich gaseous effluent, while the gasification of the carbonaceous material with air as the oxygen-containing gas stream results in a nitrogen-rich gaseous effluent. Furthermore, it can be seen that the carbonaceous materials were converted to their respective gaseous streams at high conversions.

EXAMPLE 2

This example indicates the significant increase in gasification rate of the carbonaceous materials present in a molten phosphate melt when the mole ratio of the alkali or alkaline earth metal oxide or hydroxide component to the oxide of phosphorus is at least one ($R<1$).

TABLE III

EFFECT OF ALKALI OXIDE/PHOSPHORUS OXIDE MOLE RATIO ON GASIFICATION RATE

Temperature: 1500°F.; Air Flow Rate: 2 STP 1/min. 475 grams 60:40 mole % Lithium: Potassium Phosphate; 5 weight % Fluid Coke

R Mole Ratio Alkali Oxides to P_2O_5	Oxygen Conversion %	Carbon Gasification Rate (lb./cu.ft./hr.)
0.5	12	0.5
1.0	12	0.5
2.0	55	2.9
2.5	64	3.8

As can be seen from the results as shown in Table III, the carbon gasification rate increases rapidly with the increase in the mole ratio of alkali metal oxide to phosphorus oxide (R Number). In addition, it was observed that increasing the R number ($R<1$) likewise results in a more uniform suspension of the carbonaceous materials throughout the molten medium.

EXAMPLE 3

This example indicates the effect of varying the mole ratio of the alkali metal component to the oxide of phosphorus on the gasification of carbonaceous materials in molten phosphate melts when the molten media is treated with 2 liters per minute under standard conditions of temperature and pressure with a gaseous stream containing ten percent carbon dioxide in nitrogen for a period of 2 hours in order that the molten media was employed under equilibrium carbonate conditions.

TABLE IV

EFFECT OF R NUMBER ON AIR BURNING OF COKE IN PHOSPHATE MELTS

Melt: 480 g Li/K Phosphate with Li_2O/K_2O mole Ratio equal 40/60; Temperature: 1600°F.; Air Flow Rate: 4 STP 1/min.; Coke: 20 g Fluid Coke Melt pretreated with 2 STP 1/min 10% CO_2/N_2 for 2 hours

R Number of Melt	Oxygen Conversion, %	Carbon Burning Rate (lb/cu.ft./hr.)
1.0	7	0.5
1.5	22	1.4
2.0	53	3.3
2.5	70	5.5

As can be seen from the results as shown in Table IV, above an R number (mole ratio of alkali metal component to the oxide of phosphorus) of one there occurs a significant increase in the gasification rate of carbonaceous materials present in the melt in the same manner as is shown in Table III of Example 2.

What is claimed is:

1. A process for cracking a hydrocarbon feedstock which comprises contacting said feedstock with a regenerable molten media comprising an oxide of phosphorus in combination with an alkali metal compound selected from the group consisting of alkali metal oxides, alkali metal hydroxides, alkaline earth metal oxides, alkaline earth metal hydroxides and mixtures thereof, wherein the mole ratio of the alkali metal compound expressed as the oxide thereof to the oxide of phosphorus is in the range of from about 1.2 to about 2.5, at a temperature in the range of from above the melting point of said media to about 3,000°F. for a time sufficient to form cracked hydrocarbon products and to uniformly suspend the carbonaceous materials formed during said cracking operation throughout the molten media.

2. The process of claim 1 wherein the temperature of the molten media is maintained in the range of from about 1,200° to about 2,000°F.

3. The process of claim 2 wherein said molten media contains a carbonate selected from the group consisting of alkali metal carbonates, alkaline earth metal carbonates and mixtures thereof.

4. The process of claim 2 wherein said molten media contains carbonaceous materials and is regenerated by contacting said molten media with a reagent selected from the group consisting of oxygen, steam, carbon dioxide and mixtures thereof at a temperature in the range of from about the melting point of said molten media to about 3,000°F.

5. The process of claim 4 wherein the hydrocarbon feedstock contains sulfur.

6. The process of claim 5 wherein the amount of sulfur present in the molten media is reduced by:

a. contacting the sulfur compounds in the molten media with a reducing agent; and

b. thereafter contacting the reduced sulfur compounds formed in step (a) with carbon dioxide and water to form hydrogen sulfide as a recoverable product.

7. A process for cracking a hydrocarbon feedstock which comprises contacting said hydrocarbon feedstock with a regenerable molten media comprising an oxide of phosphorus in combination with an alkali metal compound selected from the group consisting of alkali metal oxides, alkali metal hydroxides, alkaline earth metal oxides, alkaline earth metal hydroxides and mixtures thereof wherein the mole ratio of the alkali metal component expressed as the oxide thereof to the oxide of phosphorus is in the range of from about 1.2 to about 2.5, at a temperature in the range of from about the melting point of said media to about 2,500°F. to form cracked hydrocarbon products and to uniformly suspend the carbonaceous materials throughout the molten media, and thereafter gasifying said carbonaceous materials formed during said cracking process by contacting said molten media containing carbonaceous materials with a reagent selected from the group consisting of oxygen, carbon dioxide, steam and mixtures thereof at a temperature in the range of from about the melting point of said medium to about 3,000°F.

8. The process of claim 7 wherein the temperature of the molten media is maintained in the range of from about 1,200° to about 2,000°F.

9. The process of claim 8 wherein said molten media contains a carbonate selected from the group consisting of alkali metal carbonates, alkaline earth metal carbonates and mixtures thereof.

10. The process of claim 9 wherein the gasifying reagent is an oxygen containing gas stream.

11. The process of claim 10 wherein the hydrocarbon feedstock is a heavy hydrocarbon feedstock containing sulfur.

12. A process for cracking a heavy hydrocarbon feedstock containing sulfur which comprises:

a. contacting said feedstock with a regenerable molten media comprising an oxide of phosphorus in combination with an alkali metal compound selected from the group consisting of alkali metal oxides, alkali metal hydroxides, alkaline earth metal oxides, alkaline earth metal hydroxides and mixtures thereof wherein the mole ratio of the alkali metal component expressed as the oxide thereof to the oxide of phosphorus is in the range of from about 1.2 to about 2.5, at a temperature in the range of from about the melting point of said media to about **2500°F.** to form cracked hydrocarbon products and to uniformly suspend the carbonaceous materials throughout the molten media;

b. contacting the molten media containing said carbonaceous materials with a gaseous stream containing oxygen at a temperature in the range of from about above the melting point of said media to about **3000°F.** in order to gasify said carbonaceous products and to form sulfur compounds;

c. contacting the sulfur compounds formed in step (b) in the molten medium with a reducing agent; and

d. thereafter contacting the reduced sulfur compounds formed in step (c) with carbon dioxide and water to form hydrogen sulfide as a recoverable product.

13. The process of claim 12 wherein said reducing agent is carbon.

14. The process of claim 13 wherein the reduced sulfur compounds formed in step (a) are selected from the group consisting of alkali metal sulfides, alkaline earth metal sulfides and mixtures thereof.

15. The process of claim 14 wherein said oxide of phosphorus is phosphorus pentoxide.

16. The process of claim 15 wherein said molten media contains a carbonate selected from the group consisting of alkali metal carbonates, alkaline earth metal carbonates and mixtures thereof.

17. The process of claim 16 wherein the alkali metal compounds are selected from the group consisting of sodium oxide, potassium oxide, lithium oxide and mixtures thereof.

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