

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

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[22] Filed: **Mar. 28, 1973**

[21] Appl. No.: **345,642**

[52] U.S. Cl. **208/125; 48/211; 208/235; 260/683 R; 423/351; 423/572; 423/648**

[51] Int. Cl. **C10g 9/34**

[58] Field of Search **208/125, 128, 130, 107**

[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

Hydrocarbon feedstocks, preferably heavy hydrocarbon feedstocks containing sulfur, are cracked at elevated temperatures in a novel regenerable alkali metal carbonate molten medium containing a glass-forming oxide, such as an oxide of boron, to produce high yields of light olefins such as ethylene, which olefins are useful in the synthesis of polymers and other valuable chemicals. The carbonaceous materials, i.e. coke, which are formed and dispersed in the molten medium during the cracking operation are gasified by contacting a portion of said carbonaceous materials with a gaseous stream containing oxygen, steam or carbon dioxide at temperatures of from about above the melting point of said medium to about 3000°F. in order to regenerate the melt. Preferably, the amount of glass-forming oxide expressed as the oxide thereof, present in the alkali-metal carbonate melt is maintained in the range of from about 0.1 to about 25 weight percent based on the total weight of the molten medium in order to increase the overall dispersion of the carbonaceous materials which are formed in the molten medium during the cracking reaction.

15 Claims, 2 Drawing Figures

HYDROCARBON CRACKING IN A REGENERABLE MOLTEN MEDIA

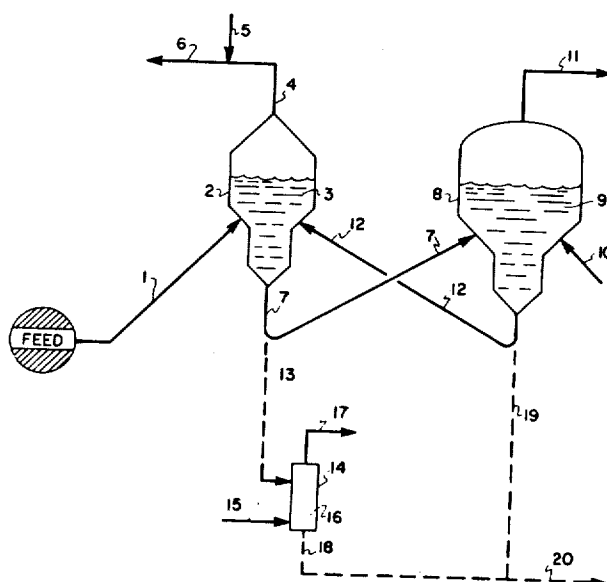


FIGURE 1

HYDROCARBON CRACKING IN A REGENERABLE MOLTEN MEDIA

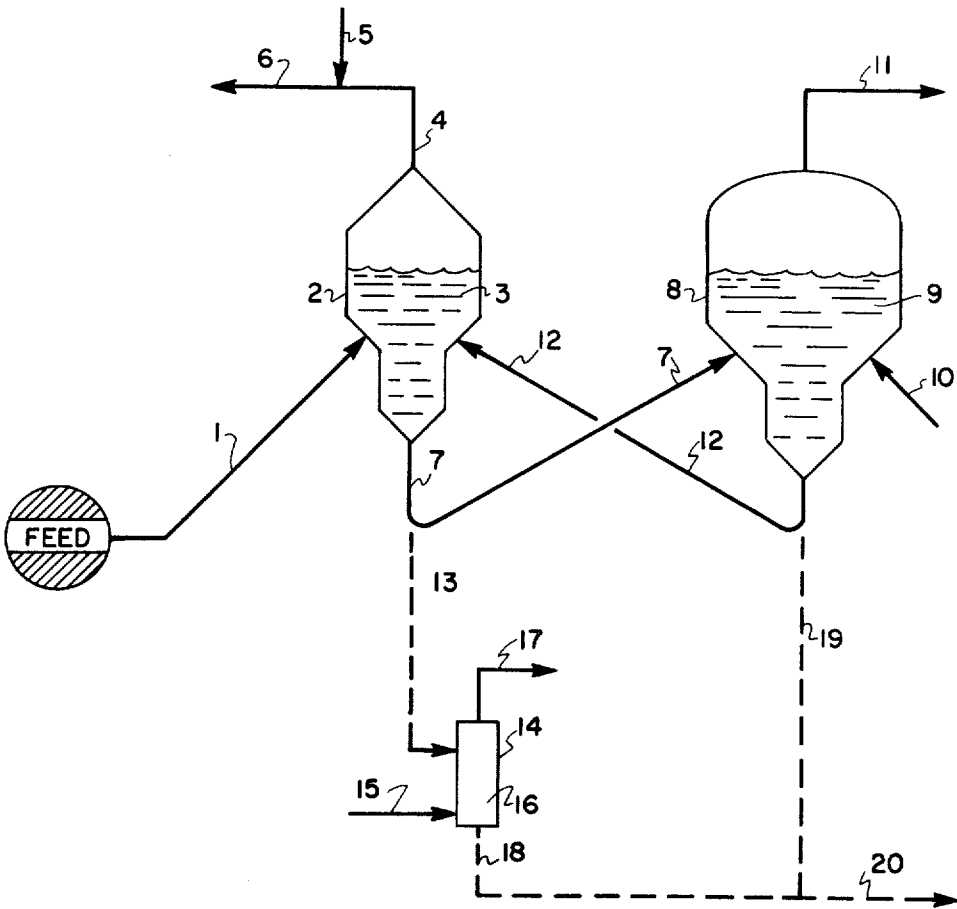
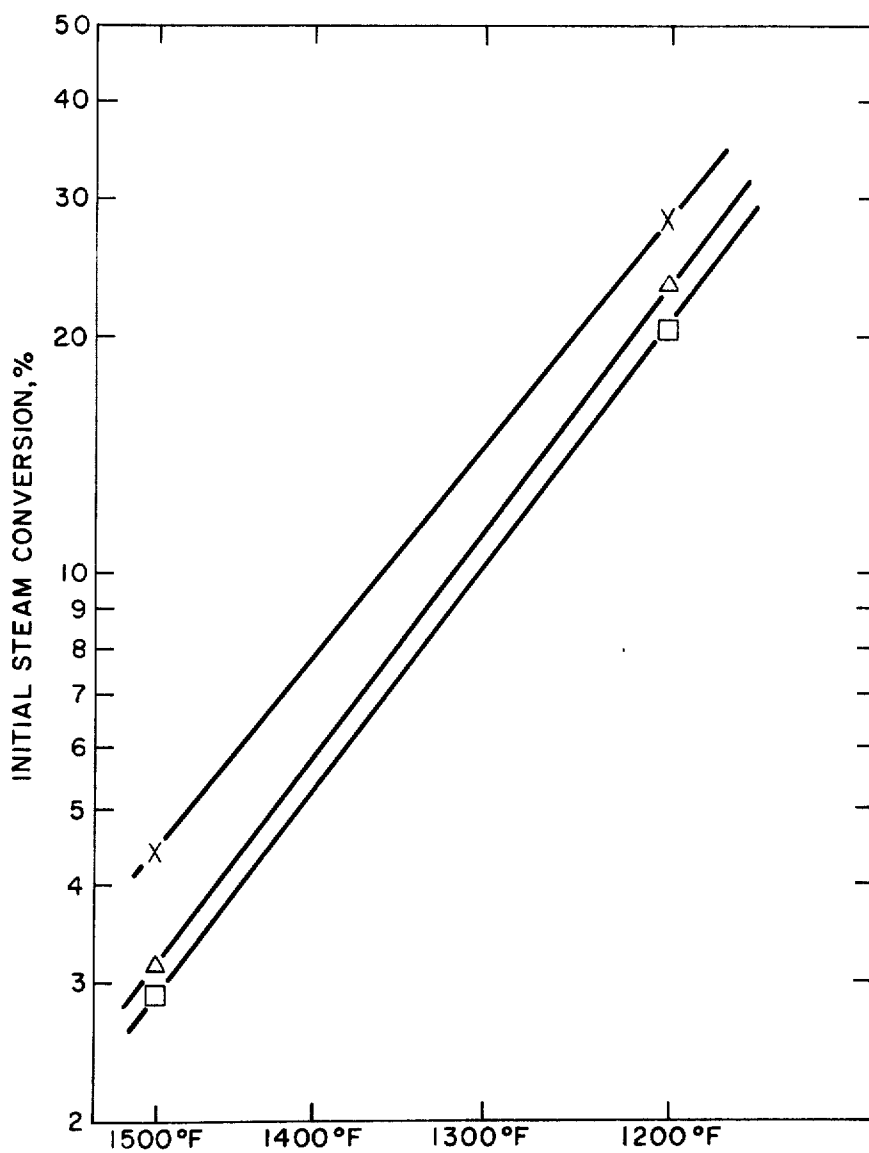


FIGURE 2
DESULFURIZATION IN MOLTEN MEDIA



HYDROCARBON CRACKING IN A REGENERABLE MOLTEN MEDIUM

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 alkali metal carbonate molten medium. 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 alkali metal carbonate molten medium containing a glass-forming oxide such as an oxide of boron to produce cracked hydrocarbon products such as ethylene and carbonaceous materials. At least a portion of the carbonaceous materials, i.e. coke which are formed during the cracking process are gasified by contacting said carbonaceous materials in the molten medium with a gaseous stream containing an oxygen, 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 in the art. The cracking of hydrocarbon feedstocks in molten heat transfer medium such as lead to produce ethylene has likewise been disclosed in the art.

However, the molten medium 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 sufficiently dispersed in the melt, but formed a separate phase which contaminated the liquid and gaseous products. Further with molten medium 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 and U.S. Pat. No. 3,647,358) in order to effectuate the thermal cleavage of hydrocarbon feedstocks.

It has been suggested that hydrocarbon feedstocks can be cracked in a molten alkali metal carbonate, alkali metal hydroxide, or a mixture thereof, to form hydrocarbon products containing ethylene and thereafter regenerating the molten medium by intimate contact with oxygen or steam (see U.S. Pat. Nos. 3,553,279; 3,252,773; 3,252,774; 3,505,018; 3,438,727; 3,438,728; 3,438,733; 3,438,734; 3,516,796; 3,551,108; *Oil and Gas Journal* Sept. 27, 1971; German DT-OS No. 2,149,291).

While molten alkali metal carbonate melts tend to absorb or disperse the coke formed during the cracking

reaction; the extent of coke dispersion is relatively low. This limited coke dispersion in the molten medium may cause process difficulties in a commercial environment.

Recently, it has been proposed to crack a hydrocarbon feedstock in a regenerable molten medium containing an alkali oxide in combination with a glass-forming oxide such as an oxide of boron. (U.S. Ser. No. 280,185, filed Aug. 14, 1972). Such a molten medium, while exhibiting sufficient coke dispersion, suffers from the disadvantage of being corrosive in nature, thereby resulting in a significant materials of construction problem.

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 contacting the hydrocarbon feedstock with an alkali-metal carbonate molten medium containing minor amounts of a glass-forming oxide selected from the group consisting of an oxide of boron, vanadium, silicon, phosphorous including mixtures thereof at a temperature in the range of from about above the melting point of the medium to about 2500°F. for a time sufficient to form cracked hydrocarbon products and carbonaceous materials. Thereafter, the carbonaceous materials formed and dispersed in the molten medium during the cracking operation are contacted with a gaseous stream containing oxygen, steam, or carbon dioxide including mixtures thereof, at a temperature in the range of from about the melting point of said medium to about 3000°F. for a period of time in order to regenerate the molten medium. It has been discovered that not all oxides of primary and secondary glass-forming compounds known in the art are amenable to the process of the instant invention. Specifically, oxides of such primary glass-forming elements as germanium, arsenic and antimony have been found unsuitable for the cracking or gasification processes described herein in that the oxides of these elements, i.e., glass-forming oxides of germanium, arsenic and antimony, are excessively reduced to their metal state in the presence of carbon at temperatures which would normally be employed to crack or gasify a hydrocarbon feedstock. Carbon in the form of coke will normally be present in the molten medium to a greater or lesser degree in the practice of the process of the instant invention, as will be hereinafter described, in view of the fact that it is preferred to gasify only that amount of coke which is being formed in cracking zone in order to achieve a heat balanced system as well as to maintain a steady state coke concentration in the melt. Further, two primary glass-forming oxides which are not significantly reduced by carbon, namely the oxides of molybdenum and tungsten are not effective in increasing the dispersion of carbonaceous materials formed during the cracking operation when employed in minor amounts in a molten alkali carbonate medium. In addition, a secondary glass-forming oxide, namely bismuth oxide, is likewise reduced in a molten medium at elevated temperatures to its metal state in the presence of carbon.

The glass-forming oxides of the instant invention are employed in combination with an alkali metal (Group IA) carbonate, that is a carbonate of lithium, sodium, potassium, cesium or mixtures thereof. The molten medium may additionally contain other Group IA or IIA constituents such as the oxides, hydroxides, sulfides,

sulfites, or sulfates of sodium, lithium, potassium, cesium, magnesium, calcium, strontium and barium. Alkali metal sulfites, sulfates and sulfides are formed in situ during the course of the cracking or subsequent gasification reactions by the reaction of the sulfur contaminants in the feedstock with the alkali or alkaline earth metal constituents of the melt. Alkali metal oxides are also generated in situ by the carbon reduction of alkali metal carbonates. Alkali metal hydroxides may be formed if water is present in the cracking or gasification zones. The amount of glass-forming oxide in the total molten media is maintained between about 0.1 to 25 weight percent, preferably between 1 to about 20 weight percent and more preferably from about 1 to about 12 weight percent calculated as the oxide thereof, e.g. B_2O_3 , V_2O_5 , SiO_2 , P_2O_5 and based on the total molten media. It should be recognized that the glass-forming element e.g. boron may exist in various valence states at various points in the process. Accordingly, the expression "oxide of boron" is intended to encompass any oxide of the applicable element e.g. boron, vanadium, silicon and phosphorous.

The advantages of cracking a hydrocarbon feedstock, particularly a heavy hydrocarbon feedstock containing sulfur, in the above-mentioned molten medium reside in the ability of the molten medium of this invention to: (a) suspend the carbonaceous materials formed in situ during the cracking operations 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 of 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 residua and crude oils 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 retaining 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 medium 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 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 medium of the instant invention, thereby effectuating a further removal of sulfur from the carbonaceous materials.

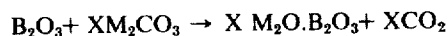
Furthermore, the molten medium of the instant invention exhibits the additional advantage of being relatively noncorrosive in nature, particularly when compared with a molten medium containing a predominant amount of a glass-forming oxide. Accordingly, maintaining the concentration of the glass-forming oxide below about 25 weight percent, preferably below about 20 weight percent, and more preferably below 12 weight percent, alleviates the containment problem associated with employing a glass-forming oxide as a

major constituent in the molten medium cracking process. Thus, it can be seen that the addition of a controlled amount of a glass-forming oxide to an alkali metal carbonate melt results in a molten medium exhibiting excellent coke dispersion properties without being extremely corrosive in nature, which properties are required for a commercial operation.

A still further advantage of employing a molten alkali metal carbonate melt containing a controlled amount of a glass-forming oxide in order to convert a heavy hydrocarbon feedstock containing sulfur to valuable chemical products resides in the fact that increased desulfurization rates are obtained at a given temperature with the molten medium of the instant invention. The fact that the desulfurization rate decreases markedly with an increase in temperature in a molten alkali carbonate medium often necessitates cooling the molten medium during the desulfurization step in order to obtain a satisfactory desulfurization rate. It has been discovered, however, that during the desulfurization of the molten medium with steam and carbon dioxide that the steam conversion and thus the overall desulfurization rate increases with the addition of a glass-forming oxide to a molten alkali carbonate medium. Thus, a molten alkali carbonate medium containing a glass-forming oxide can be desulfurized with steam and carbon dioxide at the same rate at a higher temperature than a molten alkali carbonate melt which does not contain a glass-forming oxide thereby reducing the amount of cooling and reheating required to bring the molten medium back to the desired reaction temperature.

Accordingly, the only requirement of the molten medium of this invention is that a sufficient amount of the glass-forming oxides are employed to disperse the carbonaceous materials formed during the cracking reaction uniformly throughout the melt and thereafter promote the rapid gasification of said materials upon contact with a gaseous stream containing oxygen or steam or carbon dioxide at elevated temperatures. The use of the term "glass-forming oxide" is not meant to imply that all of the molten medium described above can be rapidly cooled without crystallizing. It should be recognized, as stated above, that the molten medium of this invention may be employed in combination with other components such as metallic and nonmetallic oxides, sulfides, sulfates and various other salts in varying amounts so long as a sufficient amount of glass-forming oxide is employed to disperse by-product carbonaceous material, i.e. coke.

It is to be understood that although the molten medium of the instant invention is described in terms of an alkali metal carbonate and the glass-forming oxides, it is clearly within the scope of this invention to employ and define the molten medium of this invention with respect to the compounds which are believed to be formed when a glass-forming oxide is heated to the molten state in combination with the alkali metal carbonate or other alkali metal compounds. For example, a molten medium containing an alkali metal carbonate (M_2CO_3) and boron oxide (B_2O_3) as the glass-forming oxide can also be expressed in the molten state as an alkali metal borate, on the basis of the following reaction:



wherein X ranges from 1 to 3 depending on the alkali

metal employed. Accordingly, it is within the purview of the instant invention to employ as the molten medium of this invention an alkali metal carbonate and a glass-forming oxide, as defined above, in combination with an alkali metal or an alkali metal salt of the glass-forming oxide employed, e.g., alkali metal borate. It is to be understood that any of the molten glass melts of this invention may be prepared by fusing any combination of raw materials, which upon heating will form a glass-forming oxide or an alkali metal salt of the glass-forming oxide employed in combination with an alkali metal carbonate.

Individual regenerable molten medium which are most preferred are those obtained when an oxide of boron is employed as the glass-forming oxide. The most preferred melt system of the instant invention comprises boron oxide in combination with a carbonate of lithium, sodium and mixtures thereof. The most preferred alkali metal carbonate is a mixture of a major amount of sodium carbonate and a minor amount of lithium carbonate.

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 medium 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 that contain from about 2 to about 6 weight percent sulfur 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 medium 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 are 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 medium 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 FIG. 1 of which is a schematic flow diagram for thermally cracking a heavy hydrocarbon feedstock in the molten medium of the instant invention.

A heavy hydrocarbon residua fraction containing from about 2 to about 6 weight percent sulfur and having a boiling point at atmospheric pressure of above 650°F. and a Conradson carbon content of 12 is passed by the way of line 1 into the cracking zone 2. Within the cracking zone 2 is maintained a molten bed containing an oxide of boron and alkali metal carbonate

comprising a major amount of sodium carbonate and a minor amount of lithium carbonate. The liquid hydrocarbon feedstock passing by way of line 1 is introduced into the cracking zone 2 by bubbling the feedstock through the molten medium 3. Alternatively, the molten medium may be sprayed into the reactor or trickled down the reactor walls as the hydrocarbon feedstock passes through the reactor. The molten medium may flow either cocurrently or countercurrently to the flow of the hydrocarbon feedstock. In either event, means should be provided to secure intimate contacting of the feed with the molten medium.

The temperature of the molten medium 3 is maintained in the range of from about 1200° to about 2000°F., and more preferably from about 1300° to about 1700°F. in order to form cracked hydrocarbon products and carbonaceous materials. The temperature of the molten medium is maintained within the above-mentioned range due to the exothermic gasification reaction of a portion of the carbonaceous materials formed during the cracking reaction, as will be hereinafter described, such that the molten medium 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 medium at the desired temperature and pressure, the gaseous effluent emanating from the molten medium 3 passes overhead from the cracking zone 2 and is recovered by way of line 4. The cracked products passed 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 the 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 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 medium 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 medium. Accordingly, the molten medium containing suspended carbona-

aceous 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 medium 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 medium 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 medium 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 medium 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 medium 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 medium to 3000°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 1200° to about 2000°F., and more preferably from about 1400° to about 1800°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 medium, the amount of oxygen which must be present in the gaseous stream is in the range of from about 1 to about 100 weight % oxygen, and more preferably in the range of from about 10 to about 25 weight % oxygen. Normally, the gaseous stream containing oxygen is passed through the molten medium 9 at a rate of less than about 0.01 w/w/hr. (weight of oxygen/weight of molten medium/hour) to about 50 w/w/hr., and more preferably from about 0.01 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 1000°F. in order to effect a rapid regeneration of the molten medium.

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 medium. 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 % and

more preferably from about 50 to about 100 weight %. The steam is normally introduced by way of line 10 at a temperature in the range of from about 300° to about 1000°F., and at a pressure in the range from about 100 to about 500 psig in order to regenerate the molten medium. 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 %. 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 1000°F. and 100 to 1000 psig, respectively.

The specific gasification rate of the carbonaceous materials in individual, regenerable molten medium, 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 medium. As a general rule, the carbon gasification rate increases as the temperature 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 %, and more preferably from about 1.0 to about 20 weight %, and most preferably from about 1 to about 5 weight % in order to effect a rapid gasification thereof.

The gaseous products produced by contacting the carbonaceous materials in the molten medium with either an oxidizing gas, steam or CO₂ 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 medium of the instant invention, normally 1500°F. and atmospheric pressure, respectively, result in a gaseous effluent containing about 75 mole % hydrogen and about 24 mole % carbon oxides. Based on thermodynamic considerations, however, the gasification of carbonaceous materials with steam in the molten medium of the instant invention at lower temperatures, preferably below 1000°F., and at elevated pressures would result in formation of a methane-rich gaseous effluent.

As opposed to the production of either a hydrogen or methane-rich stream 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.

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 absorbed by the molten medium 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 medium of the instant invention effectuates the removal of sulfur and ash-forming impurities from the carbonaceous material by retaining 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 medium 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 medium from transfer line 7. The basis for this preference of removing a portion of the contaminated molten medium 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 medium, as will be hereinafter described.

The sulfur impurities present in the carbonaceous material as mentioned above are retained by the molten medium 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 medium 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 carbon dioxide and water in order to recover the sulfur impurities as hydrogen sul-

fide. 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 1800°F. Alternatively, the molten medium 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 medium 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. In either event, it is preferred that the total sulfur concentration in the molten medium be maintained below about 5.0 weight % and preferably below about 0.25 and 2.0 weight % based on the total molten media.

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 medium with a reduced sulfur content is withdrawn from the sulfur recovery zone by way of line 18, wherein this molten medium 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 medium 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.

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 2.3 grams per minute through a 1/8 inch inlet tube into a stirred reactor containing a molten alkali metal carbonaceous medium consisting of 70 mole % lithium carbonate and 30 mole % sodium carbonate to which has been added 6 wt. % of boron oxide (Run A) and 10 wt. % boron oxide, i.e. B₂O₃ as the glass-forming oxide component. The cracking zone was 4 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 molten medium connected to a portable pyrometer. The effluent gases were passed directly to a gas chromatograph for analysis. The quantity of C_3+ liquid products and carbonaceous material, namely coke, produced was also measured.

TABLE I

Feed:	650°F.+ Arabian Heavy Resid (2.3 grams/minute)	
Melt:	1900 g. Li/Na (70/30 mole %) carbonate containing B_2O_3 in stirred reactor	
Temp:	1350–1400°F. : Helium Diluent: 1.2–1.5 l/min.	
	Run A	Run B
	6	10
Wt. % B_2O_3		
Product Yield, wt.% on Feed		
H_2	0.2	0.3
Methane	6.7	8.6
CO	6.0	9.1
CO_2	10.9	11.2
Ethylene	12.7	13.0
Ethane	2.9	3.1
Propane	0.4	0.5
Propylene	9.5	8.9
Butenes	6.2	4.6
C_3+ Liquid	40.8	38.2
Coke	12	12

As can be seen from the results as shown in Table I, the cracking of a heavy hydrocarbon residua feedstock in a molten alkali carbonate medium containing 6 wt. % and 10 wt. % boron oxide results in a high conversion to C_3+ products.

EXAMPLE 2

This example indicates the carbon gasification rates that are obtainable in accordance with the instant invention when coke, which has been formed and dispersed during the cracking operation as outlined in Example 1, has been contacted with air in a molten alkali carbonate medium containing a glass-forming oxide, namely boron oxide at a temperature of 1500°F.

TABLE II

Coke Gasification		
Melt:	500 grams of melt containing 1.9 wt. % coke	
Temp:	1500°F.; Air Flow Rate: 2.0 STP Liters/min.;	
Pressure:	Atmospheric	
Molten Medium	Oxygen Conversion (%)	Carbon Gasification Rate (lb/ft. ³ /hr.)
Li-Na (70/30 mole %)	99	3.3
Carbonate containing 6 wt. % B_2O_3		

As can be seen from the results as shown in Table II, the molten alkali metal carbonate medium containing a minor amount of a glass-forming oxide results in a sufficient gasification of coke present in the melt so as to permit the facile regeneration of the melt after the melt has been employed as the cracking medium for a hydrocarbon feedstock.

EXAMPLE 3

A heavy residua hydrocarbon feedstock containing materials boiling above 650°F. was introduced into a

bubble-type, graphite-lined stirred reactor containing a molten medium in the same manner as described in Example 1. The molten medium comprised 70 % lithium carbonate and 30 mole % sodium carbonate to which 6 wt. % boron oxide, i.e. B_2O_3 had been added. The hydrocarbon feedstock was introduced along with a helium diluent (1 STP liter/minute) and cracked in this molten medium at a temperature of 1350°–1400°F. for approximately 2½ hours during which time the carbonaceous material, i.e. coke, formed during the cracking reaction was uniformly dispersed at all times throughout the medium. At the conclusion of the 2½ hour run the molten medium contained about 3 wt. % coke.

EXAMPLE 4

A heavy residua hydrocarbon feedstock was introduced into a bubble-type, stainless steel stirred reactor containing a molten medium in the same manner as described in Example 3. The molten medium comprised 70 mole % lithium carbonate and 30 mole % sodium carbonate. The hydrocarbon feedstock was introduced along with a helium diluent (1 STP liter/minute) into this molten medium and cracked at a temperature of 1350°–1400°F. for approximately 40 minutes. The carbonaceous materials, i.e. coke, formed during this cracking reaction were not uniformly dispersed throughout the molten medium such that the molten medium formed two layers, one of which was coked and one of which was relatively clear. At the conclusion of the 40-minute cracking run, the molten medium contained about 0.5 wt. % coke.

Upon carrying out the above-described cracking reaction for an extended period of time, namely for 2 hours, the carbonaceous materials became dispersed into a single homogeneous phase. At the conclusion of this 2 hour run, the molten medium contained about 2.0 wt. % coke.

EXAMPLE 5

This example indicates the increase in the desulfurization rate as measured by the steam conversion when a molten alkalimetal carbonate medium containing a minor amount of boron oxide is contacted with steam and CO_2 at a given temperature. The condition under which these runs were conducted is shown in Table III below.

TABLE III

Melt: 70 mole % Li_2CO_3 /30 mole % Na_2CO_3 Sulfur Conc. in melt: 4.8 wt. % as sulfides CO_2/H_2O feed ratio: 37/63 mole %		
	B_2O_3 Conc. wt. %	
	1200°F.	1500°F.
X	22	24
Δ	12	12
□	0	0

As can be seen from the results as shown in FIG. 2, at a given temperature, the presence of boron oxide in the molten medium increases the desulfurization rate when the molten medium containing sulfides is contacted with steam and carbon dioxide.

EXAMPLE 6

This example indicates that a molten medium containing an alkali metal carbonate in combination with an oxide of boron is significantly less corrosive to mate-

rials of containment than is a molten medium consisting of an oxide of boron in combination with an alkali oxide. The data shown below was obtained by partially submerging a sample of the refractory into the molten medium under the conditions specified in Table IV.

TABLE IV

Refractory	Melt Composition	Corrosion Test Results				Corrosion, Inches per Year Melt/Interface/Vapor
		Additive	Atmosphere	Temperature	Hours	
95% Cr ₂ O ₃	Na ₂ O—Li ₂ O—B ₂ O ₃	0.2 Cl ⁻	Air	1550°F.	50	4.2/28.8/4.7
Al ₂ O ₃	89 wt. % Li/Na ₂ CO ₃ (70/30 mole %) 11 wt. % B ₂ O ₃	—	Air	1550°F.	48	0.1/0.2/0.1
Al ₂ O ₃	83 wt. % Li/NaCO ₃ (70/30 mole %) 17 wt. % B ₂ O ₃	—	Air	1550°F.	48	.8/1.2/0.7-13.5
Al ₂ O ₃	80 wt. % Li/Na ₂ CO ₃ (70/30 mole %) 20 wt. % B ₂ O ₃	—	Air	1550°F.	49	1.2/1.2/1.2-13

As can be seen from the results as shown in Table IV, the degree of corrosion of the refractory materials is directly related to the amount of boron oxide which has been added to the molten medium.

What is claimed is:

1. A process for cracking a hydrocarbon feedstock which comprises contacting said feedstock with a regenerable alkali metal carbonate molten medium containing from about 0.1 to about 25 wt.%, calculated as oxide and based on total molten medium, of a glass-forming oxide selected from the group consisting of oxides of boron, vanadium, silicon, phosphorus and mixtures thereof at a temperature in the range of from 1200°F. to about 2500°F. to form cracked hydrocarbon products and to uniformly suspend the carbonaceous materials formed during said cracking operation throughout the molten medium and thereafter gasifying a portion of said carbonaceous materials formed during said cracking process by contacting said molten medium containing the carbonaceous materials 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 above the melting point of said medium to about 3000°F.

2. The process of claim 1 wherein the temperature of the molten medium is maintained in the range of from about 1200° to about 2000°F.

3. The process of claim 2 wherein the amount of glass-forming oxide expressed as the oxide thereof in the molten medium is in the range of from about 1 to about 20 wt. % of the total molten media.

4. The process of claim 3 wherein the alkali metal carbonate is selected from the group consisting of lithium carbonate, sodium carbonate and mixtures thereof.

5. The process of claim 4 wherein the alkali metal carbonate is a mixture of a major amount of sodium carbonate and a minor amount of lithium carbonate.

6. The process of claim 3 wherein the glass-forming oxide is an oxide of boron.

7. The process of claim 6 wherein said gasifying reagent is oxygen.

8. The process of claim 7 wherein the molten medium contains an alkali metal borate.

9. The process of claim 8 wherein the hydrocarbon feedstock is a heavy hydrocarbon feedstock containing sulfur.

10. The process of claim 9 wherein the amount of sulfur present in the molten medium is reduced by:

- a. contacting the sulfur compounds in the molten medium with a reducing agent; and
- b. thereafter contacting the reduced sulfur compounds formed in step (a) with carbon dioxide and steam to form hydrogen sulfide as a recoverable product.

11. The process of claim 10 wherein said reducing agent is carbon.

12. The process of claim 11 wherein at least a portion of said heavy hydrocarbon feedstock boils above about 650°F. at atmospheric pressure.

13. The process of claim 12 wherein said molten medium contains an oxide of boron in an amount expressed as the oxide thereof in the range of from about 1 to about 12 wt.% of the total molten media.

14. The process of claim 13 wherein the heavy hydrocarbon feedstock contains from about 2 to about 6 wt.% sulfur.

15. A process for cracking a heavy hydrocarbon feedstock comprising a component selected from the group consisting of crude oils and residua containing from about 2 to about 6 wt.% sulfur which comprises contacting said heavy hydrocarbon feedstock with a regenerable alkali metal carbonate molten medium comprising a mixture of lithium and sodium carbonates containing from about 1 to about 12 wt.%, calculated as oxide and based on the total molten medium, of an oxide of boron at a temperature in the range of from about 1300°F. to about 1700°F. to form cracked hydrocarbon products and to uniformly suspend the carbonaceous materials formed during said cracking operation throughout the molten medium and thereafter gasifying a portion of said carbonaceous materials formed during said cracking process by contacting said molten medium containing the carbonaceous materials with oxygen at a temperature in the range of from about 1400° to about 1800°F.; the amount of sulfur present in the molten medium being reduced by: (a) contacting the sulfur compounds in the molten medium with a reducing agent; and (b) thereafter contacting the reduced sulfur compounds formed in step (a) with carbon dioxide and water.

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