

- [54] MELT CRACKING FOR LUBRICATING OILS
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- [51] Int. Cl. C10g 13/04
- [58] Field of Search 208/109, 112, 125, 107; 252/416

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[57] **ABSTRACT**

Heavy hydrocarbon feed stocks such as atmospheric and vacuum residua, heavy crude oils and the like are converted to lubricating oil products by contacting said feed stocks in a reaction zone with a stable, regenerable molten medium containing a glass-forming oxide such as boron oxide at a temperature in the range of from about 600° to about 1200°F. and hydrogen. In one embodiment of the invention, the hydrogen and melt are both present in the same reaction zone. In another embodiment of the invention, the cracking operation is conducted in the substantial absence of hydrogen and the cracked effluent, thereafter, separately contacted with hydrogen in the presence of a hydrogenation catalyst. The latter embodiment is particularly preferred where the starting feed has a high sulfur, nitrogen and metals content. Preferably, the stable, regenerable molten medium comprises a glass-forming oxide in combination with an alkaline reagent. The carbonaceous materials such as coke which are formed in the molten medium during the above-described conversion process are gasified by contacting the carbonaceous materials with a gaseous stream containing oxygen such as air, steam, or carbon dioxide at temperatures of from above about the melting point of said medium to about 2000°F. thereby regenerating the molten medium.

18 Claims, 2 Drawing Figures

FIGURE 1

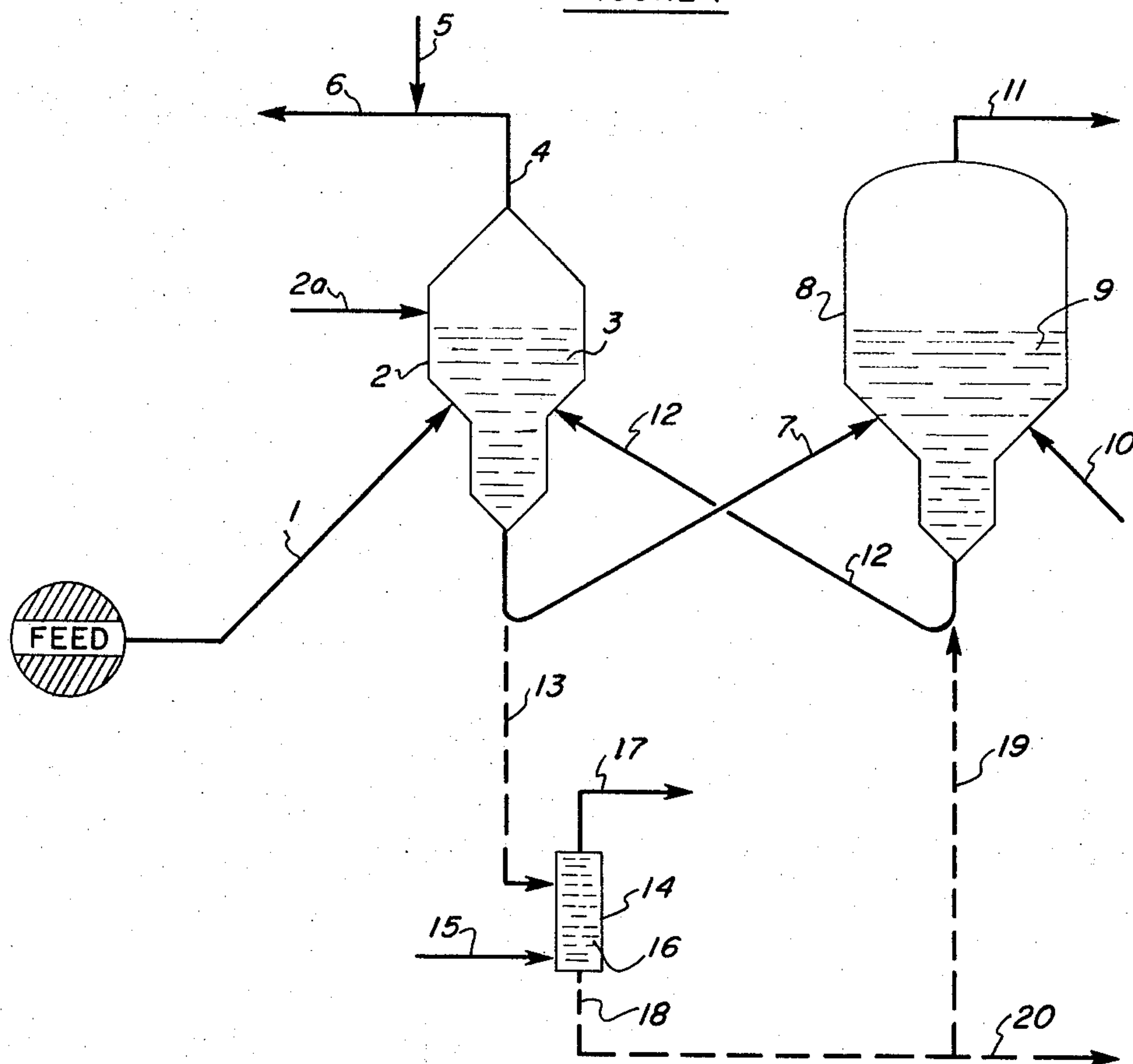
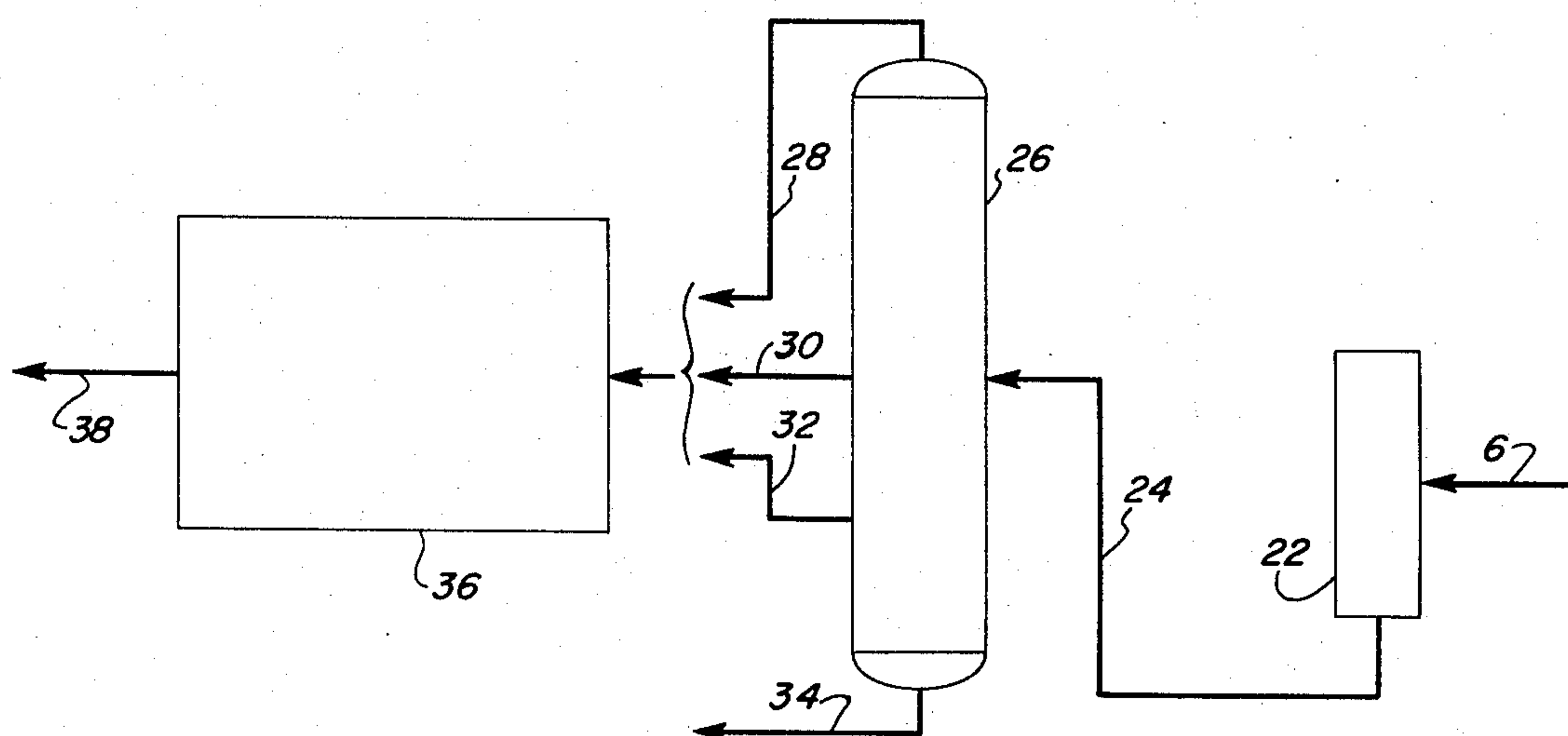


FIGURE 2



MELT CRACKING FOR LUBRICATING OILS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the conversion of a heavy hydrocarbon feedstock to produce lubricating oil stocks. More particularly, this invention relates to converting a heavy hydrocarbon feedstock to liquid hydrocarbon products containing substantial amounts of lubricating oil components by contacting the feedstock with a molten medium. Still more particularly, this invention relates to the conversion of a heavy hydrocarbon feedstock such as atmospheric and vacuum residua, crude oils and the like, in a stable, regenerable molten medium containing a glass-forming oxide such as boron oxide, to product predominantly liquid hydrocarbon products, containing substantial amounts of lubricating oil components. Carbonaceous materials, such as coke, which form during the conversion and become suspended in the molten medium, are gasified by contacting the carbonaceous materials with a gasifying reagent such as air, at elevated temperatures in order to regenerate the melt.

2. Description of the Prior Art

In the past attempts have been made to prepare lube oil base stocks from heavy hydrocarbon materials such as atmospheric or vacuum residua and the like. Typical of such attempts is that involving hydrocracking the heavy hydrocarbon material at elevated temperature and pressure in the presence of a catalyst such as an amorphous base catalyst containing a metallic hydrogenation component and a cracking component. The process results in the conversion of high molecular weight hydrocarbons to lower molecular materials containing lube oil components and in the saturation of low VI olefinic materials to the more desirable higher VI paraffinic compounds. Subsequent treatment of the hydrocrackate such as by hydrotreating, solvent extraction and/or dewaxing yields a lube oil product. The prior art hydrocracking processes, as directed to the preparations of lube oils from heavy feedstocks, have suffered from several difficulties including the tendency of the heavy feeds, particularly residua, to deposit coke and metals on the catalyst, eventually deactivating same. Other catalytic processes such as hydrodesulfurization have also encountered similar difficulties when applied to heavy feedstocks. In view of the above-mentioned difficulties, it would be desirable to develop alternative processes which would yield high quality lube oil base stock while minimizing problems relating to coke and metals deposition.

SUMMARY OF THE INVENTION

In accordance with the invention, it has now been discovered that lubricating oils may be prepared from heavy hydrocarbon feedstocks by contacting same with a molten medium as hereinafter defined, and hydrogen at elevated temperatures. The contacting results in the substantial conversion, i.e., cracking of higher molecular weight compounds contained in the feedstock, to lower molecular weight materials boiling predominantly in the lube oil range, e.g. between about 650° and 1100°F. (at atmospheric pressure). The 650°-980°F. fraction may be upgraded by further processing operation such as hydrotreating, solvent extraction, dewaxing and the like, one result of such opera-

tions being a substantial improvement in color intensity, and reductions in CCR and metals content. However, the 980°F.+ fraction contains extremely high boiling asphaltic components which substantially inhibit upgrading from operations similar to those discussed above, e.g., hydrotreating and solvent extraction. This problem can be effectively overcome by vacuum distilling the 980°F.+ fraction to ca. 50 percent overhead (1100°F-) and rejecting the bottoms as asphalt. The yield of 980°-1100°F material may be maximized by recycling the 980°F.+ fraction to the melt cracking operation and vacuum distillation the resultant product therefrom. The thus-treated 980°-1100°F. material can then be effectively subjected to further processing, as indicated, supra, if desired. It is known that the hydrogen serves, at least in part, to saturate at least a portion of the olefinic materials formed during the conversion, to yield paraffinic materials, thereby resulting in an increased yield of lube oil products and, further, in an increase in the overall viscosity index of same. Carbonaceous materials formed during the process are suspended in the molten medium and are substantially removed therefrom by contacting same with a gasifying reagent, at elevated temperature thereby regenerating the molten medium.

In some instances it may be desirable to increase the efficiency and selectivity of the hydrogenation reaction, such as by conducting same in the presence of a hydrogenation (hydrotreating) catalyst as hereinafter defined. In this embodiment of the invention, it is preferred to carry out the hydrogenation reaction (hydrotreating reaction) in a separate zone from that wherein the conversion reaction takes place. This is necessary in view of the high temperatures used in the conversion operation, which temperatures could lead to the deactivation of the hydrogenation catalyst. Thus, the hydrogenation and conversion operations could be conducted in separate reactors, or alternatively, in one reactor which is divided into a plurality of separate reaction zones.

In the process of this invention a wide variety of feedstocks may be converted to produce predominantly liquid hydrocarbon products. Generally, the hydrocarbon feedstocks of the instant invention are heavy hydrocarbon feedstocks such as crude oils, heavy residua, atmospheric and vacuum residua, crude bottoms, pitch, asphalt, other heavy hydrocarbon pitchforming residua, coal, coal tar or distillate, natural tars including mixture thereof. Preferably, a major portion of the heavy hydrocarbon feedstocks boils above about 650°F. at atmospheric pressure. Most preferably, the hydrocarbon feedstocks that can be employed in the practice of the instant invention are paraffinic or naphthenic crude oils, vacuum residua containing materials boiling above about 650°F. atmospheric pressure and the like.

Examples of suitable crude sources include Arabian Light or Heavy crudes, Kuwait, Gach Saran, Venezuelan and Western Canadian crudes such as Cold Lake and Athabasca bitumen, Bachaquero and the like. Vacuum resids from Aramco, Safaniya and Bachaquero crudes are preferred feedstocks. In general, metals content can be as high as several hundred ppm (wt. basis) and there is no real limit as to sulfur or metals content for melt processing. High contents simply mean more frequent melt regeneration.

The regenerable molten medium of the instant invention comprises a glass-forming oxide (or oxide precursor)

sor), by which is meant an oxide of silicon, germanium, boron, phosphorus, arsenic, antimony, tellurium, selenium, molybdenum, tungsten, bismuth, aluminum, gallium, vanadium, titanium, and mixtures thereof. Preferably, the glass-forming oxides are selected from the group consisting of oxides of boron, phosphorus, vanadium, silicon, tungsten, and molybdenum. An oxide of boron is the most preferred glass-forming material.

The glass-forming oxides are employed in combination with an alkaline reagent, by which term is meant (a) alkali metal (Group IA) oxides, alkali metal hydroxides and mixtures thereof, and (b) alkali metal oxides, alkali metal hydroxides and mixtures thereof in combination with alkaline earth metal (Group IIA) oxides, hydroxides and mixtures thereof. When mixtures of alkali metal compounds and alkaline earth metal compounds are employed, the mixture typically contains a minor proportion of the alkaline earth materials. Alkaline earth oxides and hydroxides have relatively high melting points and are of limited utility in this process when the reaction temperature does not exceed about 1200°F. The preferred alkali metals are sodium, lithium, potassium, cesium and mixtures thereof. The preferred alkaline earth metal materials are magnesium, calcium, strontium, and barium. The most preferred alkaline reagent comprises one or more alkali metal hydroxides or one or more alkali metal oxides in combination with major or minor amounts of one or more alkali metal oxides. Desirably, the molar ratio of alkaline reagent (calculated on the basis of the oxide thereof) to glass forming oxide present in the melt varies in the range of from about 0.01 to about 5, more preferably from about 1.5 to about 3, and most preferably from about 2.2 to about 2.7.

When a gaseous stream containing elemental oxygen, for example air, is employed in order to gasify the carbonaceous materials present in the molten medium of the instant invention, the preferred mole ratio of the alkaline reagent (calculated on the basis of the oxide thereof) to glass-forming oxide in the gasification zone is in the range of from about 0.5 to about 2.5. However, when steam is employed to gasify the carbonaceous materials, the preferred mole ratio of the alkaline reagent (calculated on the basis of the oxide thereof) to glass-forming oxide in the gasification zone is in the range from about 0.5 to about 2.0. When the mole ratio of alkaline reagent (calculated on the basis of the oxide thereof) to glass-forming oxide is within the above-described preferred ranges, there occurs a significant increase in the gasification rate of the carbonaceous materials suspended in the molten medium of the instant invention; however, the gasification process is operable if the alkaline reagent glass forming oxide ratio falls outside the preferred ranges.

The advantage of converting a heavy hydrocarbon feedstock to lube oil basestocks in the above-mentioned molten medium, in addition to providing the heat transfer medium for the conversion reactions, lies in the ability of the medium to: (a) suspend the carbonaceous materials formed in situ during the conversion operation uniformly throughout the melt, (b) abstract sulfur from the hydrocarbon materials being treated, and (c) thereafter, upon contact with a gasifying reagent at elevated temperatures to promote the rapid gasification of said carbonaceous materials. Accordingly, the instant invention is suitable for feeds containing larger amounts of catalyst-inhibiting impurities than

would be tolerable in other processes such as hydrocracking. The molten medium of the instant invention allows one to conduct conversion processes at high temperatures, thereby obtaining high conversions to lube oil materials in view of the fact that the carbonaceous materials formed during the conversion process may be gasified by contacting same with a gasifying reagent, as hereinafter defined.

In addition to promoting the gasification rate of the carbonaceous materials formed during the conversion process, the molten medium of the instant invention offers the additional advantages of significantly lowering the emission of pollutants into the atmosphere by absorbing or reacting with at least a portion of the sulfur and/or sulfur compounds produced during the actual cracking operation and/or during the combustion of carbonaceous material during the gasification phase of the process. The hydrocarbon products of the conversion process of the instant invention desirably contain a significantly reduced amount of heavy metals compared to that originally contained in the heavy hydrocarbon feed. For example, reduction of heavy metals content by melt cracking may be by as much as 90 percent, at only, say, 50 percent feed conversion. The metals distribute themselves between the coke and the melt. Furthermore, the molten medium of the instant invention possesses good thermal conductivity to allow efficient heat transfer and thermal stability to decomposition to volatile products under the conversion or gasification conditions. Thus, it is evident that these advantageous properties exhibited by the stable, regenerable molten medium of the instant invention offer significant advantages in the cracking of heavy hydrocarbon feedstocks.

The melts may contain other components such as ash constituents, metallic and nonmetallic oxides, sulfides, sulfites, sulfates and various other salts in varying amounts so long as the medium is molten at the hydrocarbon conversion conditions of the instant invention, i.e., a temperature less than about 1200°F., and preferably from about 600° to less than about 1200°F., and more preferably from about 800° to about 1100°F and provided that a sufficient amount of glass-forming oxide is employed to maintain the molten medium in a regenerable condition. One skilled in the art will readily determine the applicable components as well as the stoichiometry of the glass-forming oxides to said components which will be required in order to form the regenerable molten medium as described above. Further, various filler materials, catalysts or promoters may be added to the melt.

Typical examples of stable molten media containing alkali metal oxides in combination with glass-forming oxides that may be employed in the practice of the instant invention are shown in Table I below. The same melts could be formed from the corresponding hydroxides.

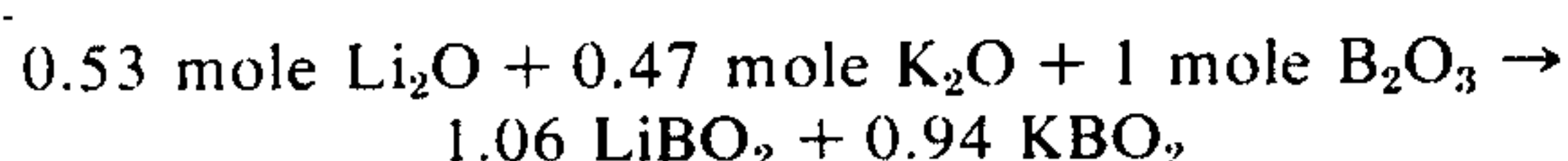
TABLE I

	Molten Glass Mixture	Composition, Mole Ratio	Approximate Melting Point, °F.
(a)	Li ₂ O·K ₂ O·B ₂ O ₃	0.5/0.5/1	1070
(b)	Li ₂ O·Cs ₂ O·B ₂ O ₃	0.3/0.7/1	1076
(c)	K ₂ O·V ₂ O ₅	0.6/1	734
(d)	Li ₂ O·Na ₂ O·WO ₃	1.1/1/2.1	917
(e)	K ₂ O·Li ₂ O·MoO ₃	0.4/1/1.4	955
(f)	Na ₂ O·SiO ₂ ·B ₂ O ₃	0.8/0.8/1	968

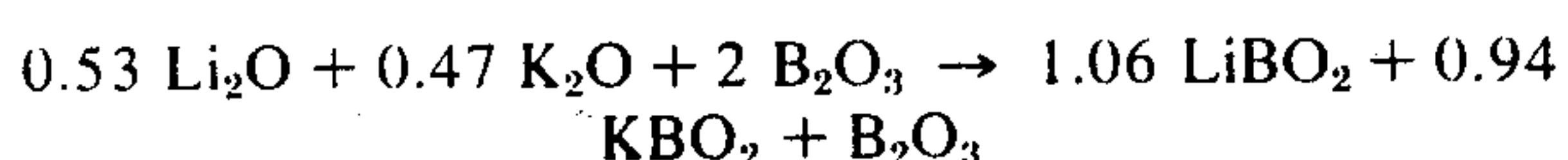
TABLE I-Continued

Molten Glass Mixture	Composition, Mole Ratio	Approximate Melting Point, °F.
(g) $\text{Li}_2\text{O} \cdot \text{K}_2\text{O} \cdot \text{B}_2\text{O}_3$	1.3/0.7/1	1000
(h) $\text{Li}_2\text{O} \cdot \text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$	1.5/0.5/1	940
(i) $\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$	1.2/1	1026
(j) $\text{Li}_2\text{O} \cdot \text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$	0.5/0.5/1	888
(k) $\text{Li}_2\text{O} \cdot \text{K}_2\text{O} \cdot \text{P}_2\text{O}_5$	0.5/0.5/1	874
(l) $\text{Li}_2\text{O} \cdot \text{K}_2\text{O} \cdot \text{SO}_3 \cdot \text{P}_2\text{O}_5$	1.4/0.5/1/1	860
(m) $\text{Li}_2\text{O} \cdot \text{Na}_2\text{O} \cdot \text{K}_2\text{O} \cdot \text{B}_2\text{O}_3$	1.1/0.8/0.6/1	850

It is to be understood that although the molten medium of the instant invention is described throughout the specification in terms of the alkaline reagent 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, i.e., the salt formed when a glass-forming oxide is heated to the molten state in combination with the alkaline reagent. For example, a molten medium consisting of lithium oxide and potassium oxide as the alkaline reagent and boron oxide as the glass-forming oxide in the following mole ratios, 0.53 Li_2O , 0.47 K_2O , 1.0 B_2O_3 , can also be expressed in the molten state as a borate, specifically a lithium potassium metaborate on the basis of the following reaction:



Hence, when a molar excess of the glass-forming oxide (B_2O_3) is employed, the melt may comprise a glass-forming oxide in combination with an alkali metal borate in accordance with the following reaction:



Accordingly, it is clearly within the purview of the instant invention to employ as the stable molten medium of this invention a glass-forming oxide, as defined above, in combination with an alkaline reagent or an alkaline reagent salts of the glass-forming oxide employed. It is to be noted 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 either alone or in combination with an alkaline reagent.

Individual regenerable stable molten systems that are most preferred are those obtained when boron oxide or phosphorus pentoxide is employed as the glass-forming oxide. The most preferred melt system of the instant invention comprises boron oxide in combination with a hydroxide of lithium, potassium, sodium and mixtures thereof as the alkaline reagent. The hydroxide may be used in combination with other alkali metal oxide. The most preferred alkaline reagent is a major amount of a mixture of lithium, potassium and sodium hydroxides and a minor amount of alkali metal oxides, e.g., melt(m) in Table I supra (about 90 percent hydroxide form, about 10 percent oxide form).

While not essential to the reaction, an inert diluent can be employed in order to regulate the hydrocarbon partial pressure in the molten media conversion zone. The inert diluent should normally be employed in a molar ratio from about 1 to about 50 moles of diluent per mole of hydrocarbon feedstock, and more preferably from about 1 to about 10 moles of diluent per mole

of hydrocarbon feed. Illustrative, nonlimiting examples of the diluents that may be employed in the practice of the instant invention include helium, carbon dioxide, nitrogen, steam, methane, and the like.

5 The cracking operation may be conducted as a fixed bed process, i.e., where the feedstock vapors pass through a stationary bed containing the molten medium or, alternatively, the molten medium may be sprayed into a reactor or trickled down the reactor wall 10 where the hydrocarbon feedstock passes through the reactor. The molten medium can flow either cocurrently or countercurrently to the hydrocarbon flow. The temperature of the molten medium is maintained in the range of from above the melting point of said medium to less than about 1200°F., and more preferably 15 from about 800° to about 1100°F. in order to form predominantly liquid hydrocarbon products and carbonaceous materials.

Depending upon the temperature and the specific 20 type of hydrocarbon feedstock, the weight ratio of molten media to hydrocarbon in the reaction zone varies in the range of from 0.1 to 1 to about 100 to 1 and preferably from 5 to 1 to 20 to 1. The reaction may be conducted at pressures ranging from subatmospheric to 25 about 50 atmospheres, preferably from about 1 to about 10 atmospheres. The reaction time is expressed in the amount of time the feedstock is in contact with the melt, i.e., residence time, and is desirably in the range of from about 0.001 to about 6 hours, and more 30 preferably from about 0.1 to about 3 hours. It is noted that since the desired products are flashed overhead from the reaction zone, residence time will vary depending on the boiling range of each component so removed.

35 In one embodiment of the invention, the hydrogenation (hydrotreating) and cracking reactions can be conducted in the same reaction zone, in the absence of a hydrogenation catalyst. Hydrogen partial pressures in the reaction zone will range between about 100 and 40 5,000 psig, preferably between 200 and 1500 psig. The space velocity will range between about 0.1 and 5, preferably 0.3 and 2 (w/w/hr). In a second embodiment of the invention, the hydrogenation (hydrotreating) reaction can be conducted in the presence of a hydrogenation 45 (hydrotreating) catalyst but in a zone separate from the conversion zone. The type of catalyst employed will be dependent, in part, on the characteristics of the product from the melt cracking operation. Thus, for example, a high sulfur product will require a sulfur-insensitive catalyst which has good desulfurization activity. The hydrogenation catalyst can be any conventional hydrogenation catalyst used in the art such as, 50 for example, a mixture comprising a major amount of an amorphous component and a minor amount of a hydrogenation component preferably comprising one or more transitional metals selected from Groups VIB and/or VII of the Periodic Table and the oxides and sulfides thereof.

60 Representative of these metals are molybdenum, chromium, tungsten, nickel, cobalt, palladium, iron, rhodium, and the like, as well as combinations of these metals and/or their oxides and/or sulfides. Preferred metals are nickel, cobalt, molybdenum and mixtures thereof. One or more of the metals, metal oxides or sulfides, alone or in combination, may be added to the support in minor proportions ranging from 1 to 25 wt. 65 percent based on the total catalyst.

The amorphous component, i.e., support, can be one or more of a large number of non-crystalline materials having high porosity. The porous material is preferably inorganic but can be organic in nature if desired. Representative porous materials that can be employed include metals and metal alloys; sintered glass; firebrick, diatomaceous earth, inorganic refractory oxides; organic resins, such as polyesters, phenolics and the like; metal phosphates such as boron phosphate, calcium phosphate and zirconium phosphate; metal sulfides such as iron sulfide and nickel sulfide; inorganic oxide gels and the like. Preferred inorganic oxide support materials include one or more oxides of metals selected from Groups IIA, IIIA and IV of the Periodic Table. Non-limiting examples of such oxides include aluminum oxide, titania, zirconia, magnesium oxide, silicon oxide, titanium oxide, silica-stabilized alumina and the like.

Preferably, the starting catalyst composition comprises a silica/alumina support containing molybdenum trioxide and nickel oxide hydrogenation components. The silica-alumina weight ratio in the amorphous support can range from 20:1 to 1:20 and preferably from 1:4 to 1:6. The molybdenum trioxide: nickel oxide weight ratio in the amorphous support can range from about 1:25 to 25:1 and preferably from 2:1 to 4:1. Finally, the weight ratio of the support to the hydrogenation component can range from about 20:1 to 1:20 and preferably from 4:1 to 6:1. A particularly preferred starting catalyst composition comprises:

NiO	4.5 wt. %
MoO ₃	13.0 wt. %
SiO ₂	14.0 wt. %
Al ₂ O ₃	68.4 wt. %

The catalyst is preferably pre-sulfided by conventional methods such as by treatment with hydrogen sulfide or carbon disulfide prior to use. The precise chemical identity of the hydrogenation constituents present on the support during the course of the hydrocracking operation is not known. However, the hydrogenation components probably exist in a mixed elemental metal/metal oxide/metal sulfide form.

The catalysts may be prepared by any of the general methods described in the art such as by cogelation of all the components, by impregnation of the support with salts of the desired hydrogenating components, by deposition, by mechanical admixture and the like.

Temperatures in the separate hydrotreating (hydrogenation) zone will range from about 400°–900°F., preferably from about 500°–800°F. Pressures will range from about 100 to 5,000 psig, preferably from about 500 to 2500 psig and flow rate will vary from about 0.1 to 5, preferably 0.3 to 2.0 V/V/Hr. The total hydrogen supply rate (makeup and recycle hydrogen) is 200–20,000 s.c.f. of hydrogen per barrel of feedstock, preferably 500 to 5,000 s.c.f.

The separate hydrotreating operation serves not only to saturate olefinic materials, but also aids in removing sulfur, nitrogen and metal compounds from the feed, thereby resulting in overall color improvement. The hydrotreating operation results in substantially no conversion of hydrocarbons to lower molecular weight materials. Thus, the overall yield of product from the hydrotreater is greater than about 99 LV%. As indicated previously, heavier melt crackate fractions (e.g., 980°F+ fraction) must be pretreated such as by recycling to the

melt cracking operation and subsequent vacuum distillation of the effluent product prior to hydrotreating (at more severe conditions than with regard to the 650°–980°F fraction) in order to achieve results parallel to those obtained with the lighter fraction.

By use of the above-described process, it is possible to obtain a lube oil product characterized by having a bromine number of less than about one in addition to having relatively low metals, sulfur and nitrogen content. A low bromine number indicates low concentrations of olefins in the product and is desirable in lube oil materials having good thermal/oxidative stability and good color characteristics.

It is to be noted that even where the hydrogenation and cracking reactions are conducted in the same reaction zone, i.e., the first embodiment, supra, it may be desirable, in some instances, such as, for example, where the process feedstock contains a large amount of nitrogen and sulfur-containing constituents to still use a subsequent hydrotreating operation to lower the sulfur and nitrogen content of the effluent.

In general, the amount of lube oil product (boiling between about 600°F. and 1100°F+ (at atmospheric pressure)) formed by the process of this invention is normally in the range of from about 10 to about 40 wt. percent of the total feedstock to the melt cracking reaction zone.

Further upgrading operations such as solvent-extracting or dewaxing may be used subsequent to the cracking (and optional hydrotreating) operation to improve the lube oil quality, if so desired. These processes are well known in the art and will, therefore, not be further described. See, for example, U.S. Pat. Nos. 1,860,823 and 2,052,196 in connection with phenol treating, U.S. Pat. No. 1,962,103 in connection with furfural treating and U.S. Pat. No. 3,105,809 in connection with solvent dewaxing, the disclosures of which are incorporated herein by reference.

A significant advantage of the instant invention is that the carbonaceous materials (coke) which are formed during the conversion process become suspended in the molten medium and can subsequently be gasified by contacting the melt with a gasifying reagent such as gaseous stream containing free or combined oxygen, i.e., air, steam, carbon dioxide, and mixtures thereof, at elevated temperatures in order to rapidly regenerate the stable molten medium. The carbonaceous materials that 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 normally formed during high temperature pyrolysis or organic compounds.

The term gasification as used herein describes the contacting of the carbonaceous materials in the molten media with a reagent containing elemental or chemically combined oxygen such as air, steam, carbon dioxide, and mixtures thereof. The gasification reaction is carried out at temperatures in the range of from above about the melting point of the molten media up to about 2000°F. or higher and at a pressure in the range of from subatmospheric to about 100 atmospheres. More preferably, the temperature at which the gasification reaction is carried out is in the range of from about 1000° to about 1800°F. and at a pressure in the range of from about 1 to about 10 atmospheres.

Normally, the amount of oxygen which must be present in the gaseous stream containing free or combined

oxygen in order to effectuate the gasification of the carbonaceous materials is in the range of from about 1 to about 100 weight percent oxygen, and more preferably from about 10 to about 25 weight percent oxygen. Normally, the gaseous stream containing oxygen is passed through the melt at a rate of from less than about 0.01 w./w./hr. to about 100 w./w./hr. More preferably, the rate at which the gaseous stream is passed through a melt system of the instant invention is in the range of from about 0.01 w./w./hr. to about 10 w./w./hr. Preferably air is employed as the gaseous stream containing oxygen in order to effect a rapid regeneration of the molten medium.

Steam or carbon dioxide, either alone or in admixture with oxygen may also be employed to gasify the carbonaceous materials present in the molten medium of the instant invention. However, as is appreciated in the art, the different gasification reagents mentioned above will each gasify the carbonaceous material at different rates. Generally, the presence of free elemental oxygen in the melt will result in higher gasification rates than with other reagents such as steam or CO₂. Thus, when steam or CO₂ is employed as the gasification reagent, more severe conditions, e.g., higher temperatures and longer residence time, will be required in order to achieve gasification rates equivalent to or higher than when, for example, air or oxygen is employed as the gasification reagent.

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 temperature of the melt, concentrations 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 about 0.1 to about 60 weight percent, and preferably from about 1.0 to about 20 weight percent, in order to effect a rapid gasification thereof. Accordingly, it can be seen that it is advantageous to carry out the gasification reaction process at temperatures above about 1000°F., and more preferably in the range of from 1000° to 1800°F., and at an oxygen gas feed rate of 0.01 to 10 w./w./hr. in the presence of from about 1.0 to about 10 weight % carbonaceous materials in order to effectuate a rapid gasification of the carbonaceous materials present in the melt. Such a rapid gasification will necessarily result in a rapid regeneration of the melt.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow diagram showing a preferred embodiment of the invention.

FIG. 2 is a flow diagram showing the incorporation of a hydrotreating step subsequent to the cracking operation.

Turning to FIG. 1 in detail, a heavy hydrocarbon residuum fraction, preferably having an initial boiling point (at atmospheric pressure) above about 650°F., is introduced to cracking zone 2 via feed line 1. Within the cracking zone is maintained a molten bed 3 con-

taining an oxide of boron and an alkaline reagent comprising a major amount of a mixture of sodium, potassium and lithium hydroxides in combination with a minor amount of sodium, potassium and lithium oxides.

The hydrocarbon feedstock may be passed upwardly through melt 3 by introducing the feedstock at a point below the upper level of the molten medium. The temperature of the molten medium 3 is maintained below about 1200°F. Hydrogen is introduced into zone 2 via line 2a. A total hydrogen pressure ranging between about 200 and 1500 psig is in the zone.

After the hydrocarbon feedstock has been at least partially reduced to lighter products through contact with the hot molten medium 3, the resulting cracked products pass overhead from cracking zone 2 via line 4. The cracked products may be cooled by indirect heat exchange or through contact with a quench medium introduced via line 5. If desired, the cracked products may be passed directly to a fractionation facility via line 6, and the lube oil components recovered and if desired further treated such as by hydrotreating, solvent extraction, dewaxing and the like.

In the cracking operation a portion of the hydrocarbon feedstock is converted to coke materials. The instant melt compositions suspend the coke by-product within the melt. The coke materials are removed from the melt by a gasification step involving contacting the coke containing melt with an oxidizing gas. In the process of the present invention, the molten medium that contains suspended carbonaceous material is withdrawn from cracking zone 2 by way of line 7 and introduced to gasification zone 8. Preferably, a vapor lift is used to circulate the melt between the cracking zone and the gasification zone. Within gasification zone 8, the coke-containing molten medium 9 is contacted with a reagent introduced into the gasification zone 8 via line 10. Preferably the reagent is elemental oxygen (or a gas stream containing elemental oxygen), steam or carbon dioxide. During contact with the gasifying reagent, the temperature within the gasification zone may be brought to about 2,000°F.

During gasification, the coke or carbonaceous material contained in the melt is combusted and the gasification products carried overhead via line 11. The chemical composition of the overhead gaseous effluent is dependent on the type of gasifying reagent employed. When oxygen or an oxygen-containing gas is employed, only a minor proportion of the total gaseous effluent is made up of sulfur-bearing materials. When the ratio of alkaline reagent, calculated on the basis of the oxides thereof, to glass-forming oxide exceeds certain minimum levels, the resulting oxygen gasification products are predominantly sulfur free (containing below about 500 vppm, generally below 200 vppm sulfur constituents). This result is believed to be achieved because the sulfur oxides formed during gasification react with a portion of the alkaline reagent constituents of the melt to form metal sulfites or sulfates. Upon recycle of the gasified melt to the cracking zone via line 12, the inorganic sulfur-bearing materials are believed to be reduced to the corresponding sulfides due to the renewed presence of carbonaceous material in the melt. When steam is used as the gasifying reagent, the sulfur impurities contained in the melt within the gasification zone 8 are not converted to sulfur oxides and are not absorbed or reacted with the melt constituents but,

rather, are converted to hydrogen sulfide which passes overhead via line 11.

During continued use the initial charge of melt material will become contaminated with larger and larger amounts of sulfur and ash-forming impurities. Accordingly, to maintain the melt in the desired active condition, a portion of the contaminated melt must be withdrawn from the system and replaced with fresh melt or, alternatively, reconditioned and returned to the system. One technique for reconditioning the contaminated melt is depicted in the figure. Specifically, a minor quantity of contaminated melt material is withdrawn from line 7 and passed to a sulfur recovery zone 14 wherein it is contacted with carbon dioxide and steam that are introduced via line 15. Typically the melt 16 contained within zone 14 is treated with the carbon dioxide/steam reagents at temperatures in the range of from about 800° to 1800°F. Provided that the bulk of the sulfur contaminants present in the melt are in the form of sulfides, contacting with the steam/carbon dioxide mixture will convert the sulfide ion to hydrogen sulfide which is removed from the treating zone via line 17. If the bulk of the sulfur sent to zone 14 is not in a metal sulfide form, it is necessary, for maximum sulfur removal, to reduce the sulfur present in the melt to a sulfide form in a reducing zone located prior to zone 14.

After treatment in zone 14, the molten medium having reduced sulfur content is withdrawn via line 18 and returned to the system via line 19. A portion of the treated effluent in line 19 may be withdrawn from the system via line 20 for treatment for the removal of ash constituents. The resulting sulfur-free, ash-free melt may be returned to the system.

In addition to the melts becoming contaminated with sulfur materials and ash constituents, a portion of the alkaline reagent constituents of the melt may be converted to the corresponding carbonates through reaction with carbon dioxide generated during the gasification portion of the integrated process. The equilibrium carbonate concentration of the melt will generally increase as the mole ratio of alkaline reagent to glass-forming oxide increases and as the molecular weight of the cation constituent of the alkaline reagent increases (a melt containing potassium will absorb more carbon dioxide than a melt containing sodium). The carbonate concentration in the molten media is preferably maintained at a minimum level and preferably comprises less than about 30 wt. percent of the total melt, more preferably about 20 wt. percent and most preferably, below about 15 wt. percent of the total melt. Since the alkali and/or alkaline earth constituents of the melt are at least partially converted to sulfates, sulfites, sulfides and carbonate materials, the mole ratio of alkaline reagent (oxides, hydroxides, and mixtures thereof) to glass-forming oxide will decrease as the sulfur and carbonate compounds are formed. Accordingly, it may be necessary to periodically add additional amounts of alkaline reagent to the melt in order to maintain the desired mole ratio of alkaline reagent to glass-forming oxide in the melt.

Turning to FIG. 2, the cracking operation is conducted, in this embodiment, in the absence of hydrogen, the hydrogen being utilized in a separate hydrogenation (hydrotreating) zone, zone 36. Preliminarily, the cracking effluent in line 6, is stripped of gaseous

materials in stripper 22 and thereafter passed to distillation tower 26 via line 24 wherein it is fractionated into lube streams 28, 30 and 32, and a bottoms stream 34. The lube components are then hydrotreated in zone 36 in the presence of hydrogen and an appropriate catalyst, defined hereinabove. The effluent exists via line 38 and may be further processed such as by dewaxing and solvent extraction to yield a high quality lube oil product. As already noted, the hydrotreating operation may be conducted within the cracking reactor. Thus, zone 2, shown in FIG. 1, could be divided into a plurality of stages, with the cracking and hydrotreating operations occurring in separate stages. The exact process sequence will depend, in large part, on the characteristics of the process feedstock and the desired product specifications.

PREFERRED EMBODIMENT

The process of the subject invention will be more apparent from the preferred embodiment and working examples set forth hereinbelow.

EXAMPLE 1

A series of tests was conducted to demonstrate the efficacy of melts containing boron oxide. The initial alkaline reagent portion of the boron-containing melt was composed of about 43 mole percent lithium as lithium hydroxide, 31 mole percent sodium as sodium hydroxide, and 26 mole percent potassium as potassium hydroxide. Sufficient boron oxide was added to the melt to bring the molar ratio of alkali compounds on an oxide:boron oxide basis to 2.5. The hydroxides/boron oxide mixture was heated in a graphite-lined reactor to a temperature ranging from 1500° to 1600°F. over a period of from 3-4 hours until a homogeneous melt is secured. Thereafter the melt was solidified by cooling, and 2,000 grams of melt particles were introduced into a graphite-lined reactor that was equipped with a stirrer and means for introducing feedstock and means for withdrawing liquid and gaseous product materials.

In each test run, 600 grams of feedstock comprising a heavy Arabian residual material having an initial boiling point of about 980°F. was continuously introduced into the reaction zone which was maintained at a temperature of about 1000°F. and atmospheric pressure over a 40 minute period. The feed material exhibited an API gravity of 4.6°, a Conradson carbon residue number (CCR) of 21 wt. percent and contained about 0.5 weight percent nitrogen, 4.8 weight percent sulfur and 280 ppm metals. The feed material was introduced into the bottom of the reactor through the feed inlet and was brought into intimate contact with the stirred melt. Product materials were continuously bled from the top of the reactor and the liquid products condensed and fractionated in vacuo for subsequent analysis. The residence time of the product materials within the reaction zone varied from an average of about 20 minutes for coke materials to several seconds for lighter products.

The results of the experiments are set forth in Table II below. The range of values presented are representative of results obtained from a number of experiments. The relatively wide range of results can be explained by the difficulty encountered in maintaining constant residence times in all of the runs.

TABLE II

Product Properties	Boron Oxide Melt		
C ₁ /C ₄ Gas, wt% on feed	5-8		
C ₅ /650°F. Naphtha + Gas Oil			
Yield, once-through (wt. % on feed)	10-20		
Gravity, °API	30-40		
S, wt.			
Metals 1.2-1.7			
N, wt. %	0.05-0.1		
Bromine No.	45-55		
Aniline Point, °F.	120-130		
650-980°F. Lube Basestock A			
Yield, once-through (wt. % on feed)	15-30		
Gravity, °API	20-25		
S, wt. %	2.5-3.5		
N, wt. %	0.1-0.2		
Bromine No.	15-30		
Aniline Point, °F.	145-155		
Carbon, wt. %	84.9		
Hydrogen, wt. %	11.6		
CCR, wt. %	<0.5		
Metals (Fe, V, Ni), ppm	<5		
980°F+ Product			
	(Vacuum Rerun, 980/1100°F. Cut)	Lube Basestock B	Still Bottoms
Yield, once-through (wt.% on feed)	12-50	6-25	1100°F+
Gravity, °API	8-12	12-15	6-25
S, wt. %	3-4	2.8-3.6	5-9
N, wt. %	0.15-0.3	0.15-0.25	
Carbon, wt. %	84	—	
Hydrogen, wt. %	9	—	
CCR, wt. %	2-10	~0	
Metals (Fe, V, Ni), ppm	7-30	<3	
Color	very dark	red-brown	black
Coke			
Yield, once-through (wt. % on feed)	20-30		
S, wt. %	1-1.5		

As shown in the above table, the boron oxide-containing melts serve as efficient means for the cracking of heavy petroleum residual materials to produce lubricating oil basestocks. The 650°/980°F. fraction of the overhead product from melt cracking is a medium viscosity lube base designated in Table I as Lube Basestock A. It has approximately 3 percent sulphur (which is less than the corresponding product made from fluid coking), 0.15 percent nitrogen, a significant content of olefins, but only traces of CCR (coke precursors) and metals (<5 ppm). Such properties render this fraction suitable for subsequent treatment by hydrogenation, dewaxing and solvent extraction techniques.

The fraction was submitted directly to phenol treating (3 × 50 and 5 × 60 volume percent solvent treats at 140°F.). The batch aqueous phenol extraction response (3% water) of the raw 650°-980°F. melt process product is presented in Table III together with the corresponding inspections for the unextracted feedstock. It may be observed that acceptable yields of high V.I. lube bases were produced at low (batch) extraction treat levels. For example, a 150 vol. percent phenol treat produced 37 wt. percent of 144 N lube of 98 viscosity index (after dewaxing with 30 percent MEK/70 percent MIBK, 2.5/1.0 solvent:oil ratio at 0°F.).

However, the extracted, dewaxed oil exhibited a high bromine number (20) thereby indicating relatively high concentrations of olefins. Assuming an average molecular weight of 375 for both oils, this corresponds to about one double bond per every two molecules. To meet 150N basestock specifications the bromine number must be quite low, e.g. about zero. Therefore the oil basestock of Example 1 was unsatisfactory as a lube

oil, particularly from the standpoint of thermal/oxidation stability.

EXAMPLE 2

The heavy feedstock of Example 1 was treated in the boron oxide melt exactly as described above and the 650°/980°F. overhead product from the reaction was then hydrotreated before dewaxing and solvent extraction. In the hydrotreating step 250 cc of the 650°/980°F. distillate was mixed with 250 cc of a nickel molybdate catalyst (Cyanamid Aero HDS-9A) in a 1 litre autoclave and stirred for 1 hr. at 550°F. and 800 psig pressure. The vapor in the reactor was replaced every 5 minutes with pure hydrogen. As indicated in Table IV, this mild treatment was adequate to saturate essentially all the olefinic components of the melt process product at a relatively low hydrogen consumption (415 SCF/B). Hydrotreating also reduced the sulphur and nitrogen contents, by 80 and 84 percent respectively. Both wax yield and dewaxed oil VI increased as a result of hydrotreating (8.2 wt. percent and 63 VI compared to 13.5 wt. percent and 76 VI respectively). Furthermore, dewaxed raffinate yield and colour were significantly improved.

Referring to Example 1, extraction of the raw melt cracking product with 150 percent aqueous phenol produced 37 wt. percent 144N lube of 98 VI and L6.5 ASTM color; extraction of the hydrotreated product at the same treat level, as in Example 2, produced 60 wt. percent of 138N lube of 100 VI and L3.5 ASTM color.

EXAMPLE 3

The heavy feedstock of Example 1, treated in the

boron oxide melt as described hereinbefore, produced as another distillate product from the reaction zone a material which after fractionation in vacuo is designated as 980°F+ product in Table II. Although an overhead product, this fraction contains many components boiling at temperatures far in excess of the melt reactor temperature (1,000°F.). Some of the components have boiling points of 1500°F. and more; these are of extremely high molecular weight and are similar to what is conventionally described as asphalt. The crude 980° vacuum F+ fraction was incapable of color improvement by any of the sequential stages of Example 2: dewaxing, hydrotreating, phenol treating and combinations thereof. The asphaltic components are believed to have inhibited color improvement. The fraction after these subsequent treatments remained almost black in color and was unsatisfactory as a lube oil.

EXAMPLE 4

The heavy fraction taken after melt cracking, as described in Example 3 was rerun by vacuum distillation to give 50 percent of a 980°/1100°F. cut designated in Table II as Lube Basestock B and a still bottoms which was blended off with asphalt. The lube base B had the properties listed in Table II. Color was improved over the original as indicated by the following analysis:

ASTM 1925-63T

Average of 3 samples, 0.01 inch thick, on microscope slides evaluated by Color-Eye

	Original	Lube Basestock B	Still Bottoms
Yellowness Index	93	67(best)	102 (worst)
Brightness or Luminosity, CIE	62	75(best)	5(worst)

It is apparent from these results that the color was markedly improved by fractionation to remove heavy asphaltic components. Subsequent hydrotreatment and solvent extraction should improve the color to that of a top quality bright stock. Other properties e.g., nitrogen and sulphur contents, viscosity, unsaturation, etc. should also be completely satisfactory. The dewaxed hydrotreated oil is particularly suited for use as a rubber processing and extender oil; and the same fraction after phenol extraction gave (a) a raffinate suitable as a paraffinic-naphthenic rubber oil and (boron in extract suitable as an aromatic extender oil.

EXAMPLE 5

The feedstock of Example 1 is introduced into the reactor containing the boron oxide melt under a hydrogen pressure of 500 psig at a temperature of 1,000°F. As the feed enters the reaction zone at a space velocity of 1.0 wt/wt melt/hr. the high molecular weight hydrocarbons are cracked and organic sulphur and nitrogen compounds, metal-containing porphyrin complexes, and coke precursors are degraded to gas, liquid, tar and coke. The liquid overhead product is fractionated and should yield lube basestocks similar in all respects to those of Examples 2 and 4 respectively.

EXAMPLE 6

The procedure is identical to that of Example 5 except that the hydrogen used in the melt processing reaction is prepared in situ by the reaction of steam on coke deposited in the melt by cracking a heavy feedstock. The products should be similar in all respects to those previously obtained.

TABLE III

LUBES FROM EXTRACTION OF 650-980°F. FRACTION FROM MELT CRACKING 980°F+ HEAVY ARABIAN RESID			
Phenol Extraction Response			
Batch Phenol Treat ⁽¹⁾ , Vol%	0	3 × 50	5 × 60
<u>Waxy Inspections</u>			
Yield on Feed, Wt. %	100	43.1	18.3
Raffinate RI at 60°C	1.5040	1.4790	1.4598
Extract RI at 60°C	—	1.5248	1.5150
Raffinate Gravity, °API	19.6	27.8	33.3
Visc. 100°F, SUS	156.3 ⁽³⁾	—	—
Color, ASTM	D8.0	L5.5	L2.0
Wax ⁽²⁾ , Wt. %	7.8	13.7	21.6
<u>Dewaxed Inspections</u>			
Yield on Feed, Wt. %	92.2	37.2	14.3
Visc. 100°F, SUS	181	144	132.2
Visc. 210°F, SUS	43.6	42.7	43.1
VI _E	63	98	124
Color, ASTM	D8.0	L6.5	L3.0
Gravity, °API	19.4	25.7	—
Bromine No. gm/100 gm	19.4	20.1	—
Saturates ⁽⁴⁾ , wt. %	38	54.5	76.5
Aromatics ⁽⁵⁾ , wt. %	62	45.5	23.5
<u>Extraction Response</u>			
Actual Batch Extraction Yield, Wt. %	92.2	37.2	14.3

⁽¹⁾ Phenol + 3% H₂O, 140°F.
⁽²⁾ 30% methyl ethyl ketone/70% methyl isobutyl ketone, 2.5 solvent to 1.0 oil at 0°F.
⁽³⁾ Waxy VI_E = 74, pour 70°F.
⁽⁴⁾ By Humble Silica Gel Separation Technique.
⁽⁵⁾ 100 - Wt. % Saturates by Silica Gel Technique.

TABLE IV

LUBES FROM HYDROTREATING-EXTRACTION OF 650-980°F
FRACTION FROM MELT CRACKING OF 980°F+HEAVY ARABIAN RESID

Batch Phenol Treat ⁽¹⁾ , Vol. %	Phenol Extraction Response			
	Raw Oil	Hydrotreated Oil		
	0	0	150	300
Waxy Inspections				
Yield on Feed, Wt. %	100	(100)	71.0	56.0
Raffinate RI at 60°C.	1.5060	1.4850	1.4711	1.4620
Extract RI at 60°C.	—	—	1.5218	1.5169
Raffinate Gravity, °API	20.7	26.6	30.1	32.5
Visc. 210°F., SUS	45.5 ⁽²⁾	40.1 ⁽⁶⁾	41.2	41.7
Color, ASTM	D8.0	L2.5	L2.0	L2.0
Wax ⁽³⁾ , Wt. %	8.2	13.5	15.6	16.9
Dewaxed Inspections				
Yield on Feed, Wt. %	91.8	86.5	59.9	46.5
Visc. 100°F, SUS	249	137.8	134.8	130.6
Visc. 210°F, SUS	43.8	41.6	42.1	42.2
VI _E	63	76	100	109
Color, ASTM	D8.0	L3.5	L3.5	L2.5
Gravity, °API	19.0	24.7	28.3	31.0
Bromine No. gm/100 gm	14.6	1.43	1.78	0.7
Saturates ⁽⁴⁾ Wt. %	36.0	44.9	56.9	68.2
Aromatics ⁽⁵⁾ Wt. %	64.0	55.1	43.1	31.8

⁽¹⁾ Batch extractions, phenol + 3% H₂O, 120°F.

⁽²⁾ Waxy VI_E = 70, pour ~70°F.

⁽³⁾ 30% MEK/70% MIBK, 2.5 solvent/ 1 oil at 0°F.

⁽⁴⁾ By Humble silica gel separation technique.

⁽⁵⁾ 100 - Wt. % saturates by silica gel technique.

⁽⁶⁾ Waxy VI_E = 92, pour 80°F.

What is claimed is:

1. In a process for the production of lubricating oils, the steps of contacting a heavy hydrocarbon feedstock in a contacting zone with a regenerable molten medium and hydrogen, said molten medium comprising a glass-forming oxide and an alkaline reagent selected from the group consisting of (a) a Group IA metal oxide, hydroxide, and mixture thereof, and (b) a Group IA metal oxide, hydroxide, and mixture thereof in combination with a Group IIA metal oxide, hydroxide, and mixture thereof, at a temperature in the range of from about the melting point of said medium to less than about 1200°F., for a time sufficient to form lighter hydrocarbons containing a substantial amount of lube oil components.
2. The process of claim 1 wherein the temperature of the regenerable molten medium is maintained in the range of from about 800° to less than about 1,200°F.
3. The process of claim 2 wherein said glass-forming oxide is selected from the group consisting of oxides of boron, phosphorus, vanadium, silicon, tungsten and molybdenum.
4. The process of claim 2 wherein said alkaline reagent is an alkali metal oxide, alkali metal hydroxide or mixtures thereof.
5. The process of claim 4 wherein said glass-forming oxide is boron oxide.
6. The process of claim 4 wherein the mole ratio of said alkaline reagent, calculated on the basis of the oxide thereof, to glass-forming oxide is in the range of from about 1.5 to about 3.
7. The process of claim 4 wherein the mole ratio of said alkaline reagent, calculated on the basis of the oxide thereof, to glass-forming oxide is in the range of from about 2.2 to about 3.
8. The process of claim 6 wherein said molten medium is regenerated after contact with said hydrocarbon feedstock by contacting said molten medium with oxygen, steam, carbon dioxide or mixtures thereof at a

temperature in the range of from above about the melting point of said medium to about 2000°F.

9. The process of claim 1 wherein the hydrogen partial pressure in said contacting zone is between about 100 and about 5,000 psig.

10. A process for converting a heavy hydrocarbon feedstock, a major portion of which boils above about 650°F. at atmospheric pressure, to lighter hydrocarbon materials containing a substantial amount of lube oil components which comprises contacting said heavy hydrocarbon feedstock in a contacting zone with hydrogen and a regenerable molten medium containing an alkaline reagent selected from the group consisting of (a) a Group IA metal oxide, hydroxide, and mixture thereof, and (b) a Group IA metal oxide, hydroxide, and mixture thereof in combination with a Group IIA metal oxide, hydroxide, and mixture thereof, and a glass-forming oxide selected from the group consisting of oxides of boron, phosphorus, vanadium, silicon, tungsten and molybdenum at a temperature in the range of from about 800° to less than about 1200°F. to form predominantly liquid hydrocarbon products containing a substantial amount of lube oil components boiling above about 650°F., and carbonaceous materials, and thereafter, gasifying at least a portion of said carbonaceous materials formed during said conversion process by contacting same with a gasification reagent including oxygen, carbon dioxide, steam or mixtures thereof at a temperature in the range of from about the melting point of said medium to about 2000°F.

11. The process of claim 10 wherein the temperature of the regenerable molten medium during contact with heavy hydrocarbon feedstock is maintained in the range of from about 800° to about 1100°F.

12. The process of claim 11 wherein said glass-forming oxide is boron oxide.

13. The process of claim 12 wherein said alkaline reagent is an alkali metal hydroxide, an alkali metal oxide or mixtures thereof.

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14. The process of claim 13 wherein the mole ratio of said alkaline reagent, calculated on the basis of the oxide thereof, to boron oxide is in the range of from about 2.2 to about 2.7.

15. The process of claim 14 wherein said gasifying reagent is a gas stream containing from about 10 to about 25 wt. percent oxygen.

16. The process of claim 10 wherein said glass-

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forming oxide is a boron oxide.

17. The process of claim 10 wherein said glass-forming oxide is an oxide of phosphorus.

18. The process of claim 11 wherein the hydrogen partial pressure in said contacting zone is between about 100 and about 5,000 psig.

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