

July 10, 1973

L. A. HEREDY ETAL

3,745,109

HYDROCARBON CONVERSION PROCESS

Filed Oct. 1. 1970

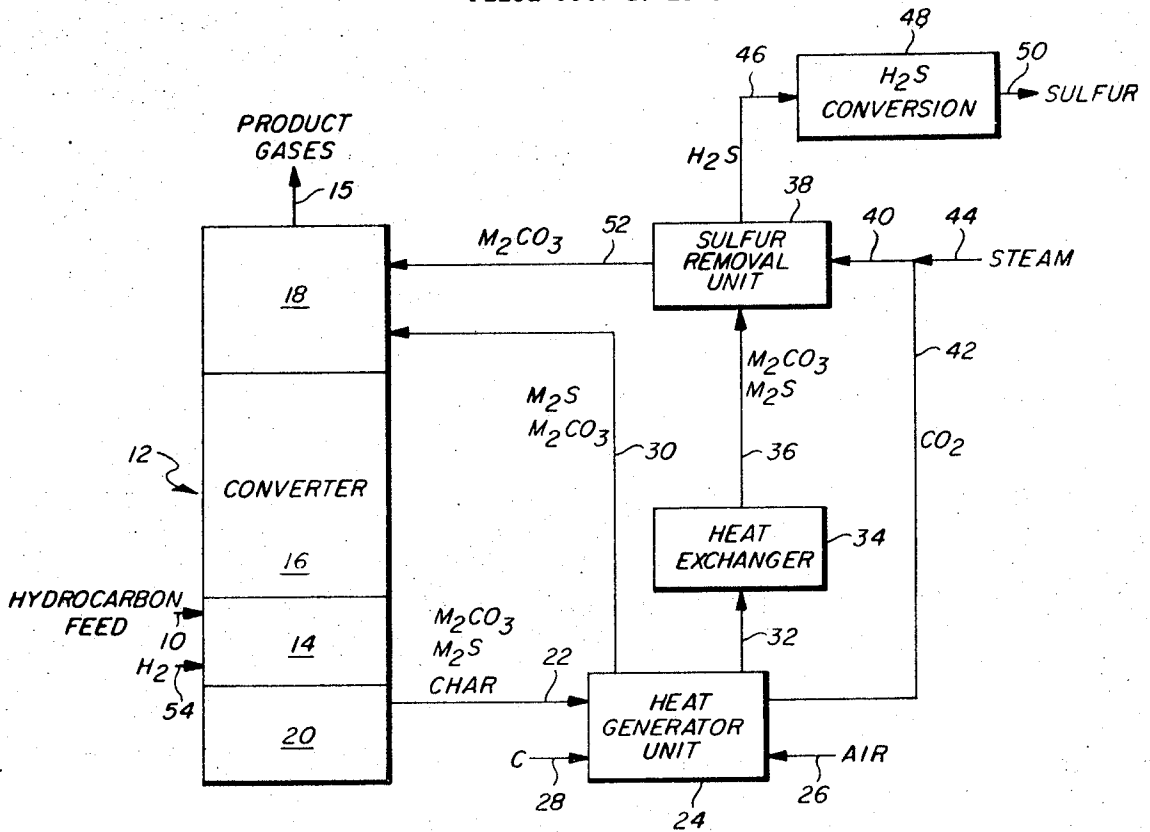


FIG. 1

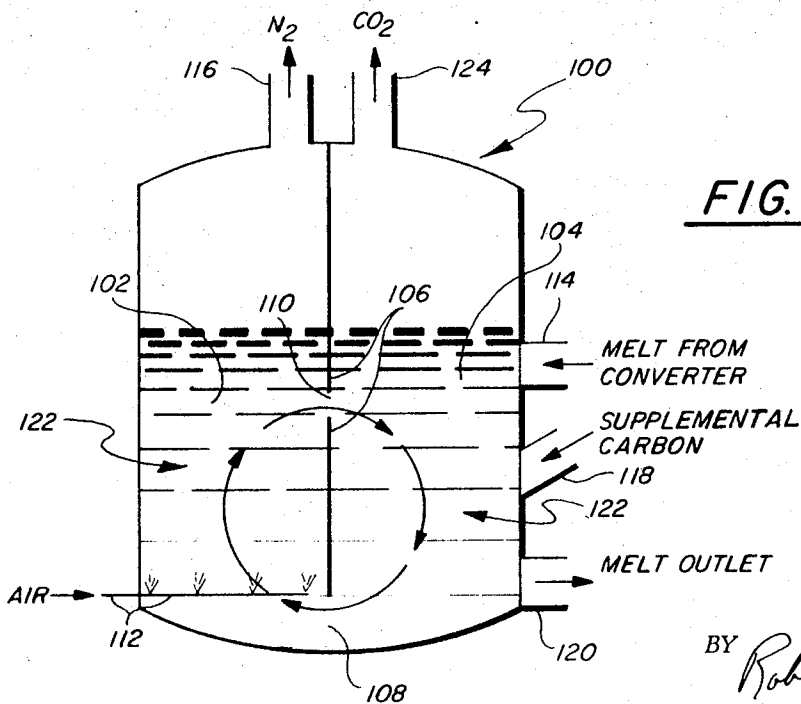


FIG. 2

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3,745,109

## HYDROCARBON CONVERSION PROCESS

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Filed Oct. 1, 1970, Ser. No. 77,170

Int. Cl. C10g 13/02, 11/00, 9/34

U.S. Cl. 208—107

12 Claims

### ABSTRACT OF THE DISCLOSURE

Hydrocarbons such as partially refined petroleum are brought into contact with a sulfide-containing alkali metal carbonate melt at elevated temperatures. Depending upon conditions, the hydrocarbons undergo thermal or catalytic cracking, hydrocracking, hydrogenation, dehydrogenation, or hydrodesulfurization. Heat is supplied to the conversion process by contacting the melt and heavy carbonaceous by-product with a reactive form of oxygen. Provision is also made for the removal of excess sulfur values.

### CROSS-REFERENCE TO RELATED APPLICATIONS

A method for producing heat by reacting a sulfide containing melt with a reactive form of oxygen and then reducing the sulfate formed back to the sulfide with a carbonaceous material is described in copending patent application Ser. No. 77,219, entitled, "Method for Producing Heat" by J. R. Birk, filed Oct. 1, 1970 and commonly assigned with the present invention.

A method for pyrolyzing carbonaceous materials with attendant recovery of pyrolysis gases wherein the pyrolysis is accomplished in a molten salt mixture containing alkali metal sulfide and sulfate is described in copending patent application Ser. No. 77,225 by J. R. Birk and D. A. Huber entitled, "Pyrolysis Method," filed Oct. 1, 1970 and commonly assigned with the present invention.

### BACKGROUND OF THE INVENTION

#### (A) Field of the invention

This invention relates to the field of hydrocarbon conversion processes. More particularly, this invention relates to the conversion of partially refined petroleum products such as distillation residuals into more valuable products by way of thermal cracking, coking, catalytic cracking, hydrocracking, hydrogenation, dehydrogenation, or hydrodesulfurization. Still further, this invention relates to a method for carrying out hydrocarbon conversion processes in a sulfide-containing alkali metal carbonate melt.

#### (B) Description of the prior art

Progress in petroleum refining is dependent to a large extent upon improvements in processes designed to convert partially refined petroleum products into more valuable products. The conversion processes all rely upon the application of heat. Two basic types are utilized, those using hydrogen and those not using hydrogen.

Among those not using hydrogen, thermal cracking is the oldest and most highly developed process. Thermal cracking involves splitting of large hydrocarbon molecules into smaller molecules at elevated temperatures. A portion of these smaller molecules represents stable light hydrocarbons such as gasoline, refinery gas, light oils, and gas oil. The remaining products are heavy oils and coke. The process is known as thermal cracking when the feed is gas oil or topped crude oil. If, on the other hand the feed consists of a residual material the thermal decomposition is known as viscosity-breaking or coking.

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The formed is a mild reduction in molecule size and is usually conducted on a once-through basis whereas the latter is a severe cracking operation. Conventional cracking processes often result in extensive coke formation, products of low grade, and the presence of sulfur-containing gases in the refinery gas product. In addition, prior art processes yield cokes containing excessive amounts of sulfur. These cokes are generally of little value.

Catalytic cracking as the name implies is the decomposition of hydrocarbons in the presence of a catalyst. Catalysts normally employed include fuller's earth, kaolin, silica-alumina, and synthetic and natural zeolites. Problems involved in catalytic cracking include coke build-up, degradation of catalyst, heat exchange and complexity of equipment.

The term dehydrogenation refers to two separate processes. The first is the conversion of alkanes and heavy alkylenes to lighter alkylenes. This process is sometimes referred to as vapor-phase cracking. Examples are the production of butadiene from butane via butene. The second type of dehydrogenation is a catalytic reforming in which a dehydrogenation of cyclic compounds occurs along with other reactions. When used herein the term dehydrogenation refers to the first of these processes. A major problem in the production of alkylenes is the low yields conventionally obtained.

Petrochemical conversion processes utilizing hydrogen include hydrocracking and hydrodesulfurization (hydrotreating).

Hydrocracking is the decomposition of hydrocarbons at high pressures and elevated temperatures with the addition of hydrogen and usually in the presence of a catalyst such as zeolites with a platinum, tungsten oxide, or nickel hydrogenation component. These catalysts may be altered by promotion with another metal or by some pretreatment such as sulfiding. Under these conditions hydrogenation occurs simultaneously with cracking. Thus, there is little build-up of tar or coke. A number of problems are involved in these processes including catalyst deterioration by sulfur, ammonia, or ash; presence of hydrogen sulfide in the products; and catalyst deactivation by coke deposition.

Hydrodesulfurization (hydrotreating) refers to a process for the removal of sulfur and nitrogen from hydrocarbons. Typical feeds for desulfurization include straight run products, cracked products, feedstocks to catalytic reforming, feedstocks to hydrocracking, lubricating oils, catalytic cracking feeds, cycle stocks, or aromatic distillates. High-sulfur residuals are also treated by this process to produce low-sulfur heating oils which can be burned without pollution by sulfur oxides. The process is similar to hydrocracking with the exception of the materials used for catalysts. In the case of hydrodesulfurization, the oxides and sulfides of iron, cobalt, tungsten, nickel, or molybdenum are commonly used. Temperatures for the process range from 290–430° C. and pressures range from 200–2000 p.s.i. Present desulfurization processes involve large capital costs and usually do not achieve the extent of desulfurization required to meet present and future standards particularly in the case of desulfurization of heavy oils and residuals.

Thus, it is seen that each of the above noted conversion processes is in need of improvements.

Until recently, the use of molten salts as a reaction medium for major industrial processes had not been considered practical. U.S. Pat. 3,438,722 suggests their use in the absorption of sulfur oxides from flue gases. U.S. Pat. No. 3,252,773 suggests the use of an alkali metal carbonate or hydroxide melt to gasify coal. U.S. Pat. 3,252,774 suggests the use of molten salts for the production of hydrogen-containing gases from hydrocarbons by a gasifica-

tion process. In addition, molten salts are being investigated for and used in a wide variety of applications. These include, for example, (1) reaction medium for production of aluminum, sodium, magnesium and fluorine; (2) media for processing spent reactor fuel elements; (3) electrolyte for fuel cells; (4) solvent for plating of refractory metals; (5) solvent for fluxing and descaling operations on metals; and (6) fuel solvent and heat transfer agent for nuclear reactors. Of importance to this disclosure is the use of molten salts for cracking hydrocarbons. Thus British Pat. 1,144,500 discusses the use of molten zinc chloride as a catalyst for hydrocracking. Although molten zinc chloride has been shown to be an effective catalyst for hydrocracking polynuclear hydrocarbons, several difficulties arise. For example, zinc chloride is deactivated by sulfur and ammonia to form zinc sulfide and ammoniates of zinc halide. In addition, regeneration of the molten salt catalyst involves either combustion with simultaneous volatilization of zinc chloride which must be recovered or dissolution of the catalyst in a two-phase (water and organic) system. In the former situation, steam generated in the combustion process hydrolyzes zinc chloride vapors to produce hydrochloric acid and zinc oxide. The hydrochloric acid must be recovered and reacted with the zinc oxide at lower temperatures to reform the zinc chloride. In addition, the sulfur product is sulfur dioxide which must be collected and reduced for reclamation of this material. The latter technique for regeneration is complex and consumes, instead of produces, energy.

Other workers have used molten carbonates for cracking light hydrocarbons such as ethane. These workers, however, did not contemplate the use of sulfide in the melt, hydrocracking, coking of residuals, or heating by internal cyclic reaction. In addition, the prior art has not provided an acceptable means for sulfur removal from the melt.

### SUMMARY OF THE INVENTION

We have now discovered that a variety of petroleum refining processes may be undertaken by contacting the feedstock with a sulfide-containing alkali metal melt, preferably a sulfide-containing alkali metal carbonate melt, under the appropriate operating conditions. These processes may be carried out with or without catalysis and with or without the addition of hydrogen. Heat for the conversion reactions is supplied by contacting the melt containing coke with a source of reactive oxygen such as air. In addition, it is possible to remove accumulated sulfurous compounds by suitable processing.

Accordingly, the objects of the invention are:

to provide an improved hydrocarbon conversion process;  
to provide an improved hydrocarbon cracking process;  
to provide an improved thermal cracking process;  
to provide an improved coking process;  
to provide an improved catalytic cracking process;  
to provide an improved dehydrogenation process;  
to provide an improved hydrocracking process;  
to provide an improved hydrodesulfurization process; and  
to provide an improved method of supplying heat for hydrocarbon conversion reactions.

These and other objects and advantages of the invention will become more apparent upon consideration of the following detailed description of the preferred embodiments of the invention wherein reference is made to the attached drawings.

### BRIEF DESCRIPTION OF THE DRAWINGS

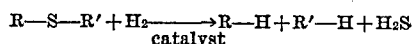
FIG. 1 is a schematic illustration of a flow plan representing the major steps of the invention.

FIG. 2 is a schematic illustration of a preferred form of reactor for reheating the melt.

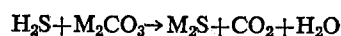
### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is broadly directed to the conversion of hydrocarbons into more valuable materials by the application of heat. Other major variables include catalyst type, pressure, temperature, and the presence of hydrogen. A schematic flow plan representing the basic process is illustrated in FIG. 1. That figure shows the basic steps of contacting a hydrocarbon with a hot melt containing an alkali metal carbonate-sulfide mixture and then withdrawing and separately heating the melt to supply heat for the conversion reaction. A hydrocarbon feed 10 is introduced into converter unit 12 at feed zone 14. The composition of this feed steam will depend upon the particular conversion process undertaken, but generally will be selected from the group consisting of methane (to produce hydrogen), ethane (to produce ethylene), light hydrocarbons, naphtha, kerosene, refinery gas, natural gas, light gas oil, heavy gas oil, atmospheric residuals, tar, vacuum residuals, and virgin hydrocarbon-containing materials such as crude oil, coal, oil shale, and tar sands. A preferable class of materials are the petroleum residuals. Once in converter 12, the feed contacts a molten salt at a temperature of from about 400° C. to about 1100° C. depending upon the conversion reaction desired. If the reaction is one which involves hydrogen, a stream of hydrogen 54 may be added to converter 12 at feed zone 14. Upon contact with the hot melt, conversion of the feed begins and the lighter hydrocarbon gases and liquids pass upwardly through packed bed portion 16 of converter 12 in a generally counter-current relationship to the hot melt. The converter is designed such that the conversion reactions are complete when the gases reach the upper part of packed portion 16 and enter plenum portion 18 of the converter reactor. The product gases are withdrawn via line 15. Heavy products such as coke remain in the melt and pass downwardly to sump portion 20 of the converter. From here, the melt and char or coke contained therein are sent via line 22 to a heat generation zone 24.

The composition of the molten salt used in these processes may vary somewhat depending upon the conversion process undertaken, particularly with respect to catalyst composition as will be described hereinafter. Nevertheless, it is critical that the melt contain from about 1 to about 25 weight percent sulfur as a sulfide. The alkali metal ions are the preferred cationic component of the melt although other metal ions may be used. A very desirable melt for most uses consists of alkali metal carbonate and alkali metal sulfide. Use of the carbonate is particularly advantageous when removal of sulfur from the products is desired, as the carbonate has the ability to absorb sulfurous compounds which are liberated from the feedstock at elevated temperatures. For example, in a hydrocracking operation the mechanism may be represented as follows:



where R and R' represent the hydrocarbon portion of a sulfur-containing molecule. The H<sub>2</sub>S which is given off is absorbed by the carbonate melt according to the reaction



where M—an alkali metal ion. This absorption reaction is equilibrium controlled. The equilibrium constant

$$[(\text{CO}_2)(\text{H}_2\text{O})(\text{M}_2\text{S})/(\text{H}_2\text{S})(\text{M}_2\text{CO}_3)]$$

and free energy of this reaction, where M is sodium, as a function of temperature are given in Table I where a negative free energy indicates a most favorable situation for the forward reaction.

TABLE I.—HYDROGEN SULFIDE ABSORPTION

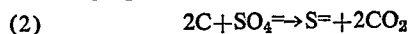
Temperature (° C.)	Equilibrium constant	Free energy (kcal./mole)
427	0.0140	+5.95
527	0.137	+3.16
627	0.744	+0.53
727	2.68	-1.96
827	7.23	-4.33
927	15.2	-6.56

At relatively high temperatures, and with low water and carbon dioxide concentrations, the absorption reaction is favored. At lower temperatures the reverse reaction (i.e., regeneration of the carbonate melt) can be carried out by adding steam and carbon dioxide. This latter reaction will be described hereinafter.

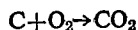
In heat generator unit 24, the withdrawn melt which contains carbonaceous char or coke is contacted with a reactive source of oxygen, preferably air 26. Because of the sulfide content of the melt, the oxygen oxidizes the sulfide in preference to the carbon contained in the melt according to the reaction:



Simultaneously, the carbon contained in the melt reacts with the sulfate formed in Reaction 1 according to the following equation:



Reaction 1 is very exothermic whereas Reaction 2 is endothermic. The composite of Reactions 1 and 2 results in the liberation of an amount of heat equivalent to that given off in the reaction:



In order to accomplish these reactions the temperature should be above 300° C. for Reaction 1 and above 600° C. for Reaction 2 and preferably between 800° C. and 1200° C. for both reactions. These temperatures are far below the operating temperatures of most furnaces and boilers. These reactions can be carried out at any practical pressures; however, increased pressure decreases the volumetric throughput of gases through the molten salt.

As a consequence of these reactions, sufficient heat is generated to sustain the conversion reactions carried out in converter 12. Because it is necessary to return the melt to converter 12 in the sulfide form, the ratio of carbon and oxygen used in heat generator unit 24 must be sufficiently high. If there is an insufficient amount of carbon contained in the melt entering heat generator unit 24 a supplementary source of carbon 28 may be provided.

Maintenance of from about 1 to 25 and preferably from 2 to 10 weight percent sulfur in the melt will assure that Reactions 1 and 2 above occur in preference to the reaction  $C + O_2 \rightarrow CO_2$ . In other words, substantially all of the carbon should be consumed by the mechanism of Reaction 2.

In addition to a carbonaceous reductant, i.e., the char resulting from the hydrocarbon conversion reaction or a supplemental carbonaceous source, it may sometimes be desirable to include a catalyst for the reduction reaction Reaction 2 in the melt. Iron has been found to be a good catalyst for the reduction reaction. Thus, an amount of iron ranging from about 0.5 to about 7 weight percent of the melt may be used. The iron may be added to the melt in the elemental form or in the form of compounds containing iron such as iron sulfide or iron sulfate which are compatible with the other melt constituents. Alternatively, the catalyst may be incorporated in or deposited on the packing used in converter 12.

FIG. 2 illustrates a preferred form of apparatus for carrying out the heat-generation reactions. There, 100 represents a reactor vessel consisting of a sulfide oxidation zone 102 and a sulfate reduction zone 104 separated by a slotted partition 106. Partition 106 is constructed with

two major openings 108 and 110 which provide fluid communication between zones 102 and 104. The sulfide oxidation zone 102 has associated therewith an air inlet and distributor system 112, and gaseous outlet 116. The sulfate reduction zone 104 has associated therewith a melt inlet 114, supplemental carbonaceous material inlet 118, a melt outlet 120 and a gaseous outlet 124.

In operation, the reactor is filled with melt 122 to a point higher than opening 110. Air is supplied to oxidation zone 102 through distributor system 112, causing sulfide salts to be oxidized to sulfate salts according to Reaction 1. The introduction of air also causes an upwardly directed flow of melt in zone 102. Nitrogen from the introduced air leaves the oxidation zone portion of the reactor via line 116. Circular flow patterns developed in the melt cause oxidized salts to flow through opening 110 to reducing zone 104. Here at inlet 114, melt containing a source of carbonaceous material or supplemental carbonaceous material 118 is added thereby causing a reduction of the sulfate to the sulfide according to Reaction 2. Carbon dioxide produced in this reaction exits the reactor vessel at 124. Reduced melt from zone 104 is carried by established flow currents through opening 108 of partition 106 to zone 102. Melt containing sulfide is removed through outlet 120 to a sulfur removal unit via heat exchanger 34 and to the converter 12. The exit gases may be heat exchanged.

Alternatively, partition 106 need not be present in reactor 100. In this situation, Reactions 1 and 2 are carried out together. In this case it is preferable that an excess of carbon be present so that under steady state operating conditions Reaction 2 is favored and the sulfur present in the melt remains in the sulfide form. Under these conditions the oxygen reacts with the sulfide in preference to reacting directly with carbon. In other words, substantially all the carbon will be consumed by the mechanism of Reaction 2.

Returning now to FIG. 1, it is seen that a portion of the heated melt from heat generator unit 24 is returned directly via line 30 to converter reactor 12. A second portion is sent via line 32 to a heat exchanger 34 where it is cooled to a temperature of from about 900 to about 450° C. From there, it is sent through line 36 to a sulfur removal unit 38. In this unit, the molten sulfide salt is contacted, preferably in a countercurrent fashion, with a stream 40 containing carbon dioxide and steam. As shown in the drawing, the carbon dioxide may be obtained from heat generator unit reactor 24 via line 42 and the steam is obtained via line 44. As a result of contact within unit 38, the following reaction occurs:



where M—the cationic content of the melt, usually a mixture of alkali metal ions. The  $H_2S$  produced in this reaction is fed via line 46 to a Claus unit 48 where sulfur 50 is produced. Alternatively, the  $H_2S$  can be utilized as the feedstock for a sulfuric acid plant. The carbonate formed in unit 38 is returned via line 52 to converter 12. The proportion of melt treated in unit 38 will depend upon the sulfur content of the feedstock. If the feed to converter 12 is sulfur-free, then a sulfur removal unit such as 38 is not necessary. If however, the feed contains sulfur, the melt circulating through converter 12 and heat generator unit 24 will experience an increase in sulfur content as the melt absorbs the sulfur from the feedstock. In such a case, it is desirable to maintain the sulfur content below about 25 weight percent.

Conditions within converter 12 will vary depending upon the feedstock and the desired conversion. Temperatures during cracking operations will vary from about 400° C.—1100° C. with the lower portion of the range representing viscosity breaking and mixed-phase cracking and the upper portion of the range representing more severe cracking operations such as coking. Catalysts may be added to the melt or incorporated into the packing of

converter 12 for the purpose of increasing the rate of the desired reactions. Preferred catalysts include oxides and sulfides of iron, cobalt, molybdenum, tin, nickel, tungsten and other transition metals. In addition, the alkali metal sulfide content of the salt has also some catalytic effect.

Conversion reactions such as hydrocracking and hydrodesulfurization (hydrotreating) which require hydrogen are accomplished by introducing a stream of hydrogen 54 into converter 12. Converter 12 is also pressurized to appropriate hydrocracking and hydrodesulfurization pressures which normally range from about 6 to about 130 atmospheres p.s.i. at temperatures of from about 450 to about 550° C. Catalysts may also be used in these processes. The preferred catalysts include oxides, halides, and sulfides of transition metal elements.

Dehydrogenation is carried out at low pressures and at temperatures of from about 450–950° C.

The operation of these hydrocarbon conversion processes according to the present invention has numerous advantages. For example, coke formation and deposition do not present a difficult problem. Coke is continuously removed from the conversion reactor with the molten salt stream and used as a reductant in the heat generation zone. Therefore, the catalysts used in the process of this invention do not undergo deterioration or fouling. In addition, due to the direct contact of the hydrocarbon with the molten salt, heat transfer in the cracking reactor is very efficient, and good temperature control can be attained. Finally, since hydrogen sulfide is completely converted to alkali metal sulfide in the conversion reactor, the gaseous products do not require desulfurization. Due to the high reactivity of the carbonate melt with organic sulfur compounds, a large fraction of the sulfur is removed from the liquid products also. Consequently, further refining of the cracking products is simpler and less expensive as compared to the refining of the products obtained by other cracking methods. In addition, all of the sulfur that is removed from the petroleum residual is recovered as hydrogen sulfide which can be conveniently converted to sulfur or sulfuric acid.

The following examples are illustrative of the basic principles of the invention.

#### EXAMPLE I

##### Thermal cracking of residual

A 550° C. + vacuum residual was thermally cracked in the presence of molten alkali metal carbonate eutectic. The residual can be described as follows:

TABLE II

##### Residual description

Yield on crude (wt. percent) -----	50.4
Yield on crude (vol. percent) -----	46.1
Rams bottom carbon residue (wt. percent) -----	25.1
Density at 15.6° C. -----	1.0689
Analysis (wt. percent):	
Sulfur -----	7.71
Carbon -----	80.36
Hydrogen -----	9.58

Fifty grams of this residual was added in 2–3 gram increments to a reservoir (10 cm. I.D. x 20 cm. height) below a packed column (5 cm. I.D. x 61 cm. height packed with 6.4 mm. alumina raschig rings). The packing was coated with 150 grams (50 g. each of Na<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub>) of alkali metal carbonate salt. The temperature of the entire system was maintained at 580° C. Helium (100 mls./min.) was used to purge the petroleum gases through (1) the packed column, (2) a water cooled condenser, (3) a Dry Ice-acetone cold trap, and (4) a gas chromatograph. The coke that was produced in the test was oxidized with oxygen and the prod-

uct, carbon dioxide, was collected and measured. The results of the test are as follows:

TABLE III

Material:	Yield (g.)
Coke -----	10.4
Oil (from condenser) -----	13.8
Light products (from cold trap) -----	6.3
Noncondensable gas -----	10.0

The remaining 20% of feed was believed to be predominantly represented by heavy tars and oils and coke which were trapped in the flow lines of the apparatus.

#### EXAMPLE II

##### Thermal cracking and dehydrogenation of ethane

Three hundred grams of a melt containing equal weights of Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub> contained in a ceramic crucible was used to crack and dehydrogenate ethane at various temperatures. The test involved purging ethane at 1 l./min. through the melt (7.5 cm. depth) and analyzing the products by gas chromatography. The reactions that took place are as follows:

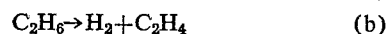


Table IV gives the results of the tests at various temperatures.

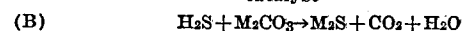
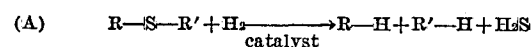
TABLE IV.—ETHANE CRACKING

Temperature (° C.)	Percent ethane reacted	Ratio, Reaction (b)/Reaction (a)
650.....	1	28
775.....	24	12
975.....	92	0.5

#### EXAMPLE III

##### Sulfur removal

The mechanism by which sulfur is removed during hydrocracking using molten carbonates may be represented as follows:



Both of these reactions have been demonstrated. For example, with the use of catalysts such as the oxides and sulfides of iron, cobalt, tungsten, nickel, and molybdenum. Reaction A is routinely carried out. Thus, it is apparent that metal sulfides can be used as catalysts. The addition of these catalysts to a molten alkali carbonate-sulfide mixture should not hinder their reactivity. In fact, sulfide, iron, and iron compounds such as iron sulfide have been found to catalyze the reduction of sulfate by hydrogen in a molten salt environment.

Reaction B has similarly been demonstrated. Thus, H<sub>2</sub>S, 130 cc./min., and CO<sub>2</sub>, 370 cc./min., were mixed in a mixing chamber and then bubbled through four inches of alkali metal carbonate melt consisting of reagent grade K<sub>2</sub>CO<sub>3</sub> (100 g.), Na<sub>2</sub>CO<sub>3</sub> (60 g.), and Li<sub>2</sub>CO<sub>3</sub> (100 g.). The reaction vessel was made of vycor and was heated to 500° C. with a Marshall electric furnace. The test was conducted for one hour, with melt samples taken at the beginning, middle, and end of the test. The evolved water was trapped with Mg (ClO<sub>4</sub>)<sub>2</sub> and the remaining gases analyzed by gas chromatography. Aliquots of the inlet and exit gases were injected into the chromatograph with a Perkin-Elmer sampling valve. Results are shown in Table V.

Initially, as indicated in the gas chromatographic results in Table V, nearly 100 percent of the H<sub>2</sub>S was absorbed, and at the end of one hour about 50 percent was still being absorbed.

TABLE V  
Inlet and Exit Gas Analysis for H<sub>2</sub>S/CO<sub>2</sub>  
Plus M<sub>2</sub>CO<sub>3</sub>

Time	CO <sub>2</sub>	H <sub>2</sub> S
Inlet.....	88	18.0
Exit 4 min.....	100	0.35
Exit 10 min.....	99	3.1
Exit 15 min.....	99	4.4
Exit 19 min.....	93	5.4
Exit 25 min.....	97	6.7
Exit 32 min.....	96	7.4
Exit 42 min.....	97	7.9
Exit 53 min.....	96	9.2

All numbers are relative peak heights on the gas chromatograph. This example illustrates the ability of an alkali metal carbonate melt to absorb H<sub>2</sub>S at elevated temperatures.

#### EXAMPLE IV

##### Heat generation

Twelve grams of coal were used to partially reduce 60 g. of sodium sulfate dissolved in 300 g. of an alkali metal carbonate melt in a ceramic crucible at a temperature of from 840–870° C. At the end of 15 minutes 44.7% of the sulfate was reduced to the sulfide; at the end of 25 minutes no further reduction of the sulfate had occurred. Therefore, the coal was assumed to have been completely expended during the reaction. The temperature of the system was allowed to stabilize. Air was then purged through the melt. At the instant the air purge was initiated, the temperature of the melt started to increase appreciably as a result of the oxidation of sulfide. It continued to increase until the air purge was stopped at which point the temperature of the melt began to decrease. For example, when air was purged through the melt at 2.1 l./min., the melt temperature rose from 891.5° C. to 918° C. in 3.0 minutes. Before and after the air purge, the melt was decreasing in temperature at a rate of about 6° C. per minute.

#### EXAMPLE V

##### Absorption of sulfur from coke during heat generation

A test was carried out in which fluidized coke was continually added to an alkali metal carbonate eutectic melt (315 g.) containing initially 15 g. sodium sulfate at 1472° F. (800° C.). At the same time air was purged through the melt in order to reoxidize the sulfide to sulfate. The test was terminated after 192.4 g. of coke had been added and all the sulfide had been converted back to sulfate. Table VI gives the results of this test.

TABLE VI

TABLE VI.—ACCUMULATION OF SULFUR IN THE MELT

	M <sub>2</sub> SO <sub>4</sub> (wt. percent)	S (wt. percent)	S (g.)	S added <sup>1</sup> (g.)
Outlet.....	4.53	1.06	3.34	0
Conclusion.....	7.50	1.76	5.54	2.67

<sup>1</sup> Assuming coke to contain 1.39% S, as stated by Phillips Petroleum Co.

These results show that the sulfur content of the melt increased by 2.2 g. while theoretically 2.7 g. of sulfur were added to the melt. The sulfur accumulation in the melt represents 81% of the theoretical addition. Therefore, during heat generation substantially all the sulfur will remain with the melt and not end up as an air pollutant.

#### EXAMPLE VI

##### Effect of temperature and iron on reduction rate

Tests were carried out to determine the effect of iron and temperature on the reduction of sulfate with coke. For the control test an alkali metal eutectic carbonate-sulfate melt containing 100.8 g. K<sub>2</sub>CO<sub>3</sub>, 11.8 g. Li<sub>2</sub>CO<sub>3</sub>, 37.0 g. Na<sub>2</sub>CO<sub>3</sub>, and 84.9 g. Na<sub>2</sub>SO<sub>4</sub> (25% M<sub>2</sub>SO<sub>4</sub>) was reduced with 2.5 times stoichiometric coke (36 grams). To determine the effect of iron on the reduction rate the melt con-

sisted initially of 100.8 g. K<sub>2</sub>CO<sub>3</sub>, 11.8 g. Li<sub>2</sub>CO<sub>3</sub>, 52.4 g. Na<sub>2</sub>CO<sub>3</sub>, 64.3 g. Na<sub>2</sub>SO<sub>4</sub>, and 40.3 g. FeSO<sub>4</sub>·7H<sub>2</sub>O (25% M<sub>2</sub>SO<sub>4</sub>). Melt samples were taken periodically throughout each test and they were analyzed for sulfate, sulfide, and carbonate. The results of these tests are presented in Table VII.

TABLE VII

##### Reductions with coke

Conditions:	Reduction time (hrs.)
600° C. ....	<sup>a</sup> 91
700° C. ....	2.9
700° C. with Fe .....	1.9
800° C. ....	0.50
800° C. with Fe <sup>b</sup> .....	0.23

<sup>a</sup> Based upon the first 31.5% reduced (28.5 hrs.).  
<sup>b</sup> Mechanical agitation, as opposed to agitation by means of a purge gas, was employed in this experiment.

The invention has been described herein with reference to preferred embodiments and specific examples. However, it will be apparent to those skilled in the art that many other modifications, adaptations and uses of this hydrocarbon conversion process are possible without departure from the spirit and scope of the invention as defined by the claims below.

We claim:

1. A closed-cycle method for the conversion of hydrocarbons into more valuable products comprising the steps of:

(a) contacting said hydrocarbons with hydrogen and an alkali metal carbonate melt containing from about 1 to 25 wt. percent sulfur in the form of alkali metal sulfide in a conversion zone at a temperature from about 400 to 1100° C. to form valuable hydrocarbons and coke,

(B) separately recovering said valuable hydrocarbons from said conversion zone,

(C) withdrawing said melt containing said coke from said conversion zone,

(D) feeding said withdrawn melt from step (C) to a heat-generation zone wherein said withdrawn melt is contacted with a reactive form of oxygen at a temperature between about 600 and 1200° C. whereby said coke and oxygen are consumer according to the reactions,



thereby heating the melt, and

(E) circulating heat-supplying melt from said heat-generation zone to said conversion zone.

2. The method of claim 1 wherein said hydrocarbons are selected from a member of the group consisting of light hydrocarbons, naphtha, kerosene, refinery gas, natural gas, light gas oil, heavy gas oil, atmospheric residuals, tar, vacuum residuals, crude oil, coal, oil shale and tar sands.

3. The method of claim 1 wherein said reactive form of oxygen is air.

4. The method of claim 1 wherein Reactions 1 and 2 are carried out in separate portions of said heat generation zone.

5. The method of claim 1 wherein said heat-generation zone is undivided, Reactions 1 and 2 being carried out together, and wherein said oxygen is controllably fed in preselected amount at less than that stoichiometrically required for oxidation of the coke present in the melt so that under steady-state operating conditions the sulfur present in the melt is maintained substantially all in sulfide form and substantially free of the sulfate form.

6. The method of claim 1 wherein said melt contains from about 0.5 to about 7 weight percent iron.

7. The method of claim 1 wherein a supplemental supply of coke is added to said heat generation zone.

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8. The method of claim 1 wherein said melt contains a catalyst selected from a member of the group consisting of oxides, halides and sulfides of a member of the group consisting of iron, cobalt, molybdenum, tin, nickel and tungsten.

9. The method of claim 1 wherein step (A) includes hydrocracking in said conversion zone.

10. The method of claim 1 wherein step (A) includes hydrodesulfurization in said conversion zone.

11. The method of claim 10 wherein a portion of said heated melt from step (D) is treated to remove a portion of its sulfur content prior to the returning of said heated melt to step (A).

12. The method of claim 11 wherein said melt from step (D) is treated with a gaseous mixture containing carbon dioxide and steam to form hydrogen sulfide gas as a recoverable product and at the same time regenerate

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alkali metal carbonate for recirculation in the process to step (A).

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U.S. Cl. X.R.

44—196, 197, 210, 211; 208—46, 106, 108, 113, 125, 213; 260—683 R

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,745,109 Dated July 10, 1973

Inventor(s) L. A. Heredy et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 1 "formed" should read --former--.  
Column 4, line 14 "steam" should read --stream--.

Column 6, line 48 delete "reactor".  
Column 10, line 30 "(a)" should read --(A)--;  
Column 10, line 44 "consumer" should read --consumed--.  
Column 12, line 8 "3,553,270" should read --3,553,279--.

Signed and sealed this 8th day of January 1974.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

RENE D. TEGTMEYER  
Acting Commissioner of Patents