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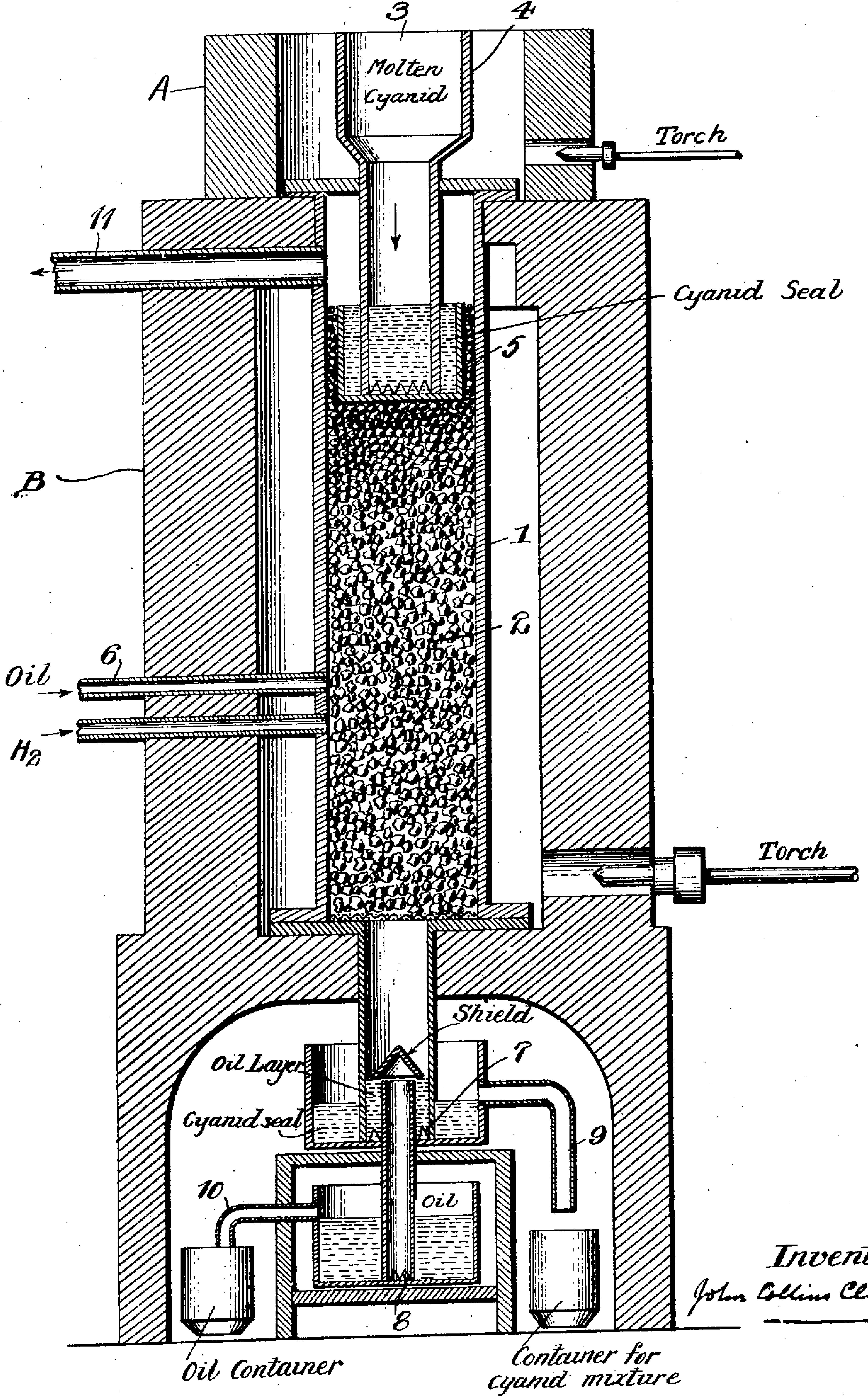

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PROCESS OF CRACKING OILS.

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This invention relates to the manufacture of gasolene from heavier oils.

Many processes have been suggested for the treatment of hydrocarbons for the production of gasolene or gasolene substitutes based on the known fact that, when the vapor of a heavier hydrocarbon, such for example, kerosene, crude oil, coal oil, tar oils, or other hydrocarbons is heated to a cracking temperature, a splitting up of the heavy molecules into molecules of lower molecular weight together with the generation of hydrogen and formation of tar and free carbon takes place. It has been recognized that the cracking action is facilitated by the presence of catalysts, such for example, as metals like nickel, cobalt, copper, silver, palladium, chromium, and manganese or the oxids of these metals. One of such processes comprises passing the oil or oil vapor over the surfaces of metal catalysts which have been formed into regular or irregular briquettes, balls, tubes, screens, fragments of heat resisting material coated with metal or with some metal compound which can be reduced to metal by the action of the hydrocarbon. These catalytic masses above referred to are introduced into tubes or pipes made of iron or earthenware heated to about red heat and traversed by the vapor of the hydrocarbon to be cracked. However, the above mentioned and other similar processes heretofore suggested suffer from the difficulties involved in keeping the catalytic surfaces free from deposited soot or carbon which coats the contact material and brings about cessation of the catalytic activity of the contact material. It is noted in this connection that aside from the deposition of soot, the sulphur present in the hydrocarbon vapor or oil being treated attacks the metal catalyst to render it non-active, commonly termed poisoned. Again, the hydrogen set free by the thermal decomposition of the hydrocarbon is prevented from functioning to hydrogenate the unsaturated hydrocarbons formed in the process owing to the coating of the catalytic surfaces with carbon and the formation of metal sulphides as aforesaid.

An object of my invention is a process for the production of gasolene from heavier oils in which some of the objectionable features of prior processes are avoided.

My process broadly comprises reacting upon a hydrocarbon oil or vapor with a molten body containing a cyanogen compound in presence of a solid catalyst. The process, more specifically, is characterized by the fact that the molten body and the hydrocarbon to be treated are contacted with each other in a reaction zone or chamber in the presence of and in contact with solid masses of catalytic material which retain their physical form and position and serve not only as a catalyst for the cracking reaction, but also as supporting and distributing packing units for the contacting of the molten body with the hydrocarbon. The process is further characterized by the fact that thiocyanates are formed by the action of the cyanid contained in the molten body with the sulphur contained in the hydrocarbon material being treated. This action of the molten cyanid forming thiocyanates with the sulphur contained in the oil keeps the catalytic surfaces free from catalyzer poisons. Still a further characteristic feature of the process is; that the cracking is effected in a reaction zone or chamber to which the molten material, such for example, a molten mixture of sodium cyanid and sodium thiocyanate is supplied through a trapped inlet and from which the molten reaction products together with the carbon (soot) and unvaporizable hydrocarbons at the temperature employed is discharged through trapped outlets, the oil or hydrocarbon to be treated being supplied to and its decomposition products withdrawn from the reaction chamber respectively without interruption or interference with the continuity and established reacting conditions of the process. Another characteristic of the process resides in the use of the molten material to hold in suspension the carbon separated in the process of cracking. This property of the molten cyanid containing material to carry considerable or substantial amounts of carbon in suspension together with its desulphurizing action on the metal sulphides formed on the catalytic units keeps the catalytic surfaces of said units free from substances which check catalysis. The obtainment of this result by the use of said molten material allows the hydrogen present in the decomposition products or the hydrogen or hydrogen containing gases which may be introduced into the reaction zone together with the hydrocarbons to be treated, the opportunity of hydrogenating the unsaturated hydrocarbons formed in the cracking operation thereby producing substantial amounts of saturated lighter hydrocarbons. Further features of this invention will appear hereinafter as the invention is described in detail.

Fused sodium cyanid in admixture with sodium thiocyanate is fed into a closed furnace shaft through a sealed inlet on to a tower filling of packing units formed of or comprising the catalytic agent heated to a temperature of 400 to 600° C. or higher. The molten material flows or trickles downwardly through the catalytic packing units and a flow of the hydrocarbon to be treated is supplied to the furnace shaft at or near the lower end. In case the hydrocarbon is supplied in the liquid phase it is immediately converted in part at least into the vapor phase, that is, the part which will vaporize at the temperature maintained in the furnace ascends while the higher boiling point or unvaporizable hydrocarbons will be discharged together with the molten material out through the trapped outlets. The lower end of the furnace is closed to the atmosphere and is provided with sealed outlets for the molten reaction products as aforesaid. At the upper end of the furnace shaft is an outlet for the gases and vapors formed by the treatment in the reaction zone. Molten material containing sodium cyanid and the oil or hydrocarbon vapor with or without admixture of hydrogen or hydrogen containing gases are continuously supplied to the furnace shaft at top and bottom respectively and the gases constituting the hydrocarbons formed in the cracking process and the molten reaction products are withdrawn from the furnace shaft at top and bottom respectively the temperature of the furnace being maintained by external heating of the retort by the burning of fuel. Obviously of course the temperature of the furnace may be maintained by the passage of an electric current through a resistor embedded in the packing units, or by using the packing units as a resistor if cheap electrical energy is available.

Sodium cyanid in admixture with sodium thiocyanate are the preferred cyanogen compounds employed in the process principally because they give satisfactory results and are inexpensive. Instead of sodium cyanid I may employ other alkali metal cyanids, such for example, potassium cyanid, alkali metal thiocyanates, as for example, sodium thiocyanate or I may employ mixtures of sodium thiocyanate with alkali cyanids. In working the process however the discharged molten material contains considerable amounts of sodium thiocyanate especially when working with oils of high sulphur content. This material after removing the carbon by filtration of the discharged molten body is used over and over again by replenishing same with fresh sodium cyanid.

I have found by numerous tests that the best results are obtained by using a mixture of 25 parts of sodium thiocyanate to 75 parts of sodium cyanid as the molten material in the cracking of hydrocarbons, by using this proportion the melting point of the cyanogen compound mixture is reduced to 400° C. or lower. The melting point of sodium cyanid by itself is around 587° C., the melting point of sodium thiocyanate approaches 300° C., it is evident that a wide range of melting points can be obtained by varying the proportion of the above mentioned compounds. The addition of small quantities of alkali salts such, for example, sodium carbonate, potassium carbonate and the like influences the melting point considerably. However, I use preferably a straight mixture of sodium cyanid and sodium thiocyanate as above referred to when working the process, as this mixture when heated to around 400° C., assumes the liquid phase and thus permits of operating with sodium cyanid in the molten state at temperatures ranging from 400 to 600° C., and higher. When the thiocyanate content of the cyanogen bearing material discharging from the furnace exceeds 25% to 30% by weight it is desulphurized by adding or fusing it with iron at a high temperature to remove the sulphur in the form of iron sulphide, the fusion product filtered from the iron sulphide can be used again as the contacting molten body for use in the process.

Among the hydrocarbons which may be used in the cracking process for the production of gasolene or a gasolene substitute are the hydrocarbons of the paraffin series such as crude petroleum, kerosene, coal tar oils, tar oils, shale oils and the like. I have obtained excellent results by spraying crude Mexican petroleum oils directly into the reaction zone in company with hydrogen and also with hydrogen containing gases such, for example, the uncondensable gases obtained after condensing out the liquid hydrocarbons from the cracked decomposition products. I have also obtained excellent results by spraying into the reaction chamber finely pulverized solid shale and also finely pulverized coal. However, the present case contemplates only the use of liquid hydrocarbons such as those above referred to and I merely mention the treatment of material containing solid hydrocarbons to show the wide applicability of the process.

With regard to the catalytic material for the process I have discovered that there are a great variety of materials which may be used and there are a number of ways of forming and handling catalytic material. The catalytic material serves two purposes in the process, first, it promotes the cracking and hydrogenation reaction, and second, it serves as a distributing contact surface for the reacting materials. The catalytic material must therefore be a material which promotes the hydrogenation reaction, and it must be capable of withstanding the temperature and the action of the molten cyanids without fusion or disintegration.

The catalytic material is employed in the physical form of packing units of either irregular or regular shapes which may be associated as a packing material in either promiscuous or a symmetrical arrangement.

The packing units may be formed wholly of one catalytic material or a mixture of two or more catalytic materials or they may comprise one or more of the catalytic materials mixed with or bonded by other non-catalytic substances, or the units may be formed of material capable of being converted to a catalytic material. For instance, units may be formed or molded from a single metal in mass or an alloy of two or more metals capable of forming the said units.

Metals which I have found to possess the required characteristics, that is, the capability of catalyzing or hydrogenizing the unsaturated hydrocarbons in presence of a molten cyanogen compound are nickel, cobalt, copper, chromium, tantalum, silver and palladium. When using the metals above referred to as packing units I prefer to shape them into forms of packing units such as the so-called Raschig rings about one inch in diameter. I also prefer a mass or column of catalytic packing units comprising a plurality of layers of different catalytic materials. For example, assuming that the distance from the bottom of the furnace is ten feet in height, the lower three feet is filled with copper packing units, the next three feet is filled with an equal mixture of units of cobalt and copper, the next four feet is filled with straight nickel packing units. The packing units are preferably as aforesaid in the form of Raschig rings about one inch in diameter. The purpose of the different catalysts in the reaction zone is to take advantage of the specific action of the different metals.

In carrying my process into practise I use an apparatus of the general type of gas scrubbing tower constructed of iron or other heat resisting materials and provided with trapped outlets and trapped inlet. The retort or scrubbing tower is filled with packing units in the manner heretofore described. The retort or scrubbing tower is heated on the outside to about 600° C. by burning fuel in a furnace built around same. In other words, the apparatus is run similarly to a gas scrubbing tower with the exception however, that it differs only in that the tower or retort is heated externally and supplied with molten cyanid through the trapped inlet instead of an aqueous liquid or the like as is ordinarily used as a scrubbing fluid in gas scrubbing tower practise.

In the drawing which forms a part hereof, I have exemplified an apparatus whereby the process may be carried into effect.

In said drawing, the figure shows a vertical cross section of a tower or retort containing the catalytic packing units, and provided with gas and other connections, hereinafter described.

The tower 1, filling of packing units 2, is heated in part by the heat contained in the previously prepared molten cyanid mixture 3, and is kept molten in the funnel charging hopper 4, by the external heat supplied by the furnace A. The molten cyanid flows over the edge of the trap pot 5, and trickles downwardly through the packing units countercurrent to a flow of hydrocarbon vapor supplied through the pipe 6, from an adjoining still or the oil may be sprayed directly into the scrubbing tower at or near the bottom as at 6. The lower end of the scrubbing tower or retort is closed to the atmosphere and is provided with the sealed outlets 7 and 8 for the molten reaction product and unvaporized oil respectively. At the upper end of the scrubbing tower or retort is an outlet 11 for the hydrocarbon vapors and gases which have undergone treatment in contact with the molten cyanid material and packing units. Molten cyanid and the hydrocarbon oil or vapor to be treated are continuously supplied as at 3 and 6 to the scrubbing tower or retort at the top and bottom respectively and converted hydrocarbons and molten reaction products are withdrawn from the scrubbing tower as at 11, 9 and 10 at the top and bottom respectively, the temperature of the scrubbing tower or retort being maintained and controlled by the heat supplied by the furnace B.

In practise I aim at making the process continuous. Under proper regulation and conditions which are readily controllable the process operates continuously with excellent yields of low boiling saturated hydrocarbons. The gases emanating from the scrubbing tower or retort may pass into a dephlegmator or fractionating column, which may be suitably arranged to yield as fractions a gas oil and unconverted kerosene, if the latter is employed as the raw material. Either or both of these products may be returned to the reaction zone for further decomposition if desired.

The lighter oils or volatile spirits are condensed in either a dephlegmator or condenser or the well known absorption process may be used and the gasolene distilled from the absorption oil used. The condensed product requires no further treatment, as for example, refining by means of sulphuric acid and alkali or like treatment. The uncondensable gases after removal of the liquefiable hydrocarbons may be used as fuel for heating purposes and also as the hydrogen containing gases used to admix with the hydrocarbons to be treated. The function of these gases as aforesaid is to effect hydrogenation by the action of their free hydrogen content when exposed to the catalytic surfaces under conditions prevailing in the herein described process.

The use of the cyanid material in the molten state, very substantially reduces the amount of fuel required for the external heating of the reaction chamber and consequently reduces the cost of operation while at the same time permitting thorough and uniform and readily controlled heating of the catalytic filling wherein the pyrogenetic decomposition of the hydrocarbon material is effected, this together with the desulphurization and hydrogenation of the hydrocarbon products produced is a very important and advantageous feature of the process.

The points to be observed for the successful operation of my process are more or less obvious in view of the foregoing description.

It will be apparent that many processes and many different forms of apparatus may be devised which will fulfill the conditions required in the process.

I claim:

1. The process of making gasolene like material from heavier hydrocarbon oil which comprises, cracking such heavier oil by commingling it with a molten body containing alkali metal cyanid in the presence of a metallic catalyst maintained at cracking temperature.

2. The process of making gasolene like material from heavier hydrocarbon oil which comprises, cracking said heavier oil by commingling it with a molten body containing sodium cyanid in the presence of a metallic catalyst maintained at cracking temperature.

3. The process of making gasolene like material from heavier hydrocarbon oil which comprises, cracking and desulfurizing such heavier oil by subjecting the same to the action of molten sodium cyanid in the presence of a metallic catalyst maintained at a cracking temperature.

4. The step in the herein described process of converting higher boiling oils into lower boiling oils which comprises, contacting such higher boiling oils with a molten body containing sodium cyanid in the presence of a metallic catalyst maintained at a cracking temperature, and collecting the evolved hydrocarbon vapors and gases.

5. The process of producing gasolene like material from heavier hydrocarbon oil which comprises, catalytically cracking such heavier oil by commingling the same with a molten body containing sodium cyanid and sodium thiocyanate in the presence of a metallic catalyst maintained at a cracking temperature.

6. The step in the herein described process of making a gasolene substitute which comprises contacting molten sodium cyanid with hydrocarbon material heavier than gasolene in the presence of a metallic catalyst maintained at cracking temperature.

7. The process of producing gasolene like material from heavier oil which comprises flowing said oil in the presence of hydrogen into contact with a molten body containing sodium cyanid through a retort filling of nickel packing units maintained at cracking temperature, supplying the said molten body to and withdrawing the reaction products comprising molten material and unvaporized oil from the retort filling of packing units through liquid sealed passages, and collecting the evolved vapors and gases from the retort.

8. The process of making a gasolene substitute the step comprising, contacting molten sodium cyanid with a hydrocarbon heavier than gasolene in the presence of a solid catalyst comprising nickel at cracking temperature.

Signed at New York city in the county of New York and State of New York, this 1st day of September, A. D. 1922.

JOHN COLLINS CLANCY.