July 25, 1944. A. J. ABRAMS 2,354,354

HYDROCARBON CONVERSION

Filed Oct. 22, 1941

Fig. 1.

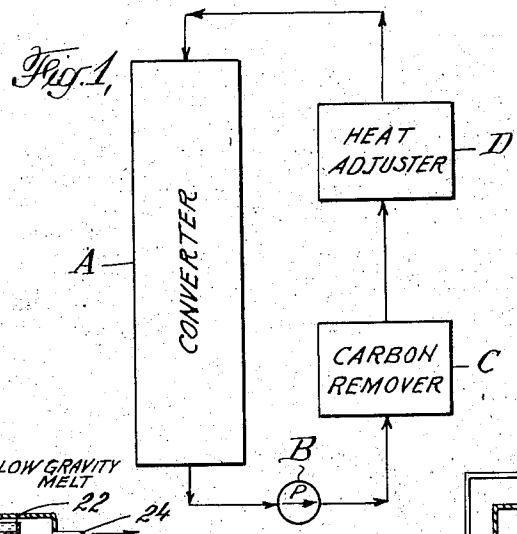


Fig. 2.

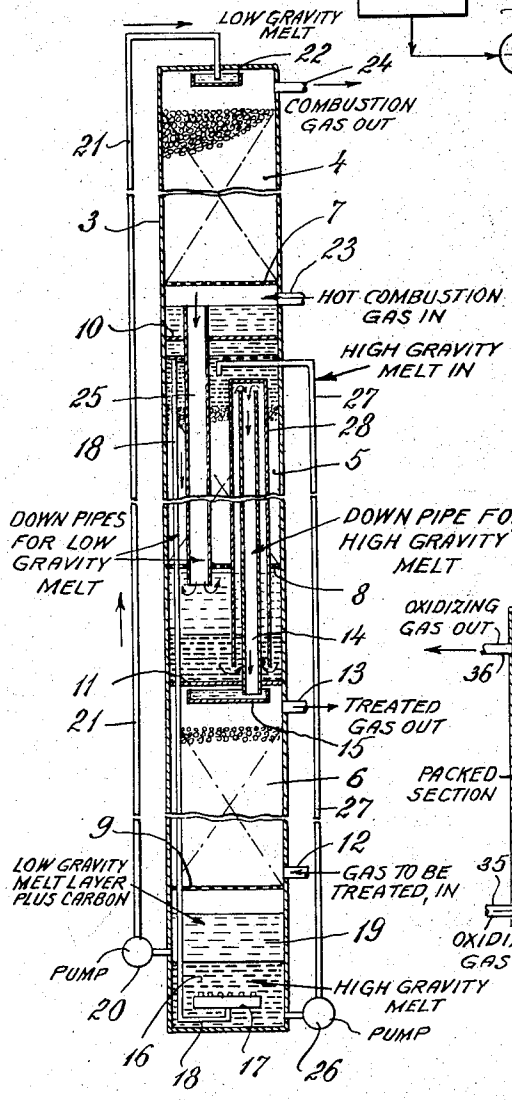
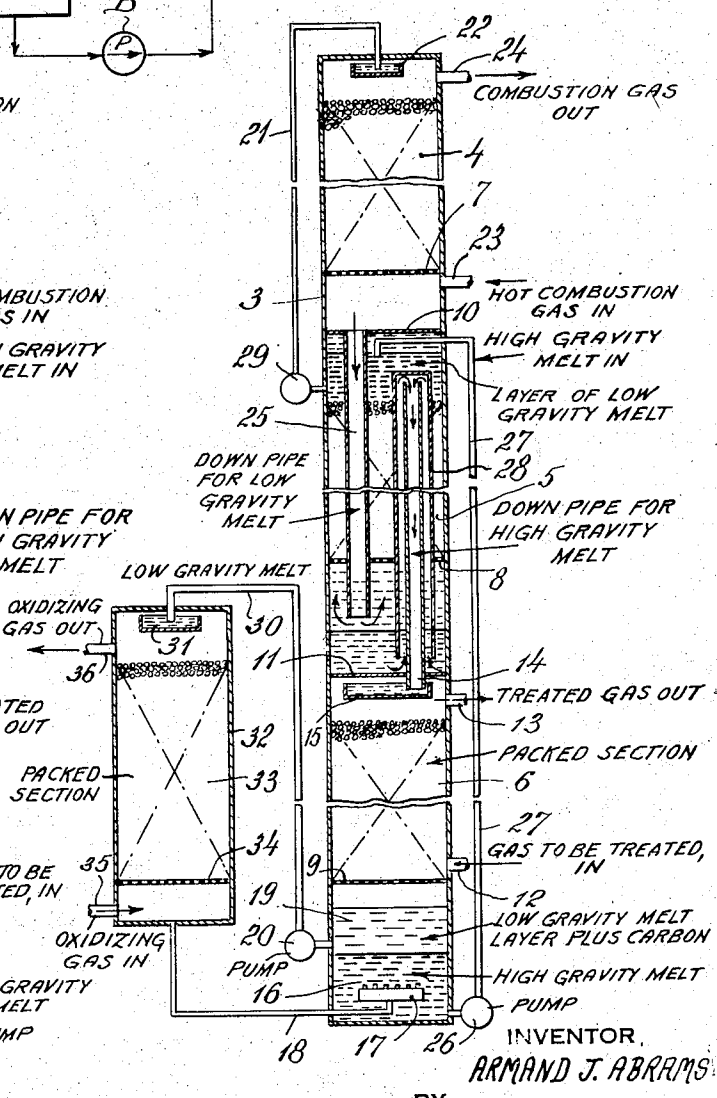


Fig. 3.



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HYDROCARBON CONVERSION

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7 Claims. (Cl. 196—70)

This invention relates to the thermal or non-catalytic conversion of hydrocarbons. More particularly, the invention is concerned with thermal conversion of hydrocarbon vapors or gases wherein heat is conveyed to the hydrocarbons by a liquid heat exchange medium in a novel and efficient manner and in a manner that is practical over a very wide range of temperatures thereby making the process applicable to all hydrocarbon conversion processes including high temperature conversion processes for the light hydrocarbon gases.

The art is replete with processes for the thermal conversion of hydrocarbons. Most of these prior art methods involve transfer of heat through a confining wall to the hydrocarbons. Such indirect heat exchange methods are subject to a practical limitation on their upper temperature and, therefore, on the operations that may be carried out. For example, in order to convert methane in this manner to valuable products would require very expensive equipment of limited life, as the refractory tube furnace involved in this operation would have to be exposed to a much higher temperature than that required by and which would reach the confined methane. On the other hand, methods have been proposed for directly contacting hydrocarbons with a heat transfer agent. This type operation has shown up in embodiments where the hydrocarbons are brought into direct contact with vapors of metals or other suitable inorganic substances, or where the hydrocarbon vapors have been bubbled through a liquid body of the heat transfer agent. It is apparent that where vapors of metals or other inorganic substances are used as a direct heat exchange agent, that the range of materials which may be used for the treatment of the lighter hydrocarbons is rather limited and that the conditions for recovery of the agent are not very favorable. Processes which use a liquid body of the heat transfer agent for direct heating of vapors passed therethrough do not seem to have made much impression on the art. A serious drawback to such methods is the carbon accumulation in the heat transfer agent. Furthermore, apparatus and operation requirements for forcing the hydrocarbons through the body of liquid are usually objectionable. Again, as these processes have been conceived heretofore, the heat transfer agent itself is usually heated by indirect means, thereby somewhat restricting their range of usefulness. None of these processes are known that have been applied successfully to the conversion of the lighter hydrocarbons such as methane, ethane and propane.

Therefore, it is an object of this invention to provide a process for the thermal conversion of hydrocarbons which provides adequate temperature control and which is capable of doing this over a very wide range of temperature, thereby making the process applicable for substantially any elevated temperature conversion process.

Another object is to afford a process for directly contacting the hydrocarbons with a liquid heat exchange medium which makes adequate provision for the removal or disposal of carbon.

The above objects and other objects will be apparent from the following description of my invention.

According to the preferred embodiment of my invention, the hydrocarbons are passed in gaseous phase through a packed conversion zone in direct contact with a liquid heat exchange medium which flows through the zone under non-flooding conditions. The packing in the zone is an inert material which is not appreciably wetted by the heat transfer agent and serves merely to spread the agent into films which provide large surface areas for contact with the hydrocarbons. In this manner I provide better contact surface for heat transfer and, therefore, better heat transfer than when hydrocarbons are passed through a flooded tower, i. e., a tower wherein all the voids are flooded with the liquid heat exchange medium. Moreover, it is much easier to pass the proper amount of hydrocarbon vapors through my non-flooded tower. Therefore, it will be understood that baffling arrangements other than packing, may be used, if desired, to provide films of heat transfer agent in the conversion zone which are exposed to hydrocarbon vapors.

My invention involves the further principal that the liquid heat transfer agent is brought into direct contact with at least a second fluid agent after leaving the conversion zone in order to recondition its physical characteristics so that it is again ready to be used in the conversion zone. This second agent may remove carbon from the heat transfer agent or it may regulate the temperature of the heat transfer agent for re-use in the conversion process or it may do both.

Therefore, perhaps, one of the simplest embodiments of my invention comprises a system in which a liquid heat exchange medium flows in a cycle through a packed conversion zone under non-flooding conditions in direct contact with

hydrocarbon vapors or gases which are converted therein, then the liquid medium flows through an external circuit in which the agent is brought into direct contact with a combustion-supporting gas under combustion conditions whereby carbon is removed from the agent and its proper heat content is restored, and then the agent passes again to the conversion zone to complete the cycle. It will be understood that if the heat furnished by the combustion step is not sufficient, additional heat may be added to the liquid heat transfer agent in suitable manner prior to its return to the conversion zone.

However, in order to attain proper temperatures or because of economic reasons, etc., it is not feasible, in many cases, to use a material for directly contacting the hydrocarbons which material can have carbon removed from it by combustion. Hence, my preferred system involves the use of at least two liquid agents. I have devised a novel manner of using these agents to attain the desired results which requires that the agents possess an appreciable difference in gravity. Thus, for example, a high gravity, oxygen-sensitive liquid agent may be used for direct heat transfer with the hydrocarbons and for carrying carbon out of the conversion chamber, and a low gravity, oxygen-insensitive liquid agent may be used for scrubbing carbon from the first agent. Then the low gravity agent may have the carbon removed from it by combustion and the high gravity agent may have its heat content restored either by directly contacting with a third fluid agent or by again directly contacting with the low gravity agent after carbon has been removed from the low gravity agent by combustion and it is at a high temperature level. It is also to be understood that the scrubbing liquid may be brought to a high temperature first whereby the heating and scrubbing of the liquid heat transfer medium is accomplished simultaneously in one step.

Another important advantage of this system is that the oxygen-insensitive agent may be brought up to desired temperature with a direct flame furnace. This would be the only furnace needed since the oxygen-sensitive agent is heated by contact with the heated, oxygen-insensitive agent. The economies in operation and furnace construction afforded by this advantage are clear.

It should be obvious, therefore, that merely by proper choice of heat transfer agents from the vast number of liquid or molten materials available of diverse boiling points that my process may be applied with ease to an operation of almost any temperature range.

I particularly prefer to use molten metals or alloys, which possess suitable melting points and boiling points for the operation in question, for the high gravity, liquid heat transfer agents. These high gravity melts should be selected, of course, so that they do not endanger the apparatus or packing to be used. Molten lead is practical for most hydrocarbon conversion processes.

If a liquid agent is to be used for scrubbing carbon from the liquid heat transfer agent, such as, for example, one of the melts mentioned above, then this scrubbing agent must be resistant to oxidation, must be of appreciably lower density than the heat transfer agent and must be immiscible therewith. In case the heat transfer agent is a high gravity molten metal or alloy, then, of course, there are many low gravity liquids that may be used for scrubbing, such as, for example, molten inorganic salts and molten salt mixtures.

In case a third liquid agent is used for heating the heat transfer agent used in the conversion zone, then this third agent must be of different gravity than the heat transfer agent and immiscible therewith. The same material which serves as a scrubbing agent is usually the most practical material to use as this third agent.

For the purpose of illustrating the invention more fully, reference is now made to the accompanying drawing which shows preferred embodiments in a diagrammatic form of suitable apparatus for carrying out the present invention.

Referring to Figure 1, there is shown essentially a flow diagram of my system. Thus, the direct heat exchange medium flows under non-flooding conditions through the conversion case A in direct contact with the hydrocarbons which are thereby converted. The heat transfer agent then is circulated by pump B through carbon remover C, heat adjuster D and back to conversion case A. As explained hereinbefore, in some instances, the heat transfer agent used in case A may not be oxygen sensitive. In this event, carbon remover C and heat adjuster D may be one and the same unit where the carbon is removed from the agent by combustion. On the other hand, if the heat transfer agent is oxygen sensitive, it may be scrubbed in C with an oxygen-insensitive agent which is later contacted with a combustion-supporting agent for removal of carbon. If this is done, the heat content of the heat transfer agent is adjusted in D by direct contact with a third agent which may or may not be the same agent used in carbon remover C. It also is to be understood that if removal of carbon is not necessary in the process being conducted, then carbon remover C may be eliminated from the system.

Turning now to Figure 2, there is disclosed a vertical structure comprising a container 3, in which there are three packed sections 4, 5, and 6, the packings therein being supported respectively by grates or screens 7, 8 and 9. These sections are isolated one from another by partitions 10 and 11. The packings may be of any kind, such as ceramic shapes, Raschig rings of ceramic or metal nature or any other kind of packing appropriate for the purpose of spreading and, in general, promoting of better physical contact.

Hydrocarbon vapors to be converted are introduced through pipe 12 and after their passage through packing 6, wherein the conversion desired is accomplished, the products of conversion depart through pipe 13. These vapors are, of course, at or near the temperature for the desired reaction when introduced at 12. Heat control of the reaction is accomplished by physically contacting the vapors while in the contact mass with a liquid heat transfer medium, such as molten lead, for example, which is introduced by pipe 14 into distributor 15 and flows down through contact mass 6 in physical contact with vapors passing therethrough and collects in pool 16 at the bottom of tower 3. Control of the temperature of this heat transfer medium is accomplished in a manner later described.

It has been discovered that the liquid heat transfer medium removes from the conversion zone, where it is in direct contact with the hydrocarbons being converted, a large proportion of the cokey and solid carbonaceous side products and residues which may be produced by the desired conversion, and therein lies a major advantage of

the process. It has further been found also that these cokey materials may be largely removed from the heat transfer medium by scrubbing with a lighter immiscible liquid. In order to take advantage of these discoveries, there is provided in pool 16 a distributor head 17, through which a lighter or lower gravity scrubbing liquid is introduced from pipe 18. This scrubbing liquid passes through pool 16 of heavy liquid and collects in pool 19. The heavy heat transfer liquid must pass through pool 19 in descending to pool 16 at the bottom of tower 3, thus effecting a liquid-liquid scrubbing which transfers cokey material from the heavy liquid to the lighter liquid. The lighter liquid is then removed from pool 19 by pump 20 and pipe 21, and introduced through spreader 22 into the top of packed section 4, where, in passing through the packing therein, it is contacted with a combustion gas or heated combustion-supporting gas, as necessary, introduced by pipe 23 and removed by pipe 24. This gas is for the double purpose of heating the low gravity liquid or melt, and for removing therefrom, by combustion, the cokey material acquired in the bottom of the reaction vessel. From the collection space above partition 10, the collected, heated, low gravity melt flows down through pipe 25 to a point below grate 8 in the central section of the tower, and up through packing in section 5, to collect in the top of this intermediate section, from which it is withdrawn by pipe 18. In this manner, the intermediate packed section 5 is maintained flooded with low gravity melt. The purpose of this intermediate packed section 5 is for the direct transfer of heat from the heated low gravity melt to the high gravity melt which latter is the liquid heat transfer medium utilized in the conversion section 6. To this end, the high gravity melt is taken from pool 16 by pump 26 and forced through pipe 27 into the upper portion of the intermediate or heat exchanger section 5, where it passes down through the packing in this section in direct contact with the heated, low gravity melt to collect in a pool above partition 11, wherefrom it is removed by the overflow tube and trap 28. The internal pipe 14 of this latter element extends through partition 11 to deliver the heated, high gravity heat transfer medium to distributor tray 15 in the conversion section 6.

In certain circumstances, it may be found that the low gravity melt most suitable for scrubbing cokey material from the high gravity melt is not the fluid most suitable for heat transfer purposes for heating the high gravity melt. In these circumstances, as shown in Figure 3, the combined regeneration and heating functions of section 4, as shown in Figure 2, may be separated. In Figure 3, the functions and internal construction of the conversion section and the heat exchanger section are materially unchanged from those of Figure 2, and the construction of the upper section 4, is materially unchanged; therefore, like numbers with like significance, are used for corresponding parts, the description of which will not be repeated. The differences are as follows:

The low gravity melt used for heat transfer in the intermediate heat exchange section 5 does not flow to the bottom of the reaction vessel to act as a scrubbing medium, but is returned to the heating step directly by pump 29 and pipe 21.

The low gravity melt used for scrubbing in the bottom of the reaction vessel and removed from pool 19 by pump 20 is passed through pipe 30 into distributor 31, located inside regenerator chamber 32 where it flows down through packing 33 supported therein on grid 34. In chamber 32, this melt is cleaned of carbonaceous material by being contacted under combustion conditions with an oxidizing gas introduced through pipe 35 and removed through pipe 36, and, after cleaning, this low gravity melt is returned to tower 3 by pipe 18 for scrubbing purposes.

In its simplest form, as explained above in discussing Figure 1, the process is one employing a liquid heat transfer medium which may be reheated and cleaned by direct methods and without the interposition of a second liquid. In this case, the apparatus would consist merely of a reaction vessel and a combined regenerator-heater, with one liquid heat transfer medium circulating over both, but since most of the materials most useful as the main liquid heat transfer medium are susceptible to oxidation, this variant will not usually be encountered.

It is to be understood that where specific materials are named herein for use as melt or packing, that they are used for exemplary purposes only, and that the invention must be understood as not being limited thereto or thereby, but as being subject only to such limitations as are expressed in the claims.

The use of an oxygen-insensitive liquid heat transfer medium and the subsequent purification and reheating of this medium directly by contact with a combustion supporting gas under combustion conditions is claimed in my copending application Serial No. 505,797 filed October 11, 1943.

I claim:

1. The process of thermally converting hydrocarbons which comprises passing the hydrocarbons in a gaseous state under conversion conditions through a conversion zone packed with inert contact material, flowing a molten metallic heat transfer medium of high gravity through said zone in direct contact with said hydrocarbons but in insufficient amount to flood the voids of the packing whereby heat is transferred to the hydrocarbons and carbonaceous residue produced as a by-product of the conversion is carried along in the liquid medium, removing high gravity melt from the conversion zone, scrubbing the removed high gravity melt in a scrubbing zone with a low gravity melt of an inorganic salt which is immiscible with the high gravity melt and which is not sensitive to oxygen under combustion conditions thereby transferring the carbonaceous residue to the low gravity melt, directly contacting said removed high gravity melt with a heated liquid of different gravity and which is immiscible therewith to adjust the heat content of such high gravity melt for re-use in the conversion zone, returning this heated high gravity melt to the conversion zone, contacting said low gravity melt scrubbing medium containing carbonaceous residue outside the scrubbing zone with an oxidizing gas under combustion conditions to remove said carbonaceous matter, and returning the resulting carbon-free low gravity scrubbing medium to the scrubbing zone.

2. The process of claim 1, wherein the heated liquid which directly contacts said removed high gravity melt for adjusting the heat content of said melt is the same liquid as said low gravity melt scrubbing medium.

3. The process of thermally converting hydrocarbons which comprises passing the hydrocarbons in a gaseous state under conversion conditions through a conversion zone packed with inert contact material, flowing a molten metallic heat transferring medium of high gravity through said zone in direct contact with said hydrocarbons

but in insufficient amount to flood the voids of the packing whereby heat is transferred to the hydrocarbons and carbonaceous residue produced as a by-product of the conversion are carried along in the molten metal medium, removing the heat transfer medium from the conversion zone, scrubbing the removed medium in a scrubbing zone with a low gravity melt of an inorganic salt which is immiscible with the high gravity medium and which is not sensitive to oxygen under combustion conditions thereby transferring the carbonaceous residue to the inorganic salt of low gravity, directly contacting said removed high gravity medium with a heated inorganic salt melt of low gravity and which is immiscible therewith to adjust the heat content of such high gravity medium for reuse in the conversion zone, and returning this heated high gravity medium to the conversion zone.

4. The process of claim 3, wherein the liquid of low gravity employed for directly heating the medium of high gravity is a salt melt of the same composition as the low gravity salt melt scrubbing medium.

5. The process of thermally converting hydrocarbons which comprises passing the hydrocarbons in a gaseous state under conversion conditions through a conversion zone packed with inert contact material, flowing a liquid heat transfer medium through said zone in direct contact with said hydrocarbons but in insufficient amount to flood the voids of the packing whereby heat is transferred to the hydrocarbons and carbonaceous residue produced as a by-product of the conversion is carried along in the liquid medium, removing liquid medium from the conversion zone, restoring the removed medium to proper temperature and carbon content for re-use in the conversion zone by direct contact with at least one other liquid medium, said latter medium being oxygen insensitive, and then returning the restored liquid heat transfer medium to the conversion zone.

6. The process of thermally converting hydrocarbons which comprises passing the hydrocarbons in a gaseous state under conversion conditions through a conversion zone, flowing a liquid heat transfer medium through said zone in the form of liquid films which are in direct contact with said hydrocarbons whereby heat is transferred to the hydrocarbons and carbonaceous residue produced as a by-product of the conversion is carried along in the liquid medium, removing liquid heat transfer medium from the conversion zone, restoring the removed medium to proper temperature and carbon content for re-use in the conversion zone by direct contact with at least one other liquid medium, said latter medium being oxygen insensitive, and then returning the restored liquid heat transfer medium to the conversion zone.

7. The process of thermally converting hydrocarbons which comprises passing the hydrocarbons in a gaseous state under conversion conditions through a conversion zone, flowing a liquid heat transfer medium through said zone in direct contact with said hydrocarbons whereby heat is transferred to the hydrocarbons and carbonaceous residue produced as a by-product of the conversion is carried along in the liquid medium, removing liquid heat transfer medium from the conversion zone, restoring the removed medium to proper temperature and carbon content for re-use in the conversion zone by direct contact with at least one other liquid medium, said latter medium being oxygen insensitive, and then returning the restored liquid heat transfer medium to the conversion zone.

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