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J. D. UPHAM

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QUENCHING OF HOT GASES

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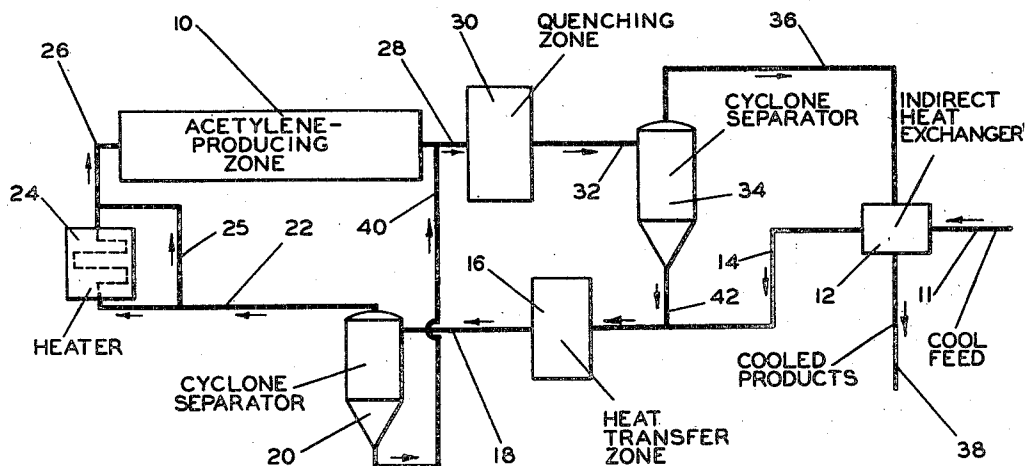


FIG. -1

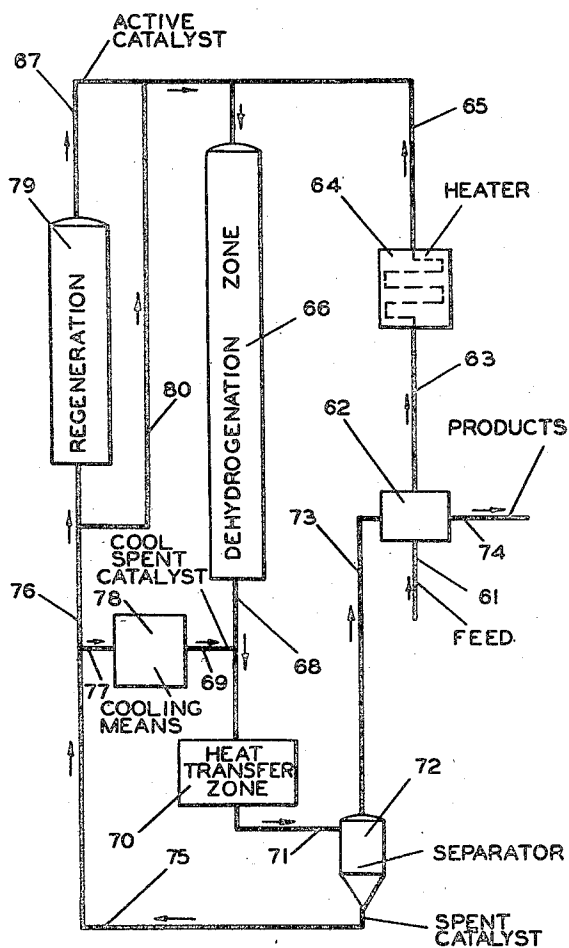


FIG. -2

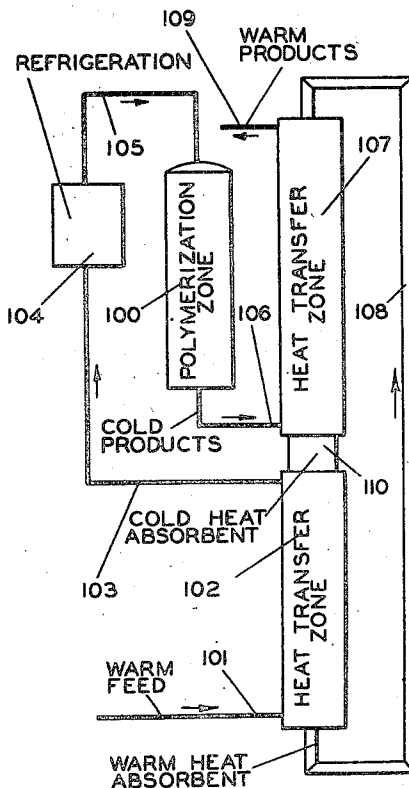


FIG. -3

INVENTOR
J. D. UPHAM

BY

Hudson, Young & Young
ATTORNEYS

UNITED STATES PATENT OFFICE

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QUENCHING OF HOT GASES

John D. Upham, Bartlesville, Okla., assignor to
Phillips Petroleum Company, a corporation of
Delaware

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This invention relates to the rapid and efficient transfer of heat between fluids and solids. In a preferred modification it relates to the quenching of hot conversion gases containing highly reactive materials such as acetylene or butadiene. A further embodiment relates to the recovery of heat from such hot gases and reutilization of such recovered heat in the conversion process.

The production of highly reactive unsaturated organic materials has become very important industrially, for example as evidenced by the increased demand for the hydrocarbons acetylene and butadiene. The highly reactive nature of these materials, which is the property which gives them their value, at the same time presents serious obstacles to their successful production. For example, most practical methods of making acetylene or butadiene from hydrocarbons, which are by far the cheapest and most abundant possible raw materials, involves a high-temperature catalytic or non-catalytic pyrolysis of the hydrocarbon feed stocks. The optimum time for these feed stocks to be held at the elevated conversion temperatures is of the order of from a few seconds down to a few hundredths of a second or even less than one hundredth of a second at the highest temperatures. Lengthened reaction periods allow secondary reactions, and decomposition or other reactions of the product, to become predominant, resulting in a decreased ultimate yield due to destruction of raw material and/or product.

Acetylene, for example, may be produced by the cracking of almost any hydrocarbon material at temperatures above about 1250° F., and fairly high yields of commercial interest may be obtained when working above about 1800° F. on up to about 3000° F. or even somewhat higher. At such elevated temperatures, however, the cracking process continues with the production of carbon and hydrogen, and the acetylene also forms polymerization and other condensation products readily. Accordingly, the residence time of the hydrocarbon reaction mixture must be quite limited, and the cracked hydrocarbons must, upon completion of the desired conversion, be immediately quenched to a temperature at least as low as about 900 to 1000° F., and preferably lower, such as down to about 550° F. This fact is well known to the art, and many methods of carrying out the quenching have been proposed.

These known methods involve quenching with liquids, for example, water, alkaline solutions, charging oil, etc. Certain defects are inherent

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in the methods heretofore proposed or used, which defects include loss of small but valuable amounts of aromatic oils, carbon black, and other components of the mixture, and loss of great amounts of heat which are absorbed by the quenching medium and either completely wasted or only very incompletely and inefficiently utilized. If the liquid to be cracked is used as quenching medium, it is apt to be contaminated by absorption therein of material from the cracked gases. Passage of the hot cracked gases over water- or air-cooled heat transfer surfaces, such as metal plates, is of course inefficient in bringing temperatures down rapidly.

Somewhat the same considerations apply in the case of diolefins such as butadiene, isoprene, piperylene, etc., formed by high-temperature conversions, which may be non-catalytic or catalytic. Polymerization and decomposition reactions normally occur at a rapid rate in the diolefin-containing effluents of such conversions. For example, in a butene dehydrogenation, vapors leaving the dehydrogenation catalyst at temperatures of about 1100 to 1300° F. may contain only traces of polymer, but rather high percentages of high-boiling polymers are found in the dehydrogenated vapors after normal cooling to temperatures in the range of say 150 to 300° F. The polymerization reactions involved may be illustrated, using general formulas, as follows:

$$\text{Monomer} \rightleftharpoons \text{dimer} \rightleftharpoons \text{higher polymers}$$

At high temperatures of the order of 1000° F. equilibrium is established in extremely short times, but the concentrations of dimer and higher polymer at equilibrium are very small. At low temperatures of the order of 200 to 300° F., the equilibrium is established so slowly that little dimer is normally formed even though equilibrium concentrations allow the formation of high percentages. At intermediate temperatures, however, both the time required to establish equilibrium and the equilibrium concentrations are favorable to dimer and higher polymer formation.

For example, at temperatures around 1200° F. the quantity of dimer formed at equilibrium from butenes is less than 1 per cent, but this quantity increases to about 5 per cent at temperatures near 700° F. Butadiene is even more readily polymerized, and at temperatures of 700 to 1000° F. a very considerable quantity of the diolefin may exist in the dimeric form at equilibrium. Copolymers formed between butenes and butadiene are also more readily formed than butene

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polymers, and may account for a further amount of polymer formation. Thus it has been found that serious losses of butadiene may occur subsequent to the catalytic dehydrogenation step while the effluent vapors are being cooled if sufficient time elapses for equilibrium concentrations of polymers to be attained in the temperature range of rapid polymerization.

The polymerization reaction velocity is enormously greater at temperatures just below the dehydrogenation range than it is at low temperatures such as those finally attained by the cooling system. Consequently, the formation of large amounts of polymer in the cold effluents does not occur in the absence of catalyst, even over very long periods of time. On the other hand, in the range from dehydrogenation temperatures down to about 600 to 800° F. polymerization reaction rates are still extremely high so that equilibrium concentrations are approached in a few seconds or less. The large quantities of polymer formed are therefore accounted for by equilibrium concentrations of polymers being formed as the gases are brought down through this active temperature range in conventional cooling equipment, wherein the cooling period is relatively long. Below about 600 to 700° F. the reaction velocity of polymerization becomes too small to cause measurable losses, even when the cooling period is prolonged. It has been noted that when carrying out the dehydrogenation of butene quantities of polymer varying from about two to about ten per cent of the butene charge are often formed while conversion to butadiene is only of the order of about fourteen to twenty-four per cent. Thus, the loss of diolefin due to polymerization which may largely occur after the effluent vapors leave the catalyst may be seen to be very serious.

In quenching hot butadiene-containing streams in conventional manner, much the same defects or disadvantages are encountered as those recited above with respect to conventional quenching of acetylene-containing streams. Inasmuch as most processes for converting hydrocarbons to diolefins or acetylenes at elevated temperatures involve relatively low per-pass conversions to the desired products, normally ranging from say 15 to 40 or 45 per cent, unconverted components are separated from the conversion effluents and recycled for further conversion. This entails a heating of 100 parts of hydrocarbon to conversion temperature to produce, for example, 30 parts of product. The 30 parts of product, together with 70 parts of unconverted material, disregarding losses by side reaction and as by-products, are quenched, and the 70 parts must be re-heated. In other words, in this typical instance, for each 30 parts of product formed, about 70 parts of material are heated to a high temperature and then cooled without having undergone useful conversion. The wastage of heat involved, if adequate means are not provided for its recovery and reuse, is apparent. These various problems are encountered not only in the non-catalytic formation of acetylene by pyrolysis and the catalytic formation of butadiene by dehydrogenation, but also to a greater or lesser extent in any high-temperature catalytic or non-catalytic process wherein highly reactive materials, such as vinyl acetylene, methylacetylene, isoprene, piperylene, acrylonitrile, styrene, ethylene oxide, etc., are formed to an appreciable extent.

It is an object of this invention to quench hot gases containing highly reactive materials in an

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effective manner. Another object is to accomplish such quenching without encountering certain defects of conventional methods. A further object is to quench hot diolefin- and/or acetylene-containing conversion mixtures with adequate rapidity to avoid undesired side reactions and/or decomposition or polymerization of the products, and further to recover a substantial proportion of the heat content of such mixtures for re-use in the conversion. Another object is to provide a complete cyclic heat transfer process wherein cold or heat is imparted to a stream by a direct transfer step, the stream is then utilized in desired manner, and at least a portion of the cold or heat imparted thereto is then recovered by a direct heat transfer step for reuse. Other objects and advantages of the present invention will be obvious, to one skilled in the art, from the accompanying disclosure and description.

Briefly stated, in preferred embodiment my invention contemplates effecting a direct admixture of relatively cool mobile solid heat retentive or absorptive material with a hot hydrocarbon conversion effluent which it is desired to quench, said heat retentive material being used in such quantities and at such a temperature, and having such a specific heat and heat conductivity, as to effect an adequately rapid or substantially instantaneous quenching of the hot effluents to a temperature level sufficiently low as to avoid undesired reactions. This direct admixture is accomplished by passing separate streams of hot effluents and of relatively cool mobile heat retentive or absorptive material into a common mixing zone. By a mobile solid heat retentive material I mean a solid material, having desirable thermal properties as described below, and in particulate form so that it may be readily moved as a flowing stream through the system. The individual particles of the heat retentive material may, under various circumstances, range from a few microns in diameter up to fairly large particles of say about one inch or even somewhat more in diameter. The choice of particle size for any particular application will be governed by factors to be discussed more fully hereinafter.

After a thermal equilibrium has been substantially established between the heat retaining material and the effluent conversion stream in the mixing zone referred to, which is accomplished quite efficiently due to the direct transfer of heat between fluid and solid, the quenched effluent stream is separated from the heat absorbent and passed to further treatment as required. The so-separated heat absorbent, having taken up a substantial amount of the sensible heat of the hot hydrocarbon effluents and being thus heated, is next passed in a stream into a second mixing zone wherein it is contacted with cool fluid hydrocarbon feed which is to be converted. In this mixing or heat-transfer zone the relatively hot heat retentive material is cooled by the feed stream, which concomitantly becomes heated by contact with the heat absorbent. It will be seen that a substantial amount of the heat absorbed from the conversion effluents is thus directly and accordingly efficiently transferred to the incoming feed and conserved for re-use in the conversion. After approaching thermal equilibrium as closely as desired in the second mixing zone, the hydrocarbon feed stream is separated from the stream of heat absorbent and passed to the conversion step, ordinarily first undergoing additional heating to supply heat for the conversion which is usually endothermic and to make

up for heat losses in the system. The cooled heat absorbent is returned for use as quenching medium as described.

Having given a brief description of the mode of operation involved in one embodiment of the invention, I shall now describe in more detail the particular characteristics of the mobile-solid heat absorptive material which may be utilized. Desirable thermal qualities in such a material involve a high specific heat, high density, and high heat conductivity. It will be appreciated that the term "high" is a relative one, and that accordingly a wide range of materials may be useful in carrying out the invention, the choice of a particular heat absorbent being dependent on the conditions under which it is to be applied. It will further be understood that a given heat absorbent may be entirely satisfactory in one situation but not so suitable or even entirely unsuitable in a different situation. The material must of course have a melting point appreciably above the maximum temperature which is likely to be encountered, and must also be able to withstand such maximum temperatures without undergoing other undesirable changes. Ordinarily the heat retentive material is substantially inert under the conditions of use with respect to the fluids to be contacted and to the apparatus, and is preferably of a non-adsorptive nature. However, in accordance with certain modifications of the invention, a material having a catalytic or other effect upon one or more of the fluids contacted is used. With these general limitations in mind, a listing may be made of some examples of materials suitable under various conditions for use in carrying out the invention. This listing is, of course, not intended to be all-inclusive, and many other suitable materials will be suggested to one skilled in the art by the disclosures offered herein.

The metals may be cited as one class of materials. With respect to thermal properties, the metals are more desirable than any other class of solids. However, certain of the metals are highly reactive, and hence may not be suitable for use in the presence of oxidizing or other active gases, such as those containing free halogens, acids, etc. Furthermore, the melting points of the metals are of course to be taken into consideration in making a choice for a specific quenching or other heat transfer step. The metals, and in fact all solids, vary between one another in heat conductivity much more than in specific heat or density. For example, most metals operative in this invention have specific heats, at elevated temperatures of the order of 800° F., of between about 0.1 and 0.3 B. t. u. per pound per degree Fahrenheit, and few solids of any kind have specific heats much above about 0.4 under similar conditions. The densities of most metals are roughly in the range of about 400 pounds per cubic foot, although the lighter metals may be less than 200 pounds per cubic foot, and most non-metallic refractory solids which may be used in the present process have densities between about 100 and 200 pounds per cubic foot. In contrast, the heat conductivities of suitable metals may vary from about 200 B. t. u./hr./sq. ft./°F./inch in one case up to over 2000 in another case, and non-metallic solids which may be given consideration for use in carrying out my invention may have heat conductivities as low as 1. It is accordingly apparent that in selecting a group of solids having properties other than thermal properties suitable for a given application, most of the solids in the group will be simi-

lar with respect to density and specific heat, while they may be quite dissimilar with respect to heat conductivity. From such a group, then, with due consideration being given to cost and other such factors, a solid having a high heat conductivity would ordinarily be selected for actual use, and specific heat and/or density would play a part in the final selection only in deciding between two or more solids of similar high heat conductivity.

Returning now to the metals, the following may be mentioned merely as examples having relatively high melting point, and are listed approximately in decreasing order of heat conductivity, that is from the highest to the lowest: copper, aluminum, brass, nickel, iron, mild steel, chromium alloys, etc. The thermal conductivity of the highest in this list, copper, is more than ten times that of the lowest in the list, chromium alloys, the former having a conductivity at 1000° F. of about 2400 B. t. u./hr./sq. ft./°F./in., and the latter having a conductivity of about 200. The above list of course is not exhaustive but merely suggestive, to one skilled in the art, of the wide variety of materials available and their range of properties. Choice of a metal for a specific quenching or other heat transfer step or cycle carried out in accordance with the teachings of this disclosure is made by taking into consideration first the melting point as compared with maximum temperatures prevailing in the system, then the chemical suitability. After some metals are thus eliminated, consideration is given to the availability and cost of the remaining suitable metals in desired particle size and/or shape, then the heat conductivity and finally, if more than one metal still appears suitable, the density and specific heat are taken among the determining factors.

Considering now the non-metallic solids, it is immediately apparent that a lower order of heat conductivity is involved. However, due to factors such as cost, chemical inertness, resistance to attrition, and particularly to refractory qualities at high temperatures, a non-metallic solid is frequently more desirable than a metal. Artificial graphite and silicon carbide ("Carborundum") are outstanding in that their heat conductivities are far above those of any other non-metallic solid investigated. Graphite ranks with most of the metals, while silicon carbide is below the metals but still far above other non-metals. Due to its inertness, heat stability, and mechanical strength, silicon carbide is usually preferred over graphite in the practice of my invention. The heat conductivity of silicon carbide varies considerably with temperature, but generally speaking is within the range of about 100 (in the units used above), varying from 75 at 2500° F. to 125 at 1100° F. The reasons for my preference for silicon carbide thus become apparent when its thermal, mechanical, and chemical characteristics are considered.

Other non-metallic solids available for use in various modifications of the invention include the following examples listed in approximate decreasing order of heat conductivity (at elevated temperatures of 1500 to 2000° F.), which ranges from about 25 to 30 on down to about 1 to 2: petroleum coke, fused alumina, magnesite, quartz, other forms of dense silica, fire clay, porcelain, rocks of various kinds, diatomaceous earth (fired), etc.

The methods of handling any of the foregoing or other heat absorptive materials depends, among other factors, upon the particle size utilized. Typical methods of handling particle sizes rang-

ing from a fine powder up to balls one inch in diameter are described in the examples shown in the drawings, and will be considered in detail below. Choice of particle size will be based primarily on the rapidity of heat transfer required, with secondary consideration being given to the thermal properties of solids available, particularly if the number of suitable solids is somewhat limited. For a very rapid quenching, such as is required for example in the case of an acetylene-containing stream obtained by pyrolysis of an oil in the electric arc, small particle size is most advantageous and indeed almost essential. Thus, in a preferred embodiment described below a moving stream of finely comminuted solid heat absorbent is injected into the hot converted stream whereby the hydrocarbons are almost immediately reduced to the desired low temperature. As another example, wherein quenching is not of such importance or of no importance, but wherein a most complete utilization of heat or cold is desired, relatively large particles of heat absorbent are caused to pass counter-current to a hot or cold fluid, sufficient residence time being allowed to obtain substantially complete thermal equilibrium at the various points within the heat transfer zone. In any case, the particle size, heat conductivity, and heat capacity of the solid material are correlated to give the desired rate of heat transfer. Under the term "mobile solid heat absorbent" may also be included chains, continuous ribbons of metal, continuous sheets of metal wool, etc., which by suitable mechanical means may be caused to flow as rapidly as desired as a stream through the required apparatus in direct contact with fluids. However, somewhat complicated driving and guiding means are generally required; and due particularly to the ease and flexibility in handling, as well as generally superior heat transfer properties, a large number of separate, individual particles, as described above, is ordinarily preferred.

It is felt that a more complete understanding of the principles of the invention may now be obtained, based on the foregoing disclosures, by examining the operation of certain processes wherein said principles are relied upon in attaining the objects of the invention. Reference is accordingly made to the accompanying drawings, which portray in a schematic manner principal elements of equipment in which the invention may be practiced. It will be appreciated that the representations in the drawings are diagrammatic in nature, and that numerous additional pieces of equipment, such as heaters, pumps, control instruments, valves, insulation, flow rate regulators, product separators, steam lines, etc. will be used in any given operation. However, the supplying of such items is well within the skill of the art, and further mention need not be made of them in view of the detailed and adequate disclosure presented herein of various preferred modes of carrying the invention into practice.

Figure 1 shows diagrammatically apparatus used in producing acetylene by non-catalytic pyrolysis of hydrocarbons, wherein quenching and heat recovery are effected in accordance with the invention.

Figure 2 shows diagrammatically apparatus used in producing butadiene by the dehydrogenation of butene in the presence of a powdered dehydrogenation catalyst, wherein quenching and heat recovery are effected in accordance with the invention.

Figure 3 shows diagrammatically apparatus

used in producing olefinic polymers at low sub-atmospheric temperatures, wherein a very efficient cooling of feed and subsequent recovery of cold from the product is effected in a complete cycle in accordance with the invention.

In Figure 1, a cracking zone 10, designed in accordance with principles well known in the art, is provided for producing acetylene by pyrolysis of a hydrocarbon feed stock which enters the system through line 11. The hydrocarbon feed may range from substantially pure methane up to heavy reduced crude oil or other heavy liquid hydrocarbons, and may comprise one or a plurality of individual hydrocarbons. It will be appreciated that the exact methods of operating will vary in accordance with the nature of the feed stock, as will the temperature and residence time in the conversion zone. Frequently steam, hydrogen, and/or other diluents will be used in conjunction with the hydrocarbon material. Partial oxidation with oxygen-containing gases may also be used in order to attain the required high cracking temperatures. In addition to acetylene (C_2H_2), other higher acetylenic hydrocarbons will be produced in smaller quantities, as will monoolefins, diolefins, other unsaturates, aromatic oils, relatively large quantities of hydrogen, etc. Depending upon pyrolysis conditions, appreciable amounts of carbon black may be formed. The cracking zone 10 may comprise an electric arc, but preferably comprises a regenerative-type furnace containing refractory brickwork or the like which is alternately blasted with hot combustion gases or flame and then used for passage of the cracking stock therethrough wherein the desired cracking occurs due to the high temperature of the refractory material. The construction and operation of one such furnace is described by Hasche et al. in U. S. Patent 2,319,679. Reference may be had to the literature for a complete discussion of charging stocks, diluents, partial combustion, arcs, furnaces, temperatures, reaction times, products, product separation, etc., and these aspects will not be further described here. Ellis, "The Chemistry of Petroleum Derivatives," volumes I and II and references cited therein; numerous patents to Wulff such as 2,037,056, etc.; Metzger, 2,179,379; are cited as examples of the literature dealing with acetylene production and related subjects.

Although the extreme temperature used in producing acetylene are not ordinarily attained, the embodiment of the invention illustrated in Figure 1 may also be readily applied to the catalytic or non-catalytic production of butadiene. Higher temperatures are encountered when gases or oils are non-catalytically cracked, frequently in the presence of superheated steam or oxygen. By way of examples may be mentioned the processes disclosed in copending application by Allen and Wolk, Serial No. 496,090 now U. S. Patent 2,377,847, and by Allen, Serial No. 493,671 now U. S. Patent 2,387,731. Frolich et al. disclose a high-temperature, low contact time pyrolysis of butene-2 to produce butadiene in U. S. Patent 2,322,122. Other processes are known to the art, such as those mentioned by Ellis in "The Chemistry of Petroleum Derivatives."

In the embodiment shown in Figure 1 as applied to acetylene production, a finely divided heat absorbent is used for quenching and heat recovery. Due to the extremely high temperatures involved, which may in some cases range as high as 3000° F., I prefer to use silicon carbide particles as heat absorbent. Inasmuch as a very

rapid quenching is required, particles which will pass through about a 100 mesh screen, or at least through a 60 mesh screen, are used. Silicon carbide or "Carborundum" powder of 200-300 mesh is advantageously employed. The small particle size, coupled with the high heat conductivity of silicon carbide, makes possible the highly satisfactory results which are obtained. The silicon carbide is substantially non-catalytic and hence desirable for this reason also.

Reactants and reaction products pass through the system in the following order: enter through line 11, pass through indirect heat exchanger 12, line 14, heat transfer zone 16, line 18, separator 20, line 22, heater 24 if required or by-pass line 25, line 26, cracking zone 10, line 28, quenching and heat transfer zone 30, line 32, separator 34, line 36, indirect heat exchanger 12, and out via line 38 to conventional separation and recovery treatments. Into the extremely hot conversion effluents stream passing through line 28 is continuously injected a stream of relatively cool heat absorbent powder from line 40. The powder, becoming immediately suspended in the gases, effects a very rapid quenching to a temperature, such as 800° F., at which undesired reactions are minimized or stopped entirely. The direct heat transfer involved between gas and solid is highly efficient in obtaining the desired results. The mixture of gas and solids is allowed to remain in heat transfer zone 30 for a sufficient length of time for substantial attainment of thermal equilibrium, or at least until the gas is cooled to the desired low temperature. The time required for this is quite short, such as one or two tenths (0.1-0.2) of a second or less, and the size of zone 30 is determined by the rate of flow through the system; the quenching zone 30 may actually consist merely of a sufficient length of conduit, rather than a separate chamber as shown. The streams 28 and 40 may be injected separately or together into the quenching zone.

In case a hot stream from a butadiene-producing conversion is being quenched, the hot butadiene-containing gases are preferably quenched to a temperature below about 700° F. within a period of time less than about one second, and preferably less than about 0.2 second.

The mixture of vapors and solid particles is next passed into separator 34, which may be a filter, electrical precipitator, or other suitable means, but which preferably comprises a cyclone separator. From this separator the quenched gases, now substantially free from the powdered heat absorbent, may be passed through indirect heat exchanger 12 for imparting some of its residual sensible heat to the incoming feed, and then on to suitable treatment known to the art for recovering the desired products and recycle stock, if any. The gases leaving separator 34 may in some cases require additional treatment by means not shown for removal and recovery therefrom of traces of powdered heat retainer. Under severe conditions of pyrolysis in zone 10, appreciable amounts of carbon may be formed. This carbon may at least partially pass through separator 34 and be recovered from the quenched gases by known means, whereas if a liquid quenching medium were used the carbon would be retained in admixture with the liquid. Any carbon separating with the heat absorbent powder in separator 34 is readily recovered therefrom by virtue of density differences.

The powdered silicon carbide or the like recovered in separator 34 is now at a considerably

more elevated temperature than prior to its use in quenching zone 30, and has absorbed a substantial proportion of the sensible heat of the conversion mixture. This recovered heat is re-used in the process by passing the powder through a complete cycle including another heat transfer zone 16. The hot powder is passed via line 42 into admixture with the relatively cool incoming feed in line 14, and the mixture resides in heat transfer zone 16 for a sufficient time to reach or at least approach thermal equilibrium. By this means the recovered heat is re-imparted to the feed, and the hot absorbent is concomitantly cooled by the cool feed and thus reconditioned for use as a quenching medium. Effluents from zone 16 pass via line 18 into separator 20, which is preferably a cyclone separator similar to unit 34, and the thus-preheated feed exits through line 22 and may be passed directly via lines 25 and 26 to the cracking zone, or may be given additional preheat in heater 24, depending upon the characteristics of the cracking system. Cooled powder from separator 20 is passed via line 40 for reuse as a quenching and heat recovering medium in zone 30 as described. The powder may be additionally cooled by means (not shown) inserted in line 40 if desired.

The powdered heat absorbent may be conveyed through its cycle by any means known to the art. This may include mechanical means such as screw conveyors, etc., supplied within lines 40 and 42. Preferably gravity is relied on to carry the stream of powder in one or both of these lines. The gas-lift principle may be utilized if desired in moving the powder in known manner. Due to the abrasive character of silicon carbide, suitable protection is provided for equipment carrying the powdered solid. Preferably this comprises a lining of silicon carbide. It will be understood that in view of the extreme temperatures involved, the equipment comprising cracking zone 10, as well as line 28, and zone 30 and line 26 if required will be lined with silicon carbide or other refractory.

The inert nature of silicon carbide is highly advantageous in this process as compared with the usually used liquid quenching media such as water or oil. Water and oil enter into many reactions with components of the acetylene-containing gas. By the practice of my invention a simpler, more complete control of the effluents' composition is had. The formation of carbon is not catalyzed by my quenching medium. Furthermore, any carbon present in the effluents is readily separated from the heat carrier powder. Aromatic and/or unconverted cycle oils which it may be desired to recover are simply separated from the carborundum. Due to its non-adsorptive nature, very little of this type of material is picked up. A periodic washing of the powder with suitable solvent may be used to recover such material from admixture therewith in certain cases. Also, in the event a carbonaceous coating is developed on the silicon carbide powder, an occasional oxidation will serve to remove same.

While silicon carbide has been described as the preferred material to use as a mobile solid heat carrier in the embodiment of the invention shown in Figure 1, other refractory material, such as alumina, fireclay, silica, fine quartz sand, etc., may be used with suitable modifications in the quantities used, and with due consideration being given to the temperature involved.

Turning now to Figure 2, for a consideration of another embodiment of my invention, the flow of

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materials for the catalytic dehydrogenation of butenes to butadiene is shown in diagrammatic form. The conditions required and the numerous catalysts which may be utilized, the use of diluents and various other modifications, will not be discussed in detail, inasmuch as these factors are well known and it is clearly within the skill of the art at this time to practice butene dehydrogenation in the presence of a powdered catalyst to produce butadiene. To amplify the details further would only encumber the present disclosure without furthering an understanding of the invention. In this embodiment, the mobile heat absorbent material used for quenching and heat recovery is the catalyst itself. The catalyst is obviously capable of withstanding the temperatures to be encountered. Sufficient is used to provide a heat capacity great enough to quench the dehydrogenation effluents to the desired temperature. Preferably substantially "spent" catalyst, that is, catalyst which because of carbonaceous deposits is incapable of furthering the dehydrogenation reaction efficiently, is utilized. The advantage gained is that the quenching material may then be considered to be a substantially inert or non-catalytic, and yet no extraneous material is brought into the system. Carry-over of catalyst powder into the heat transfer system, or of heat absorbent powder into the catalytic system, accordingly need not be feared, and preferably the two systems named are inter-connected, and in fact are overlapping in the embodiment shown in Figure 2.

As catalyst and heat absorbent may be mentioned merely by way of example composites of chromium oxide with a major proportion of alumina, preferably treated with minor amounts of alkali metal hydroxide or other alkaline material, and containing limited amounts of barium or strontium oxide. Such a catalyst is preferably used in conjunction with steam as a diluent for the olefinic dehydrogenation feed. Numerous other dehydrogenation catalysts might be mentioned without adding to the knowledge of the art, for any suitable dehydrogenation catalyst may be used with suitable modification. A mesh size of 200-300 is satisfactory, although other sizes may also be used. Any known manner of handling the mobile catalyst may be used. Dehydrogenation temperatures of 1100 to 1300° F. are suitable for the production of butadiene, although dehydrogenation temperatures outside this range are also operative. For the dehydrogenation of pentenes to produce pentadienes, for example, somewhat similar temperatures are suitable. The feed stocks need not necessarily be entirely olefinic, for normal butane may be dehydrogenated in a single stage to butadiene, preferably with recycle of butenes. Moderate super-atmospheric pressures, such as 50 to 100 pounds per square inch absolute, are ordinarily used, although somewhat higher or lower pressures, even sub-atmospheric pressures, are sometimes used.

In Figure 2, normal butene feed, which may be 1-butene, 2-butenes, or mixtures thereof, together with propylene, hydrogen, steam, carbon dioxide, or other diluents and/or hydrogen acceptors as desired, is passed via line 61, through indirect heat exchanger 62, through line 63, heater 64, and line 65 to dehydrogenation zone 66. Powdered catalyst from conduit 67 is introduced, as by injection, into the gases in line 65 just prior to entrance into zone 66, or directly into zone 66. The suspension of catalyst in re-

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actants passes through zone 66, wherein the desired dehydrogenation takes place.

This suspension then leaves zone 66 via line 68, into which is introduced from line 69 a relatively large quantity of additional powdered catalyst which is initially at a temperature well below that of the dehydrogenation effluents. The resulting mixture resides in heat transfer zone 70 until thermal equilibrium is substantially attained. The injection of cool catalyst in this manner very rapidly quenches the reaction mixture to a temperature below that at which undesired reaction occurs. The mixture passes from zone 70 via line 71 into separator 72, preferably a cyclone separator. Gases leave separator 72 substantially free from catalyst, via line 73, heat exchanger 62 and line 74. These gases are then subjected to conventional treatment for recovery of components including butadiene, hydrogen, and recycle stock. If desired, methods now known to the "fluid catalyst" art for effecting complete separation of dehydrogenation catalyst from reaction zone effluents may supplement the separation effected in separator 72. Such methods include partial condensation of the gases, electrical precipitation, scrubbing with liquids, etc.

Catalyst leaves separator 72 via line 75 and passes partly into line 76 and partly into line 77. From line 77, catalyst passes through cooling means 78, and thence into line 69 for re-use as quenching medium as described. Catalyst from line 78 passes to line 67 either through regeneration zone 79 or through by-pass line 80, or both. From line 67 it is again used in the reaction zone. In regenerator zone 79, carbonaceous matter is burned off, as by suspension of the catalyst in hot oxygen-containing gases, in known manner. If the heat thus generated is insufficient to bring the temperature of the catalyst up to the desired value near the dehydrogenation temperature, additional heating of the recycled catalyst may be accomplished by means not shown, or the pre-heat of the gaseous feed to the dehydrogenation may be sufficient to give the desired temperature in the reaction zone.

It will be seen that an effective quenching is readily attained, without the necessity of introducing any extraneous substance into the reaction zone effluents. The catalyst is continuously flowing in a closed circuit, including an internal "quenching circuit." The catalyst for quenching may be obtained from regenerated catalyst, rather than as shown, but this is generally not so desirable, for fresh catalyst would at first, at least, encourage further reaction, while spent catalyst is relatively inactive. An advantageous operation, not shown for the sake of simplicity in the drawing, is to effect cooling of the quench catalyst stream in unit 78 by indirect, or preferably direct, heat exchange with cold incoming reactants in line 61, thus giving efficient heat recovery and utilization. This and other modifications, as well as the use of auxiliary equipment as required, will be obvious to one skilled in the art in view of the detailed disclosure of principles and specific methods herein.

In case it is desirable to avoid cooling the main stream of catalyst upon leaving the dehydrogenation zone and prior to recycle of the same to the dehydrogenation, the method shown in Figure 2 may be modified somewhat, particularly when very little deactivation of catalyst occurs upon one pass through the reactor, so that most of the catalyst is recycled without regeneration. In

such an operation, the total effluents from the dehydrogenation zone may first have at least the bulk, and preferably substantially all, of the catalyst separated therefrom and recycled. The gaseous conversion products still hot and just separated from the catalyst, are then quenched by suspension therein of cool, deactivated catalyst. The deactivated catalyst thus used for quenching is separated from the quenched gases, and is preferably maintained in a circuit of its own substantially separate from the hot catalyst circuit. Small amounts of catalyst may be carried into the quenching circuit, and corresponding amounts may be withdrawn therefrom, regenerated and returned to the active catalyst cycle.

By suitable modification of equipment, the methods just described for powdered catalysts may be extended to moving beds of catalyst of larger particle size, such as from 4 to 60 mesh, as exemplified by the so-called TCC process. In such an instance, a larger particle size of heat absorbent would necessitate a great quantity thereof over the amount of powder required in order to obtain a given rapidity of quenching. Longer residence times in zone 70 would also be utilized.

The apparatus shown diagrammatically in Figure 3 may be used for carrying out a low-temperature catalytic olefin polymerization process, whereby an efficient conservation of refrigeration is obtained. A modification of my invention is thus shown which, although utilizing certain principles common to all modifications, never the less differs substantially in some respects from the modifications of Figures 1 and 2. In this instance it is not heat, but cold, which it is desired to conserve. It is realized that strictly speaking, according to the usually accepted scientific terminology, cold is not transferred from a first point to a second point but rather heat is transferred from the second point to the first point. However, when refrigeration is involved and temperatures below normal prevail in a system, it is convenient to refer to the imparting and transferring of cold or refrigeration, since it is the refrigeration which is expensive and which accordingly it is desired to conserve. With this explanation it is believed that one skilled in the art will readily understand what is meant when such terminology is used. In the process illustrated by Figure 3, a quenching step is not required, but a most complete transfer of heat (or cold) within a continuous cycle is desired.

A polymerization zone or system, represented schematically in the drawing by the rectangle 100, is provided, which may involve any of the features of processes of this kind which are known to the art. The desired polymerization of olefins is carried out in this system at sub-atmospheric temperatures which may range from say 40° F. on down to say -160° F. or even lower, depending on the feed stock, catalyst, and product desired. It is well known that a great variety of polymers may be prepared by the catalytic polymerization or copolymerization of one or more olefins or olefinic materials such as isobutylene, normal butenes, ethylene, butadiene, vinyl chloride, styrene, etc. The polymerization is frequently carried out at depressed temperatures in the presence of relatively large volumes of solvent, using a Friedel-Crafts type metal or metalloid halide catalyst such as boron trifluoride, aluminum chloride, aluminum bromide, tin tetrahalides, zirconium tetrachloride, etc. Promoters

such as the lower alkyl halides, hydrogen halides, certain ketones, etc., are sometimes used. Generally speaking, the lower the temperature of reaction the higher the average molecular weight of the polymer, other factors being equal. Soluble and/or insoluble polymers may be formed, depending upon conditions. Ellis, "Chemistry of Petroleum Derivatives," and other patent and non-patent literature may be referred to for additional details. The method to be described is particularly applicable to processes which produce soluble polymers, although with suitable modification it may be applied to insoluble polymers, such as "butyl rubber," which is a copolymer of isobutylene with small amounts of a diolefin.

By way of example may be described the polymerization of a hydrocarbon mixture containing a substantial proportion of butenes, preferably isobutylene although normal butenes may also be present. Ordinarily a C₄ fraction is used which contains substantial amounts of butanes, which serve as diluent and solvent for the high molecular weight polymers formed. If such butanes are not available in sufficient quantity admixed with the butenes, they may be supplied, or pentane or other suitable saturated hydrocarbon solvent may be used. The butenes and accompanying hydrocarbon material, preferably in liquid phase, enter via line 101 from any suitable source, and flow through heat transfer zone 102 countercurrently to a downwardly flowing mass of cold solid heat retentive material, such as for example metal shot, chains, metal wool, metal turnings, rocks, quartz, clay, etc. Aluminum spheres of about one inch diameter are preferred, due to the high heat conductivity of aluminum, its inertness to the reactants, its cheapness, and the ease of handling and flowing such spheres. The stream of heat carrier enters the top of zone 102 at approximately reaction temperature, which may for example be about -25° F., and in flowing countercurrent to the incoming fluid reactants imparts cold thereto and thus cools the same by very efficient direct contact. The thus precooled reactants leave the top of heat transfer zone 102 via line 103 and pass through refrigeration means 104 wherein a further lowering of temperature to or somewhat below reaction temperature is accomplished. Means 104 furnishes sufficient refrigeration to overcome the heat liberated by the exothermic polymerization reaction and also the heat entering the system from the surroundings, largely due to lack of perfect insulation.

The cold reactants next pass via line 105 into reaction zone 100, wherein they are subjected to the action of a polymerizing catalyst such as boron fluoride or a solution of aluminum chloride in methyl chloride. Substantially complete polymerization of the butenes occurs to form polymers of a molecular weight suitable for use as lubricating oils, additives to oils, etc. A part of the refrigeration may be supplied directly to the reaction zone by means other than super-cooling of feed if desired. It is preferred to carry out the reaction as nearly isothermally as possible, for close temperature control is essential for good product control. For example, the product formed at -25° F. may have an average molecular weight several times that of the product formed at +25° F. After a suitable residence time, the cold products of reaction, comprising a solution of polymers in liquid low-boiling hydrocarbons, leaves

the zone 100 via line 106 and enters the bottom of heat exchange zone 107. In this zone a substantial proportion of the cold previously imparted to the feed as in zone 102 is recovered for reuse.

The stream of mobile heat absorbent such as the aluminum spheres referred to above leaves the first-mentioned heat exchange zone 102 at a temperature well above reaction temperature. This stream is transported via conduit 108, which may have associated therewith means (not shown) such as screw conveyor, bucket lift, or the like, to the top of zone 107. By flowing downward in zone 107 countercurrent to the cold reaction effluents, the heat absorbent becomes cooled, while the products are warmed to somewhere near room temperature, the final temperature of the products which exit via line 109 being dependent on the rate of flow of absorbent and the rate of flow of hydrocarbons through the system. Effluent products from which the cold has been recovered are passed to conventional means for recovering and purifying desired polymers, solvent, etc. The stream of cooled aluminum spheres passes from zone 107 into zone 102 through a means 110 which may be a mechanical closure such as a revolving lock more or less fluid-tight or other suitable means. A certain amount of leakage of liquid through unit 110 in either direction is allowable since effluents leaking through will merely be recycled to the reaction zone, while incoming liquid leaking through will simply by-pass the reaction zone, and be treated along with the effluents in conventional manner.

The countercurrent flow just described is the most efficient for recovering the cold or utilizing the refrigeration, inasmuch as the mobile heat absorbent leaves zone 107 at approximately the temperature of the reaction effluents, while it leaves zone 102 at approximately the temperature of the incoming feed, having given up substantially all of its cold thereto. Looked at from another viewpoint, the warm incoming feed passes in zone 102 progressively into contact with colder and colder heat retainer, being thereby cooled to a final low temperature; the cold liquid effluent from reaction zone 100 passes in zone 107 progressively into contact with warmer and warmer heat retainer, being finally brought to a relatively warm temperature. The method of operating just described with reference to Figure 3, as well as other embodiments of my invention, are highly advantageous in that most efficient heat transfer is obtained by the direct intermingling of fluids and mobile solids.

The heat transfer method illustrated in Figure 3 may, by suitable modification, be utilized in recovering and re-using heat in a process carried out at elevated temperatures, rather than for the recovery and re-use of refrigeration as described.

It will frequently be most efficient in practice to separate the treated fluids from the heat absorbent material before complete thermal equilibrium is established. In such cases, the temperatures of the two streams leaving the separating zones, for example, will differ by from one or two to fifty or even more degrees Fahrenheit. The closeness to which temperature equalization is approached will of course be dependent upon economic factors involving equipment capacities, heating or cooling costs, etc., for any particular process. Generally when a powdered heat carrier is utilized, the heat transfer is sufficiently

rapid that thermal equilibrium is substantially accomplished in a very short time.

The invention, although particularly applicable thereto, is not necessarily limited to the conversion of hydrocarbons, or even to processes involving chemical reactions. It may be used to advantage in various situations wherein an efficient heat transfer or rapid cooling, or rapid heating, or all are desired.

One mode of operation which may be used quite advantageously in some cases is to introduce the mobile heat retentive or absorbent material into contact with fluids to be heated or cooled at a plurality of points spaced along the line of flow. Thus, several streams of heat absorbent may enter a heat transfer zone at different points, and then flow either concurrent with or countercurrently to the said fluid. In this way the amount of heat transfer occurring at all points in the heat transfer zone is readily controlled. The quantity and/or temperature of the heat absorbent introduced may vary from one point of introduction to another.

It is to be understood that various heat retentive materials are not necessarily equivalent in effectiveness or applicability to a given process. The particle size of solid material used, its heat capacity, its heat conductivity, its mechanical strength and resistance to comminution or agglomeration, and its stability at the temperature to be encountered are among the most important factors to be considered in choosing a solid heat absorbent for use in a particular process. It will also be appreciated that a powdered solid and a solid of relatively large particle size are not necessarily equivalents, for each form has among its advantages some not possessed by the other, with intermediate particle sizes having such advantages in proportion to their approach to one or the other extreme.

I claim:

1. A continuous method for bringing an organic fluid to a conversion temperature, effecting a desired conversion thereof, and then rapidly altering the temperature thereof and recovering a substantial amount of the heat or cold imparted thereto, which comprises continuously passing a stream comprising such an organic fluid serially through a first heat transfer zone, a second heat transfer zone, a conversion zone, and a third heat transfer zone, continuously passing a stream of solid mobile heat absorbent through a closed circuit including said first and third heat transfer zones, continuously maintaining the temperature of said stream of solid heat absorbent entering said first heat transfer zone at a level different from that of said stream of organic fluid entering said first heat transfer zone, continuously maintaining said organic fluid and said solid heat absorbent within said first heat transfer zone in intimate contact for a sufficient time to alter the temperature of said organic fluid toward said conversion temperature by direct heat exchange between same and said heat absorbent, continuously further altering the temperature of said organic fluid in said second heat transfer zone to bring same to said conversion temperature, continuously maintaining said organic fluid in said conversion zone at said conversion temperature under conditions effecting the desired conversion thereof, and rapidly and intimately contacting within said third heat transfer zone said organic fluid effluent from said conversion with said heat absorbent in such quantity and at such a temperature as to rapidly alter the temperature

of the conversion effluent fluid away from said conversion temperature and to recover at least a portion of the heat or cold imparted to said organic fluid in said second heat transfer zone by direct heat exchange between said fluid and said heat absorbent.

2. In the production of butadiene by the high-temperature conversion of hydrocarbons, the improvement which comprises rapidly effecting a suspension of silicon carbide particles smaller than about 60 mesh in a hot gaseous stream of butadiene-containing conversion effluents, said particles being at such a temperature and in such quantity as to cool said effluents to a temperature at least as low as about 700° F. at which undesired reactions are inhibited in a period of time less than about one second, separating the resulting suspension of powdered silicon carbide in gases into heated silicon carbide particles and quenched gases, recovering butadiene from said quenched gases, suspending said heated silicon carbide particles in cool fluid hydrocarbon feed to said conversion to partially heat said feed and to cool said silicon carbide powder, separating the resulting suspension into heated feed and cooled silicon carbide particles, and again utilizing the latter for said quenching.

3. A method according to claim 1 wherein said organic fluid is heated in said first and second heat transfer zones and is cooled in said third heat transfer zone.

4. A method according to claim 3 wherein an unsaturated hydrocarbon material is produced by conversion of an organic fluid at elevated temperatures.

5. A method according to claim 3 wherein said organic fluid is quenched in said third heat transfer zone by intimate contact with said solid mobile heat absorbent in finely divided form.

6. A method according to claim 1 wherein said organic fluid is cooled in said first and second heat transfer zones and is heated in said third heat transfer zone.

7. A method according to claim 6 wherein said conversion is a polymerization reaction.

8. In the production of acetylene by the high-temperature conversion of hydrocarbons, the improvement which comprises rapidly effecting a suspension of silicon carbide particles smaller than about 60 mesh in a hot gaseous stream of acetylene-containing conversion effluents, said particles being at such a temperature and in such a quantity as to cool said effluents to a temperature at least as low as about 1,000° F. at which undesired reactions are inhibited in a period of time less than about 0.2 second, separating the resulting suspension of powdered silicon carbide in gases into heated silicon carbide particles and quenched gases, recovering acetylene from said quenched gases, suspending said heated silicon carbide particles in cool fluid hydrocarbon feed to said conversion to partially heat said feed and to cool said

silicon carbide powder, separating the resulting suspension into heated feed and cooled silicon carbide particles, and again utilizing the latter for said quenching.

9. In the production of highly reactive organic materials by the high-temperature conversion of organic fluids, the improvement which comprises rapidly effecting a suspension of silicon carbide particles smaller than about 60 mesh in a hot gaseous stream of conversion effluents containing said highly reactive organic material, said particles being at such a temperature and in such quantity as to cool said effluents in a sufficiently short period of time to a sufficiently low temperature to inhibit undesired reactions, separating the resulting suspension of powdered silicon carbide in gases into heated silicon carbide particles and quenched gases, recovering said highly reactive organic material from said quenched gases, suspending said heated silicon carbide particles in cool fluid organic feed to said conversion to partially heat said feed and to cool said silicon carbide powder, separating the resulting suspension into heated feed and cooled silicon carbide particles, and again utilizing the latter for said quenching.

10. A method according to claim 3 wherein said solid mobile heat absorbent comprises particles of fused alumina.

11. A method according to claim 1 wherein said organic fluid passes countercurrently to a stream of solid mobile heat absorbent in particulate form in said first and third heat transfer zones.

12. A method according to claim 11 wherein said organic fluid is contacted with refrigerated aluminum spheres as said heat absorbent at temperatures below normal.

JOHN D. UPHAM.

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Certificate of Correction

Patent No. 2,443,210.

June 15, 1948.

JOHN D. UPHAM

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 2, line 46, for "a" before the word "temperatures" read *at*; column 3, line 32, for "butene" read *butenes*; column 8, line 51, for "temperature" read *temperatures*; column 13, line 23, for "great" read *greater*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 16th day of November, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.