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Jacoby

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[54] **CARRYING OUT HEAT-PROMOTABLE CHEMICAL REACTIONS IN SODIUM CHLORIDE FORMATION CAVERN**

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[52] **U.S. Cl.**..... **61/.5**, 165/45, 166/302, 166/256, 23/299, 23/272 A, 60/641, 423/659, 299/4, 299/5, 159/1 G

[51] **Int. Cl.**..... **E21b 43/00**, B65g 5/00, B01j 1/00

[58] **Field of Search**..... 23/312 AH, 302, 309, 293, 23/299; 159/1 G; 299/4, 5; 60/26, 641; 165/45, 106, 132; 166/302, 256, 259; 61/.5; 210/63; 423/659

[56] **References Cited**

UNITED STATES PATENTS

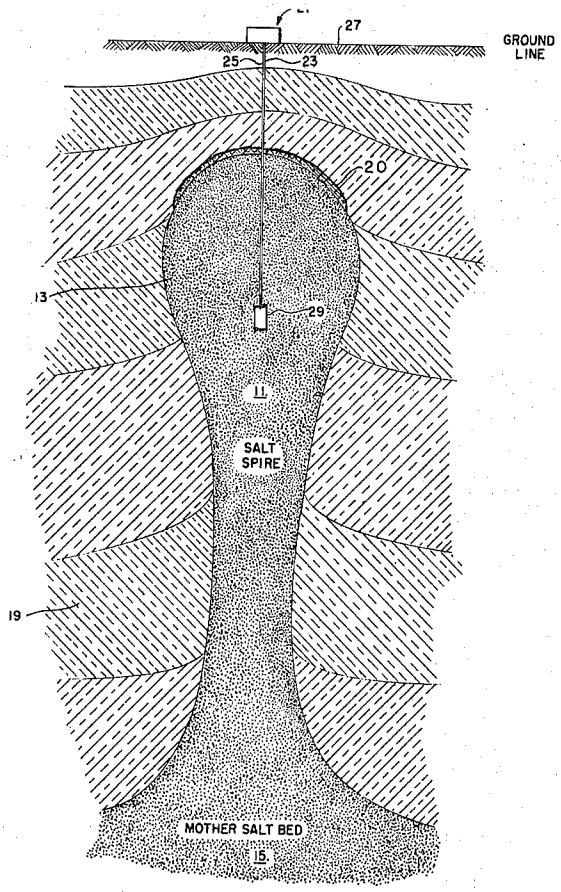
1,917,154	7/1933	Porter	159/1 G
2,461,449	2/1949	Smith	166/57 X
2,930,197	3/1960	Carpenter	61/.5
2,994,200	8/1961	Carpenter	299/5 X
3,140,986	7/1964	Hubbard	60/26 X
3,278,234	10/1966	Helvenston	299/5
3,284,137	11/1966	Wolber	299/5
3,348,883	10/1967	Jacoby	299/4
3,410,604	11/1968	White	299/4
3,421,794	1/1969	Jacoby	299/5
3,432,205	3/1969	Hottman	299/4
3,449,247	6/1969	Bauer	110/8 X
3,470,943	10/1969	Huisen	159/1 G
3,552,128	1/1971	Shook	61/.5

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[57] **ABSTRACT**

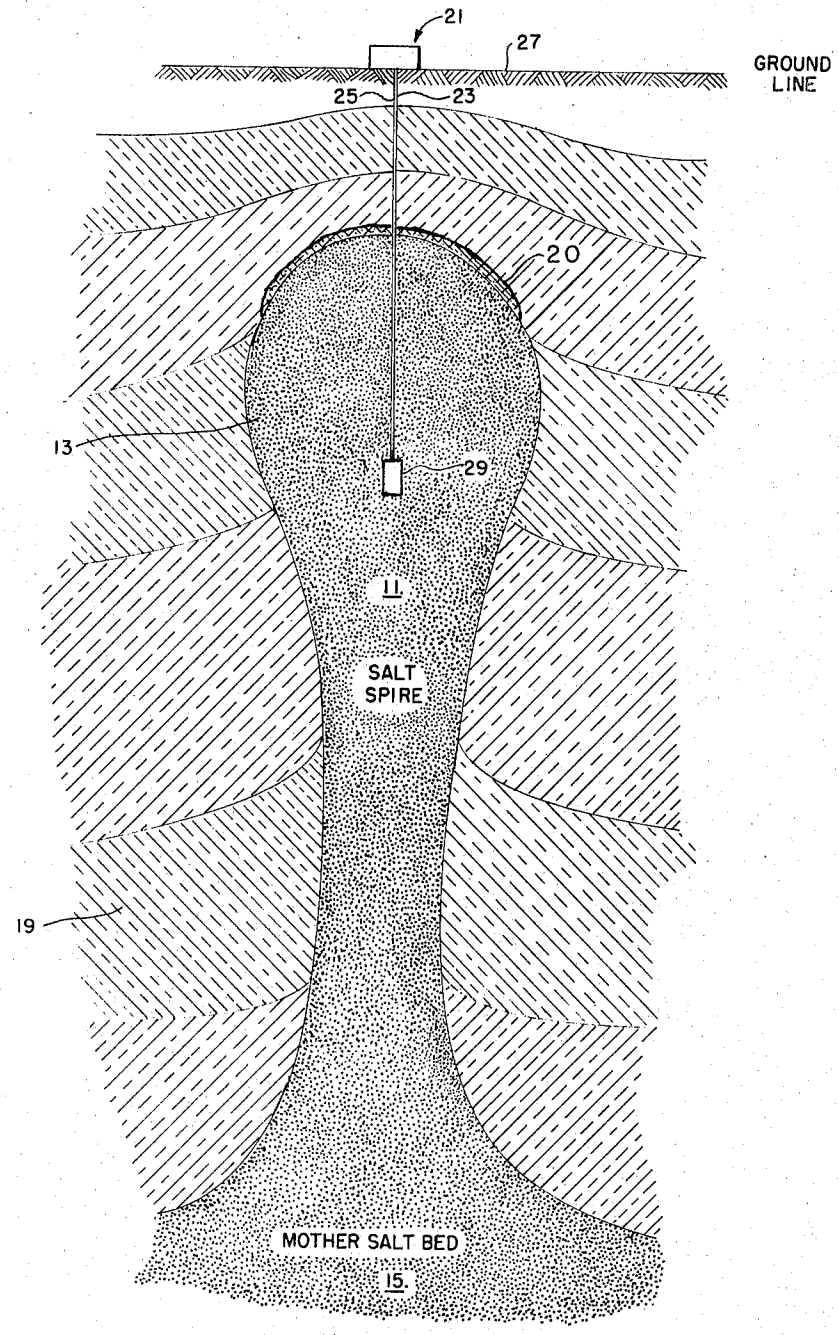
Chemical reactions, requiring heat are effected without air pollution contributions at reaction sites in underground cavities which are uniquely located to take advantage of little known and rarely occurring subterranean heat supply and heat conducting characteristics of certain geological structures extending in thermal continuity with heat sources far below reach of modern bore hole drilling techniques. Reactants are fed to the cavity and products are removed therefrom by means of passageways through bore holes extending from the earth's surface into the cavities. The activities are located at such depths, in highly heat conductive mineral spires or domes or the like which occur in thermal continuity with othewise inaccessible geological formations comprising unlimited sources of earth core heat, as to draw upon such unlimited supplies of heat at such rates and temperatures as will promote the desired chemical reaction.

7 Claims, 5 Drawing Figures



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FIG. 1

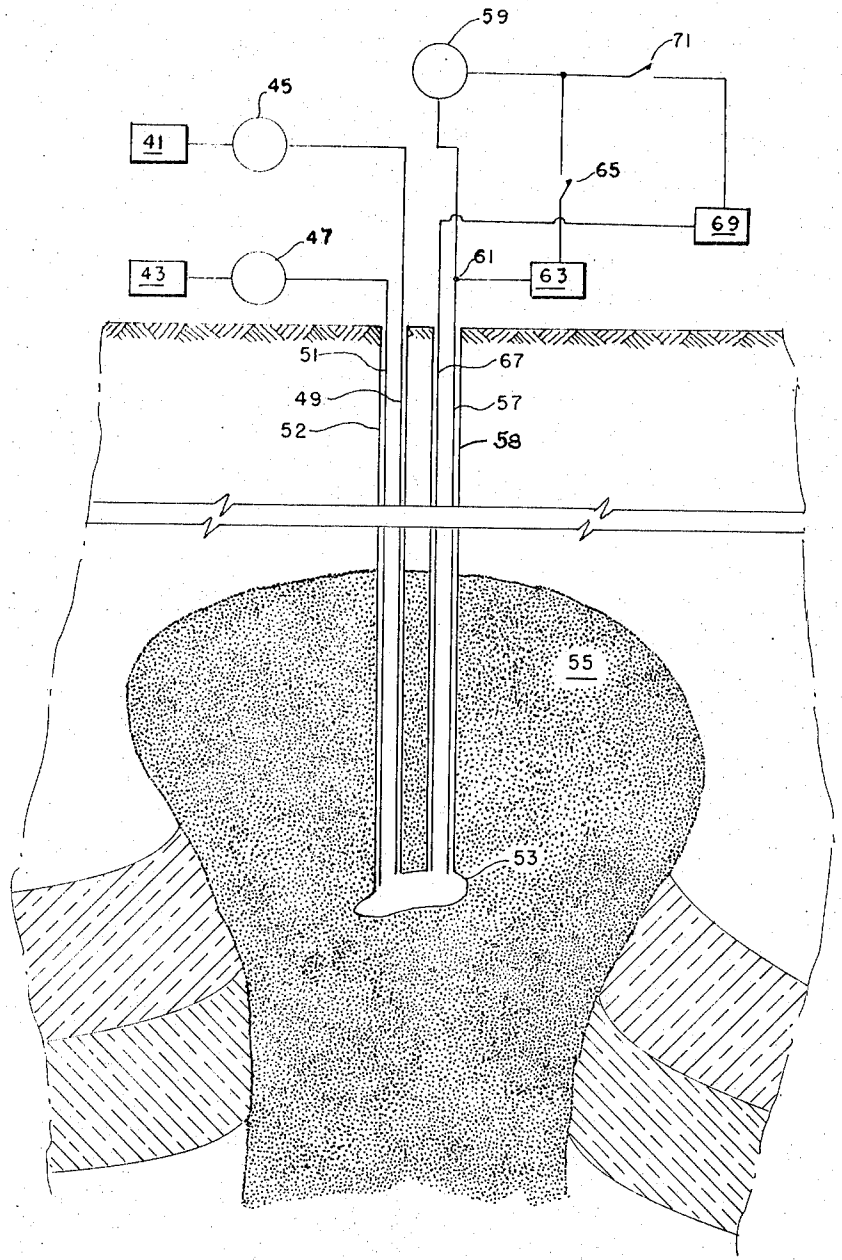


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FIG. 2



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FIG. 4

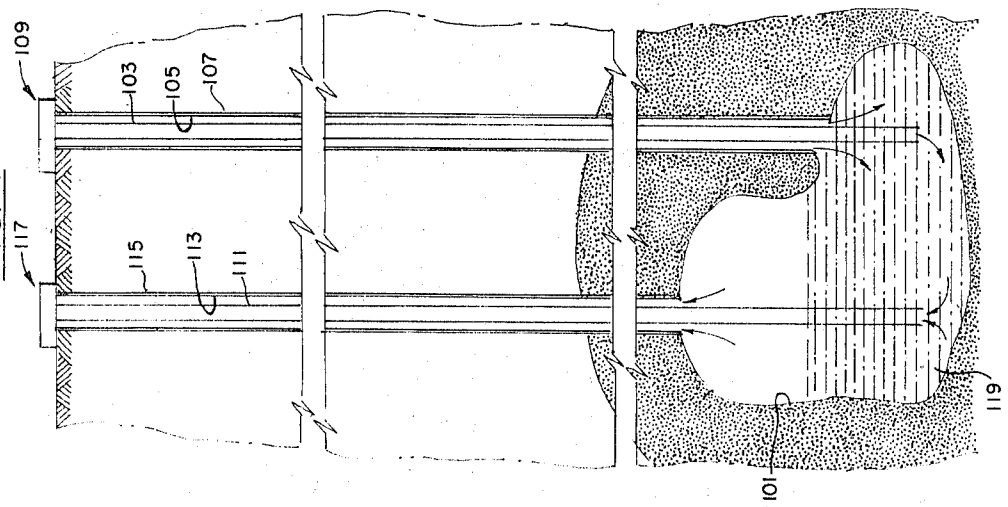


FIG. 3

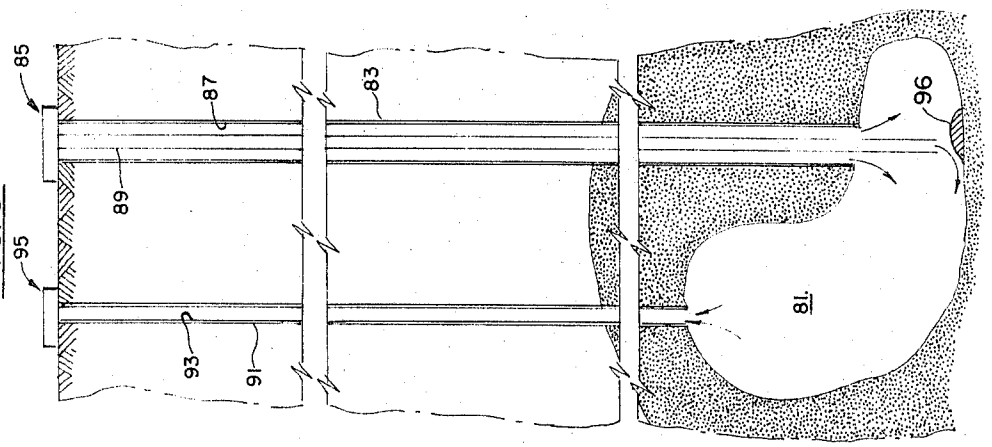
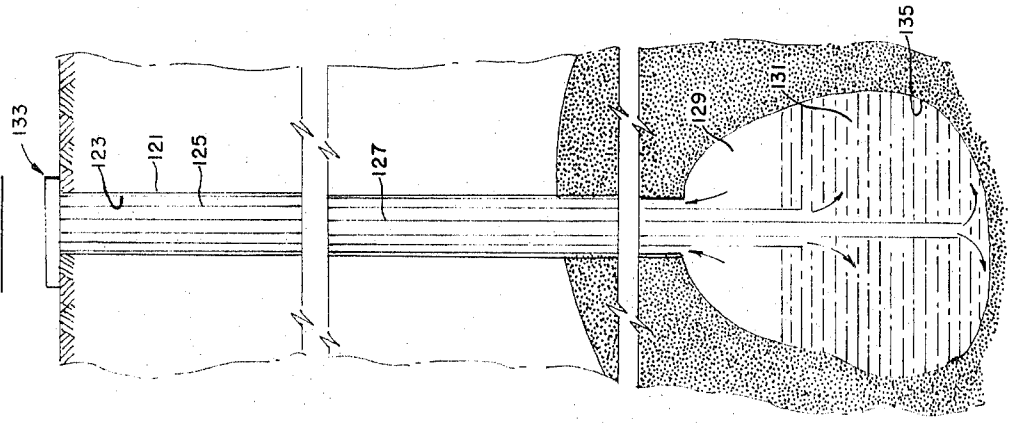


FIG. 5



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CARRYING OUT HEAT-PROMOTABLE CHEMICAL REACTIONS IN SODIUM CHLORIDE FORMATION CAVERN

In a preferred embodiment of the invention, the reaction site cavity will be formed in a "hot" sodium chloride rock salt spire or dome which is of highly heat conductive capabilities and in thermal communication with a lower geologic formation which transmits its heat through the dome or spire to the reaction cavity. In a similar manner, reaction cavities may be utilized in other highly heat conductive geologic formations of the spire, vein, or dome type.

Also included within the invention are various apparatuses for effecting the desired reaction and passage of materials to and from the reaction cavity. Specific geologic formations and the chemical reactions which best lend themselves to the practice of the invention are also disclosed.

BACKGROUND OF THE INVENTION

Chemical reactions, in which molecular configurations of atoms are changed, often require the addition of energy in the form of heat which is normally obtained by combustion of fuels with air. The combustion of fuels invariably gives rise to pollutant products which ultimately are released to the atmosphere. To a certain extent undesirable emissions can be controlled by utilizing nuclear energy as a source of heat, but even in such cases there are often thermal pollution problems associated with the operation of the nuclear plant.

It is to be especially noted that because of the continuing increase in technological processes and production, whereby manufacturing and chemical operations are expected to increase substantially in future years, pollution of the atmosphere and waterways would be expected to correspondingly continue to increase. Accordingly, it is important to develop improved reaction processes in which releases of pollutants are eliminated or at least minimized. When such processes can be employed economically or, as in the present case, exceptionally economically, their physio-social and economic values from many standpoints are manifoldly increased.

It is known that the interior of the earth comprises a tremendous source of heat, some of which is conveyed through the crust structure and to the surface of the earth, although the effects of this heat are hardly apparent at the earth's surface or in modern well drilled bore holes, or in so-called "deep" mines. The temperatures in such holes, even at the greatest economically marginal depths thereof, are not high enough, nor are the heat supply recuperative powers thereof sufficient that the heat energy to be abstracted therefrom may be usefully employed. For example, it has been found that at depths of 5,000 feet or more, the underground temperatures in normally encountered strata will sometimes be as high as 110°–115°F or thereabouts. Although efforts have been made to recover such heat energy from the earth, as from hot springs, and volcanoes, etc., past efforts have been economically unsuccessful.

Typically, present-day methods for recovery of geothermal energy require that geothermal heat is transported to its point of use in a mobile carrier such as a gas or liquid, thereby involving certain inadequacies and/or disadvantages. For example, if gas is employed, there must be sufficient pressure to allow sustained production from the well, and the gas must contain sufficient energy to drive a prime mover engine. Or, if the heat is contained for example in an aqueous hot brine, the temperature must be sufficiently high to permit flashing of the water content of the brine into steam for driving a steam engine or the like. The separated steam must not contain an undue amount of corrosive salts or gas such as ammonia or hydrogen sulfide, and the waste water/brines must be disposable without polluting surface or other potable waters. In contrast, the present invention avoids liberation at the earth's surface of any geothermal vapors or liquids; being a completely "closed system" whereby the heat removed from the earth's core is utilized as desired without polluting the earth's surface atmosphere.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the utilization of geothermal energy of the "clean heat" type for chemical reaction purposes, and provides a system avoiding the liberation of any reaction and/or geothermal vapors or fluids, such as would otherwise contaminate the earth'surface surface atmosphere.

As a result of this invention, a chemical reaction which requires heat can be undertaken within a reaction vessel developed in an environment furnishing a free and continuous and virtually inexhastible source of heat. Such reaction is controllable, and various reagents can be employed at different times for reaction in the same reaction vessel. It is adaptable to both batch and continuous processes. Furthermore, the geological formations most favorable to use in the present reaction often occur adjacent to sources of raw materials for the reaction, e.g., liquid or gaseous hydrocarbons.

In accordance with the present invention, a method of promoting a chemical reaction comprises feeding one or more reactants of a heat-promotable chemical reaction to an underground site of geothermal energy; which site is at a temperature high enough to promote the heat-promotable chemical reaction while holding the reactant in communication with such site of geothermal energy for a period of time sufficient to raise the temperature of the reaction; then removing a reaction product from such communication with the site of geothermal energy after said reaction; and finally cooling the reaction product.

Although the invention contemplates, broadly, that whereas chemical reactions have not heretofore been performed in a reaction site as set forth herein, it also includes many more specific subinventions involving factors such as the types of sites employed; direct contact of the chemical reactants with the natural walls of such site; the method by which the reactants are transported to the site, and by which the product is removed; the uses of reactants; and the production of products in certain physical states to facilitate transport to and from the reaction site. Also, the apparatus employed to effect the transport of reactants and to control the chemical reaction; and the uses of particular chemicals in the reactions which are compatible with the chemical composition of the rock wall structure at the reaction site.

It has been found that a cavern for the chemical reaction may be located at a depth of from about 5,000 to about 20,000 feet below sea level; which depths can be reached by economical and feasible drilling techniques.

Thus for example, in a salt spire or dome, or in other geologic formations in which the heat conductive mineral extends farther down than from a 20,000 foot level into heat conductive continuity with more intensely heated lower geologic sections such as at 40,000 or 50,000 feet below sea level, heat is conducted from such lower levels to such upper levels through the intermediate highly heat conductive dome or spire of salt or the like. Such a salt formation, being somewhat plastic under pressure, forms an excellent vitreous-like vessel for the intended chemical reaction, especially when the reactions involve organic materials such as will not dissolve or react with salt. Unlike typical "sedimentary strata" for example, rock salt and certain other igneous and metamorphic formations are so-called "competent" and provide leakproof wall surfaces preventing escape of reactants or loss of pressure through the walls of a reaction cavern fabricated therein in accordance with the present invention. Furthermore, the water soluble rock salt deposite referred to lend themselves readily to mining techniques which do not require the presence of men or heavy equipment underground. Thus, a reaction cavern can be formed in such formations by solution mining techniques, such as wherein water is injected through a bore hole to dissolve out salt, which is then removed as brine and thereby creating a cavern. As an additional benefit of this method, the salt removed is a useful product of commercial value. Or, the cavern may be formed by a chemical/nuclear explosive device.

Various means for transporting reactants and products from the underground reaction site may be employed, as may be different means for controlling the reactions. For example, the reactants may be kept apart until they reach the reaction site, or they may be blended in an inlet feed pipe. The product (s) may be removed through a separate casing in the inlet bore hole, or it may be taken out through a different exit line in a separate bore hole. The exit pipes may be so located in the cavern as to remove either gases or liquids, selectively. Controls may be employed to regulate the flows of reactants and the withdrawals of products so as to best maintain the reaction time for most efficient and/or complete reaction. The dwell or detention time of the reactants in the cavern is of course a function of the volume of the cavern and the flow rates, and this can be controlled so that the heat extracted in the reaction is continually replaced by a replenishment heat flow through the conductive mineral to the cavern from the greater depth.

It is a particular feature of the invention that when the reaction chamber of the system is fabricated within the "hot" portion of a heat conducting spire as explained hereinabove, the reaction chamber may be fabricated either by a solution mining process or by a mechanical "under-reaming" process; and that in either case the size and shape and wall surface area of the cavity can be constructed exactly in accordance with previously calculated data so as to insure that the reaction cavity will continuously furnish the desired heat supply.

Although the use of liquid reagents and the removal of liquid product are contemplated as within the invention, for most efficient continuous processes it may be preferred to employ gaseous reagents and to obtain a gaseous product. By doing so, if the product volume is less or if the average temperature thereof is higher than that of the reagents, flow will be facilitated in the outlet and inlet passageways, respectively. Normally, it will be preferred to avoid reactions which generate solid products because these will tend to fill in the cavern, and will not be recoverable unless they are suspended in liquid products or are periodically flushed out. In some enbodiments of the invention, as where gaseous products are made, to facilitate heat transfer from the walls of the cavern to the reactants the cavern may preliminarily be at least partially filled with a heat conductive fluid, e.g., diphenyl; and the reagents may be bubbled through this in contact with each other, to better absorb heat therefrom and to promote the desired reaction.

The general nature of the present invention and some exemplary embodiments thereof have been described, but a more detailed description of the invention, together with specific preferred embodiments and examples will now be given. Some of the more specific aspects of the invention will be exemplified, setting forth by way of examples reactions in a cavern in a salt spire or dome. It will be understood that these are also applicable to less preferred reaction sites in other materials, which will be of sufficiently high heat conductivity as to continuously replenish the heat extracted. The invention will be readily understood from the following descriptions, in conjunction with the drawing in which:

THE DRAWING

FIG. **1** is a geological sectional view of a salt spire containing a reaction site or cavern in accordance with the present invention, and a dual bore hole system for adding reactants and removing products to an aboveground facility;

FIG. **2** is a schematic diagram, illustrating means for addition of reactants and removal of product from the reaction cavern site, together with controls to regulate the process and the reaction temperature;

FIG. **3** is a vertical section of apparatus of this invention, showing the use of plural bore holes with separate addition of reactants through plural passageways in one bore hole and removal of product or product mixtures through the other bore hole;

FIG. **4** illustrates the use of plural bore holes communicating with different remote portions of a reaction cavity, showing two reagents entering through separate passageways in one bore hole and two products, one in gaseous form and the other in liquid form, being removed through separate passageways in the other bore hole; and

FIG. **5** is a vertical section of another well-cavern apparatus of the invention, wherein the single bore hole contains three passageways, in which reagents enter the cavity through the central casing and the middle passageway and the product leaves through the external annular passageway.

As is shown by way of example in FIG. **1**, a salt spire **11**, culminating in a dome **13**, rises out of a mother bed **15** through comparatively non-conductive heat-insulating rock formations **19** to a topmost point beneath a cap rock **20** (FIG. **1**,) such as typically exists above the dome. At the earth's surface above the salt spire is illustrated schematically the reagent input and reaction control and product output facility, as indicated generally at **21** comprising a housing accommodating the various facilities and controls for operation of the process and apparatus of the invention. Bore holes **23** and **25** descend from the surface of the earth

27 through the cap rock 20 and into a cavity or cavern 29 in the salt spire. Such cavity as illustrated herein may be established by solution mining out a portion of the salt from the spire 11 by pumping water through bore hole 23 whereupon it dissolves the salt at the bottom of the hole producing a brine which is then removed through bore hole 25. As stated hereinabove, however, it is to be understood that in lieu of use of a solution mining technique, the cavity 29 may be established by other means; such as by under-reaming an uncased lower end portion of one or both of the bore holes. A pipe string or casing (not illustrated) will preferably be installed to maintain the integrity of the size and shape of the passageways to and from the reaction cavity.

As represented in the drawing herewith, the cavern 29 is at a depth of say 15,000 feet below sea level, which is in the desired range of over 5,000 feet below sea level and preferably between 10,000 and 20,000 feet. For best results the cavern will perhaps be at a depth greater than 12,000 feet below sea level, depending upon how "hot" the dome is. The mother salt bed is shown as being at a depth of several miles below the earth surface. To make the invention operative in a most useful form, wherein heat is communicated as contemplated herein to the cavern 29 from hotter portions of the spire below the cavern, the spire should probably extend at least 40,000 feet below the earth surface, and preferably even deeper than that.

The requisite pumps, blowers, fans, etc. for feeding reactant liquids or gases to the reaction cavern 29 through passageway 23 and for removing products of reaction through passageway 25 are conveniently located in the housing 21; as well as tanks or other containers for the reactants and for storage of the product, as may be required. The facility will also include analytical means for monitoring the contents of the product as it emerges from passageway 25 to the aboveground facility. Equipment is also provided to control the flow of the reaction products, as by appropriately operating the pumps, blowers or fans; either to speed up or slow down the flow of materials through the cavern in response to variations in analysis of the product. Thus, for example if at any time it is indicated that the reaction is not proceeding as completely as is desired, the analytical equipment will operate a control to slow down the passage of reactants and product through the cavern; thereby increasing the dwell time therein to obtain a more complete reaction.

Similarly, when the reaction process is proceeding to completion, the speed of the materials through the cavern will be automatically controlled so that the most efficient overall operation for the prevailing conditions will be maintained. Also, thermostatic controls may be used to raise or lower the temperatures of the reactants in the cavern for best effect, by varying the speed of passage of the reactants through the cavern. Or, if preferred, a diluent gas or liquid might be fed into the cavern with the reactants to absorb heat, in order to lower the cavern temperature to maintain the most efficient temperature for the desired reaction. Exemplary contents of the building and the relationship thereof to the bore holes and to the reaction cavity site are illustrated schematically in FIG. 2.

Thus, for example as illustrated in FIG. 2, vessels 41 and 43 are shown to contain gaseous reactants that are sent by blowers 45 and 47, respectively, through concentric passageways 49 and 51 in a single bore hole 52 leading into a cavern 53 which is located in a salt spire 55 as explained hereinabove. Thus, heat conducted to the cavern 53 from the lower reaches of the spire operates to promote the desired reaction; and the reaction products or products are withdrawn through passageway 57 in bore hole 58 by means of fan or blower 59. Pumps will be normally used when the materials being reacted are liquids and the products are liquids; whereas when they are gases, blowers or fans will be preferred. In lieu of such means for moving the materials through the reaction cavern 53, a natural chimney effect may be employed, such as may be created by reason of the lower density of the product than of the feed; and in any event the rate of circulation through the cavern may be controlled by baffles or valves or pumps or blowers or fans, or the like, so as to properly maintain the requisite circulation and temperature and pressure on the reaction.

As shown at FIG. 2, as the reaction product is raised through passageway 57 it is automatically sampled at 61 and analyzed by analyzer 63 to determine the extent of completion of the reaction and the degree of obtaining of desired product. Analyzer 63 signals blower 59 to slow down when the desired product is not being obtained in a sufficient proportion, due to the reaction time being too short. Also, when more than the optimum quantity of product is obtained or when near the maximum proportion of desired prodict is in the reaction product mixture being removed, the analyzer 63 will signal the blower 59 to speed up so as to operate more efficiently and produce more of the desired product, assuming of course that the reaction time can be shortened without interfering with completion of the desired reaction. Switch 65 is normally closed when the analyzer is controlling the operation of the blower, pump or other means, for regulating flow of the reactants and products.

Instead of controlling the flow rate in response to analysis of the product, it may be controlled by the temperature of the reaction cavern, or by the temperature of the reactants or of the products at other points in the system. For example, as illustrated, a thermocouple probe 67 may be provided to extend to cavern 53 to measure the temperature at the top thereof. The thermocouple operates a relay controller 69 which speeds or slows the rate of flow of materials through the cavern so as to increase or reduce the heating process. Switch 71 allows isolation of the thermocouple control from the blower, as switch 65 allows isolation of the analyzer control from the blower. In addition to the control means shown, other mechanisms may be employed to regulate the reaction by varying the proportionings of the reactants; by adding diluents or by externally cooling or heating the reactants; etc. Such controls may be operated automatically or manually or semi-automatically.

In FIG. 3, 81 represents a salt cavern to which bore hole 83 connects from an aboveground installation 85. The bore hole is fitted with concentric casings as indicated at 87 and 89, to separately convey reactants to the reaction site cavern. The reactants may be either gaseous or liquid, and as illustrated in this figure the product is gaseous and is withdrawn through bore hole 91 which is cased by a single string of pipe 93 operating to intercommunicate the top of the cavern to which the lighter gases rise and the aboveground installation 95.

Appropriate auxiliary equipment are not illustrated in these views since the primary purpose of the drawing is to show only some preferred arrangements for carrying reactants and products to and from the reaction site.

FIG. 4 illustrates a reaction cavity **101** which may have been formed either naturally; by solution mining; blasting; or by any other suitable technique in a suitable heat conductive mineral formation as explained hereinabove. Reactants, either liquids or gases, are fed to the cavern through passageways **103** and **105**; and bore hole **107** intercommunicating the cavern and the aboveground installation **109.** Products of the reaction are removed through passageways **111** and **113** in the bore hole **115,** and delivered to the surface installation **117.** As illustrated, the bottom of the cavern is filled with a liquid **119,** which may be either a reactant or product, or some other medium utilized to assist heat transfer from the walls of the cavern. If the product of reaction is a gas, it is removed through annular passageway **113.** If the product is a liquid, it may be removed through tube **111** by sealing off annular passageway **113** and applying pressure through passageways **103** and **105.**

FIG. **5** illustrates the use of a single bore hole **121** containing a main string of pipe **123,** a hanging string of pipe **125** and central tubing **127.** These define passageways, through the central two of which reactants are fed, and through the external annulus of which product is removed. As shown, the product **129** is a gas and the reagents are fed into a liquid zone **131.** Reactants are fed to and product is removed from installation **133** aboveground, which is in communication with cavern **135** through the passageways defined by the pipes and tubing as shown.

From the foregoing general description and from the illustrative examples of preferred embodiments of the processes and the apparatuses of this invention, it is seen that an economical method is provided whereby chemical reactions can be effected in certain geologic formations as explained hereinabove, utilizing the materials of certain mineral formations as reaction vessels while at the same time utilizing otherwise unavailable heat to promote the reactions. A primary advantage of locating such a reaction site or cavern in the mineral formations referred to is to take advantage of heat source which is available for replenishment of the heat extracted from the cavern, so that the heat constantly available from the reaction cavity will not diminish below that required for the programmed reaction.

Such reactions may be effected without pollution of the earth land surfaces or atmosphere or waterways, such as accompanies emission of products of combustion such as result from the generation of heat by the burning of fossil fuels or the like. Also, the invention operates without thermal pollution of waterways such as often attends the employment of nuclear reactants to generate heat. Also, it will be appreciated that in accordance with the present invention a virtually explosion-proof reaction vessel is provided, while requiring no specifically complicated and/or expensive fabrication. Many variations of the invention may be successfully employed according to various cavern material and reactant and product conditions. Some of these will be outlined below in detail, and specific working examples will be furnished to illustrate certain preferred methods as contemplated by the invention.

The reaction site or cavern will in accordance with the present invention be located in a geologic formation which is characterized by being highly heat conductive and such formation should perhaps extend below the cavern to a distance of say 40,000 or 50,000 feet, whereby the more intense heat available from such depths furnishes a constantly available supply of heat such as will maintain the temperature of the cavern high enough to promote the desired chemical reactions involving large quantities of reactants. For example, it has been found that formations having conductivities of at least 12×10^{-3} calories per centimeter per second per °C. are sufficiently conductive to readily replenish heat to a reaction cavern for the purposes of the invention. Exemplary of materials having such high conductivity rates in addition to the preferred rock salt domes or spires, are hematite, magnetite, grossularite, anhydrite, chlorite, quartzite, rutile, dolomite, calcareous mica phyllite. Thus, it is contemplated that the conducting of heat through thermally integrated deposits of such materials to the reaction cavern is within the invention.

However, the creation of a reaction cavern in a salt spire for the purposes of the present invention is considered to be the most preferred embodiment thereof. Such spires often extend from the near the surface of the earth for distances of miles therebelow. For example in the Gulf Coast region of the United States, the formations of salt extend under the Gulf of Mexico, and the spires thereof rise vertically for miles from the "mother beds" thereof to the earth's surface, such as in Louisiana and neighboring states.

The employment of salt spires as sites for reaction caverns is advantageous in many ways. The drilling or boring of a well into a deep salt deposit is fairly easily done, since salt is not as resistant to drilling as many other mineral formations. Because of its plastic nature at great depth, rock salt closes in on the casing of a bore hole and holds it firmly in place, thereby improving the heat conduction therebetween. Whenever a cavity wall in rock salt becomes cracked, it instantly tends to re-seal. Further, because of the solubility of salt in water, a cavern at the bottom of a bore hole can be readily created by forcing water into the hole and removing the resultant brine solution.

A single bore hole may be employed to create the reaction cavern. In this case a central casing is inserted within the outer casing and water may then be forced down the center casing and removed through the annulus, or vice versa. By employing directing nozzles or other such means at the base of the well, the water may be so aimed at the walls of rock salt as to create a cavern of the desired shape. Such a cavern ultimately may for example be from 10 to 500 feet in diameter, and from 100 to 10,000 feet long. It is presently preferred to employ caverns which are about 50 to 200 feet in diameter and from 500 to 5,000 feet long. Generally, the shape of the cavern will approximate a vertically cylindrical shape, but horizontally extended caverns also may be used.

The cavern may if desired be lined with a suitable material, such as a polymeric synthetic organic plastic, rubber, metal, or other lining material such as can be plated or otherwise deposited or chemically formed upon the walls thereof after creation of the cavern. The bore hole or bore holes leading to the cavern may contain separate conduits or ducts or passageways for con-

veyance of different reactants or diluents to the cavern, and the materials of construction that will be employed may be of any of various types, such as stainless steel, synthetic organic plastics, e.g., polyester resins containing chopped glass fibers, or the like. The materials will be selected to withstand chemical reaction with the materials to be brought into contact therewith, and to be of sufficient strength to withstand the physical rigors of the operation.

In addition to utilizing a single cavern with one or tow bore holes as illustrated in the drawing, caverns with many more bore holes, judiciously located, may also be employed. Products may be selectively withdrawn therefrom depending on the height to which they rise in the cavern, which again will depend on their physical states and densities. In addition to utilizing plural bore holes, serially connected plural cavities may be employed, which may be interconnected by relatively small passageways. Such caverns may be at different heights and may be located in different geologic formations so as to be operative at different temperatures for plural stage reactions. The sizes of the caverns will be such as to result in the desired dwell time of reactants in each one, serially. Also, a plurality of caverns may be employed in parallel, when so desired.

The preferred rate of flow of heat to a reaction cavern as contemplated by the present invention will occur when the path from the lower heat source is minimally of a cross sectional area at least equal to the surface area of the cavern boundaries. Also, the reaction cavern should usually be of a volume greater than the sum of the bore hole volumes, to better function as a combination reaction vessel and heat source.

The reactions to be completed in the underground caverns of this invention will most probably involve fluids. Thus, for example, gaseous reactants may be employed and gaseous products obtained in a preferred embodiment of the invention. In such an embodiment it is highly desirable for the densities of the different gases to be sufficiently different so that they will gravitate to different portions of the cavern, from which they may be selectively removed. Of course, the points of addition will be located in a corresponding manner, so that between inlet and outlet there will be sufficient room for reaction. Also, of special interest are reactions in which the reactants are liquids and the products are gases. The reverse type reactions, wherein gaseous reactants yield liquid products aare also feasible, although more power will be required to force the liquid out of the cavern unless the reaction generates gas pressures such as will aid in expulsion of the product. Liquid reactants yielding liquid products are also contemplated by the invention, but again, density differences are desired so as to enable selective removal of product. In such cases multiple caverns interconnected through restricted openings would provde useful means for preventing the discharge of reactants rather than the product, from the cavern.

Desirably, the production of solids will be avoided, but if and whenever they are produced in conjunction with liquids, they will be suspended therein and removed with the liquids. In other cases, inert liquids may be beneficially added to the cavern to help wash out any solid products of reaction. Such a liquid may preferably be a brine solution, such as will not further dissolve the walls of the cavern. Such solutions may also be used as reaction media, or as inert diluents and/or may aid in heat transfer to the reactants. Although continuous processes are considered preferable, batch processes may also be performed; and between batches the presence of a brine solution or other inert liquid materials such as a petroleum oil, diphenyl, diphenyl either or the like will aid in extracting heat from the walls of the cavern, and will make the heat more readily available to the reactants when subsequently added. Although the preceding discussion has been with respect to a plurality of reactants and products, it will be understood that the invention also applies to those reactions wherein a single reactant and/or product is involved.

Among control facilities contemplated in connection with operation of the invention are thermocouples, analyzers, relays integrators, computers, cooling devices, clocks, enthalpy measuring devices, and flow meters. Also storage vessels, tanks, pressurizing means, mixers, heaters, coolers, filters and purifying equipment may be used, but will not be described herein in detail inasmuch as use thereof will be evident from this specification to one of skill in the art. Such controls may be utilized to regulate the rates of flow, reaction times, reaction temperatures, etc., so as to best use the heat furnished by the reaction cavern. Temperatures can be controlled by either speeding or slowing the flow of reactants through the cavern; by preheating or cooling the reactants; by heating or cooling the product; or by changing the direction of flow or the distance travelled by the reactants when together in the cavern before removal therefrom.

The type of chemical reactions that may be effected in the underground heat caverns are manifestly diverse. They include all the actions in which heat is a useful promoter, whether the reaction is ultimately exothermic or endothermic. Such reactions include for example halogenations of hydrocarbons, esterifications, etherifications, hydrogenations, polymerizations, condensations and nitrations; all of which may be performed in caverns of the present invention. Such are only a few of the various types of reactions which may be performed.

Preferably, the temperature in the reaction cavern will be maintained at over 100° and usually over 120°C. Constant temperatures of 150°C. or more are quite possible, and in some cases even higher temperatures, e.g., 200° to 250°C. are preferred. In reactions that require the addition of water, this may be added as a salt brine; but in such cases temperatures will have to be relatively low or a suitable pressure maintained to prevent boiling off of the water. Such brines, being saturated with salt, will not dissolve salt from the cavern walls, and thus the cavern will remain constant in size and shape.

In some cases catalytic reactions may be performed, whereupon suitable catalyst may be placed in any preferred manner in the cavern, such as by lowering a deposit thereof as illustrated by way of example at **96** (FIG. 3). Catalysts for such reactions may be activated carbon, platinum on carbon, alumina, highly porous silica, rhodium on alumina, ruthenium on silica, platinum on asbestos, ar any other catalysts such as may be required according to the reaction to be performed.

In addition to the features hereinafter referred to, including the advantage of lack of pollution problems, the present invention provides an overall improved safety factor. For example, reactions involving the creation of explosive compounds or flammable materials

may be effected in the caverns of the invention without fear that if there is an explosion, it will have a devastating effect on personnel working on the project or on nearby property. In fact, if an explosion does occur within a cavern in a salt spire, the plastic salt will immediately reseal the cavern, allowing it to be used again as if nothing had happened. Also, a cavern of this type is not subject to leakages in or out, whereby the reaction products are not lost and remain free of contaminations from exteriorly of the reaction chamber. If the reaction is exothermic the product may be passed through the exterior annular passageway of the concentrically cased exit bore hole, and will be thereby cooled as it travels through the cooler portions of the earth structure approaching the earth's surface. Thus, in many instances, no special product cooling steps will be required.

The following working examples illustrate a few specific embodiments of the present invention. These examples are illustrative only and are not to be considered as limiting the invention, especially since it is evident that the invention involves a broad concept of which many other embodiments thereof are practicable.

EXAMPLE 1

A reaction site is prepared in a Gulf Coast salt spire which extends from about 200 feet below the surface to about 80,000 feet below sea level. The reaction site is developed by first boring a ten inch diameter bore hole down to 12,000 feet below sea level in a central portion of the salt spire; then casing the hole and then directing fresh water to flow through the bore hole so as to dissolve the salt at the bottom of the hole. The brine so produced is removed by means of a 6 inch string of tubing suspended in the center of the cased borehole. At the bottom of the water inlet pipe a deflector may be set up to aim the inflowing water radially, and to thereby increase the horizontal cross section of the cavern being created. The water pipe is progressively lowered to increase the depth of the cavern to the desired size. The system may then be allowed to "rest" for awhile while full of water, so as to dissolve salt from the sides thereof and provide a smoothly walled cavern. This technique will create a reaction cavern extending along a substantially vertical axis, from say the 12,000 foot depth to 14,000 feet below sea level, and about 100 feet in diameter. Thus, the volume of such a cavern would be about 15 million cubic feet; capable of holding about 20,000 lb. moles of gaseous materials. The temperature in the lower part of such a cavern would be of the order of about 250°C.

After preparation of the cavern and removal of the brine therefrom, the pipes, casings and tubing, as illustrated in FIG. **5**, are installed; the outer pipe being of the order of 10 inches in diameter; the middle tubing being about 6 inches in diameter; and the intervening pipe being about 8 inches in diameter. The central tube extends to within about 100 feet of the bottom of the cavity, and the middle pipe extends to about 400 feet from the bottom of the cavity. Operational controls employed are those such as are illustrated in FIG. **2**, with the exception that no thermocouple is shown since the control of the process is illustrated as being regulated by the analysis of the products, only.

Stoichiometric proportions of methane and chlorine to make carbon tetrachloride are led through central tubing **127** and the interior annulus defined by the hanging string of pipe **125** and central tube **127**, respectively. The methane, being lighter, rises through the chlorine and reacts therewith to form a plurality of chlorinated hydrocarbons and hydrogen chloride byproduct. The feed rates of the gases are regulated so as to allow sufficient reaction time in the cavern for desired reaction. Thus, to allow as much as ½ hour total reaction time, the feed rates total about 15 lb. moles per second. Since such feed rates require high gas flow rates through the inlet passageways, in some instances it is found desirable to raise the outlet portions of the passageways so that a smaller proportion of the cavern is employed for a particular short-time reaction. In other cases, an inert compound, such as a brine solution in lower temperature reactions, or a high boiling liquid organic material in higher temperature reactions, may be employed to take up some of the cavern volume and thereby diminish dwell time. However, the present apparatus is most useful in those reactions of gaseous phase materials requiring longer reaction times, since the large volume available, once filled with reactants, allows good production rates with long dwells at elevated temperatures. The products of the reaction are removed through the external annulus defined by pipes **123** and **125.** They include methyl chloride, methylene chloride, chloroform and carbon tetrachloride.

At the top of the installation, product is automatically sampled at **61** (FIG. **2**) and analyzed by analyzer **63** to determine the content of carbon tetrachloride, and flow rates of materials are adjusted accordingly. The carbon tetrachloride is separated from the other chlorinated methane derivatives and the less highly chlorinated products are recycled to the reaction zone, with either of the reagents, usually preferably the chlorine, to undergo further chlorination. In the event that the temperature of the reaction site is not high enough to yield a sufficiently high proportion of carbon tetrachloride, the flow rate of reagents is slowed, and in some cases additional heat may be supplied to the cavern by lowering heating means thereinto.

By following the described procedure and utilizing recycle, almost stoichiometric yields of the desired carbon tetrachloride and byproduct HCl are obtained. The hydrogen chloride may be utilized as such in other chemical operations at the surface facility, or may be reconverted to chlorine and employed further to chlorinate more hydrocarbon. In similar manner the reaction site may be employed for the halogenation of other hydrocarbons, such as homologues of methane; of unsaturated hydrocarbons, especially lower hydrocarbons; and other chlorinatable organic materials. Depending upon the physical states of the reagents and the products, the arrangements of the reactant input and product outlet passageways may be adjusted to be similar to those shown in FIGS. **3–5,** or modifications thereof, as may be indicated for best performance in any case.

The procedure described hereinabove is also applicable to various other chemical reactions, such as the burning of hydrogen and chlorine to form hydrogen chloride; the oxidation of ethanol to form acetaldehyde; the oxidation of formaldehyde to formic acid; addition reactions to acetylene; the nitration of glycerine; tri-nitration of toluene; the dehydration of maleic acid; the production of water gas; the production of hydrochloric acid from sodium chloride and sulfuric acid; the

manufacture of amines from nitro compounds by reduction with hydrogen; and many other reactions, including metathetical, rearrangement, condensation, and replacement reactions.

The reactions described may be conducted at substantially atmospheric pressure or slightly above, due to the gas column at the top of the cavern; but to facilitate pressure responsive reactions additional pressure may be applied to the reaction site. Thus, by filling the well passageways with reactant/product fluids, the weights of the fluid columns may be as much as 600 atmospheres at a 20,000 foot depth, if the liquids are of the density of water.

Although a preferred embodiment of the invention will involve those reactions which require additional heat, to promote some reactions to go most efficiently, catalysts are required. For example, using the apparatus described in this example, ortho-xylene, as a liquid, is added to the reaction cavern together with air or oxygen, with the proportion of air being in great excess to avoid explosions, and the reaction mixture is passed over a catalyst bed as indicated at **96** (FIG. **3**). A preferred catalyst in such case is vanadium pentoxide on a suitable base, such as a highly porous inert substrate. In lieu of the arrangement shown, the catalyst may be located in the inlet or the exit passageway instead of in the reactor itself; but in any case in such manner that the reagents pass through it after being heated. The product phthalic anhydride, being above its boiling point, may be removed as a gas. Or, when a liquid is produced, due to lower cavern temperature, it may be pumped out of the cavern or driven out by application of pressure as explained hereinabove. If liquid, the passageway design may be varied to have the exit passageway communicate with the liquid at the bottom of the cavern, as illustrated in FIG. **4**.

EXAMPLE 2

A dual well reaction site is prepared in a Gulf Coast salt spire of the type described in Example 1, to produce a reaction cavern and associated passageways as shown in FIG. **4**. The wells extend to a depth of about 12,000 feet below sea level and lead into a cavern having a total volume of about 4 million cubic feet. The outer casing comprises a 12 inch diameter pipe, and the inner casing is of about 6 inch diameter. The cavern is made by boring separate wells **105, 115**; extracting salt from below them by circulating water through them as described in Example 1, and thus causing the wells to communicate with each other, as shown.

For the reaction of ortho-xylene and oxygen to produce phthalic anhydride, as described in Example 1, air and ortho-xylene are delivered into the cavern through the inlet passageways, and by maintaining the temperature in the cavern below the boiling point of phthalic anhydride, the phthalic anhydride collects as a liquid in the bottom of the cavern and is removed through passageway **111**, while the unused nitrogen is removed through passageway **113**. As mentioned in Example 1, a catalyst is employed to promote the reaction. Also, controls are employed to optimize the reaction, as in Example 1.

Instead of the production of phthalic anhydride, the method of this example may be applied to the manufacture of other chemical compounds, such as ammonia from nitrogen and hydrogen; formaldehyde from alcohol and air; lower polymers of ethylene from ethylene; dimethyl ether from methanol and diethyl; ether from ethanol by catalytic dehydration of alcohols; of methanol from natural gas by use of a pressure of 750 lbs. per square inch and a deposited copper catalyst; plus many other commercial organic and inorganic reactions. In those instances where no liquid products are produced, all the gaseous product may be removed through passageway **113**.

By utilizing the two-well system of this example, a clearly defined path including a horizontal component, is required to be traversed by the reactants before removal from the reaction site. This allows a greater flexibility of operations of the chemical reactions; permits the uses of caverns of different shape designs and volumes; and in some cases allows two-stage reactions to proceed sequentially; the first reaction being effected in a comparatively small volume under the inlet pipes and tubes, and the second reaction in the larger cavern portion.

EXAMPLE 3

A reaction cavity of the order of 2 million cubic foot capacity is prepared by boring into a deposit of quartzite at a depth of about 10,000 feet below sea level and blasting a cavity therein. The crushed rock is removed by mechanical means, when feasible, or by chemical means, e.g., dissolving in suitable acid. Also, it may be removed while suspended in a heavy fluid such as an aqueous gel, pumped through the cavity. After creation of the cavity, chemical reactions such as those described in Examples 1 and 2 are conducted therein. As a specific embodiment of such types of reactions, utilizing passageways such as shown in FIG. **3**, wherein the tubing is 6 inches in diameter and the pipes are 12 inches in diameter, ethylene oxide is made from ethylene and air, using a silver catalyst promoted with an alkaline earth metal oxide, supported on alumina. The temperature of the reaction and of the reaction cavern, is about 230°C. and the pressure is about atmospheric. The feeds of ethylene and oxygen are in substantially stoichiometric proportions, at rates designed to produce short reactions times, e.g., from 5 to 45 minutes.

Another reaction such as may be effected in this apparatus is that wherein ethyl acetate is produced from ethanol and acetic acid. Although this reaction does not require heat to make it go, the use of the present reaction cavern, usually of comparatively small volume, serves to furnish not only a ready-made reaction vessel, but also a useful regulator of the temperature of the reaction. The product is cooled to near room temperature by its passage to the aboveground facility through the exit pipe which is in heat exchange relation with the relatively cool environmental earth structure. Also, chemical reactions wherein heat is operative to vaporize a liquid reactant may be practiced herein, even if, once vaporized, no further heat is needed to complete the reaction. Similarly, reactions effected by heat and conducted in conjunction with physical separations of materials are usefully effected by the method of this invention. For example, solvents may be partially removed from reactants by vaporization thereof by application of the cavern heat, and the more concentrated solutions resulting may be more reactive.

Among other reactions that may be effected in caverns of the invention are neutralizations, acidifications, hydrogenations, dehydrogenations, etherifications, esterifications, isomerizations, nitrations, carbonylations,

oxidations, reductions, catalytic reactions, pressure reactions, high temperature and low temperature reactions, etc.

I claim:

1. A method of performing a chemical reaction which comprises:

determining the location of an underground sodium chloride salt formation having heat conductivity characteristics much higher than the surrounding geologic structures, said formation extending downwardly into thermal connection with a deep seated heat source, said heat source being at a depth which is inaccessible by commercially practicable bore hole drilling techniques, said formation extending upwardly to a level which is accessible by commercially practicable bore hole drilling techniques,

dissolving a cavity to form a reaction cavern of selected size within said formation at a depth of at least 10,000 feet below sea level sufficient to insure a selected temperature of at least 100°C in said cavern and terminating the dissolution of said cavity at a selected size which provides a heat transfer area such that heat energy will flow from said source to said cavern at a selected rate so as substantially continuously to replenish heat abstracted therefrom at said selected rate and maintain said selected temperature within said cavern,

feeding material which is inert with respect to the salt and is a reactant of a heat-promotable chemical reaction which will occur at said selected temperature through a passageway to said cavern at such rate as to elevate the temperature thereof to the reaction temperature and thereby initiate and maintain the chemical reaction while holding the reactant in said cavern for a sufficient period of time to produce a reaction product,

and removing the reaction product from the cavern at a rate insufficient to abstract heat energy therefrom at said selected rate.

2. A method according to claim 1 wherein a plurality of reactants is fed to the cavern, at least one of which is fed from aboveground, and a reaction product is partially cooled by passage through the ground from the cavern to aboveground by heat transfer to the intervening rock.

3. A method according to claim 1 wherein the plurality of reactants is fed to the cavern from aboveground through separate passageways, and remain separate until they enter the cavern, where they are mixed together and the temperature thereof is raised to a temperature which is high enough to promote the heat-promotable chemical reaction, and a product of the reaction is sent aboveground by passage through a separate passageway from those through which the reactants are fed from aboveground to the cavern.

4. A method according to claim 1 wherein a plurality of reactants is fed to the cavern through a single passageway, in which they are mixed before reaching the cavern.

5. A method according to claim 1 wherein the flows of reactant(s) and product(s) are so controlled that the dwell time of the reaction mixture in the cavern is sufficient to promote substantial completion of the chemical reaction.

6. A method according to claim 1 including the step of analizing the chemical composition of the product and controlling the flows of reactants and products so as to regulate the reaction temperature and/or dwell of the reactant (s) in the reaction cavern to obtain a satisfactory yield of product (s).

7. A method according to claim 6 wherein the proportions of reactants are maintained substantially constant and the flow thereof and of the reaction product are regulated in response to a monitoring of the composition of a reaction product being discharged from the passageway from the cavern to aboveground.

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