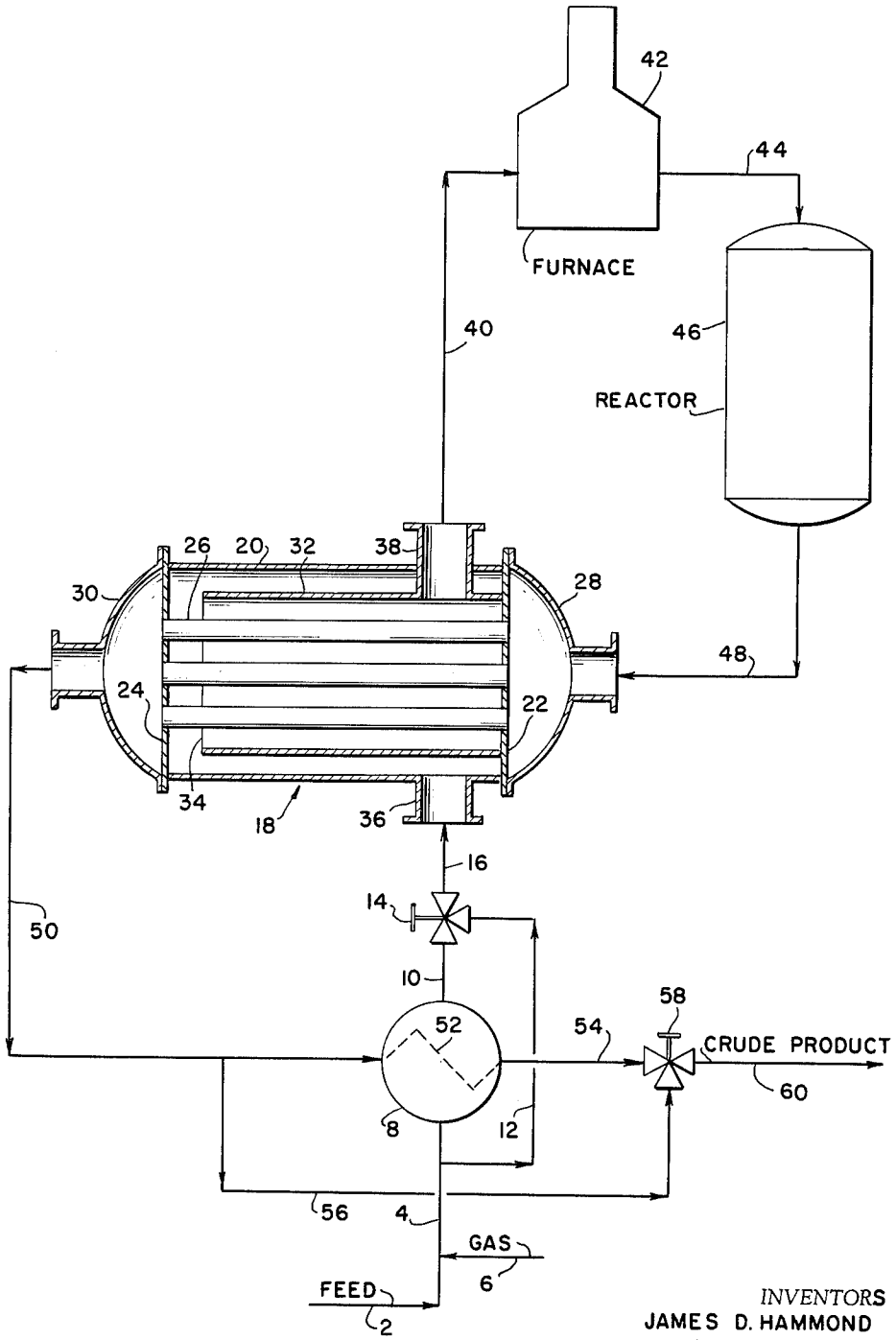
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HIGH TEMPERATURE HEAT EXCHANGE

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HIGH TEMPERATURE HEAT EXCHANGE

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The present invention relates to a process for exchanging heat between fluid streams and the equipment for carrying it out. It is particularly concerned with the exchange of heat in high temperature systems and especially those operating under high pressure.

Many systems have been devised for the economic utilization of heat in chemical processes and it is common to employ heat exchanges wherein one fluid stream is cooled by transferring a substantial portion of its heat content to one or more colder streams. For example, the heat of reaction products frequently is transferred to cold reactants through the tube walls of indirect heat exchangers. This heat exchange may be used to supply much or all of the heat necessary to bring the reactants up to reaction temperature with a consequent saving in fuel costs. Meanwhile, the desirable function of cooling the reaction products to temperatures suitable for storage or for other processing is accomplished simultaneously, at least in part, without involving any expenditure for cooling water or for the forced circulation of cool air.

Despite continuing progress in heat transfer, many serious problems still exist, particularly when high temperatures are involved. These problems are aggravated by other severe conditions as exemplified by high pressures and the presence of agents that attack the heat transfer surfaces. For example, hydrogen is known to have an embrittling effect on ordinary carbon steel at high temperatures. In the past, the solution of such problems has usually been to utilize expensive alloys, such as austenitic stainless steel, in the construction of high temperature exchange equipment, especially where the heat transfer surfaces were subjected to any chemical attack. Operations at high pressures require heavy wall thicknesses in such equipment and this further increases the cost.

An object of the invention is to provide an improved heat transfer process, and a system for carrying it out.

Another object of the invention is to provide a process for the transfer of heat at high temperatures which permits utilizing inexpensive construction materials to the maximum extent.

A further object of the invention is to provide improved control of the temperature of fluids in a combination of two or more exchanges of heat.

Still another object of the invention is to provide a high temperature heat exchange system in which relatively inexpensive construction materials may be utilized with safety at high pressures.

Further objects and advantages of the invention will be apparent to those skilled in the art on consideration of the detailed disclosure hereinafter in which all temperatures given in degrees Fahrenheit unless otherwise stated.

The present invention concerns transferring heat from the effluent of a high temperature reaction in the vapor phase to the stream of normally liquid material and a gas being charged to said reaction and particularly the improvement which comprises vaporizing liquid from a mixed phase stream by heating the mixture in a first indirect heat exchanger, and introducing the resulting wholly gaseous stream into a second indirect heat exchanger at a temperature less than about 650°, heating said gaseous stream in the second exchanger by the transfer of heat from said reaction effluent which is thereby cooled from a temperature above 900° (sometimes above 1200 or even 1300°) to less than about 800°, and passing the partially cooled reaction effluent from the second exchanger to the first exchanger to heat said mixed phase stream. Control of said vaporizing step may be accomplished by diverting a stream of fluid around said first exchanger to control said heat transfer. This stream is desirably a part of the mixed phase one, but the partially cooled heating medium stream may be diverted or a portion of both streams can be separately by-passed for obtaining that vaporization control.

Narrower aspects of the invention include the uniquely suitable application of the aforesaid heat transfer in a thermal hydrodealkylation process involving high hydrogen partial pressure and a highly exothermic reaction, a shroud or cylindrical baffle surrounding the tubes in the high temperature heat exchanger in order to cool the shell thereof, as well as the preferred regulation of the temperature below about 480° in the partially heated gaseous stream that is supplied to the high temperature or second heat exchanger for further heating as the heating medium there is cooled to a temperature that is preferably below about 650°.

For a better understanding of the nature and objects of this invention reference should be had to the accompanying drawing in which the figure is a flow sheet or schematic representation of a portion of a plant for producing benzene by the thermal hydrodealkylation of toluene with one component illustrated in longitudinal cross section. For simplicity and greater clarity, a number of valves, controllers of the flow, temperature and pressure as well as other conventional accessories have been omitted from the drawing.

In the flow sheet, a stream of nitration grade toluene is pumped from the supply line **2** into the conduit **4** where it meets a stream of hydrogen from pipe **6**. The molar ratio of hydrogen to toluene is maintained at 4:1–6:1. The mixture of liquid and gaseous material in line **4** is at a temperature level of 120° F. and under a pressure of 660 pounds per square inch gauge (hereinafter abbreviated as p.s.i.g.). Most of this stream is passed through the shell side of the conventional tube and shell type indirect heat exchanger **8**, and it emerges in conduit **10** entirely in the gasiform state after being heated by a 630° gaseous stream described hereinafter.

The heat exchanger **8** is constructed of an inexpensive alloy of moderate heat resistance, namely carbon steel with a content of 0.5% by weight molybdenum and 1.25% chromium; the latter alloying component is included as a safety factor for it is not considered to be needed under normal conditions for the temperature service mentioned. It is a distinct advantage that an expensive stainless steel or other metal of high heat resistance is not required here as would otherwise be the case if the heating stream were at a temperature above 800°.

Usually a minor portion, that is less than half, of the mixed phase material is diverted around heat exchanger **8** without heating through the by-pass **12** to the 3-way valve **14** where it rejoins the remainder of the charge in line **16**. In the instant illustration, 35% of the charge is by-passed into line **12**. While traversing the heat exchanger **8**, all of the liquid in the mixed phase stream is vaporized and the resulting gaseous stream in conduit **10** is under a pressure of 655 p.s.i.g. and the relatively high temperature of 540°. After rejoinder, the commingled streams in the line **16** leading out of the 3-way valve are at 375° under a pressure of 645 p.s.i.g. This temperature is relatively near to the minimum suitable at this stage for the particular charge selected as it is just considered adequate to maintain all of the feed stock in the gaseous phase at this point. Any significant amount of liquid phase material would be undesirable inside the high temperature

second heat exchanger **18** because such liquid would vaporize so quickly upon contact with the very hot metal surface as to produce rapid cooling and consequently extremely heavy stresses therein. Also such liquid would be much more likely to produce coke or other solid deposits upon vaporizing in the high temperature exchanger than it would at the more moderate temperatures in the first heat exchanger.

Heat exchanger **18** is depicted in a schematic cross-sectional view to illustrate the course of the heat exchanging fluids passing therethrough. It is heavily constructed throughout of an austenitic stainless steel containing about 18% chromium and 8% nickel to withstand the high temperatures and high pressures involved as well as to resist attack by the hydrogen in the vapor streams passing therethrough.

This exchanger comprises the cylindrical shell **20** with the tube sheets **22** and **24** at each end connected by a plurality heat transfer tubes **26** in known manner to provide communication between the inlet and outlet headers **28** and **30**, respectively, for the heating medium. One end of a shroud or cylindrical baffle **32** is integrally attached to the tube sheet **22** and the other end **34** of the baffle is open. This baffle surrounds the tubes **26** for the greater part of their length and divides the interior of the shell into an outer empty annular zone and an inner cylindrical zone containing the tubes **26** that transfer the major portion of heat exchanged by the device. The inlet flange **36** which admits the stream to be heated opens directly into the annular zone next to the shell whereas the outlet connection **38** for this stream passes through both the shell and the baffle and communicates only with the interior zone within the cylindrical baffle **32**.

The charge of toluene vapor and hydrogen enters the shell **20** through the inlet connection **36** and passes first through the annular zone bounded by the interior surface of shell **20** and the exterior of baffle **32**. Since this zone is shielded by the baffle from the heat transfer tubes, the gaseous material flowing through the annular region is neither exposed to contact with tubes **26** nor to heat radiated directly therefrom; hence this material remains considerably cooler than the internal streams and structural elements of the heat exchanger. This annular flow serves to cool the shell **20** which is the largest member that is exposed to a high pressure differential, namely about 645 p.s.i.g., in the apparatus. Such cooling of the shell not only reduces the strains therein but also conserves heat as radiation losses from the cooler shell are lower. When the gas stream reaches the end **34** of the baffle, it turns inwardly and its course is reversed as it passes through the central zone within baffle **32** and amongst the heat transfer tubes **26** until it reaches the outlet connection **38**. This reverse flow through the inner zone is in a direction countercurrent to the flow of heating medium through the interior of tubes **26** and thus promotes maximum efficiency in the transfer of heat through those tubes.

The charge leaves the high temperature heat exchanger **18** in conduit **40** at a temperature of 910° under a pressure of 625 p.s.i.g. on its way to the furnace **42** where it is further heated. This heated charge then passes through the line **44** to the reactor **46** where it undergoes a thermal hydrodealkylation reaction at temperatures in the 1200–1400° range and a reaction pressure of 575 p.s.i.g. in which a major percentage of the toluene is converted into benzene with the attendant production of methane and consumption of a minor proportion of the large volume of hydrogen charged.

The effluent reaction products leave in line **48** and serve as the heating medium for exchanger **18**. When a liquid quench, such as the normally liquid fraction of the crude benzene product of the instant process after suitable cooling, is employed in this process, the temperature of the heating stream entering header **28** of the high temperature exchanger is 975° and the pressure is 560 p.s.i.g.

From inlet header **28** of the high temperature heat exchanger **18**, the heating stream passes through the heat transfer tubes **26** to the outlet header **39**. Next, this benzene-rich product stream is carried to heat exchanger **8** in line **50** at a temperature of 630° and pressure of 555 p.s.i.g. In exchanger **8** also, this heating medium passes through the interiors of the tubes **52** which are schematically represented in the drawing and the cooled heating medium exits at a temperature of 410° and pressure of about 545 p.s.i.g. in conduit **54**.

In controlling the heat transfer at moderate temperatures in exchanger **8**, an optional by-pass **56** is provided to convey a portion of the product stream around exchanger **8** to the 3-way valve **58** if desired. The crude benzene product stream passing through valve **58** is withdrawn in conduit **60** for further processing which typically involves separation of the gas, stabilizing in a tower and cooling.

In illustrating the present invention in a thermal hydrodealkylation reaction with no quenching of the reaction products, the mixture of toluene and hydrogen in a molar ratio of 6:1 passes through conduit **4** at a temperature of 120°. Ninety percent of this material is passed through the first exchanger **8** and it emerges in line **10** at a temperature of 490° while the remainder is diverted through by-pass **12** and rejoins at valve **14**. This remixing vaporizes all of the liquid phase material entering this valve from the by-pass and reduces the temperature of the gaseous stream in pipe **10** to a level of 450° by the time the inlet **36** of the second heat exchanger **18** is reached. The hotter heating medium in this modification of the invention increases the heat duty of this exchanger and, of course, substantially increases the temperature rise of the charge passing through this heat exchange device over the temperature increase described earlier. Accordingly, the charge now leaves in line **40** at a temperature of 1130°; and this is further increased to 1260° in passing through the furnace **42**. The peak reaction temperature in reactor **46** is 1350°, and the effluent products enter the header **28** of the heat exchanger at substantially this temperature since relatively little heat is lost during passage through the short line **48**. The partially cooled heating medium emerges from header **30** into line **50** at a temperature of 715°, and thus does not require the use of stainless steel or other high alloy structural material in the moderate heat exchanger **8** as would have been necessary if this stream were at a temperature level of above 800° F. The heat exchanger **8** reduces the temperature of this heat medium to 340° by the time that it reaches the conduit **60**, and the crude products receive further processing as before. The pressures maintained through the system correspond with those given hereinbefore.

Two by-passes around heat exchanger **8** have been described both controlled by 3-way valves. One diverts the charge stream being heated and the other is for the products stream that is being cooled. Either one or both of these by-passes may be used in regulating the amount of heat transferred within the moderate temperature heat exchanger **8**. It is generally preferable to by-pass a part of the mixed phase charge rather than the crude product stream because it is somewhat easier to manipulate the 3-way valve **14** in handling streams in pipes **10** and **12** which are considerably cooler than the 630° stream which would be diverted through by-pass **56** by adjusting the 3-way valve **58**.

Such valves function in known manner to reduce the area of the opening therein communicating with the main supply pipe and to increase the opening that communicates with the by-pass supply pipe when the valve is turned in one direction and conversely when it is turned in the opposite direction. The exit aperture through which the fluid leaves the valve is not altered by such regulation.

It is a simple matter to manually adjust the valve **14** by reference to a thermometer (not shown) in conduit **16** to insure that the temperature is sufficiently high (i.e. free of all liquids) in the commingled streams about to enter the high temperature heat exchanger **18**—375° F. in the specific embodiment described—and not over 480°. If desired, automatic control of either 3-way valve may be substituted for manual operation by the use of conventional automatic valves which may be regulated in response to a temperature sensing element located downstream of the valve in conduit **16** or **60**, respectively. However, for most purposes it will be found that the manual valve **14** or **58** can be easily adjusted for any given process and charge stock, and that readjustment of the valve will only be needed on rare occasions.

Although a 3-way valve is greatly preferred from a standpoint of safety and also to simplify regulation of the by-pass, ordinary cocks, gate or globe valves may be employed to accomplish the same result by installing one in each supply line. For example, 3-way valve **14** may be replaced by a T connection plus a globe valve in each of lines **10** and **12**, and regulation of the amount of mixed phase material diverted around exchanger **18** will then require adjustment of the two valves.

To obtain the full economic benefits of the present invention, the partially cooled heating medium leaving the high temperature heat exchanger **18** should be at a temperature less than about 800° F. at elevated pressures of the order of 500 or 600 p.s.i.g. to avoid the necessity for stainless steel or other special heat resistant alloys being used in the moderate temperature heat exchanger **8**. In the case of quenched reaction products serving as the heating medium, the stream to be heated may enter exchanger **18** at a temperature as high as about 650°; but in the case of unquenched reaction products entering this exchanger at a temperature above about 1200° F., the relatively cool stream to be heated should not enter at a higher temperature level than about 480° F. In a preferred modification, it is desirable to cool the effluent reaction products to a temperature below about 650° in high temperature exchanger **18** in order that the exchanger **8** may not even require any chromium in the composition of the structural metal, and in this instance also, the stream in conduit **16** to be heated should not be hotter than about 480°. An ordinary molybdenum steel containing about 0.5% molybdenum is suitable for exposure to temperatures up to about 650° F. with gaseous streams of the type disclosed herein. Thus, control of the heating of the charge in exchanger **8** is quite significant in obtaining the full advantages of this invention. Such control is reflected in good regulation of the temperature of the gaseous stream in line **16** by suitable adjustment of the 3-way valve **14**.

While the instant heat transfer process and system are particularly adapted for use with the thermal hydrodealkylation process set forth hereinbefore, it is obvious that the present invention is not limited to this particular reaction and that such heat exchange has wide utility in connection with cooling and heating fluid streams employed in other high temperature operations of either the exothermic or endothermic type. Accordingly, this invention is not to be construed as limited in any manner except in accordance with the language of the appended claims and as may be required by the prior art.

We claim:

1. In a process for the thermal reaction entirely in the vapor phase of normally liquid material and a gas at a temperature substantially above 900° F. wherein said reactants are at least partially preheated and the reaction effluent is cooled by heat exchange therebetween, the improvement which comprises vaporizing liquid in a mixed phase stream of said normally liquid material and gas by heating in a first indirect heat exchanger, introducing the resulting wholly gaseous stream into a second indirect heat exchanger at a temperature less than about 650° F., heating said gaseous stream in the second exchanger by the transfer of heat from said reaction effluent which is thereby cooled from a temperature above 900° F. to less than about 800° F., and passing the partially cooled reaction effluent from the second exchanger to the first exchanger to heat said mixed phase stream.

2. In a process for the thermal reaction entirely in the vapor phase of normally liquid material and a gas at a temperature substantially above 900° F. wherein said reactants are at least partially preheated and the reaction effluent is cooled by heat exchange therebetween, the improvement which comprises vaporizing liquid in a mixed phase stream of said normally liquid material and gas by transferring heat into said mixed phase stream in a first indirect heat exchanger, diverting a stream of fluid around said first exchanger to control said heat transfer to provide a wholly gaseous stream at a temperature less than about 650° F., heating said gaseous stream in a second indirect heat exchanger by the transfer of heat from said reaction effluent which is thereby cooled from a temperature above 900° F. to less than about 800° F., and passing the partially cooled reaction effluent from the second exchanger to the first exchanger to heat said mixed phase stream.

3. A process according to claim **2** in which the heating of said mixed phase stream is controlled by diverting a portion of said mixed phase stream around said first exchanger, and thereafter blending said diverted portion and said vaporized stream upstream of said second exchanger to form said wholly gaseous stream.

4. A high pressure process according to claim **2** in which said gaseous stream immediately after entering said second heat exchanger cools a structural member that is subjected to a substantial pressure differential by passing through a zone bounded in part by the interior surface of said member while said gaseous stream is shielded from exposure to the principal transfer of heat from said reaction effluent in said second exchanger, and thereafter effecting said principal transfer of heat into said gaseous stream in said second exchanger.

5. In a process for the thermal hydrodealkylation of an alkyl aromatic hydrocarbon entirely in the vapor phase at a temperature above about 1200° F. in the presence of hydrogen at a partial pressure of at least about 200 p.s.i. wherein said hydrocarbon and hydrogen reactants are at least partially preheated and the hydrodealkylation effluent is cooled by heat exchange therebetween, the improvement which comprises vaporizing liquid in a mixed phase stream of said hydrocarbon and hydrogen by heating in a first indirect heat exchanger, introducing the resulting wholly gaseous stream into a second indirect heat exchanger at a temperature less than about 650° F., heating said gaseous stream in the second exchanger by the transfer of heat from said hydrodealkylation effluent which is thereby cooled from a temperature above 900° F. to less than about 800° F., and passing the partially cooled hydrodealkylation effluent from the second exchanger to the first exchanger to heat said mixed phase stream.

6. In a process for the thermal hydrodealkylation of an alkyl aromatic hydrocarbon entirely in the vapor phase at a temperature above about 1200° F. in the presence of hydrogen at a partial pressure of at least about 200 p.s.i. wherein said hydrocarbon and hydrogen reactants are at least partially preheated and the hydrodealkylation effluent is cooled by heat exchange therebetween, the improvement which comprises vaporizing liquid in a mixed phase stream of said hydrocarbon and hydrogen by transferring heat into said mixed phase stream in a first indirect heat exchanger, diverting a stream of fluid around said first exchanger to control said heat transfer to provide a wholly gaseous stream at a temperature less than about 650° F., heating said gaseous stream in a second indirect heat exchanger by the transfer of heat from said hydrodealkylation effluent which is thereby cooled from a temperature above 900° F. to less than about 800° F., and

passing the partially cooled hydrodealkylation effluent from the second exchanger to the first exchanger to heat said mixed phase stream.

7. A process according to claim 6 in which the heating of said mixed phase stream is controlled by diverting a portion of said mixed phase stream around said first exchanger, and thereafter blending said diverted portion and said vaporized stream upstream of said second exchanger to form said wholly gaseous stream.

8. A process according to claim 6 in which the heating of said mixed phase stream is controlled by diverting a portion of said partially cooled hydrodealkylation effluent around said first exchanger.

9. A process according to claim 6 in which said gaseous stream enters said second exchanger at a temperature less than about 480° F. and said hydrodealkylation effluent is cooled therein to a temperature less than about 650° F.

10. A process according to claim 6 in which said gaseous stream immediately after entering said second heat exchanger cools a structural member that is subjected to a pressure differential in excess of about 200 p.s.i. by passing through a zone bounded in part by the interior surface of said member while said gaseous stream is shielded from exposure to the principal transfer of heat from said hydrodealkylation effluent in said second exchanger, and thereafter effecting said principal transfer of heat into said gaseous stream in said second exchanger.

11. A process according to claim 6 in which at least a major part of the preheating of said hydrocarbon and hydrogen to hydrodealkylation temperature is effected by heat interchange with said hydrodealkylation effluent.

12. A process according to claim 6 in which substantially all of said hydrodealkylation effluent is passed through said second heat exchanger.

13. A process according to claim 6 in which the initial substantial cooling of said hydrodealkylation effluent by indirect heat exchange is effected in said second exchanger.

14. In a process for the thermal hydrodealkylation of an alkyl aromatic hydrocarbon entirely in the vapor phase at a temperature above about 1200° F. in the presence of hydrogen at a partial pressure of at least about 200 p.s.i. wherein said hydrocarbon and hydrogen reactants are at least partially preheated and the hydrodealkylation effluent is cooled by heat exchange therebetween, the improvement which comprises effecting at least a major part of the preheating of said reactants to hydrodealkylation temperature by vaporizing liquid in a mixed phase stream of said hydrocarbon and hydrogen by transferring heat into a portion of said mixed phase stream in a first indirect heat exchanger, diverting another portion of said mixed phase around said first exchanger to control said heat transfer to provide a wholly gaseous stream at a temperature less than about 480° F., heating said gaseous stream in a second indirect heat exchanger by the transfer of heat from substantially all of said hydrodealkylation effluent which is thereby cooled from a temperature above 900° F. to less than about 800° F. in an initial indirect substantial cooling of said hydrodealkylation effluent, and passing the partially cooled hydrodealkylation effluent from the second exchanger to the first exchanger to heat said mixed phase stream.

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