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(71) Applicant: **TPC GROUP LLC** [US/US]; 5151 San Felipe, Suite 800, Houston, TX 77056 (US).

(72) Inventors: **CACIULA, Liana**; 1600 Eldridge Parkway, Apt. 1907, Houston, TX 77077 (US). **DUFF, Joseph, G.**; 1319 Bayport Lane, League City, TX 77573-6266 (US). **BALLARD, Elizabeth**; 14627 St. Cloud Drive, Houston, TX 77062 (US). **POTTER, Mark**; 923 Pebbleshire Drive, Houston, TX 77062 (US). **CHADA, Sirisha**; 14223 Wildwood Springs Lane, Houston, TX 77044 (US).

(74) Agent: **FERRELL, Michael, W.**; Ferrells, PLLC, P.O. Box 312, Clifton, VA 20124-1706 (US).

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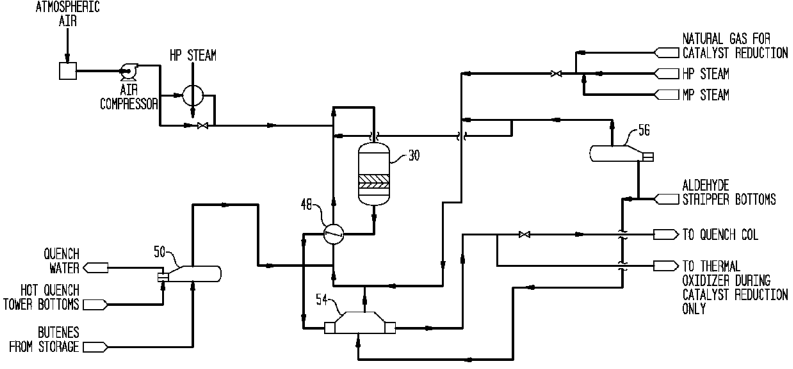
(54) Title: LOW EMISSIONS OXIDATIVE DEHYDROGENATION PROCESS FOR PRODUCING BUTADIENE

FIG. 2



(57) Abstract: Butadiene is formed by dehydrogenation of butenes which are mixed with steam and oxygen then converted to butadiene by oxidative dehydrogenation over a ferritic oxide catalyst, wherein the sensible heat in the oxidative dehydrogenation reaction product is utilized along with heat produced by thermal oxidation of low value volatile products formed to reduce energy requirements and CO2 emissions. Sensible heat is utilized at high temperature for purposes of superheating feed and at somewhat lower temperatures for purposes of vaporizing feed at sequential locations in the process.

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LOW EMISSIONS
OXIDATIVE DEHYDROGENATION PROCESS
FOR
PRODUCING BUTADIENE

CROSS-REFERENCE TO RELATED APPLICATION(S)

This international patent application is based on co-pending US Provisional Patent Application Serial No. 61/617,506 of the same title (Attorney Docket No. TPC-10-25), filed March 29, 2012, the priority of which is hereby claimed and the disclosure of which is incorporated herein by reference in its entirety.

This international patent application is also based on co-pending US Provisional Patent Application Serial No. 61/617,535 (Attorney Docket No. TPC-11-8), entitled, "IMPROVED CONTROLLABILITY OXIDATIVE DEHYDROGENATION PROCESS FOR PRODUCING BUTADIENE", filed March 29, 2012, the priority of which is hereby claimed and the disclosure of which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

The present invention relates to oxidative dehydrogenation of butenes to make butadienes. The butadiene enriched product stream is used to provide heat for the reaction section by staged indirect heat exchange. Thermal oxidation of organic compounds separated from the butadiene enriched product stream also provides energy to the reaction section.

BACKGROUND OF THE INVENTION

Previously known oxidative dehydrogenation processes for producing butadiene from hydrocarbons have used natural gas fired heaters to vaporize and superheat the reaction feed streams and consequently have produced emissions, particularly CO_2 emissions, far in excess of the level acceptable in today's climate. In particular, previous processes typically used natural gas to vaporize butene and heat a mixture of hydrocarbons, preferably butenes, oxygen and steam to a temperature in excess of 260°C (500°F), more commonly in excess of about 315°C (600 °F), and preferably over about 345°C (650° F) or, in some cases, even over 371°C (700° F). In a typical process, the reaction mixture includes butenes, oxygen in an amount of from about 0.4 moles to about 0.8 moles, more typically from slightly in excess of 0.5 moles up to about 0.65 moles of oxygen for each mole of butene in the butene rich hydrocarbonaceous feed, and superheated steam in amounts of from about 12:1 to about 16:1. Subsequent to reaction, the reaction product mixture is cooled and butadiene separated by oil absorption and subsequent fractionation. Typically, these processes produce crude butadiene at a purity ranging from about 50 to about 70%, more typically from about 55 to about 65%, which is passed onward in the plant for further processing using known technologies.

References of interest are discussed below.

Lewis; HYDROCARBON CONVERSION PROCESS USING NOVEL METALLO MANGANESE OXIDES; United States Patent No. 5,772,898;Jun. 30, 1998; relates to a hydrocarbon conversion process comprising contacting a hydrocarbon feed with a catalyst comprising a crystalline metallo manganese oxide composition having a three-dimensional framework structure, an intracrystalline pore system and an empirical chemical composition on an anhydrous basis expressed by the formula:

$$A_yMn_{8-x}M_x\,O_{16}$$

where A is a templating agent selected from alkali metals, alkaline earth metals and ammonium ion, "y" is the moles of A and varies from the group consisting of about 0.5 to about 2.0, M is a metal selected from the group consisting of chromium, zirconium, tin, platinum, rhodium, niobium, tantalum, vanadium, antimony, ruthenium, gallium and germanium, "x" is the moles of M and varies from about 0.01 to about 4.0 and characterized in that manganese has a valence of +3, or +4, M has a valence of +3, +4 or +5 and the composition has the hollandite structure.

Sasaki et al.; IRON-ANTIMONY-CONTAINING METAL OXIDE CATALYST COMPOSITION AND PROCESS FOR PRODUCING THE SAME; United States Patent

No. 5,139,988; Aug. 18, 1992; relates to a composition which contains as essential components: crystalline iron antimonate and at least one element selected from the group consisting of vanadium, molybdenum, and tungsten; is useful as a catalyst in the oxidation reaction of organic compounds. Also, a process for producing the composition is disclosed.

Dejaifve et al.; CATALYST FOR DEHYDROGENATING ORGANIC COMPOUNDS, A PROCESS FOR ITS PREPARATION AND ITS USE; United States Patent No. 4,975,407; Dec. 4,1990; relates to a catalyst derived from iron oxides providing agents and potassium oxide providing agents, characterized in that the molar ratio is in the range of from 1.5 to 60 and that a potassium ferrite $K_2Fe_{12}O_{19}$ phase is present supported on an octahedral Fe_3O_4 matrix, showing crystalline epitaxy between the hexagonal structure of $K_2Fe_{12}O_{19}$ and the (111) planes of the Fe_3O_4 spinel structure.

McFarland; OXIDATIVE DEHYDROGENATION OF AMYLENES; United States Patent No. 4,973,793; Nov. 27, 1990; realtes to an oxidative dehydrogenation process wherein butylenes are cofed with amylenes in a catalytic oxidative dehydrogenation reaction which is said to substantially improve the conversion of the amylenes. The improved amylene conversion is obtained by the oxidative dehydrogenation of mixtures of amylenes and from 10 to 95 mole % butylenes.

Helberg, United States Patent no. 4,067,921, discloses heat recovery in connection with a butadiene production operation. See Figure 4 and the text at Col. 6, lines 20-38.

Miklas, METHOD OF ACTIVATING ZINC-FERRITE OXIDATIVE DEHYDROGENATION CATALYST; United States Patent No. 3,953,370; April 27, 1976, relates to use of steam at a temperature of from 370-700°C (700-

1300°F) to activate a zinc ferrite oxidative dehydrogenation catalyst for preparation of butadiene from C_4-C_8 hydrocarbons.

Tschopp; DIOLEFIN PRODUCTION AND PURIFICATION; United States Patent No. 3,943,185; Mar. 9, 1976 relates to a process for producing a stream of oxidatively dehydrogenated C_4 hydrocarbons substantially free of oxygen and inert noncondensable gases removed comprising absorbing the C_4 hydrocarbons in an absorber oil in a first zone; stripping oxygen and inert noncondensable gases from the mixture of adsorber oil and C_4 hydrocarbons in a second zone which is operated under conditions of temperature and pressure to maintain an aqueous phase in the second zone; and withdrawing (1) a predominately aqueous phase from the second zone, (2) an overhead of predominately all of the oxygen and inert noncondensable gases and a bottoms of adsorber oil and C4 hydrocarbon substantially free of oxygen and inert noncondensable gases.

In *Croce et al.*; SULFUR PROMOTED OXIDATIVE DEHYDROGENATION; United States Patent No. 3,937,746; Feb. 10, 1976; the yield in oxidative dehydrogenation of organic compounds is improved by having a sulfur promoter present either as part of the catalyst or added to the reaction with the reactants.

In *Marsheck*; OXIDATIVE DEHYDROGENATION OF ORGANIC COMPOUNDS; United States Patent No. 3,801,671; Apr. 2, 1974; it is reported that the oxidative dehydrogenation of paraffinic hydrocarbons to diolefins can be improved by effecting such dehydrogenation in the presence of a fluidized mixed catalyst system consisting essentially of at least one catalyst active for the conversion of paraffins in admixture with at least one catalyst active for the conversion of monoolefins.

In *Bertus, et al.*; OXIDATIVE DEHYDROGENATION OF PARAFFINIC HYDROCARBONS; United States Patent No. 3,745,194; July 10, 1973; organic compounds are dehydrogenated to compounds having a higher degree of unsaturation by contacting the feedstock in the vapor phase in the presence of an oxygen containing gas with a catalyst containing tin in an oxidized state in combination with at least one of the metals bismuth, cobalt, or nickel in an oxidized state. Representative of such conversions is the oxidative dehydrogenation of butane to 1,3-butadiene over a nickel stannate-containing catalyst.

In *Woerner et al*; PURIFICATION OF UNSATURATED HYDROCARBONS BY EXTRACTIVE DISTILLATION WITH ADDITION OF LIQUID SOLVENT TO STRIPPER OVERHEAD; United States Patent No. 3,496,070; Feb. 17, 1970, a hydrocarbon separation process is provided for the separation of a hydrocarbon mixture comprising 4 to 5 carbon atoms including unsaturated hydrocarbons which comprises: extractively distilling the hydrocarbon mixture with a selective solvent in an extractive distillation column whereby hydrocarbon is selectively extracted in the extractive distillation column to form a hydrocarbon-rich solvent fraction which is fed to a solvent stripping column with said solvent being taken off as a bottoms from said stripping column and a vaporous hydrocarbon fraction being taken as an overhead fraction from said stripping column; adding said selective solvent in liquid phase to the vaporous overhead from the solvent stripper to lower the pressure in the overhead condenser of the solvent stripper column and in the solvent stripper.

Bajars; DEHYDROGENATION WITH MAGNESIUM FERRITE; United States Patent No. 3,284,536; Nov. 8, 1966 relates to dehydrogenating hydrocarbons in the vapor phase at elevated temperatures in the presence of oxygen and a catalyst containing magnesium ferrite. Hydrocarbons to be dehydrogenated according to the process are hydrocarbons of 4 to 7 carbon atoms, preferably aliphatic hydrocarbons selected from the group consisting of saturated hydrocarbons, monoolefins, diolefins and mixtures thereof of 4 to 5 or 6 carbon atoms having a straight chain of at least four carbon atoms, and cycloaliphatic hydrocarbons. Oxygen is present in the reaction zone in an amount within the range of 0.2 to 2.5 mols of oxygen per mol of hydrocarbon to be dehydrogenated. The temperature for the dehydrogenation reaction will be greater than 250°C, such as greater than about 300°C or 375°C, and the maximum temperature in the reactor may be about 650° C or 750° C or perhaps higher under certain circumstances.

Gay; DEHYDROGENATION IN THE PRESENCE OF OXYGEN AND AN AMMONIUM HALIDE ; United States Patent No. 3,207,805; Sept. 21, 1965 relates to a process for dehydrogenating organic compounds and relates more particularly to the dehydrogenation of dehydrogenatable organic compounds at elevated temperatures in the presence of oxygen and an ammonium halide.

Welch, et al., in "BUTADIENE VIA OXIDATIVE DEHYDROGENATION", Hydrocarbon Processing, Nov. 1978, pp. 131-136; discuss an oxidative dehydrogenation process, in which steam, air or oxygen, and normal butenes are heated and passed over an undisclosed autoregenerative heterogeneous catalyst at around 430°C (800°F) using steam as a heat sink to moderate the temperature rise in the adiabatic reactor system without using gas phase additives such as halogen and sulfur compounds. The process is said to consume essentially all of the oxygen in the feed usually leaving oxygen levels in the effluent below 0.3 percent. Acetylenes and oxygenated byproducts are major by products.

SUMMARY OF THE INVENTION

The present invention provides a low emissions method of manufacturing butadiene from a butene rich feed, wherein butenes are mixed with steam and oxygen then converted to butadiene by oxidative dehydrogenation over a ferritic oxide catalyst. Sensible heat in the oxidative dehydrogenation reaction product is utilized along with heat produced by thermal oxidation of low value volatile products formed to reduce energy requirements and CO_2 emissions. Sensible heat is utilized at high temperature for purposes of superheating feed and at somewhat lower temperatures for purposes of vaporizing feed.

A typical process includes providing a butene rich hydrocarbonaceous feed, vaporizing and superheating said hydrocarbonaceous butene rich feed to a temperature of at least about 205°C (400°F), mixing said hydrocarbonaceous butene rich feed with superheated steam and an oxygen rich gas to form a reactor feed stream, the moles of oxygen in said reactor feed stream being controlled to fall in the range of at least about 0.4, more preferably at least about 0.5 moles of oxygen per mole of hydrocarbonaceous butene rich feed, reacting said reactor feed stream over a ferritic oxide catalyst, preferably an oxide catalyst comprising: a major proportion of iron; a minor proportion of zinc; and smaller amounts of manganese; phosphorus derived from a phosphorus source such as phosphoric acid; and preferably calcium derived from a non-nitrogenous calcium precursor such as calcium acetate; thereby forming a butadiene enriched product stream, wherein: the catalyst bed is preheated to a temperature which is sufficient to initiate the oxidative dehydrogenation reaction by passing an inert or reductive feed stream, often natural gas , but possibly butene if more convenient, and steam in the absence of oxygen, through the catalyst bed until it reaches a temperature of about 345°C (650° F) up to a bed temperature of at least about 425°C – 455°C (800 ° F - 850 °F), depending on the activity of the catalyst. The steam in the flow used for getting the catalyst bed up to temperature is superheated using natural gas or some other convenient external energy source. Once the catalyst bed has been adequately heated, if the reductive agent is natural gas, it is replaced by butenes. In the case where butene has been used as the reductive agent, air containing the oxygen required for the reaction is introduced, and the superheated steam flow is controlled to maintain the mixed reactor feed temperature at desired level. The reactor effluent used to provide heat required to the feed, usually heating the reactor feed stream to at least about 315°C to 345°C (600°F to 650° F). The butadiene rich reactor effluent, which is typically at about 595°C (1100° F), is used on the hot side of a series of heat exchangers; passing first through a reactor feed superheater in which the combined flow of butenes and steam directed to the reactor is usually superheated to at least about 205°C (400°F), usually from about 315°C to 345°C (600° F to 650°F), by indirect heat exchange with said butadiene enriched product stream. In some cases, the butadiene enriched product stream passes next through a recycle condensate vaporizer in which steam is generated by indirect heat exchange (as mentioned, the steam being subsequently mixed with butenes and the resulting mixture being superheated by said butadiene enriched product stream just prior to entering the reactor); the butadiene enriched product stream, after cooling to a temperature in the range of 175°C to about 125°C (350°F to about 260°F), preferably about 130°C to 150°C (280°F to 300°F), being directed through a quench column, in which heat is removed from the butadiene enriched product stream and steam content thereof condensed. It is often preferable to vaporize aqueous condensate with high pressure steam generated by combustion of low value organics removed from the process stream as described below.

After passing through the quench column, the butadiene enriched product stream may be conducted to a suction drum in which any liquids entrained in the product stream are removed prior to passing through a two-stage compressor with inter-stage cooling. Alternatively, the suction drum may be dispensed with if the top of the quench tower is correctly sized for vapor/liquid disengagement and a demister pad is provided to intercept suspended droplets that might otherwise pass from the quench tower to the compressor. After being compressed to about 1140 kPa abs. (150 psig), the butadiene enriched product stream is directed to an aldehyde scrubber, and ultimately, a C4 absorber. After removal of aldehydes in the aldehyde scrubber, the C4 species contained in the butadiene enriched product stream are removed in the C4 absorber column by absorption into a compatible absorption oil, which is adapted to preferentially absorb butadiene and other C4's, leaving nitrogen, hydrogen, and lighter hydrocarbon species to be removed in a gaseous overhead stream which is directed to a thermal oxidizer equipped with heat recovery to supply high pressure steam to be used to supply heat, as mentioned previously particularly heat for vaporizing recovered aqueous condensate used producing the superheated steam needed for the oxidative dehydrogenation reaction. Preferably, off-gases having more value as fuel than as products or reactants removed during other processing steps or in other operations in the plant are also directed to the thermal oxidizer; but a large source of the energy in the feed to the thermal oxidizer derives from the gaseous products not absorbed in the C4 absorber column. In some cases, it will be expedient to augment the feed to the thermal oxidizer with natural gas or some other vaporous feed so that a stable flame is obtained in the thermal oxidizer. In this case, the heat value obtained by combustion of the recovered low value organics can supply a large portion of the heat required for vaporization of the recovered aqueous condensate, the energy required for this vaporization being a large component of the energy needs of the process, although since the BTUs are of course fungible, it may not be possible to directly track them to the vaporizer. A particularly useful source of combustible organics for the thermal oxidizer lies in the downstream processes for purification of crude butadiene into salable product. In cases, where alkanes are dehydrogenated on site to provide the butenes fed to the oxidative dehydrogenation process, the off-gases from that process can be another useful source of energy.

After passing through the C4 absorber column, the absorber oil having butadiene dissolved therein is directed to a degasser tower where carbon dioxide, residual nitrogen and hydrogen are removed overhead and sent back to the second stage of the gas compressor, the absorber oil being passed thence to a C4 stripper wherein dispersed organics dissolved in the absorber oil are stripped out, the absorber oil being cooled and recirculated to the C4 absorber via the lean oil surge drum. Preferably, during steady operation of the plant which normally continues for many months at a time, over 40% of the heat required to vaporize both the hydrocarbonaceous butene rich feed and the condensate recovered from the butadiene enriched product stream is primarily supplied by sensible heat recovered from the butadiene enriched product stream as well as by heat generated by thermal oxidation of undesired products removed from two sources: (1) the butadiene enriched product stream, and (2) undesired products created during production of butenes from alkanes, such that at least 40%, preferably at least about 45%, of the energy required for manufacturing butadiene is supplied by the energy content of the feed stocks for the operation as the vast majority of the energy required is used for vaporizing and superheating the feeds to the reactor. For example in a plant having a capacity of about 32,000 kg of butadiene per hour (70 thousand lbs of butadiene per hour), approximately 21,000 kJ are required for each kg (9000 BTUs are required for each lb) of butadiene produced; so at least about 3800 kJ to about 4200 kJ (about 3600 BTUs to about 4000 BTUs) can be supplied by recovery of sensible heat from the reactor effluent. In this regard, it is considered significant that much of the energy recovered comes from a high to medium quality heat source at about 595°C (1100°F) and is only required to pass through one tube wall in the recovery process. Further, by separating combustible organics from the condensate, the water content of the butadiene enriched product stream is cleaned so that it can be vaporized to generate steam and reused as required for the oxidative dehydrogenation reactors, so that, as compared to prior art processes, the net energy and water usage of the process of the present invention can be very low. In cases, where a thermal oxidizer is used, an additional 10 to 40% of the energy required, about 2100 to about 8400 kJ/kg (about 900 to about 3600 BTUs per lb) of butadiene, depending on the size of the thermal oxidizer, can be supplied by combustion of combustible organics.

In one embodiment of the present invention, the heat required to vaporize both the hydrocarbonaceous butene rich feed and the water stripped from the butadiene enriched product stream is augmented by available heat generated by associated plant equipment such that in steady operation, the energy required for manufacturing crude butadiene from a butene rich feed is supplied by the energy content of the feed to the combined dehydrogenation and oxidative dehydrogenation process as well as available heat generated by associated plant equipment with less than about 12,800 kJ/kg (about 5500 BTUs per lb) of butadiene, preferably less than about 11,500 kJ/kg (about

5000 BTUs per lb) of butadiene, being supplied by fossil fuels. In cases where a thermal oxidizer is employed, the energy required from fossil fuels can be less than about 10,500 kJ/kg (about 4500 BTU per pound) of butadiene down to less than 5800 kJ/kg (2500 BTUs per pound) of butadiene.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is described in detail below with reference to numerous examples and the appended **Figures** wherein like numbers designate similar parts throughout and wherein:

Figure 1 is a schematic sectional view of a preferred reactor for use in the practice of the present invention.

Figure 2 is a flow diagram of the reactor section of a crude butadiene battery illustrating the reactor and the pretreatment equipment for bringing the butene rich feed to the entry conditions required for operation of the reactor.

Figure 3 is a flow diagram of a portion of a crude butadiene battery illustrating the Gas Compressing and Scrubbing equipment for initial processing of a butadiene enriched product stream produced by the reactor section of Figure **2**.

Figure 4 is a flow diagram of a portion of a crude butadiene battery illustrating the aldehyde stripper and associated equipment for processing of a butadiene enriched product stream after processing by the Gas Compressing and Scrubbing section of Figure **3**.

Figure 5 is a flow diagram of a portion of a crude butadiene battery illustrating the C4 absorption and stripping equipment for production of a crude stream of about 50% butadiene by processing of a butadiene enriched product stream received from the aldehyde stripper section of Figure **4**.

Figure 6 is a flow diagram of a portion of a crude butadiene battery illustrating portions of the system used for handling of absorption oil after stripping of C4's therefrom.

DETAILED DESCRIPTION

The invention is described in detail below in connection with the **Figures** for purposes of illustration, only. The invention is defined in the appended claims. Terminology used throughout the specification and claims herein are given their ordinary meanings, for example, "indirect heat transfer" refers to heat transfer from one medium to another medium through a heat exchanger wall and pressures refer to gauge pressures unless otherwise indicated. When carrying out the inventive process, preferably heat is transferred through a single heat exchanger wall from a higher temperature stream to a lower temperature stream, such as from reactor effluent to reactor feed in a feed superheater as described hereinafter. Indirect heat transfer may be carried out in accordance with the invention using any suitable equipment such as tube and shell heat exchangers or plate and frame heat exchangers.

Unless otherwise indicated, "butadiene" or "BD" refers to 1,3 butadiene or mixtures comprising 1,3 butadiene.

"Temperature delta" refers to a temperature difference, for example, the temperature difference between the input temperature of a stream provided to a heat exchange device and the output (exit) temperature of that stream from that heat exchange device. A temperature delta of a stream though a heat exchanger is thus the difference between the inlet temperature and outlet temperature of that stream.

The front end of butadiene production system of the present invention comprises multiple largely identical process trains, each process train having one reactor **30** producing a butadiene enriched product stream from which useful heat is extracted by indirect heat exchange before entering quench tower **64** at which point all process streams are combined in our preferred embodiment. Only one train will be illustrated to avoid needless over-complication.

In Figure 2, butene rich feed is vaporized in butene vaporizer **50** in which the heat required for vaporization is supplied by removal of heat from bottoms of quench tower **64** which, as will be discussed later, is heated by contact with the hot reaction product once a steady state operation has been achieve in the current process. After passing through butene vaporizer **50,** the vaporized butene feed is mixed with steam, the steam being generated in two recycle condensate vaporizers **54** and **56**. The steam generated in recycle condensate vaporizer **54** is produced by indirect heat exchange with butadiene enriched product stream leaving reactor feed superheater **48.** The heat required to generate the steam in recycle condensate vaporizer **56** is preferably supplied by steam either from the plant grid or preferably from the thermal oxidizer or some other conveniently available source. Preferably, the steam is completely vaporized in recycle condensate vaporizer **56** prior to being mixed with vaporized butene before passage through reactor feed superheater **48** in which the reactor feed is preheated by indirect heat exchange with the butadiene enriched product stream exiting reactor **30** with the resultant combined entry stream having a temperature of at least about 345°C (about 650°F), preferably in the range of from about 345°C to 400°C (from about 650°F to 750°F). Thus the feed to reactor **30** is heated to the required temperature by indirect heat exchange with the exit stream which, as will be discussed later, is usually at a temperature in excess of 535°C (1000°F), more typically around 595°C (1100°F). Significantly, the recovered heat passes through only a single tube wall in contrast to schemes in which an intermediate fluid is used. Preheated reactor feed leaving the reactor feed superheater **48** is mixed with compressed oxygen bearing gas, typically air, with the amount of air feed being carefully controlled so that approximately 0.5 to 0.6 moles of oxygen are supplied for each mole of hydrocarbon in the feed passed to the reactors. In some cases, it will be convenient to preheat the oxygen bearing gas to from about 205 to about 235°C (about 400 to about 450°F) using high pressure steam. After mixing, the reaction feed stream is passed to refractory lined adiabatic reactor **30** illustrated in **Figure 1**, where butene/steam/air feed inside reactor **30** passes first through: an inert flow distribution layer **32** then to an oxidative-dehydrogenation catalyst layer **34**, having a depth of 83.8 cm (33 inches) or so; an aldehyde and acetylene removal (AAR) catalyst layer **36** and an inert support (alumina spheres) layer **38.**

Further details of the preferred reactor **30** and method of operating it are provided in US Provisional Patent Application Serial No. 61/617,535 (Attorney Docket No. TPC-11-8), entitled, "IMPROVED CONTROLLABILITY OXIDATIVE DEHYDROGENATION PROCESS FOR PRODUCING BUTADIENE", filed March 29, 2012. It is desired that the catalyst particles used in connection with the present invention be slightly larger than commonly used in previous practice to limit the pressure drop through the catalyst bed as we prefer to use a catalyst bed which is deeper than commonly used previously. Higher pressure drop requires higher pressure in the system which reduces selectivity. We also prefer to use catalyst particles having two key differences from previous practice: (1) the particles are "pre-reduced" or otherwise heat treated prior to loading to give them the crush strength necessary to be usable in a bed having a depth of from about 50 cm to about 150 cm (from about 20" up to about 60''), preferably a depth of from about 65 cm to about 130 cm (from about 25" to about 50"), more preferably from about 75 cm to about 100 cm (from about 30" to about 40"); while the bulk density of the calcined particles is no more than about 1100 kg/m^3 (about 70 lbs/ft^3), preferably between about 880 kg/m^3 and 1050 kg/m^3 (about 55 lbs/ft^3 and 65 lbs/ft^3) and still more preferably is between about 920 kg/m^3 and 1010 kg/m^3 (about 58 lbs/ft^3 and 63 lbs/ft^3) and (2) we prefer to avoid the use of nitrates that are conventionally used as precursors for the calcium compounds often incorporated into these catalysts. We have found that calcium acetate is a suitable precursor in this regard and has the advantage of reducing NOx emissions, while calcium chloride and calcium carbonate are also suitable.

Flow distribution is also important for avoiding channeling and hot spots in the catalyst bed. The preferred flow regime is fully turbulent and is enhanced by the presence of the inlet distributor. That is, an inlet distributor is advantageously provided to insure uniform flow distribution through the catalyst bed and prevent channeling and the potential creation of hot spots, which are likely to shorten the catalyst life. One preferred design for this inlet distributor device is in the form of baffles and rings which is mounted in the vapor space above the catalyst bed to promote even distribution of flow and to minimize inlet pressure losses.

Suitable catalysts are also described in *Miklas*, METHOD OF ACTIVATING ZINC-FERRITE OXIDATIVE DEHYDROGENATION CATALYST; United States Patent No. 3,953,370; April 27, 1976, which relates to use of steam at a temperature of from 371-704°C (700-1300°F) to activate a zinc ferrite oxidative dehydrogenation catalyst for preparation of butadiene from C_4-C_8 hydrocarbons as well as *Bajars et al*; DEHYDROGENATION WITH MAGNESIUM FERRITE; United States Patent No. 3,284,536; United States Patent no. 4,083,844 to Purdy entitled CALCIUM OXIDE MODIFIED ZINC FERRITE OXIDATIVE DEHYDROGENATION CATALYSTS AND USE as well as CATALYTIC OXIDATIVE DEHYDROGENATION PROCESS; United States Patent No. 4,658,074, the disclosures of which are incorporated herein by reference. Acetylene and aldehyde (AAR) removal catalysts and their usage are described in pending Application No. PCT/US2011/000624, the disclosure of which is also incorporated by reference.

In reactor **30**, butenes react with oxygen in a series of reactions ultimately producing a stream in which there is very little, if any, oxygen but a greatly increased concentration of butadiene and greatly reduced amounts of butenes. The reaction product also comprises contaminants which would greatly interfere with use of the butadiene as a feed to a polymerization process if not removed as described hereinafter. Since the reactions occurring in reactor **30** are intensely exothermic, the stream leaving reactor **30** is at a quite elevated temperature usually in excess of 540°C (1000° F), more typically closer to 595°C (1100°F). By judiciously transferring much of the sensible heat in the stream leaving reactor **30** to portions of the streams being combined to form the feed to reactor **30,** it is possible to not only improve the process economics but also to greatly reduce if not eliminate use of natural gas during steady operation. When combined with other means of recovering energy discussed herein, it becomes possible to vaporize and superheat the feed stream to the butene conversion section of the process largely without consumption of energy other than that inherently supplied in the stream of hydrocarbons used to produce the butene rich feed to the process.

The location of the intensely exothermic reaction occurring in each reactor is monitored through a number of remotely readable thermocouples **40** spaced along the height of oxidation-dehydrogenation layer **34** so that the location of the reaction zone therein may be determined as hereinafter described. The amount of oxygen remaining in the product stream is monitored with oxygen analyzer **42** located near the bottom of layer **34** so that oxygen breakthrough into AAR layer **36** is avoided as discussed hereinafter in more detail. Also provided is a lower sample port **44** for a convergence analyzer in layer **36** so that composition may be monitored at the lower extreme of the reactor.

As mentioned previously, the hot reaction product stream from reactor **30** passes through reactor feed superheater **48** (**Figure 2)** which supplies a portion of the heat used to bring the feed to reactor **30** up to the requisite operating temperature and thence the reaction product exiting reactor feed superheater **48** passes through steam generator **54** wherein a portion of the sensible heat contained therein is used to vaporize and/or superheat the steam passing to reactor **30**.

Subsequently, butadiene enriched reaction product exiting from steam generator **54** passes to quench tower **64** (**Figure 3)** entering at a height slightly above the maximum liquid level expected during normal operation. As mentioned, in our preferred embodiment, butadiene enriched product stream from reactor **30** is combined with other butadiene enriched product streams from the other reactors (not shown) prior to entering quench tower **64.** In one embodiment, bottom section **66** of quench tower **64** is equipped with valve trays while top section **70** is equipped with a corrugated metallic structured packing such as Koch Flexipac®, similar to that described in *Lantz, et al.*, US Patent 6,874,769, Structured Packing Plate and Element and Method of Fabricating Same or Rukovena, US Patent 4,740,334. Alternatively, spray nozzles may be used for the entire tower. It is anticipated that in many cases, it will be possible to feed the mixture of vaporous and liquid reaction product effluent directly into quench tower **64** without any preliminary phase separation; but such preliminary phase separation can be easily accommodated, if expedient, by incorporation of a flash tank or similar phase separation device. The condensate liquid phase collected at lower exit **67** of quench tower **64** comprising primarily of condensed steam and quench water is fed back through the hot side of butene vaporizer **50** with cooled liquid return being passed back via quench condensate air cooler **76** and thence to quench tower circulating cooler **78** before being fed into quench tower **64** at a location well above the top of the packed section **70** of quench tower **64** but below demister pad **83**. Preferably quench condensate air cooler **76** is equipped with modular tube banks, individually controlled fans, and variable pitch fan blades to facilitate temperature control in a variety of ambient conditions. In many cases, it will be possible to extract additional heat from Quench Tower bottoms stream **64** for uses elsewhere in the associated plant reducing size and cost of Quench Tower Coolers **76** and **78**.

Crude butadiene vapor leaves top section **70** of quench tower **64** (**Figure 3**) passing through demister pad **83**, which is included primarily to protect gas compressor **84** from any entrained liquid droplets, and enters on the suction side of two-stage centrifugal gas compressor **84**. Indirect inter-stage cooling is provided by compressor inter-stage coolers **88** and **89** with cooling to compressor inter-stage cooler **88** being supplied by a process stream leaving stripped water cooler **99** and the heated stream from the shell side of compressor inter- stage cooler **88** being fed to aldehyde stripper **98** (**Figure 4**). Cooling to inter-stage cooler **89** is conveniently supplied by plant cooling tower water.

Entrained liquid droplets coalesced on demister pad **83** are refluxed through quench tower **64** while compressed vaporous butadiene enriched product compressed to 1140 kPa abs. (about 150 psig) leaves the second stage of the gas compressor and it is passed to aldehyde scrubber **92** of which top portion **93** is preferably packed with structured packing which may be similar to Norton Intallox structured packing or those packings described above. A portion of the bottoms from aldehyde scrubber **92** is recycled through the structured packing via aldehyde scrubber bottoms cooler **95** while the remainder is passed to aldehyde stripper **98** via aldehyde scrubber bottoms separator **96** (**Figure 4)** which receives liquid from the quench tower **64** bottoms via quench tower bottoms pump **65** as well as from gas compressor **84** second stage knock out drum. The water contents of the aldehyde scrubber bottoms separator **96** may be returned to quench tower **64** at a location below demister pad **83**. It is an important aspect of this invention that in those cases where substantial amounts of hydrocarbons lighter than C4 or other low value volatiles can be removed from various streams herein, those off gases are fed to a thermal oxidizer where they are combusted to produce steam which can be used to supply heat as needed for various portions of the overall process thereby greatly reducing need for natural gas combustion in steady operation and thereby also reducing concomitant generation of carbon monoxide and carbon dioxide.

Aldehyde stripper (**Figure 4**) receives the water phase from the aldehyde scrubber bottoms after the oil phase has been skimmed out. This stream is pumped first to the shell side of stripped water cooler **99**, from whence it reaches the shell side of compressor interstage cooler **88**, which helps to increase its temperature via heat integration before being fed to aldehyde stripper **98**, a portion of this overhead vapor from aldehyde stripper **98** going to aldehyde stripper overhead condenser **100** and thence being returned to aldehyde stripper **98** as reflux to maintain the vapor/liquid equilibrium in the column and drive overhead the aldehydes contained in the feed to this tower **98**. The balance of the overhead vapor stream from aldehyde stripper **98** bypassing overhead condenser **100** is combined with other low value combustibles and directed to a thermal oxidizer (not shown) for production of superheated steam. Heavier hydrocarbons entrained in the condensed overhead stream from overhead condenser **100** are collected by bottoms coalescer and are also disposed of by treatment at a conventional oily water facility (not shown). Aldehyde stripper reboiler **102** uses steam, advantageously medium pressure steam, to vaporize a portion of aldehyde stripper bottoms from aldehyde stripper **98** and reintroduces the vapor below bottom tray of aldehyde stripper **98** while the remainder is pumped using aldehyde stripper bottoms pump **105** to two locations: (1) back to the aldehyde scrubber **92** bottoms below the packing via two stripped water coolers (not shown), and (2) to the recycle condensate vaporizers, where it generates the vast bulk, if not all, of the steam used for the oxidative dehydrogenation reaction.

Reaction product from aldehyde scrubber **92** (**Figure 3**) overhead is passed to the bottom of C4 absorber **110** (**Figure 5**) containing numerous trays or other known devices for promoting gas liquid contact and equipped with at least one intercooler **111.** Absorber oil (also sometimes referred to as lean oil) used in absorber **110** can suitably be paraffinic, or a mixture of paraffins and aromatics, although it seems like better results are obtained using oils which are richer in, or possibly even entirely, vinyl cyclohexene (butadiene dimer). Good commercial results have been obtained when the fresh absorber oil is primarily Espersol 250, an aromatic Naphtha product with a boiling range of 90°C to 150 °C (200°F to 300°F) having the composition shown in Table 1 (Celsius Boiling Points provided in Table 1A).

Table 1 Absorber Oil Composition

Component	Molecular Weight	N.B. Point (°F)	Specific Gravity	Chroma. %	Assumed Wt %	Mole %	Vol. %
Benzene	78.11	176.2	0.8845	6	5	6.8	5
Cyclohexane	84.16	178	0.783	3	2	2.5	2.3
Methyl Cyclohexane	98.18	213.7	0.774	1	1	1.1	1.1
Toluene	92.13	231	0.872	12	13	15	13.2
2,2,4-Trimethyl Pentane	114.23	236.1	0.696	1	2	1.9	2.6
Vinyl Cyclohexane	108.18	262.1	0.8335	3	5	4.9	5.3
Ethyl Cyclohexane	112.22	269.2	0.788	1	1	0.9	1.1
M&P-Xylene	106.16	281	0.867	19	20	20.1	20.4
O-Xylene	106.16	291	0.885	17	18	18.1	18
Styrene	104.14	294	0.911	10	12	12.3	11.6
Propyl Benzene	120.19	318.6	0.862	1	2	1.8	2.1
Butyl Benzene	134.21	361.4	0.864	4	6	4.8	6.1
"Heavies" (Assume 2-M Naphthalene)	142.2	466	1.029	22	13	9.7	11.2

Table 1A Absorber Oil Composition (Celsius Boiling Points)

Component	Molecular Weight	N.B. Point (°C)	Specific Gravity	Chroma. %	Assumed Wt %	Mole %	Vol. %
Benzene	78.11	80.11	0.8845	6	5	6.8	5
Cyclohexane	84.16	81.1	0.783	3	2	2.5	2.3
Methyl Cyclohexane	98.18	100.9	0.774	1	1	1.1	1.1
Toluene	92.13	111	0.872	12	13	15	13.2
2,2,4-Trimethyl Pentane	114.23	113.4	0.696	1	2	1.9	2.6
Vinyl Cyclohexane	108.18	127.8	0.8335	3	5	4.9	5.3
Ethyl Cyclohexane	112.22	131.8	0.788	1	1	0.9	1.1
M&P-Xylene	106.16	138	0.867	19	20	20.1	20.4
O-Xylene	106.16	144	0.885	17	18	18.1	18
Styrene	104.14	146	0.911	10	12	12.3	11.6
Propyl Benzene	120.19	159.2	0.862	1	2	1.8	2.1
Butyl Benzene	134.21	183	0.864	4	6	4.8	6.1
"Heavies" (Assume 2-M Naphthalene)	142.2	241	1.029	22	13	9.7	11.2

Butadiene in the product stream is absorbed in absorber oil introduced at the top of C4 absorber **110**, the bottoms from which is pumped to the top of degasser tower **116** through C4 absorber bottoms pump **113** and degasser feed cooler **115**. Degasser tower **116** operates at lower pressure to facilitate the removal of residual gases, particularly carbon dioxide, nitrogen and hydrogen, which are passed through inter-stage cooler **88** of two-stage gas compressor **84** to the butadiene enriched product stream prior to passage through aldehyde scrubber **92**. Degasser overhead gas from degasser **116** is recycled back to the second stage of compressor **84** and thence to scrubber **92** and absorber **110** whence it will ultimately find its way to thermal oxidizer **114**. Degasser reboiler **122** maintains the temperature in the liquid phase of degasser tower **116** sufficiently high to allow residual gases to be flashed out passing to thermal oxidizer **114** as described above. The bottoms from degasser tower **116** largely comprising crude butadiene and miscellaneous C4's in absorber oil are passed to C4 stripper **124** through C4 stripper feed bottoms interchanger **127** where this bottoms stream is heated by passage of hot absorber oil from the bottoms of C4 stripper **124** through the tubes of C4 stripper feed/bottoms interchanger **127**. Heated degasser bottoms are introduced into C4 stripper **124** at an intermediate height. Crude butadiene and C4's are stripped from heated absorber oil in C4 stripper **124,** passing out as overhead to C4 stripper overhead condenser **130** while depleted absorber oil collected in the bottoms from C4 stripper **124** is reheated in C4 stripper reboiler **128;** and the overhead vapor from C4 stripper **124** is condensed in C4 stripper overhead condenser 1**30** with a portion of the condensed liquid being accumulated in C4 stripper reflux drum **125**,where residual water can be separated from the hydrocarbon phase and sent back to aldehyde stripper tower **98**,while crude butadiene product is pumped through C4 stripper reflux pump **123** to further processing, while sufficient crude butadiene is being recirculated as reflux to ensure that sufficient separation is attained in C4 stripper **124**.

Bottoms leaving C4 stripper **124** comprise absorber oil having butadiene and other C4s stripped therefrom which is divided into three portions, one of which is recirculated to C4 stripper **124** through C4 stripper reboiler **128**, a second portion being passed to absorber oil surge drum **142**, (**Figure 6)** the remaining portion being used as mentioned previously to heat butadiene/absorption oil mixture upon passage through C4 stripper feed/bottoms interchanger **127** where it, and oil being recycled from absorption oil surge drum **142,** are passed to absorption oil air cooler **131** and absorption oil cooler **133** before being returned to C4 absorber **110** for reuse. As absorber oil breaks down, forming heavier molecules, fresh oil make-up is introduced into the system while the balance is directed to a re-run column for heavies cleanup. Upon sufficient accumulation of heavies in the absorption oil to justify, or necessitate, operation of absorber oil re-run tower **132**, a portion of the oil being recirculated from absorption oil surge drum **142** is distilled to remove heavier components in absorber oil re-run tower bottoms with the overhead being pumped back to absorber oil recirculation loop. Occasionally the recovered oil could be pumped to storage tank **140** where the fresh absorber oil is stored.

Tables 2 and 2A sets forth an energy balance for three possible plant configurations for 23,000 kg/hr (50,600 lb/hr) of butadiene production: one having no thermal oxidizer; one having a small thermal oxidizer sized primarily for the low value combustibles produced in the process of converting butene to butadiene; and one sized for both the low value combustibles produced in the process of converting butene to butadiene as well as those produced in the process of purifying crude butadiene to a saleable grade. It can be appreciated that the energy requirement for vaporizing and superheating the various streams fed to the reactor during steady operation of the process for converting butenes to butadiene is surprisingly small when sensible heat in the reaction product stream is combined with the energy resulting from thermal oxidation of low value combustibles from both butadiene production and purification.

Table 2

Low Emissions/Heat Integration for Oxidative Dehydrogenation of Butene

BD Production:	50,600 LB/HR
Total Energy† Required:	**432,112,000** BTU/HR
Energy provided by Sensible Heat in Butadiene Enriched Product Stream (BTU/HR)	
Butene Vaporizer **50**	14,558,000
Superheater **48** (Butene)	--
Superheater **48** (Steam)	95,783,000
Condensate Vaporizer **54**	111,613,000
SubTotal†	221,954,000
Additional Energy Required to Vaporize Steam for Reactor Feed (BTU/HR) *	
Condensate Vaporizer **56**	210,159, 000

* Energy calculated based on 150# superheated steam @ 810°F generated by combination of thermal oxidation of by-products from butene and butadiene production as supplemented by combustion of natural gas at 21,000 BTU/LB as fuel for steam boiler to produce 1112 BTU/LB of Steam during first phase of steady operation

Thermal Oxidizer Size:	Energy Contribution from Combustion of By-Products (Supplied via Steam)	% Energy from Process Sources	% Energy from Fossil fuel	Lbs. of NG required for each lb of Butadiene Produced	% Energy for Vaporizing Recycle Condensate and Superheating Feed from Thermal Oxidizer	% Energy for Vaporizing Recycle Condensate and Superheating Feed from Reactor Effluent
none	0	51	48	0.20	--	51
offgases from Crude BD production only	150,000 #/hr 150# Steam	61	39	0.16	10	51
Offgases from production and purification of Crude BD	250,000 #/hr 150# Steam	91	9	0.04	40	51

† Totals do not agree perfectly due to rounding.

Table 2A (Metric Units)

Low Emissions/Heat Integration for Oxidative Dehydrogenation of Butene

BD Production:	23,000 kg/HR
Total Energy† Required:	**455,597,000** kJ/HR
Energy provided by Sensible Heat in Butadiene Enriched Product Stream (kJ/HR)	
Butene Vaporizer **50**	15,349,000
Superheater **48** (Butene)	--
Superheater **48** (Steam)	100,988,000
Condensate Vaporizer **54**	117,679,100
SubTotal†	234,017,000
Additional Energy Required to Vaporize Steam for Reactor Feed (kJ/HR) *	
Condensate Vaporizer **56**	221,581,000

* Energy calculated based on 68.0 kg superheated steam @ 432°C generated by combination of thermal oxidation of by-products from butene and butadiene production as supplemented by combustion of natural gas at 48,813 kJ/kg as fuel for steam boiler to produce 2585 kJ/kg of Steam during first phase of steady operation

Thermal Oxidizer Size:	Energy Contribution from Combustion of By-Products (Supplied via Steam)	% Energy from Process Sources	% Energy from Fossil fuel	kg. of NG required for each kg of Butadiene Produced	% Energy for Vaporizing Recycle Condensate and Superheating Feed from Thermal Oxidizer	% Energy for Vaporizing Recycle Condensate and Superheating Feed from Reactor Effluent
none	0	51	48	0.20	--	51
offgases from Crude BD production only	68,039 kg/hr 1.034 MPa Steam	61	39	0.16	10	51
Offgases from production and purification of Crude BD	113,398 kg/hr 1.034 MPa Steam	91	9	0.04	40	51

Energy requirements for the reaction section can also be expressed in kJ/kg (BTU/LB) BD (butadiene) produced as set forth in **Tables 3** and **3A** below.

Table 3 – Reaction Section Energy Utilization

Total Energy required*:	8540 BTU/LB BD
Energy for Superheater **48**	1890 BTU/LB BD
Energy for Vaporizer **50**	288 BTU/LB BD
Energy for Vaporizer **54**	2200 BTU/LB BD
Energy for Vaporizer **56**	4150 BTU/LB BD

*Approx. values

Table 3A, Metric Units

Total Energy required*:	19,900 kJ/kg BD
Energy for Superheater **48**	4,400 kJ/kg BD
Energy for Vaporizer **50**	670 kJ/kg BD
Energy for Vaporizer **54**	5,130 kJ/kg BD
Energy for Vaporizer **56**	9,650 kJ/kg BD

*Approx. values

The data in Tables 2, 2A , 3 and 3A reflects process modeling using fresh catalyst.

All of the energy for Superheater **48,** over 4400 kJ/kg (1900 BTU per pound) of butadiene, may be supplied by indirect heat transfer of sensible heat from the reactor effluent stream at high temperature, with the effluent product stream well above 370°C (700°F). Likewise, all of the energy for vaporizer **54** may similarly be supplied by indirect heat transfer at a somewhat lower temperature of the effluent product stream. Heat recovery from the process stream is enhanced by extracting heat from the effluent stream when the stream is at a relatively high temperature for purposes of superheating the feed and then extracting heat from the reactor effluent at a relatively lower temperature for purposes of vaporizing feed. Energy for vaporizer **56** may be supplied from a plant steam grid which draws heat from thermal oxidation of volatile organic compounds generated in connection with the oxidative dehydration process as described herein.

In preferred embodiments, the vaporized and superheated hydrocarbonaceous butene rich feed is brought to a temperature of at least about 205°C (about 400°F), more preferably 260°C (500 °F), still more preferably at least about 315°C (about 600°F), most preferably about 345°C (about 650°F), mixed with hydrocarbonaceous butene rich feed, superheated steam and an oxygen rich gas to form a reactor feed stream and the moles of oxygen in said reactor feed stream being controlled to fall in the range of at least about 0.4 moles, more preferably at least about 0.5 moles and most preferably about 0.55 moles of oxygen per mole of hydrocarbonaceous butene rich feed.

Preferably the feed mixture comprising butenes, steam, and oxygen is oxidatively dehydrogenated over a ferritic oxide catalyst consisting essentially of: oxygen, a major proportion of iron; a minor proportion of zinc; and smaller amounts of manganese; phosphorus, with the residue of a nitrate free calcium precursor, thereby forming a butadiene enriched product stream. The use of substantially nitrate free oxidative dehydrogenation catalyst is extremely advantageous.

The energy content of the butadiene enriched product stream is used to provide heat for the reaction feed stream by a combination of indirect heat exchange to remove sensible heat from the butadiene enriched product stream and thermal oxidation of undesired hydrocarbonaceous products separated from the butadiene enriched product stream by first passing the butadiene enriched product stream through a reactor feed superheater in which a mixture of steam and butene enriched hydrocarbons entering the reactor is superheated by indirect heat exchange with said butadiene enriched product stream to a temperature of at least 205°C (400 °F), preferably at least 260°C (500 °F), more preferably at least about 315°C (about 600 °F) and most preferably to about 345°C (about 650°F) ;

Subsequently, the butadiene enriched product stream is next passed through a steam generator in which water, preferably water condensed from the process stream, is vaporized by indirect heat exchange with the butadiene enriched product stream.

The butadiene enriched product stream is subsequently quenched is a quench tower, compressed, scrubbed to remove aldehydes and passed through a C4 absorber wherein C4 species including butadiene are absorbed in an absorption oil which is sometimes also referred to as lean oil.

The butadiene is recovered by passing the absorption oils through a degasser tower in which non-C4 volatiles are removed; a C4 stripper in which C4's including butadiene are desorbed or stripped from said absorption oil under reduced pressure. Preferably, dispersed volatile lower organics are stripped from the liquid stripped from the butadiene enriched product stream and the resultant aqueous stream is recycled to the steam generator while the volatile organics are oxidized to generate steam used to supply the heat required to vaporize water supplied to the steam generator.

Thermal oxidation of low value products recovered from (1) the butadiene enriched product stream, and (2) by-products of the purification of crude butadiene into the salable butadiene generates sufficient heat so that in steady operation, the energy content of the feed to the oxidative dehydrogenation process supplies at least 60%, preferably 70% and more preferably 85% of the energy required for (1) vaporizing and superheating said hydrocarbonaceous butene rich feed; and (2) vaporizing and superheating the water used to supply said superheated steam in said reactor feed stream during steady operation in the production cycle.

In our preferred processes, for each kg of butadiene produced, less than 0.15 kg, more preferably less than 0.10 kg, most preferably less than 0.05 kg of natural gas is consumed in (a) vaporizing and superheating the butene rich feed and (b) vaporizing and superheating the water used to supply the superheated steam in said reactor feed stream as the energy required therefore is supplied by the energy content of the butene rich feed to the oxidative dehydrogenation process.

By thermal oxidation of dispersed volatile lower organics removed from the butadiene enriched product stream at various stages of the process during steady operation, it is possible to recover sufficient energy in steady operation that the total heat required to both vaporize and superheat the butene rich feed as well as to vaporize and superheat the water used to supply the superheated steam supplied to the reactor feed stream is no more than 130%, preferably no more than 110% of the sum of (1) the sensible heat extracted from the butadiene enriched product stream and (2) the heat generated by thermal oxidation of (a) undesired products removed from the butadiene enriched product stream, and (b) by-products of the conversion of alkanes into the butenes enriched stream supplying the butene rich feed.

In preferred configurations, at least 75% of the heat required to vaporize the water stripped from the butadiene enriched product stream is supplied by a combination of: (1) sensible heat in said butadiene enriched product stream; (2) thermal oxidation of undesired volatiles from the butadiene enriched product stream.

More preferably, at least about 50% the heat required to vaporize the water stripped from the butadiene enriched product stream is supplied by:

(a) sensible heat in said butadiene enriched product stream;

(b) heat obtained from thermal oxidation of undesired volatile products obtained from the butadiene enriched product stream.

Even more preferably, at least about 75% of the energy required to vaporize and superheat said hydrocarbonaceous butene rich feed; and superheat the water used to supply said superheated steam in said reactor feed stream is supplied by the energy content of said butene rich feed to the oxidative dehydrogenation process.

While the invention has been described in detail, modifications within the spirit and scope of the invention will be readily apparent to those of skill in the art. In view of the foregoing discussion, relevant knowledge in the art and references, including co-pending applications, discussed above in connection with the Background and Detailed Description, the disclosures of which are all incorporated herein by reference, further description is deemed unnecessary. In addition, it should be understood that aspects of the invention and portions of various embodiments may be combined or interchanged either in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention.

AS OUR INVENTION, WE CLAIM:

1. An improved low emissions method of converting a hydrocarbonaceous butene rich feed into butadiene, wherein the improvement comprises the steps of:

vaporizing and superheating said hydrocarbonaceous butene rich feed to a temperature of at least 205°C (400°F), mixing said hydrocarbonaceous butene rich feed with superheated steam and an oxygen rich gas to form a reactor feed stream;

oxidatively dehydrogenating said reactor feed stream over a ferritic catalyst thereby forming a butadiene enriched product stream;

wherein:

the butadiene enriched product stream is used to provide heat for the reaction feed stream by a combination of indirect heat exchange to remove sensible heat from the butadiene enriched product stream and thermal oxidation of undesired hydrocarbonaceous products separated from the butadiene enriched product stream;

said butadiene enriched product stream at a temperature of at least about 510°C (950°F) passes first through a reactor feed superheater in which a mixture of steam and butene enriched hydrocarbons entering the reactor is superheated by indirect heat exchange with said butadiene enriched product stream to at least 345°C (650° F);

the butadiene enriched product stream exiting said reactor feed superheater passes next through a steam generator in which water is vaporized by indirect heat exchange with said butadiene enriched product stream;

the butadiene enriched product stream passes subsequently through a C4 absorber wherein C4's including butadiene are absorbed in a compatible absorption oil,

the absorption oil passes through: a degasser tower in which non-C4 volatiles are removed; a C4 stripper in which C4's including butadiene are desorbed/stripped from said absorption oil under reduced pressure, wherein dispersed volatile lower organics are stripped from aqueous liquid stripped from the butadiene enriched product stream and the resultant aqueous stream is recycled to the steam generator;

such that in steady operation, the energy content of said butene rich feed to the oxidative dehydrogenation reactor supplies at least 40% of the energy required for:

vaporizing and superheating said hydrocarbonaceous butene rich feed; and

vaporizing and superheating the water used to supply said superheated steam in said reactor feed stream.

2. The improved low emissions method of converting a hydrocarbonaceous butene rich feed into butadiene by oxidative dehydrogenation of that hydrocarbonaceous butene rich feed into butadiene of claim 1, wherein the heat required to vaporize water supplied to the steam generator is supplied at least in part by heat generated by thermal oxidation of undesired products removed from the butadiene enriched product stream.

3. The improved low emissions method of converting a hydrocarbonaceous butene rich feed into butadiene by oxidative dehydrogenation of that hydrocarbonaceous butene rich feed into butadiene of claim 1, wherein the ferritic catalyst is a ferritic oxide catalyst consisting essentially of: oxygen, a major proportion of iron; a minor proportion of zinc; and smaller amounts of manganese; phosphorus, and the residue of a nitrate free calcium precursor.

4. The improved low emissions method of converting a hydrocarbonaceous butene rich feed into butadiene by oxidative dehydrogenation of that hydrocarbonaceous butene rich feed into butadiene of claim 1, wherein during steady operation, the energy content of said butene rich feed supplies at least 45% of the energy required for:

vaporizing and superheating said hydrocarbonaceous butene rich feed; and vaporizing and superheating the water used to supply said superheated steam in said reactor feed stream.

5. The improved low emissions method of converting a hydrocarbonaceous butene rich feed into butadiene by oxidative dehydrogenation of that hydrocarbonaceous butene rich feed into butadiene of claim 1, wherein during the first phase of steady operation, the energy content of said butene rich feed supplies at least 50% of the energy required for:

vaporizing and superheating said hydrocarbonaceous butene rich feed; and

vaporizing and superheating the water used to supply said superheated steam in said reactor feed stream.

6. The improved low emissions method of converting a hydrocarbonaceous butene rich feed into butadiene by oxidative dehydrogenation of that hydrocarbonaceous butene rich feed into butadiene of claim 1, wherein the energy content of said butene rich feed supplies such a proportion of the energy required for:

(a) vaporizing and superheating said hydrocarbonaceous butene rich feed; and

(b) vaporizing and superheating the water used to supply said superheated steam in said reactor feed stream

that less than 0.35 kg of natural gas is consumed in (a) and (b) for each kg of butadiene produced.

7. The improved low emissions method of converting a hydrocarbonaceous butene rich feed into butadiene by oxidative dehydrogenation of that hydrocarbonaceous butene rich feed into butadiene of claim 1, wherein the energy content of said butene rich hydrocarbonaceous feed supplies such a proportion of the energy required for:

(a) vaporizing and superheating said hydrocarbonaceous butene rich feed; and

(b) vaporizing and superheating the water used to supply said superheated steam in said reactor feed stream that less than 0.3 kg of natural gas are consumed in (a) and (b) for each kg of butadiene produced.

8. The improved low emissions method of converting a hydrocarbonaceous butene rich feed into butadiene by oxidative dehydrogenation of that hydrocarbonaceous butene rich feed into butadiene of claim 1, wherein the energy content of said butene rich hydrocarbonaceous feed supplies such a proportion of the energy required for:

(a) vaporizing and superheating said hydrocarbonaceous butene rich feed; and

(b) vaporizing and superheating the water used to supply said superheated steam in said reactor feed stream

that less than 0.25 kg of natural gas are consumed in (a) and (b) for each kg of butadiene produced.

9. An improved low emissions method of manufacturing butadiene by oxidative dehydrogenation of a hydrocarbonaceous butene rich feed, wherein the improvement comprises the steps of:

vaporizing said hydrocarbonaceous butene rich feed, mixing said hydrocarbonaceous butene rich feed with superheated steam and an oxygen rich gas to form a reactor feed stream, superheating said reactor feed stream to a temperature of at least 345°C (650°F);

oxidatively dehydrogenating said reactor feed stream over a ferritic oxide catalyst thereby forming a butadiene enriched product stream;

wherein: the butadiene enriched product stream is used to provide heat for the reaction feed stream by a combination of indirect heat exchange to remove sensible heat from the butadiene enriched product stream and thermal oxidation of hydrocarbonaceous products separated from the butadiene enriched product stream;

said butadiene enriched product stream at a temperature of at least about 510°C (about 950°F) passing first through a reactor feed superheater in which a mixture of steam and butene enriched hydrocarbons entering the reactor is superheated by indirect heat exchange with said butadiene enriched product stream to at least 345°C (650° F) ;

the butadiene enriched product stream passing next through a steam generator in which water is vaporized and/or superheated by indirect heat exchange with said butadiene enriched product stream;

the butadiene enriched product stream passing subsequently through a quench tower, a compressor, an aldehyde scrubber and a C4 absorber wherein butadiene and C4's are preferentially absorbed into absorption oil with the overhead from said C4 absorber being passed to a thermal oxidizer and used to generate steam to supply heat used in the process, the absorption oil passing to: a degasser tower wherein residual nitrogen, hydrogen, and carbon dioxide is removed from the butadiene enriched absorption oil; a C4 stripper wherein butadiene and C4's are stripped from the absorption oil and recovered as a crude butadiene product stream,

wherein dispersed volatile lower organics are stripped from aqueous liquid stripped from the butadiene enriched product stream at various stages of the process and the resultant aqueous stream is provided to the steam generator; and wherein, during the first phase of steady operation,

the additional heat required to:

vaporize and superheat said hydrocarbonaceous butene rich feed; and

vaporize and superheat the water used to supply said superheated steam in said reactor feed stream;

is no more than 130% of the sum of (1) the sensible heat extracted from the butadiene enriched product stream and (2) the heat generated by thermal oxidation of volatile products removed from the butadiene enriched product stream.

10. The improved low emissions method of converting a hydrocarbonaceous butene rich feed into butadiene by oxidative dehydrogenation of that hydrocarbonaceous butene rich feed into butadiene of claim 9, wherein the ferritic catalyst is a ferritic oxide catalyst consisting

essentially of: oxygen, a major proportion of iron; a minor proportion of zinc; and smaller amounts of manganese; phosphorus, and the residue of a nitrate free calcium precursor.

11. The improved low emissions method of manufacturing butadiene from a butene rich feed by oxidative dehydrogenation of that butene enriched feed into butadiene of claim 9, wherein the additional energy required for conversion of said butene rich feed into a butadiene enriched stream is no more than 110% of the sum of: (1) the sensible heat derived from the butadiene enriched product stream and (2) the heat generated by thermal oxidation of (a) volatile products removed from the butadiene enriched product stream.

12. An improved low emissions method of converting the hydrocarbonaceous butene rich feed into butadiene by oxidative dehydrogenation, wherein the improvement comprises the steps of:

providing a butene rich hydrocarbonaceous feed, vaporizing and superheating said hydrocarbonaceous butene rich feed to a temperature of at least about 205°C (about 400°F), mixing said hydrocarbonaceous butene rich feed with superheated steam and an oxygen rich gas to form a reactor feed stream;

oxidatively dehydrogenating said reactor feed stream over a catalyst comprising: a major proportion of iron oxide; a minor proportion of zinc oxide; and smaller amounts of manganese oxide; and phosphoric acid, and thereby forming a butadiene enriched product stream; wherein:

the sensible heat in said butadiene enriched product stream is used to provide heat for the reaction feed stream by indirect heat exchange;

said butadiene enriched product stream passing through a reactor feed superheater in which a stream comprising vaporized butenes and steam is superheated by indirect heat exchange with said butadiene enriched product stream to at least 205°C (400° F);

the butadiene enriched product stream subsequently passing next through a steam generator in which steam is generated by indirect heat exchange with said butadiene enriched product stream;

the butadiene enriched product stream passing subsequently through a quench tower, a compressor, an aldehyde scrubber, a C4 absorber, a degasser tower; a C4 stripper, wherein dispersed organics are stripped from aqueous liquid stripped from the butadiene enriched product stream and the resultant aqueous stream is provided to the stripped water steam heater; and wherein

at least 75% of the heat required to vaporize the water stripped from the butadiene enriched product stream is supplied by a combination of:

sensible heat in said butadiene enriched product stream; and

thermal oxidation of undesired volatiles from the butadiene enriched product stream.

13. An improved low emissions method of converting ahydrocarbonaceous butene rich feed into butadiene by oxidative dehydrogenation, wherein the improvement comprises the steps of:

providing a butene rich hydrocarbonaceous feed, vaporizing and superheating said hydrocarbonaceous butene rich feed to a temperature of at least about 205°C (about 400°F), mixing said hydrocarbonaceous butene rich feed with superheated steam and an oxygen rich gas to form a reactor feed stream;

oxidatively dehydrogenating said reactor feed stream over a catalyst comprising: a major proportion of iron oxide; a minor proportion of zinc oxide; and smaller amounts of manganese oxide; and phosphoric acid, and thereby forming a butadiene enriched product stream; wherein:

the sensible heat in said butadiene enriched product stream is used to provide heat for the reaction feed stream by indirect heat exchange;

said butadiene enriched product stream passes first through a reactor feed superheater in which reactor feed comprising vaporized butenes and steam entering the reactor is superheated by indirect heat exchange with said butadiene enriched product stream to at least 205°C (400° F);

the butadiene enriched product stream thereafter passes through a steam generator in which steam is superheated by indirect heat exchange with said butadiene enriched product stream ;

the butadiene enriched product stream passing subsequently through a quench tower, a compressor, an aldehyde scrubber, a C4 absorber, a degasser tower; a C4 stripper, wherein dispersed organics are stripped from aqueous liquid stripped from the butadiene enriched product stream and the resultant aqueous stream is provided to the stripped water steam heater; and wherein:

at least about 50% of the additional heat required to vaporize the water stripped from the butadiene enriched product stream is supplied by:

(a) sensible heat in said butadiene enriched product stream; and

(b) heat obtained from thermal oxidation of undesired volatile products obtained from the butadiene enriched product stream.

14. In a process for producing butadiene by converting butenes from a butene rich stream into butadiene by oxidatively dehydrogenating said butenes in a reaction system which includes a superheater for superheating feed and one or more feed vaporizers for vaporizing feed, the improvement comprising:

(a) reacting said butene rich feed stream in an oxidative dehydrogenation reactor to form a butadiene enriched product effluent stream which exits said reactor at an elevated temperature ;

(b) feeding said butadiene enriched product effluent stream to a feed superheater, wherein the butadiene enriched product effluent stream is provided to the superheater at a temperature of 425°C (800 ˚F) or more, reactor feed also being provided to the superheater;

(c) superheating reactor feed in the superheater to a temperature of at least 260°C (500 ˚F) with indirect heat transfer of sensible heat from the butadiene enriched product effluent stream to the feed;

(d) subsequent to step (c), feeding the butadiene enriched product effluent stream exiting the superheater to a feed vaporizer, wherein the butadiene enriched product effluent stream entering the vaporizer is at a temperature of at least 205°C (400 °F); and

(e) vaporizing feed in the vaporizer with indirect heat transfer of sensible heat from the butadiene enriched product effluent stream to the feed.

15. The improvement according to Claim 14, wherein the butadiene enriched product effluent stream is provided to the superheater at a temperature of 485°C (900 °F) or more.

16. The improvement according to Claim 15, wherein the butadiene enriched product effluent stream is provided to the superheater at a temperature of 540°C (1000 °F) or more.

17. The improvement according to Claim 16, wherein the butadiene enriched product effluent stream is provided to the superheater at a temperature of 595°C (1100 °F) or more.

18. The improvement according to Claim 14, wherein the butadiene enriched product effluent stream is provided to the superheater at a temperature of from 480°C to 760°C (900 °F to 1400 °F).

19. The improvement according to Claim 14, wherein the butadiene enriched product effluent stream is provided to the vaporizer at a temperature of at least 290°C (550°F).

20. The improvement according to Claim 19, wherein the butadiene enriched product effluent stream is provided to the vaporizer at a temperature of at least 315°C (600°F).

21. The improvement according to Claim 20, wherein the butadiene enriched product stream is provided to the vaporizer at a temperature of at least 345°C (650°F).

22. The improvement according to Claim 14, wherein the butadiene enriched product stream is provided to the vaporizer at a temperature of from 260°C to 425°C (500°F to 800°F).

23. The improvement according to Claim 14, wherein feed is heated in the superheater to a temperature of at least 290°C (550°F).

24. The improvement according to Claim 23, wherein feed is heated in the superheater to a temperature of at least 316°C (600°F).

25. The improvement according to Claim 24, wherein feed is heated in the superheater to a temperature of at least 345°C (650°F).

26. The improvement according to Claim 14, wherein the feed is heated in the superheater to a temperature of from 260°C to 485°C (500°F to 900°F).

27. The improvement according to Claim 14, wherein the temperature delta of the butadiene enriched product effluent stream through the superheater is at least 120°C (220°F).

28. The improvement according to Claim 27, wherein the temperature delta of the butadiene enriched product effluent stream through the superheater is at least 150°C (270°F).

29. The improvement according to Claim 28, wherein the temperature delta of the butadiene enriched product effluent stream through the superheater is at least 180°C (325°F).

30. The improvement according to Claim 14, wherein the temperature delta of the butadiene enriched product effluent stream through the superheater is from 120°C to 235°C (220°F to 425°F).

31. The improvement according to Claim 14, wherein at least 2300 kJ/kg (1000 BTU/LB) BD produced is transferred from the butadiene enriched product effluent stream to feed in the superheater by indirect heat exchange.

32. The improvement according to Claim 31, wherein at least 3500 kJ/kg (1500 BTU/LB) BD produced is transferred from the butadiene enriched product effluent stream to feed in the superheater by indirect heat exchange.

33. The improvement according to Claim 14, wherein at least 2300 kJ/kg (1000 BTU/LB) BD produced is transferred from the butadiene enriched product stream to feed in the vaporizer by indirect heat exchange.

34. The improvement according to Claim 33, wherein at least 3500 kJ/kg (1500 BTU/LB) BD produced is transferred from the butadiene enriched product stream to feed in the vaporizer by indirect heat exchange.

35. The improvement according to Claim 34, wherein at least 4100 kJ/kg (1750 BTU/LB) BD produced is transferred from the butadiene enriched product stream to feed in the vaporizer by indirect heat exchange.

36. The improvement according to Claim 14, wherein from 2300 to 5800 kJ/kg (1000 to 2500 BTU/LB) BD produced is transferred from the butadiene enriched product effluent stream to feed in the superheater by indirect heat exchange and from 2300 to 7000 kJ/kg (1000 to 3000 BTU/LB) BD produced is transferred from the butadiene enriched product stream to feed in the vaporizer by indirect heat exchange.

37. An apparatus for producing butadiene by way of oxidative dehydrogenation of a butane-rich feed stream comprising:

(a) a reactor adapted for receiving said butane-rich feed stream and converting butenes to butadiene by oxidative dehydrogenation, thereby providing a butadiene enriched product effluent stream which exits the reactor at an elevated temperature;

(b) a superheater coupled to the reactor to receive the butadiene enriched product effluent stream from the reactor at elevated temperature as well as being configured to receive reactor feed, said superheater being adapted to transfer sensible heat from the butadiene enriched product effluent stream to reactor feed and provide superheated feed to the reactor;

(c) a first vaporizer coupled to the reactor to receive the butadiene enriched product effluent stream as it exits the superheater and to transfer sensible heat from the butadiene enriched product effluent stream to reactor feed;

(d) a second vaporizer coupled to the reactor for providing vapor feed thereto;

(e) a purification train for recovering butadiene from the butadiene enriched product effluent stream; and

(f) a thermal oxidizer for recovering energy by way of oxidizing by-products from the purification train and providing energy for said second vaporizer.

38. The apparatus for producing butadiene by way of oxidative dehydrogenation of a butane-rich feed stream according to Claim 37, wherein the superheater is adapted to transfer at least 2300 kJ/kg (1000 BTU/LB) BD produced from the butadiene enriched product effluent stream to feed by indirect heat exchange.

39. The apparatus for producing butadiene by way of oxidative dehydrogenation of a butane-rich feed stream according to Claim 38, wherein the superheater is adapted to transfer at least 3500 kJ/kg (1500 BTU/LB) BD produced from the butadiene enriched product effluent stream to feed by indirect heat exchange.

40. The apparatus for producing butadiene by way of oxidative dehydrogenation of a butane-rich feed stream according to Claim 37, wherein the first vaporizer is adapted to transfer at least 2300 kJ/kg (1000 BTU/LB) BD produced from the butadiene enriched product effluent stream to feed by indirect heat exchange.

41. The apparatus for producing butadiene by way of oxidative dehydrogenation of a butane-rich feed stream according to Claim 40, wherein the first vaporizer is adapted to transfer at least 3500 kJ/kg (1500 BTU/LB) BD produced from the butadiene enriched product effluent stream to feed by indirect heat exchange.

42. The apparatus for producing butadiene by way of oxidative dehydrogenation of a butane-rich feed stream according to Claim 41, wherein the first vaporizer is adapted to transfer at least 4300 kJ/kg (1850 BTU/LB) BD produced from the butadiene enriched product effluent stream to feed by indirect heat exchange.

43. The apparatus for producing butadiene by way of oxidative dehydrogenation of a butane-rich feed stream according to Claim 37, wherein the superheater is adapted to transfer from 2300 to 8100 kJ/kg (1000 to 3500 BTU/LB) BD produced from the butadiene enriched product effluent stream to feed by indirect heat exchange and the first vaporizer is adapted to transfer from 2300 to 10,500 kJ/kg (1000 to 4500 BTU/LB) BD produced from the butadiene enriched product effluent stream to feed by indirect heat exchange.

44. The apparatus for producing butadiene by way of oxidative dehydrogenation of a butane-rich feed stream according to Claim 37, wherein the thermal oxidizer is adapted to provide at least 930 kJ/kg (400 BTU/LB) BD produced to said second vaporizer.

45. The apparatus for producing butadiene by way of oxidative dehydrogenation of a butane-rich feed stream according to Claim 44, wherein the thermal oxidizer is adapted to provide at least 1800 kJ/kg (800 BTU/LB) BD produced to said second vaporizer.

46. The apparatus for producing butadiene by way of oxidative dehydrogenation of a butane-rich feed stream according to Claim 45, wherein the thermal oxidizer is adapted to provide at least 3700 kJ/kg (1600 BTU/LB) BD produced to said second vaporizer.

47. The apparatus for producing butadiene by way of oxidative dehydrogenation of a butane-rich feed stream according to Claim 46, wherein the thermal oxidizer is adapted to provide at least 4600 kJ/kg (2000 BTU/LB) BD produced to said second vaporizer.

48. The apparatus for producing butadiene by way of oxidative dehydrogenation of a butane-rich feed stream according to Claim 47, wherein the thermal oxidizer is adapted to provide at least 6500 kJ/kg (2800 BTU/LB) BD produced to said second vaporizer.

49. The apparatus for producing butadiene by way of oxidative dehydrogenation of a butane-rich feed stream according to Claim 37, wherein the superheater is adapted to transfer from 2300 to 8000 kJ/kg (1000 to 3500 BTU/LB) BD produced from the butadiene enriched product effluent stream to feed by indirect heat exchange and the first vaporizer is adapted to transfer from 2300 to 10,500 kJ/kg (1000 to 4500 BTU/LB) BD produced from the butadiene enriched product effluent stream to feed by indirect heat exchange and the thermal oxidizer is adapted to provide at least 930 kJ/kg (400 BTU/LB) BD produced to said second vaporizer.

50. The apparatus for producing butadiene by way of oxidative dehydrogenation of a butane-rich feed stream according to Claim 49, wherein the superheater is adapted to transfer from 2300 to 8000 kJ/kg (1000 to 3500 BTU/LB) BD produced from the butadiene enriched product effluent stream to feed by indirect heat exchange and the first vaporizer is adapted to transfer from 2300 to 10,500 kJ/kg (1000 to 4500 BTU/LB) BD produced from the butadiene enriched product effluent stream to feed by indirect heat exchange and the thermal oxidizer is adapted to provide at least 4600 kJ/kg (2000 BTU/LB) BD produced to said second vaporizer.

FIG. 1

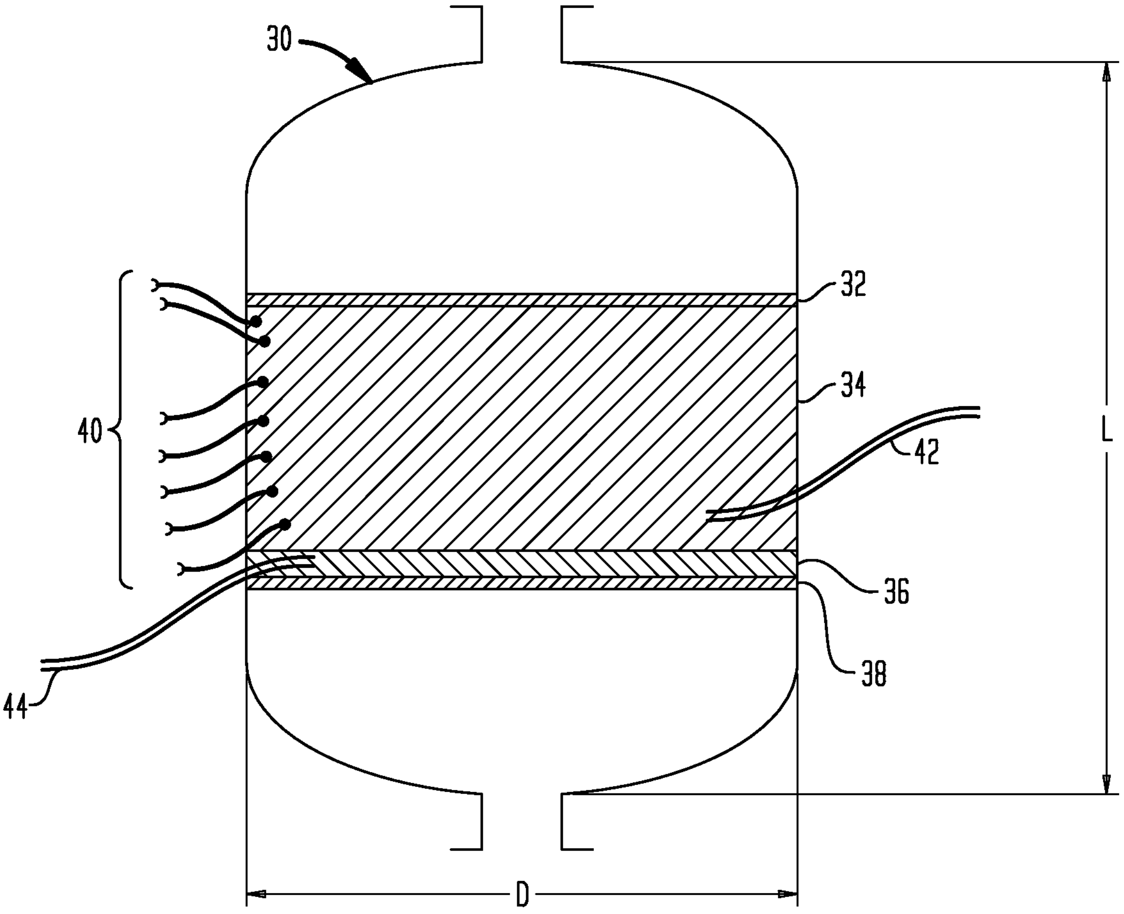


FIG. 2

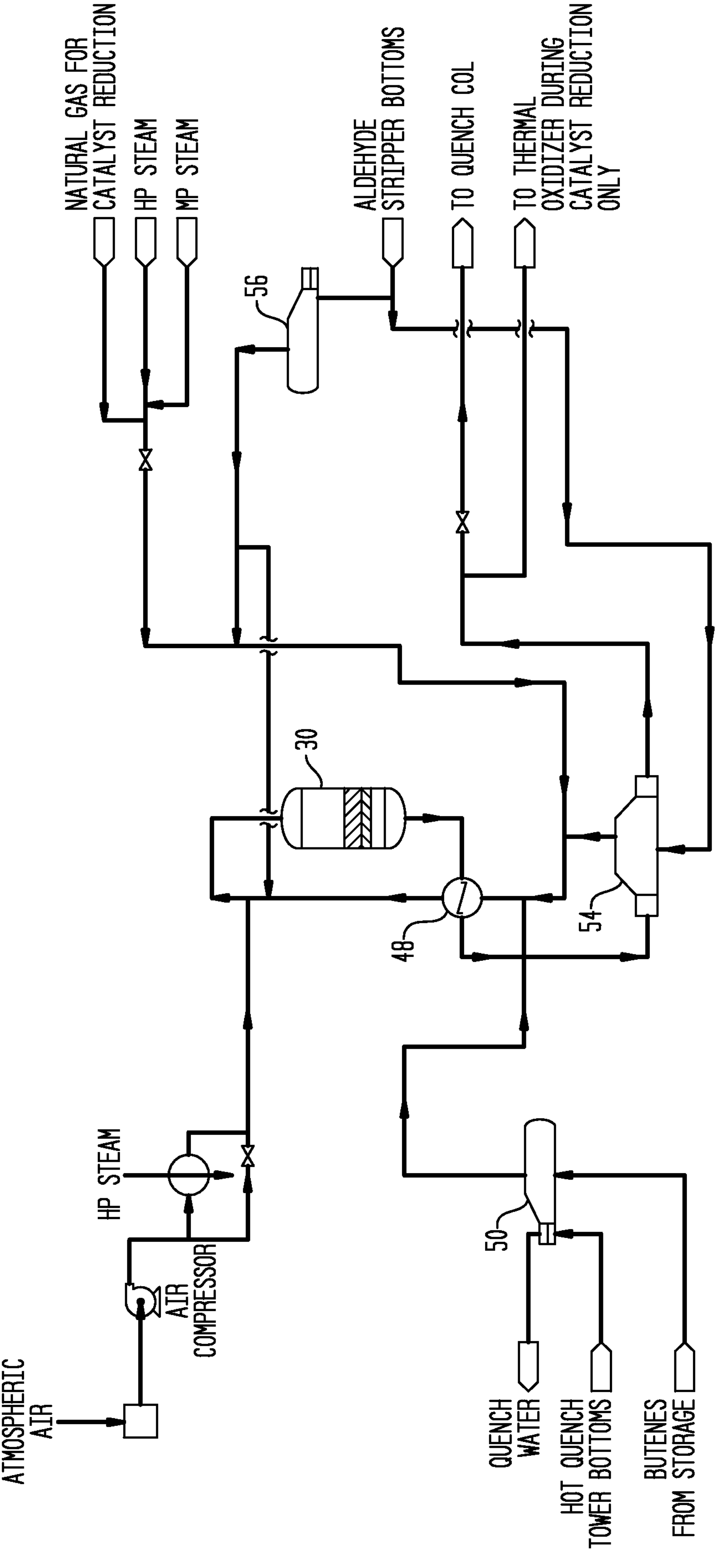

NATURAL GAS FOR CATALYST REDUCTION
HP STEAM
MP STEAM
ALDEHYDE STRIPPER BOTTOMS
TO QUENCH COL
TO THERMAL OXIDIZER DURING CATALYST REDUCTION ONLY
56
30
48
54
50
HP STEAM
AIR COMPRESSOR
ATMOSPHERIC AIR
QUENCH WATER
HOT QUENCH TOWER BOTTOMS
BUTENES FROM STORAGE

FIG. 3

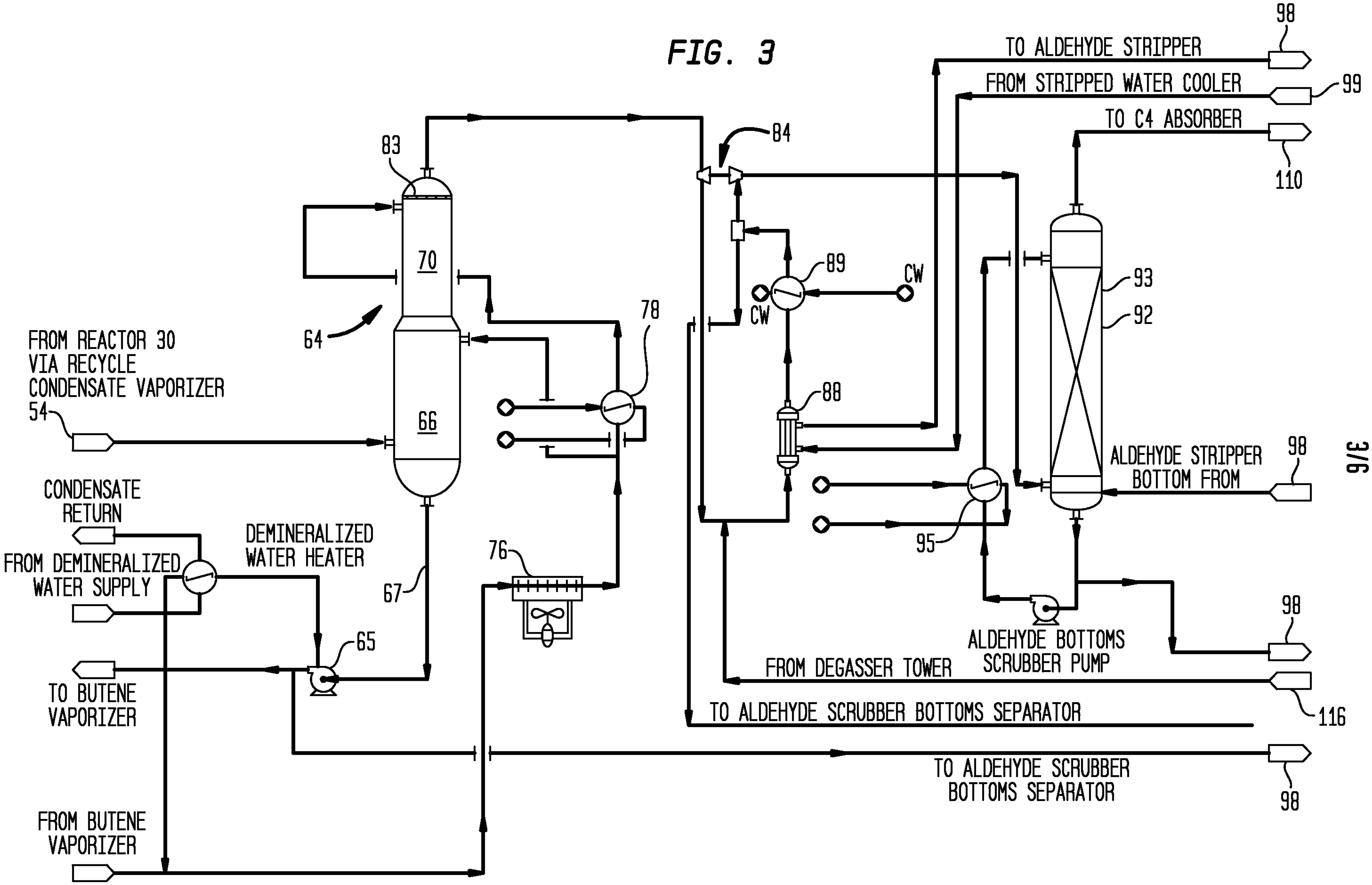

98
TO ALDEHYDE STRIPPER
FROM STRIPPED WATER COOLER
99
TO C4 ABSORBER
110
84
83
70
64
89
CW
CW
78
93
92
FROM REACTOR 30
VIA RECYCLE
CONDENSATE VAPORIZER
54
66
88
ALDEHYDE STRIPPER
BOTTOM FROM
98
95
CONDENSATE
RETURN
FROM DEMINERALIZED
WATER SUPPLY
DEMINERALIZED
WATER HEATER
67
76
65
ALDEHYDE BOTTOMS
SCRUBBER PUMP
98
TO BUTENE
VAPORIZER
FROM DEGASSER TOWER
116
TO ALDEHYDE SCRUBBER BOTTOMS SEPARATOR
TO ALDEHYDE SCRUBBER
BOTTOMS SEPARATOR
98
FROM BUTENE
VAPORIZER

FIG. 4

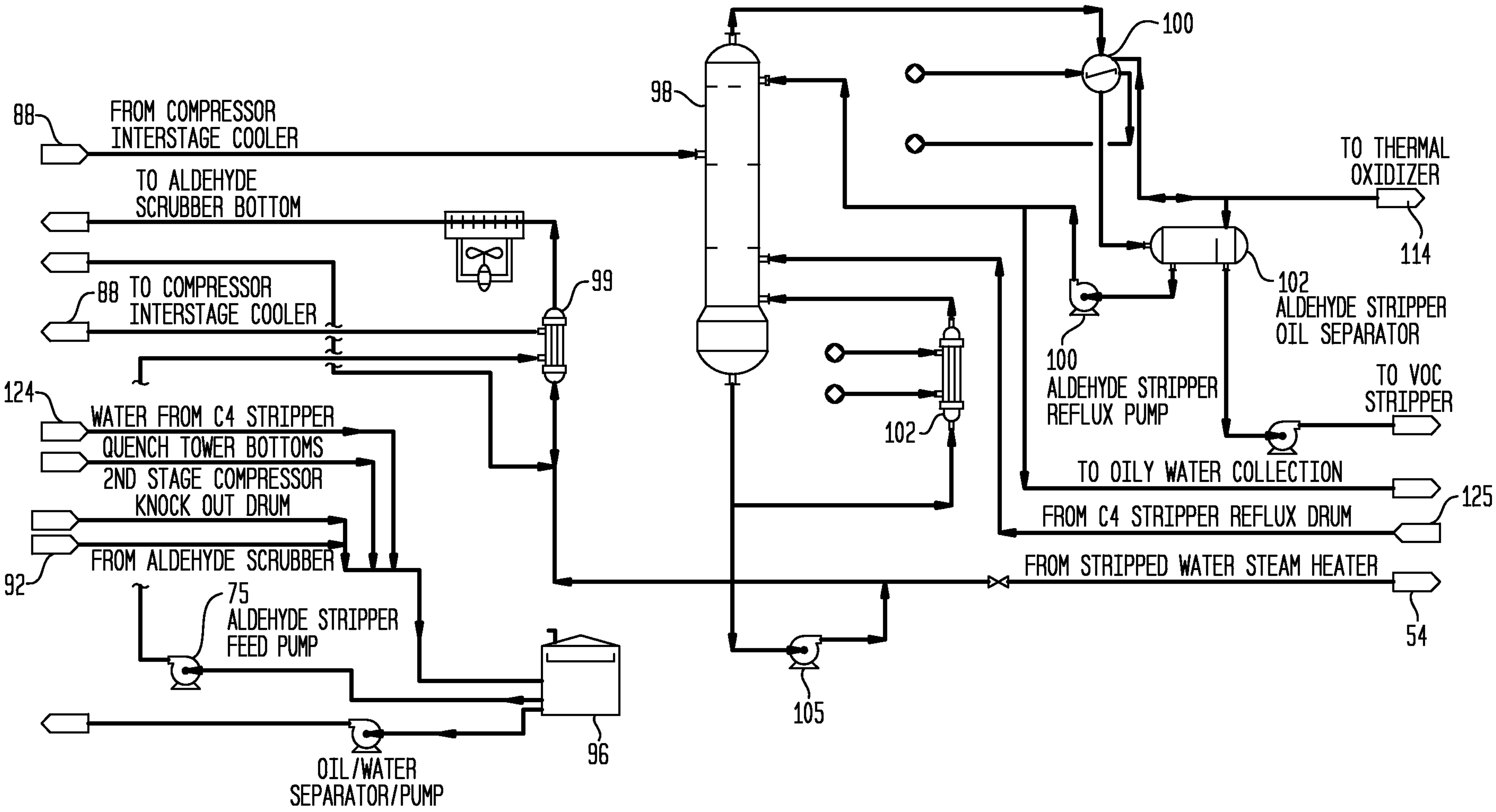

88
FROM COMPRESSOR INTERSTAGE COOLER
TO ALDEHYDE SCRUBBER BOTTOM
88 TO COMPRESSOR INTERSTAGE COOLER
124
WATER FROM C4 STRIPPER
QUENCH TOWER BOTTOMS
2ND STAGE COMPRESSOR KNOCK OUT DRUM
92
FROM ALDEHYDE SCRUBBER
75
ALDEHYDE STRIPPER FEED PUMP
OIL/WATER SEPARATOR/PUMP
96
99
98
105
102
100
100
ALDEHYDE STRIPPER REFLUX PUMP
102
ALDEHYDE STRIPPER OIL SEPARATOR
TO THERMAL OXIDIZER
114
TO VOC STRIPPER
TO OILY WATER COLLECTION
FROM C4 STRIPPER REFLUX DRUM
125
FROM STRIPPED WATER STEAM HEATER
54

FIG. 5

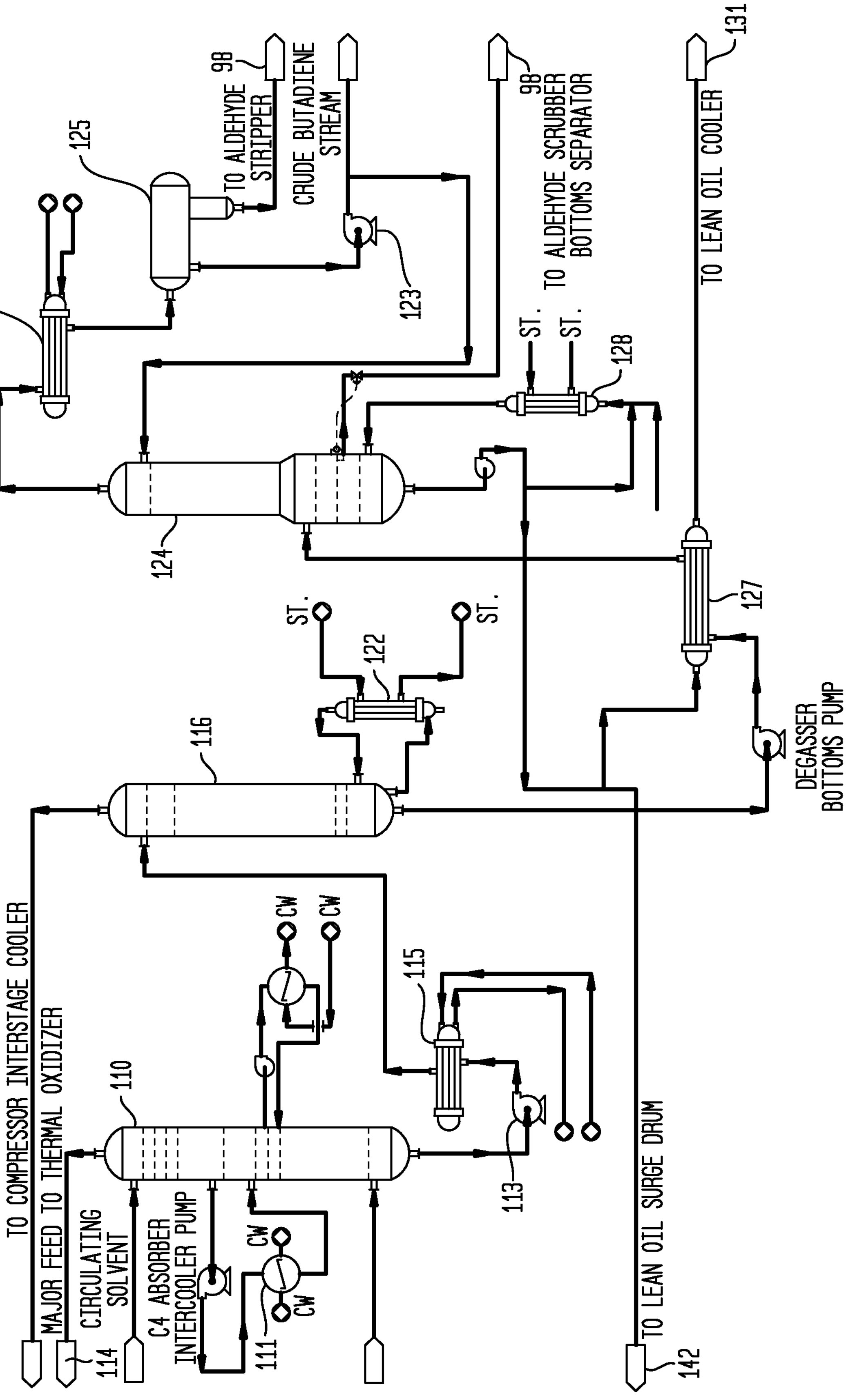
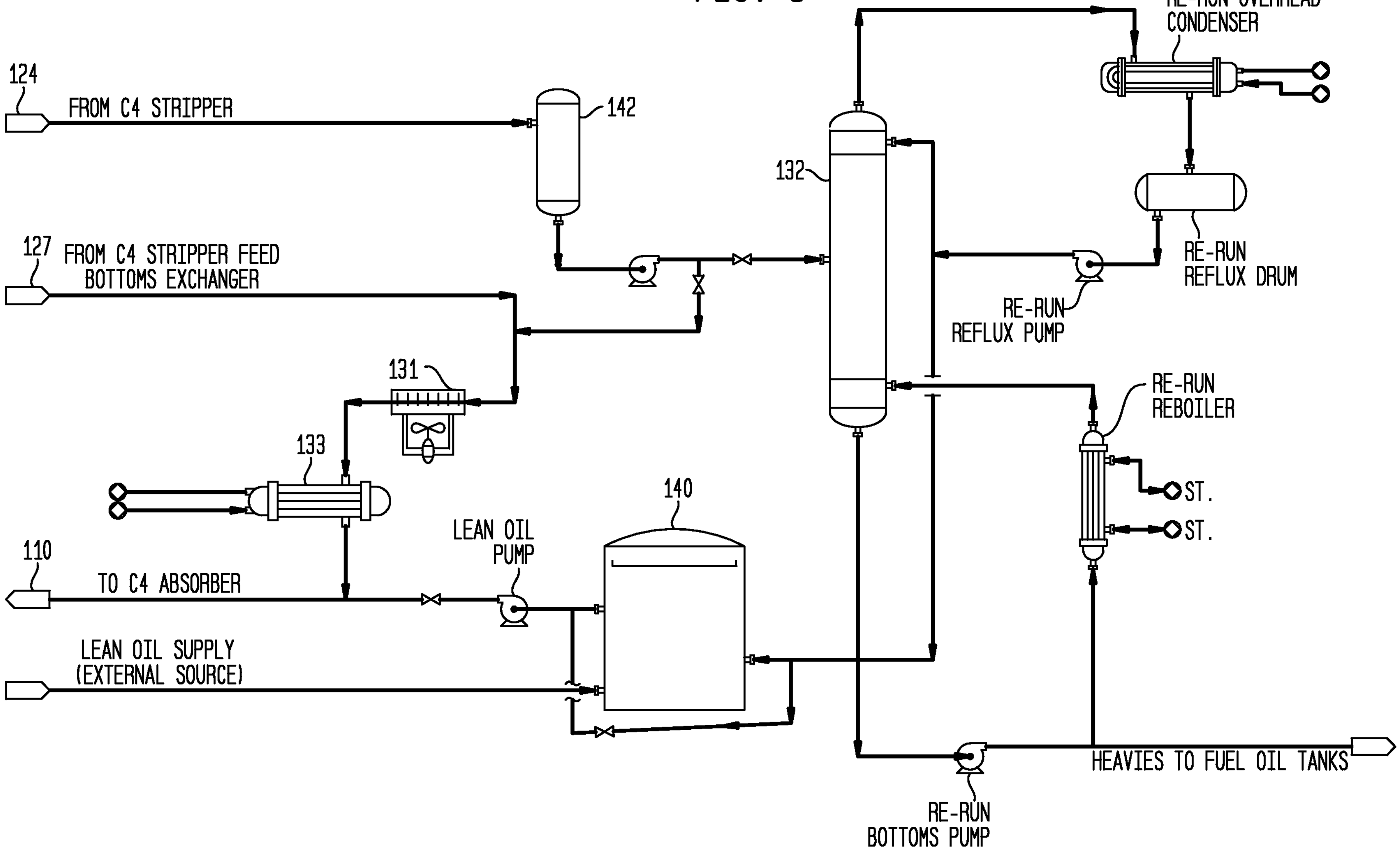

130
125
TO ALDEHYDE STRIPPER
98
CRUDE BUTADIENE STREAM
98
TO ALDEHYDE SCRUBBER BOTTOMS SEPARATOR
TO LEAN OIL COOLER
131
123
ST.
ST.
128
124
ST.
122
ST.
127
116
DEGASSER BOTTOMS PUMP
TO COMPRESSOR INTERSTAGE COOLER
MAJOR FEED TO THERMAL OXIDIZER
110
CW
CW
115
CIRCULATING SOLVENT
114
C4 ABSORBER INTERCOOLER PUMP
CW
CW
111
113
TO LEAN OIL SURGE DRUM
142

FIG. 6


124
FROM C4 STRIPPER
142
127
FROM C4 STRIPPER FEED BOTTOMS EXCHANGER
131
133
110
TO C4 ABSORBER
LEAN OIL PUMP
140
LEAN OIL SUPPLY (EXTERNAL SOURCE)
132
RE-RUN OVERHEAD CONDENSER
RE-RUN REFLUX DRUM
RE-RUN REFLUX PUMP
RE-RUN REBOILER
ST.
ST.
RE-RUN BOTTOMS PUMP
HEAVIES TO FUEL OIL TANKS

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/034205

A. CLASSIFICATION OF SUBJECT MATTER

C07C 5/333(2006.01)i, C07C 11/167(2006.01)i, C07C 11/08(2006.01)i, B01J 23/745(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C 5/333; C07C 5/03; C07C 11/167; C07C 11/08; B01J 23/745

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: butene , butadiene, oxidative dehydrogenation , catalyst, heat exchange, sensible heat

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011-0245568 A1 (KHABASHESKU OLGA et al.) 06 October 2011 See abstract, paragraph [0036]-[0040] and claims	1-50
A	US 3159688 A (THOMAS J.JENNINGS et al.) 01 December 1964 See column 2, line 12 - line 36, column 5, line 59 - column 8, line 8 and claims	1-50
A	US 3320330 A (JAMES LOUIS CALLAHAN et al.) 16 May 1967 See column 6, line 44 - line 68 and claims	1-50
A	US 3110746 A (HENRY H.VOGE et al.) 12 November 1963 See column 7, line 70 - column 8, line 2 and claims	1-50
A	US 7495138 B2 (CRONE SVEN et al.) 24 February 2009 See abstract and claims	1-50

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
28 August 2013 (28.08.2013)

Date of mailing of the international search report
28 August 2013 (28.08.2013)

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City,
302-701, Republic of Korea
Facsimile No. +82-42-472-7140

Authorized officer
LEE Chang Nam
Telephone No. +82-42-481-5527

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/034205

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011-0245568 A1	06/10/2011	None	
US 3159688 A	01/12/1964	BE 615319 A	20/03/1962
		GB 938320 A	20/03/1962
US 3320330 A	16/05/1967	None	
US 3110746 A	12/11/1963	None	
US 7495138 B2	24/02/2009	AT 409680 T	15/10/2008
		BR PI0519153 A2	30/12/2008
		CN 101084174 A0	05/12/2007
		CN 101084174 B	17/11/2010
		DE 102004061514 A1	06/07/2006
		DE 502005005572 D1	13/11/2008
		EA 010744 B1	30/10/2008
		EA 200701050 A1	28/12/2007
		EP 1831134 A1	12/09/2007
		EP 1831134 B1	01/10/2008
		ES 2312042 T3	16/02/2009
		KR 10-1272387 B1	10/06/2013
		KR 20070089177 A	30/08/2007
		MY 141055 A	25/02/2010
		US 2008-0119680 A1	22/05/2008
		WO 2006-066848 A1	29/06/2006