

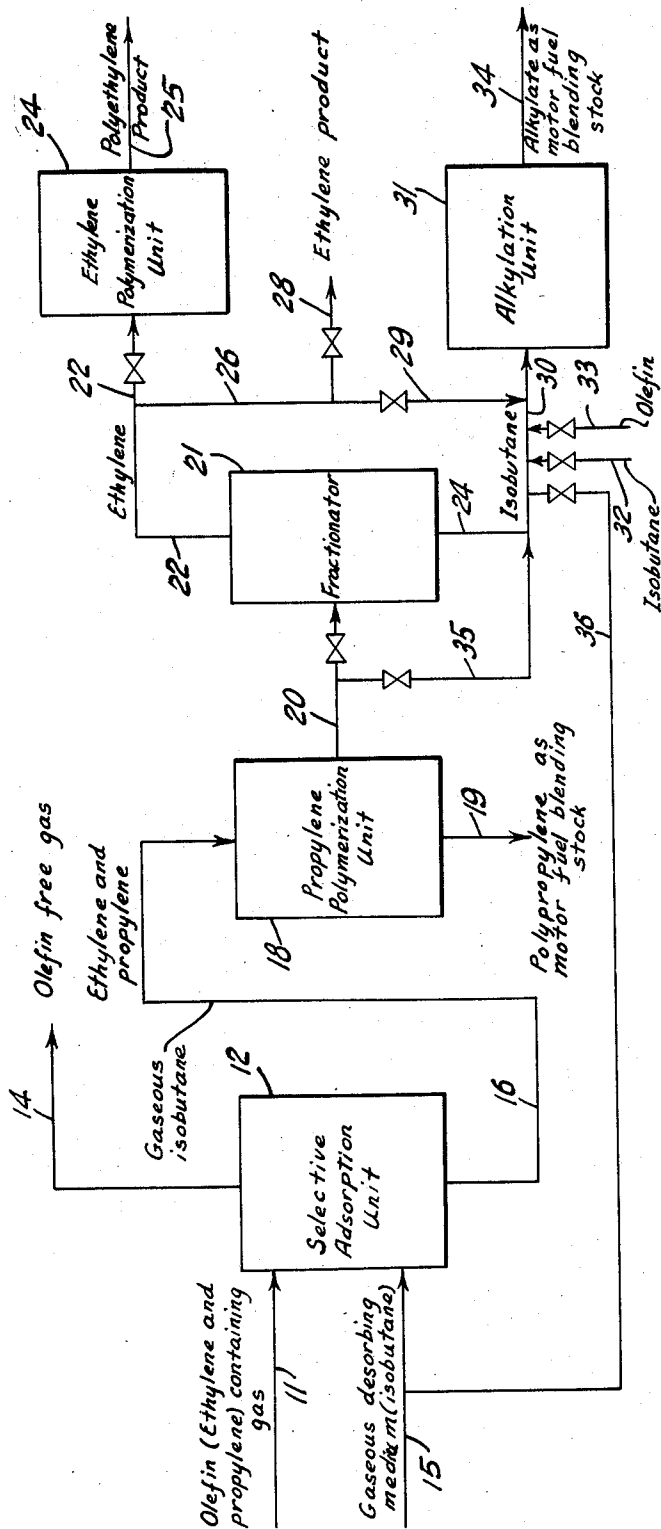
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RECOVERY AND UTILIZATION OF NORMALLY GASEOUS OLEFINS

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RECOVERY AND UTILIZATION OF NORMALLY GASEOUS OLEFINS

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This invention relates to a method of treating gaseous streams containing normally gaseous olefins, such as ethylene and propylene. More particularly, this invention relates to a method for separating and utilizing the olefin content (ethylene and propylene) of gaseous streams such as are available at a petroleum refinery. In accordance with one embodiment this invention is concerned with the recovery of ethylene and propylene from the residue gases of a petroleum treating process such as the gases from a fluid catalytic cracking unit. In accordance with still another embodiment this invention is directed to a method of upgrading an olefin-containing fuel gas by the recovery of the normally gaseous olefins therefrom and separately treating the recovered olefins for the production of more valuable chemicals and/or materials therefrom.

In a petroleum refinery operation there are produced numerous gaseous hydrocarbon-containing streams which per se have substantially little value and, accordingly, are often employed as fuel. Many of these gaseous hydrocarbon-containing streams contain normally gaseous olefins, such as ethylene and propylene, in substantial, although minor, amounts, such as amounts in the range of 2–15 volume percent, respectively. Heretofore frequently because of the difficulties involved in the separation of these normally gaseous olefins from such streams, the olefins therein, despite the fact that they are particularly desirable when in substantially pure or concentrated amounts as chemical feed stocks for the preparation of plastics and motor fuel components, relatively little utilization of these normally gaseous olefins has been made or attempted. For example, in some refinery operations it has been the practice heretofore to employ the fluid catalytic cracker adsorber tail gas as a fuel gas despite the fact that this tail gas contains substantial, although minor, amounts of ethylene and propylene and despite the fact that this tail gas is available in very substantial quantities.

Accordingly, it is an object of this invention to provide an improved process for the treatment of gaseous streams containing normally gaseous olefins, such as ethylene and propylene.

Another object of this invention is to provide an improved process for the recovery of ethylene and propylene from petroleum refinery streams.

Still another object of this invention is to provide a process for upgrading normally gaseous olefin-containing gaseous streams into more valuable products.

Again another object of this invention is to provide an improved process for the utilization of gaseous refinery streams, such as a fluid catalytic cracker adsorber tail gas containing minor amounts of ethylene and propylene.

How these and other objects of this invention are accomplished will become more apparent with reference to the accompanying disclosure and drawing wherein there is schematically illustrated one embodiment of a process in accordance with this invention directed specifically to the separation of ethylene and propylene from a gaseous stream containing the same and the

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eventual production of a propylene polymer particularly suitable as a motor fuel component, and ethylene polymer (polyethylene), a very useful plastic-like material and/or, if desired, a relatively high octane number alkylate desirable as a component in a motor fuel.

We have provided a process for treating a gaseous admixture containing ethylene and propylene wherein the gaseous admixture is contacted with a special selective adsorbent which selectively adsorbs ethylene and propylene in preference to the other components making up the gaseous admixture. Following the selective adsorption of ethylene and propylene from the gaseous admixture which might also include other gaseous materials and hydrocarbons, such as nitrogen, carbon monoxide, oxygen, hydrogen, methane, ethane, propane, n-butane, isobutane, the butenes and similar higher molecular weight hydrocarbons (paraffins and olefins), the ethylene and propylene are desorbed.

The resulting desorption effluent containing ethylene and propylene is then passed to a catalytic polymerization unit wherein the propylene content of the desorption effluent is polymerized to form a normally liquid propylene polymer (polypropylene). The resulting normally liquid propylene polymer which is particularly suitable as a motor fuel component by virtue of its relatively high octane rating is then separately recovered. Following the propylene polymerization process wherein the propylene was polymerized in the presence of ethylene, the residual ethylene stream, after separation of the propylene polymer therefrom, together with the gaseous desorption fluid, which might have been employed to desorb the ethylene and propylene from the selective adsorbent, is treated, as by fractionation, to yield a gaseous stream comprising essentially only ethylene. This gaseous stream comprising essentially only ethylene is subjected, if desired, to well known high pressure or low pressure polymerization operations wherein the ethylene is polymerized to form an ethylene polymer (polyethylene) which is recovered as product. If desired, a portion of the ethylene-containing stream may be employed to alkylate an isoparaffinic hydrocarbon, such as isobutane, in a catalytic alkylation unit for the production of a normally liquid alkylate, i.e., a branched chain paraffinic hydrocarbon which is particularly useful as a motor fuel component. The operation wherein a portion of the ethylene is employed to alkylate an isoparaffinic hydrocarbon, such as isobutane, is particularly desirable when the gaseous desorption fluid employed to desorb ethylene and propylene from the selective adsorbent is isobutane. When isobutane is thus employed the gaseous desorption effluent would initially comprise ethylene, propylene and isobutane. As indicated hereinabove, the propylene contained in this desorption effluent is separately catalytically polymerized in the presence of the ethylene and the isobutane.

The special selective adsorbent employed in the practice of this invention is a solid, particle-form selective adsorbent which preferentially adsorbs ethylene and propylene over normally gaseous materials, such as methane, ethane, oxygen, nitrogen and the like. Particularly suitable as the special selective adsorbent in the practice of this invention is a dehydrated crystallized sodium aluminosilicate sold by Linde Air Products Company under the trade name Linde type 4A molecular sieve. This particular dehydrated crystalline sodium aluminosilicate is a porous crystalline material wherein the pores of the crystals are of molecular dimension and of uniform size, approximately 4.0 Angstrom units, a pore size sufficiently large to admit such materials as carbon monoxide, hydrogen sulfide, nitrogen, oxygen, methane, ethane, ethylene, acetylene, propylene, but sufficiently small to exclude the relatively high molecular weight hydrocarbons (i.e.,

those hydrocarbons having a molecular weight greater than propylene), such as propane, n-butane, isobutane, the butenes, cyclopropane and higher molecular weight paraffins (n-paraffins, isoparaffins), and olefins. This same dehydrated crystalline sodium aluminosilicate material having a uniform pore size of about 4 Angstrom units preferentially adsorbs the unsaturated hydrocarbons, such as ethylene and propylene, over the saturated hydrocarbons, such as methane and ethane, and other gaseous materials such as nitrogen and oxygen. The naturally occurring zeolite (sodium aluminosilicate), analcite, exhibits the property of preferentially adsorbing ethylene and propylene over methane and ethane and is a suitable selective adsorbent for use in the practice of this invention.

The selective adsorption operation in accordance with this invention is carried out in the gaseous phase, preferably at a relatively low temperature, such as a temperature in the range 50° F.-400° F., more or less. Although higher or lower temperatures might also be employed it is preferred to carry out the selective adsorption separation operation at about ambient temperature, such as a temperature in the range 75-200° F.

The materials preferentially adsorbed on the particular solid selective adsorbents employed in the practice of this invention may be desorbed therefrom by any suitable means, e.g., high temperature, vacuum desorption or combination of high temperature and vacuum desorption. Preferably the adsorbed ethylene and propylene are desorbed by contact with a suitable, readily separable (such as by distillation, condensation, extraction and the like) hot gaseous fluid such as carbon dioxide, which is separable from admixture with the resulting desorbed ethylene and propylene by aqueous caustic wash. The normally gaseous hydrocarbons, such as ethane, propane, n-butane, isobutane, n-octane, isooctane and the like, are particularly useful in the practice of this invention. The desorption operation may be carried out at subatmospheric, atmospheric or supraatmospheric pressure. Generally it is preferred to effect the desorption operation at a temperature greater than that employed during the adsorption operation. More particularly, it is preferred to carry out the desorption operation at a temperature in the range 200-750° F., more or less, preferably 50-250 degrees Fahrenheit higher than the adsorption temperature employed.

As indicated herein, the adsorption and desorption operations may be carried out as isothermal and/or isobaric operations, i.e., the same temperature may be employed during the desorption and desorption operations and/or the same pressure may be employed during the adsorption and desorption operations. In accordance with one embodiment of the practice of this invention it is preferred to carry out the desorption operation at a relatively reduced pressure with respect to the adsorption operation, preferably at a subatmospheric pressure, such as a pressure in the range 2-12 p.s.i.a.

Various gaseous ethylene and propylene-containing streams can be satisfactorily treated and employed in the practice of this invention. The practice of this invention is particularly applicable to those gaseous streams which contain minor amounts of ethylene and propylene, such as amounts of ethylene and propylene in the range 1-15% by volume. Gaseous streams containing in combination major amounts of ethylene and propylene, e.g., total ethylene and propylene content in the range 50-85% by volume ethylene and propylene, however, are also satisfactorily treated in accordance with this invention.

Referring now in detail to the drawing which schematically illustrates one embodiment of the practice of this invention as directed to the upgrading of an ethylene and propylene-containing stream, such as may be found in a fluid catalytic cracker adsorber tail gas, a gaseous stream having the following composition as set forth in accompanying Table I is introduced via line 11 into selec-

tive adsorption unit 12 wherein this gaseous stream is contacted with a selective adsorbent of the type Linde type 4A molecular sieve, which selectively adsorbs substantially only ethylene and propylene from the aforesaid gaseous stream.

Table I

Component:	Volume percent
N ₂ +CO-----	20.8
H ₂ -----	17.5
Methane-----	35.3
Ethylene-----	6.1
Ethane-----	9.6
Propylene-----	5.9
Propane-----	3.4
Isobutane-----	0.4
n-Butane and heavier-----	1.0
	100.0

There is recovered as effluent from adsorption unit 12 via line 14 a gaseous stream having a substantially reduced ethylene and propylene content and which is suitably employed as fuel gas. The composition of this effluent gas is indicated in accompanying Table II.

Table II

Component:	Volume percent
N ₂ +CO-----	23.6
H ₂ -----	21.1
Methane-----	36.4
Ethylene-----	0.0
Ethane-----	9.1
Propylene-----	2.5
Propane-----	3.9
Isobutane-----	0.6
n-Butane and heavier-----	2.8
	100.0

Adsorbed gas 4.2 pounds/100 pounds selective adsorbent.

The preferentially adsorbed ethylene and propylene are desorbed from the selective adsorbent employed in selective adsorption unit 12 by contact with a relatively hot, readily separable gaseous desorbing medium, such as isobutane, which is introduced into selective adsorption unit 12 via line 15. With isobutane employed as the gaseous desorption fluid at a temperature in the range 220-425° F. there issues from adsorption unit 12 via line 16 a gaseous desorption effluent comprising principally isobutane, ethylene and propylene. The isobutane is separated by fractional distillation by means not shown, if desired.

The gaseous desorption effluent in line 16 is introduced into the propylene catalytic polymerization unit 18 which is provided with a solid propylene polymerization catalyst, e.g., UOP polymerization catalyst which comprises phosphoric acid deposited on kieselguhr. The propylene catalytic polymerization unit 18 is operated under suitable polymerization conditions of temperature and pressure, such as a pressure in the range 20-400 p.s.i.g. and a temperature in the range 200-400° F. There is recovered from polymerization unit 16 via line 19 the resulting polymerized propylene, a polypropylene such as a trimer of propylene or tetramer of propylene together with varying amounts of propylene dimer, depending upon the polymerization conditions employed, etc.

There is recovered from polymerization unit 18 via line 20 a residual effluent comprising essentially only ethylene and a minor amount of higher molecular weight hydrocarbons from propylene polymerization unit 18. In accordance with one embodiment of the practice of this invention this residual effluent is introduced via line 20 directly into fractionator 21 wherein the gaseous residue is fractionated into an overhead fraction via line 22 consisting essentially only of ethylene and a bottoms fraction via line 24 consisting essentially of higher molecular weight hydrocarbons such as isobutane.

The overhead ethylene fraction in accordance with one embodiment may be introduced directly via line 22 into ethylene polymerization unit 24 wherein it is polymerized under suitable conditions of temperature and pressure and in the presence of a suitable catalyst to yield a polyethylene product which is separately recovered via line 25. The polymerization catalyst employed within ethylene polymerization unit 24 may be the well known Ziegler type ethylene polymerization catalyst whereby ethylene under relatively low pressure, in the range 50-550 p.s.i.g., and relatively low temperature is polymerized. A suitable Ziegler type catalyst for use within ethylene polymerization unit 24 comprises a metal alkyl and a metal compound selected from a metal in the groups IV-VIII, e.g., a catalyst comprising aluminum triethyl and titanium tetrachloride.

If desired, a portion of the ethylene stream in line 22 may be diverted via lines 26 and 28 as ethylene product. Further, if desired, another portion of the ethylene in line 22 may be diverted via lines 26, 29 and 30 into alkylation unit 31 wherein it is employed as the alkylating agent (olefin) to alkylate an isoparaffinic hydrocarbon, such as isobutane, introduced therein via lines 32 and 30. Any suitable alkylation catalyst may be employed within alkylation unit 21. Exemplary alkylation catalysts which might be suitably employed within alkylation unit 31 include aluminum chloride and the like. If desired, normally gaseous olefins, such as ethylene, propylene, butenes and the like, from an extraneous source may be introduced into alkylation unit 31 via lines 33 and 30 in order to adjust the olefin-isoparaffin ratio within alkylation unit 31 to a preferred value. There is recovered from alkylation unit 31 a normally liquid alkylate stream, such as 2,3 dimethyl butane, via line 34. The alkylate recovered via line 34 is particularly valuable as a motor fuel component by virtue of its relatively high octane rating.

Still in accordance with another embodiment of the practice of this invention, particularly when isobutane is employed as the gaseous desorbing fluid, the resulting gaseous residue from propylene polymerization unit 18 may be passed directly via lines 20, 35 and 30 into alkylation unit 31 wherein the ethylene is advantageously employed to alkylate the isobutane. Further, still in accordance with a practice of this invention, the gaseous residue containing substantially only isobutane and ethylene in line 20 may be fractionated in fractionator 21 to recover as previously-described an overhead ethylene fraction via line 22 and a bottoms isobutane fraction via line 24. A portion of the overhead ethylene fraction in line 22 may be admixed via lines 26, 29 and 30 with the bottoms isobutane fraction in line 24 and introduced via line 30 into alkylation unit 31. As shown in the drawing, a portion of the isobutane recovered from fractionator 21 via line 24 may be recycled via lines 24, 36 and 15 to selective adsorption unit 12 wherein it is re-employed as the desorbing fluid to effect the desorption of ethylene and propylene from the selective adsorbent employed therein.

As will be apparent to those skilled in the art many substitutions, changes and alterations are possible without departing from the spirit or scope of this invention.

We claim:

1. A method of treating a gaseous stream comprising minor amounts of ethylene and propylene in admixture with other gaseous hydrocarbons which comprises contacting said gaseous stream with a particle-form dehydrated crystalline sodium aluminosilicate selective adsorbent which selectively adsorbs ethylene and propylene to the substantial exclusion of other normally gaseous hydrocarbons in said stream to yield a gaseous residue having a substantially reduced ethylene and propylene content, desorbing the adsorbed ethylene and propylene by contacting said adsorbent with gaseous isobutane at an elevated temperature to yield a gaseous desorption effluent

consisting essentially of isobutane, ethylene and propylene, subsequently separately polymerizing said propylene in said gaseous effluent in the presence of said isobutane and ethylene by contact with a solid phosphoric acid type polymerization catalyst to yield a normally liquid propylene polymer and a gaseous admixture consisting essentially of ethylene and isobutane, fractionating said gaseous admixture to separate a stream consisting essentially of isobutane and a stream consisting essentially of ethylene, employing a portion of said fractionated isobutane to desorb the adsorbed ethylene and propylene from said adsorbent, separately polymerizing a portion of said fractionated ethylene to form an ethylene polymer, contacting another portion of said fractionated ethylene with another portion of said fractionated isobutane in the presence of an alkylation catalyst to alkylate said isobutane with ethylene to form a normally liquid alkylate suitable as a gasoline component.

2. A method of treating a gaseous stream recovered from a fluid catalytic cracking unit which stream contains a minor amount of ethylene and propylene in admixture with nitrogen, carbon monoxide, hydrogen, methane, ethane, propane which comprises contacting said gaseous stream with a particle-form aluminosilicate adsorbent made up of porous crystals wherein the pores of the crystals are of uniform size and have a pore size of about 4.0 Angstrom units, a pore size sufficient to admit ethylene and propylene to the substantial exclusion of other higher molecular weight hydrocarbons, and which preferentially adsorbs ethylene and propylene over the aforesaid components of said gaseous stream, to adsorb ethylene and propylene and to yield a gaseous residue substantially free of ethylene and propylene, desorbing the adsorbed ethylene and propylene from said adsorbent by contacting said adsorbent with gaseous isobutane at an elevated temperature to yield a gaseous desorption effluent consisting essentially of isobutane, ethylene and propylene, subsequently separately polymerizing said propylene in said gaseous desorption effluent in the presence of said isobutane and ethylene to yield a normally liquid propylene polymer and a gaseous admixture consisting essentially of isobutane and ethylene, fractionating said gaseous admixture to separate overhead a stream consisting essentially of ethylene and a bottoms fraction consisting essentially of isobutane, separately polymerizing a portion of said fractionated ethylene to form an ethylene polymer, employing a portion of said fractionated isobutane to desorb the adsorbed ethylene and propylene from said adsorbent, admixing another portion of said fractionated ethylene and another portion of said fractionated isobutane, introducing the resulting admixture of ethylene and isobutane to an alkylation zone for the formation of a normally liquid alkylate suitable as a gasoline component.

3. A process in accordance with claim 2 wherein said propylene is polymerized by contact with a propylene polymerization catalyst containing phosphoric acid.

4. A process in accordance with claim 2 wherein said ethylene is polymerized in the presence of a catalyst comprising a metal alkyl and a metal compound selected from a metal in the groups IV-VIII.

5. A method in accordance with claim 4 wherein said metal alkyl is aluminum triethyl and wherein said metal compound is titanium tetrachloride.

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