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#### (54) Title: MORE ENERGY EFFICIENT C5 HYDROGENATION PROCESS

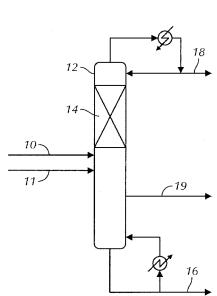


FIG. 1

(57) Abstract: A process for the conversion of linear pentenes to propylene is disclosed. The process may include feeding hydrogen and a C5-olefm containing stream comprising linear pentenes, dienes, acetylenes, and cyclopentene to a catalytic distillation reactor system. Concurrently in the catalytic distillation reactor system, the acetylenes and dienes may be hydrogenated and the C5-olefin containing stream may be fractionated, thereby recovering an overheads fraction comprising the linear pentenes, a side draw fraction comprising the cyclopentene, and a bottoms fraction. In some embodiments, at least a portion of the overheads fraction may then be fed to a metathesis reactor for converting the linear pentenes to propylene.



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# MORE ENERGY EFFICIENT C5 HYDROGENATION PROCESS

# FIELD OF THE DISCLOSURE

[0001] Embodiments disclosed herein relate generally to an energy efficient process to produce linear C5 olefins with a very low level of cyclopentene. The linear C5 olefins may be suitable for use in a downstream metathesis unit for the production of propylene, for example.

#### **BACKGROUND**

Crude streams for the commercial production of olefins contain various compounds as impurities. Acetylenic and diene impurities need to be removed from the streams to produce acceptable quality olefin products. To produce olefins such as ethylene, propylene, butadiene, pentenes and the like, acetylenic impurities such as acetylene, methyl acetylene, vinyl acetylene, ethyl acetylene, 2-methyl-1-buten-3-yne and the like, as well as diene compounds, such as butadiene, propadiene, and the like, in various crude mixed C2-C5 streams need to be removed with minimum loss of useful materials such as ethylene, propylene, butenes, pentenes, and the like in the feed streams. The preferred technique for the purification in commercial practice is the selective hydrogenation of acetylenic and diene compounds over hydrogenation catalysts.

[0003] Crude C5 olefin-containing streams may include various dienes and acetylenes, which often must be removed before use of the C5 olefin-containing stream in downstream processing units, such s a downstream metathesis unit. In addition to the need to remove dienes and acetylenes, which produce coke and shorten metathesis catalyst run length, cyclopentene must also be removed from the C5 feed to a very low level, such as less than 0.5 wt.%, as cyclopentene may undergo undesirable ring-opening metathesis polymerization in the downstream metathesis unit. The very close boiling points of linear C5 olefins and cylcopentene, however, require that a very high reflux ratio be used during fractionation or catalytic distillation to sufficiently separate the cyclopentene, recovered in the bottoms fraction, from the linear pentenes, recovered in the overheads fraction.

# SUMMARY OF THE CLAIMED EMBODIMENTS

[0004] It has been found that, for a catalytic distillation reactor system, concurrently selectively hydrogenating the acetylenic and diene impurities and separating the linear pentenes from cyclopentene, withdrawing a side draw fraction from the column at a location where cyclopentene is at a high concentration may greatly improve separation efficiency and/or reduce operating costs

[0005] In one aspect, embodiments disclosed herein relate to a process for the selective hydrogenation of acetylenes and dienes in a C5 hydrocarbon stream. The process may include feeding hydrogen and a C5-olefin containing stream comprising linear pentenes, dienes, acetylenes, and cyclopentene to a catalytic distillation reactor system. Concurrently in the catalytic distillation reactor system, the acetylenes and dienes may be hydrogenated and the C5-olefin containing stream may be fractionated, thereby recovering an overheads fraction comprising the linear pentenes, a side draw fraction comprising the cyclopentene, and a bottoms fraction.

[0006] In another aspect, embodiments disclosed herein relate to a process for the conversion of linear pentenes to propylene. The process may include feeding hydrogen and a C5-olefin containing stream comprising linear pentenes, dienes, acetylenes, and cyclopentene to a catalytic distillation reactor system. Concurrently in the catalytic distillation reactor system, the acetylenes and dienes may be hydrogenated and the the C5-olefin containing stream may be fractionated, thereby recovering an overheads fraction comprising the linear pentenes, a side draw fraction comprising the cyclopentene, and a bottoms fraction. At least a portion of the overheads fraction may then be fed to a metathesis reactor for converting the linear pentenes to propylene.

[0007] In another aspect, embodiments disclosed herein relate to a system for the selective hydrogenation of acetylenes and dienes in a C5 hydrocarbon stream. The system may include: one or more flow lines for feeding hydrogen and a C5-olefin containing stream comprising linear pentenes, dienes, acetylenes, and cyclopentene to a catalytic distillation reactor system; the catalytic distillation reactor system, for concurrently: hydrogenating the acetylenes and dienes; and fractionating the C5-olefin containing stream; an overheads system fluidly connected to the catalytic distillation reactor system for recovering an overheads fraction comprising the linear

pentenes; a flow line for recovering a side draw fraction comprising the cyclopentene from the catalytic distillation reactor system; and a bottoms system for recovering a bottoms fraction from the catalytic distillation reactor system.

[0008] Other aspects and advantages will be apparent from the following description and the appended claims.

# BRIEF DESCRIPTION OF DRAWINGS

- [0009] Figure 1 is a simplified process flow diagram of a process for selectively hydrogenating acetylenes and dienes in a crude C5 stream according to embodiments disclosed herein.
- [0010] Figure 2 is a simplified process flow diagram of a process for selectively hydrogenating acetylenes and dienes in a crude C5 stream according to embodiments disclosed herein.
- [0011] Figure 3 presents simulation results for a comparative column, without a side draw.
- [0012] Figures 4-6 present simulation results for a catalytic distillation reactor system including a side draw for selectively hydrogenating acetylenes and dienes in crude C5 stream according to embodiments disclosed herein.

# **DETAILED DESCRIPTION**

- [0013] In one aspect, embodiments herein relate to an energy efficient process to produce linear C5 olefins with a very low level of cyclopentene. The linear C5 olefins may be suitable for use in a downstream metathesis unit for the production of propylene, for example.
- [0014] Within the scope of this application, the expression "catalytic distillation reactor system" denotes an apparatus in which the catalytic reaction and the separation of the products take place at least partially simultaneously. The apparatus may comprise a conventional catalytic distillation column reactor, where the reaction and distillation are concurrently taking place at boiling point conditions, or a distillation column combined with at least one side reactor, where the side reactor may be operated as a liquid phase reactor or a boiling point reactor. While both catalytic distillation reactor systems described may be preferred over conventional liquid phase reaction followed by separations, a catalytic distillation column reactor may have the advantages of decreased piece count, reduced capital cost, increased

catalyst productivity per pound of catalyst, efficient heat removal (heat of reaction may be absorbed into the heat of vaporization of the mixture), and a potential for shifting equilibrium. Divided wall distillation columns, where at least one section of the divided wall column contains a catalytic distillation structure, may also be used, and are considered "catalytic distillation reactor systems" herein.

- [0015] Feed streams according to embodiments disclosed herein may include various refinery stream containing C5 olefins and various dienes and acetylenic compounds. For example, a C4-C6 cut, a C5 cut, a C5-C6 cut or other various C5 olefin-containing mixtures may be used. In some embodiments, the feed stream is a C5 fraction containing linear pentenes, cyclopentene, as well as diene and/or acetylenic compounds. Mixed pentene feedstocks useful in embodiments disclosed herein may include linear pentenes and isopentenes. Mixed pentene feedstocks may also include various other hydrocarbon components, including C4 to C6 paraffins and olefins. In some embodiments, the mixed pentene feedstock may be a C5 hydrocarbon fraction from a catalytic or steam cracker, where the C5 fraction may include linear pentenes, isopentene, n-pentanes, and isopentanes.
- [0016] Figure 1 illustrates a simplified process flow diagram of a process for selectively hydrogenating acetylenes and dienes in a crude C5 stream according to embodiments disclosed herein. A C5 olefin-containing feed and hydrogen are fed via flow lines 10 and 11, respectively, to a catalytic distillation reactor system 12 including one or more hydrogenation reaction zones. As illustrated in Figure 1, catalytic distillation reactor system 12 includes a reaction zone 14 located above the feed location.
- [0017] In catalytic distillation reactor system 12, the C5 olefin-containing feed is concurrently fractionated and selectively hydrogenated. The lighter components in the C5 olefin-containing feed traverse up the column, where any acetylenes and dienes may be reacted with hydrogen to produce additional olefins and paraffins, before being recovered as an overheads fraction 18. The heavier components in the C5 olefin-containing feed traversed down the column and are fractionated to produce a cyclopentene-rich side draw 19 and a bottoms fraction 16.
- [0018] Side draw 19 is located intermediate the feed elevation and the bottom draw. In some embodiments, the side draw may be located proximate an elevation at which

the concentration of cyclopentene is elevated within the column, relative to the feed. In some embodiments, the side draw is located below the feed stage and proximate an elevation of maximum cylcopentene concentration determined as if the side draw were not present. As used herein, "proximate an elevation" means within a few distillation stages, such as within about 10 or 15 stages for a column having 100 stages, for example, where the term "stage" or "distillation stage" refers to actual distillation trays or an equivalent (theoretical or otherwise) height of packing, for example. As an example, for a given C5-olefin containing feed, it may be determined, such as via simulation or sampling, that the cyclopentene is at a peak concentration within the column at stage 80; the sidedraw may thus be located between stages 70 and 90, for example. As a further example, Figure 3 illustrates a composition profile within a column, showing peak cyclopentene concentration proximate stages 88 and 89; the side draw may be located between stages 85 and 90, for example.

[0019] Withdrawing a cyclopentene-rich stream as a side draw from the column may enhance separation efficiency, decreasing the overall traffic of cyclopentene within the column. As a result, it may be possible to decrease the concentration of cyclopentene in the overheads fraction 18 as compared to a column without a side draw under similar operating conditions (i.e., similar overheads pressure, feed rate, reboiler duty, and reflux ratio). Alternatively, the reduction in cyclopentene traffic within the column may allow one to reduce overhead condenser and/or reboiler duties, as compared to a column without a side draw, while achieving a similar concentration of cyclopentene in the overheads fraction; in some embodiments, overhead condenser and reboiler duties may be reduced by as much as 20%, 25%, 30% or greater while achieving a similar concentration of cyclopentene in the overheads fraction.

[0020] The side draw stream may be relatively small even while achieving the above noted efficiencies. In some embodiments, the side draw may be less than about 10 mol% of the total feed. In other embodiments, a ratio of the side draw rate to the feed rate (mol side draw / mol feed) may be in the range from about 0.001 to about 0.01, such as in the range from about 0.002 to about 0.005.

linear olefins as well as dienes and acetylenes from the column. However, where the side draw is located relatively remote from the feed location, the loss of linear olefins through the side draw may be relatively small, such as less than 0.01% to 0.1%, such as about 0.02% to about 0.03%. These negligible losses in linear olefins are relatively insignificant as compared to the gains in separation efficiency or decreases in duties that may be achieved via use of a side draw. Thus, in some embodiments, the side draw may be (a) located below the feed stage, and (b) proximate an elevation of (i) maximum cylcopentene concentration determined as if the side draw were not present and (ii) a low or minimum concentration of linear olefins.

[0022] As noted above, dienes and acetylenes may be withdrawn from the column along with the cyclopentene in the side draw. This may be due to column dynamics, as well as a result of the particular feedstock, which may include heavier acetylenic and diene compounds that do not boil up into the hydrogenation reaction zone. As the cyclopentene side draw may be useful as a feedstock in various downstream operations, it may be desirable to reduce or eliminate acetylenes and dienes that may be withdrawn from the column in the side draw. Location of the feed proximate or within the hydrogenation reaction zone may be used to reduce the concentration of acetylenes and dienes in side draw 19. Alternatively, a second hydrogenation reaction zone 20 may be used in the column, intermediate the feed point and side draw location or proximate the side draw location, such as illustrated in Figure 2, where like numerals represent like parts. Use of a second hydrogenation reaction zone may effectively hydrogenate acetylenes and dienes traversing downward through the column, providing for a cyclopentene-rich side draw product substantially free of acetylenes and dienes. As used herein, substantially free of dienes and acetylenes is defined as being less than about 0.5 wt.% dienes and acetylenes.

[0023] Catalysts useful in the hydrogenation reaction zone(s) may include Group 8 metals, such as cobalt, nickel, palladium, or platinum, alone or in combination, and/or Group 1B metals, such as copper, and/or other metals, such as a Group 5A or Group 6A metals, such as molybdenum or tungsten, on a suitable support, such as alumina, silica, titania, silica-alumina, titania-alumina, titania-zirconia, or the like. Normally the catalytic metals are provided as the oxides of the metals supported on extrudates

or spheres. The metals may be reduced to the hydride form or other active states, if necessary, prior to use by exposure to hydrogen, for example.

[0024] The particular catalyst(s) and operating conditions in the hydrogenation reaction zone(s) may depend upon the particular C5-olefing containing feed(s) used, the overall flow scheme (i.e., use of or lack of guard beds, etc.), the desired conversion and selectivity, and the tolerance in end products for any isomerization that may occur under hydrogenation conditions, among other variables. Typical hydrogenation reaction zone operating conditions include temperatures in the range from 30°C to 500°C and pressures ranging from 1 to 100 bar.

[0025] In some embodiments, hydrogenation reaction zone temperatures may range from about 30°C to about 300°C. In other embodiments, hydrogenation reaction zone temperatures may range from about 40°C to about 250°C; from about 50°C to about 200°C in other embodiments; and from about 75°C to about 175°C in yet other embodiments. In embodiments where an upper and lower reaction zone are provided, the temperature in the lower bed will be greater than that of the upper bed, both of which are generally captured by the above ranges. Overheads and bottoms temperatures of the column may be greater than or less than the temperatures indicated above, the bottoms operating at a temperature proximate the boiling range of the heavier feed components at column pressure, and the overheads operating at a temperature proximate the boiling range of the lighter feed components and reaction products at column pressure.

[0026] In some embodiments, distillation column reaction system may operate at an overhead pressure in the range from about 1 bar to about 50 bar (absolute). In other embodiments, hydrogenation reactor pressures may range from about 2 bar to about 30 bar; from about 3 bar to about 20 bar in other embodiments; and from about 5 to about 10 bar, such as about 7 to 9 bar, in yet other embodiments.

[0027] Following selective hydrogenation of the acetylenic and diene compounds and separation of the linear pentenes from cyclopentene, the resulting C5 olefin-containing product may be fed to a metathesis reactor for the production of propylene. For example, the linear pentenes may be reacted with ethylene in the presence of a metathesis catalyst or a combined metathesis / isomerization catalyst to produce

propylene. When linear pentenes are fed to a conventional metathesis reactor, the following reactions may occur:

- (a) 1-pentene  $\rightarrow$  2-pentene (Isomerization);
- (b) 2-pentene + ethylene -→ 1-butene + propylene (Metathesis);
  - (c) 1-butene  $\rightarrow$  2-butene (Isomerization);
  - (d) 2-butene + ethylene  $\rightarrow$  2 propylene (Metathesis).

1-Pentene is isomerized to 2-pentene. The metathesis reaction of 1-pentene with ethylene is non-productive (products are same as reactants). The overall linear C5 olefin reaction can thus be shown as:

1 linear pentene + 2 ethylene - $\rightarrow$  3 propylene.

- [0028] The metathesis reaction products, including unreacted ethylene, propylene, butenes, and unreacted pentenes may then be recovered and forwarded to a separation zone, which may include one or more distillation columns and/or extractive distillation columns for separating the metathesis reactor effluent into various desired fractions, which may include an ethylene fraction, a propylene fraction, a butene and/or pentene fraction, and a heavies fraction. The ethylene fraction and butene / pentene fraction(s) may be recycled to the metathesis reaction zone for continued production of propylene.
- [0029] Catalysts useful in the metathesis reactor may include any known metathesis catalyst, including oxides of Group VIA and Group VIIA metals on supports. Catalyst supports can be of any type and could include alumina, silica, mixtures thereof, zirconia, and zeolites. In addition to the metathesis catalyst, the catalyst contained in the metathesis reactor may include a double bond isomerization catalyst such as magnesium oxide or calcium oxide, for converting 1-butene and 1-pentene to 2-butene and 2-pentene, allowing for increased production of propylene via metathesis with ethylene. In some embodiments, the catalyst may include a promoter to reduce acidity; for example, an alkali metal (sodium, potassium or lithium), cesium, a rare earth, etc. In some embodiments, the metathesis or mixed metathesis/double bond isomerization catalyst may include those described in US20110021858 or US20100056839, for example.
- [0030] The metathesis reactor may operate at a pressure between 1 and 40 bar in some embodiments, and between 5 and 15 bar in other embodiments. The metathesis

reactor may be operated such that the reaction temperature is within the range from about 50°C to about 600°C; within the range from about 200°C to about 450°C in other embodiments; and from about 250°C to about 400°C in yet other embodiments. The metathesis reaction may be performed at a weight hourly space velocity (WHSV) in the range from about 3 to about 200 in some embodiments, and from about 6 to about 40 in other embodiments. The reaction may be carried out in the liquid phase or the gas phase, depending on structure and molecular weight of the olefin(s), by contacting the olefin(s) with the metathesis catalyst. If the reaction is carried out in the liquid phase, solvents or diluents for the reaction can be used, such as aliphatic saturated hydrocarbons, e.g., pentanes, hexanes, cyclohexanes, dodecanes, and aromatic hydrocarbons such as benzene and toluene are suitable. If the reaction is carried out in the gaseous phase, diluents such as saturated aliphatic hydrocarbons, for example, methane, ethane, and/or substantially inert gases, such as nitrogen and argon, may be present. For high product yield, the reaction may be conducted in the absence of significant amounts of deactivating materials such as water and oxygen.

[0031] Examples

[0032] Simulations were conducted to compare the performance of a catalytic distillation reactor system for selectively hydrogenating a C5 feed stream with and without a side draw. The C5 feed composition is shown in Table 1. Simulations were carried out in ASPEN PLUS 7.2 (Aspen Technology, Inc., Burlington, Massachusetts). Simulations for columns with a side draw were performed with the column configuration as shown in Figure 1. Simulation results are compared in Table 2.

[0033] It can be seen from Table 2 and the Figures 3-6 that with the same cyclopentene concentration in the distillate (0.5 wt%), the reboiler duty can be significantly decreased from 31,571 btu/h (Case I) to 23,498 btu/h (Case 4) by taking a small side draw enriched in cyclopentene. Interestingly the total linear C5 olefin loss through the side draw is negligible (0.08 wt%). If using the same reflux ratio and reboiler duty as shown in Cases 2 and 3, an overhead product with a much less concentration of cyclopentene is produced by taking a small sidestream enriched in cyclopentene from the column.

Table 1. C5 Feed Composition (wt.%)

Component	Wt.%	Component	Wt.%	Component	Wt.%
1-butene	0.0525	3-methyl 1-butene	0.7513	cis 2-butene	0.5753
isobutene	0.5477	trans 2-butene	0.6300	Isobutane	0.0290
n-butane	0.1405	cyclopentadiene	0.0170	1,2-pentadiene	0.0150
1,4-pentadiene	0.0064	1,5-hexadiene	0.0119	2-methyl 1,3-	0.1105
		;		butadiene	
cis 1,3-pentadiene	0.0775	trans 1,3-pentadiene	0.1408	1-pentene	2.8576
2-methyl 1-butene	5.0019	2-methyl 2-butene	14.1153	3-methyl 1-	0.6446
				pentene	
4-methyl 1-pentene	0.4733	cis 2-pentene	4.9555	cyclopentane	0.6256
cyclopentene	1.8741	trans 2-pentene	9.4822	isopentane	20.6196
n-pentane	3.6866	1,4-hexadiene	0.0053	2-methyl 1,4-	0.0270
				pentadiene	
3-methyl 1,3-	0.0335	3-methyl 1,4-	0.0710	3-methyl	0.0060
pentadiene		pentadiene		cyclopentene	
trans 1,3-hexadiene	0.1525	1-hexene	0.4480	1-methyl	0.4961
				cyclopentene	
2,3-dimethyl 1-	0.5611	2-ethyl 1-butene	0.0300	2-methyl 1-	1.0288
butene		·		pentene	
2-methyl 2-pentene	2.1323	3,3-dimethyl 1-	0.1055	3-methyl pentane	4.2233
		butene			
cis 2-hexene	0.9268	cis 3-hexene	0.2812	cis 3-methyl 2-	1.2823
				pentene	
cis 4-methyl 2-	0.4486	methyl	1.3342	trans 2-hexene	1.7921
pentene		cylcopentane	•		
trans 3-hexene	0.8618	trans 3-methyl 2-	1.3668	trans 4-methyl 2-	1.7264
		pentene		pentene	
2,2-dimethylbutane	0.1158	2,3-dimethylbutane	2.0282	20methyl pentane	8.2805
n-hexane	1.2040	2,4-dimethyl 1-	0.0243	3,3-dimethyl 1-	0.0080
		pentene		pentene	
2,2,3-	0.0360	2,4-dimethylpentane	0.3495	Benzene	0.7423
trimethylbutane					
Toluene	0.0463	heavies	0.3828		

Table 2. Simulation Conditions

Case Number	1	2	3	4
Column Stages	102	102	102	102
C5 Feed Stage	42	42	42	42
Hydrogen Feed Stage	45	45	45	45
Reaction Zone Stages		30-37	30-37	30-37
Cyclopentene in Overheads (wt%)	0.50	0.28	0.34	0.50
Pressure (psia)		114.7	114.7	114.7
Reflux Ratio	10	10.05	10.05	7.3
Average partial pressure of hydrogen (psi)	0.505	0.505	0.505	0.505
Bottoms vs. Feed ratio (mol/mol)	0.306	0.306	0.306	0.306
Reboiler Duty (but/h)	31571	31571	31571	23498
Side Draw Stage	N/A	86	86	86
Side Draw vs. Feed Ratio (mol/mol)	N/A	0.0046	0.0023	0.0023
Total linear olefin loss to side draw (wt.%)	N/A	0.16	0.05	0.08

[0034] As described above, embodiments disclosed herein provide an efficient process for selectively hydrogenating dienes and acetylenes in a crude C5 hydrocarbon stream. Advantageously, the use of a side draw may provide for greater separation efficiency and/or reduced operating duties as compared to catalytic distillation reactor systems without a side draw.

[0035] While the disclosure includes a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments may be devised which do not depart from the scope of the present disclosure. Accordingly, the scope should be limited only by the attached claims.

#### **CLAIMS**

#### What is claimed:

1. A process for the selective hydrogenation of acetylenes and dienes in a C5 hydrocarbon stream, comprising:

feeding hydrogen and a C5-olefin containing stream comprising linear pentenes, dienes, acetylenes, and cyclopentene to a catalytic distillation reactor system;

concurrently in the catalytic distillation reactor system:

hydrogenating the acetylenes and dienes; and fractionating the C5-olefin containing stream;

recovering an overheads fraction comprising the linear pentenes; recovering a side draw fraction comprising the cyclopentene; and recovering a bottoms fraction.

- 2. The process of claim 1, wherein the side draw is located intermediate a feed location of the C5-olefin containing stream and a bottoms draw location.
- 3. The process of claim 1, wherein the side draw is located below the feed stage and proximate an elevation of maximum cylcopentene concentration determined as if the side draw were not present.
- 4. The process of claim 1, wherein a mole ratio of the side draw rate to the feed rate is in the range from about 0.001 to about 0.01.
- 5. The process of claim 1, wherein a mole ratio of the side draw rate to the feed rate is in the range from about 0.002 to about 0.005.
- 6. The process of claim 1, wherein the catalytic distillation reactor system comprises a hydrogenation reaction zone located above a feed location of the C5-olefin containing stream.
- 7. The process of claim 6, wherein the catalytic distillation reactor system further comprises a hydrogenation reaction zone located below a feed location of the C5-olefin containing stream and above or proximate an elevation of the side draw.
- 8. The process of claim 1, wherein the side draw is substantially free of acetylenes and dienes.
- 9. A process for the conversion of linear pentenes to propylene, comprising:

feeding hydrogen and a C5-olefin containing stream comprising linear pentenes, dienes, acetylenes, and cyclopentene to a catalytic distillation reactor system;

concurrently in the catalytic distillation reactor system:

hydrogenating the acetylenes and dienes; and fractionating the C5-olefin containing stream;

recovering an overheads fraction comprising the linear pentenes; recovering a side draw fraction comprising the cyclopentene; recovering a bottoms fraction; and

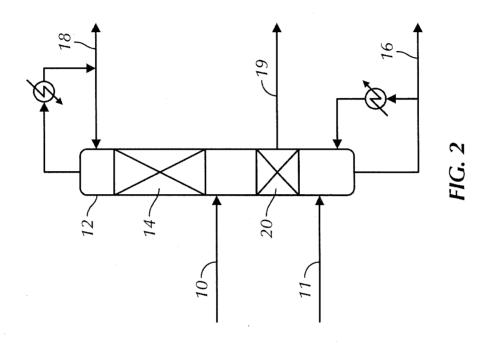
feeding at least a portion of the overheads fraction to a metathesis reactor.

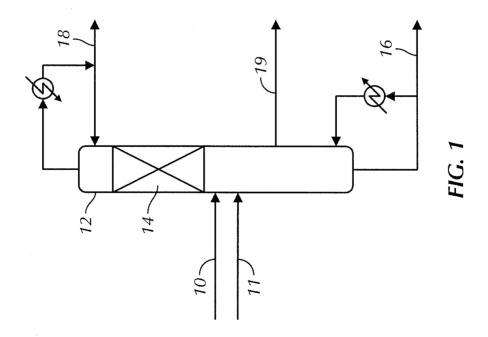
- 10. The process of claim 9, wherein the side draw is located intermediate a feed location of the C5-olefin containing stream and a bottoms draw location.
- 11. The process of claim 9, wherein the side draw is located below the feed stage and proximate an elevation of maximum cylcopentene concentration determined as if the side draw were not present.
- 12. The process of claim 9, wherein a mole ratio of the side draw rate to the feed rate is in the range from about 0.001 to about 0.01.
- 13. The process of claim 9, wherein a mole ratio of the side draw rate to the feed rate is in the range from about 0.002 to about 0.005.
- 14. The process of claim 9, wherein the catalytic distillation reactor system comprises a hydrogenation reaction zone located above a feed location of the C5-olefin containing stream.
- 15. The process of claim 14, wherein the catalytic distillation reactor system further comprises a hydrogenation reaction zone located below a feed location of the C5-olefin containing stream and above or proximate an elevation of the side draw.
- 16. The process of claim 9, wherein the side draw is substantially free of acetylenes and dienes.
- 17. A system for the selective hydrogenation of acetylenes and dienes in a C5 hydrocarbon stream, comprising:
  - one or more flow lines for feeding hydrogen and a C5-olefin containing stream comprising linear pentenes, dienes, acetylenes, and cyclopentene to a catalytic distillation reactor system;

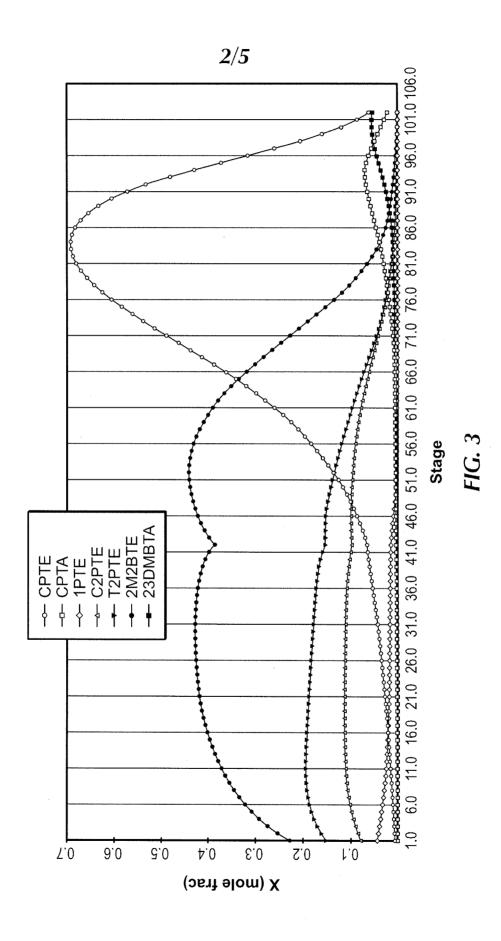
the catalytic distillation reactor system, for concurrently:

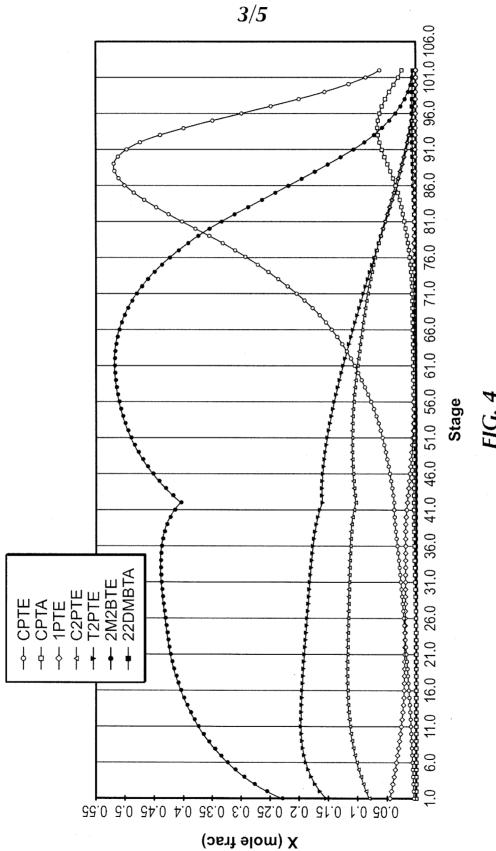
hydrogenating the acetylenes and dienes; and fractionating the C5-olefin containing stream;

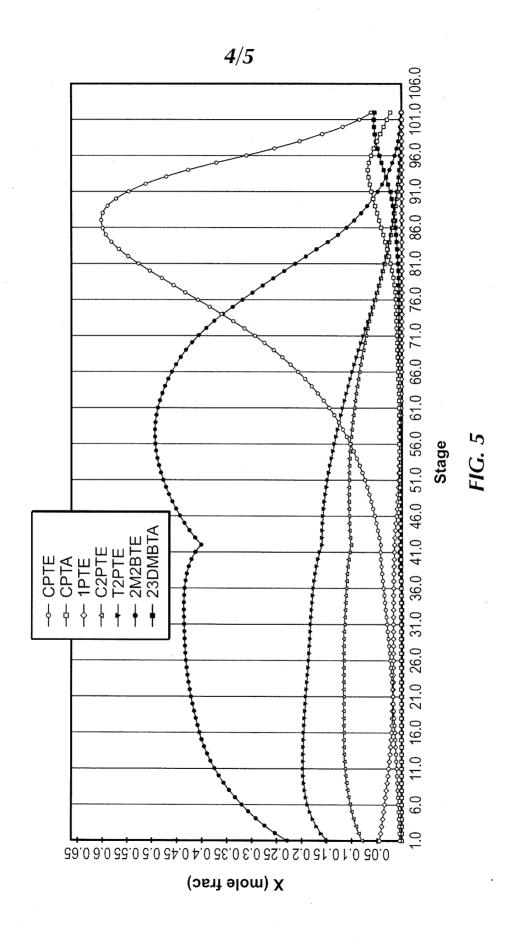
- an overheads system fluidly connected to the catalytic distillation reactor system for recovering an overheads fraction comprising the linear pentenes;
- a flow line for recovering a side draw fraction comprising the cyclopentene from the catalytic distillation reactor system; and
- a bottoms system for recovering a bottoms fraction from the catalytic distillation reactor system.
- 18. The system of claim 17, wherein the side draw is located intermediate a feed location of the C5-olefin containing stream and a bottoms draw location.
- 19. The system of claim 17, wherein the side draw is located below the feed stage and proximate an elevation of maximum cylcopentene concentration determined as if the side draw were not present.
- 20. The system of claim 17, wherein the catalytic distillation reactor system comprises a hydrogenation reaction zone located above a feed location of the C5-olefin containing stream.
- 21. The system of claim 20, wherein the catalytic distillation reactor system further comprises a hydrogenation reaction zone located below a feed location of the C5-olefin containing stream and above or proximate an elevation of the side draw.

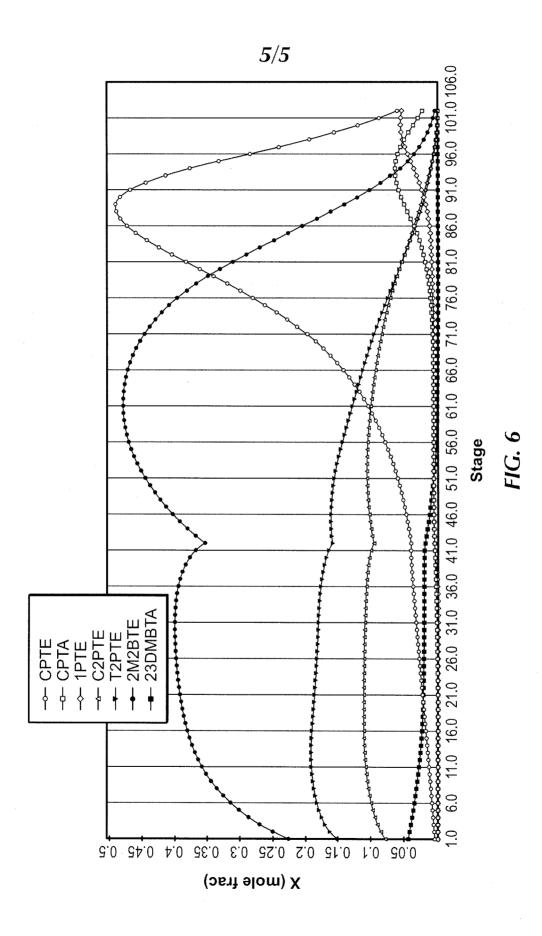












International application No. **PCT/US2013/049925** 

#### A. CLASSIFICATION OF SUBJECT MATTER

C10G 45/58(2006.01)i, C10G 47/22(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)

C10G 45/58; C07C 11/02; C07C 4/06; B01D 3/34; C07C 5/08; C10G 45/32; C07C 7/163; C07C 5/03; C07C 2/00; C10G 47/22

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:olefin, cyclopentene, pentene, catalystic distillation, fractionnation, hydrogenation, C5, acetylene, diene

#### C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2010-107675 A2 (LUMMUS TECHNOLOGY INC.) 23 September 2010 See abstract, paragraphs [0047], [0052], [0053], [0057] and claim 19.	1-21
Y	EP 0556025 A1 (CHEMICAL RESEARCH & LICENSING COMPANY) 9 February 1993 See abstract, figure 3 and claims 1, 11.	1-21
Y	US 2005-0222475 A1 (DUPLAN, J. L. et al.) 6 October 2005 See abstract, paragraphs [0001], [0019] and claims 1, 5, 10.	9-16
A	see abstract, paragraphs [0001], [0019] and craims 1, 3, 10.	1-8,17-21
A	US 2003-0233017 A1 (GELBEIN, A. P. et al.) 18 December 2003 See abstract and claims 1, 4.	1-21
A	US 5877363 A (GILDERT, G. R. et al.) 2 March 1999 See abstract and claims 1, 11.	1-21

	Further documents are listed in the continuation of Box C.		$\boxtimes$	See patent family annex.
*	Special categories of cited documents:	"T"	later d	document published after the international filing date or priority
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	to be of particular relevance		the pri	inciple or theory underlying the invention
"E"	earlier application or patent but published on or after the international	"X"	docun	nent of particular relevance; the claimed invention cannot be
	filing date		consid	lered novel or cannot be considered to involve an inventive
"L"	document which may throw doubts on priority claim(s) or which is		step v	when the document is taken alone
	cited to establish the publication date of citation or other	"Y"	docun	nent of particular relevance; the claimed invention cannot be
	special reason (as specified)		consid	lered to involve an inventive step when the document is
"O"	document referring to an oral disclosure, use, exhibition or other		combi	ned with one or more other such documents, such combination
	means		being	obvious to a person skilled in the art
"P"	document published prior to the international filing date but later	"&"	docun	nent member of the same patent family
	than the priority date claimed			
Date	e of the actual completion of the international search	Date	of ma	iling of the international search report
	21 October 2013 (21.10.2013)		,	22 October 2013 (22.10.2013)

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/049925

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010-107675 A2	23/09/2010	AR 077169 A1 CA 2748570 A1 CN 102356053 A EP 2408725 A2 EP 2408725 A4 JP 2012-520929 A KR 10-2011-0139740 A KR 10-2013-0096771 A MX 2011008983 A SG 174127 A1 TW 201038520 A US 2010-0240937 A1 US 2012-330079 A1 US 8314280 B2 US 8389789 B2 WO 2010-107675 A3	10/08/2011 23/09/2010 15/02/2012 25/01/2012 28/11/2012 10/09/2012 29/12/2011 30/08/2013 15/09/2011 28/10/2011 01/11/2010 23/09/2010 27/12/2012 20/11/2012 05/03/2013 13/01/2011
EP 0556025 A1	18/08/1993	AU 3280393 A AU 654757 B2 BR 9300505 A CA 2089113 A1 CA 2089113 C DE 69315362 D1 DE 69315362 T2 EP 0556025 B1 JP 03-224444B2 JP 05-294851A KR 10-0245018 B1 MX 9300698 A MY 116459 A RU 2120931 C1 US 6169218 B1 US 6495732 B1 WO 94-04477 A1	12/08/1993 17/11/1994 17/08/1993 11/08/1993 21/12/2004 08/01/1998 19/03/1998 26/11/1997 29/10/2001 09/11/1993 15/02/2000 29/07/1994 28/02/2004 27/10/1998 02/01/2001 17/12/2002 03/03/1994
US 2005-0222475 A1	06/10/2005	AU 2003-227818 A1 CN 100475755 C CN 1642887 A CN 1642887 C0 DE 60316415 D1 DE 60316415 T2 EP 1487768 A1 EP 1487768 B1 FR 2837199 A1 FR 2837199 B1 JP 04-665397 B2 JP 2005-520874 A RU 2004130481 A RU 2299191 C2	29/09/2003 08/04/2009 20/07/2005 20/07/2005 31/10/2007 17/01/2008 22/12/2004 19/09/2007 19/09/2003 16/09/2005 06/04/2011 14/07/2005 20/07/2005 20/05/2007

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/049925

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
		US 7262332 B2	28/08/2007	
		WO 03-078364 A1	25/09/2003	
US 2003-0233017 A1	18/12/2003	AR 043554A1	03/08/2005	
		AU 2004-219723 A1	23/09/2004	
		BR PI0400329A	04/01/2005	
		CA 2518260 A1	23/09/2004	
		CN 1759083 A	12/04/2006	
		CN 1759083 CO	27/02/2008	
		EG 23539 A	26/04/2006	
		EP 1618082 A2	25/01/2006	
		JP 2006-522120 A	28/09/2006	
		KR 10-2005-0106112 A	08/11/2005	
		MX PA05009270 A	19/10/2005	
		PL 378808 A1	15/05/2006	
		RU 2005131579 A	10/02/2006	
		RU 2325429 C2	27/05/2008	
		US 2005-0090701 A1	28/04/2005	
		US 6867338 B2	15/03/2005	
		US 7368617 B2	06/05/2008	
		WO 2004-081149 A2	23/09/2004	
		WO 2004-081149 A3	13/01/2005	
US 05877363 A	02/03/1999	AU 1997-41664 B2	09/12/1999	
		CA 2264137 A1	26/03/1998	
		CA 2264137 C	21/02/2006	
		CN 1085193 C	22/05/2002	
		CN 1231654 A	13/10/1999	
		CN 1231654 CO	13/10/1999	
		EP 0931042 A1	24/07/2002	
		EP 0931042 B1	24/07/2002	
		JP 04-606521 B2	05/01/2011	
		JP 2001-500522 A	16/01/2001	
		KR 10-0563577 B1	22/03/2006	
		TW 430651 A	21/04/2001	
		TW 430651 B	21/04/2001	
		WO 98-12160 A1	26/03/1998	