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(54) Title: A PROCESS FOR THE PREPARATION OF CONJUGATED DIENE

(57) Abstract: The present disclosure provides a process for preparing a conjugated diene from a C4. feed; said process comprising contacting said C4 feed with at least one catalyst selected from the group consisting of oxides of Gr. IIB metals and Gr. VIII metals under a set of pre-determined dehydrogenating conditions followed by passing at least one oxygenate selected from the group consisting of steam, carbon dioxide (CO₂), oxygen, carbon monoxide through the C4 feed to obtain the conjugated diene.



WO 2014/128718 A2

A PROCESS FOR THE PREPARATION OF CONJUGATED DIENE

Field:

The present disclosure relates to a process for the preparation of a conjugated diene.

Background:

In petrochemical industries 1,3-Butadiene is an important raw material for the production of a range of valuable materials and chemicals like polybutadiene rubber, styrene-butadiene rubber etc. which find applications mostly in automobile industries.

The primary source of Butadiene is steam cracking of liquid hydrocarbons which produces Butadiene as a byproduct. Commercially, Butadiene is produced as a by-product during the production of ethylene from naptha cracking. In the present scenario there is an increased demand of Butadiene end products like rubber etc. However, the traditional Butadiene production route is incapable of satisfying the demand of Butadiene. This eventually increases the price of Butadiene. On the other hand, the shift of new and forthcoming refineries from catalytic to steam cracking, which give lower yields of C4s also results in reduction of Butadiene supply. Due to such uncertainty of Butadiene supply, the Butadiene price fluctuates significantly.

Therefore, it is highly desirable to develop a dedicated "on-purpose" process for the production of Butadiene to meet the global market demand and supply as well as to have stable global Butadiene price. The catalytic oxidative dehydrogenation (ODH) process provides an excellent platform for producing a variety of alkene, alkadiene etc. from low-valued corresponding alkanes etc. Oxidative dehydrogenation process is an advancement of the dehydrogenation process which overcomes the thermodynamic limitation of the latter process. In the present scenario, the on-purpose production of Butadiene via catalytic oxidative dehydrogenation reaction from n-butane and butenes (1-butene, cis- and trans-2-butene) seems to be the most economically and commercially viable approach to fulfill the present stringent Butadiene supply and demand.

In recent years, a variety of catalytic oxidative dehydrogenation processes were reported for the manufacture of 1,3-Butadiene from n-butane/butenes/C₄-feeds stream. Most of these processes were conducted by using n-butane/butenes/C₄-feed stream with/without an oxidant such as air, oxygen and the like or with/without a diluent such as steam and the like.

One prior art patent document discloses a method of producing 1,3 Butadiene using a continuous-flow dual bed reactor which comprises a) charging the continuous-flow dual bed reactor with a bismuth molybdate-based first catalyst and a ferrite-based second catalyst layer to form a first catalyst layer and a second catalyst layer such that a quartz layer is disposed between the first and the second catalyst layers to separate the first and the second catalyst layers; b) passing a reactant including a C₄ mixture containing n-butene, air and steam through the catalyst layers of the continuous-flow dual bed reactor to conduct an oxidative dehydrogenation reaction; and c) obtaining 1,3-Butadiene by the oxidative dehydrogenation reaction.

Another prior art patent document discloses a method of preparing 1,3-Butadiene which comprises subjecting a C₄ mixture to oxidative dehydrogenation in the presence of a mixed-phase bismuth molybdate catalyst comprising α -bismuth molybdate and γ -bismuth molybdate.

Still another prior art patent document discloses a method of producing a zinc ferrite catalyst for preparing 1,3-Butadiene. 1,3-Butadiene is prepared by passing a mixed gas of a C₄ mixture, air and steam through a catalyst layer supported with the zinc ferrite catalyst to conduct an oxidative dehydrogenation reaction.

A further prior art patent document discloses a process for the dehydrogenation of a hydrocarbon such as n-butene, isoamylene or ethyl benzene by contacting the hydrocarbon in the presence of a hydrogen acceptor comprising carbon dioxide with a catalyst comprising an oxide of a transition metal (zinc or lead) deposited on a support comprising alumina or silica.

Still further, a process for the preparation of butadiene from n-butane comprising non-oxidative, catalytic dehydrogenation followed by oxidative dehydrogenation in the

first and second dehydrogenation respectively is disclosed in one of the prior art patent documents. Though it discloses optional use of CO₂ in the non-oxidative dehydrogenation process, it does not specifically mention any catalyst. Further, this process focuses on compressing the resultant feed of two dehydrogenation zones and subsequently recycling to the first dehydrogenation zone then dehydrogenating n-butane in the presence of CO₂.

Similarly, another patent document discloses dehydrogenation of alkane with a chromium-based catalyst in the presence of carbon dioxide. Though the patent mentions improved olefin selectivity it does not teach or suggest about diene preparation or its selectivity.

From the representative prior art patent documents, it is clear that CO₂ has been used in the dehydrogenation reaction. However, none of the documents disclose a process for the preparation of butadiene with higher selectivity or which prevent hydrocarbon burning losses.

Objects

Some of the objects of the present disclosure are discussed herein below.

It is an object of the present disclosure to provide a catalytic process for the preparation of a conjugated diene with higher selectivity from C4 feed.

Another object of the present disclosure is to provide a simple and safer catalytic process for selectively preparing conjugated diene from C4 feed.

Still another object of the present disclosure is to provide a catalytic process for the selective preparation of conjugated diene from C4 feed with reduced hydrocarbon burning losses.

A still further object of the present disclosure is to provide a catalytic process for the preparation of butadiene with high yield from C4-feed stream.

Other objects and advantages of the present disclosure will be more apparent from the following description when read in conjunction with the accompanying figures which are not intended to limit the scope of the present disclosure.

Summary

In accordance with the present disclosure there is provided a process for preparing a conjugated diene from a C4 feed; said process comprising contacting said C4 feed with at least one catalyst selected from the group consisting of oxides of Gr. IIB metals and Gr. VIII metals under a set of pre-determined dehydrogenating conditions followed by passing at least one oxygenate selected from the group consisting of steam, carbon dioxide (CO₂), oxygen, carbon monoxide through the C4 feed to obtain the conjugated diene.

Typically, the C4 feed comprises at least one compound selected from the group consisting of butanes and butenes.

Typically, the butane is at least one compound selected from the group consisting of n-butane and isobutane.

Typically, the butene is at least one compound selected from the group consisting of n-butene, isobutene, trans-2-butene and cis-2-butene.

Typically, the dehydrogenation is carried out at a temperature of 300 to 600°C.

Typically, the dehydrogenation is carried out at a pressure of 0.1 to 3.0 kg/cm².

Typically, the dehydrogenation is carried out for a time period of 3 to 24 hours.

In accordance with one embodiment of the present disclosure the dehydrogenation is carried out in the presence of CO₂ without air or oxygen and steam.

In accordance with another embodiment of the present disclosure the dehydrogenation is carried out in the presence of CO₂, air or oxygen and steam.

In one of the embodiments of the present disclosure the catalyst is an extruded catalyst comprising a mixture of oxides of zinc and iron with or without at least one binder selected from the group consisting of alumina, silica and clays.

Typically, the yield of conjugated diene is at least 40 %.

Typically, the isomeric purity of conjugated diene is 98 to 99.8%.

Typically, the molar ratio of C4 feed to carbon dioxide is 1:1 to 1:100.

Typically, the molar ratio of C4 feed to oxygen is 1:0.1 to 1:0.9.

Typically, the molar ratio of C4 feed to steam is 1:10 to 1:20.

Typically, the dehydrogenation is carried out at a space velocity of 300 to 3000 h⁻¹.

Typically, the selectivity of the process towards conjugated diene is at least 80%.

Typically, the conjugated diene is 1,3-butadiene.

Typically, the proportion of catalyst with respect to C4 feed ranges between 22 and 1100.

Brief description of accompanying drawings:

Figure 1 illustrates a comparative result of the process of the present disclosure and the process of the prior art.

Detailed Description

In order to overcome the problems associated with the known catalytic oxidative dehydrogenation processes such a low selectivity, less conversion and high cost, the inventors of the present disclosure developed a safer, novel and highly selective catalytic process for preparing conjugated diene from a low-valued C4 feed such as normal-butane, 1-butene, trans-2-butene, cis-2-butene and mixtures thereof. The process involves contacting the C4 feed with at least one catalyst selected from the group consisting of oxides of Gr. IIB metals and Gr. VIII metals under a set of pre-

determined dehydrogenating conditions followed by passing at least one oxygenate selected from the group consisting of steam, carbon dioxide (CO₂), oxygen, carbon monoxide through the C4 feed to obtain the conjugated diene.

In accordance with the present disclosure the C4 feed comprises at least one compound selected from the group consisting of butanes and butenes. The butane is at least one compound selected from the group consisting of n-butane and isobutene and the butene is at least one compound selected from the group consisting of n-butene, isobutene, trans-2-butene and cis-2-butene.

In accordance with one embodiment of the present disclosure the dehydrogenation is carried out in the presence of CO₂ without air or oxygen and steam.

In accordance with another embodiment of the present disclosure the dehydrogenation is carried out in the presence of CO₂, air or oxygen and steam.

The dehydrogenation of C4 feed is carried out at a temperature of 300 to 600°C and at a pressure of 0.1 to 3.0 kg/cm² for a time period of 3 to 24 hours. Typically, the dehydrogenation is carried out at a space velocity of 300 to 3000 h⁻¹.

In accordance with the present disclosure the molar ratio of C4 feed to carbon dioxide is maintained between 1:1 and 1:100, the molar ratio of C4 feed to oxygen is maintained between 1:0.1 and 1:0.9, and the molar ratio of C4 feed to steam is maintained between 1:10 and 1:20.

In one of the embodiments of the present disclosure the catalyst is an extruded catalyst comprising a mixture of oxides of zinc and iron with or without at least one binder selected from the group consisting of alumina, silica and clays. Typically, the proportion of catalyst with respect to C4 feed ranges between 22 and 1100.

In accordance with the present disclosure the yield of conjugated diene is at least 40 % and its isomeric purity is 98 to 99.8%. Further, the selectivity of the process of the present disclosure towards conjugated diene is at least 80%.

In accordance with one embodiment of the present disclosure the conjugated diene is 1,3-butadiene.

Hereinafter, the present disclosure will be described in more detail with reference to the following Examples, but the scope of the present disclosure is not limited thereto.

Example 1: Catalytic Oxidative Dehydrogenation of C4 feed using Carbon Dioxide (CO₂)*

The oxidative dehydrogenation reaction of C4 feed was conducted by using an extruded catalyst comprising a mixture of oxides of zinc and iron with a binder selected from the group consisting of alumina, silica, clays or combinations thereof and CO₂.

Oxidative dehydrogenation of C4 feed to 1,3-Butadiene was carried out in continuous flow fixed-bed reactor. In a catalytic run, 0.05 Liter of an extruded mixture containing oxides of zinc and iron, and alumina was charged into a tubular SS reactor. The catalyst was preheated at 500⁰C for 2hrs with air/oxygen stream (20 L_N/hour). A mixture of C4 feed and carbon dioxide was continuously fed into the reactor. Experiments were conducted at various feed compositions, temperatures and GHSV (gas hourly space velocity) on the basis of C4 feed. Reaction products were periodically sampled and analyzed using on-line gas chromatography (GC). Conversion of C4 feed and selectivity of various products were calculated on the basis of carbon balance as follows.

Conversion of 1-butene = (moles of C4 feed such as normal-butane, 1-butene, trans-2-butene, cis-2-butene and a mixture of thereof reacted)/(moles of C4 feed such as normal-butane, 1-butene, trans-2-butene, cis-2-butene and a mixture thereof supplied)

Selectivity of 1,3-Butadiene = (moles of 1,3-Butadiene formed)/(moles of C4 feed such as normal-butane, 1-butene, trans-2-butene, cis-2-butene and a mixture thereof reacted)

Selectivity of 2-butenes = (moles of 2-butenes formed)/(moles of C4 feed such as normal-butane, 1-butene, trans-2-butene, cis-2-butene and a mixture thereof reacted)

Selectivity of carbon dioxide = (moles of carbon dioxide)/(moles of C4 feed such as normal-butane, 1-butene, trans-2-butene, cis-2-butene and a mixture thereof reacted)

The reaction conditions and results are provided in the Table No. 1 and 2

Table No. 1

Reaction condition -1 (Variation of Run time)*							
	UOM (unit of measure)	Values					
Reaction temperature	Deg. Cent.	505					
Ratio of C4 feed:Carbon dioxide (CO2)	Molar	1:44					
C4 feed GHSV	per Hour	42					
Auto-generated Reaction Pressure	kg/cm2	1.4					
Results							
	UOM	Values					
Run time	(Hour)	0.5	1	1.5	2	2.5	3
Average conversion of 2-Butenes	%	84	76	67	61	56	51
Selectivity of 1,3-Butadiene	%	70	85	84	82	78	75
Yield of 1,3-Butadiene	%	59	64	56	50	44	38
Selectivity of 1-Butene	%	10	10	11	12	14	15
Selectivity of total hydrocarbon produced	%	80	95	95	94	92	90
Selectivity of COx	%	20	5	5	6	8	10

Table No. 2

Reaction condition -2 (Variation of Feed GHSV)*				
Reaction temperature	505°C			
Carbon dioxide flow rate	60 Ln/H			
Auto-generated reaction Pressure	1.4 kg/cm ²			
Results				
C4 feed GHSV/hour	21	42	63	84
% Average conversion of 2-butenes	49	76	49	35
% Selectivity of 1,3-Butadiene	80	72	56	37
% yield of 1,3-Butadine	39	55	27	13
% Selectivity of 1-Butene	16	17	31	43
% Selectivity of Total Hydrocarbon produced	96	89	87	80
% Selectivity of COx	4	11	13	20

*After approximately 3 hour run time catalyst regeneration is required while conducting ODH reaction using CO₂.

*After regeneration with Air the catalyst activity can be recovered back.

Example 2:

The oxidative dehydrogenation reaction of C4 feed was conducted by using an extruded catalyst comprising a mixture of oxides of zinc and iron with a binder selected from the group consisting of alumina, silica, clays or combinations thereof, and air/oxygen, CO₂ and steam.

Oxidative dehydrogenation of C4 feed to 1,3-Butadiene was carried out in continuous flow fixed-bed reactor. In a catalytic run, 0.05 Liter of an extruded mixture containing oxides of zinc and iron, and aluminum was charged into a tubular SS (stainless steel) reactor. The catalyst was preheated at 500°C for 2hrs with air/oxygen stream (20 L_N/hour). A superheated steam was prepared from water by passing it through a pre-heated zone (at 180°C) and was continuously fed into the reactor together with C4 feed, air/oxygen and carbon dioxide. Air was used as an oxygen source and nitrogen present in air served as a carrier gas. Experiments were conducted at various feed compositions, temperatures and GHSV (gas hourly space velocity) on the basis of C4 feed. Reaction products were periodically sampled and analyzed using on-line gas chromatography (GC). Conversion of C4 feed and selectivity of various products were calculated on the basis of carbon balance as described in Example 1. Yield of 1,3-Butadiene was calculated by multiplying conversion and selectivity.

The reaction conditions and results are provided in the Table No. 3 and 4.

Table 3:

Reaction condition -1 (Variation of CO₂ flow rate)	
	Values
Reaction temperature	353°C
C4 feed GHSV	227/hour
Flow rate of C4 feed at NTP	0.44 Mole/Hour
Flow rate of Air at NTP	0.44 Mole/Hour
Flow rate of steam	5.6 Mole/Hour
Auto-generated Reaction Pressure	1.8 kg/cm ²

Results						
	Values					
Carbon dioxide (CO ₂) flow rate [Mole/Hour]	0.53	0.76	1.30	1.96	3.03	3.48
% average conversion of 2-Butenes	67	63	61	53	50	48
% Selectivity of 1,3-Butadiene	56	64	78	86	91	93
% yield of 1,3-Butadiene	38	40	47	46	44	45
% Selectivity of 1-Butene	3	4	4	4	4	3
% Selectivity of total hydrocarbon produced	59	68	82	90	95	96
% Selectivity of CO _x	41	32	18	10	5	4

Table 4:

Reaction condition -2 (Variation of Reaction temperature)	
	Values
C4 feed GHSV	41/hour
Flow rate of C4 feed at NTP	0.44 Mole/Hour
Flow rate of Air at NTP	0.44 Mole/Hour
Flow rate of Carbon dioxide (CO ₂) at NTP	3.03 Mole/Hour
Flow rate of Water	5.6 Mole/Hour
Auto-generated reaction Pressure (maximum)	1.8 kg/cm ²

Results						
	Values					
Reaction temperature °C	293	311	330	353	403	420
% average conversion of 2-Butenes	17	24	39	50	87	91
% Selectivity of 1,3- Butadiene	83	88	80	91	41	29
% yield of 1,3-Butadiene	14	21	31	44	35	26
% Selectivity of 1- Butene	7	4	3	4	1	1
% Selectivity of total hydrocarbon produced	90	92	83	95	42	30
% Selectivity of COx	10	8	17	5	58	70

Example 3:

The oxidative dehydrogenation reaction of C4 feed was conducted by using an extruded catalyst, comprising a mixture of oxides of zinc and iron with a binder selected from the group consisting of alumina, silica, clays or combinations thereof and air/oxygen and water.

Oxidative dehydrogenation of C4 feed to 1,3-Butadiene was carried out in continuous flow fixed-bed reactor. In a catalytic run, 0.05 Liter of an extruded mixture containing oxides of zinc and iron and alumina was charged into a tubular SS reactor. The catalyst was preheated at 500°C for 2 hrs with air/oxygen stream (20 L_N/hour). A superheated steam was prepared from water by passing through a pre-heating zone (at 180°C) and was continuously fed into the reactor together with C4 feed and air/oxygen. Air was used as an oxygen source and the nitrogen present in air served as a carrier gas. Experiments were conducted at various feed compositions, temperatures and GHSV (gas hourly space velocity) on the basis of C4 feed. Reaction products

were periodically sampled and analyzed using on-line gas chromatography (GC). Conversion of C4-feed and selectivity of various products were calculated on the basis of carbon balance as described in Example 1. Yield of 1,3-Butadiene was calculated by multiplying conversion and selectivity.

The reaction conditions and results are provided in the Table No. 5 and 6

Table 5:

Reaction condition -1 (Variation of feed composition)			
	Values		
Reaction temperature °C	345		
C4 feed GHSV	227/hour		
Auto-generated Reaction Pressure	0.8 kg/cm ²		
Results			
	Values		
Molar Ratio of C4 feed-3:Oxygen:steam	1:0.75:13	1:0.64:13	1:0.22:13
% average conversion of 2-Butene	61	69	65
% Selectivity of 1,3-Butadiene	67	62	48
% Selectivity of 1-Butene	4	5	3
% yield of 1,3-Butadiene	41	42	31

% Selectivity of total hydrocarbon produced	71	67	51
% Selectivity of COx	29	33	49

Table 6:

Reaction condition -2 (Variation of reaction temperature)						
	Values					
Molar Ratio of C ₄ Raffinate- 3:Oxygen:steam	1:0.64:13					
C4 feed GHSV	227/hour					
Reaction Pressure	0.8 kg/cm ²					
Results						
Reaction temperature °C	336	345	363	373	383	393
% average conversion of 2-Butenes	66	69	68	79	61	58
% Selectivity of 1,3- Butadiene	61	62	57	50	47	41
% yield of 1,3-Butadine	40	42	39	39	29	24
% Selectivity of 1- Butene	2	5	6	9	13	14
% Selectivity of Total Hydrocarbon produced	63	67	63	59	60	55
% Selectivity of CO _x	37	33	37	41	40	45

From the results as shown in above tables and figure 1, it is clear that the process of the present disclosure is highly selective compared to the known processes.

Technical advance and economic significance:

- The present disclosure provides a novel, simple and safer process for the preparation of conjugated diene with higher selectivity from C4 feed such as normal-butane, 1-butene, trans-2-butene, cis-2-butene and a mixture thereof.
- In the process of the present disclosure hydrocarbon burning loss is negligible.
- The process of the present disclosure is carried out optionally in the presence of air/oxygen and steam.
- The process of the present disclosure is cost effective as it is selective, high yielding and carried with or without air/oxygen and steam.

Throughout this specification the word “comprise”, or variations such as “comprises” or “comprising”, will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

The use of the expression “a”, “at least” or “at least one” suggests the use of one or more elements or ingredients or quantities, as the use may be in the embodiment of the disclosure to achieve one or more of the desired objects or results.

The numerical values given for various physical parameters, dimensions and quantities are only approximate values and it is envisaged that the values higher or lower than the numerical value assigned to the physical parameters, dimensions and quantities fall within the scope of the disclosure and the claims unless there is a statement in the specification to the contrary.

While certain embodiments of the disclosure have been described, these embodiments have been presented by way of examples only, and are not intended to limit the scope of the disclosure. Variations or modifications in the process of this disclosure, within the scope of the disclosure, may occur to those skilled in the art upon reviewing the disclosure herein. Such variations or modifications are well within the spirit of this disclosure.

Claims:

1. A process for preparing a conjugated diene from a C4 feed; said process comprising contacting said C4 feed with at least one catalyst selected from the group consisting of oxides of Gr. IIB metals and Gr. VIII metals under a set of pre-determined dehydrogenating conditions followed by passing at least one oxygenate selected from the group consisting of steam, carbon dioxide (CO₂), oxygen, carbon monoxide through the C4 feed to obtain the conjugated diene.
2. The process as claimed in claim 1, wherein the C4 feed comprises at least one compound selected from the group consisting of butanes and butenes.
3. The process as claimed in claim 2, wherein the butane is at least one compound selected from the group consisting of n-butane and isobutane.
4. The process as claimed in claim 2, wherein the butene is at least one compound selected from the group consisting of n-butene, isobutene, trans-2-butene and cis-2-butene.
5. The process as claimed in claim 1, wherein the dehydrogenation is carried out at a temperature of 300 to 600°C.
6. The process as claimed in claim 1, wherein the dehydrogenation is carried out at a pressure of 0.1 to 3.0 kg/cm².
7. The process as claimed in claim 1, wherein the dehydrogenation is carried out for a time period of 3 to 24 hours.
8. The process as claimed in claim 1, wherein the dehydrogenation is carried out in the presence of CO₂ without air or oxygen and steam.

9. The process as claimed in claim 1, wherein the dehydrogenation is carried out in the presence of CO₂, air or oxygen and steam.
10. The process as claimed in claim 1, wherein the catalyst is an extruded catalyst comprising a mixture of oxides of zinc and iron with or without at least one binder selected from the group consisting of alumina, silica and clays.
11. The process as claimed in claim 1, wherein the yield of said conjugated diene is at least 40 %.
12. The process as claimed in claim 1, wherein the isomeric purity of said conjugated diene is 98 to 99.8%.
13. The process as claimed in claim 1, wherein the molar ratio of C4 feed to carbon dioxide is 1:1 to 1:100.
14. The process as claimed in claim 1, wherein the molar ratio of C4 feed to oxygen is 1:0.1 to 1:0.9.
15. The process as claimed in claim 1, wherein the molar ratio of C4 feed to steam is 1:10 to 1:20.
16. The process as claimed in claim 1, wherein the dehydrogenation is carried out at a space velocity of 300 to 3000 h⁻¹.
17. The process as claimed in claim 1, wherein the selectivity of the process towards conjugated diene is at least 80%.

18. The process as claimed in claim 1, wherein the conjugated diene is 1,3-Butadiene.

19. The process as claimed in claim 1, wherein the proportion of catalyst with respect to C4 feed ranges between 22 and 1100.

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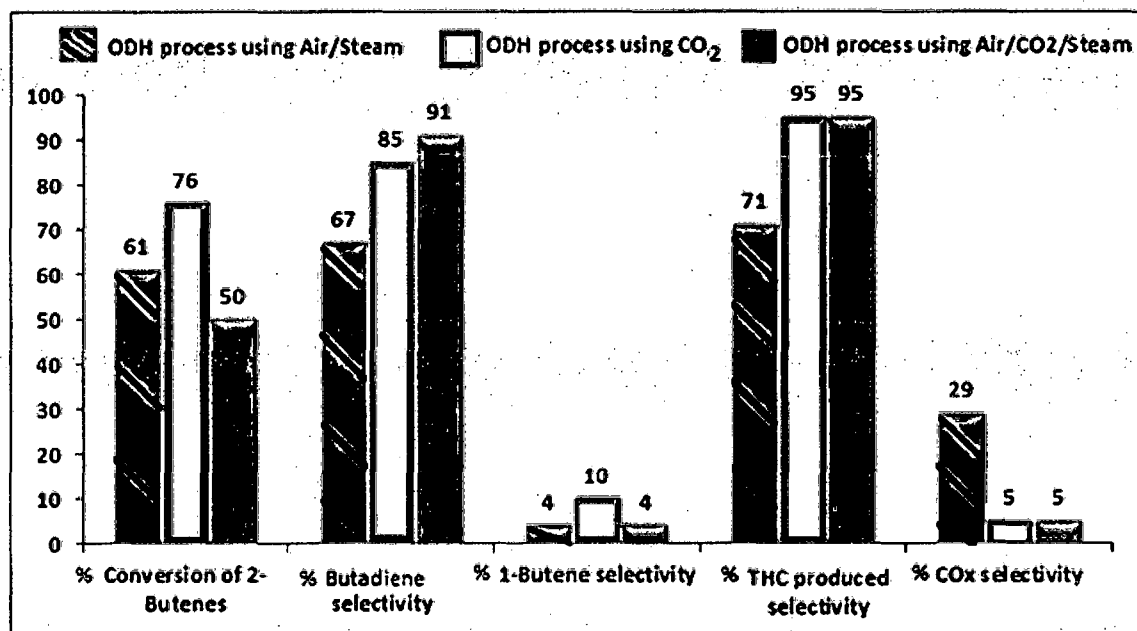


FIGURE 1