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[Continued on next page]

(54) Title: PROCESS FOR PREPARATION OF 1,3-BUTADIENE



(I)

1,3-butadiene

(57) **Abstract:** The present disclosure relates to a process for preparation of 1,3-butadiene. The present disclosure relates to a process for the preparation of 1,3-butadiene which involves conversion of at least one carbohydrate to erythritol by fermentation. Further, erythritol is converted to 1,3-butadiene by reacting it with at least one iodinating agent and at least one base in the presence of at least one fluid medium. The process for the preparation of 1,3-butadiene is simple and employs an inexpensive and readily available raw material. 1,3-butadiene (I).



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PROCESS FOR PREPARATION OF 1,3-BUTADIENE

FIELD

The present disclosure relates to a process for preparation of 1,3-butadiene.

BACKGROUND

5 1,3-Butadiene is a conjugated diene and it is an important industrial intermediate. 1,3-Butadiene is commercially used in the preparation of polymers and synthetic rubber. It is also used as an intermediate in petrochemical industry.

Typically, 1,3-butadiene is produced as a by-product during the preparation of ethylene and other olefins by the steam cracking of petroleum feedstocks. 1,3-butadiene can also be
10 prepared from erythritol. The catalysts used in the preparation of butadiene from erythritol are manufactured using multi step synthesis. The methods for the preparation of 1,3-butadiene are complex, involve the use of expensive raw materials and require stringent conditions.

Thus, there is felt a need to develop a process for the preparation of 1,3-butadiene which is
15 simple and utilizes an inexpensive and readily available raw material.

OBJECTS

Some of the objects of the present disclosure, which at least one embodiment herein satisfies, are as follows:

It is an object of the present disclosure to ameliorate one or more problems of the prior art or
20 to at least provide a useful alternative.

An object of the present disclosure is to provide a process for the preparation of 1,3-butadiene from an inexpensive and easily available raw material.

Another object of the present disclosure is to provide a simple process for the preparation of 1,3-butadiene.

25 Other objects and advantages of the present disclosure will be more apparent from the following description, which is not intended to limit the scope of the present disclosure.

SUMMARY

The present disclosure relates to a process for preparing 1,3-butadiene. The process comprises fermenting at least one carbohydrate present in a fermentation medium using at least one yeast, to obtain erythritol. The fermentation medium further comprises at least one nitrogen source and at least one inorganic salt. Erythritol is reacted with at least one iodinating agent and at least one base, in the presence of at least one fluid medium at a temperature in the range of 20 °C to 100 °C for a predetermined time, to obtain 1,3-butadiene.

The step of fermenting comprises inoculating the fermentation medium with at least one yeast, and incubating the inoculated fermentation medium for a time period in the range of 24 hours to 120 hours, at a temperature in the range of 25 °C to 40 °C, at a pH in the range of 5 to 7 while stirring at a speed in the range of 100 rpm to 500 rpm, to obtain a fermented product mass. The fermented product mass is centrifuged to obtain a solid mass and a cell-free supernatant comprising erythritol, followed by isolating erythritol from the cell-free supernatant.

The at least one yeast is selected from the group consisting of *Yarrowia lipolytica*, *Candida bombicola*, *Candida magnoliae*, *Debaryomyces polymorphus*, *Debaryomyces castellii*, *Debaryomyces hansenii*, *Debaryomyces merma*, *Debaryomyces vanriji*, *Hanseniaspora osmophila*, *Hanseniaspora vineae*, *Hansenula anomala*, *Hansenula polymorpha*, *Issatchenkia orientalis*, *Metschnikowia refaufii*, and *Trigonopsis variabilis*.

In one embodiment of the present disclosure, the yeast used for fermenting carbohydrate to erythritol is *Yarrowia lipolytica* (NCIM Number: 3472).

The at least one carbohydrate is selected from the group consisting of glucose and xylose. The concentration of the at least one carbohydrate in the fermentation medium is in the range of 25 g/L to 300 g/L. The at least one nitrogen source is selected from the group consisting of yeast extract, beef extract, tryptone, casein enzyme digest, peptone, brain heart infusion, aqueous ammonia, urea, and ammonium sulfate. The concentration of the at least one nitrogen source in the fermentation medium is in the range of 2 g/L to 30 g/L. The at least one inorganic salt is selected from the group consisting of potassium dihydrogen phosphate, and magnesium sulfate heptahydrate. The concentration of the at least one inorganic salt in the fermentation medium is in the range of 0.25 g/L to 20 g/L.

The at least one iodinating agent is selected from the group consisting of iodine, triphenylphosphine/iodine, triphenylphosphine/*N*-iodosuccinimide, aqueous hydroiodic acid, boron trifluoride etherate (BF₃-Et₂O)/sodium iodide, magnesium iodide, trimethylsilyl chloride (ClSiMe₃)/sodium iodide, boron trifluoride etherate (BF₃-Et₂O)/potassium iodide, and zirconium tetrachloride (ZrCl₄)/ sodium iodide. The molar ratio of erythritol to the at least one iodinating agent is in the range of 1:4 to 1:12.

In one embodiment of the present disclosure, the step of reacting erythritol is carried out using triphenylphosphine/iodine.

The predetermined time for reacting erythritol with at least one iodinating agent is in the range of 2 hours to 60 hours.

The at least one base is selected from the group consisting of pyridine, triethylamine (TEA), *N,N*-diisopropylethylamine (DIPEA), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and aqueous bases. The ratio of erythritol to the at least one base is in the range of 1:0.5 to 1:5 v/v. The fluid medium is at least one selected from the group consisting of chloroform, pyridine, ethyl acetate, acetonitrile, dichloromethane, dimethyl formamide, dioxane, and tetrahydrofuran.

The yield of 1,3-butadiene from erythritol is in the range from 40 % to 80 % on mole basis.

BRIEF DESCRIPTION OF ACCOMPANYING DRAWING

The process for preparation of 1,3-butadiene of the present disclosure will now be described with the help of the accompanying drawing, in which:

Figure 1 illustrates a standard plot for the amount of 1,3-butadiene with area under curve as analyzed by Gas Chromatography, wherein the “amount of 1,3-butadiene (in mg)” is provided on X-axis and the corresponding “Area under curve” is provided on Y-axis.

Figure 2 illustrates proton NMR of 1,3-butadiene obtained by the process of present disclosure.

Figure 3 illustrates gas chromatograph for 1,3-butadiene obtained by the process of present disclosure.

DETAILED DESCRIPTION

1,3-Butadiene is produced as a by-product during the preparation of ethylene and other olefins by the steam cracking of petroleum feedstocks. 1,3-Butadiene can also be prepared from erythritol. The catalysts used in the preparation of butadiene from erythritol are manufactured using multi step synthesis. The methods for the preparation of 1,3-butadiene are complex, involve the use of expensive raw materials and require stringent conditions.

The present disclosure envisages a new approach for the preparation of 1,3-butadiene to mitigate the drawbacks mentioned herein above.

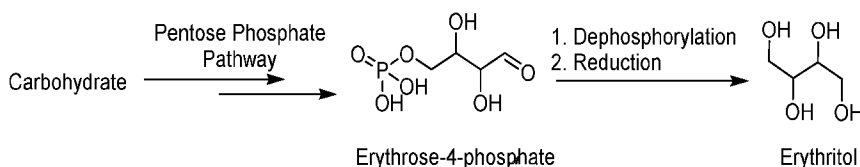
In accordance with the present disclosure, a process for the preparation of 1,3-butadiene is provided. The process for the preparation of 1,3-butadiene comprises the following steps.

At least one carbohydrate present in fermentation medium is fermented using at least one yeast to obtain erythritol. The fermentation medium further comprises at least one nitrogen source and at least one inorganic salt.

The step of fermenting the carbohydrate to erythritol comprises inoculating the fermentation medium with at least one yeast, and incubating the inoculated fermentation medium for a time period in the range of 24 hours to 120 hours, at a temperature in the range of 25 °C to 40 °C, at a pH in the range of 5 to 7, while stirring at a speed in the range of 100 rpm to 500 rpm, to obtain a fermented product mass. The fermented product mass is centrifuged to obtain a solid mass and a cell-free supernatant comprising erythritol, followed by isolating the erythritol from the cell-free supernatant.

During fermentation, yeast utilizes the carbohydrate such as glucose and/or xylose, as the main carbon source and produces erythritol. Carbohydrate is converted to erythrose-4-phosphate via the pentose phosphate pathway. Erythrose-4-phosphate undergoes dephosphorylation, followed by reduction, to form erythritol. Yeast secretes erythritol in the fermentation medium. The process for the conversion of carbohydrate to erythritol is represented in **Scheme 1**.

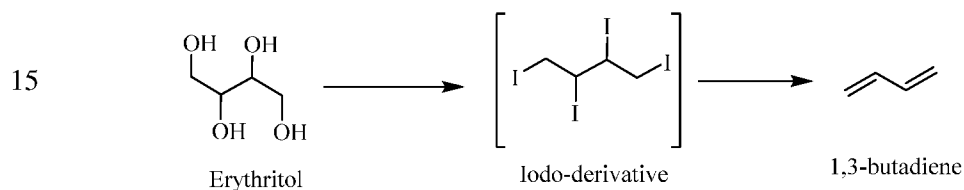
Scheme 1



Erythritol is reacted with at least one iodinating agent and at least one base, in the presence of at least one fluid medium at a temperature in the range of 20 °C to 100 °C for a predetermined time to obtain 1,3-butadiene.

To convert erythritol to 1,3-butadiene in a single step using simple reaction conditions, erythritol is first converted into an iodo-derivative. An iodo-derivative of erythritol has at least one hydroxyl group of erythritol displaced by the iodide group. One such iodo-derivative of erythritol, wherein all four hydroxyl groups on erythritol are displaced by iodide is shown, herein below. The process for the conversion of erythritol to 1,3-butadiene is represented in **Scheme 2**.

Scheme 2



In accordance with the embodiments of present disclosure, the at least one yeast is selected from the group consisting of *Yarrowia lipolytica*, *Candida bombicola*, *Candida magnoliae*, *Debaryomyces polymorphus*, *Debaryomyces castellii*, *Debaryomyces hansenii*, *Debaryomyces merma*, *Debaryomyces vanriji*, *Hanseniaspora osmophila*, *Hanseniaspora vineae*, *Hansenula anomala*, *Hansenula polymorpha*, *Issatchenkia orientalis*, *Metschnikowia refaufii*, and *Trigonopsis variabilis*.

In accordance with one embodiment of the present disclosure, the yeast used for fermenting
25 carbohydrate to erythritol is *Yarrowia lipolytica*.

Yarrowia lipolytica (NCIM Number: 3472) was obtained from National Chemical Laboratory (NCL), Pune.

In accordance with the embodiments of present disclosure, the at least one carbohydrate is selected from the group consisting of glucose and xylose.

The concentration of the at least one carbohydrate in the fermentation medium is in the range of 25 g/L to 300 g/L.

In accordance with one embodiment of the present disclosure, the carbohydrate is glucose and the concentration of glucose in the fermentation medium is 150 g/L.

- 5 In accordance with another embodiment of the present disclosure, the carbohydrate is xylose and the concentration of xylose in the fermentation medium is 150 g/L.

It was observed that, in the process of the present disclosure the fermentation of xylose as the carbon source produces higher amounts of erythritol as compared to that produced during fermentation of glucose as the carbon source.

- 10 In accordance with the embodiments of present disclosure, the at least one nitrogen source is selected from the group consisting of yeast extract, beef extract, tryptone, casein enzyme digest, peptone, brain heart infusion, aqueous ammonia, urea, and ammonium sulfate.

The concentration of at least one nitrogen source in the fermentation medium is in the range of 2 g/L to 30 g/L.

- 15 In accordance with one embodiment of the present disclosure, the nitrogen source is yeast extract and the concentration of yeast extract in the fermentation medium is 20 g/L.

In accordance with the embodiments of present disclosure, the at least one inorganic salt is selected from the group consisting of potassium dihydrogen phosphate, and magnesium sulfate heptahydrate. The concentration of at least one inorganic salt in the fermentation

- 20 medium is in the range of 0.25 g/L to 20 g/L.

In accordance with one embodiment of the present disclosure, the inorganic salts are potassium dihydrogen phosphate and magnesium sulfate heptahydrate. The concentration of potassium dihydrogen phosphate and magnesium sulfate heptahydrate in the fermentation medium is 10 g/L and 1 g/L respectively.

- 25 In accordance with the embodiments of present disclosure, the at least one iodinating agent is selected from the group consisting of iodine, triphenylphosphine/iodine, triphenylphosphine/*N*-iodosuccinimide, aqueous hydroiodic acid, boron trifluoride etherate (BF₃-Et₂O)/sodium iodide, magnesium iodide, trimethylsilyl chloride (ClSiMe₃)/sodium

iodide, boron trifluoride etherate (BF₃-Et₂O)/potassium iodide, and zirconium tetrachloride (ZrCl₄)/ sodium iodide.

In accordance with one embodiment of the present disclosure, the iodinating agent is triphenylphosphine/iodine.

- 5 The molar ratio of erythritol to the at least one iodinating agent is in the range of 1:4 to 1:12.

In accordance with one embodiment of the present disclosure, the molar ratio of erythritol to the iodinating agent is 1:4.1.

- The predetermined time for reacting erythritol with at least one iodinating agent is in the range of 2 hours to 60 hours. The 1,3-butadiene produced during the reaction increases with
10 time.

The conversion of erythritol to 1,3-butadiene is high when reaction is carried out at a temperature of 70 °C and 80 °C.

In accordance with one embodiment of the present disclosure, the predetermined time for reacting erythritol with at least one iodinating agent is 8 hours.

- 15 The at least one base is selected from the group consisting of pyridine, triethylamine, *N,N*-diisopropylethylamine, 1,8-diazabicyclo[5.4.0]undec-7-ene, and aqueous bases.

In accordance with one embodiment of the present disclosure, the base is pyridine.

- The conversion of erythritol to 1,3-butadiene was higher when pyridine was used as base as compared the use of triethylamine, *N,N*-diisopropylethylamine, 1,8-diazabicyclo[5.4.0]undec-
20 7-ene as a base.

The ratio of the amount of erythritol to the at least one base is in the range of 1:0.5 to 1:5 v/v.

In accordance with one embodiment of the present disclosure, the ratio of erythritol to the base is 1:2.5 v/v.

- The fluid medium is at least one selected from the group consisting of chloroform, pyridine, ethyl acetate, acetonitrile, dichloromethane, dimethyl formamide, dioxane, and tetrahydrofuran.
25

In accordance with one embodiment of the present disclosure, the fluid medium is chloroform.

The yield of 1,3-butadiene from erythritol is in the range from 40 % to 80 % on mole basis.

5 The process of the present disclosure for preparation of 1,3-butadiene is simple. The raw materials used for fermenting carbohydrate to erythritol (Step 1) and for conversion of erythritol to 1,3-butadiene (Step 2) are inexpensive and easily available.

10 The present disclosure is further described in light of the following experiments which are set forth for illustration purpose only and not to be construed for limiting the scope of the disclosure. The following experiments can be scaled up to industrial/commercial scale and the results obtained can be extrapolated to industrial scale.

EXPERIMENT:

Step 1: Erythritol production

15 *Yarrowia lipolytica* (NCIM Number: 3472) was obtained from National Chemical Laboratory (NCL), Pune.

Experiment 1: Production of erythritol from D-(+) glucose:

20 The yeast *Yarrowia lipolytica* was inoculated in 200 mL of fermentation medium containing 150g/L of glucose, 20 g/L of yeast extract, 10 g/L of potassium dihydrogen phosphate and 1 g/L of magnesium sulphate heptahydrate. The inoculated fermentation medium was incubated at 30 °C while maintaining the pH at 6 and with continuous stirring at 200 rpm for 72 hours, to obtain a fermented product mass. The fermented product mass was centrifuged to obtain a solid mass in the form of pellet and a cell-free supernatant comprising erythritol. The cell-free supernatant was lyophilized (10 mL). Further, 25 mL of methanol was added to the lyophilized cell-free supernatant (10 mL) to isolate erythritol. The titre value of isolated
25 erythritol was 2 g/L (**Table 1**, Entry 1) in experiment 1.

The amounts of carbohydrate and erythritol in the fermentation medium were analyzed by high pressure liquid chromatography (HPLC). The column used for HPLC was an anion exchange column, and the mobile phase used was 5 mM sulfuric acid solution with a flow rate of 0.6 mL/min. Column temperature was maintained at 50 °C.

Experiment 2, 3, and 4: Production of erythritol from a mixture of D-(+) glucose and D-(+) xylose

The process for the production of erythritol was similar to **Experiment 1** except for the carbon source. In **experiment 2**, the carbohydrate used was a mixture of glucose and xylose in the molar ratio of 3:1. In **experiment 3**, the carbohydrate used was a mixture of glucose and xylose in the molar ratio of 1:1. In **experiment 4**, the carbohydrate used was a mixture of glucose and xylose in the molar ratio of 1:3.

The amount of erythritol produced during **experiments 2 to 4** is provided below in **table 1** (Entries 2, 3, and 4).

Experiment 5: Production of erythritol from D-(+)-xylose:

The yeast *Yarrowia lipolytica* was inoculated in 200 mL of fermentation medium containing 150g/L of xylose, 20 g/L of yeast extract, 10 g/L of potassium dihydrogen phosphate and 1 g/L of magnesium sulphate heptahydrate. The inoculated fermentation medium was incubated at 30 °C while maintaining the pH at 6 and with continuous stirring at 200 rpm for 72 hours, to obtain a fermented product mass. The fermented product mass was centrifuged to obtain a solid mass in the form of pellet and a cell-free supernatant comprising erythritol. The cell-free supernatant was lyophilized (10 mL). Further, 25 mL of methanol was added to the lyophilized cell-free supernatant (10 mL) to isolate erythritol. The titre value of isolated erythritol was 8.17 g/L (**Table 1**, Entry 5) in **experiment 5**.

Erythritol production in **experiments 1 to 5** is given in below **Table 1**.

Table 1: Effect of using different types of carbohydrates on erythritol production

Experiment No.	Carbohydrate	Ratio of glucose to xylose	Erythritol titre value (g/L)
Experiment 1	Glucose	-	2.0 g/L
Experiment 2	Glucose and Xylose	3:1	1.80 g/L
Experiment 3	Glucose and Xylose	1:1	2.2 g/L
Experiment 4	Glucose and Xylose	1:3	4.0 g/L

	Xylose		
Experiment 5	Xylose	-	8.17 g/L

From **table 1**, it is evident that erythritol production is higher when xylose is used as the carbon source, as compared to glucose.

Step 2: Conversion of erythritol to 1,3-butadiene

Experiment 6: Procedure for the conversion of erythritol to 1,3-butadiene

5 In a reaction vial, iodine (1.66 g, 0.0066 moles) was added slowly to a stirred solution of triphenylphosphine (1.76 g, 0.0066 moles) in 9.5 ml of chloroform (CHCl_3), at 0 °C. To this mixture, erythritol (200 mg, 0.0016 moles) and pyridine (0.5 ml) were added. The reaction vial was sealed with a rubber plug and steel crimp, and heated at 80 °C for 8 hours. The progress of the reaction was monitored using gas chromatography (GC) by injecting an
10 aliquot (0.1 mL) of samples drawn from the headspace of the reaction vial. After 8 hours, upon getting a constant value of the area under the curve in GC, the reaction was terminated. The yield of 1,3-butadiene was 74 % (66 mg).

^1H -NMR sample preparation: The head space aliquot was drawn using an air tight syringe, bubbled into the CDCl_3 solvent in NMR tube at -10 °C. The NMR tube was sealed and
15 recorded straightaway using NMR instrument.

1,3-Butadiene was characterized using ^1H -NMR and GC. The ^1H -NMR of 1,3-butadiene obtained by **experiment 6** is shown in **figure 2**. ^1H -NMR (400 MHz, CDCl_3): δ = 6.23-6.33 (m, 2H), 5.13-5.19 (m, 2H), 5.03-5.08 (m, 2H) ppm.

The GC chromatogram of 1,3-butadiene obtained by **experiment 6** is shown in **figure 3**,
20 wherein **A** corresponds to 1,3-butadiene and **B** corresponds to nitrogen.

The reaction progress was analyzed by GC (DB-1 column, 100 x 0.5 mm, ID: 0.25 mm). Parameters for GC analysis were: FID detector temperature: 160 °C, column temperature: 50 °C, gas flow rate: 25 mL/min.

Reaction yield was derived from the standard graph of 1,3-butadiene as given in **figure 1**,
25 wherein the “amount of 1,3-butadiene (in mg)” is provided on X-axis and corresponding “area under curve” is provided on Y-axis.

2.1: Optimization of reaction conditions for the conversion of erythritol to 1,3-butadiene.

Experiment 7-11: Optimization of the base and the amount of fluid medium

The process used for conversion of erythritol to 1,3-butadiene was similar to **experiment 6** except for the base used and/or amount of the base. The bases and fluid media used in **experiments 7 to 11** are given in **Table 2** along with corresponding amounts of 1,3-butadiene produced during **experiments 7 to 11**.

Table 2: Optimization of base and fluid medium

Experiment No.	Base	Fluid medium	Yield
Optimization of base			
Experiment 6	Pyridine (0.5 ml)	Chloroform (9.5 ml)	74 %
Experiment 7	TEA (0.5 ml)	Chloroform (9.5 ml)	48 %
Experiment 8	DIPEA (0.5 ml)	Chloroform (9.5 ml)	28 %
Experiment 9	DBU (0.5 ml)	Chloroform (9.5 ml)	33 %
Effect of amount of base			
Experiment 10	Pyridine (5.0 ml)	Chloroform (5.0 ml)	62%
Experiment 11	Pyridine (10ml)		60%
Control experiment			
Experiment 12	Pyridine (0 ml)	Chloroform (10.0 ml)	0%

From **table 2**, it is evident that the conversion of erythritol to 1,3-butadiene is higher when pyridine is used as base as compared the use of TEA, DIPEA and DBU as a base. Further, on comparing **experiment 6** with **experiments 10** and **11**, it was observed that an increase in the amount of pyridine with concomitant decrease in the amount of the fluid medium led to a lower conversion of erythritol to 1,3-butadiene. The presence of base is mandatory for the conversion of erythritol to 1,3-butadiene as seen in **experiment 12**.

Experiment 13-18: Optimization of temperature

The process used for the conversion of erythritol to 1,3-butadiene was similar to **experiment 6** except for the temperature of the reaction. A set of reactions were carried out at different temperatures. The amount of 1,3-butadiene production is given in **table 3**.

Table 3: Optimization of temperature

Experiment No.	Temperature	Reaction time (h)	Yield
Experiment 13	24 °C	8	15 %
Experiment 14	50 °C	8	38 %
Experiment 15	60 °C	8	44 %
Experiment 16	70 °C	8	68 %
Experiment 17	100 °C	8	28 %
Experiment 18	24 °C	24	62 %

From **table 3**, it is evident that the conversion of erythritol to 1,3-butadiene is high when reaction is carried out between the temperature range of 70 °C and 80 °C.

On comparing **experiment 13** with **experiment 18**, it is clear that the 1,3-butadiene production increases with time.

5 **2.2 Scale up: Procedure for the conversion of erythritol to 1,3-butadiene**

In a reaction vessel containing a stirred solution of triphenylphosphine (17.6 g, 0.066 moles) in 95 ml of chloroform, was added iodine (16.6 g, 0.066 moles) slowly at 0 °C followed by the addition of erythritol (2.0 g, 0.016 moles) and pyridine (5 ml) at 20 °C . The reaction vessel was sealed and then heated at 80 °C for 8 hours. The reaction mixture was cooled and then distilled using a short vigreux column by keeping the bath temperature at 60 °C. The distillate fraction was collected at -20 °C. The product was characterized using GC-MS. The yield of the reaction was 72 % (637 mg).

Overall, the process of the present disclosure for preparation of 1,3-butadiene is simple. The raw materials used in the process of present disclosure for fermenting carbohydrate to erythritol (Step 1) and for conversion of erythritol to 1,3-butadiene (Step 2) are inexpensive and easily available.

TECHNICAL ADVANCES AND ECONOMICAL SIGNIFICANCE

The present disclosure described herein above has several technical advantages including, but not limited to, the realization of preparation of 1,3-butadiene:

- a. from inexpensive and readily available raw materials; and

b. by a simple process.

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 “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.

Any discussion of documents, acts, materials, devices, articles or the like that has been included in this specification is solely for the purpose of providing a context for the disclosure. It is not to be taken as an admission that any or all of these matters form a part of the prior art base or were common general knowledge in the field relevant to the disclosure as it existed anywhere before the priority date of this application.

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

While considerable emphasis has been placed herein on the components and component parts of the preferred embodiments, it will be appreciated that many embodiments can be made and that many changes can be made in the preferred embodiments without departing from the principles of the disclosure. These and other changes in the preferred embodiment as well as other embodiments of the disclosure will be apparent to those skilled in the art from the disclosure herein, whereby it is to be distinctly understood that the foregoing descriptive matter is to be interpreted merely as illustrative of the disclosure and not as a limitation.

CLAIMS:

1. A process for the preparation of 1,3-butadiene, said process comprising the following steps:
 - i. fermenting at least one carbohydrate present in a fermentation medium using
5 at least one yeast, to obtain erythritol,
wherein said fermentation medium further comprises at least one nitrogen source and at least one inorganic salt; and
 - ii. reacting erythritol with at least one iodinating agent and at least one base, in
the presence of at least one fluid medium at a temperature in the range of 20
10 °C to 100 °C for a predetermined time, to obtain 1,3-butadiene.
2. The process as claimed in claim 1, wherein the step of fermenting comprises the following sub-steps:
 - a. inoculating said fermentation medium with at least one yeast, and incubating
said inoculated fermentation medium for a time period in the range of 24
15 hours to 120 hours, at a temperature in the range of 25 °C to 40 °C, at a pH in the range of 5 to 7, and at a stirring speed in the range of 100 rpm to 500 rpm, to obtain a fermented product mass;
 - b. centrifuging said fermented product mass to obtain a solid mass and a cell-free supernatant comprising erythritol; and
 - 20 c. isolating erythritol from said cell-free supernatant.
3. The process as claimed in claim 1, wherein said at least one yeast is selected from the group consisting of *Yarrowia lipolytica*, *Candida bombicola*, *Candida magnoliae*, *Debaryomyces polymorphus*, *Debaryomyces castellii*, *Debaryomyces hansenii*, *Debaryomyces merma*, *Debaryomyces vanriji*, *Hanseniaspora osmophila*,
25 *Hanseniaspora vineae*, *Hansenula anomala*, *Hansenula polymorpha*, *Issatchenkia orientalis*, *Metschnikowia refaufii*, and *Trigonopsis variabilis*.
4. The process as claimed in claim 1, wherein said yeast is *Yarrowia lipolytica* (NCIM Number: 3472).
5. The process as claimed in claim 1, wherein said at least one carbohydrate is selected
30 from the group consisting of glucose and xylose.
6. The process as claimed in claim 1, wherein the concentration of said at least one carbohydrate in said fermentation medium is in the range of 25 g/L to 300 g/L.

7. The process as claimed in claim 1, wherein said at least one nitrogen source is selected from the group consisting of yeast extract, beef extract, tryptone, casein enzyme digest, peptone, brain heart infusion, aqueous ammonia, urea, and ammonium sulfate.
- 5 8. The process as claimed in claim 1, wherein the concentration of said at least one nitrogen source in said fermentation medium is in the range of 2 g/L to 30 g/L.
9. The process as claimed in claim 1, wherein said at least one inorganic salt is selected from the group consisting of potassium dihydrogen phosphate, and magnesium sulfate heptahydrate.
- 10 10. The process as claimed in claim 1, wherein the concentration of said at least one inorganic salt in said fermentation medium is in the range of 0.25 g/L to 20 g/L.
11. The process as claimed in claim 1, wherein said at least one iodinating agent is selected from the group consisting of iodine, triphenylphosphine/iodine, triphenylphosphine/*N*-iodosuccinimide, aqueous hydroiodic acid, boron trifluoride etherate (BF₃-Et₂O)/sodium iodide, magnesium iodide, trimethylsilyl chloride (ClSiMe₃)/sodium iodide, boron trifluoride etherate (BF₃-Et₂O)/potassium iodide, and zirconium tetrachloride (ZrCl₄)/ sodium iodide.
- 15 12. The process as claimed in claim 1, wherein the molar ratio of erythritol to said at least one iodinating agent is in the range of 1:4 to 1:12.
- 20 13. The process as claimed in claim 1, wherein said step of reacting erythritol is carried out using iodine and triphenylphosphine.
14. The process as claimed in claim 1, wherein said at least one base is selected from the group consisting of pyridine, triethylamine, *N,N*-diisopropylethylamine, 1,8-diazabicyclo[5.4.0]undec-7-ene, and aqueous bases.
- 25 15. The process as claimed in claim 1, wherein the ratio of erythritol to said at least one base is in the range of 1:0.5 to 1:5 v/v.
16. The process as claimed in claim 1, wherein said predetermined time is in the range of 2 hours to 60 hours.
17. The process as claimed in claim 1, wherein said at least one fluid medium is selected from the group consisting of chloroform, pyridine, ethyl acetate, acetonitrile, dichloromethane, dimethyl formamide, dioxane, and tetrahydrofuran.
- 30 18. The process as claimed in claim 1, wherein the yield of 1,3-butadiene from erythritol is in the range from 40 % to 80 % on mole basis.

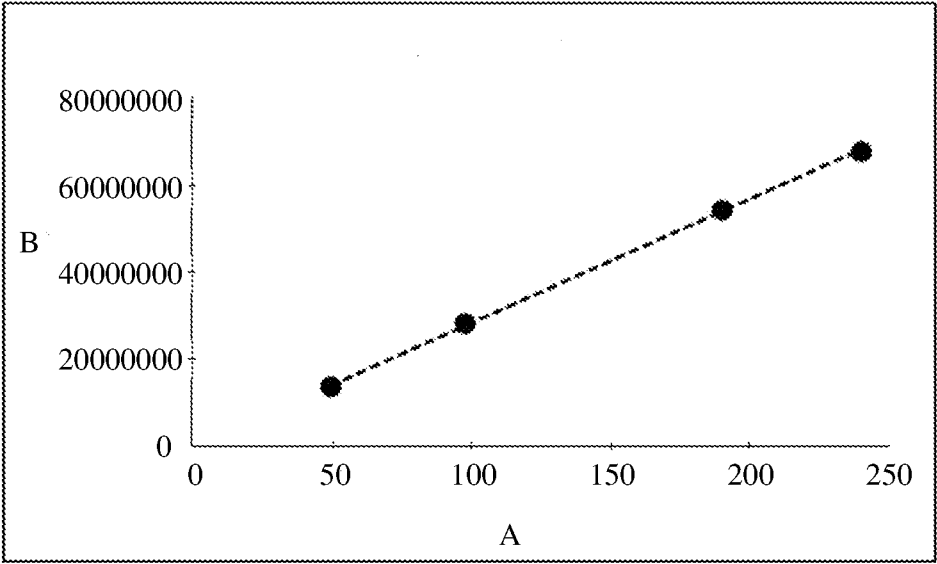
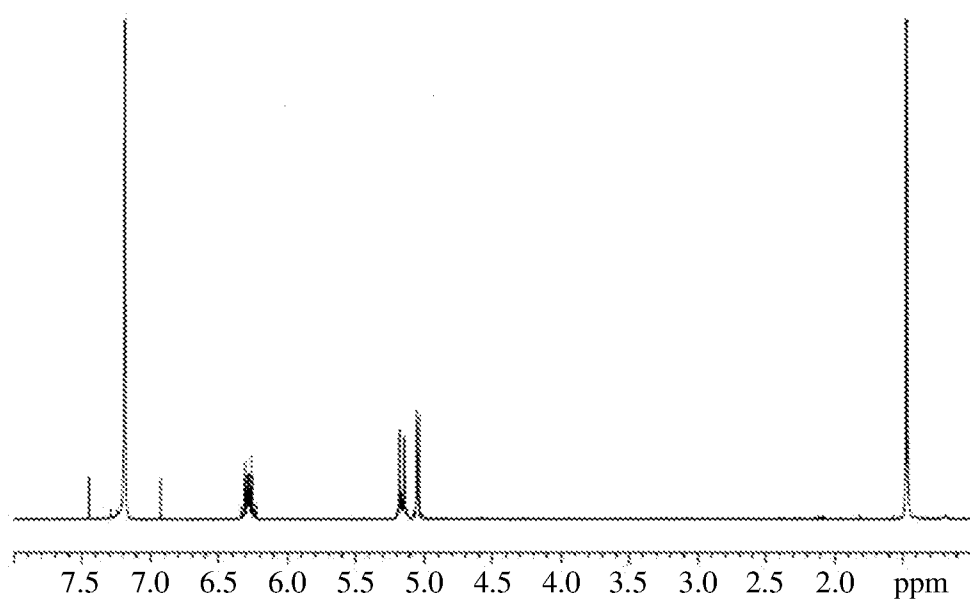
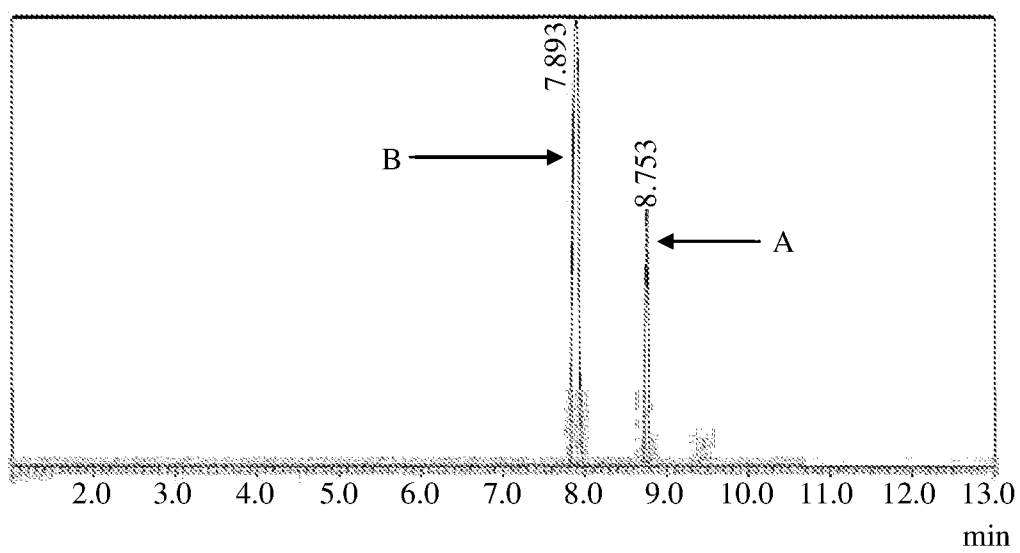


Figure 1

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**Figure 2**

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**Figure 3**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2016/056052

A. CLASSIFICATION OF SUBJECT MATTER
C12P5/00, C12P1/00 Version=2017.01

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)

C12P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

C12N

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Patseer, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2012177710 A1 (GENOMATICA INC AT AL), 27 Dec 2012 (2012-12-27) Abstract; Para 5, page 1; line 10, page 6; para 5, page 1; line 5-10, page 39	1-18
Y	WO 2013071074 A1 (INVISTA NORTH AMERICA SARL), 16 May 2013 (2013-05-16), Family: NONE Abstract; line 29, page 7-line 5, page 8; line 5, page 7; page 13; line 25-30, page 27	1-18
Y	US 2011300597 A1 (BURK MARK J ET AL), 08 Dec 2011 (2011-12-08) Abstract; Para [0065]-[0067]	1-18

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

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
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"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	

Date of the actual completion of the international search

03-01-2017

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IB2016/056052

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