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(54) Keksinnön nimitys - Uppfinningens benämning - Title of the invention
Prosessi 2-butanolin tuottamiseksi gammavalerolaktonista
Process för att producera 2-butanol av gammavalerolakton
A process for producing 2-butanol from gammavalerolactone

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ROZENBLIT, A. et al. Reaction mechanism of aqueous-phase conversion of γ -valerolactone (GVL) over a Ru/C catalyst. In: Journal of Energy Chemistry 2016-11-23, Vol. 25, 1008-1014, <DOI:10.1016/j.jechem.2016.11.010>, BABABRIK, R. M. et al. Reaction Mechanism for the Conversion of γ -Valerolactone (GVL) over a Ru Catalyst: A First-Principles Study. In: Industrial & Engineering Chemistry Research 2017-03-06, Vol. 56, No. 12, 3217-3222, <DOI:10.1021/acs.iecr.7b00196>, YAN, K. et al. Catalytic reactions of gamma-valerolactone: A platform to fuels and value-added chemicals. In: Applied Catalysis B: Environmental 179 (2015) 292-304 2015-05-21, Vol. 179, 292-304, <DOI:10.1016/j.apcatb.2015.04.030>

(57) Tiivistelmä - Sammandrag - Abstract

Prosessi 2-butanolin tuottamiseksi selektiivisesti GLA:sta käyttäen vähintään yhtä siirtymämetallikatalyyttiä, joka valitaan ryhmästä jossa ovat rauta, rutenium, koboltti, rodium ja iridium.

A process is disclosed for selectively producing 2-butanol from GVL by using at least one transition metal catalyst selected from the group consisting of iron, ruthenium, cobalt, rhodium and iridium.

A PROCESS FOR PRODUCING 2-BUTANOL FROM GAMMAVALEROLACTONE

5 FIELD OF THE INVENTION

The present invention relates to selective production of 2-butanol from γ -valerolactone (GVL) with a catalyst.

BACKGROUND

2-Butanol (sec-butanol, sec-butyl alcohol, methyl ethyl carbinol; $C_4H_{10}O$) is a
10 colourless solvent with a characteristic alcohol odor. It is only moderately miscible with water but is miscible in all proportions with many organic solvents.

2-Butanol is produced commercially by the indirect hydration of fossil C-4 streams, usually n-butene. In production, butadiene and isobutylene are removed from the C-4 stream and the remaining butanes-butylenes stream (raffinate-2), usually rich
15 in butene-2, is reacted with sulphuric acid. Addition of water hydrolyses the resulting sec-butyl hydrogen sulphate and di-sec-butyl sulphate to 2-butanol and sulphuric acid; di-sec-butyl ether is a by-product of side reactions.

Most of the industrially produced 2-butanol is used to make methyl ethyl ketone, which is used in surface coatings, adhesives, lube oil dewaxing, magnetic tape
20 manufacture, printing inks, and in chemical uses. A minor amount of 2-butanol is employed as a direct solvent, as well as in blends with aromatic hydrocarbons, ketones and other alcohols. 2-Butanol is also used as an intermediate for manufacturing chemicals that are used for solvent applications, such as blended with aromatic hydrocarbons, ketones, and other alcohols for use as a solvent for
25 nitrocellulosic and acrylic lacquers, and as a coupling agent for applications in hydraulic brake fluids, industrial cleaning compounds, and paint remover. 2-Butanol is also used as a raw material in the manufacture of sec-butyl acetate and in the production of a xanthate derivative that is a collector in ore flotation. Other uses include the manufacture of perfumes, fruit essences, dyestuffs, and wetting
30 agents.

The 2-butanol synthesis route described above is based on fossil sources. Hence, for renewable fuels and chemicals use of fossil 2-butanol is problematic because of its fossil origin, and renewable 2-butanol would be desirable for such uses.

It is thus an object of the present invention to provide a method for selectively
5 producing 2-butanol from a renewable feedstock.

ROZENBLIT, A. et al. discloses a reaction mechanism of aqueous-phase conversion of γ -valerolactone (GVL) over a Ru/C catalyst, see Journal of Energy Chemistry 2016-11-23, Vol. 25, 1008-1014.

BABABRIK, R. M. et al. discloses a reaction Mechanism for the Conversion of γ -
10 Valerolactone (GVL) over a Ru Catalyst: A First-Principles Study, see Industrial & Engineering Chemistry Research 2017-03-06, Vol. 56, No. 12, 3217-3222.

YAN, K. et al. discloses catalytic reactions of gamma-valerolactone: A platform to fuels and value-added chemicals, see Applied Catalysis B: Environmental 179 (2015) 292-304 2015-05-21, Vol. 179, 292-304.

15 US 5883266 discloses hydrogenated 5-carbon compounds and methods of for making them.

SUMMARY

According to the first aspect is provided a process for selective production of 2-butanol from γ -valerolactone (GVL) comprising:

- 20 a. Providing in a reactor at least one transition metal catalyst selected from the group consisting of iron, ruthenium, cobalt, rhodium and iridium;
- b. Heating a feedstock containing GVL, thereby forming a heated GVL feedstock;
- c. Forming a reaction mixture by feeding into the reactor:
 - 25 i. The heated GVL feedstock; and
 - ii. Hydrogen gas; and
- d. Maintaining the temperature of the reaction mixture in the range 200-300°C to allow selective production of reaction products comprising 2-butanol.

An advantage of the present process is that an effective and selective process for producing 2-butanol from a renewable feedstock in a controlled manner is achieved. With the present invention it is possible to use GVL derived from a lignocellulosic source to produce 2-butanol and co-products. Thus, drawbacks
5 relating to fossil raw materials can be avoided.

According to the second aspect is provided a use of a catalyst comprising at least one transition metal selected from the group consisting of iron, ruthenium, cobalt, rhodium and iridium, in a selective production of 2-butanol from GVL.

According to another aspect is provided a use of a catalyst comprising at least one
10 transition metal selected from the group consisting of iron, cobalt, rhodium and iridium, in a selective production of 2-butanol from GVL.

An advantage of present use is high selectivity of 2-butanol production, and possibility to control co-product production by process conditions.

FIGURES

15 Figures 1A and 1B show product distribution (according to GC-MS) in GVL hydrogenation experiments over Rh/ZrO₂ and Ru/ZrO₂ catalysts for liquid products obtained at 225 and 250 °C.

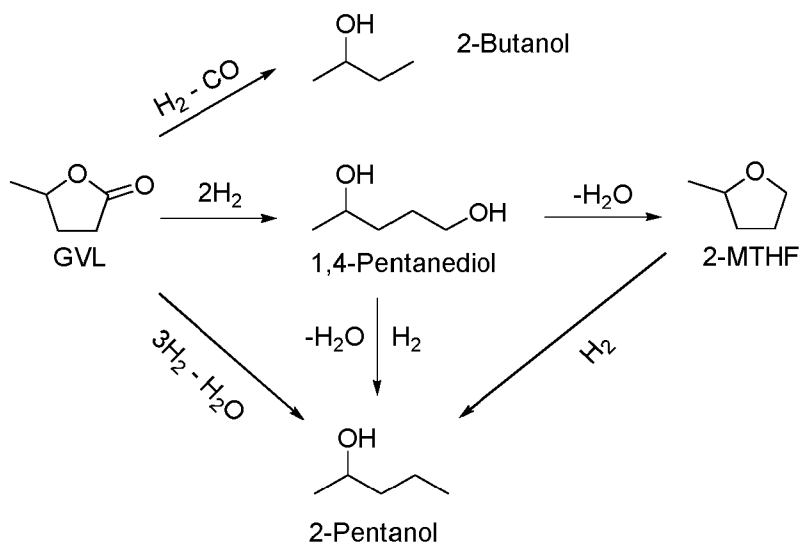
DETAILED DESCRIPTION OF THE INVENTION

As used herein, the term "comprising" includes the broader meanings of
20 "including", "containing", and "comprehending", as well as the narrower expressions "consisting of" and "consisting only of".

In an embodiment the selectivity of 2-butanol production is at least 50% analysed as GC-MS area-%.

With the obtained high selectivity of 2-butanol production it is possible to decrease
25 formation of co-products and to have a process, which provides primarily 2-butanol as the reaction product. Thus, in an embodiment the present process can be optimised for 2-butanol production, which is advantageous when co-products are not desired.

Scheme 1 shows a simplified reaction scheme according to the invention, which depicts part of the compounds formed from GVL by the present selective hydrogenation. Compounds derived from pentanoic acid - also a hydrogenation product from GVL - are not included as they are of minor importance for the Rh- and Ru- catalysts.



Scheme 1. Selective hydrogenation products from GVL.

GC-MS area-% can be calculated as follows: the relative amount (area-%) of each compound in the product stream was determined by GC-MS. Each peak was integrated (<https://goldbook.iupac.org/html/P/P04453.html>) and the relative amount (area-%) was obtained by comparing the area of a single peak to the sum of the peaks in the GC-MS chromatogram.

As the skilled person understands, depending on the process conditions inside the reactor, distribution of the compounds between liquid and gas phase may vary. For example GVL and 2-butanol may be present primarily in the liquid phase, but to some degree also in the gas phase. Similarly, lightest compounds such as methane and hydrogen, are primarily present in the gas phase.

In an embodiment the feedstock contains at least 80 wt-% GVL.

High GVL content of the feedstock is advantageous to provide a catalytic reaction process, which proceeds efficiently from GVL as the starting material to reaction products, in particular 2-butanol. The remaining part of the feedstock may contain

water, levulinic acid, pentanoic acid, furfural, and/or sulphuric acid. Thus, the process can be used to process GVL-containing feed which contains further substances in addition to GVL.

In an embodiment the process conditions provide 2-butanol in a liquid phase, wherein the ratio of 2-butanol to 2-methyltetrahydrofuran is at least 2 analysed as GC-MS area-%. In another embodiment the ratio of 2-butanol to 2-methyltetrahydrofuran is at least 2.0, 2.5, 3, 3.5, 4, 4.5, 5, 5.5 or 6 analysed as GC-MS area-%. Thus, the process can advantageously be used to produce high amount of 2-butanol. This can be achieved by selection of the catalyst and reaction conditions, such as temperature. Suitable reaction conditions can be selected by preferring process conditions that drive the reaction into the direction of 2-butanol production instead of 2-MTHF in Scheme 1.

In an embodiment the process conditions provide 2-butanol in a liquid phase, and wherein the liquid phase comprises GVL, 2-butanol, 2-methyltetrahydrofuran and pentanol such as 1-pentanol or 2-pentanol.

In an embodiment the liquid phase contains less than 80 GC-MS area-% GVL, preferably less than 80, 70, 60, 50, 40, 30 or 25 GC-MS area-% GVL.

In an embodiment the liquid phase contains at least 15 GC-MS area-% 2-butanol.

In an embodiment the liquid phase contains at least 10 GC-MS area-% 2-butanol, preferably at least 10, 15, 20, 25, 30, 40, 50, 55 or 60 GC-MS area-% 2-butanol.

In an embodiment the liquid phase contains 3-15 GC-MS area-% 2-MTHF, preferably 3-8, 4-6, 4-10, 5-15, 5-10, 6-11, 7-11, 7-10, or less than 15, less than 10, less than 8, less than 6 or less than 5 GC-MS area-% 2-2-MTHF.

In an embodiment the liquid phase contains 2-8 GC-MS area-% 1-/2-pentanol, preferably 2-7 or 2.5-6.5 GC-MS area-% 1-/2-pentanol.

In an embodiment the catalyst comprises Rh, Ru, or a combination thereof.

An advantage of having Ru and/or Rh in the catalyst is high selectivity and yield of 2-butanol production.

In an embodiment the catalyst is provided on a support. In another embodiment the support is a solid porous support. This has an advantage of improved

availability of the catalytically active metal by its dispersion on a porous solid material. Further, porous support may improve activity and selectivity of the catalyst.

In an embodiment the support comprises Zr oxide, Al oxide, Ti oxide, silica, or a
5 combination thereof.

In an embodiment the catalyst comprises Rh/ZrO₂ or Ru/ZrO₂, or a combination thereof. This has an advantage of high selectivity and yield.

In an embodiment the temperature is maintained in the range 215-270 °C during production of 2-butanol. In a preferred embodiment the temperature is maintained
10 in the range 220-255°C. In this temperature 2-butanol production pathway is preferred (see Scheme 1).

In an embodiment the temperature is maintained in the range 240-260°C during production of 2-butanol. In this temperature 2-butanol production pathway is even more preferred.

15 In an embodiment the temperature is maintained at the selected range by cooling and heating the feedstock containing GVL. Optionally the temperature of the reactor is controlled by heat transfer by conduction, preferably through reactor walls. In another embodiment, or in addition to the above means, the temperature is controlled by diluting the feedstock. As the skilled person knows, hydrogenation
20 is typically an exothermic reaction, and temperature rise inside the reactor can be controlled by diluting the feedstock, which slows down the reaction and the resulting heat.

In an embodiment the liquid phase comprises 2-butanol, 2-methyltetrahydrofuran, 2-pentanol, 1-pentanol, 2-butanone, pentanoic acid 2-penten-1-ylester, pentanoic
25 acid pentylester.

The inventors found that lower reaction temperature results into lower yield of 2-butanol with higher selectivity, whereas a higher temperature results into higher yield of 2-butanol and other reaction products. Thus, a higher temperature can be used to increase yield of 2-butanol, to produce further reaction products and to
30 convert more GVL into reaction products. Accordingly, a lower reaction

temperature can be selected to obtain a more selective 2-butanol production and less other reaction products.

In an embodiment the feedstock containing GVL is heated to a temperature in the range 215-270°C, preferably in the range 215-235, 220-230, 240-260, or 245-
5 255°C, or about 225 or 250°C

In an embodiment the temperature is maintained in the range 215-235, 220-230, 240-260, or 245-255°C, or about 225 or 250°C.

In a preferred embodiment the temperature is maintained at 220-230°C, more preferably at about 225°C. In this temperature the process provides a liquid phase
10 containing GVL, 2-butanol, 2-methyltetrahydrofuran and 2-pentanol.

In a preferred embodiment the temperature is maintained at 245-255°C, more preferably at about 250°C. In this temperature the process provides a liquid phase containing 2-butanol, 2-methyltetrahydrofuran, 2-pentanol, 1-pentanol, 2-butanone, pentanoic acid 2-penten-1-ylester, and pentanoic acid pentylester.

15 In an embodiment a pressure selected from the range 40-100 bar, preferably 50-90 bar, is maintained inside the reactor during production of 2-butanol. In another embodiment a pressure of 70-90 bar, 75-85 or about 80 bar is maintained inside the reactor.

In an embodiment the process is a continuous process. Compared to batch
20 processes, such as laboratory scale batch processes, carrying out the present invention as a continuous process is advantageous. For example, the temperature of the process can be controlled by controlling the temperature of the feed which enters the reactor.

In an embodiment the present process is carried out without adding further
25 solvents.

In an embodiment the present process is carried out without adding water, i.e. it is a "dry process". In previous processes water has been identified as essential component to achieve selectivity to 2-butanol production. Surprisingly, the present process was selective for 2-butanol.

30 In an embodiment the process is a continuous flow process and the reactor is a fixed bed reactor.

In an embodiment the selectivity is determined by determining the relative amount (area-%) of each compound in the product stream by GC-MS, integrating each peak, and comparing the area of a single peak to the sum of the peaks in the GC-MS chromatogram.

- 5 In an embodiment the reaction mixture contains at least 25 GC-MS area-% GVL.

In an embodiment at least part of the unreacted GVL present in the liquid phase is recycled into the reactor. This has an advantage of higher total conversion of GVL, resulting into improved efficiency of the process.

- 10 In an embodiment the liquid phase contains at least 15 % 2-butanol analysed as GC-MS area-%.

In an embodiment the pressure inside the reactor is controlled, and methane formed during the process is converted to hydrogen gas. With the combined production of hydrogen gas the total conversion of GVL into reaction product is improved, thus improving efficiency of the process.

- 15 In an embodiment methane formed in the process is conducted outside the reactor through an outlet in the reactor wall, and conversion into hydrogen is carried out in a further conversion unit. In an embodiment the further conversion unit is in fluid connection with the reactor via at least one piping, such as a discharge piping for removing fluid from the reactor, and optionally via inlet piping for loading fluids into
20 the reactor.

In an embodiment at least part of the hydrogen gas obtained from methane is recycled to the reactor. In an embodiment the hydrogen gas is purified before feeding into the reactor.

- 25 An advantage of obtaining methane and converting it to hydrogen gas is improved process economy.

In an embodiment at least one further reaction product selected from 2-MTHF, 2-butanone, and pentyl pentanoate is recovered.

Recovery of said further reaction products is advantageous because they can be used e.g. in manufacturing of solvents and flavouring agents.

- 30 In an embodiment GVL is derived from a lignocellulosic source.

An advantage of using GVL from a lignocellulosic source is that the produced 2-butanol is produced from a renewable source. Thus, problems relating to fossil feedstocks can be avoided.

In an embodiment the reaction product is at least one of 2-MTHF, 2-butanone, and
5 pentyl pentanoate.

In an embodiment the process comprises a further step of distilling and/or extracting the liquid phase to fractionate 2-butanol and other components.

In an embodiment the amount of metal in the catalyst is less than 5 wt-%. In another embodiment the amount of metal in catalyst is less than 4 wt-%, 3 wt-%,
10 2 wt-%, 1 wt-% or 0.5 wt-%, preferably about 1 wt-%.

In an embodiment the reactor is operated in a continuous mode.

In an embodiment the reactor is a fixed bed reactor

In an embodiment 2-butanol is recovered from the reactor in liquid phase.

In an embodiment the process involves a step of separating a gas phase from a
15 liquid phase. In an embodiment the gas phase is separated from the liquid phase to separate reaction products.

In an embodiment reaction products are recovered from the reactor by conducting them into a product container. In an embodiment the product container is kept at an atmospheric pressure. In another embodiment the pressure of the reaction
20 product feed from the reactor is reduced in a controlled manner before feeding into the product container, and gas-liquid separation is carried out to the reaction product feed before storing in the product container. Preferably light co-products in the gas phase and optionally in the liquid phase are stored in a cooled product container.

25 In an embodiment at least part of the gas phase obtained during gas-liquid separation is recovered. In another embodiment selected co-products present in the gas phase are recovered by condensation

In an embodiment H_2 /feed ratio is about 2000. In another embodiment the ratio is about 100-2000, preferably about 200-1000.

The H₂/feed can be calculated as follows: H₂/feed ratio (NL/L) = H₂ flow rate (NL/h) / GVL flow rate (ml/h) x 1000

In an embodiment the liquid phase contains pentanoic acid 2-penten-1-ylester, 2-pentanol, pentanoic acid pentylester, 1-pentanol, 2-butanone, 2-butanol, 2-MTHF
5 and GVL.

In an embodiment at least part of the 2-butanol produced in the process is used to manufacture chemicals, fuels or fuel blends.

Thus, with the present process using GVL derived from lignocellulosic source it is possible to obtain a renewable source of 2-butanol and co-products.

10 In an embodiment the process is carried out at an industrial scale.

In an embodiment the steps a-c of the present process are carried out in the said sequence.

EXAMPLES

The following examples are provided to illustrate various aspects of the present
15 invention. They are not intended to limit the invention, which is defined by the accompanying claims.

Example 1 - Production of 2-butanol from GVL over Rh/ZrO₂ and Ru/ZrO₂ catalysts

Catalyst preparation

20 The Ru/ZrO₂ and Rh/ZrO₂ catalysts were prepared using RuCl₃·nH₂O and Rh(NO₃)₃, respectively, as metal precursors. The ZrO₂ support material was ground and sieved to the target particle size of 0.125-0.180 mm and calcined at 600 °C. The metal precursor was added by incipient wetness impregnation on the support and then dried at 100 °C overnight and calcined in air at 450 °C for 2 hours.
25 The metal contents measured for the final catalysts were 0.85 wt-% Ru and 0.86 wt-% Rh.

The hydrogenation of GVL over Rh/ZrO₂ and Ru/ZrO₂ was conducted in continuous flow fixed bed reactors. Five grams of catalyst was packed in the reactor without any inert material dilution. Commercial γ-valerolactone (Sigma-
30 Aldrich ≥99 %) was used as received without any dilution. The catalysts were dried

under nitrogen flow (10 l/h) at 120 °C for 1 hour. Heating rate was 0.5 °C/min. After drying, hydrogen flow was adjusted to 10 l/h and pressure was increased to 15 bar. The catalysts were reduced at 400 °C for 5 hours. Heating rate was 3 °C/min. After cooling down and soaking of the catalyst at 100 °C, test conditions were
 5 adjusted to WHSV 0.5 h⁻¹, H₂/feed ratio 2000 NL/L and pressure 80 bar. Only the temperature was varied during the hydrogenation experiment.

Reaction conditions and test procedure

The reaction conditions used in the experiments are shown in Table 1.

10 **Table 1.** Reaction conditions for the preparation of 2-butanol from GVL (the density of GVL used was 1.0259 g/cm³ (50 °C)).

Reaction condition	Unit	Value
Temperature	°C	225 and 250
Pressure	bar	80
Catalyst amount	g	5
GVL feed rate	g/h	2.5
	ml/h	2.44
WHSV	1/h	0.5
H ₂ flow rate	g/h	0.43
	NL/h	4.8
H ₂ /feed ratio	NL/L	~2000

$$\text{GVL feed rate (ml/h)} = \text{GVL feed rate (g/h)} / \text{GVL density (1.0259 g/cm}^3\text{)}$$

Weight-hourly-space-velocity is the mass flow rate of the reactants divided by the
 15 mass of the catalyst in the reactor,

$$\text{WHSV (1/h)} = \text{GVL flow rate (g/h)} / \text{Catalyst amount (g)}$$

$$\text{H}_2 \text{ flow rate (g/h)} = \text{H}_2 \text{ flow rate (NL/h)} / 22.41 \text{ (L/mol)} \times \text{molecular weight H}_2 \text{ (g/mol)}$$

$$\text{H}_2/\text{feed ratio (NL/L)} = \text{H}_2 \text{ flow rate (NL/h)} / \text{GVL flow rate (ml/h)} \times 1000$$

20 Example 2 - Sample analysis

The product distributions obtained in GVL hydrogenation over Rh/ZrO₂ and Ru/ZrO₂ catalysts at 225 and 250 °C are shown in Figure 1A and 1B and in Table 2.

According to GC-MS results the GVL conversion as well as the 2-butanol yield increased when the hydrogenation temperature increased from 225 to 250 °C.

The liquid product stream obtained in the hydrogenation experiment was analysed with offline Gas Chromatography - Mass Spectrometry, GC-MS (Agilent GC 6890A mit MSD 5973). Peaks in the GC chromatogram were assigned to various compounds by MS. The relative amount (area-%) of each compound in the product stream was determined by GC-MS. Each peak was integrated (<https://goldbook.iupac.org/html/P/P04453.html>) and the relative amount (area-%) was obtained by comparing the area of a single peak to the sum of the peaks in the GC-MS chromatogram. The amount of GVL (wt-%) was determined quantitatively with GC-FID from response factor that was calibrated with pure GVL.

Gas Chromatography – Flame Ionization Detector or GC-FID is a very common analytical technique that is widely used in the petrochemical, pharmaceutical and natural gas markets.

An FID typically uses a Hydrogen/Air flame into which the sample is passed to oxidise organic molecules and produces electrically charged particles (ions). The ions are collected and produce an electrical signal which is then measured.

The conversion of GVL calculated from the quantitative amount of GVL remaining in the product was 50.5 and 69.8 wt-% for Rh/ZrO₂ at 225 and 250 °C, respectively, and 42.8 and 78.7 wt-% for Ru/ZrO₂ at 225 and 250 °C, respectively.

Table 2. Product distribution, 2-butanol selectivity and 2-butanol-to-MTHF-ratio in organic liquid phases obtained at 225 and 250 °C with Rh/ZrO₂ and Ru/ZrO₂ catalysts (in GC area-%).

		Rh/ZrO₂ at 225°C	Rh/ZrO₂ at 250°C	Ru/ZrO₂ at 225°C	Ru/ZrO₂ at 250°C
GVL	area-%	75.4	58.0	69.1	29.1
2-MTHF	area-%	5.7	4.8	7.6	9.5
2-Butanol	area-%	16.1	25.7	20.7	51.2
1-/2-Pentanol	area-%	2.8	4.8	2.6	6.2
Butanone	area-%	-	1.6	-	3.3
Esters	area-%	-	3.6	-	-
Other minor	area-%	-	0.55	-	0.79
Unknowns	area-%	-	0.97	-	-
2-Butanol selectivity	area-%	65.4	61.2	67.0	72.2
2-Butanol-to- MTHF-ratio	area-%	2.8	5.4	2.7	5.4

5

High selectivity for 2-butanol was achieved in the hydrogenation reactions carried out at 225-250 °C and 80 bar. At these temperatures the selectivity for 2-butanol over Rh/ZrO₂ was 61-65 area-% and over Ru/ZrO₂ 67-72 area-%. The selectivity obtained in these reactions is highly improved compared to 2-butanol selectivity values found in the literature for GVL hydrogenation. For example, Al-Shaal et al. (Green Chem., 2014, 16, 1358) have reported the formation of mainly 2-MTHF and 2-butanol at 190 °C and 100 bar when using 5 wt-% Ru/C as GVL hydrogenation metal. At the highest GVL conversion reported almost equal amounts of 2-MTHF (43 %) and 2-butanol (36 %) were obtained (with a butanol-to-MTHF-ratio of 0.8).

Based on the 2-butanol-to-MTHF-ratios (=2.7-5.4) of the Rh/ZrO₂ and Ru/ZrO₂ catalysts it is proposed that the reaction route giving 2-butanol is preferred over the route leading to 2-MTHF. Further, with said catalysts, it is possible to direct the catalytic process to higher selectivity for 2-butanol, or higher yield of 2-butanol, simply by changing temperature. For the Ru/C catalyst with a 2-butanol-to-MTHF-ratio of 0.8, both routes are proposed to occur with almost equal probability and no selectivity is obtained.

As the examples indicate, in the present invention highly improved selectivities for 2-butanol formation from GVL was achieved. In particular Rh/ZrO₂ and Ru/ZrO₂ catalysts were superior in selectivity compared to selectivity values reported in the literature (e.g. over 5 wt-% Ru/C). In the present invention a much lower amount
5 of catalyst, i.e. 1 wt-% Rh/ZrO₂ and Ru/ZrO₂, was sufficient to achieve high selectivity and yield of the 2-butanol production.

Different non-binding example aspects and embodiments of the present invention have been illustrated in the foregoing. The embodiments are used merely to explain selected aspects or steps that may be utilized when implementing the
10 present invention. Some embodiments may be presented herein only with a reference to a certain aspect of the invention. It should be appreciated that the embodiments may apply to other aspects of the present invention, as well. Consequently, any appropriate combination of the embodiments and the aspects may be formed. Any combination of aspects or embodiments as disclosed herein
15 may also be made without at least one non-essential feature disclosed in an aspect or embodiment.

Claims

1. A process for selective production of 2-butanol from γ -valerolactone (GVL) comprising:
 - a. Providing in a reactor at least one transition metal catalyst selected from the group consisting of iron, ruthenium, cobalt, rhodium and iridium;
 - b. Heating a feedstock containing GVL, thereby forming a heated GVL feedstock;
 - c. Forming a reaction mixture by feeding into the reactor:
 - i. The heated GVL feedstock; and
 - ii. Hydrogen gas; and
 - d. Maintaining the temperature of the reaction mixture in the range 215-270°C to allow selective production of reaction products comprising 2-butanol.
2. The process of claim 1, wherein the selectivity of 2-butanol production is at least 50% analysed as GC-MS area-% by determining the relative amount (area-%) of each compound in the product stream by GC-MS, integrating each peak, and comparing the area of a single peak to the sum of the peaks in the GC-MS chromatogram.
3. The process of any one of claims 1-2, wherein the feedstock contains at least 80 wt-% GVL.
4. The process of any one of claims 1-3, wherein in the process conditions provide 2-butanol in a liquid phase, wherein the ratio of 2-butanol to 2-methyltetrahydrofuran is at least 2 analysed as GC-MS area-% by determining the relative amount (area-%) of each compound in the product stream by GC-MS, integrating each peak, and comparing the area of a single peak to the sum of the peaks in the GC-MS chromatogram.
5. The process of any one of claims 1-4, wherein the catalyst comprises Rh, Ru, or a combination thereof.

6. The process of any one of claims 1-5, wherein the catalyst is provided on a support.
7. The process of claim 6, wherein the support comprises Zr oxide, Al oxide, Ti oxide, silica, or a combination thereof.
- 5 8. The process of any one of claims 1-7, wherein the catalyst comprises Rh/ZrO₂ or Ru/ZrO₂, or a combination thereof.
9. The process of any one claims 1-8, wherein the temperature is maintained in the range 240-260 °C during production of 2-butanol.
10. The process of any one of claims 1-9, wherein in the process conditions
10 provide 2-butanol in a liquid phase, and wherein the liquid phase comprises GVL, 2-butanol, 2-methyltetrahydrofuran and 2-pentanol.
11. The process of claim 10, wherein the liquid phase comprises 2-butanol, 2-methyltetrahydrofuran, 2-pentanol, 1-pentanol, 2-butanone, pentanoic acid 2-penten-1-ylester, and pentanoic acid pentylester.
- 15 12. The process of any one of claims 1-11 wherein a pressure selected from the range 40-100 bar, preferably 50-90 bar, is maintained inside the reactor during production of 2-butanol.
13. The process of any one claims 1-12, wherein the process is a continuous process.
- 20 14. The process of claim 13 wherein at least part of the unreacted GVL present in the liquid phase is recycled into the reactor.
15. The process of any one of claims 4-14, wherein the liquid phase contains at least 15 % 2-butanol analysed as GC-MS area-% by determining the relative amount (area-%) of each compound in the product stream by GC-MS, integrating
25 each peak, and comparing the area of a single peak to the sum of the peaks in the GC-MS chromatogram.
16. The process of any one of claims 12-15 wherein the pressure inside the reactor is controlled, and methane formed during the process is converted to hydrogen gas.

17. The process of claims 1-16 wherein at least one further reaction product selected from 2-MTHF, 2-butanone, and pentyl pentanoate is recovered.

18. The process of any one of claim 1-17 wherein GVL is derived from a lignocellulosic source.

Patenttivaatimukset

1. Prosessi 2-butanolin tuottamiseksi selektiivisesti γ -valerolaktonista (GVL) käsittäen:

- a. tarjotaan käyttöön reaktorissa vähintään yksi siirtymämetallikatalyytti, joka on
5 valittu ryhmästä, jossa ovat rauta, rutenium, koboltti, rodium ja iridium;
- b. kuumennetaan GVL:a sisältävää raaka-ainetta, jolloin muodostuu kuumennettu GVL-raaka-aine;
- c. muodostetaan reaktioseos syöttämällä reaktoriin:
 - i. kuumennettua GVL-raaka-ainetta; ja
 - 10 ii. vetykaasua; ja
- d. säilytetään reaktioseoksen lämpötila välillä 215 - 700 °C, jotta mahdollistetaan 2-butanolia käsittävien reaktiotuotteiden selektiivinen tuottaminen.

2. Patenttivaatimuksen 1 mukainen prosessi, jossa 2-butanolin tuottamisen
15 selektiivisyys on vähintään 50 % analysoituna GC-MS ala-%:na määrittämällä kunkin yhdisteen suhteellinen määrä (ala-%) tuotevirrassa GC-MS:llä, integroimalla kukin piikki, ja vertaamalla yksittäisen piikin alaa GC-MS-kromatogrammin piikkien summaan.

3. Minkä tahansa patenttivaatimusten 1-2 mukainen prosessi, jossa raaka-aine
20 sisältää vähintään 80 wt-% GVL:a.

4. Minkä tahansa patenttivaatimusten 1-3 mukainen prosessi, jossa prosessiolosuhteissa 2-butanoli tuotetaan nestefaasissa, missä 2-butanolin suhde 2-metyylitetrahydrofuraaniin on vähintään 2 analysoituna GC-MS ala-%:na
25 määrittämällä kunkin yhdisteen suhteellinen määrä (ala-%) tuotevirrassa GC-MS:llä, integroimalla kukin piikki, ja vertaamalla yksittäisen piikin alaa GC-MS-kromatogrammin piikkien summaan.

5. Minkä tahansa patenttivaatimusten 1-4 mukainen prosessi, jossa katalyytti käsittää Rh:a, Ru:a tai niiden seosta.

6. Minkä tahansa patenttivaatimusten 1-5 mukainen prosessi, jossa katalyytti
30 tarjotaan käyttöön kantoaineella.

7. Patenttivaatimuksen 6 mukainen prosessi, jossa kantoaine käsittää Zr-oksidia, Al-oksidia, Ti-oksidia, silikaa tai näiden seosta.
8. Minkä tahansa patenttivaatimusten 1-7 mukainen prosessi, jossa katalyytti käsittää Rh/ZrO₂:ta tai Ru/ZrO₂:ta tai näiden seosta.
- 5 9. Minkä tahansa patenttivaatimusten 1-8 mukainen prosessi, jossa lämpötila säilytetään välillä 240 - 260 °C 2-butanolin tuottamisen aikana.
10. Minkä tahansa patenttivaatimusten 1-9 mukainen prosessi, jossa prosessiolosuhteet tarjoavat 2-butanolin käyttöön nestefaasissa, ja missä nestefaasi käsittää GVL:a, 2-butanolia, 2-metyylitetrahydrofuraania ja 2-
- 10 pentanolia.
11. Patenttivaatimuksen 10 mukainen prosessi, jossa nestefaasi käsittää 2-butanolia, 2-metyylitetrahydrofuraania, 2-pentanolia, 1-pentanolia, 2-butanonia, pentaanihapon 2-penten-1-yyliesteriä ja pentaanihapon pentyyliesteriä.
12. Minkä tahansa patenttivaatimusten 1-11 mukainen prosessi, jossa paine joka
- 15 on valittu väliltä 40-100 bar, edullisesti 50-90 bar, säilytetään reaktorin sisällä 2-butanolin tuottamisen aikana.
13. Minkä tahansa patenttivaatimusten 1-12 mukainen prosessi, jossa prosessi on jatkuva prosessi.
14. Patenttivaatimuksen 13 mukainen prosessi, jossa vähintään reagoimaton
- 20 GVL, joka on läsnä nestefaasissa, kierrätetään reaktoriin.
15. Minkä tahansa patenttivaatimusten 4-14 mukainen prosessi, jossa nestefaasi sisältää vähintään 15 % 2-butanolia analysoituna GC-MS ala-%:na määrittämällä kunkin yhdisteen suhteellinen määrä (ala-%) tuotevirrassa GC-MS:llä, integroimalla kukin piikki, ja vertaamalla yksittäisen piikin alaa GC-MS-
- 25 kromatogrammin piikkien summaan.
16. Minkä tahansa patenttivaatimusten 12-15 mukainen prosessi, jossa reaktorin sisällä olevaa painetta kontrolloidaan ja prosessin aikana muodostunut metaani muutetaan vetykaasuksi.

17. Minkä tahansa patenttivaatimusten 1-16 mukainen prosessi, jossa kerätään lisäksi talteen vähintään yksi reaktiotuote joka valitaan seuraavista: 2-MTHF, 2-butanoni ja pentyylipentanoaatti.

18. Minkä tahansa patenttivaatimusten 1-17 mukainen prosessi, jossa GVL on
5 johdettu lignoselluloosalähteestä.

GVL reaction at 225 oC

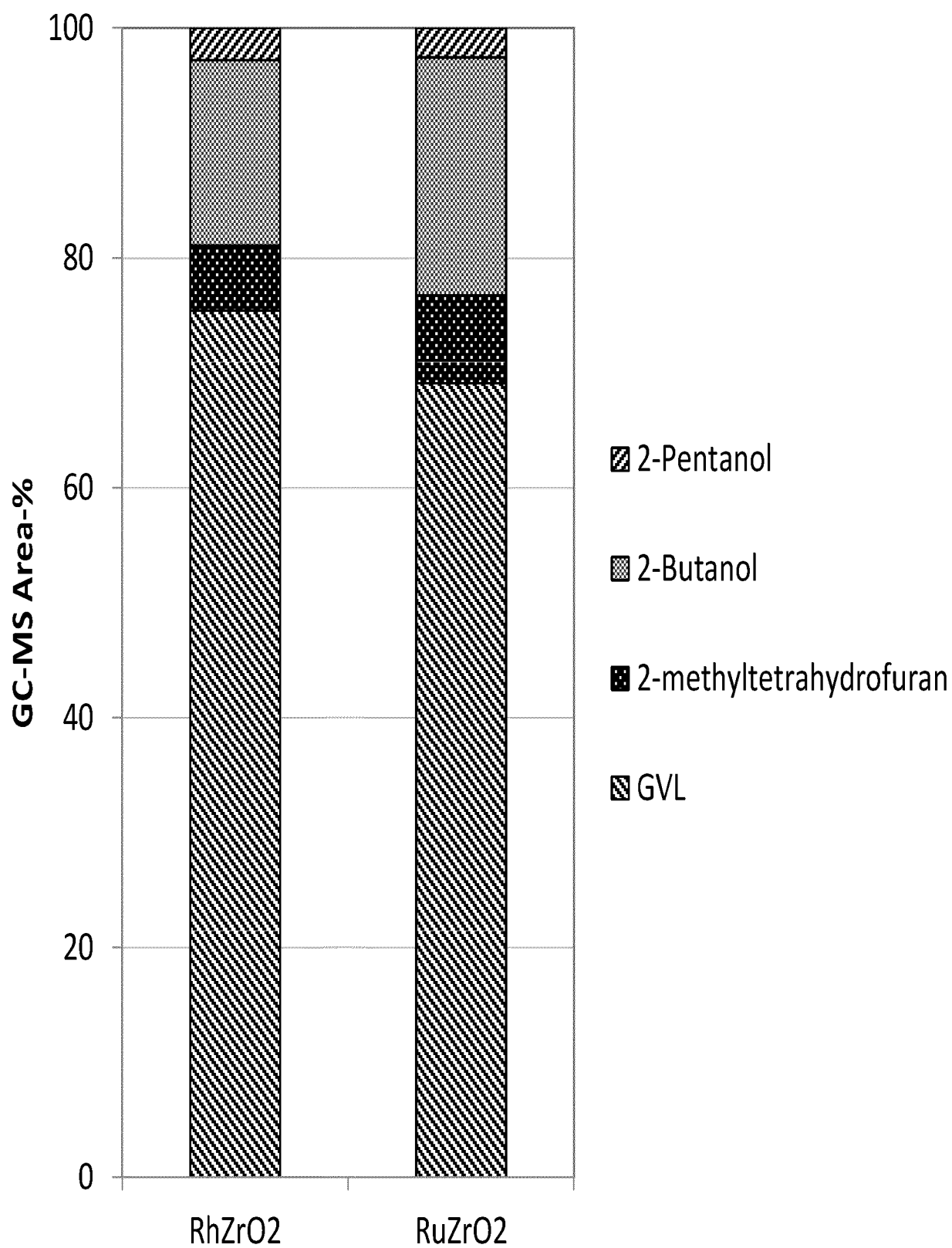


Fig 1A

GVL reaction at 250 oC

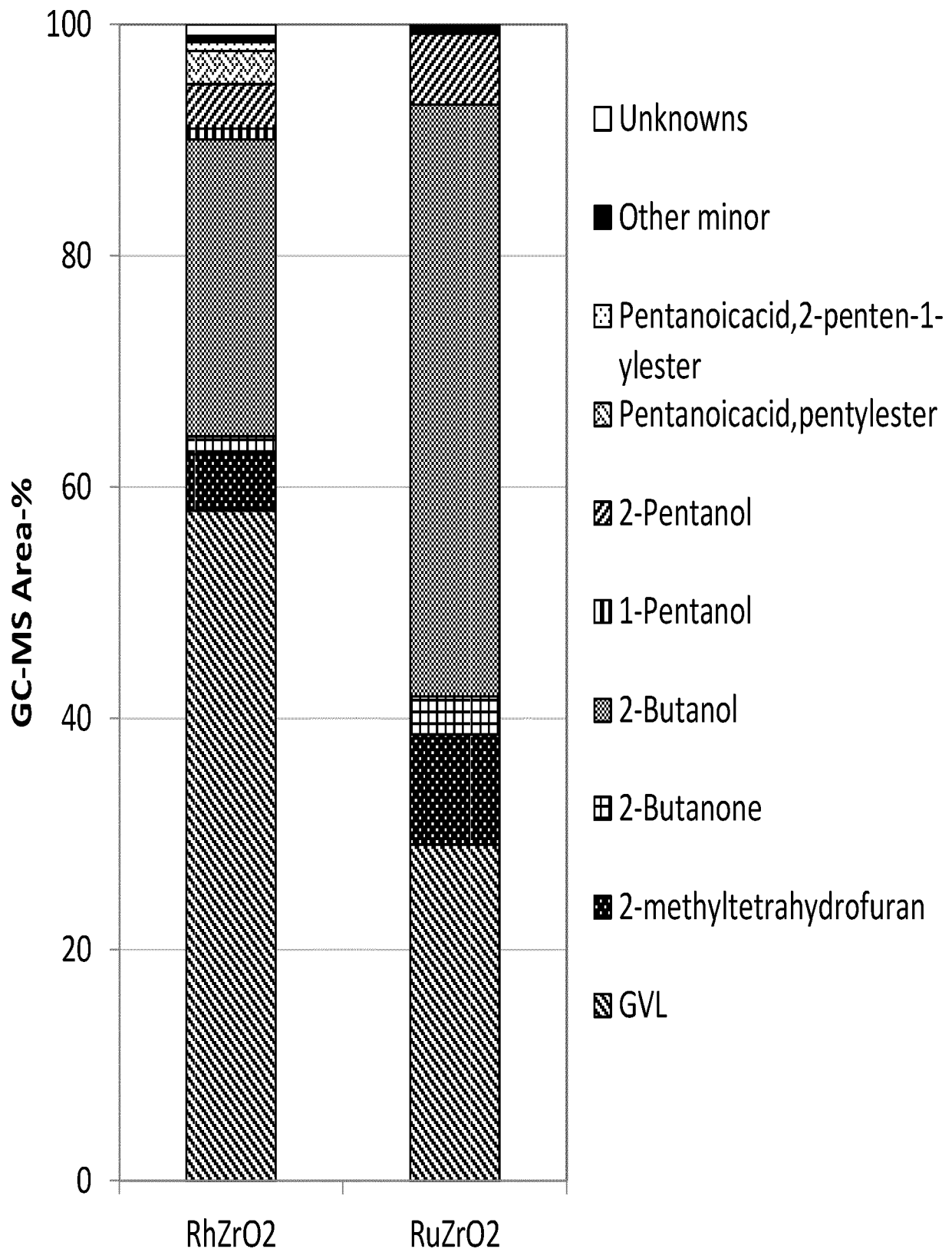


Fig 1B