

**PROCESS FOR THE CO-PRODUCTION OF DIALKYL SUCCINATE AND
1,4-BUTANEDIOL BY HYDROGENATING DIALKYL MALEATE IN TWO
STAGES**

DESCRIPTION

The present invention relates to a process for the efficient co-production of dialkyl-succinate and 1,4-butanediol by catalytic hydrogenation of dialkyl maleate.

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FIELD OF THE INVENTION

Embodiments disclosed herein relate generally to process and equipment to co-produce 1,4-butanediol, together with dialkyl succinate as co-product, by
10 reacting a feed, consisting of alkyl maleate, with hydrogen gas in a two stages reaction over suitable catalysts.

BACKGROUND OF THE INVENTION

Over the last decades, the world production of
15 plastic materials and, therefore, of plastic waste is dramatically increased.

Consequently, the biodegradable and the biodegradable/compostable polymers have attracted wide attention, as substitutes of the traditional and durable plastic polymers.

5 In the scenario of new biodegradable plastics, the polybutylene succinate (PBS) is one of the most interesting products, thanks to the combination of its excellent characteristics, as easily compostable material, its mechanical properties, its compatibility
10 with other polymers and its processability.

Polybutylene succinate may be used for many applications, particularly for agricultural film, rather than LDPE, and for food contact applications.

The paper "Biodegradability of Plastics,
15 International Journal of Molecular Sciences, 2009 Aug.29, by Y. Tokiwa et al.", besides describing the mechanism of biodegradation of PBS and other plastics, highlights the advantages of the biodegradable plastics, as increased soil fertility, low
20 accumulation of bulky plastic materials in the environment and reduction of cost of waste management. Furthermore, biodegradable plastics can be recycled to useful metabolites (monomers and oligomers) by microorganisms and enzymes.

25 The polybutylene succinate is produced by using 1,4 butanediol (BDO) and succinic acid (SA) as raw materials, through an esterification/polycondensation process with production of water; as alternative, the PBS may also be produced from butanediol and dimethyl
30 succinate (DMS), by a transesterification/poly-

condensation process with production of methanol, rather than water.

The polybutylene succinate may be produced as a pure polymer or also as a copolymer, as for example
5 the poly-butylene succinate-co-butylene terephthalate (PBST), using the co-esterification with terephthalic acid (PTA), or the poly-butylene succinate-co-adipate (PBSA), using adipic acid (AA). A further option is the production in blend with other polymer, as for
10 example the polybutylene succinate (PBS) and polybutylene adipate-co-terephthalate (PBAT) blend.

Unfortunately, even if the interest in PBS is large, the high price of the raw materials is deeply affecting the competitiveness of PBS and it is
15 limiting its production. Particularly, both the succinic acid and the dimethyl succinate have today a very high price. Most of the succinic acid today in the market is bio-produced by fermentation, with very high production cost. The dimethyl succinate, which
20 today is mostly produced by esterification of the bio-SA with methanol through a dedicated plant, has even higher cost.

Therefore, it would be desirable to providing new processes or improved processes, in order to
25 simplifying the industrial process of manufacturing the raw materials of the PBS products and to decreasing their production cost.

1,4-butanediol (BDO) is a versatile chemical intermediate, thanks to its terminal, primary hydroxyl
30 groups and to its chemical resistant nature.

BDO is an important raw material in the synthesis of technically relevant polymers such as thermoplastic urethanes and polyesters, mainly polybutylene terephthalate (PBT), polyester plasticizers, paints, 5 coatings and adhesives.

In the past years the largest consumer of BDO was tetrahydrofuran (THF), used to produce poly-tetramethylene ether glycol (PTMEG), a key raw material for spandex fibers. Substantial quantities of 10 BDO go into the manufacture of gamma-butyrolactone (GBL), which is in turn the main raw material used to manufacture N-methyl-pyrrolidone (NMP) and other pyrrolidones.

Another important downstream derivative of BDO is 15 the polybutylene terephthalate (PBT).

There are a number of routes to manufacture BDO: the first commercial route was the Reppe process from acetylene and formaldehyde. Other technologies include the production from butadiene, from propylene oxide, 20 from allyl alcohol and more recently through biotransformation process.

Thanks to the availability and low cost of the raw material, in the last thirty years and in the next future the processes based on butane/maleic anhydride 25 tend to dominate the market.

As described in EP2782893 B1 of the same Applicant, the processes based on butane/maleic anhydride comprise two main groups.

The first group includes all processes based on 30 the esterification of the maleic anhydride by

methanol, ethanol or other alcohols and the following hydrogenation of the dialkyl ester, usually as dimethyl maleate (DMM), to butanediol and/or, depending on the conditions of pressure and
5 temperature and on the catalyst, to tetrahydrofuran and gamma-butyrolactone.

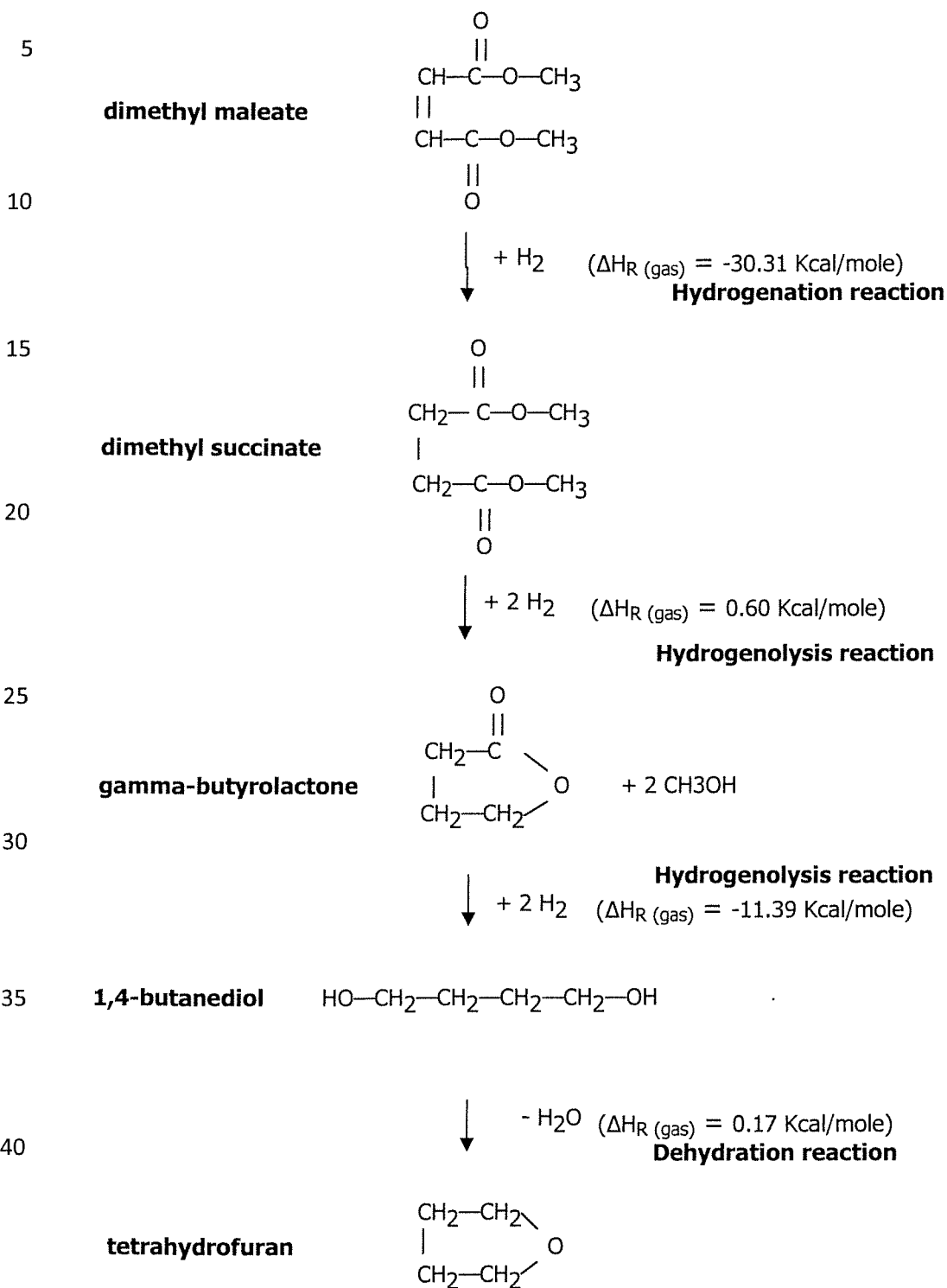
The second group on the contrary includes the processes based on the direct hydrogenation of the maleic anhydride or maleic acid to BDO and/or THF and
10 GBL. Even if theoretically these processes appear to be simpler, with fewer processing steps (both the maleic anhydride purification and the esterification are not necessary), in the industrial application they met with poor success, probably due to the high cost
15 of the catalyst and of the sophisticated materials of construction necessary in presence of maleic acid at high temperature .

Considering again the processes of the first group based on the esterification of the maleic
20 anhydride, another distinction can be made between the processes based on the hydrogenation in vapor phase and the processes based on the hydrogenation in mixed liquid/vapor phase.

The new process introduced in the present
25 invention for the co-production of BDO and DMS belongs to the hydrogenation processes of diesters of the maleic anhydride in mixed phase.

Irrespective of the vapor or mixed phase, it is believed that the reaction of dimethyl maleate to 1,4-

butanediol proceeds through at least two intermediates, as follows:



In conclusion, dimethyl succinate, 1,4-butanediol, tetrahydrofuran and gamma-butyrolactone are products of reaction which are converted one to another by addition/subtraction of hydrogen and/or
5 water. The products distribution changes, by adjusting the operating parameters of the hydrogenolysis reaction or the type of catalysts.

In particular, dimethyl succinate represents the first product of hydrogenation and its final content
10 in the reaction product is, in the common practice, very low, below 10% or even below 2%. The residual amount of DMS is lower, as the temperature and pressure are higher and as the space velocity is lower.

15 In the prior art several inventions have been applied on the hydrogenation of maleic anhydride esters to produce 1,4-butanediol or, in some cases, to produce dimethyl succinate.

US patent 2,110,488 can be considered the first
20 application concerning the hydrogenation of an ester of aliphatic carboxylic acids to produce aliphatic alcohols using a catalyst consisting of copper oxide and chromium oxide, within a temperature range from 250 to 300 °C and within a pressure range from 150 to
25 300 atmospheres.

On the other hand, US patent 4,032,458 is the first application on the production of 1,4-butanediol, where a solution containing maleic acid is first subject to esterification by a monohydric alcohol. The
30 resulting dialkyl ester of maleic acid is hydrogenated

in two reaction steps, the first step to saturate the double bond present in the maleic acid and the second step to produce 1,4-butanediol and the monohydric alcohol. Both reaction steps uses a copper-chromite catalyst. Reaction temperatures are in the range from 100 to 300 °C, reaction pressures from 172 to 241 barg, being the catalyst dissolved in slurry. Moreover, since the catalyst of the first reaction step is copper chromite, the selectivity to DMS is low, with the resulting formation of hydroxyl group. WO patent 82/03854 is a generic process to hydrogenate a carboxylic acid ester in vapor phase with a catalyst comprising a mixture of copper oxide and zinc oxide. One of the several possible applications concerns the production of 1,4-butanediol from an ester of maleic, fumaric or succinic acid.

US patent 4,584,419 consists in a process to hydrogenate an ester of maleic anhydride to butanediol in vapor phase in the presence of a copper chromite catalyst.

US patent 4,656,297 is another process to produce butanediol by the hydrogenation in vapor phase of dimethyl succinate with copper chromite catalyst, by adding methanol to the ester feed.

US patent 4,751,334 is also an hydrogenation process in vapor phase with Cu-Cr or Cu-Zn oxide catalyst, to produce 1,4-butanediol from diethyl maleate in two or three adiabatic hydrogenolysis zones in series.

US patents 5,606,099 and 5,872,276 refers to a process to hydrogenate dialkyl maleate to dialkyl succinate in liquid phase at a pressure of from 50 to 400 bar, at temperature of from 30 to 160 °C and at
5 hydrogen/feed molar ratio from 20 to 40. The catalyst consists of pressed powders of the elements of the iron subgroup with addition of elements of transition groups IV or V or elements of sub-group VI, having particular compressive strength and internal surface
10 area.

US patents 6,100,410, 6,239,292, 6,274,743, 6,350,924, 6,433,192 and 6,433,193 describe different special integrations between a maleic anhydride plant and a BDO production plant, wherein the maleic
15 anhydride absorbed in an organic solvent is first esterified and the resulting maleic ester is stripped by a stream of hydrogen and then subject to an hydrogenation in vapor phase.

US patent 6,191,322 is a process for the
20 production of BDO by mixed phase catalytic hydrogenation of gamma-butyrolactone or succinic anhydride esters or their mixtures in two catalytic beds in series with injection of cold hydrogen between the reaction stages, at pressure of from 75 to 90 bar
25 and temperature between 160 and 250°C. The catalyst can be selected between copper and zinc oxide or copper chromite.

US patent 6,248,906 is a process where the maleic anhydride ester is subject to two subsequent
30 hydrogenation steps, where the primary hydrogenation

produces mainly GBL and THF and the secondary hydrogenation converts a fraction of GBL to BDO. The first reaction zone of the primary hydrogenation fully hydrogenates DMM to DMS, by using a noble metal based catalyst, in vapor phase, under moderate pressure, 3 to 40 bar, and high molar ratio hydrogen/ester feed. US patent 6,989,455 refers to a two stages hydrogenation process to butanediol, specific for a feedstream comprising maleic acid in water solution. The first reaction stage product comprises succinic acid. Owing of the corrosive effects of the maleic acid, the temperature of the first stage does not exceed 130°C. However, the process had not commercial application due to the poor resistance of catalysts applied in aqueous maleic acid solution.

US patent 7,598,404 refers to a process targeted to producing mainly tetrahydrofuran with enhanced utilization of the heat of reaction. The feed is first hydrogenated in a pre-reactor zone comprising catalyst, which favors the carbon double bond saturation, i.e. the production of dimethyl succinate from dimethyl maleate. In this way, the heat of reaction may be utilized in the evaporation of some of the liquid feed. Accordingly, in the second reaction zone, where THF and optionally diol and/or lactone are produced, the reaction occurs strictly under conditions of complete vaporization.

CN patent 101747149 discloses a method for prepare BDO by two stages hydrogenation in series, by using maleic acid dialkyl ester, where the effluent

from the first reaction step separates in two phases and the resulting liquid product is contacted again with hydrogen in the second hydrogenation section. The scope is to obtain high conversion and selectivity.

5 However, the 1,4 butanediol is the main product of both first and second reaction steps.

EP 2782893, similarly to US 7,598,404 relates to a first stage of reaction wherein the hydrogen saturates the double bond and produces preferentially dimethyl succinate and wherein one of the scopes is the improved use of the heat of reaction. Both stages of reaction operate in mixed liquid-vapor phase.

10 CN102070448 discloses a method for preparing dimethyl succinate, which includes two reaction steps of esterification and hydrogenation. The process is dedicated to a single product (DMS), and therefore in combination with a dedicated BDO plant to produce PBS it requires large investment.

CN102190582 relates to a method of simultaneously producing DMS, at low pressure, and BDO, at medium pressure, from DMM. However, two pressure levels are required and, therefore, the number of hydrogen compressors needs to be doubled accordingly.

25 CN 104193619 describes a process to produce dimethyl succinate, by hydrogenation and purification, using as raw material an intermediate product, a stream rich in dimethyl maleate and methanol, produced in the esterification unit of a butanediol plant. Rather than a real co-production of DMS and BDO in a single plant, the invention consists in two

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hydrogenation units, each one with independent reactor, compressor, heat exchangers and other equipment, connected in parallel.

Most of the above mentioned and other patents not
5 included in this application refer to the production of butanediol and/or tetrahydrofuran by hydrogenation of dialkyl maleate, mostly in vapor phase or, in few cases, in liquid or mixed phase. The reference to the formation of dimethyl succinate in a separate reaction
10 step, as for example in US 4,032,458, US 6,248,906, US 7,598,404 and EP 2782893, is always occasional and not addressed to the production or co-production of dimethyl succinate. Only CN102190582 and CN 104193619 introduce the co-production of BDO and DMS. However,
15 in both applications, the two products needs two separated hydrogenation compressor units, with evident higher investment and production costs.

Few other patents, for example US 5,606,099, US 5,872,276 and CN 102070448 relate only to the
20 production of dimethyl succinate, by hydrogenation of dimethyl maleate.

Matter of the present invention is a method of efficient and low cost co-production of 1,4-butanediol and dialkyl succinate from dialkyl maleates in a
25 single hydrogenation plant, by using the less expensive process in liquid-vapor mixed phase.

SUMMARY OF THE DISCLOSURE

The present invention relates to a process for the co-production of 1,4-butanediol and dialkyl

succinate by catalytic hydrogenation of dialkyl maleates.

The process consists essentially in the following steps:

- 5 a) hydrogenating a stream of dialkyl maleate in a first stage of reaction over suitable catalyst to produce dialkyl succinate;
- b) separating the effluent from the first stage of reaction in a flash vessel to produce a liquid
10 stream, rich in dialkyl succinate, and splitting this stream in three portions:
 - i) a first part, corresponding to less than 50 % by mol of total production, is further subject to low pressure phase separation, to separate the
15 absorbed hydrogen, and to distillation to produce high purity dialkyl succinate
 - ii) a second part is sent to the second stage of reaction
 - iii) a recirculation liquid, which by a pump is
20 cooled in a heat exchanger and sent back to the inlet of the first stage of reaction
- c) further hydrogenating the above second part of the dialkyl succinate produced in the first stage of reaction in a second stage of reaction, by using a
25 different suitable catalyst, for producing mainly 1,4-butanediol, together with minor amounts of gamma-butyrolactone and tetrahydrofuran as co-products; the effluent is subject to cooling, phase separation and distillation to produce 1,4-
30 butanediol

wherein,

the first stage of reaction operates from 80 to 130 °C
as inlet temperature, from 30 to 80 bar as pressure
and with liquid hourly space velocity from 0.5 to
5 2.0;

the second stage of reaction operates from 160 to 190
°C as inlet temperature, from 30 to 80 bar as
pressure and with liquid hourly space velocity from
0.1 to 0.3;

10 the hydrogen/organic feed molar ratio is in the range
from 15 to 30 in the first stage of reaction and
from 30 to 60 in the second stage of reaction;

the amount of dimethyl succinate, not converted in the
second stage of reaction and separated by
15 distillation in mixture with some amount of gamma-
butyrolactone, is recycled to the second stage of
reaction;

in both stages of reaction, the conditions as
hydrogen/organic feed ratio, pressure and
20 temperature are such to maintain the reactors in
mixed liquid/vapor phase.

The above-described operation in mixed
liquid/vapor phase represents one of the fundamental
aspects of the process presented in this application.

25 In fact, in most of the patents and in most of the
industrial plants for the production of BDO from
maleic anhydride, via dimethyl maleate as intermediate
product, the hydrogenation step occurs in vapor phase.
Because of the very large amount of circulating
30 hydrogen gas, both the reactants and the products of

reaction are in vapor phase. The possible dimethyl succinate produced in a hypothetical first stage of reaction could be separated from the reaction gas only by means of a substantial cooling and condensation
5 step, followed to a subsequent further stage of heating of the fraction of DMS fed to the hydrogenolysis stage for the production of butanediol. In conclusion, the process of the present application, characterized by DMS separation obtained with a simple
10 phases separation, is practicable only for reaction with relatively low circulation of hydrogen and with the hydrogenation reactions in mixed phase.

Anyhow, the practice in mixed phase does not constitute a limitation of the application. On the
15 contrary, as well described in EP 2782893, the hydrogenation in liquid/vapor phases, compared to the vapor phase, offers different advantages in terms of reduced investment cost, reduced energy consumption, higher reaction selectivity, better quality of the BDO
20 product and lower tendency of catalysts to fouling and deactivation problems.

Moreover, the advantages introduced by the present invention are also particularly enhanced when the process is applied to a dialkyl maleate feedstock
25 characterized by high purity. As a matter of fact, if the very high selectivity of the first stage of reaction, using a dedicated catalyst specialized for the hydrogenation of the double bond, meets a high purity of the feedstock, the result is a product of
30 exceptional purity. The resulting dialkyl succinate

needs a very simple purification or even it can be used as it is, without any purification.

The high purity dialkyl maleate could be produced for example according to U.S. patent No. 6,392,088, wherein the dialkyl ester produced by esterification of a dicarboxylic anhydride with methanol in a two stages reactive distillation system. The reaction product is afterward subject to an atmospheric stripping, to remove the excess of methanol, and then to a vacuum distillation, to separate as bottom product the homogeneous catalyst and the residual monoalkyl ester. The pure dimethyl ester is recovered as an overhead stream of the vacuum distillation column.

In order to preserve the high purity of the dialkyl succinate produced, the recycle of unconverted DMS to the hydrogenation, differently from the prior art, shall be sent to the second stage, rather than to first one. In fact, since the DMS forms an azeotropic mixture with GBL, the recycle stream is inevitably mixed with some amount of GBL, which, if recycled to the first stage of reaction, should deteriorate the quality of the DMS produced.

The two stages reaction system, as proposed in this invention, permits the co-production of DMS and BDO, used in mixture as raw materials for the production of polybutylene succinate, in a single industrial plant by using single compressor for the circulation of hydrogen. Moreover, the proposed method minimizes the amount of circulation hydrogen,

by using a lower hydrogen/organic feed molar ratio in the first stage of reaction, where the organic feed flowrate is higher. The molar ratio is higher in the second stage, where the organic feed flowrate, after the draw-off of the part of the product corresponding to the desired DMS production, is lower and where the reaction conditions and catalyst require a higher hydrogen amount.

Examples of suitable catalysts to be used in the first stage include low content palladium catalysts supported on carbon or on alumina or other noble metal, ruthenium or platinum, supported on carbon, alumina or silica. The content of noble metal is between 0.1 to 2.0 % by weight, relative to the total weight of the catalyst.

Examples of suitable catalysts for the hydrogenolysis reaction in the second stage include copper containing catalysts, such as copper-chromite catalysts or copper-zinc oxide catalysts.

Typically, the hydrogen used in the process is commercial pure hydrogen, with low content of inerts and other hydrocarbon components. Its amount is controlled to have a small stoichiometric excess but sufficient to ensure the completion of the reaction.

Both reaction zones operate at a pressure of 30 to 80 bar, preferably of 50 to 75 bar. Too low pressure increases the GBL yield and does not permit to maintain the reaction components in liquid phase. Pressure higher than 80 bar does not produce evident

yields advantage and causes only increased capital and operating costs.

The reaction temperatures are maintained at the inlet of the first reactor between 80 to 130 °C and
5 at the inlet of the second reactor between 160 and 190°C. Due to the exothermicity of the hydrogenation reactions, the outlet temperature in both stages is higher than the inlet temperature. A recirculation of cooled product in the first stage and the injection
10 of minor amounts of cold hydrogen recycle gas in the second stage permit the control of the reaction outlet temperatures.

One fundamental aspect of the present process is the use of different hydrogen/organic feed molar
15 ration in the two stages of reaction. In the first stage of reaction, where the organic feed flowrate is higher, the ratio is 15 to 30. In the second stage, where the reaction conditions and the catalyst require a higher hydrogen amount, the molar ratio is
20 30 to 60.

The contact time with catalyst, expressed in terms of liquid space velocity, is 0.5 to 2.0 hr⁻¹ in the first stage of reaction and 0.1 to 0.3 hr⁻¹ in the second stage of reaction.

25 The process of this invention allows modifying the relative molar ratio of dimethyl succinate and butanediol produced in a very simple manner: just by changing the flow rate of the DMS extracted at the outlet of the first stage of reaction. Therefore,
30 according to the present application, the DMS/BDO

ratio can be adjusted from 0.05, in case of a relative small production of PBS and a relative high production of BDO, used for other BDO derivatives or also, as pure product, for market sale, to around about 0.4 to 5 0.5, when all the production is intended for PBS production. When the final destination is the production of polyester co-polymers, as PBST or PBSA, or of blends of PBS with other polyesters using BDO, for instance a blend of PBS and PBAT, the process 10 permits the adjustment of molar ratio DMS/BDO at a value between 0.05 and 0.40, depending on the characteristics of the final copolymer or polymers blend.

According to the common knowledge described by 15 the technical literature and old applications, the process can also co-produce, besides DMS and BDO, also variable amounts of tetrahydrofuran (THF) and gamma-butyrolactone (GBL)

According for example to the process described in 20 EP 2782893, the THF/BDO ratio may be modified by means of moisture removal from the recycle gas. The THF production increases even by subjecting the butanediol to a process of dehydration at moderate temperature, 120 to 250 °C, which may occur by contact with an 25 acidic catalyst of the silica-alumina type or of the polymer-based resin with sulfonic acid group.

Moreover, the (THF+GBL)/BDO ratio may increase by lowering the pressure of the hydrogenation reaction.

Moreover, also the production of gamma- 30 butyrolactone may change from zero to around 5 to 15

percent, by adjusting its recycle rate, between full recycle to zero recycle, from the purification to the hydrogenation section.

5 BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a simplified process flow diagram of the hydrogenation system, as described in the summary of the disclosure points (a), (b) and (c), to co-produce dialkyl succinate and 1,4-butanediol and, optionally, gamma-butyrolactone and/or tetrahydrofuran by catalytic hydrogenation of dialkyl maleates;

Figure 2 represents the prior art, in three different configurations, as:

Fig. 2A is a block diagram, showing the production of PBS from n-butane, via maleic anhydride and two different hydrogenation plants, one to produce BDO and one to produce succinic acid;

Fig. 2B is a block diagram, showing the production of PBS, using as raw materials n-butane for the production of succinic acid and natural gas and/or coal to produce butanediol by the Reppe process;

Fig. 2C is a block diagram for the production of PBS, using renewable raw materials, commonly defined as bio-based materials;

Fig 3 is a block diagram according to the present process, with co-production of butanediol and dimethyl succinate used as raw materials for the polybutylene succinate manufacturing.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be now described with reference to the drawings.

Figure 1 illustrates a plant according to the invention for the co-production of DMS, BDO and, optionally GBL and THF, by catalytic reaction of a dialkyl maleate, typically dimethyl maleate, with hydrogen in mixed liquid-vapor phase.

The figure shows only the main unit operations relevant to the process of the present application, without including, for scope of clarity, the service equipment, as pumps or heat exchangers, which are normally included in an industrial plant, according to the chemical engineering principles.

The dimethyl maleate, produced by catalytic esterification of maleic anhydride, is fed as stream 1 in liquid phase. Stream 1 is mixed with stream 12, which represents the mixture of the fresh hydrogen stream 2 with the recycle gas stream 11.

The resulting stream 3 is therefore a mixed liquid/vapor fluid. After joining the cooled recirculation liquid stream 7 from the outlet of the first hydrogenation reactor, the resulting mixture stream 4 enters the first stage of reaction 21. It is a downflow fixed bed adiabatic reactor, containing a specific catalyst highly selective for the saturation of the carbon double bond contained in the dialkyl-maleate.

In the catalyst bed of reactor 21, the dimethyl maleate reacts to dimethyl succinate with very high

conversion and selectivity. This reaction is highly exothermic and therefore the outlet temperature of the effluent stream **5** is somewhat higher than the temperature of the inlet stream **4**. In a preferred embodiment of this process, the outlet temperature of the first reactor stage matches the inlet temperature of the second reaction stage and, therefore, no heating or cooling is necessary between the two stages of reaction. However, for scope of control in all possible plant modes of operation, a heat exchanger, even if not operated under the normal conditions of operation, may contribute to a better temperature control.

The effluent from the reactor first stage **5**, under controlled temperature, is a liquid/vapor mixture, where the liquid phase is mostly dimethyl succinate and the vapor phase is mostly hydrogen.

The effluent from the first stage of reaction enters a flash vessel to produce a liquid stream, rich in dialkyl succinate, which is divided in three portions. A first part stream **8**, corresponding to 5 to 50 mol% of the total production, is the raw DMS produced in the unit. It is further subject to low-pressure phase separation, to separate the absorbed hydrogen, and to distillation to produce high purity dialkyl succinate (not represented in the figure).

A second part of the liquid, stream **15**, is sent to the second stage of reaction, through for example an overflow pipe or a downcomer installed in a chimney

tray above the catalyst bed of the second stage of reaction.

A third part, the recirculation liquid steam 7, after cooling is sent back to the inlet of the first
5 stage of reaction, together with stream 3.

In Figure 1, the flash of the first reactor effluent occurs in an enlarged top section of the second stage of reaction, equipped with a chimney tray, including an overflow device, of pipe or
10 downcomer type. Thanks to the enlarged section of the reactor, the vapor phase, mostly hydrogen, and the liquid phase, mostly dimethyl succinate, separate each other. The vapor phase, stream 16, passes through the single chimney or multiple chimneys of the tray. The
15 liquid phase accumulates on the tray, which level is controlled by the overflow device. Part of the liquid, the first, stream 8, and the third part, stream 7, previously described, are extracted from a lateral nozzle, both of them under control of flowrate. The
20 liquid in excess stream 15, together with the vapor phase stream 16, enter the catalyst bed of the second stage reactor 22.

The enlarged top section of the reactor, as described in the figure 1, is the better and
25 economical solution for the separation of the phases. Of course, the process can use different engineering solutions, as the use of a flash vessel, separated from the reactor, to obtain the same results.

A further solution consists in the use of two stacked reactors, with intermediate separation of phases.

The liquid stream **14**, containing a minor amount
5 of unconverted DMS recycled back from the purification section of the plant, normally in mixture with some amount of GBL, also enters the catalyst bed of reactor **22**.

Efficient liquid distributor on top of the
10 catalyst bed of the reactor is used to prevent channeling effects.

Reactor **22** is also a downflow fixed bed adiabatic reactor, containing a catalyst different from the first stage and, more specifically, a catalyst
15 suitable for the hydrogenolysis of the dimethyl succinate to 1,4-butanediol; depending from the conditions of pressure and temperature, together with BDO, variable amounts of gamma-butyrolactone and/or tetrahydrofuran can be produced.

20 Product stream **9** from the reactor is first cooled and then it enters the separator vessel **23**, where the crude liquid product **13**, containing mostly BDO with lower percentages of gamma-butyrolactone, tetrahydrofuran, methanol, water, unreacted dimethyl
25 succinate and impurities, separates from the vapor phase stream **10**, consisting essentially in hydrogen, with lower amounts of methanol, tetrahydrofuran and water. The gaseous stream **10** is then recycled back via the compressor **20**, which differential pressure
30 corresponds to the total pressure drop, due to

reactors, heat exchangers, separators, piping and control valves, of the plant.

The discharge stream **11** from the compressor, together with the fresh hydrogen stream **2**, constitutes the overall reaction gas **12** used in the hydrogenation reactors.

EXAMPLE

The process of this application is now described by means of examples, with reference to the Fig.2A, 2B and 2C. that represent the prior art, in three different configurations, while fig.3 is a block scheme of the plants configuration, according to the steps and the operating conditions described in this invention.

For scope of clarity, the figures 2A, 2B, 2C and 3 use the same nomenclature, as follows:

the numbers identified by multiples of ten represent the units of production:

10 is a maleic anhydride production unit, by n-butane oxidation

20 is a succinic acid production unit, by hydrogenation of maleic anhydride

30A is a butanediol production unit, by esterification of MA with methanol to produce dimethyl maleate and by hydrogenolysis of DMM to BDO, according to the prior art

30B is a butanediol production unit, by esterification of succinic acid with methanol to produce dimethyl succinate and by hydrogenolysis of DMS to BDO

40 is a polybutylene succinate unit, through catalytic polycondensation of butanediol with succinic acid or with dimethyl succinate

50 is a methanol plant, starting from natural gas or other raw material

60 is a formaldehyde unit, using methanol feedstock

70 is an acetylene unit, starting from natural gas or coal

80 is butanediol unit, using the Reppe process

90 is a succinic acid unit, using a bio-process from renewable raw materials

100 is a butanediol production unit, by esterification of MA with methanol to produce dimethyl maleate and by co-production of dimethyl succinate and butanediol by two steps hydrogenation, according to the process of this application

The numbers from 1 to 5 are the original raw materials, fossil or renewable, used for the manufacture of PBS, as follows:

Stream 1 is the n-butane used for the production of maleic anhydride by catalytic oxidation in gas phase

Stream 2 is the hydrogen used for the hydrogenation/hydrogenolysis of maleic anhydride to succinic acid and to butanediol

Stream 3 is the natural gas used for production of methanol

Stream 4 is natural gas or coal used for production of acetylene

Stream **5** is a renewable raw material used for production of bio-succinic acid

Other numbers identify intermediate products, final product or recycle streams, as follows:

5 Stream **11** is the maleic anhydride produced from n-butane

Stream **12** is the maleic anhydride used for the production of succinic acid

10 Stream **13** is the maleic anhydride used for the production of butanediol

Stream **21** is the succinic acid produced from maleic anhydride

Stream **31** is the butanediol produced from maleic anhydride

15 Stream **32** is the butanediol produced from bio-succinic acid

Stream **41** is in both Figures 2 and 3 the final product, polybutylene succinate

20 Stream **42** represents the methanol recycled from the PBS unit to the BDO unit, according to the process described in this invention

Stream **51** is the methanol produced from natural gas

Stream **61** is the formaldehyde produced from methanol

25 Stream **71** is the acetylene produced from coal or from natural gas

Stream **81** is the butanediol produced from formaldehyde and acetylene, by the Reppe process

30 Stream **91** is the total bio-succinic acid produced from a renewable resource

Stream **92** is the fraction of bio-succinic acid used as feedstock for the PBS manufacture

Stream **93** is the fraction of bio-succinic acid used as feedstock for the production of butanediol

5 Stream **101** is the dimethyl succinate co-produced according to the process described in this invention

Stream **102** is the butanediol co-produced according to the process described in this invention.

10 Figure 2A represents the block diagrams showing the sequence of a plant for the production of PBS, according to a first option of the prior art, where the starting raw materials are n-butane, stream **1** and hydrogen, streams **2a** and **2b**. The n-butane enters the
15 plant **10**, where it produces by catalytic oxidation with air or oxygen, raw maleic anhydride, which is then recovered by organic solvent and purified, to produce maleic anhydride in liquid state, as stream **11**. The stream **11** is divided in two parts. The stream
20 **12** enters the plant **20**, where it is hydrogenated to succinic anhydride and hydrated to succinic acid, stream **21**. The second fraction of maleic anhydride stream **13** enters the butanediol plant **30A**, where it is transformed, through a process of esterification,
25 hydrogenation and distillation, to high purity butanediol, stream **31**. Stream **21** and **31** are the raw materials for the manufacture of polybutylene succinate stream **41** in the polycondensation plant **40**.

30 Figure 2B shows a second option according to the prior art, where the production of succinic acid

stream **21** follows the same route described in Fig. 2A, while the BDO is produced in plant **80** according to the Reppe route. Reppe route uses formaldehyde, stream **61**, and acetylene, stream **71**, as raw materials. In turn, the formaldehyde is produced from methanol stream **51** in the plant **60** and the methanol from natural gas stream **3** in plant **50**. Acetylene stream **71** is produced from coal or natural gas stream **3** in plant **50**. Totally, seven different plants are connected in series or parallel to finally produce PBS.

Fig. 2C is a third option, more popular and eco-friendly method of manufacturing PBS: corn, sugarcane molasses or other bio-masses, stream **5**, are transformed by fermentation and several steps of purification in plant **90**, to produce high purity solid succinic acid, stream **91**. Part of the SA is fed as stream **93** to a BDO plant **30B**, where by esterification, hydrogenation and purification, it is transformed in high purity BDO stream **32**. The BDO, together with the remaining part of SA stream **92**, enters the polycondensation plant **40**, where PBS, stream **41**, is produced by esterification and polycondensation. The scheme is seemingly very simple: the PBS is produced only by three units. Unfortunately, the complexity and the low selectivity of the bio-fermentation process cause a very high production cost of the succinic acid, which today limits the commercial success of this route.

Of course, the block schemes of Fig.2A, 2B and 2C do not represent the complete scenario of the prior

art for the production of PBS. For example in a combination of Fig.2B and Fig.2C, the BDO is produced by the Reppe process and the SA by bio-fermentation, with production of PBS partially from fossil material and partially from renewable resource.

In a different example, the bio-route of Fig.2C is modified, since the BDO may be produced directly by fermentation of biomasses without the intermediate production of succinic acid. In this option the unit **90** and **30B** are in parallel, rather than in series.

Whichever is the combination between bio-processes and conventional petrochemical processes, the result is a variable but always high cost of the final PBS product.

Finally, the Figure 3 illustrates the block scheme of the plants configuration, including the co-production of butanediol and dimethyl succinate, according to the steps and the operating conditions described in this invention. Same as in Figure 2A, the unit **10** represents a maleic anhydride production unit through catalytic oxidation of n-butane stream **1**. The maleic anhydride stream **11** enter the BDO plant **100**, which details are described in Figure 1. The two co-products from unit **100**, DMS stream **101** and BDO stream **102**, enter together the unit **40**, where is produced polybutylene succinate, stream **41**. The methanol, stream **42**, produced by transesterification reaction is recycled back to the BDO plant 100 and used for the esterification of the maleic anhydride to dimethyl maleate.

Incidentally, it should be noted that the production of PBS using dimethyl succinate rather than succinic acid offer two advantages.

First, while the succinic acid is a solid, the
5 dimethyl succinate is a liquid at ambient conditions and, therefore, it can be handled and well mixed with the other reagent, butanediol, much easier and efficiently compared to a solid material.

The second advantage is related to the expected
10 lower amount, approximately half, of tetrahydrofuran produced during the synthesis of PBS, compared to the use of succinic acid. Tetrahydrofuran is a by-product derived from the dehydration of butanediol and, therefore, the use of DMS contribute to the reduction
15 of the specific consumption of BDO and, by cascade, of hydrogen, maleic anhydride and n-butane.

Example 1 according to the invention.

In a units configuration according to Fig.3, 100
Kg/h of n-butane (stream **1**), with 97% purity, are
20 oxidized by air in a maleic anhydride plant **10**, to produce 100 kg/h of purified maleic anhydride, stream **11**, having a purity of 99.9%. The maleic anhydride enters the BDO synthesis plant **100**, together with 6.5 Kg/h of hydrogen, stream **2**, and 29.1 Kg/h of recycle
25 methanol, stream **42**, from the PBS unit **40**. All the gamma-butyrolactone produced in the hydrogenation and the unconverted DMS are separated in the distillation section of the unit and then recycled to the second hydrogenation reactor. The products from the BDO plant
30 to the PBS polycondensation unit **40** are 66.6 Kg/h of

DMS, stream **101**, and 45.4 Kg/h of BDO, stream **102**. The molar fraction of DMS, in the total feed to PBS unit, is around 0.47.

The polybutylene succinate product, stream **41**, is
5 around 77.4 Kg/h.

As summary, in this example, 100 Kg/h of n-butane produce 77.4 Kg/h of polymer.

Of course, the material balance of this example is simplified, since it does not show the oxygen
10 consumed, the unconverted n-butane and the water/carbon monoxide/carbon dioxide/organic acids produced in unit **10**, the THF and the small amount of by-products of unit **100**, the THF produced in unit **40** and other minor losses.

15 Example 2 according to the invention

In a process configuration in accordance with the present invention and as shown in Figure 1:

2 Kmole/h of dimethyl maleate, at 99 % purity, stream **1**, and 6.4 Kmole/h of hydrogen, at 99.99% purity
20 (stream **2**), join a hydrogen rich recycle stream **11**, containing 45 Kmole/h of hydrogen, and 10 Kmole/h of dimethyl succinate, stream **7**, recycled from the outlet of the first reactor.

The resulting combined temperature at the inlet
25 of the first stage of reaction **21** (stream **4**) is around 120 °C. The first reactor contains a single catalytic bed, consisting of ruthenium supported on alumina.

The outlet from the first stage of reaction, stream **5**, is flashed in a vessel for the separation of
30 the vapor phase, stream **16**.

The resulting liquid is divided in three parts, as follows:

Stream **7**: 10 Km³/h are cooled and recycled at the inlet of the first stage

5 Stream **8**: 0.9 Km³/h are separated as crude DMS product

The remaining liquid portion, stream **15**, enters the second reactor **22**, together with the hydrogen gas, stream **16**, separated in the flash vessel.

10 The second reactor contains a copper chromite catalyst in a single bed. The inlet temperature is 170 °C.

The pressure in both stages of reaction is 70 barg, with a slightly lower pressure in the second
15 stage due to the pressure drop.

The effluent from reactor **22** (stream **9**), after cooling at around 40 to 50 °C, not shown in Fig.1, enters the separation vessel **23**, where the crude liquid BDO, stream **13**, separates from the recycle gas
20 **10**.

The crude BDO is then sent to the distillation columns (not shown in the drawing), for the separation of THF, methanol, water, GBL/DMS azeotropic mixture, recycled back as stream **14** to the second reactor **22**.
25 Finally, the butanediol is separated from the light and heavy by-products.

The hydrogen rich gas stream **10** enters the compressor **20**. The compressed gas **11** joins the fresh hydrogen **2** and the resulting stream **12**, after heating

(not shown in the drawing), represents the total hydrogen gas entering the first stage reactor **21**.

The attached Table 1 and Table 2 summarize the main results of the operation, as conversion,
5 selectivity and operating parameters.

TABLE 1

First reactor-DMM Hydrogenation

	Fresh feed flowrate (DMM)	288.3 Kg/h
10	Hydrogen flowrate	
	Fresh	6.4 Kmole/h
	Recycle	45 Kmole/h
	Total	51.4 Kmole/h
	Temperature in/out	120/170 °C
15	Pressure	70 barg
	Liquid hourly Space Velocity	2.0 hr ⁻¹
	Molar ratio H ₂ /DMM	25.7
	DMM conversion	100 %
	Selectivity to DMS	higher than 99%
20	Crude DMS product	
	Flowrate	131.5 Kg/h
	Purity	98.5 wt %

TABLE 2

25 Second reactor-DMS Hydrogenolysis

	Fresh feed flowrate (DMS)	162 Kg/h
	Hydrogen flowrate	49.4 Kmole/h
	Temperature in/out	170/180 °C
	Pressure	69.8 barg
30	Liquid hourly Space Velocity	0.2 hr ⁻¹

Molar ratio H ₂ /DMS	44.9
DMS conversion	97.5 %
Selectivity to BDO	93 % (referred to the operation with total GBL recycle)

5 Crude BDO product

Flowrate	170 kg/h
Purity	53 wt %
(referred to the overall product, including methanol and water)	

10

CLAIMS

1. A process for co-producing, from dialkyl maleates and hydrogen, dialkyl succinate and 1,4-butanediol, said process comprising the following steps:

- 5 a) hydrogenating a stream of dialkyl maleate in a first stage of reaction over suitable catalyst to produce dialkyl succinate;
- b) further hydrogenating part of the dialkyl succinate produced in the first stage of reaction in a second stage of reaction, by using a different suitable catalyst, for producing an effluent comprising mainly 1,4-butanediol, together with minor amounts of gamma-butyrolactone and tetrahydrofuran as co-products; the effluent is subject to cooling, phase separation and distillation to produce 1,4-butanediol,
- 15 wherein,
- the first stage of reaction operates from 80 to 130 °C as inlet temperature, from 30 to 80 bar as pressure and with liquid hourly space velocity from 0.5 to 2.0
- 20 the second stage of reaction operates from 160 to 190 °C as inlet temperature, from 30 to 80 bar as pressure and with liquid hourly space velocity from 0.1 to 0.3 hr⁻¹
- 25 in both stages of reaction, the conditions as hydrogen/organic feed ratio, pressure and temperature are such to maintain the reactors in mixed liquid/vapor phase
- 30

characterized in that:

the effluent from the first stage of reaction is separated in a flash vessel to produce a vapor phase and a liquid phase stream, rich in dialkyl succinate, and splitting this stream in three portions:

i) a first part, corresponding to less than 50 %mol of total production, is further subject to low pressure phase separation, to separate the absorbed hydrogen, and to distillation to produce high purity dialkyl succinate;

ii) a second part is sent to the second stage of reaction;

iii) a recirculation liquid, which by a pump is cooled in a heat exchanger and sent back to the inlet of the first stage of reaction;

the hydrogen/dialkyl maleate feed molar ratio is in the range from 15 to 30 in the first stage of reaction and from 30 to 60 in the second stage of reaction; and

the dialkyl succinate, not converted in the second stage of reaction and separated in the distillation section in mixture with some amount of gamma-butyrolactone, is recycled to the second stage of reaction.

2. The process according to claim 1, wherein the operation is performed on a continuous basis.

3. The process according to claim 1, wherein the catalyst used in the first stage of reaction comprises a low content between 0.1 and 2.0 % by weight, relative to the total weight of the catalyst, of an active metal selected from the group consisting of palladium, ruthenium, platinum or mixture thereof, applied to a support material comprising carbon, aluminum oxide, silicon oxide.
4. The process according to claim 1, wherein the catalyst used for hydrogenolysis in the second stage is a copper containing catalyst, selected from a copper-chromite and a copper-zinc oxide catalyst.
5. The process according to claim 1 the dialkyl maleate is dimethyl maleate and dialkyl succinate is dimethyl succinate.
6. The process according to claim 5, wherein the dimethyl maleate has very high purity, not less than 97 wt%.
7. The process according to any of claims 1 to 6, wherein both reaction stages are fixed bed adiabatic reactors.
8. The process according to any of claims 1 to 7, wherein the inlet temperature to the second stage of reaction is controlled by the recirculation rate at the first stage of reaction.
9. The process according to any of claims 1 to 8 wherein the amount of the liquid recirculated from the outlet to the inlet of the first stage of reaction is from 1 to 10 times the weight amount of the compound to be hydrogenated.

10. The process according to claim 9, wherein the amount of the liquid recirculated from the outlet to the inlet of the first stage of reaction is from 2 to 4 times the weight amount of the compound to be hydrogenated.

11. The process according to any of claims 1 to 10, wherein the required hydrogen/dialkyl maleate feed molar ratio is achieved by cooling the effluent from the second stage of reaction at a temperature between 20 to 60 °C, by separating the resulting liquid and gaseous phases in a dedicated vessel, by recirculating the gaseous phase through a recycle compressor.

12. The process according to any of claims 1 to 11, wherein both the purified dimethyl succinate produced in the first stage of reaction and the purified 1,4-butanediol produced in the second stage of reaction are used as raw materials of a polyester unit, producing polybutylene succinate alone or, by using butanediol, dimethyl succinate together with terephthalic acid or adipic acid or esters of the two dicarboxylic acids, as co-polymer.

13. The process according to claim 12 wherein the methanol produced in the polybutylene succinate unit by transesterification is used together with maleic anhydride for producing the dimethyl maleate fed to the first stage of hydrogenation.

14. The process according to claim 1 wherein the flash of the first reactor effluent occurs in an enlarged top section of the second stage of reaction,

equipped with a chimney tray, including an overflow device, of pipe or downcomer type.

15. The process according to claim 1 wherein the separation of the vapor phase and liquid phase is
5 obtained using two stacked reactors, with intermediate separation of phases.