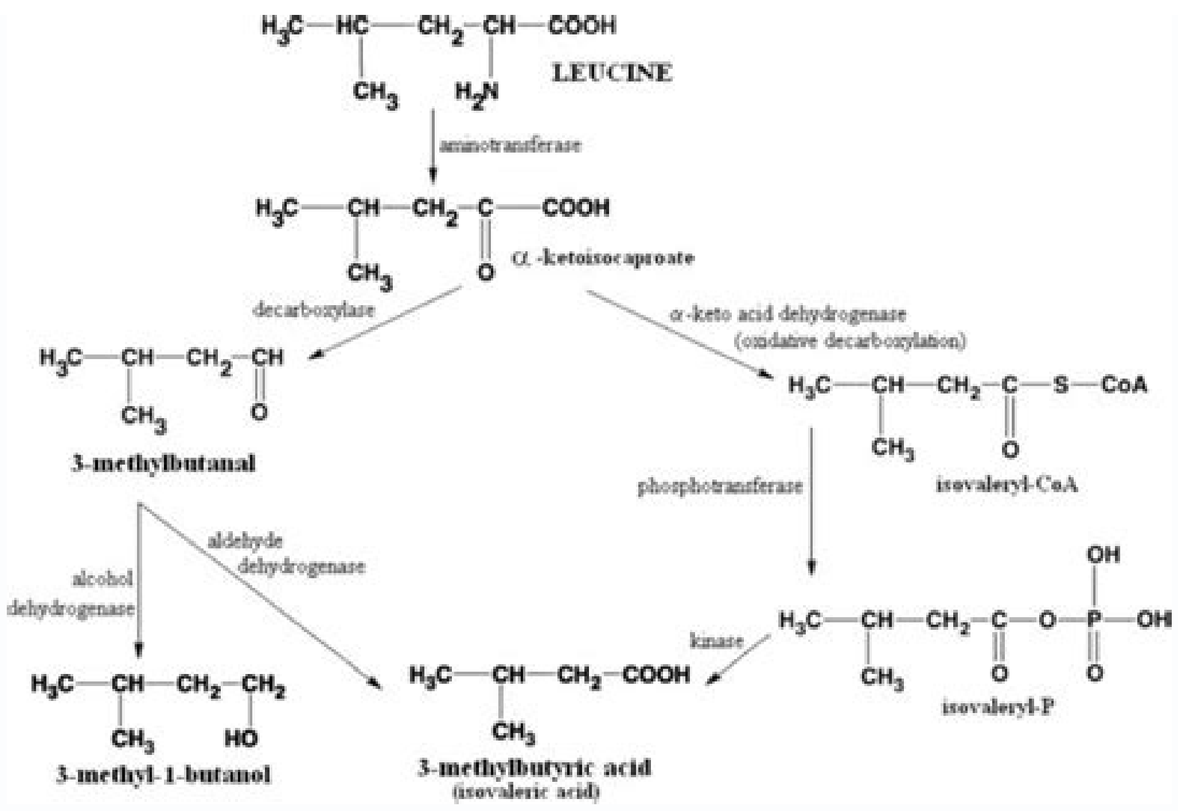
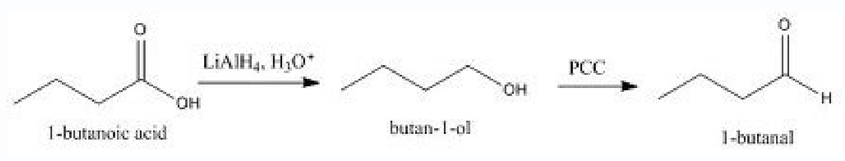
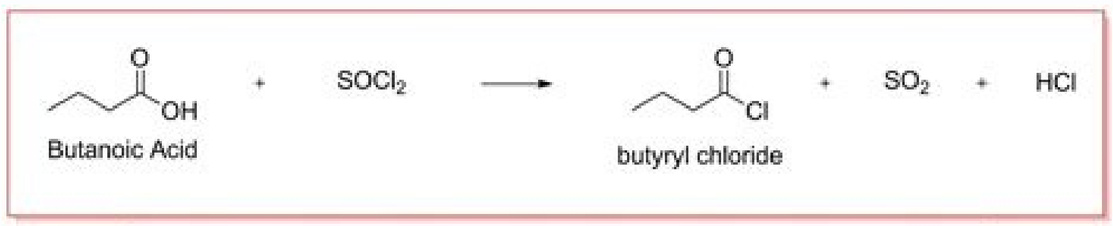
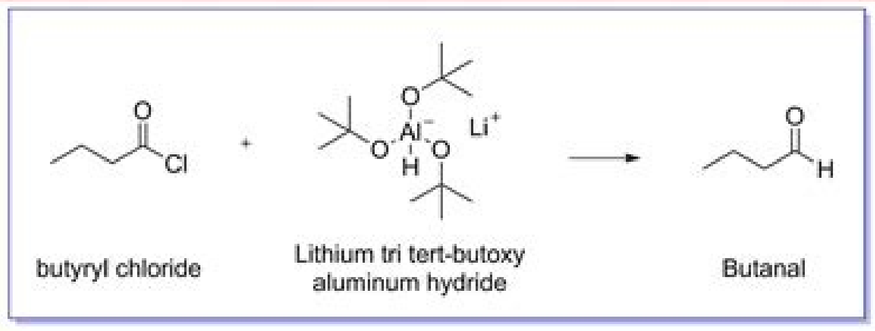
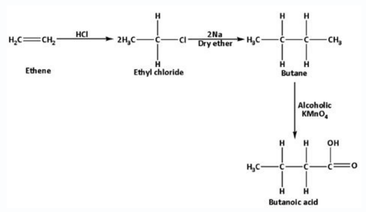
Formation of butanoic acid from butanol

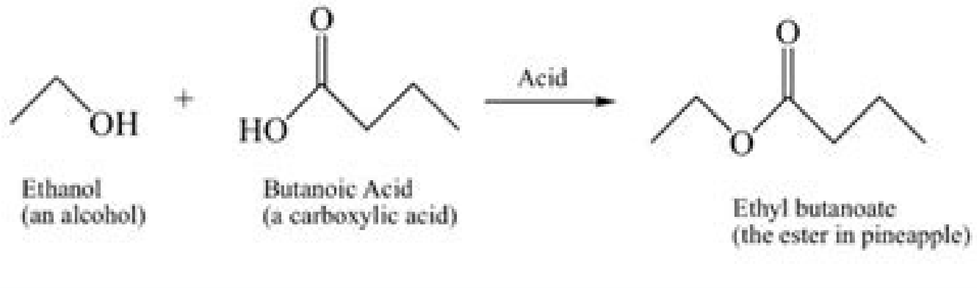












Formation of ethanoic acid.

Access through your institutionVolume 53, February 2017, Pages 194-200 rights and contentView full text Poly(β-hydroxy butyric acid) can be isolated from a suspension of bacterial cells, that is, Alcaligens eutrophus, by allowing the cells to flocculate by pH modification, followed by extraction of the polymer from the flocculated cells.From: Biopolymer Composites in Electronics, 2017 Novel and neglected issues of acetone-butanol-ethanol (ABE) fermentation by clostridia: Clostridium metabolic diversity, tools for process mapping and continuous fermentation systems. Patakova P, Linhova M, Rychtera M, Paulova L, Melzoch K. Patakova P, et al. Biotechnol Adv. 2013 Jan-Feb;31(1):58-67. doi: 10.1016/j.biotechadv.2012.01.010. Epub 2012 Jan 28. Biotechnol Adv. 2013. PMID: 22306328 Review. AnswerVerifiedHint: Butanoic acid is also known as butyric acid. Butanoic acid is a colourless clear liquid and has an unpleasant odour. The molecular formula for butanoic acid is ${\text{C}}{{\text{H}}_{\text{3}}} - {\text{C}}{{\text{H}}_{\text{2}}} - {\text{C}}{{\text{H}}_{\text{2}}} - {\text{C}}{{\text{H}}_{\text{2}}} - {\text{COOH}}$. We have to write the preparation reaction of butanoic acid from alcohol, alkyl halide and alkene.Complete step-by-step answer:We have to write the preparation reaction of butanoic acid from alcohol, alkyl halide and alkene.i.Butanoic acid can be prepared from an alcohol as follows:Butanoic acid can be prepared from butanol which is an alcohol. Butanol reacts with acidified potassium dichromate and produces butanoic acid. The reaction is as follows: In this reaction, acidified potassium dichromate acts as an oxidising agent which oxidises butanol to butanoic acid.ii.Butanoic acid can be prepared from an alkyl halide as follows:Butanoic acid can be prepared from ethyl chloride which is an alkyl halide. Ethyl chloride reacts with sodium metal in presence of dry ether and produces butane. Butane on reaction with alcohol potassium permanganate produces butanoic acid. The reaction is as follows: In this reaction, alcoholic potassium permanganate acts as an oxidising agent which oxidises butane to butanoic acid.iii.Butanoic acid can be prepared from an alkene as follows:Butanoic acid can be prepared from ethene which is an alkene. Ethene reacts with hydrochloric acid and produces ethyl chloride. Ethyl chloride reacts with sodium metal in presence of dry ether and produces butane. Butane in reaction with alcohol potassium permanganate produces butanoic acid. The reaction is as follows: In this reaction, alcoholic potassium permanganate acts as an oxidising agent which oxidises butane to butanoic acid.Note: Ethene reacts with hydrochloric acid according to the Markownikoff rule. The Markownikoff rule states that when an asymmetrical alkene reacts with an asymmetrical reagent, the negative part of the reagent gets attached to that carbon atom which has less number of hydrogen atoms. OSTI.GOV Journal Article: Bioalcohol production from acidogenic products via a two-step process: A case study of butyric acid to butanol This article presents the full study (lab-scale experimental study and large-scale techno-economic analysis) results of a two-step catalytic process for the conversion of organic waste–derived butyric acid to butanol. Butanol from biomass resources like organic waste promise to become an attractive and sustainable fuel and industrial precursor due to an increase in greenhouse gas content in the atmosphere. Therefore, research in this field is important for energy applications and reduction in greenhouse gas emissions. In this regard, a two-step process was applied in this study to produce butanol from butyric acid that can potentially be derived from organic waste. The two-step process consists of the (1) esterification of butyric acid to methyl butyrate and (2) hydrogenolysis of this methyl butyrate to butanol. The first reaction, esterification of butyric acid, was optimized using carbon-based catalysts. The production of butanol from methyl butyrate via hydrogenolysis was investigated using bimetallic Pt–Co catalysts. The hydrogenolysis of methyl butyrate on these catalysts under optimal conditions of 250 °C, 5 MPa H2, and a feed/catalyst weight ratio of 11.2 led to 54.1% selectivity toward 1-butanol. Based on the experimental results, an integrated process simulation model was developed to determine the economic potential of the two-step productionmore » of butanol from butyric acid. Using this model, the techno-economic feasibility of the two-step process was analyzed. Here, the minimum selling price (MSP) of 1-butanol produced from butyric acid using this process was US dollars 3.388 per gallon of gasoline equivalent (GGE). This MSP is in the range of recent biofuel market prices of US dollars 2.03/GGE to US dollars 3.83/GGE.« less Authors: Cho, Seong-Heon [1]; Kim, Juyeon [2]; Han, Jeehoon [2]; Lee, Daewon [3]; Kim, Hyung Ju [3]; Kim, Yong Tae [3]; Cheng, Xun [4]; Xu, Ye [4]; Lee, Jechan [5]; Kwon, Eilhann E. [1] Sejong Univ., Seoul (Korea) Chonbuk National Univ., Jeonju (Korea) Korea Research Inst. of Chemical Technology, Daejeon (Korea) Louisiana State Univ., Baton Rouge, LA (United States) Ajou Univ., Suwon (Korea) Publication Date: Wed Jul 03 00:00:00 EDT 2019 Research Org.: Louisiana State Univ., Baton Rouge, LA (United States) Sponsoring Org.: USDOE Office of Science (SC), Basic Energy Sciences (BES). Chemical Sciences, Geosciences & Biosciences Division; USDOE Office of Science (SC), Basic Energy Sciences (BES). Chemical Sciences, Geosciences, and Biosciences Division OSTI Identifier: 1656771 Alternate Identifier(s): OSTI ID: 1594044; OSTI ID: 1874081 Grant/Contract Number: SC0018408; 20163010092290; 2018R1D1A1A09082841 Resource Type: Journal Article: Accepted Manuscript Journal Name: Applied Energy Additional Journal Information: Journal Volume: 252; Journal ID: ISSN 0306-2619 Publisher: Elsevier Country of Publication: United States Language: English Subject: 09 BIOMASS FUELS; Short-chain fatty acid; Waste-to-energy; Techno-economic analysis; Biofuel; Butanol Cho, Seong-Heon, Kim, Juyeon, Han, Jeehoon, Lee, Daewon, Kim, Hyung Ju, Kim, Yong Tae, Cheng, Xun, Xu, Ye, Lee, Jechan, and Kwon, Eilhann E. Bioalcohol production from acidogenic products via a two-step process: A case study of butyric acid to butanol. United States: N. p., 2019. Web. doi:10.1016/j.apenergy.2019.113482. Cho, Seong-Heon, Kim, Juyeon, Han, Jeehoon, Lee, Daewon, Kim, Hyung Ju, Kim, Yong Tae, Cheng, Xun, Xu, Ye, Lee, Jechan, & Kwon, Eilhann E. Bioalcohol production from acidogenic products via a two-step process: A case study of butyric acid to butanol. United States. Cho, Seong-Heon, Kim, Juyeon, Han, Jeehoon, Lee, Daewon, Kim, Hyung Ju, Kim, Yong Tae, Cheng, Xun, Xu, Ye, Lee, Jechan, and Kwon, Eilhann E. 2019. "Bioalcohol production from acidogenic products via a two-step process: A case study of butyric acid to butanol". United States. . . @article{osti_1656771, title = {Bioalcohol production from acidogenic products via a two-step process: A case study of butyric acid to butanol}, author = {Cho, Seong-Heon and Kim, Juyeon and Han, Jeehoon and Lee, Daewon and Kim, Hyung Ju and Kim, Yong Tae and Cheng, Xun and Xu, Ye and Lee, Jechan and Kwon, Eilhann E.}, abstractNote = {This article presents the full study (lab-scale experimental study and large-scale techno-economic analysis) results of a two-step catalytic process for the conversion of organic waste–derived butyric acid to butanol. Butanol from biomass resources like organic waste promise to become an attractive and sustainable fuel and industrial precursor due to an increase in greenhouse gas content in the atmosphere. Therefore, research in this field is important for energy applications and reduction in greenhouse gas emissions. In this regard, a two-step process was applied in this study to produce butanol from butyric acid that can potentially be derived from organic waste. The two-step process consists of the (1) esterification of butyric acid to methyl butyrate and (2) hydrogenolysis of this methyl butyrate to butanol. The first reaction, esterification of butyric acid, was optimized using carbon-based catalysts. The production of butanol from methyl butyrate via hydrogenolysis was investigated using bimetallic Pt–Co catalysts. The hydrogenolysis of methyl butyrate on these catalysts under optimal conditions of 250 °C, 5 MPa H2, and a feed/catalyst weight ratio of 11.2 led to 54.1% selectivity toward 1-butanol. Based on the experimental results, an integrated process simulation model was developed to determine the economic potential of the two-step production of butanol from butyric acid. Using this model, the techno-economic feasibility of the two-step process was analyzed. Here, the minimum selling price (MSP) of 1-butanol produced from butyric acid using this process was US dollars 3.388 per gallon of gasoline equivalent (GGE). This MSP is in the range of recent biofuel market prices of US dollars 2.03/GGE to US dollars 3.83/GGE.}, doi = {10.1016/j.apenergy.2019.113482}, url = { , journal = {Applied Energy}, issn = {0306-2619}, number = , volume = 252, place = {United States}, year = {Wed Jul 03 00:00:00 EDT 2019}, month = {Wed Jul 03 00:00:00 EDT 2019} } Similar records in OSTI.GOV collections: Biochemical Process Engineering, Division of Chemical Engineering, Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, SE-971 87 Luleå, SwedenCorresponding author.*Corresponding author: Biochemical Process Engineering, Division of Chemical Engineering, Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, SE-971 87 Luleå, Sweden. Tel: +46920491012; Fax: +46920491399; Revised 2016 Feb 15; Accepted 2016 Mar 15.This is an Open Access article distributed under the terms of the Creative Commons Attribution License (, which permits unrestricted reuse, distribution, and reproduction in any medium, provided the original work is properly cited.Fermentation-based production of butyric acid is robust and efficient. Modern catalytic technologies make it possible to convert butyric acid to important fine chemicals and biofuels. Here, current chemocatalytic and biocatalytic conversion methods are reviewed with a focus on upgrading butyric acid to 1-butanol or butyl-butyrate. Supported Ruthenium- and Platinum-based catalyst and lipase exhibit important activities which can pave the way for more sustainable process concepts for the production of green fuels and chemicals.Keywords: butyric acid, butanol, catalytic upgrade, butyl-butyrate, esterification, lipaseFrom the perspective of a biobased economy, it is imperative to utilize renewable resources and to find efficient and innovative value chains from biomass to commodity chemicals and biofuels (Koutinas et al. 2014; Straathof 2014). Carboxylic acids are an important group of organic acids which are extensively used in the food and chemical industry. Fermentative production of organic acids can be very efficient and several, including citric acid, lactic acid, itaconic acid, succinic acid etc., are being produced on a commercial scale (López-Garzón and Straathof 2014). In principle, the functionality of carboxylic acids facilitates catalytic upgrading to broad range of compounds including aldehydes, esters, ketones, alcohols, alkanes, alkenes and olefins (Fig. 1) (Eggeman and Verser 2005). Fermentative production of organic acids is generally more efficient in comparison with the production of their corresponding aldehyde, alcohol, alkene or alkane. For example, the maximum concentration of 1-butanol obtained during fermentation is usually between 10 and 20 g L−1 whereas that of butyric acid is close to 90 g L−1 (Straathof 2014). Similarly, the obtainable concentration of propionic acid is about 105 g L−1 whereas it is 10.8 g L−1 for 1-propanol (Straathof 2014). Other groups of compounds such as esters and ketones are also very interesting target products which can be derived from carboxylic acids and used as commodity chemicals and biofuels (Gaertner et al. 2009; Ju et al. 2010; Chuck and Donnelly 2014). Hence, there is a great interest to explore methods to upgrade carboxylic acids to its derivatives as means for more efficient process concepts. This paper will review current state of the art technologies for the catalytic upgrading of butyric acid with particular focus on 1-butanol or butyl-butyrate as the target products. Both chemocatalytic and biocatalytic strategies will be covered.Butyric acid is an ill-smelling 4-carbon carboxylic acid which has important applications in the solvent, polymer and specialty chemical market and is currently produced by petrochemical means through the oxy process (Mascal 2012). Microbial production of butyric acid production is performed anaerobically and is generally robust and straight forward with acetic acid being the most notable side product (Fayolle, Marchal and Ballerini 1990). Clostridium tyrobutyricum has been identified as the most efficient producer of butyrate, reaching concentrations up to about 60 g L−1 in batch fermentation and up to about 73 g L−1 in fed-batch cultivation using glucose as the carbon/energy source with the corresponding productivities of 0.78 and 1.41 g L−1·h, respectively (Song et al. 2010). Using C. tyrobutyricum immobilized on fibrous beds and a repeated fed-batch technique a butyric acid concentration of 87 g L−1 could be reached on glucose with a productivity of 1.1 g L−1·h (Jiang et al. 2011). Continuous production with cell recycle has been used to reach a productivity of 9.5 g L−1·h while maintaining a butyrate concentration of 29.7 g L−1 (Michel-Savin, Marchal and van de Casteele 1990). Clostridium tyrobutyricum can utilize several sugars including glucose, fructose, xylose and arabinose (although some of them may not be co-utilized) and is hence well suited to ferment lignocellulosic hydrolysates (Zhu, Wu and Yang 2002; Huang et al. 2011). For example, using a fed-batch process and a combination of sweet sorghum stalk hydrolysate and beet molasses as feed-stock a butyric acid concentration of 58.8 g L−1 was achieved with corresponding yield and productivity 0.52 g g−1 fermented sugars and 1.9 g L−1·h, respectively (Sjöblom et al. 2015).Recovery costs are generally in the range of 30%–40% of the total production cost for carboxylic acids, and it is hence crucial to find competitive process concepts in order to make biobased production economically feasible (López-Garzón and Straathof 2014). Product recovery of carboxylic acids from fermentation broths is challenging as they are highly water soluble, can shift between the carboxylate and acid form and are often diluted. Extraction and adsorption are the most prevalent recovery methods although the requirement to completely convert the carboxylate into its acid or carboxylate form before recovery may consume substantial amounts of mineral acids or bases (López-Garzón and Straathof 2014).Considering biobutanol or butyl-butyrate production from butyric acid, reactive extraction and reactive regeneration by esterification has received attention as they can minimize waste and material use (Eggeman and Verser 2005). In a patent application (Kang et al. 2011), a method was described where butyric acid was complexed with tripentylamine forming a water insoluble phase which subsequently was decomposed in a distillation column enabling reuse of the amine and recovery of pure butyric acid in the top. Extraction trials made with tripentylamine showed that 99% of the butyric acid could be recovered in the amine layer.Aqueous two-phase partition is a liquid–liquid extraction method which was evaluated for the separation between butyric acid and acetic acid in fermentation broth (Wu et al. 2010). Exploiting the tendency for acetic acid to remain in the aqueous salt solution, butyric acid could selectively be salted out of the aqueous solution by the addition of calcium chloride causing two phases to appear where the upper phase is enriched in the butyric acid. With this method, the ratio BA/AA could be increased from 4.02 to 8.9 in the upper phase of the fermentation broth. Extraction of butyric acid from C. tyrobutyricum fermentation broths were also studied in a polyethylene glycol/Na2SO4 aqueous two-phase system (Wu et al. 2015). In this method, Na2SO4 was first added to salt out cell protein, sugars and nitrogen compounds, followed by filtration and transferring to PEG. The major components of the resulting PEG-rich phase were butyric acid, acetic acid and butanol. The PEG was precipitated with an iodine solution and filtered. The filtrate was subsequently distilled to separate butyric acid, where at the optimal conditions a yield as high as 91.74% ± 0.46% was demonstrated.Zeolites could be a possible option for recovery of butyric acid from fermentation broths by adsorption. When a hydrophobic MFI type zeolite was investigated for the selective adsorption of 1-butanol from model ABE fermentation broths, butyric acid was co-adsorbed with 1-butanol (Faisal et al. 2014). Without butanol present, selective adsorption of butyric acid could be accomplished. The results obtained are encouraging; however, more experiments should be performed using real fermentation broths and column breakthrough experiments.The upgrading of carboxylic acids to their corresponding aldehydes, alcohols and hydrocarbons require carefully balanced oxygen removal reactions. Several catalytic routes can be applied for this purpose including dehydration, hydrogenolysis and hydrogenation (De, Saha and Luque 2015). In order to produce larger molecules appropriate for use as diesel and jet fuels, C–C coupling reactions such as ketonization or esterification reactions can be exploited (Gaertner et al. 2009; Ju et al. 2011; Chuck and Donnelly 2014). In the literature, there are several patents and reports describing the preparation and application of mixed heterogeneous metal catalysts on various supports (for example, RuCoPdZn/Al2O3, Co-Pt/SiO2 and Ru-Sn/Al2O3) for the hydrogenation of C1-C6 carboxylic acids to produce biofuels (Pesa, Graham and Kliewer 1984; Yang 2008; Johnston et al. 2009). By carefully adjusting the reaction conditions and the composition of the catalysts, the activity and selectivity can be adjusted to favor the aldehyde, ester or alcohol. For example, whereas Ru/TiO2 showed 98% selectivity toward ethylacetate, Pt-Sn/TiO2 displayed 99% selectivity for ethanol during catalytic hydrogenation of acetate (Mclachlan, Pimblett and Price 1991).Development of a catalyst with the proper activity, selectivity and stability is challenging, particularly considering the corrosive nature of monocarboxylic acids and the low reactivity of the carboxyl group in comparison to other carbonyl groups such as ketones and aldehydes (Manyar et al. 2010; Lee et al. 2014). Catalyst poisoning, oxidation of the metal, loss of metal due to leaching, loss of metal specific surface area due to sintering or pore occlusion and coke formation must be minimized to prevent deactivation of the catalyst (Santillan-Jimenez and Crocker 2012). In order for chemocatalytic upgrading to be commercially applicable, efficient recovery processes of the carboxylic acid in combination with cost effective catalytic systems must be developed. Integrated recovery and upgrading systems are highly attractive as they can minimize waste and energy consumption.For the conversion of acetic-, hexanoic-, nonanoic- and dodecanoic acid to their corresponding aldehydes, the oxide catalysts Fe2O3, Cr2O3, Cr2O3/TiO2 and V2O5/TiO2 have shown high selectivity. Ru-Sn/Al2O3 the conversion of acetic acid was 85% with a selectivity of 59% for the aldehyde at 300°C (Yokoyama and Yamagata 2001).Reactive extraction of butyric acid with a trialkylamine followed by esterification and hydrogenolysis was previously mentioned as an interesting route for biobased production of butyl-butyrate or 1-butanol from butyric acid. In principle, 1 mol of butyric acid and 1 mol of 1-butanol are esterified to 1 mol of butyl-butyrate which subsequently is hydrogenolyzed to 2 mol of 1-butanol (Ju et al. 2010; Kang et al. 2011). One part of the butanol is then used as a product and one part is used for the esterification reaction. The intermediate step of esterification allows milder conditions to be used compared to direct catalytic conversion to butanol, although the development of new catalysts and process design may level this difference. The hydrogen produced by C. tyrobutyricum could in principle be used for the hydrogenolysis reaction making the process more sustainable (Kang et al. 2011).Esterification trials between butyric acid and 1-butanol have been made using various catalysts including the commercially available strong ion exchange resin catalyst DOWEX 50WX8-400, DOWEX 50WX2-400, Amberlyst 70 and Amberlyst 121 at different temperatures (100°C –120°C) and different butanol to butyric acid molar ratios (2 and 3). Conversion, selectivity and yield of butyl-butyrate were found to be high, typically ranging between 90% and 99% (Table 1) (Kang et al. 2011). The stability was reported to be good with a conversion and selectivity of 99% and 97%, respectively, over 1 month with Amberlyst 70 and a reaction temperature of 110°C.Summary of data for chemocatalytic upgrading of butyric acid to various derivatives.TargetTPressConversionSelectivity forYieldCatalystReactionproduct(°C)(atm)(%)target prd (%)(%)ReferenceDowex 50Wx8-400Esterification of BA and ButOHBuB100na97.399.496.7Kang et al. (2011)Dowex 50Wx2-400Esterification of BA and ButOHBuB120na97.598.996.4Kang et al. (2011)Amberlyst 70Esterification of BA and ButOHBuB110na98.298.096Kang et al. (2011)Amberlyst 121Esterification of BA and ButOHBuB110na96.299.195.3Kang et al. (2011)1%Pa-Cu/ZnO/Al2O3Hydrogenolysis of BuBButOH1751098.799.898.5Kang et al. (2011)Ru/ZnOHydrogenation of BAButOH2652562.497.8NaLee et al. (2014)1Ru-2Sn/ZnOHydrogenation of BAButOH2652599.998.6NaLee et al. (2014)1.0Ru/CAPHDO of BAButOH1906393.53.3NaChen et al. (2011)MnOx/CeO2Ketonization of BA4HN410128>98NaMurkete, Jackson and Miller (2011)CM-HMSKetonization of BA4HN410136>98NaMurkete, Jackson and Miller (2011)CM-MCM-41Ketonization of BA4HN410131>98NaMurkete, Jackson and Miller (2011)Subsequent hydrogenolysis of butyl-butyrate to butanol was tested with a commercially available Cu/ZnO/Al2O3 catalyst prepared with 1.0 wt% palladium. With a downstream reactor pressure of 10 atm, the hydrogenolysis reaction was favored when the temperature increased from 150°C to 200°C, the hydrogen to butyl-butyrate ratio increased from 10 to 35 and the space velocity was decreased from 1 to 0.3 h−1. The yield for the hydrogenolysis reaction was decreased from about 92% to 86% over 720 h.There are also promising catalysts for direct conversion of butyric acid to 1-butanol using ZnO supported Ruthenium–Tin bimetallic catalysts (Lee et al. 2014). At 265°C and a hydrogen pressure of 25atm, vapor phase hydrogenation showed 99.9% conversion of butyric acid with a selectivity of 98.6% for 1-butanol. Lasting for 145 days without significant deactivation, the 1Ru-2Sn/ZnO catalyst showed a very high stability and durability. The direct conversion could facilitate a simpler process design and a better economy compared intermediate esterification.Liquid phase hydrogenation using titania supported Pt and Pt-Re bimetallic catalysts were evaluated on a selection of aliphatic and cyclic carboxylic acids (Manyar et al. 2010). These catalysts exhibited high activity at relatively mild conditions (130°C and a hydrogen pressure of 19.7atm). Generally, it was observed that the Pt-Re/TiO2 catalysts had reduced selectivity toward the alcohol compared to the Pt/TiO2 catalysts. Aqueous phase hydrogenation or hydrodeoxygentation (APHDO) is very important reactions because they would allow the catalytic upgrading to occur in water solutions, which is the intrinsic solvent of carboxylic acids produced by fermentation, hence, reducing energy intensive and costly water removal operations (Chen et al. 2011). Carbon supported Ruthenium (Ru/C) catalysts that have shown promising results for the aqueous phase hydrogenation of lactic acid to propylene glycol performed at 100°C – 170°C and hydrogen pressures of 7–14MPa, displaying selecitivies of 90%–95% and nearly complete conversion (Zhang, Jackson and Miller 2001).APHDO of mono carboxylic acids in order to produce their corresponding alcohols or alkanes was investigated using Ru/C, Ru/ZrO2 and Ru/Al2O3 catalysts at a hydrogen pressure of 6.4 MPa (63.2 atm) (Chen et al. 2011). With C2–C4 carboxylic acids and 1.0Ru/C catalysts, it was generally found that when the reaction temperature increased from 150°C –190°C the conversion increased at the expense of the selectivity for the alcohol. At the high temperature, the C–C bond cleavage reaction was dominant and the major products were alkanes with one less carbon than the original acid. For butyric acid, the conversion was 93.5% but the selectivity for 1-butanol was only 3.3%, with 22.3% for methane, 0.2% for ethane, 64.4% for propane and 9.6% for butane. Further, studies on propionic acid showed that the use of Al2O3 support could largely inhibit the C–C bond cleavage reaction in contrast to C or ZrO2 supports.In addition to esterification, ketonization is another interesting C–C coupling reaction which could be used to create larger chain molecules appropriate for diesel and jet fuels (Gaertner et al. 2009). Ceria-zirconia catalysts and supported mesoporous solid base catalysts are promising for ketonization reactions (Gaertner et al. 2009; Murkete, Jackson and Miller 2011). The synthesis of 4-heptanon from butyric acid was investigated using supported mesoporous solid base catalysts at 410°C and atmospheric pressure (Murkete, Jackson and Miller 2011). The conversion was about 30% with a selectivity larger than 98% toward 4-heptanone in all cases.Enzymatic catalysis is gaining increasing attention as it is considered to be more environmental friendly compared to the chemical catalysis. Normally, lower temperatures are required compared to chemical catalysis and there is no need for use of harsh chemicals, preventing also the generation of wastes that need to be further treated. Moreover, enzymatic reactions are very selective, minimizing the formation of by-products. Esterification of organic molecules (e.g. butanol) can yield esters, like butyl-butyrate, with excellent characteristics as fuel additives. These esterification reactions are carried out by lipases (triacylglycerol acylhydrolase; EC 3.1.1.3). Although the mode of action of lipases involves the hydrolysis of ester bonds they differ from the other esterases due to the fact that they demonstrate a unique action in the interface of aqueous and organic solutions (Pandey et al. 1999). Lipases are catalyzing both hydrolysis and esterification reactions depending on the reaction conditions.Lipases have the ability to perform esterification between a wide variety of alcohols (acceptor) and organic acids (donor). For example, Martins et al. (2014) evaluated the esterification efficiency of different commercial lipases (Novozym 435, Lipozyme RM-IM and Lipozyme TL-IM) on a variety of alcohols (ethanol, isopropyl alcohol, butanol and pentanol) and organic acids (acetic, propionic and butyric acid). Butanol was an excellent candidate as it was efficiently esterified with all the acids.Novozym 435 (Candida antartica lipase B) was used for the esterification of 1-butanol with acetic acid and the formation of butyl-acetate by Martins et al. (2011), where a high conversion rate (91.5%) was achieved (Table 2). Moreover, the authors demonstrated that the lipase can be re-used for several cycles without significant loss in activity if a washing step with solvent takes place between batches. This positive effect of ‘solvent-washing’ step was also demonstrated in another work of Rodrigues et al. (2008). Re-use of the lipase is of great importance for industrial applications, as it reduces the operational costs. In another work with the same enzyme, Martins et al. (2013c) examined the effect of low-frequency ultrasound (40 kHz) on the efficiency of butyl-acetate formation. The authors demonstrated that the ultrasound improved the process not only by increasing the productivity (7.5-fold higher compared to the control), but also by improving the stability of the enzyme in higher amounts of acetic acid (2M instead of 0.3M) and also by enabling the direct re-use of the lipase. Ultrasounds (40 kHz, 220W ultrasonic bath) were also used by Paludo et al. (2015). Moreover, they demonstrated that the use of molecular sieves during esterification can provide a water-free environment, as it removes the water released during the esterification, and resulted in re-using the lipase for ten cycles without any loss of activity. Another enzyme that was used for the preparation of butyl-acetate is Lipozyme IM20 (lipase from Rhizomucor miehei) (Kumar and Rao 2003). Among the different solvents evaluated, n-hexane, isooctane, cyclohexane and n-heptane were the most efficient, whereas chloroform, dioxane and THF resulted in very poor esterification due to the destruction of the essential hydration layer and subsequently deactivating the lipase.Summary of data for enzymatic upgrading of butyric acid and butanol to various derivatives.ProductDonorAcceptorLipaseSystemYield (Time)T (°C)ReferenceButyl-acetateAcetic acidButanolNovozym 435Hexane91.5% (2.5 h)40Martins et al. (2011)Butyl-acetateAcetic acidButanolNovozym 435Hexane94% (2.5 h)46Martins et al. (2013a)Butyl-acetateAcetic acidButanolLipozyme IM20Hexane90% (96 h)45Kumar and Rao (2003)Butyl-butyrateButyric acidButanolType VIIHeptane75% (24 h)41Santos and de Castro

(2006)Butyl-butyrateButyric acidButanolLipozyme RM-IMHexane>90% (16 h)40Lorenzoni et al. (2012)94.8% (24 h)Butyl-butyrateButyric acidButanolLipozyme TL-IM or MCI-TLLHexane~95% (7 ha)50Martins et al. (2013b)Butyl-butyrateButyric acidButanolLipozyme TL-IMHexane95% (3 h)48Martins et al. (2013c)Butyl-butyrateButyric acidButanol Mucor sp. lipaseCyclohexan95% (24 h)35Abbas and Comeau (2003)Butyl-caproateCaproic acidButanol Mucor sp. lipaseCyclohexan100% (24 h)35Abbas and Comeau (2003)Ethyl-butyrateButyric acidEthanolLipozyme TL-IMSolvent-free90% (6 h)30Paludo et al. (2015)Butyl-butyrateButyric acidButanolNovozym 435Hexadecane in aqueous broth media34 mM37van den Berg et al. (2012)Santos and de Castro (2006) used a lipase from C. rugosa (lipase type VII) for the formation of butyl-butyrate esters resulting in a concentration of 32.4 g L−1. Another lipase from R. miehei (Lipozyme RM-IM) was used for the same esterification by Lorenzoni et al. (2012). This lipase presented high efficiency toward butyl-butyrate resulting in a concentration of 948 mM (24 h) with a productivity of 1.22 and 0.85 mmol of ester/(g of catalyst)ċh after 16 and 24 h, respectively. Another commercial lipase that was used for the preparation of butyl-butyrate was Lipozyme TL-IM (from Thermomyces lanuginosus lipase—TLL). Martins et al. (2013a) compared an in house immobilized TLL with MCI GEL CHP20P (MCI-TLL) and an already immobilized TLL in silicate support (Lipozyme TL-IM). Although with both support materials the TLL resulted in the same conversion (around 95%), the initial conversion rates of MCI-TLL were higher and the productivity of MCI-TLL was 14.5 mmol g−1·h compared to 3.2 mmol g−1·h of the Lipozyme TL-IM. This difference in productivity was a result of the ability of MCI-TLL to act with higher concentrations of butyric acid, underpinning the importance of appropriate selection of supporting material for immobilization. The same lipase was efficiently used by another work, demonstrating high re-usability when washed with n-hexane (Martins et al. 2013b). Finally, a non-commercial lipase from Mucor sp. was also evaluated in a combinations of acids (propionic, butyric and caproic) and alcohols (methanol, ethanol, allyl, butanol, isoamyl, geraniol, citronellol and farnesol) resulting in high yield of esters (Abbas and Comeau 2003).All the aforementioned works performed the esterification in ‘pure’ 1-butanol. On the other hand, due to the relative low concentrations of 1-butanol in the fermentation broths of ABE, there is a great interest to enable the direct esterification of 1-butanol and butyric acid in situ, avoiding energy demanding downstream processes of separation. By applying this process not only the cost of the process is reduced, but also the levels of 1-butanol are kept low minimizing the inhibitory effect toward the fermenting bacteria. A phase of an organic solvent is also necessary in order to enable the esterification to take place. When aiming for diesel enrichment with butyl-butyrate, the possibility of direct esterification in the diesel is interesting as there would be no need to separate the ester after its synthesis, hence, leading to more practical and economical systems for the production of ‘green’ fuels. An interesting feature about lipases is that they catalyze the ester synthesis particularly well in inorganic solvents including n-alkanes such as hexane, dodecane and hexadecane, which are major constituents of petroleum fuels (Zaks and Klibanov 1985). The fact that the enzyme catalyzed synthesis of butyl-butyrate could be performed in these types of hydrocarbons opens up the possibility for one-pot diesel enrichment with butyl-butyrate. This process was evaluated by van den Berg et al. (2012) by using Novozym 435 to directly esterify 1-butanol and butyric acid that are produced during ABE fermentation in a hexadecane phase. The highest concentration that was detected in the hexadecane phase was 4.9 g L−1 (34 mM), which although is not very high, and it is a first step for the development of an efficient one-pot process. Preliminary work by the authors have demonstrated that esterification of 1-butanol and butyric acid to butyl-butyrate could be performed directly in diesel fuel with a conversion efficiency of 70%–80% using Novozym 435 (work in progress).Another approach of biological conversion of butyric acid to 1-butanol involves the whole-cell catalysis with the hyperthermophile Pyrococcus furiosus, which has the ability to hydrogenate carboxylic acids selectively to the corresponding alcohols (Ni et al. 2012). More specifically, the authors mentioned that P. furiosus has the ability to couple H2 oxidation with the reduction of carboxylic acids under highly chemoselective conditions. Although the conversion of butyric acid to 1-butanol was only 28% (compared to, e.g. pentanoic acid to n-pentanol which accounted for >99%), it was an important discovery and further improvements can be made.The ability to increase the reduction potential of microorganisms having butanol as an intermediate in their metabolic pathways using electricity has shown that it possible to produce 1-butanol from butyric acid or glycerol (Sharma et al. 2013; Choi et al. 2014). Hence, coupling electricity derived from wind-, hydro- and solar power, with microbial reduction of various carbon sources could be an efficient way of storing excess electrical energy in the form of biofuel molecules and organic commodities.The research in catalytic upgrading of carboxylic acids has made a very important progress during the last years. Upgrade can be performed with both chemical and biological routes. Ru-Sn/Al2O3 catalyts may be a good starting point for upgrading of butyric acid to butanal through hydrogentation. For direct catalytic conversion of butyric acid to 1-butanol 1Ru-2Sn/ZnO and Pt/TiO2 catalysts are promising. For APHDO, Ru/Al2O3 appear promising for conversion of BA to 1-butanol. For esterification of BA and 1-butanol DOWEX 50WX8-400, DOWEX 50WX2-400, Amberlyst 70 and Amberlyst 121 have shown good results. Ketonization to 4-heptanone may be performed with ceria-zirkonia or supported mesoporous solid base catalysts. On the other hand, biological catalysis can take place with either enzymes or whole cells. Different enzymes have been used, which resulted in high conversion rates. One important aspect of enzyme use is the ability to re-cycle and re-use the catalyst for several catalysis cycles. This was demonstrated by either applying a solvent washing step or by using ultrasounds. On the other hand, whole-cell catalysis is a ‘technology’ not fully explored and its maximum potential needs to be discovered.We thank Bio4Energy, a strategic research environment appointed by the Swedish government, for supporting this work. Conflict of interest. None declared.Abbas H, Comeau L. Aroma synthesis by immobilized lipase from Mucor sp. Enzyme Microb Tech. 2003;32:589–95. [Google Scholar]Chen L, Zhu Y, Zheng H, et al. Aqueous-phase hydrodeoxygenation of carboxylic acids to alcohols or alkanes over supported Ru catalysts. J Mol Catal A-Chem. 2011;351:217–27. [Google Scholar]Choi O, Kim T, Woo HM, et al. Electricity-driven metabolic shift through direct electron uptake by electroactive heterotroph Clostridium pasteurianum. Sci Rep. 2014;4:6961. doi: 10.1038/srep06961. [PMC free article] [PubMed] [CrossRef] [Google Scholar]Chuck CJ, Donnelly J. The compatibility of potential bioderived fuels with jet A-1 aviation kerosene. Appl Energ. 2014;118:83–91. [Google Scholar]De S, Saha B, Luque R. Hydrodeoxygenation processes: advances on catalytic transformations of biomass-derived platform chemicals into hydrocarbon fuels. Bioresource Technol. 2015;178:108–18. [PubMed] [Google Scholar]Eggeman T, Verser D. Recovery of organic acids from fermentation broths. In: Davison BH, Evans BR, Finkelstein M, et al., editors. Twenty-Sixth Symposium on Biotechnology for Fuels and Chemicals. New York City: Humana Press; 2005. pp. 605–18. [Google Scholar]Fayolle F, Marchal R, Ballerini D. Effect of controlled substrate feeding on butyric acid production by Clostridium tyrobutyricum. J Ind Microbiol. 1990;6:179–83. [Google Scholar]Faisal A, Zerbeska A, Saremi P, et al. MFI zeolite as adsorbent for selective recovery of hydrocarbons from ABE fermentation broths. Adsorption. 2014;20:465–70. [Google Scholar]Gaertner CA, Serrano-Ruiz JC, Braden DJ, et al. Catalytic coupling of carboxylic acids by ketonization as a processing step in biomass conversion. J Catal. 2009;266:71–8. [Google Scholar]Huang L, Xiang Y, Cai J, et al. Effects of three main sugars in cane molasses on the production of butyric acid with Clostridium tyrobutyricum. Korean J Chem Eng. 2011;28:2312–5. [Google Scholar]Jiang L, Wang J, Liang S, et al. Enhanced butyric acid tolerance and bioproduction by Clostridium tyrobutyricum immobilized in a fibrous bed bioreactor. Biotechnol Bioeng. 2011;108:31–40. [PubMed] [Google Scholar]Johnston VJ, Chapman JT, Chen L, et al. Ethanol Production From Acetic Acid Utilizing A Cobalt Catalyst. 2009. United States Patent US 7,608,744 B1, October 27.Ju IB, Jeon W, Park MJ, et al. Kinetic studies of vapor-phase hydrogenolysis of butyl butyrate to butanol over Cu/ZnO/Al2O3 catalyst. Appl Catal A-Gen. 2010;387:100–6. [Google Scholar]Ju IB, Lim HW, Jeon W, et al. Kinetic study of catalytic esterification of butyric acid and n-butanol over Dowex 50Wx8-400. Chem Eng J. 2011;168:293–302. [Google Scholar]Kang SY, Park CH, Yoon YS, et al. Method of Extracting Butyric Acid from Fermented Liquid and Chemically Converting Butyric Acid into Biofuel. 2011. United States Patent Application US20110294176A1, December 1.Koutinas AA, Vlysidis A, Pleissner D, et al. Valorization of industrial waste and by-product streams via fermentation for the production of chemicals and biopolymers. Chem Soc Rev. 2014;43:2587–627. [PubMed] [Google Scholar]Kumar GV, Rao MN. Enzymatic synthesis of butyl acetate using Rhizomucor miehei lipase: parametric study. Indian J Chem. 2003;42B:2577–82. [Google Scholar]Lee JM, Upare PP, Chang JS, et al. Direct hydrogenation of biomass-derived butyric acid to n-butanol over a ruthenium–tin bimetallic catalyst. ChemSusChem. 2014;7:2998–3001. [PubMed] [Google Scholar]López-Garzón CS, Straathof AJ. Recovery of carboxylic acids produced by fermentation. Biotechnol Adv. 2014;32:873–904. [PubMed] [Google Scholar]Lorenzoni ASG, Graebin NG, Martins AB, et al. Optimization of pineapple flavor synthesis by esterification catalysed by immobilized lipase from Rhizomucor miehei. Flavour Frag J. 2012;27:196–200. [Google Scholar]Mclachlan KA, Pimblett G, Price PJ. Ester Production by Hydrogenation of Carboxylic Acids and Anhydrides. 1991. Patent EP0372847 A3.Manyar HG, Paun C, Pilus R, et al. Highly selective and efficient hydrogenation of carboxylic acids to alcohols using titania supported pt catalysts. Chem Commun. 2010;46:6279–81. [PubMed] [Google Scholar]Martins AB, da Solva AM, Schein MF, et al. Comparison of the performances of commercial immobilized lipases in the synthesis of different flavor esters. J Mol Catal B-Enzym. 2014;105:18–25. [Google Scholar]Martins AB, Friedrich JLR, Cavalheiro JC, et al. Improved production of butyl butyrate with lipase from Thermomyces lanuginosus immobilized on styrene-divinylbenzene beads. Bioresource Technol. 2013a;134:417–22. [PubMed] [Google Scholar]Martins AB, Friedrich JLR, Rodrigues RC, et al. Optimized butyl butyrate synthesis catalyzed by Thermomyces lanuginosus lipase. Biotechnol Progr. 2013b;29:1416–21. [PubMed] [Google Scholar]Martins AB, Graebin NG, Lorenzoni ASG, et al. Rapid and high yields of synthesis of butyl acetate catalyzed by Novozym 435: reaction optimization by response surface methodology. Process Biochem. 2011;46:2311–6. [Google Scholar]Martins AB, Schein MF, Friedrich JLR, et al. Ultrasound-assisted butyl acetate synthesis catalyzed by Novozym 435: enhanced activity and operational stability. Ultrason Sonochem. 2013c;20:1155–60. [PubMed] [Google Scholar]Mascal M. Chemicals from biobutanol: technologies and markets. Biofuel Bioprod Bior. 2012;6:483–93. [Google Scholar]Michel-Savin D, Marchal R, van de Casteele JP. Butyric fermentation - metabolic behavior and production performance of Clostridium tyrobutyricum in a continuous culture with cell recycle. Appl Microbiol Biot. 1990;34:172–7. [Google Scholar]Murkete AD, Jackson JE, Miller DJ. Supported mesoporous solid base catalysts for condensation of carboxylic acids. J Catal. 2011;278:189–99. [Google Scholar]Ni Y, Hagedoorn PL, Xu JH, et al. A biocatalytic hydrogenation of carboxylic acids. Chem Commun. 2012;48:12056–8. [PubMed] [Google Scholar]Paludo N, Alves JS, Altmann C, et al. The combined use of ultrasound and molecular sieves improves the synthesis of ethyl butyrate catalyzed by immobilized Thermomyces lanuginosus lipase. Ultrason Sonochem. 2015;22:89–94. [PubMed] [Google Scholar]Pandey A, Benjamin S, Soccol CR, et al. The realm of microbial lipases in biotechnology. Biotechnol Appl Bioc. 1999;29:119–31. [PubMed] [Google Scholar]Pesa FA, Graham AM, Kliewer WR. Hydrogenation of Carboxylic Acids. 1984. United States Patent US4443639 A, April 17.Rodrigues RC, Volpato G, Wada K, et al. Enzymatic synthesis of biodiesel from esterification reactions of vegetable oils and short chain alcohols. J Am Oil Chem Soc. 2008;85:925–30. [Google Scholar]Santillan-Jimenez E, Crocker M. Catalytic deoxygenation of fatty acids and their derivatives to hydrocarbon fuels via decarboxylation/decarbonylation. J Chem Technol Biot. 2012;87:1041–50. [Google Scholar]Santos JC, de Castro HF. Optimization of lipase-catalysed synthesis of butyl butyrate using a factorial design. World J Microb Biot. 2006;22:1007–11. [Google Scholar]Sharma M, Aryal N, Sarma PM, et al. Bioelectrocatalyzed reduction of acetic and butyric acids via direct electron transfer using a mixed culture of sulfate-reducers drives electrosynthesis of alcohols and acetone. Chem Commun. 2013;49:6495–7. [PubMed] [Google Scholar]Sjöblom M, Matsakas L, Christakopoulos P, et al. Production of butyric acid by Clostridium tyrobutyricum (ATCC25755) using sweet sorghum stalks and beet molasses. Ind Crop Prod. 2015;74:535–44. [Google Scholar]Song H, Eom MH, Lee S, et al. Modeling of batch experimental kinetics and application to fed-batch fermentation of Clostridium tyrobutyricum for enhanced butyric acid production. Biochem Eng J. 2010;53:71–6. [Google Scholar]Straathof AAJ. Transformation of biomass into commodity chemicals using enzymes or cells. Chem Rev. 2014;114:1871–908. [PubMed] [Google Scholar]Van Den Berg C, Heeres AS, van der Wielen LA, et al. Simultaneous clostridial fermentation, lipase-catalyzed esterification, and ester extraction to enrich diesel with butyl butyrate. Biotechnol Bioeng. 2012;110:137–42. [PubMed] [Google Scholar]Wu D, Chen H, Jiang L, et al. Efficient separation of butyric acid by an aqueous two-phase system with calcium chloride. Sep Sci Eng. 2010;18:533–7. [Google Scholar]Wu X, Li G, Yang H, et al. Study on extraction and separation of butyric acid from Clostridium tyrobutyricum fermentation broth in PEG/Na2SO4 aqueous two-phase system. Fluid Phase Equilibr. 2015;403:36–42. [Google Scholar]Yang ST. Methods of Producing Butanol. 2008. United States Patent Application US 20080248540 A1, October 9.Yokoyama T, Yamagata N. Hydrogenation of carboxylic acids to the corresponding aldehydes. Appl Catal. 2001;221:227–39. [Google Scholar]Zaks A, Klibanov AM. Enzyme-catalyzed processes in organic solvents. P Natl Acad Sci USA. 1985;82:3192–6. [PMC free article] [PubMed] [Google Scholar]Zhang Z, Jackson JE, Miller DJ. Aqueous-phase hydrogenation of lactic acid to propylene glycol. Appl Catal A-Gen. 2001;219:89–98. [Google Scholar]Zhu Y, Wu ZT, Yang ST. Butyric Acid production from acid hydrolysate of corn fibre by Clostridium tyrobutyricum in a fibrous-bed bioreactor. Process Biochem. 2002;38:657–66. [Google Scholar]