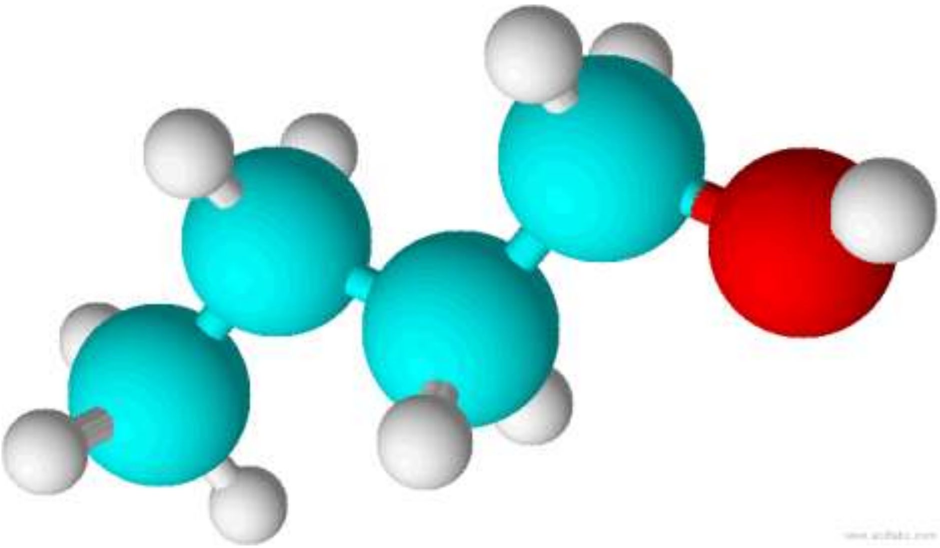
REPORT

f3 2014:01

AN INVENTORY AND COMPARISON OF SWEDISH BIOBUTANOL PROJECTS RELATIVE GLOBAL BIOBUTANOL PRODUCTION, RESEARCH AND DEVELOPMENT

Report from an f3 project



Authors:

Niklas Strömberg & Anders Loren, SP Technical Research Institute of Sweden

Lars Lind, Perstorp Bioproducts

THE SWEDISH KNOWLEDGE CENTRE
FOR RENEWABLE TRANSPORTATION FUELS

PREFACE

This report is the result of a cooperation project within the Swedish Knowledge Centre for Renewable Transportation Fuels (f3). The f3 Centre is a nationwide centre, which through cooperation and a systems approach contributes to the development of sustainable fossil-free fuels for transportation. The centre is financed by the Swedish Energy Agency, the Region Västra Götaland and the f3 Partners, including universities, research institutes, and industry (see www.f3centre.se).

The material processed and presented in this report is based on interviews, documents from the Swedish companies Protista and Perstorp, data mining on the Internet studying patents, prospects, press releases, translated Chinese documents and research articles. It should be noted that regarding the reference sources to biobutanol production in China and Soviet Union, there are too few to give a secured judgment of the ABE development in these regions of the world. Throughout this report the term “ABE solvents” refers to the sum of acetone, butanol and ethanol. Tools used in the report are ACD ChemSketch, Scopus and Googel Trends.

This report shoud be cited as:

Strömberg, N., Loren, A. and Lind, L. (2014) *An Inventory and Comparison of Swedish Biobutanol Projects Relative Global Biobutanol Production, Research and Development.* Report No 2014:01, f3 The Swedish Knowledge Centre for Renewable Transportation Fuels, Sweden. Available at www.f3centre.se.

SUMMARY

With respect to the large supply of cellulosic waste materials in Sweden and potential use and benefits from iso- and n-butanols as biofuels/biochemicals, the objective of this report was to investigate the production and research efforts on biobutanol in Sweden and relate these to corresponding efforts for biobutanol globally.

Butanols are four carbon alcohols available in four isomeric forms that mainly find use as solvents or as starting chemicals in lacquers and plastics. Production of the most widely used isomer, n-butanol, is currently largely based on petroleum but can also be produced at an industrial scale through Acetone: Butanol: Ethanol (ABE) fermentation of sugars from cellulosic substrates, or through chemical synthesis (condensation) of cellulosic ethanol. Compared to ethanol and methanol, butanols have a higher energy content and better water separating properties and are as well less corrosive. Thereby, the use of butanols as a fuel or fuel blend component is technically more promising than methanol and ethanol. However, the greatest advantage of butanols is that they can be used in both diesel and gasoline engines and the fuel can be delivered through present infrastructure.

The outcome of the survey reveals that Sweden has no or little tradition on biobutanol production as well as no focused research in the field. Greatest increase in biobutanol production occurs in China, where commercial production sites for biobutanol based on corn feedstock are in operation. Recently (December 2013) also ligno-cellulosic waste has been used as feedstock for ABE fermentation at scale. The research regarding butanol fermentation is dominating in the US, Germany and Asia. Finally it seems likely that we are presently witnessing a revival of the old ABE-fermentation technology with significant improvements gained from today’s process technologies along with the development of natural and genetically modified bacteria or yeasts.

SAMMANFATTNING

Med tanke på den stora tillgången på cellulosaavfall i Sverige och den potentiella användningen av iso- och n-butanoler som biodrivmedel/biokemikalier är syftet med denna rapport att undersöka forskningsaktiviteten och utvecklingen av biobutanolproduktion i Sverige och relatera denna till motsvarade globala utveckling av biobutanol.

Butanoler är alkoholer bestående av fyra kolatomer och finns tillgängliga i fyra strukturella former, vilka idag huvudsakligen används som lösningsmedel eller utgångskemikalier i lacker och plaster. Produktionen av n- butanol baseras för närvarande i hög grad på petroleum, men n-butanol kan också framställas i industriell skala via Aceton:Butanol:Etanol jäsning (s.k. ABE) av både C5 och C6 socker från cellulosasubstrat eller genom kemisk syntes (kondensering) av cellulosaetanol. Jämfört med etanol och metanol har butanol högre energiinnehåll och bättre vattenseparerande egenskaper, samt är mindre korrosivt. Därmed är användningen av butanoler som drivmedel eller drivmedelskomponent tekniskt sett mer lovande än metanol och etanol. Den kanske största fördelen med butanol är att den kan användas i både diesel- och bensinmotorer och bränslet kan levereras via befintlig infrastruktur (d.v.s. cisterner, rör och drivmedelspumpar) utan modifiering Sammantaget har således butanol stora marknadsfördelar med avseende på lagring, distribution och drivmedelsinblandning samt har dessutom attraktiva alternativa tillämpningar som baskemikalie till biomaterial.

Resultatet från undersökningen visar att Sverige inte har någon tradition av att producera biobutanol och saknar fokuserad forskning på området. Den största ökningen av biobutanolproduktion sker i Kina, som nyligen har byggt kommersiella produktionsanläggningar för biobutanol. Som råvara för butanoltillverkning via ABE-jäsning används idag inte bara majs som var vanligt tidigare, utan också lignocellulosaavfall. Forskningen kring butanoljäsning dominerar annars i USA, Tyskland och Asien. (Sverige är tillsammans med Danmark på sista plats.) Slutligen verkar det troligt att vi nu bevittnar ett återupplivande av den gamla ABE-jäsningstekniken, med betydande förbättringar av processtekniken, tillsammans med utveckling av naturliga och genetiskt modifierade bakterier/gäststammar.

CONTENTS

1 INTRODUCTION

We are presently witnessing a global warming caused by massive past and present use of fossil energy. To mitigate this, the EU has set a mandatory target (Directive 2009/28/EC) that at least 10% of the energy used for transport should come from renewable sources by 2020. A prerequisite for future biofuels is that the feedstock does not compete with food crops and thus, unless fallow land areas are cultivated with energy crops or using marine resources, the fuel feedstock demand must to a large extent be met by biofuels from cellulosic waste materials.

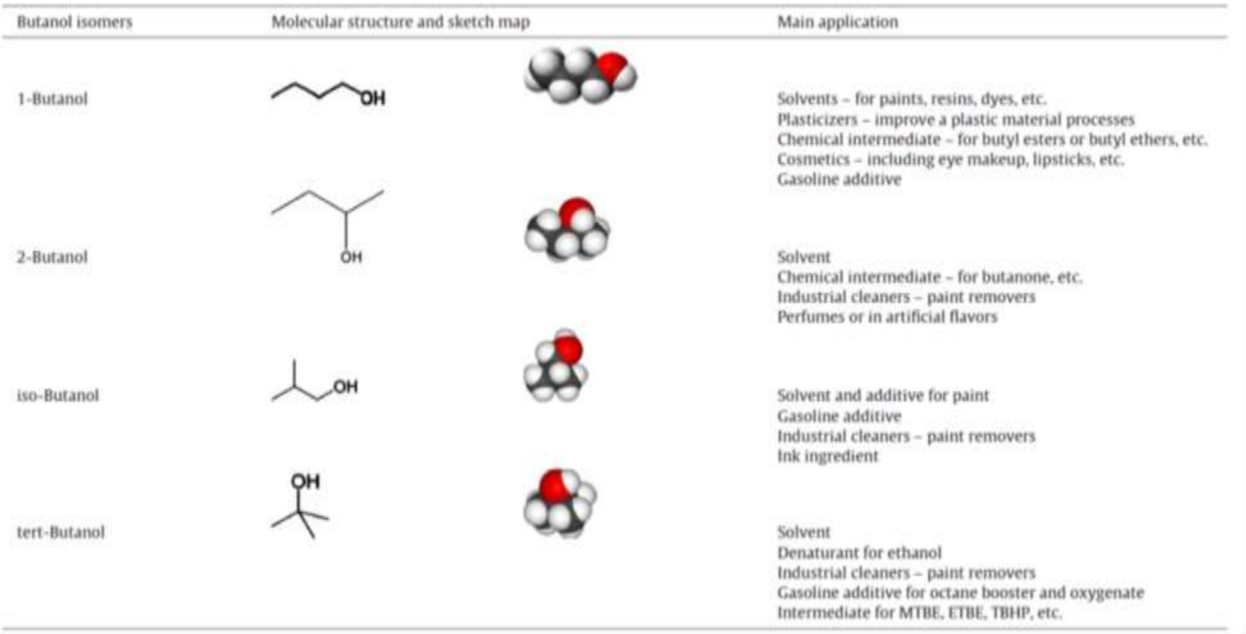
So far the solution to this problem, especially in Sweden, has been cellulosic bioethanol that in addition has been most studied. However, there might be other attractive liquid energy carriers that better fit the conversion processes of lignocellulosic biomass as well as present and future engine technologies and fuel infrastructures. As such, butanols constitute one of the most interesting candidates for viable fuel production.

Butanols are four carbon alcohols available in four isomeric forms (Figure 1) that mainly find use as solvents or as starting bulk chemicals in lacquers and plastics. The most commonly used isomer, 1-butanol (n-butanol), is currently mainly made from petroleum but they can also be produced through so called Acetone:Butanol:Ethanol (ABE) fermentation in the molar proportion 3:6:1. Butanols can be produced from agricultural crops such as corn, molasses, and whey permeate using bacteria Clostridium acetobutylicum or C. beijerinckii. The advantage of using these and some other butanol-producing bacteria is that they can utilize both lignocellulosic hydrolysate sugars (hexoses and pentoses), as opposed to traditional ethanol-producing yeast strains that do not easily ferment pentoses at all [1]. Butanols can today also be produced from genetically modified bacteria such as *E-coli* or modified yeasts cells such as *S. cerevisiae*[2]. The demand for n-butanol has increased (dramatically) and is approximately 5-6 million tonnes/year globally [3, 4]. The global (mostly located in China) biobased n-butanol production in 2008 reached 120 000 tons [5] corresponding to about 2% of the global total n-butanol production (petro+bio) [3, 4]. The potential global supply of biobutanol (n-butanol) is however expected to increase to > 1 million tonnes/year in 2020, to be sold as a chemical and later on as a fuel [5]. A recent study on the US potential for butanol concluded that up to 30% of the national fuel demand can be secured by butanol fermentation of waste materials alone [6].

The objective of this report was to gather the knowledge and activities regarding biobutanol production and research in Sweden and compare the result with the global biobutanol production, research and development.

1.1 MOTIVATORS FOR BUTANOL AS A MOTOR FUEL

Though the demand for n-butanol has increased lately, its present and dominating production route relies on petroleum, and alternative routes based on biomass are sought after today. As such, biobutanol constitutes one of the most interesting alternatives to petroleum based transport fuels and of the four different isomers, iso-butanol and n-butanol are the most promising candidates (Figure 1).



Butanol isomers	Molecular structure and sketch map	Main application
1-Butanol	OH	Solvents – for paints, resins, dyes, etc. Plasticizers – improve a plastic material processes Chemical intermediate – for butyl esters or butyl ethers, etc. Cosmetics – including eye makeup, lipsticks, etc. Gasoline additive
2-Butanol	OH	Solvent Chemical intermediate – for butanone, etc. Industrial cleaners – paint removers Perfumes or in artificial flavors
iso-Butanol	OH	Solvent and additive for paint Gasoline additive Industrial cleaners – paint removers Ink ingredient
tert-Butanol	OH	Solvent Denaturant for ethanol Industrial cleaners – paint removers Gasoline additive for octane booster and oxygenate Intermediate for MTBE, ETBE, TBHP, etc.

Figure 1. The different structures of butanols and their use in various products from reference [7].

Compared to ethanol and methanol, butanols have a higher energy content and better water separating properties as well as less risk for causing corrosion. It should, however, be noted that 100% water (absolute) free 1-butanol dissolves aluminum [8] that may become a serious problem if water is constantly removed e.g. trough distillation, but in reality there is always traces of water that efficiently prevents aluminum dissolution. Despite this issue, the use of butanols as a fuel blend component is technically more promising than methanol and ethanol. However, the greatest advantage of butanol is that it can be used in both diesel and gasoline engines and the distribution of it can be fitted into present infrastructural systems. Butanol can be blended seamlessly with gasoline up to 100% [9] and diesel up to 20% [10-12] with minor or no changes in the engine design. It also can be pumped without risk in pipelines, which is not possible for ethanol and methanol [7]. As a result of these investigations the American Society for Testing and Materials (ASTM) released a standard (ASTM D7862) for blends of butanol with gasoline at 1-12.5 vol. %. The specification covers three butanol isomers: 1-butanol, 2-butanol, and 2-methyl-1-propanol but excludes the use of 2-methyl-2-propanol (tert-butyl alcohol).

1.2 PRODUCTION OF BUTANOL THROUGH CHEMICAL REACTIONS

Most n-butanol produced today is synthetic and derived from a petrochemical route based on propene oxo synthesis (see Figure) and thus linked to the propene market. In oxo synthesis, carbon monoxide and hydrogen (syngas) react to a carbon–carbon double bond using catalysts. Aldehyde mixtures are obtained in the first reaction step, which is followed by hydrogenation for the production of butanol. Depending on reaction conditions (pressure, temperature) as well as the catalyst, different isomeric ratios of butanols are obtained.

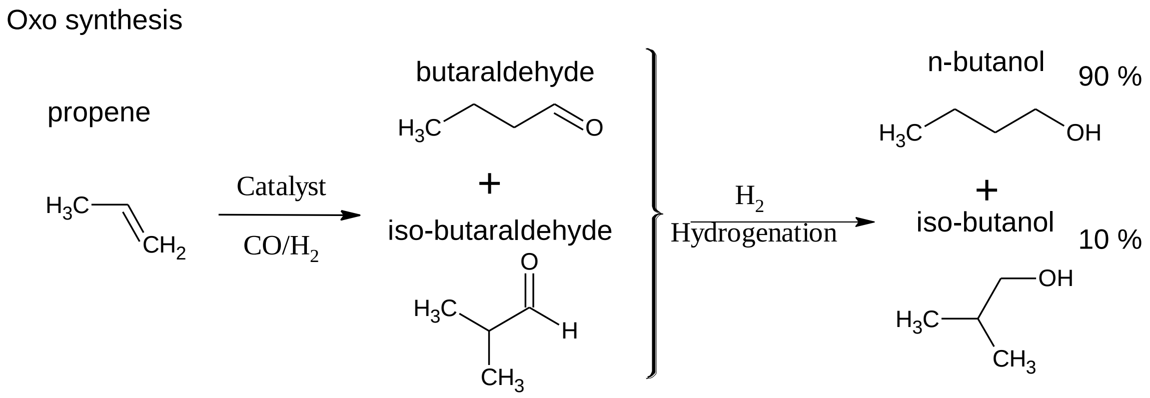


Figure 2. Chemical synthesis of n and iso-butanol from propene through the Oxo route.

Another way of using propene as a start material is through the less used Reppe process (Figure 3), where propene, carbon monoxide and water are reacted in the presence of a catalyst [13]. The Reppe process directly produces butanol at low temperature and pressure but this process has not been commercially successful due to the costly process technology [13].

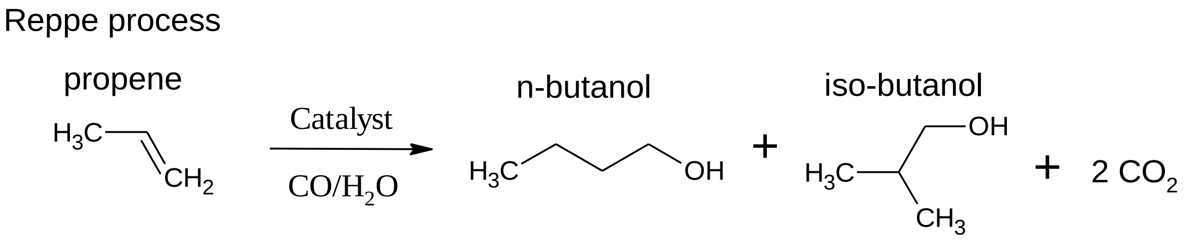


Figure 3. Production of n-butanols and iso-butanols from propene through the Reppe process.

A few decades ago, the common route for butanol synthesis was from acetaldehyde (Figure 4). The process consists of aldol condensation, dehydration and hydrogenation [13]. The reaction opens up many ways to produce longer alcohols from various starting materials such as e.g. two (2) ethanols using catalysis through the so called Guerbert reaction (Figure 4) that lately gained new interest.

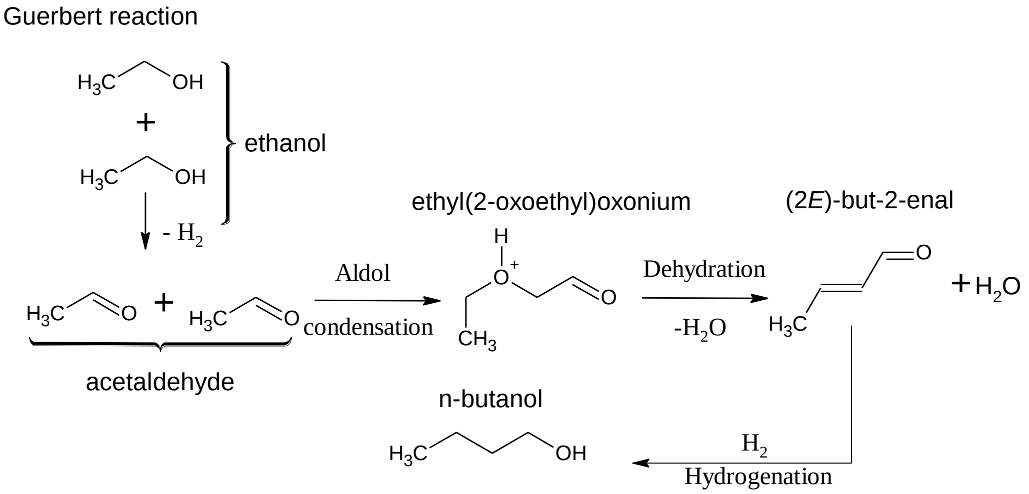


Figure 4. Production of n-butanol from ethanol to acetaldehyde via the Guerbert reaction. Note that other starting alcohols can be used e.g. glycerol and methanol.

While most of today’s processes rely on petroleum based starting materials, the Guerbert process (Figure 4) provides an alternative route from ethanol. In this case, ethanol is dehydrogenated to form acetaldehyde from which the synthesis can proceed [14]. The Guerbert reaction is improved with various catalysts [15] and in 2013 a new catalyst was developed by the Spanish company Abengoa that in addition has patented the entire process. Abengoa announced that it has produced butanol with 99.8% purity from ethanol and plans to start commercial-scale production of butanol in 2015 at the Revenna Nebraska plant [16]. The process allows a butanol plant to be built as an 'add on' to an existing commercial ethanol plant (see Figure 5), enabling the production of butanol without having to halt the ethanol production process.

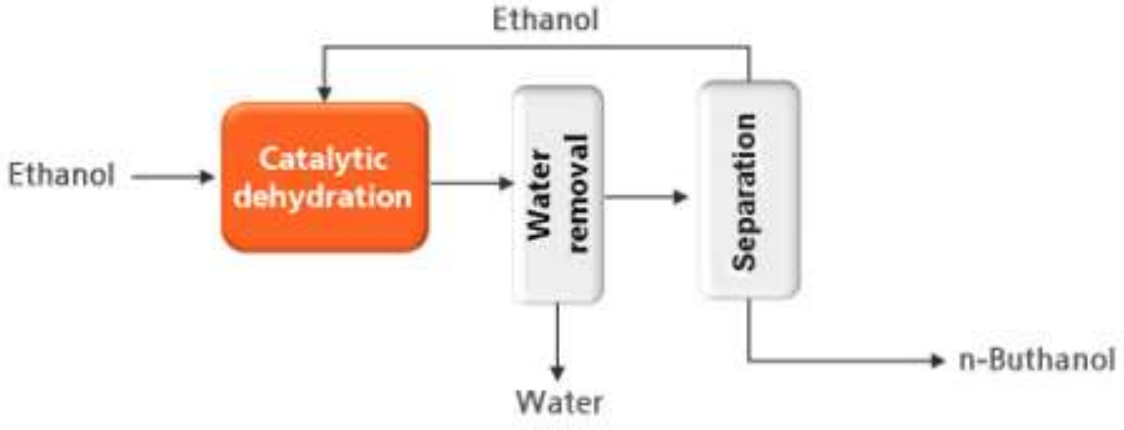


Figure 5. Schematics of the ethanol to butanol conversion process as an add-on to an ethanol plant [17]. The process behind the schematic drawing is in principle the Guerbert reaction (Figure 4) but with a patented catalyst and process technology.

It shall also be mentioned that recently iso-butanol was made from glycerol and methanol as presented in a previous f3-report [18], where glycerol and methanol were converted to aldehydes, condensed to methacrolein and hydrogenated to iso-butanol. Thus, the process is in principle according to the Guerbert reaction (Figure 4) but with different starting materials. Glycerol constitutes a 10% by-product from the transesterification process during biodiesel production from oils and fat. Thus, the availability of glycerol is largely dependent on biodiesel production quantity as well as to what prices glycerol can be sold. The major outcome from that study was that iso-butanol production cost from glycerol was calculated to be significantly higher than for corresponding ethanol production.

1.3 PRODUCTION OF BIOBUTANOL THROUGH FERMENTATION (BACTERIA AND MODIFIED YEASTS)

There are two major ways to ferment biobutanol (here referring to both n-butanol and iso-butanol), i.e. the ABE process using wild bacteria strains for n-butanol, and the process using genetically modified bacteria or yeasts for Iso butanol and n-butanol production. The use and development of modified bacteria is popular in USA in order to produce especially **iso-butanol** from mainly corn and the techniques are secured by special strains and processes. However, the much older ABE process relies on anaerobe fermentation using *Clostridia* bacteria strains that in turn produces solvents of Acetone:**n-butanol**:Ethanol in the molar proportion 3:6:1 from various substrates. In addition, fermentation gases are produced such as CO_2 and H_2 that may be used to either aid the fermentation or produce chemicals through e.g. hydrogenation, heating or solvent stripping. A most remarkable feature with ABE fermentation is that unlike natural yeasts, the ABE fermenting organisms (*Clostridia* bacteria strains) can not only be used on simple C6 sugars (hexoses), as for ethanol, but also through direct fermentation of C5 sugars (pentoses) from starch and lignocellulosic materials, providing a powerful and versatile carbohydrate to bulk chemical conversion [19]. Much of the research today focuses on how to modify yeast in order to tolerate toxic substances from lignocellulosic materials, while some *Clostridia* strains in fact have a natural tolerance for such substrates [19].

However, strain selection of the fermenting organisms and new refinement technologies for butanol have lately increased production yields dramatically and e.g. adjusted ABE- as well as yeast fermentation routes for industrial butanol production. Still, one of the major costs of butanol fermentation is the feedstock. In this respect hydrolysates of ligno-cellulosic biomass wastes from forestry and agriculture are highly interesting as they can provide fermentable sugars, e.g. glucose (C6), mannose (C6), galactose (C6), arabinose (C5) and xylose (C5).

1.4 THE BOTTLENECKS OF ABE FERMENTATION AND MODIFIED YEASTS

Both the ABE and modified yeast/bacteria processes for butanol production contain some bottlenecks that need to be surpassed in order to make it cost competitive with the petrochemical production method. Two major challenges to solve are **product inhibition** and **inhibition from organic compounds** present in the fermentation substrate.

Product inhibition is caused by the toxic effect of the solvent butanol on the fermenting organism and for an increased yield, the ABE fermentation products must be continuously removed during fermentation. Since the tolerable concentration of butanol is low (~2%), and in addition, butanol and water forms an azeotropic mixture, product recovery through distillation combined with liquid-liquid phase separation is possible, but at a high energy cost. In a recent study [20] fed-batch fermentation and gas-stripping with CO_2 in combination with liquid-liquid extraction and conventional distillation was shown to be a promising route for production. However, a most attractive future route for efficient product recovery seems to be based on adsorption and membrane processes [21]. In particular, hydrophobic silicalite-1 zeolite has been reported to selectively adsorb butanol from dilute water mixtures.

Inhibition from organic compounds present in the fermentation substrate originates from the structure of lignocellulose feedstocks, which are chemically more complex to ferment than starches. The breakdown of cellulose requires various pretreatments as steam explosion, acid- or enzyme hydrolysis. These pre-treatment steps, in addition to carbohydrates, also release organic compounds which can inhibit the subsequent butanol and biogas production. Known inhibitors are furan aldehydes, organic acids and phenolic compounds.

2 LEARNING FROM THE HISTORY OF ABE FERMENTATION

Genetically modified organisms such as yeasts/bacteria used for isobutanol production is a relatively new way of producing biobutanol while on the other hand the ABE fermentation dates back to laboratory scale attempts by L. Pasteur who in 1861 discovered the identified the first clostridial species, *Clostridium butyricum butyricum* [22]. The fermentation of starch to the solvents acetone, butanol, and ethanol (ABE-solvents) was further developed by C. Weizman in 1912 at Manchester University into an industrial process [23]. He isolated the wild strain which was later called *Clostridium acetobutylicum* and ran the first production plant for acetone production from starch. The demand for acetone was great at that time as it was crucial in the manufacturing process of the smokeless gunpowder in ammunition used during World War I. More specifically, acetone was used in order to extrude spaghetti-like rods initially called "cord powder" composed of nitroglycerine, nitrocellulose and petroleum jelly that later on was abbreviated to "Cordite". Due to the great demand for acetone at that time, butanol was considered as by-product with little or no specific use.

After the Weizmann patent expired in the 1930s, large production facilities were established in USA, Japan (Kyowa Hakko started ABE in 1948 and used mainly used syrup as feedstock), and South Africa (National Chemical Products in Germiston, established 1937), among others in order to provide the growing automotive industry with rubber (butadiene) and varnish based on n-butanol. Thus, butanol had found its use as starting material for a polymer and as a solvent, which during the mid-1940s led to that butanol constituted the largest fermentative bulk chemical, only superseded by ethanol. Two thirds of industrially used butanol was produced by ABE fermentation in U.S in 1945 [12].

Due to the competition with petrochemicals during the 1950s and 1960s, the ABE fermentation industry completely ceased in Europe, America and Japan, however, the production continued in Egypt, the Soviet Union (late 1980s) and South Africa (1983) [24]. In China, the development of ABE started at the time when it was abandoned in the rest of the world and was only stopped temporarily in 2004 to just two years later be re-established.

In conclusion much of the industrial ABE fermentation technology has been performed at scale in China and Soviet Union and their development is discussed separately in the following sections together with other nations that have started or plan to start butanol or isobutanol industrial plants. The Swedish efforts on butanol fermentation are also described for comparison.

2.1 SOVIET UNION

Recently an effort was made to shed some light over the ABE industry in Soviet Union [25]. It should be emphasized that the following information is based on this limited source only.

The ABE industry was first established during the period 1929-1935 and used a starch-based (wheat and rye) fermentation that was essentially the same as the Weizmann process developed in England, Canada, and the USA during the World War I. A number of plants were established throughout the country based on this concept, however, the fermentation method was found inefficient and the large amounts of starch necessary for an industrial butanol production resulted in shortages of substrates for ABE and led to competition with food.

To solve these issues, an early system for continuous/semi-continuous fermentation was developed by linking fermenters together and in addition an effort was made to use pentose hydrolyzates of hemp waste, corncobs, and sunflower shells. The Dokshukino plant, where the continuous fermentation using hydrolysates was conducted, has been considered as the first plant (1962) using agricultural waste materials routinely in a full-scale industrial process [25].

Another remarkable feature was the early biorefinery concepts introduced in the plants. It remains (in the reference) unclear if H_2 was used, but the CO_2 was collected from the fermentation gases and sold as dry ice and liquid CO_2. Biogas was produced in large quantities from the fermentation sludge through anaerobe digestion and the methane was used to provide process heat in sterilization and distillation at the plant.

The early biorefinery concept has been documented for the Evremovo plant [25] where about 40 500 tons of starch equivalents (about 90 000 tons of flour dry weight, partially substituted by molasses and hydrolysate) per year were sterilized in 880 000 tons of liquid substrate and fermented to 15 000 tons of solvents containing 4 140 tonnes acetone, 8 550 tonnes butanol, 2 310 tonnes ethanol , 8.7 million m^3 H_2, and 13.1 million m^3 CO_2. The fermentation broth was used for the production of 11 million m^3 biogas (methane) and an unknown amount of vitamin B12. In addition, fodder yeast was produced. If assuming that these figures are representative for all of the operation plants an annual national production of about 70 000 tons n-butanol may be estimated. The eight industrial ABE fermentation plants in operation were gradually shut down in the end of the 1980s.

2.2 USA

As already mentioned, several ABE fermentation plants were shut down in USA during the 1950s. Today, commercial ABE seems to be increasing but the biggest focus is on the development on iso-butanol and genetically modifications of various organisms.

Gevo Inc. has engineered E. coli to produce iso-butanol [26] and recently acquired a commercial-scale ethanol plant in Luverne, Minnesota, that was retrofitted to produce iso-butanol. The predicted annual production capacity of the iso-butanol in the Luverne plant was 84 000 tons [27] but the plant ran into operational problems. In 2012 and the latter part of 2013, gevo modified their plant to both producing biobutanol and ethanol side by side in order to gain flexibility. Presently the plant has a capability to produce about 45 000 tonnes of ethanol and 6000-9000 tonnes of isobutanol.

DuPont has also engineered several biocatalysts for iso-butanol [3] and assigned the technology to ButamaxTM Advanced Biofuels[28], a joint venture between BP and Dupont. DuPont is collaborating with Kingston Research Limited, another BP–Dupont joint venture, to build a demonstration plant in the UK [29].

BP and DuPont have been working together since 2003; in 2006 they created a partnership to develop, produce and market a next generation of biofuels, with the first planned commercialization being biobutanol. Under the partnership, there are patents in the areas of biology, fermentation processing, chemistry and end uses for 1-butanol, iso-butanol and 2-butanol. BP and DuPont have secured various patents on different butanol isomers and ended up selecting iso-butanol for commercialization. In 2013 DuPont and BP, together with Highwater Ethanol LLC, a producer of first-generation corn ethanol, begun to retrofit Highwater's ethanol plant in Lamberton, Minnesota, for the production of bio-isobutanol. The idea is to continue use corn starch as feedstock for the fermentation [28].

Gevo and DuPont/GP are since 2011 in dispute over the iso-butanol technology.

2.3 CHINA

China developed its own ABE industry rather late and after plants in Europe were put out of use around 1960. Plants were built in Shanghai, Beijing, and Wuxi, each with an annual production of 1 000 tonnes ABE solvents. Between 1965 and 1970, ten more plants were constructed. The total national annual production was about 40 000–50 000 tonnes of ABE solvents. The Shanghai Solvent was the largest producer with about 10 000 tonnes of ABE solvents.

From 1980, the ABE industry underwent tremendous changes, many plants left big cities for agricultural districts, moving from Southern to Northern China, close to corn farmland and coal production sites. At the same time, new plants were established in Shandong, Hebei, North-Eastern provinces, each with a yearly output of 5 000–10 000 tons of ABE solvents. The total national annual production of ABE solvents reached 170 000 tons, corresponding to approximately 100 000 tons of n-butanol.

However, also China was affected by the petrochemical synthetic process but this happened much later than for the rest of the world, during the end of 20th century. Industrial ABE fermentation gradually ceased, and in 2004 all plants were closed. Just after ending the era of ABE industry in China, the national demand for n-butanol almost doubled from 280 000 tons in 2000, to 520 000 tons in 2005. However, the annual production of synthetic butanol reached 500 000 tons, leading to a balance between supply and demand [24].

These figures likely made the decision makers in China to reconsider commercial ABE fermentation processes. In 2006 China resumed ABE production with plants [30] that mainly operated in a semi-continuous fashion with each fermentation lasting up to 21 days. The plants typically house up to eight fermentation tanks (300–400 m^3 volumes) linked together in series to produce n-butanol initially from corn starch [29, 30]. Fresh feedstock transfers together with the seed culture through the fermentors at a pace that is enough for re-assimilation of acids to solvents.

The total annual ABE production capacity from ten plants has reached 210 000 tons and the total ABE solvent production was expected to be extended to 1 000 000 tons, based on the available data as of September 2008 [30].

According to the independent market firm Chemical Market Associates Inc, Cathay Industrial Biotech was the largest global producer of biobutanol in the world in 2011, with 65 000 tons of bio n-butanol (100 000 tons of ABE solvents) produced at their plant in the Jilin province. Cathay plans to double the production of bio n-butanol to 130 000 tons (200 000 tons of ABE solvents) in the future [31]. Thus, today (2011) one plant in China almost exceeds the former (before 2004) historical annual national production maximum. However Cathay Industrial Biotech key raw material used in their biobutanol production is corn [31] though their goal is to use cellulosic materials in the future. A transfer from food feedstocks to cellulosic materials is likely critically important in the densely populated China (compare with the development in the Soviet Union in the 1960s that led to starvation) during the likely expansion of the ABE technology in the future.

In China there is about 600 million tons of straw [32] with low utilization rate and recent test show a 80% sugar conversion using steam hydrolysis to produce good hydrolysate for ABE fermentation [33].

Based on the technology of steam explosion to convert hemicellulose to fermentable sugars for butanol, Laihe Chemical Ltd. Co. in Songyuan City, Jilin Province, in August 2010 established a plant with an capacity of processing 300 000 tons of straw per year producing 50 000 tons of n-butanol, 50 000 tons of polyols and 20 000 tons of phenolic aldehyde glue using straw as feedstock [33]. In 2012 the company fused to Laihe Rockley Bio-Chemicals Co., Ltd. (LRB), which is a joint venture company established by Jilin Toprank Agricultural Development Co., Ltd, Guangzhou Dachen Venture Capital Limited Partners and Rockley China Fund of Rockley Group, UK. LRB joint venture plans to build two ABE fermentation plants with annual capacity of 100 000 tons of ABE solvents each designed for agricultural waste materials. The total refining capacity of agricultural wastes (including corn stalks, corn cob and corn shell) will be 800 000 tons of biomass when the whole project is completed. One of the production lines in the plants with an annual capacity of 40 000 tons of ABE solvents has been built and was in successful trial production using waste materials until June 2012. It is now in use for commercial production since December 2013.

Though production in the Soviet Union did make use of cellulose hydrolysate as an ABE substrate, the LRB plant in the Jilin Province is the first commercial production site with an annual bio n-butanol capacity over 10 000 tons based on a complete non-food feedstock [34]. Using the production figures in the Chinese plants and all the available straw [32] in China for butanol production gives a theoretical maximum production of 100 million tons of n-butanol made from straw. However, these figures just show the potential and does not consider other potential uses of straw, e.g. as soil improver or feed.

2.4 BRAZIL

A relatively new plant has been built in Brazil and is operated by HC Sucroquimica. The plant produces 8,000 tons of ABE solvents from sugar cane juice and is located next to an ethanol distillery and sugar mill [29]. Cobalt and Rhodia have formed a partnership to develop a demonstration plant in Brazil to convert sugarcane bagasse and other non-food feedstocks into biobutanol.

2.5 SWEDEN

Despite the demand or potential growth, commercial biobutanol production in Sweden is today nonexistent, largely and likely due to limited research regarding the ABE fermentation process and obviously also a strong tradition on ethanol production.

Today Perstorp AB provides petroleum based n-butanol through the Stenungsund plant, annually producing about 70 000-90 000 tons of n-butanol, which is mainly sold on the Swedish market.

Attempts to produce domestic biobutanol in Sweden started in 2008 through a joint venture called Stella. In this rather ambitious initiative taken by Protista International AB and Perstorp AB, the two partners began studying microbial production of biobutanol from renewable raw materials. The result from this investment was a multi-step continuous and fully computerized pilot plant (total volume ~200 liter). Unfortunately Protista went bankrupt in 2015 despite large efforts for commercializing the pilot plant.

The pilot-plant core was a packed bed reactor, in which e.g. *Clostridium acetobutylicum* was immobilized. By optimizing media composition, flow rates and cultivation procedures, the butanol (and ABE-) yields obtained by Stella were unique and competitive since the bacterium used has a wild strain genome. When comparing results reported by well-known academic groups found in the US or elsewhere [35, 36], the Stella concept had a very competitive production rates. Nevertheless, Protista and Perstorp estimated that the butanol productivity must be further increased from about 3,2 g/ L&h, actual result, up to ~ 4 g/L&h, in order for the process to become economically feasible at 2010 price level and taxation. At the same time, the process must rely on renewable raw materials that do not interfere with the food production.

Therefore, the Stella process had to be adapted for use with lignocellulose-based renewable raw materials, like waste material from forestry, paper and pulp, agriculture or municipal household wastes[37, 38]. In addition to the huge waste streams from forestry in Sweden, the more easily accessible surplus straw available for energy production was estimated to approx. 1 million tons/yr, equaling 3-4 TWh/yr [39]. An extrapolation of the annual surplus straw in Sweden [39] and an industrial productivity conversion of 1/6 (as in the China calculation) [33] from straw biomass, would result in about 160 000 tons of bio-n butanol, i.e. well exceeding the annual petro n-butanol production in Sweden.

Another facility that has produced hydrolysates from lignocellulosic substrates a relatively large scale (2 tons of biomass/day) is the SP Biorefinery plant in Örnsköldsvik that today (2015) is operated by SP Technical Research Institute of Sweden. The plant was previously used for ethanol production from wood substrates but the plant could be retrofitted to butanol production.

3 GLOBAL SCOPE AND DISSEMINATION OF BUTANOL FERMENTATION RESEARCH

3.1 METHOD

The global research interest (Impact) on biobutanol is evaluated by using Scopus and search terms 1) “butanol and fermentation” and 2) “ethanol and fermentation” on all text parts of the documents (abstract, keywords, body text etc). Thus, the filter is very coarse and publications that just briefly mention e.g. “butanol” and “fermentation” will result in hits. The number of hits for search term 1 is normalized with search term 1+2 in order to see interest of butanol research relative to the ethanol + butanol research area.

The interest of butanol has also been evaluated between 2004 and 2014 by using Google trends that measure the search term popularity on internet. The results were compared with search term “ethanol” and the interest for Shale gas (search term “Shale gas”). The search terms was categorized under “Business & Industrial” in Google trends in order to avoid irrelevant hits.

3.2 RESULTS AND DISCUSSION

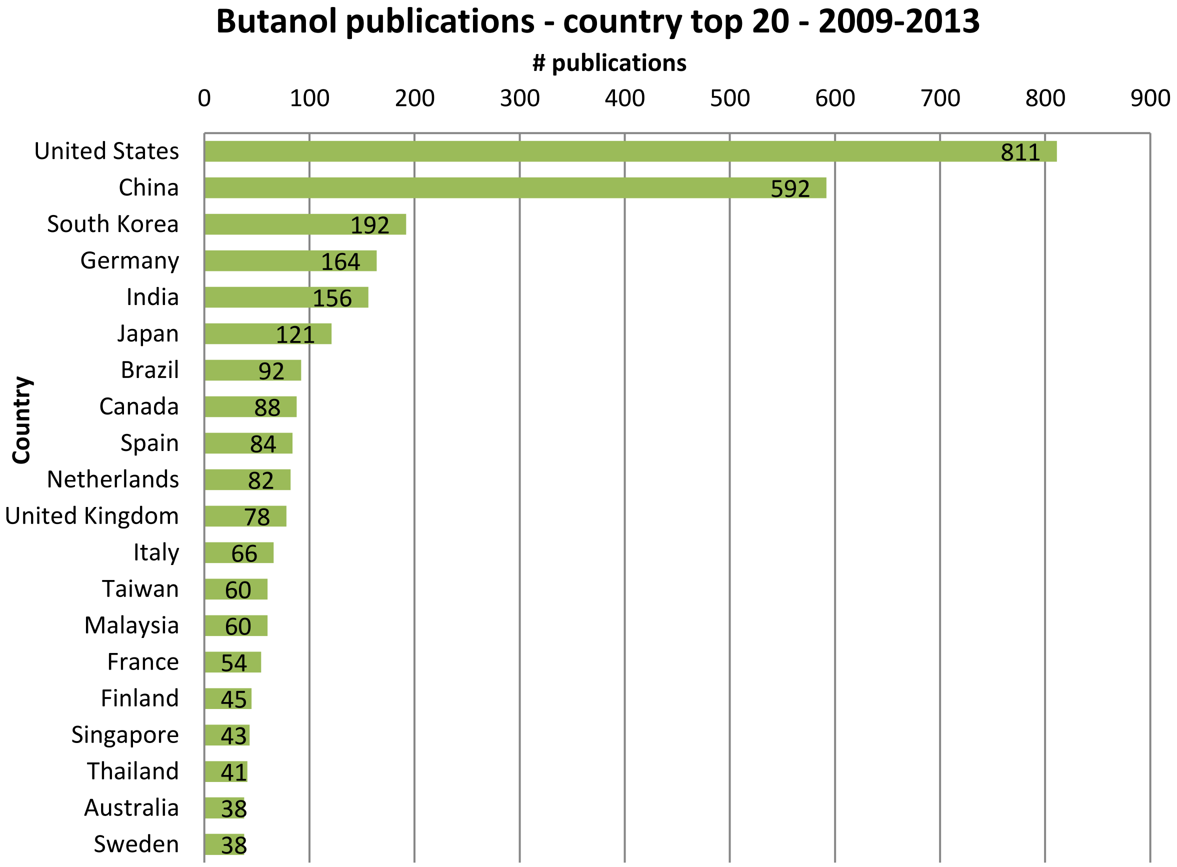


Figure 6. Peer review publications and their global national distribution based on the search terms “Butanol” and “Fermentation” in Scopus database between 2009 and 2013.

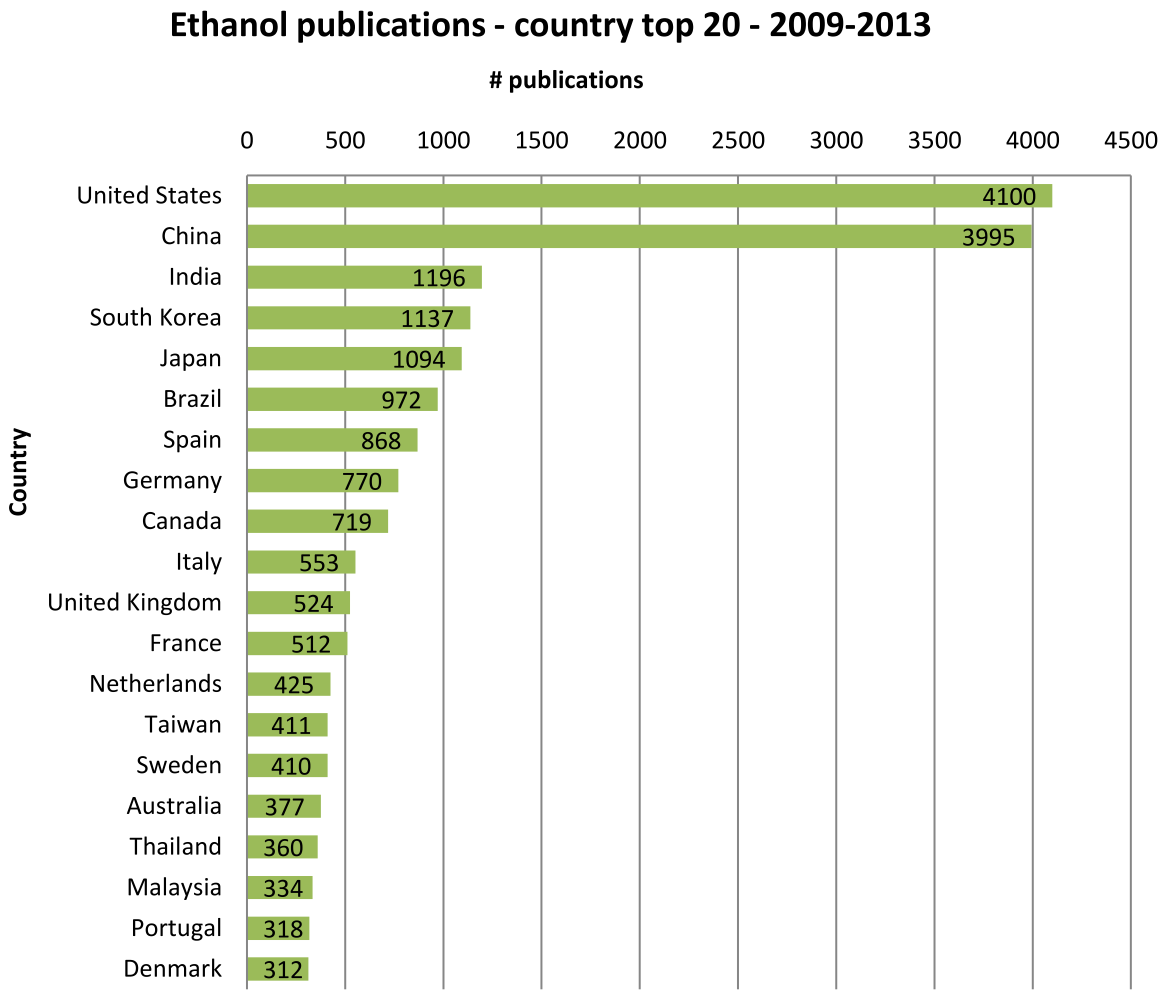


Figure 7. Peer review publications and their global national distribution based on the search terms “Ethanol” and “Fermentation” in Scopus database between 2009 and 2013.

The research on fermentation of biomass to alcohols is the strongest in US and China in absolute numbers of peer reviewed publications, followed by South Korea and Germany (Figure 6 and Figure 7).

As described in the method section (3.1), butanol fermentation was normalized to ethanol fermentation. In this way it was possible to evaluate the interests for butanol relative to ethanol between countries regardless the absolute number of publications (Figure 8). Due to the limited space in the tables, countries needed annually atleast five search term hits of “butanol+ fermentation” to be listed.

Using this methodology, we found a high relative interest for butanol in Singapore and Russian Federation, followed by Germany, US and Netherlands. In conclusion, most research regarding butanol, considering both the absolute and the relative evaluations, was found in US, Germany and in Asia. Of the Nordic countries most interest for butanol was found in Finland (both relative and in absolute numbers). It is noteworthy that Denmark and Sweden show a very low interest in butanol fermentation.

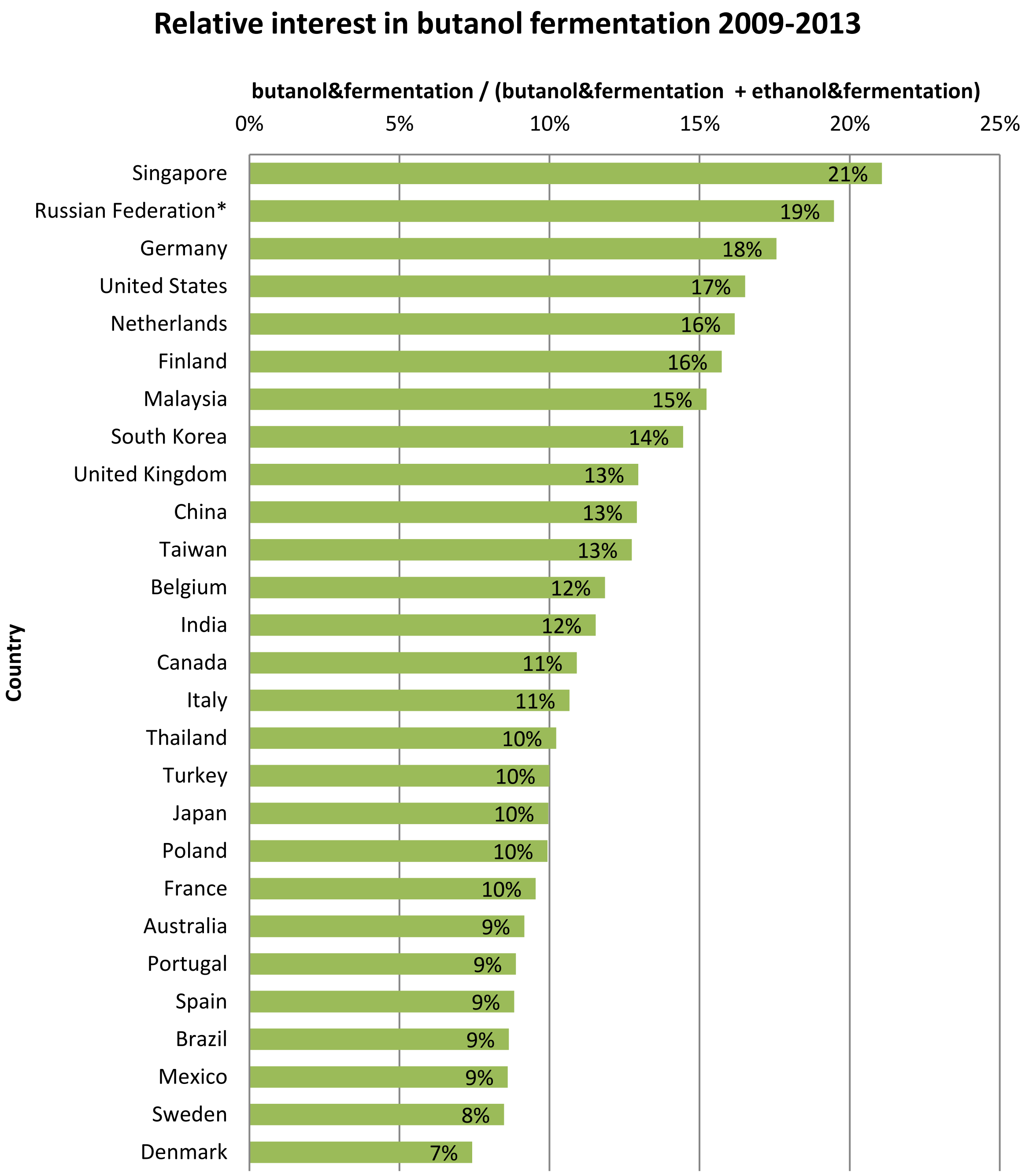


Figure 8. The relative national interest for butanol and fermentation relative to the butanol and ethanol fermentation field, presented as a publication ratio using publications from Scopus database between 2009 and 2013. *Note that considering the history in ABE fermentation and available wood biomass, there are few publications in the Russian Federation (they are not on the top 20 list of butanol publications in Figure 7).

A hypothesis in this study was that a large interest in ethanol fermentation would give an interest in butanol fermentation as well. However, based on the survey it becomes clear that even though this is true for many nations, it is not the case for Sweden and Brazil which have entirely focused on ethanol production.

While considering the benefits of butanol as an energy carrier for biofuels and a starting chemical for bio plastics, it would be relevant to evaluate the global search behaviour on interent for butanol and other biofuels compared to upcoming non-renewable petroleum sources.

One of the most discussed and highly criticized new carbon sources lately is shale gas, with a high methane content that can be converted to plastics and fuels through e.g. the Fischer-Tropsch process and thus for a long period of time support us with low cost petroleum-based products (fuels and materials). Shale gas appeared first as a search term 2005 in Google trends (figure 9) but started rise from 2009 coinciding with the decline of interest of the search term “biofuels”. In 2011 the search term “biofuels” was exceeded by “Shale gas”. Linking the use of search terms to the degree of interest, “Butanol” and “Ethanol” follow the same trend when compared with “Shale gas” (Figure 10).

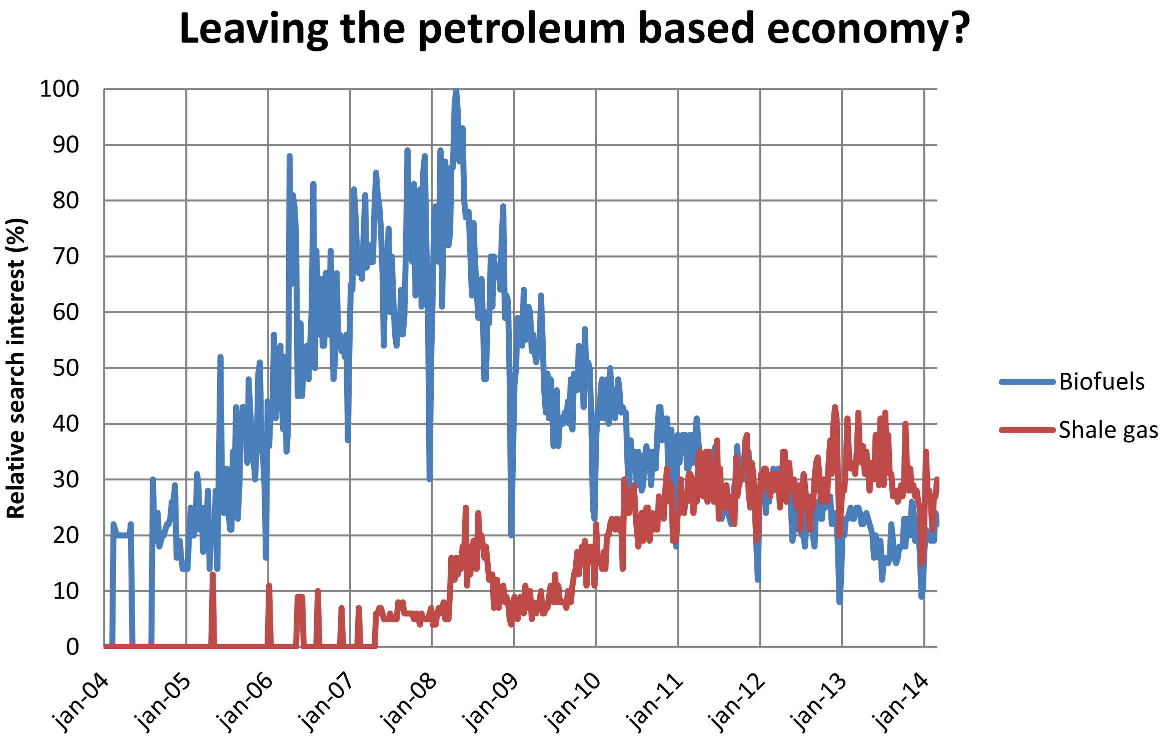


Figure 9. The graph shows relative search interest for the terms “Biofuels” and “Shale gas” within the category “Business & Industrial” in Google Trends between January 2004 and January 2014. Numbers represent search interest relative to the highest point that appears on the chart i.e. normalized to the peak of the search term “Biofuels” in 2008. In 2011, the search interest for the search term “Shale gas” exceeded the search term “Biofuels”.

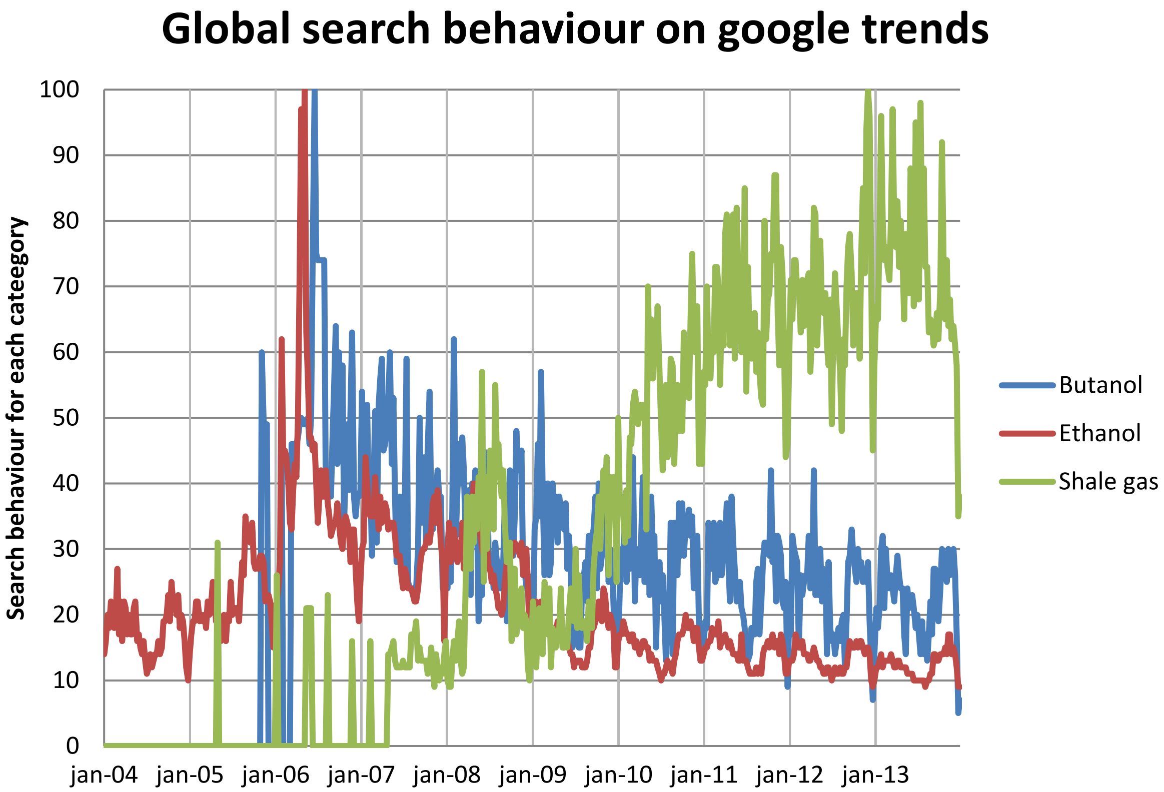


Figure 10. Search behavior based on the search terms “Butanol”, “Ethanol” and “Shale gas” in the category “Business & Industrial” in Google trends between January 2004 and January 2014. The graph indicates a paradigm shift in the biofuel economy. Note that each parameter now is expressed relative its individual maximum search interest (“Butanol” & Ethanol” ~2006 and “Shale gas” in ~2013) in order to more efficiently show the trend shift. The average relative interest for Butanol:Ethanol:Shale gas was 1:29:2, thus of the searches, the ethanol interest was in absolute numbers greatest.

4 CONCLUSIONS

Butanol production through chemical conversions as well as using the ABE-production route has been demonstrated historically at an industrial scale. With present enormous development of novel yeast strains and process control, it would be interesting to further investigate the butanol production potential from cellulosic wastes materials to support production of bulk chemicals and fuels in the future.

The global (mostly located in China) biobased n-butanol production in 2008 reached 120 000 tons [5] corresponding to about 2% of the global total n-butanol production (petro+bio) [3, 4]. The potential global supply of biobutanol (n-butanol) is however expected to increase to > 1 million tonnes/year in 2020, to be sold as a chemical and later on as a fuel [5].

Recently butanol may be used up to 12 % in spark ignition engines. Thus, considering the allowed blending proportions in the fuels and the large efforts for increasing the bio butanol capacities in Asia, an up to tenfold increase in biobutanol production by 2020 is not unrealistic. This means that we can expect a dramatic increase of the biogenic content in the butanol industry in the near future.

The outcome of this inventory of biobutanol activities reveals that Sweden has no tradition in producing biobutanol and only limited research into the field of production. Sweden has a dominant position regarding ethanol research in the world considering the size and population of the country. However, this report reveals that the large interest in ethanol production from cellulosic biomass has not spilled over to research on the potential for butanol. The same phenomena can be seen for Brazil that also focuses on ethanol. Projects in USA are focused on isobutanol fermentation using modified yeast and mainly corn while China has re-initiated commercial production sites for bio-n-butanol not only from corn but also recently (December 2013) from lignocellulosic waste using ABE fermentation. Finally, it seems likely that we are presently witnessing a revival of this old fermentation technology with significant improvements in process technologies along with the development of natural and genetically modified bacterial/yeast strains.

REFERENCES

[1] Qureshi, N. and T.C. Ezeji, *Butanol, 'a superior biofuel' production from agricultural residues (renewable biomass): recent progress in technology*. Biofuels, Bioproducts and Biorefining, 2008. **2**(4): p. 319-330.

[2] Steen, E.J., et al., *Metabolic engineering of Saccharomyces cerevisiae for the production of n-butanol.* Microb Cell Fact, 2008. **7**(1): p. 36.

[3] Donaldson, G.K., et al., *Fermentive production of four carbon alcohols*, 2010, Google Patents.

[4] DONALDSON, G., et al., *FERMENTIVE PRODUCTION OF FOUR CARBON ALCOHOLS*, 2007, WO Patent 2,007,041,269.

[5] Cascone, R., *Biobutanol: A Replacement for Bioethanol?* Chemical engineering progress, 2008. **104**(8).

[6] Minty, J.J., et al., *Design and characterization of synthetic fungal-bacterial consortia for direct production of isobutanol from cellulosic biomass.* Proceedings of the National Academy of Sciences, 2013. **110**(36): p. 14592-14597.

[7] Jin, C., et al., *Progress in the production and application of n-butanol as a biofuel.* Renewable and Sustainable Energy Reviews, 2011. **15**(8): p. 4080-4106.

[8] Simensen, C.J., P. Fartum, and A. Andersen, *Analysis of intermetallic particles in aluminium by dissolution of the sample in butanol.* Fresenius' Zeitschrift für analytische Chemie, 1984. **319**(3): p. 286-292.

[9] Ramey, D. and S.-T. Yang, *Production of butyric acid and butanol from biomass.* final report to the US Department of Energy, Contract No.: DE-F-G02-00ER86106, 2004.

[10] Merola, S.S., et al., *Combustion process investigation in a high speed diesel engine fuelled with n-butanol diesel blend by conventional methods and optical diagnostics.* Renewable Energy, 2014. **64**(0): p. 225-237.

[11] Rakopoulos, D.C., et al., *Investigation of the performance and emissions of bus engine operating on butanol/diesel fuel blends.* Fuel, 2010. **89**(10): p. 2781-2790.

[12] Rakopoulos, D.C., et al., *Effects of butanol–diesel fuel blends on the performance and emissions of a high-speed DI diesel engine.* Energy Conversion and Management, 2010. **51**(10): p. 1989-1997.

[13] Cotton, F.A., et al., *Advanced inorganic chemistry*. Vol. 5. 1988: Wiley New York.

[14] Lee, S.Y., et al., *Fermentative butanol production by clostridia.* Biotechnology and Bioengineering, 2008. **101**(2): p. 209-228.

[15] Burk, P.L., R.L. Pruett, and K.S. Campo, *The rhodium-promoted guerbet reaction: Part I. Higher alcohols from lower alcohols.* Journal of molecular catalysis, 1985. **33**(1): p. 1-14.

[16] Voegele, E., *Abengoa to Begin Cellulosic ethanol production in April*, in *Ethanol Producer Magazine*2013.

[17] Abengoa. *Abengoa launches a technology development project for catalytic conversion of ethanol to biobutanol*. 2013 2014-01-29]; Available from: http://www.abengoa.es/htmlsites/boletines/en/febrero2013/tecnologia/.

[18] Bauer, F. and C. Hulteberg, *Glycerol-based Isobutanol*. 2013.

[19] Ezeji, T., N. Qureshi, and H.P. Blaschek, *Butanol production from agricultural residues: Impact of degradation products on Clostridium beijerinckii growth and butanol fermentation.* Biotechnology and Bioengineering, 2007. **97**(6): p. 1460-1469.

[20] van der Merwe, A., et al., *Comparison of energy efficiency and economics of process designs for biobutanol production from sugarcane molasses.* Fuel, 2012.

[21] Oudshoorn, A., L.A.M. van der Wielen, and A.J.J. Straathof, *Assessment of options for selective 1-butanol recovery from aqueous solution.* Industrial & Engineering Chemistry Research, 2009. **48**(15): p. 7325-7336.

[22] Pastèur, M.L. and M. C, *Ulla natura delle fermentazioni; Esperienze e idee nuove.* Il Nuovo Cimento, 1861. **14**(1): p. 74-76.

[23] Dürre, P., *Biobutanol: an attractive biofuel.* Biotechnology journal, 2007. **2**(12): p. 1525-1534.

[24] Chiao, J.-s. and Z.-h. Sun, *History of the acetone-butanol-ethanol fermentation industry in China: development of continuous production technology.* Journal of Molecular Microbiology and Biotechnology, 2007. **13**(1-3): p. 12-14.

[25] Zverlov, V., et al., *Bacterial acetone and butanol production by industrial fermentation in the Soviet Union: use of hydrolyzed agricultural waste for biorefinery.* Applied Microbiology and Biotechnology, 2006. **71**(5): p. 587-597.

[26] Evanko, W.A., et al., *Recovery of higher alcohols from dilute aqueous solutions*, 2012, Google Patents.

[27] Gevo. *Production-sites*. [WWW] 2014 [cited 2014 20140108]; WEB]. Available from: http://www.gevo.com/about/our-business/production-sites/.

[28] Butamax. *Latest Updates, Press releases*. [WWW] 2013 [cited 2014 20140108]; WEB]. Available from: http://www.butamax.com/latest-news-updates.aspx.

[29] Green, E.M., *Fermentative production of butanol—the industrial perspective.* Current Opinion in Biotechnology, 2011. **22**(3): p. 337-343.

[30] Ni, Y. and Z. Sun, *Recent progress on industrial fermentative production of acetone–butanol–ethanol by Clostridium acetobutylicum in China.* Applied Microbiology and Biotechnology, 2009. **83**(3): p. 415-423.

[31] Ltd., C.I.B. *PROSPECTUS FORM F-1*. 2011 [cited 2014 2014-04-08]; Available from: http://www.sec.gov/Archives/edgar/data/1517546/000104746911006440/a2204377zf-1.htm.

[32] Zeng, X., Y. Ma, and L. Ma, *Utilization of straw in biomass energy in China.* Renewable and Sustainable Energy Reviews, 2007. **11**(5): p. 976-987.

[33] Engineering, I.o.P. *Zou Jiahua Attended the Special Reports Meeting on Steam Explosion Industrialization*. [WWW] 2011 [cited 2014 20140108]; WEB]. Available from: http://english.ipe.cas.cn/ns/Events/201104/t20110425_68140.html.

[34] Lahie Rockley Bio-Chemicals Co., L. *Rockley China and Jilin Songyuan Laihe Chemicals Co Ltd announce Joint Venture to produce Industrial Scale Biobutanol from Agricultural Waste*. [WWW] 2012 [cited 2014 20140108]; WEB]. Available from: http://www.laiherockley.com/en/index.php?a=newscon&id=351&oneid=179.

[35] Ezeji, T.C., N. Qureshi, and H.P. Blaschek, *Bioproduction of butanol from biomass: from genes to bioreactors.* Current Opinion in Biotechnology, 2007. **18**(3): p. 220-227.

[36] Berezina, O.V., et al., *Reconstructing the clostridial n-butanol metabolic pathway in Lactobacillus brevis.* Applied Microbiology and Biotechnology, 2010. **87**(2): p. 635-646.

[37] Raganati, F., et al., *Butanol Production from Lignocellulosic-based Hexoses and Pentoses by Fermentation of Clostridium Acetobutylicum.* CHEMICAL ENGINEERING, 2012. **27**.

[38] Niemistö, J., et al., *Biobutanol as a potential sustainable biofuel-Assessment of lignocellulosic and waste-based feedstocks.* Fuel, 2013. **1**(1): p. 27-45.

[39] Nilsson, D. and S. Bernesson, *Halm som bränsle.* 2009.