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COMPARATIVE SYSTEM ANALYSIS OF CARBON PRESERVING FERMENTATIONS FOR BIOFUEL PRODUCTION

Report from an f3 project

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THE SWEDISH KNOWLEDGE CENTRE
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PREFACE

This project was funded by the Swedish knowledge centre for renewable transportation fuels, f3 (Fossil Free Fuels). The f3 centre is a Swedish nationwide centre that contributes to the development of sustainable transportation fuels by initiating research projects and syntheses of current research.

In this final report from the research project entitled “Carbon preserving fermentation”, focusing on the production of 1-butanol. Luleå University of Technology, Lund University and SEKAB have been active partners. A reference group has reviewed the material presented in this report and provided valuable feedback to the authors. The members of the reference group are listed below.

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SUMMARY

Today it is mutual understanding that we need to find replacements for the crude oil and natural gas in order to produce fuel and valuable chemicals even in the future. In Sweden, we are able to reduce the environmental impact and use of fossil raw material by improving the use of biomass from the forest and other origin. New systems for conversion of biomass at the Swedish pulp and paper mills, power plants among other constitute the foundation for an alternative development into a sustainable society. Fuel production from biomass has largely been focused on ethanol production. Limitations in type of raw material required for ethanol production at the large plants made butanol to a very good complement. Butanol has better fuel properties than ethanol both regarding energy content as well as handling. The established production and distribution of ethanol can be shared for cost efficient production. Recently published data suggest that a combined plant with both ethanol and butanol production by fermentation is economically attractive. The traditional and ones again interesting butanol (ABE) fermentation has a general low yield and releases carbon dioxide. The bacterial strains that are used in butanol fermentations can on the other hand utilize the sugars released from hemicellulose. Hemicellulose represents today the largest fraction of waste at the ethanol plants. Hemicellulose is also the wood component that can be easily extracted from waste generated by the forest industry.

We have in this study chosen to investigate the possibility to produce butanol via a novel hybrid process to reduce the raw material need and increase the yield of butanol. In the proposed process the conversion of biomass are made in two steps, first a fermentation that consumes carbon dioxide (succinic acid fermentation) and a second catalytic reduction step generate butanol. The project has been limited to use wheat straw as raw material. At present there are no data available that would enable a similar study based on forest feedstock. However both feedstock's' require similar pretreatment. In the report traditional butanol fermentation is compared to the suggested hybrid process both adapted for an annual production of 10 000 ton of butanol.

As a starting-point, the butanol fermentation that have been simulated in so called fed-batch mode with gas stripping in product recovery generated made the production cost for this stand-alone plant in the margin of being economically feasible. The low price on butanol produced by the petrochemical industry is today 1 000-1 650 $/ton and would only be achieved by lowered price on the feedstock or integration into larger biorefineries. The modulated process shows a raw material need of 43 500 ton of substrate (sugar) and release of approximately 24 000 ton of carbon dioxide. During butanol fermentation considerable amounts of acetone and some ethanol is also produced. In the modelled scenario 4 600 ton of acetone and 200 ton of ethanol are produced that helps in reducing the overall production cost of butanol. In the hybrid process that is presented in the report several reaction steps to convert succinic acid are combined to a unique route. In similarity with the butanol fermentation raw material cost is a major portion of the production cost. Almost 70% of the production cost is raw material cost. To lower the production cost, the succinic acid recovery process would be directly linked to the catalytic conversion. The current study was though focused at the conversion of solid, purified succinic acid and shows an improved conservation of carbon from sugar to butanol. The catalytic conversion has a predicted carbon conservation of 67 mole %. Additional improvements in this yield can significantly reduce the required amount of raw material and reduce carbon dioxide emission. The report shows that the hybrid process would need 22% less

raw material than the butanol fermentation at a succinic acid fermentation yield of 0.7 g/g substrate. In this scenario the carbon dioxide fixation would be 6 000-20 000 ton depending on the conditions during succinic acid fermentation.

A mission for the project was also to evaluate the possible co-production of chemical intermediates formed in the catalytic step. The intermediates of interest were γ-butyrolactone (GBL), tetrahydrofurane (THF). The compounds are used as solvents, in the pharmaceutical chemistry and for other applications. Changing the process to enable the production of these other compounds as well would mean significant changes, mainly regarding separation and purification units – a more complex separation scheme would have to be implemented. Thus, as the process would become more complex, the complexity and increased operating cost would have to be balanced by a significantly higher price for the new products than for butanol.

The reduced need for raw material with the hybrid process should be evaluated in a larger perspective. Life-cycle assessment including reduced greenhouse gas emissions associated with transportations would certainly show additional benefits with the proposed hybrid process.

SAMMANFATTNING

Det är i dag vedertaget att vi måste hitta ersättningar till råoljan och naturgasen för att även i fortsättningen kunna producera bränsle och andra produkter som baseras på dessa ändliga råvaror. Vi kan i Sverige minska klimatpåverkan och användningen av fossila utgångsmaterial genom att effektivisera nyttjandet av skogsråvaran och andra biomassor. Nya system för konvertering av biomassan vid landets massa- och pappersbruk, kraftvärmeverk etc. utgör grunden för en omställning till en sådan utveckling. Bränsleproduktion från biomassa har till största delen fokuserats på etanol produktion. Begränsningar i vilken råvara som kan användas till anläggningarna för etanolproduktion har föranlett att butanol utsetts som ett mycket bra komplement. Butanol har dessutom bättre bränsleegenskaper än etanol både ur energisynpunkt och hantering. Den etablerade produktionen och distributionen av etanol kan samnyttjas för kostnadseffektiv samproduktion. Forskningsresultat visar att en kombinerad anläggning för produktion av etanol och butanol genom fermentering är kommersiellt lönsam. Den traditionella och åter intressanta butanol (ABE) fermenteringen har ett generellt lågt utbyte och avger koldioxid. Bakteriestammarna som används för butanol fermenteringen kan dock omvandla det socker som utgör huvuddelen av hemicellulosan. Hemicellulosa representerar i dag den största andelen avfall som genereras vid etanolanläggningarna. Hemicellulosa är också den vedsubstans som lätt kan extraheras från skogsindustrins restavfall.

Vi har i denna studie valt att undersöka möjligheten att producera butanol genom en ny hybridprocess för att minska råvarubehovet och öka utbytet av butanol. I den föreslagna processen sker omvandlingen av biomassan i två steg, först sker en fermentering av hydrolyserad biomassa till bärnstenssyra som i ett andra katalytiskt steg genererar butanol. Projektet har begränsats till att studera utfallet med vetehalm som råmaterial. Det finns för närvarande inga grunddata som kan möjliggöra en komplett studie för skogsråvara. Båda råvarorna har dock liknande behov av förbehandling. I rapporten jämförs butanol fermenteringen med den föreslagna hybridprocessen anpassad för en produktionskapacitet på 10 000 ton butanol per år.

Med utgångspunkt från butanol fermenteringen som simulerats som en så kallad fed-batch fermentering med gas stripping för produktseparering visar rapporten att produktionskostnaden i en fristående anläggning ligger på marginalen för att vara ekonomiskt lönsam. Det låga priset på butanol framställ petrokemiskt ligger i dag på 1 000-1 650 $/ton vilket endast kan uppnås genom sänkta råvarupriser och integrering i större bioraffinaderier. Den modulerade butanol fermenteringen visar att råvarubehovet skulle uppgå till 43 500 ton substrat (socker) och avge ca 24 000 ton koldioxid. Vid butanol fermenteringen genereras också betydande mängder aceton och en del etanol. I detta scenario produceras 4 600 ton aceton och 200 ton etanol som bidrar till att reducera produktionskostnaderna. I hybridprocessen som presenteras i rapporten har flera reaktionssteg för omvandling av bärnstenssyra till butanol kombinerats till en unik process. I likhet med den jämförda butanolfermenteringen utgör råvaran det klart största delen av produktionskostnaden. Upp till 70% av priset för butanol framställd genom katalytisk omvandling av bärnstenssyra är kopplad till råmaterialkostnaden. För att minska produktionskostnaden i detta fall bör produktseparering och upprening av bärnstenssyran efter fermenteringen vara direkt integrerad med det katalytiska steget. Den aktuella processen har dock utgått från fast upprenad bärnstenssyra men visar på ett högt utbyte (67 mol%). Bara små förbättringar i detta utbyte innebär signifikanta vinster i det totala utbytet och utsläppet av koldioxid. Med samma förutsättningar som den traditionella processen vid butanolfermentering visar rapporten att hybridprocessens behov av substrat skulle vara 22% lägre vid ett totalt utbyte i bärnstenssyra fermentationen på 0.7 gram per gram substrat. I detta scenario bedöms

också att en koldioxidfixering åstadkommas på 6 000 – 20 000 ton beroende på betingelserna vid bärnstenssyra fermentationen.

I uppdraget för projektet har också värdet av intermediära kemikalier i den katalytiska omvandlingen bedömts. Bland dessa kemikalier återfinns γ-butyrolakton (GBL), tetrahydrofuran (THF) och 1,4-butandiol (BDO). En separering och upprening av dessa biprodukter skulle innebära omfattande ändringar i processen som medför ökade kostnader. Bedömningen är att dessa intermediat inte är fördelaktiga att samproducera med butanol.

De vinster som kan uppnås med ett reducerat behov av råmaterial med hybridprocessen bör utvärderas i ett större perspektiv. En livscykelanalys där hänsyn tas till minskat transportbehov bör visa på ytterligare fördelar med processen.

CONTENTS

1 INTRODUCTION

Production of second-generation biofuels from lignocellulosic biomass such as wood, energy crops, agricultural residues, and municipal solid waste is of global interest. The International Energy Agency (IEA) see a rapid increase in biofuel demand, in particular for second-generation biofuels, in an energy sector that aims on stabilising atmospheric CO_2 concentration at 450 parts per million (ppm). In a scenario 2030 where 10% of global forestry and agricultural residues, respectively, are assumed to be available for biofuel production, around 5% of the transportation fuel demand would be covered [1]. The calculations are made for production of lignocellulosic-ethanol. Constraints in biofuel production volumes are related to the availability of additional land to generate new feedstock. Industries are there for recommended to focus on currently available feedstock sources in the initial stage of development. The overall greenhouse gas impacts of lignocellulosic ethanol production based on lifecycle analyses indicate that lignocellulosic ethanol generates 91% less greenhouse gases than fossil-based petrol or diesel [2]. In this calculations the release of CO_2 during ethanol fermentation are included. An alternative alcohol also produced by fermentation is butanol. Butanol as fuel replacement to gasoline outcompete ethanol, biodiesel and hydrogen when its safety and simplicity of use are recognised. It is also compatible in different blends with ethanol and diesel with improved combustion characteristics [2]. A general advantage of using oxygenated fuels compared to hydrocarbon fuels, are reduced level of contaminants, particularly sulphur and nitrogen. The oxygen containing fuels lower the peak combustion temperature reducing emissions [3]. The conventional butanol fermentation have two main disadvantages compared to ethanol fermentation; first it has lower yield (maximum 0.41 g butanol and 0.51 g ethanol g-1 glucose), secondly it generates a lower titre 1.5-2% compared to ethanol 4-12%, resulting in higher recovery cost [4]. It is in this context we have investigated a novel, hybrid process that utilizes a fermentation that consumes CO_2 and uses subsequent catalytic reduction steps to add hydrogen to form butanol. The main issue is whether the use of hydrogen and its costs are economically advantageous. Hydrogen production from biomass can be achieved by several different processes from thermo catalytic processes to biological processes [5]. The fermentation process we selected to analyse is the use of bacteria to convert sugars and CO_2 to succinic acid (SA) which can then be converted through a series of chemical reactions to butanol (Figure 1).

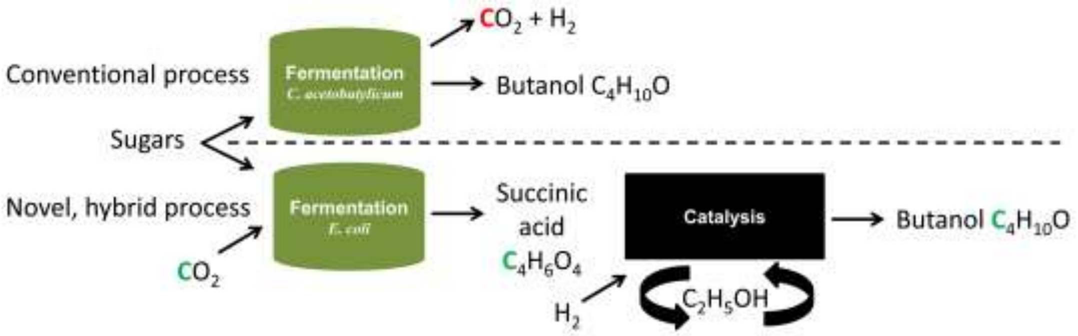


Figure 1 Overview of conventional and novel hybrid process for butanol production. In the conventional butanol fermentation process CO_2 is released from metabolized sugars. Seen in the hybrid process, CO_2 is fixed during fermentation and the carbon maintained to final product.

Within this process scheme, tetrahydrofuran (THF) is produced by the hydrogenolysis of succinate esters. Hansen *et al.* (2005) [6] reported that THF is an effective co-solvent for ethanol in diesel. Furthermore, Berglund (2004, 2009) [7, 8] reported that diethyl succinate and dibutyl succinate, respectively, could be used directly in diesel fuel to reduce particulate emissions. The production of succinic acid by fermentation is being pursued commercially by a number of companies (BASF, DSM, BioAmber) using starch as a raw materials, but no detailed economic models are publicly available. The novel process holds the potential of simultaneous biofuel and biochemical production. Biological recycling and detoxification of unwanted by-products in the same line of bioprocessing are further benefits.

1.1 AIM AND METHOD

The aim of this project is to address the primary research questions:

- What are the comparative economics of the succinic acid process as compared to the “conventional” process for the production of butanol?
- What business opportunities for chemical intermediates and diesel fuel additives are created in a biorefinery context by these processes that are not available in the current approach?

The project has developed two ASPEN (Aspen Plus® process design software, AspenTech) based process models for comparative studies on the process economics and feasibility. The first model simulates a direct sugar to butanol fermentation process and the second model conversion of succinic acid to butanol. The butanol fermentation model is scaled to manage 10 thousand tonnes butanol per year with a purity of 99.9%. Production was evaluated on sugars from wheat straw hydrolysate (WSH). The parallel process to generate butanol from succinic acid is adjusted to manage same production level and purity. The overall comparison is managed in the section called complementary analysis covering the succinic acid fermentation and both models.

2 RAW MATERIAL

To produce butanol or succinic acid by fermentation, sugar must be provided from a steady and sustainable source. In Sweden, the abundant lignocellulose produced in the cell walls of softwoods (spruce and pine) and hardwoods (birch, poplar and others) can be used. Residues from agricultural production, e.g. straw and stover, also constitute a possible source of lignocellulose in the form of straw, but will compete with its use as animal feed. The cell walls of these stocks contain cellulose, hemicelluloses and lignin (polyphenols). The ratio between these components are summarised in Figure 2. The main challenge for using lignocellulosic materials is their resistance to efficient degradation to monomeric sugars. The dominating method to liberate fibres in pulp and paper production, sulphate pulping, is efficient at selectively degrading the hemicellulose. Released carbohydrates (from hemicellulose) and lignin is typically used as fuel in the recovery boilers at the pulp mills. Different research projects; pre-extraction of wood chips [9] and black liquor fractionation have shown the potential of utilizing this flow to generate fermentable sugars by hydrolysing the released carbohydrates [9-11]. The thermochemical processes found in the industry sector associated with the pulp and paper industry, forest products, food and chemicals are highly energy efficient in biomass conversion [2]. New ways to integrate and exploit these established industries for biofuel production is attractive.

Total degradation of both cellulose and hemicellulose is the target in dedicated biorefineries. Methods used in biorefineries are described in section 2.1 Pre-treatment and hydrolysis.

The most profound difference in the raw material is the hemicellulose composition. Depending of refining method, selective or total degradation, the hemicellulose composition will influence the sugar composition. Hemicelluloses contain substituted glucans, xylans and/or mannans, and anionic components such as the galacturonic acid-containing pectic polysaccharides. The overall composition in hardwood, softwood and wheat straw is shown in Figure 2.

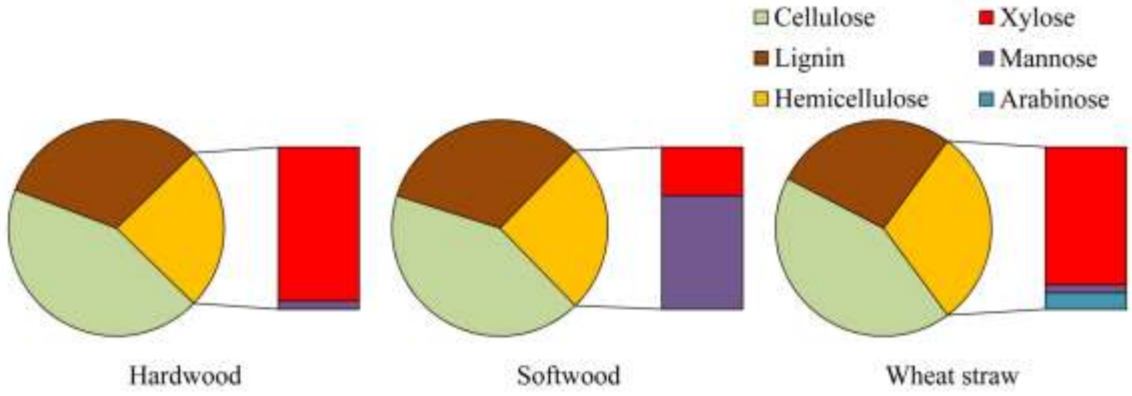


Figure 2 Cell-wall polymer composition (cellulose, hemicellulose and lignin) and hemicellulose composition (adapted from [12]).

2.1 PRE-TREATMENT AND HYDROLYSIS

Methods used to hydrolyse both the cellulose and hemicelluloses are utilized in biorefinery plants. Softwoods are more difficult to hydrolyse compared to hardwoods and agricultural residues like wheat straw due to the structure of the material. In any use of these lignocellulose materials, some type of mechanical treatment to generate fine particles is usually needed. Subsequent treatment is aimed at the fractionation of cellulose, hemicellulose and lignin in order to maximise fermentation yields and rates. Lignocellulose conversions can be combined with the fermentation through different concepts; separate hydrolysis & fermentation (SHF), simultaneous saccharification & fermentation (SSF), simultaneous saccharification & co-fermentation (SSCF) and consolidated bioprocessing (CBP) are all applicable [13].

In the current study separate hydrolysis and fermentation are considered to simplify comparison between the two different fermentations. Research and applications of SSF, SSCF and CBP on the specific fermentations are likewise limited.

In tree out of eight demonstration and pilot plants for conversion of lignocellulose to ethanol, wheat straw is used as raw material [2]. Pre-treatment is generally performed by a hydrothermal treatment (steam explosion) including weak acid hydrolysis following enzymatic hydrolysis. However in this facilities a separation of the pentose sugars are typically implemented. Pentoses sugars cannot be fermented by the yeast *Saccharomyces cerevisiae* employed in ethanol plants. The utilization of all carbohydrates is possible with Clostridium strains (butanol) [2, 14] and adapted *E. coli* strains (succinic acid) [15-17]. A schematic overview of wheat straw pre-treatment modified for butanol/succinic acid fermentation Figure 3.

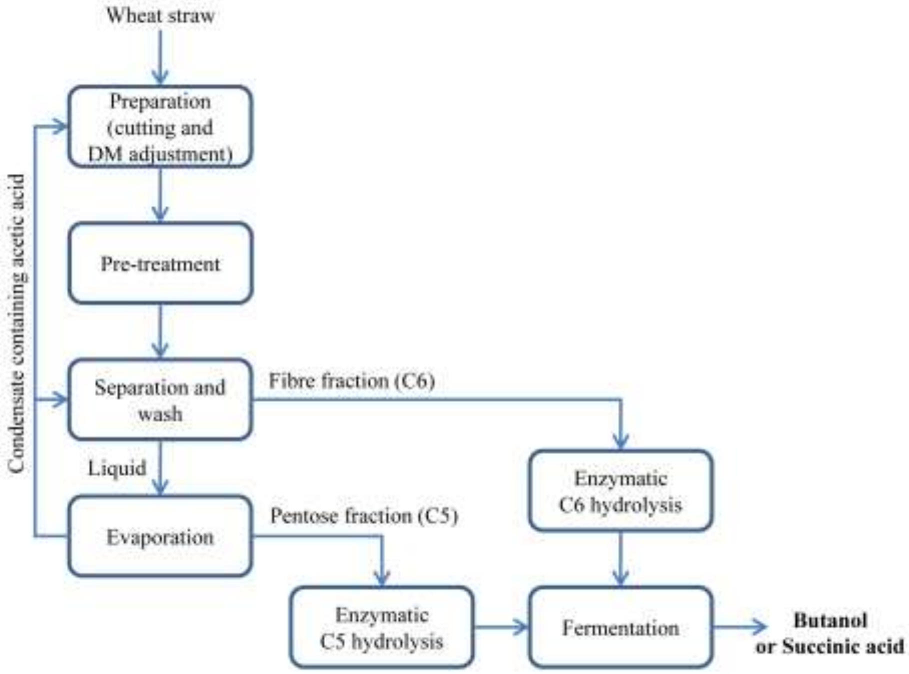


Figure 3 Overview of a pre-treatment process for wheat straw [18, 19]. The C5 and C6 fractions can also be processed simultaneously in one enzymatic hydrolysis step but most likely with lower yield. DM = Dimension adjustment to approx. 5 cm pieces.

3 THE BUTANOL FERMENTATION PROCESS

Butanol (1-butanol, *n*-butanol) can play an important role in alleviating the dependence on fossil derivatives for transportation fuel. It can be either synthesized through thermochemical routes or produced through fermentation of sugar. The latter is the focus in this work. 1-butanol with molecular formula C_4H_9OH (MW 74.12) and boiling point of 118 ^{0}C has an energy density about three fourths of gasoline. Butanol can exceed the blending limit of ethanol with gasoline (normally less than 10%) without inducing significant impact on the Otto engine performance [20, 21].

3.1 BIOBUTANOL FROM FERMENTATION

The butanol fermentation process often referred as the ABE fermentation after its main chemical products: acetone, butanol and ethanol has been practiced since 1912 when it was developed in the UK [22]. It was challenged by the petrochemical synthetic butanol production in the 1950s but still fermentative production remained until early 1980s in China, Russia and South Africa. Today fermentative production has re-emerged and is able to compete with synthetic butanol with a feedstock from starch and sugar [21, 23]. The cheaper agricultural residues; corn cobs, corn stover, sugar cane bagasse, wheat straw and municipal solid waste can be used as alternatives. Feedstock materials derived from wood and forest residues containing lignocellulose present an even larger source. Limiting the use of lignocellulose is the lack of efficient pre-treatment methods that can liberate fermentable sugars without by-products affecting the bacterial growth and productivity.

The main issues that pose problems in fermentative biobutanol production using clostridial cultures include the toxicity of butanol to the culture (maximum concentration tolerable, 10-12 g/l butanol or 20 g/l total ABE), low yield, and the production of considerable amounts of other solvents along with butanol (the main ones being acetone (C_3H_6O) and ethanol (C_2H_5OH)). In addition, acetic and butyric acid are also formed in the process. An obvious solution to inhibition would be to continuously remove the solvents from the broth or to engineer clostridia culture with high tolerance to the fermentation solvents. Recent reports on fermentative bio-butanol production from cellulosic feedstock's have indicated considerable improvements both from yield and solvent recovery point of views [24-29]. Several plausible solvent recovery technologies have also been reported in the literature, amongst others gas stripping [29, 30], pervaporation [27], liquid-liquid extraction [31], and adsorption [32] can be listed. Further details on the different recovery technologies can be found in [33-35]. Of all the techniques, gas stripping has been reported as one of the promising in situ recovery technologies both from operability and economic point of views [24, 26, 29, 30, 35].

3.2 ABE FERMENTATION USING DIFFERENT SUBSTRATES

There have been several reports on the fermentation of different feedstock's into biobutanol using clostridial cultures [2]. The fermentation process largely depends on the sugar content of the feedstock, pre-treatment process by which fermentable sugars are liberated, and the clostridial culture used. Table 1 summarizes reports on experimental results of biobutanol fermentation with in situ gas stripping for different substrates. The composition of the product condensate i.e. concentration fractions of acetone, butanol and ethanol to the total ABE in all the reports fairly agree (Figure 4).

Table 1 Fermentation of different substrates with in-situ gas stripping

Operation mode		**Fed-batch**				**Batch**		
Substrate		Glucose	Cassava		Starch	Glucose	WSH+G	Corn
Fermentation Time	hrs.	201	169	263	138	127	132	66
Glucose initial	g/l	100						
Glucose final	g/l	26.1						
Glucose utilized	g/l	500.1	245	337	226	162	129	65
Total ABE	g/l	233	90.3	109	81.3	75.9	47.6	26.5
Productivity	g/l/h	1.16	0.53	0.41	0.59	0.60	0.36	0.40
Yield (ABE)	g/g	0.47	0.37	0.32	0.36	0.47	0.37	0.41
Acetone	g/l	77.7	25.7	27.0	24.1	24.7		8.30
Butanol	g/l	152	59.8	76.4	56.2	46.4		17.6
Ethanol	g/l	3.40	4.78	5.09	1.00	4.80		0.60
Butyric acid	g/l	4.20	3.82	1.97				
Gas flow rate	l/min/l	3.00	1.25	1.25				
Acetic acid	g/l	4.30	4.29	5.24				
References		[24]	[26]		[25]	[33]	[28]	[25]

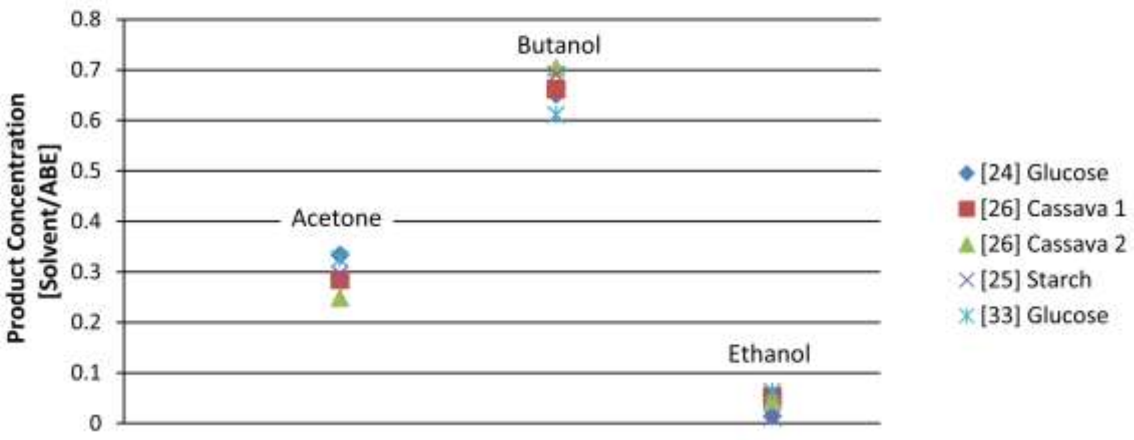


Figure 4 Composition of product condensate i.e. concentration fractions of acetone, butanol and ethanol to the total ABE.

The model initially developed is based on fermentation of glucose substrate has been adapted to handle pentose sugars conversion process. The model is built in Aspen Plus. It is a steady-state flowsheet model based on a stoichiometric reactor approach. The fermentation stoichiometry is rather a qualitative representation and the yield is controlled according to the experimental data reported by Ezeji *et al*. in [33], for hexose, as well as pentose sugars in [36]. According to the experimental data the fermentation of glucose yields 0.303, 0.155 and 0.007 in g/g-glucose of butanol, acetone and ethanol, respectively. The yields from the model are actually lower following the assumed stoichiometry summarized in Table 2 which resulted in more hexose (about 20.5% more) and pentose (about 5% more) inputs compared to the experimental ones. In fact, given the feedstock composition in this work, the conservative yield estimates that resulted due to the assumed stoichiometry maybe more realistic. In addition, it should be noted that the conversion of pentose to butanol is only balanced for the carbon atom.

The reactor is assumed to be operated on a fed-batch mode and the conditions are maintained at a temperature of 35^0C and a pressure of 1 atm, as reported in [33]. The total fermentation time is 200 hrs and stripping starts after 22 hrs. In order to render a continuous process, the overall productivity in the model is maintained using average mass flow rates over the total fermentation time. Thus, the mass flow rate of products from the fermenter is 0.556%, (=1/180, the stripping process is operated for 180 hrs.), of the fermentation broth. For the same reason, the substrate intermittently added during the fed-batch fermentation process is simulated as a continuous addition using averaged mass flow rates over the entire fermentation period. Furthermore, the glucose utilization rate is set to 95% and that of pentose sugars is set to 90% [33, 36].

Table 2 Fermentation stoichiometry for hexoses and pentoses

Product	**Stoichiometric reaction**	**Fractional conversion**	**Yield g/g glucose**
Acetone	$C_6H_{12}O_6 + H_2O \rightarrow C_3H_6O + 3\ CO_2 + 4\ H_2$	0.364	0.123
Butanol	$C_6H_{12}O_6 \rightarrow C_4H_{10}O + 2\ CO_2 + H_2O$	0.557	0.241
Ethanol	$C_6H_{12}O_6 \rightarrow 2\ C_2H_6O + 2\ CO_2$	0.010	0.005
Butyric acid	$C_6H_{12}O_6 \rightarrow C_4H_8O_2 + 2\ CO_2 + 2\ H_2$	0.013	0.007
Acetic acid	$C_6H_{12}O_6 \rightarrow 3\ C_2H_4O_2$	0.006	0.007
Acetone	$C_5H_{10}O_5 \rightarrow C_3H_6O + 2\ CO_2 + 2\ H_2$	0.343	0.148
Butanol	$C_5H_{10}O_5 \rightarrow C_4H_{10}O + CO_2 + X$	0.524	0.288
Ethanol	$C_5H_{10}O_5 \rightarrow 5C_2H_6O + 5\ CO_2$	0.011	0.006
Butyric acid	$C_5H_{10}O_5 \rightarrow C_4H_8O_2 + CO_2 + H_2O$	0.012	0.008
Acetic acid	$C_5H_{10}O_5 + H_2O \rightarrow 2\ C_2H_4O_2 + CO_2 + 2\ H_2$	0.009	0.008

3.3 IN SITU GAS STRIPPING

Gas stripping is a simple technique of recovering solvents from the fermentation broth. An inert gas, such as N_2 or CO_2, is sparged through the broth so that volatile solvents are removed continuously. Gas stripping can be applied to reactors operated on batch, fed-batch or continuous basis. It is favourable since it does not remove reaction intermediates from the fermentation broth [30]. The main disadvantage of gas stripping is that it disfavours butanol, due to the fact that butanol has the highest boiling point of the solvents present in the fermentation broth [30]. The selectivity of the stripping process for a specific compound can be calculated as described below.

Selectivity = $[y/(1-y)]/[x/(1-x)]$

Where:

y-the concentration of 1-butanol in the condensate (%wt)

x-the concentration of 1-butanol in the fermentation broth (%wt)

ABE is selectively removed during the fermentation process. In the fed-batch fermentation (22–201 h), butanol selectivity's were reported in the range of 10–22. Acetone and ethanol selectivity's ranged over 6.69–12.72 and 4.45–11.16, respectively. Furthermore, the results did not show any direct relationship between fermentation broth ABE concentration and each component's respective selectivity [24].

In the model, the gas stripper is represented as a separator with 1-butanol selectivity set to 20 [24, 30]. The selectivity of butanol is set as a design specification. In addition, no selectivity's have been assigned to the butyric and acetic acids since presence of both is not reported in the condensate [24]. The selectivity's for acetone and ethanol are set in the separator as split fractions such that their amounts in the condensate correspond to the reported values.

The stripper gas is composed of the fermentation products CO_2 (97%wt) and H_2. The gas recycle rate is 3 l/min per litre of fermentation broth [24]. According to the model more gases are produced than required for the gas stripping process and consequently part of it is bled-off. The alcohols are recovered by condensing the gases flowing out of the fermenter to a temperature of 2°C.

3.4 DOWNSTREAM PROCESSING

The downstream process is operated on a continuous basis. Five distillation columns and a triple phase decanter are used. All the columns are modelled using the RadFrac model in Aspen Plus. The product condensate are fed to the first column that separates the light components (acetone and ethanol) as overheads and the heavy ones (butanol and water) as bottoms. The overhead from the first column is fed to the second column where acetone with a purity of 99.9 wt.% is separated as overheads and hydrous ethanol as bottoms. The hydrous ethanol is fed to the third column and ethanol with a purity of 94 wt.% is fractionated as overhead. The bottoms from the third column is a mixture of water and butanol which is then mixed with the bottoms from the first column and let into the downstream processing.

3.5 BUTANOL/WATER AZEOTROPE

A triple phase flash decanter and two distillation columns are used to separate the azeotropic mixture of butanol and water. This arrangement is reported in [23]. The mixture of water and butanol enters the decanter where it is split into an aqueous and an organic stream. The organic stream is fed to a butanol stripper which separates butanol with a purity of 99.9 wt.% as bottoms and a mixture of water/butanol as overhead. The aqueous stream is also sent to water stripping that separates water with a purity of 99.9 wt.% as bottoms and water/butanol as overhead. The overheads from the two columns have almost the same composition with significant butanol concentration (~25 vol.%) concentration. They are mixed, cooled and recycled to the decanter.

3.6 INPUT-OUTPUT STRUCTURE

The overall target has been to produce 10 000 ton/year of biobutanol through the fermentation and recovery processes described in the previous sections. The feed pre-treatment and WSH preparation are not included in the analysis. Assuming 8000 operational hours per year, the input-output data are summarized in Table 3.

Table 3 Main input-output flows of the butanol fermentation unit.

Input (WSH)	**ton/h**	**ton/year**
Water	88.04	672.5
Glucose	0.58	4.6
Xylose	4.05	32.4
Arabinose	0.81	6.5
Furfural	0.02	0.2
HMF	0.01	0.1
Acetic acid	0.62	5.0
Output		
Butanol	1.25	10
Acetone	0.57	4.6
Ethanol	0.02	0.2
Off-Gas (CO_2 & H_2)	2.7	21.6
Waste water	1.83	14.7

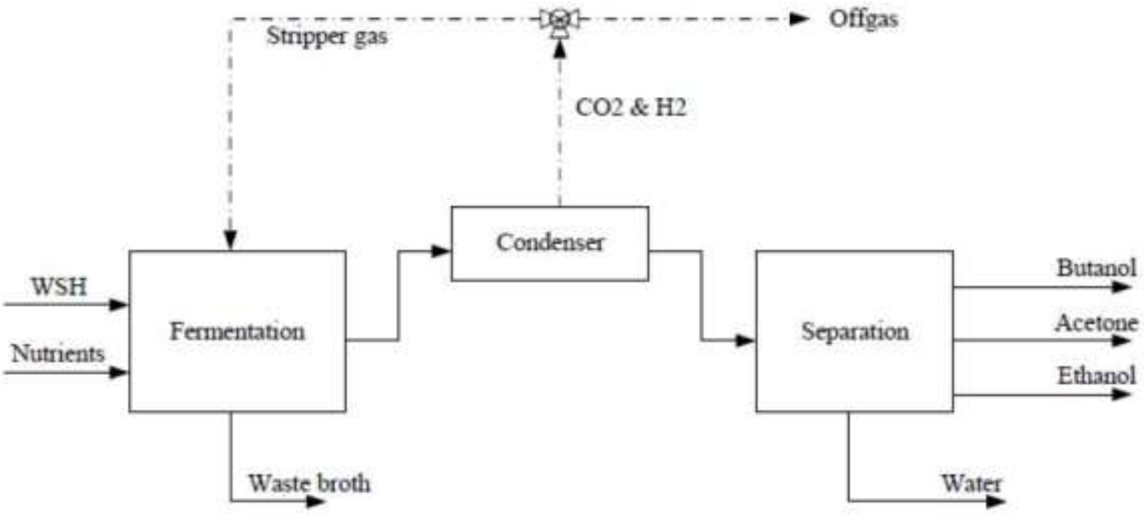


Figure 5 Schematics of the butanol fermentation process.

3.7 KEY MODEL PARAMETERS

Based on the mass and energy balance results some key characteristics of the mathematical model are tabulated in Table 4. Considering the energy content of biobutanol and wheat straw powder, the overall energy conversion efficiency is calculated to be around 32%. If acetone and ethanol are included in the analysis the overall conversion efficiency increases to about 44%.

Table 4 Model parameters.

Wheat straw hydrolysate	
Mass flow rate (T/h)	90.1
Volume flow rate (m^3/h)	89.9
Wheat Straw powder (T/h)	7.7
Energy density (MJ/kg)	18
Total Energy (GJ/h)	13.9
1-Butanol	
Mass flow rate (T/h)	1.25
Volume flow rate at 20 °C (m^3/h)	1.54
Energy density (MJ/L) [3]	*29*
Total Energy (GJ/h)	41
Conversion (MJ/L butanol)	0.32
Utility	
MP steam (MJ/h)	0.02
Electricity (GJ/h)	2.25
Energy input (MJ/L butanol)	1.5
Overall energy efficiency	0.315
Fermenter	
Holding time (h)	180
Working volume (x10^3 m^3)	11
Total Fermenter volume (x10^3 m^3)	13

3.8 TECHNO-ECONOMIC EVALUATION

The assessment is performed by estimating the cost of unit operations involved in the process, based on the flowsheet developed in Aspen Plus, and by applying factorial methods to evaluate the investment cost. The sizing of the components is also based on the mass and energy balance reported above. Further, since the fermentation process is operated on a fed-batch mode a schedule for rendering continuous operation has been assumed and evaluated during the economic assessment. The capital cost is estimated according to the following expression:

$$Capital\,cost = \sum\left[(Equipment\ purchase\ cost \times h_f \times f_m)\right] \times f_i \times f_b \times f_p$$

Where:

h_f - Hand factor, f_m - material factor, f_i - instrumentation factor, f_b - building factor and f_p - place factor.

3.8.1 Investment cost

The cost of equipment for the unit operations involved in the process is estimated using correlations and data available in literature [37]. The initial estimates have been corrected to match the pressure and material requirements of the current process using factors reported in the same literature. The estimated costs are based on chemical engineering plant cost index (CEPCI) 460 (year 2005) and are adjusted for inflation and are reported for the year 2011 (CEPCI 586). The resulting cost is then multiplied with a hand factor for the equipment type to account for piping, insurances, installations etc. The hand factors used in the analysis are summarized in Table 5.

Table 5 Hand factor for carbon-steel (CS) equipment's [37].

Equipment type	Hand factor
Fractionation column	4
Pressure vessels/tanks	4
Heat exchangers	3.5
Pumps	4
Compressors	2.5
Reactors	4

The final project capital cost is estimated to be 62.04 MUSD (Table 6). It should be noted that the largest share (about 80%) of the equipment cost results from the fermenters. 10% and 15% of the investment cost are added to the investment cost estimate to account for the start-up [37] and working capital [38], respectively. Assuming 13% interest rate of return and 15 years economic life time, the annuity becomes 9.60 MUSD.

Table 6 Equipment costs, investment cost and overall initial capital cost.

Equipment type	MUSD
Reactors (agitated)	17.5
Heat Exchangers	0.11
Pumps	0.12
Compressors	0.95
Evaporator and Decanter vessels	0.14
Storage vessels	0.61
Columns (including accessories)	2.38
Total equipment cost	**21.78**
Instrumentation factor	1.55
Buildings factor	1.47
Total investment cost	**49.64**
Start-up cost	4.96
Working capital	7.45
Overall initial capital cost	**62.04**

3.8.2 Production costs

The production cost accounts mainly for the costs incurred by the purchase of raw materials, utilities (HP, MP and LP steam, water, electricity, refrigeration etc.) and labour. The process requires MP steam for heating, cooling water, electricity and refrigeration. Since a heat pump has been included in the process design, the refrigeration demand is accounted by the electricity demand of the compressor. The costs for raw materials and utilities have been accounted according to the unit costs summarized in Table 7.

Table 7 Prices used in the economic analysis

Type	Unit Cost
WSH diluted ($/tonne)	30
Electricity ($/kWh)	0.06
HP steam ($/tonne)	100
MP steam ($/tonne)	50
LP steam ($/tonne)	0
Water ($/tonen)	0.2

The required number of personnel has been estimated using the data available in literature [27] where fractions are assigned for personnel per unit operation per shift. These fractions are multiplied with the number of unit operations of each type and with the number shifts and summed up to obtain the total number of persons needed. Accordingly, there are 9 compressors (0.09 persons/shift/unit), 20 reactors (0.25 persons/shift/unit), 5 distillation towers (0.25 persons/shift/unit), 6 heat exchangers (0.05 persons/shift/unit), and 2 evaporators (0.15 persons/shift/unit). Assuming 5 shifts, about 41 personnel are required. This has been accounted in the production cost estimation by assigning USD 71 500 per person per year. The production cost is summarized in Table 8.

Table 8 Production cost of butanol with and without acetone/ethanol included.

Input	$/m^3 butanol	$/m^3 ABE
WSH ($/tonne)	1753	1178
Electricity ($/kWh)	24	16
MP steam ($/tonne)	275	185
Water ($/tonne)	50	34
Capital cost	778	522
Labour	220	148
Total	**3100**	**2082**

It can be inferred from the results that the production cost is largely affected by the raw material cost (57%) followed by the capital costs (25%), MP steam (9%) and labour costs (7%). As it can also be perceived from Table 8, the production cost of biobutanol reduces significantly (by about 33%) when acetone and ethanol are included in the analysis as main products.

3.8.3 Sensitivity Analysis

A sensitivity analysis has been carried out towards the parameters which largely affect the production cost. The cost of raw material is one of the main contributors to the cost of production consequently a sensitivity analysis is performed by varying it from $1/ton to $50/tonne-WSH and is presented in Figure 6.

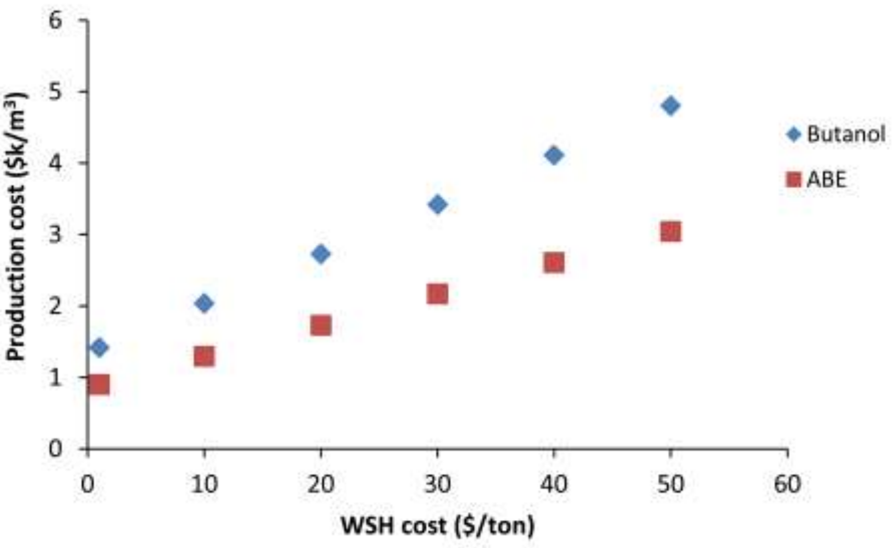


Figure 6 Sensitivity of butanol production costs to feedstock costs.

The economy of biobutanol production through fermentation is largely affected by the capital costs which are mainly incurred due to the large volumes of fermenters required as a result of the long holding time during fermentation. However, there are several reports for batch fermentation which require shorter fermentation time than used in the current work. A sensitivity analysis has also been performed to emphasize on the effect of the fermentation time on the production costs (Figure 7).

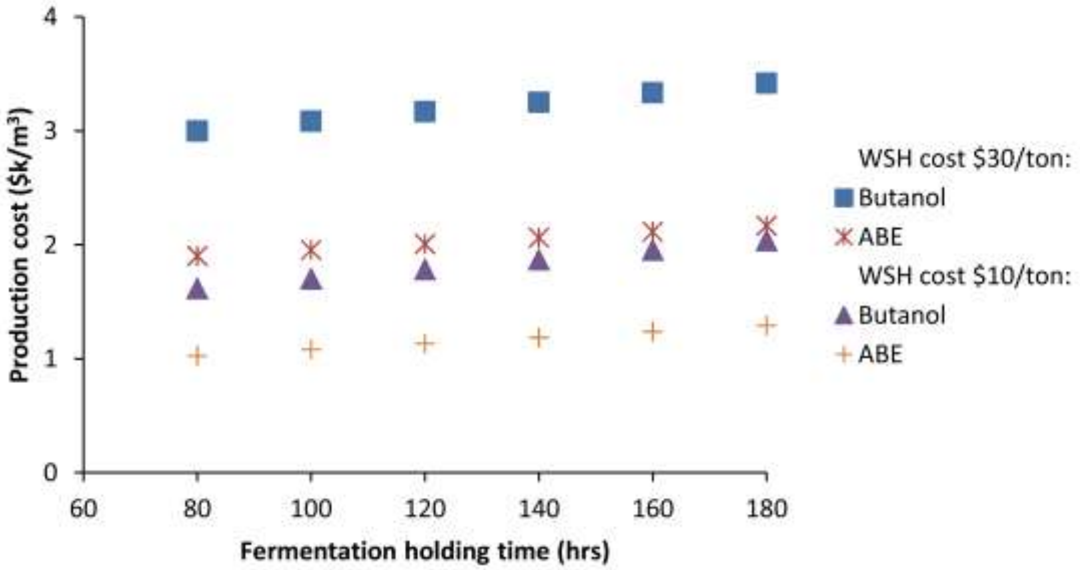
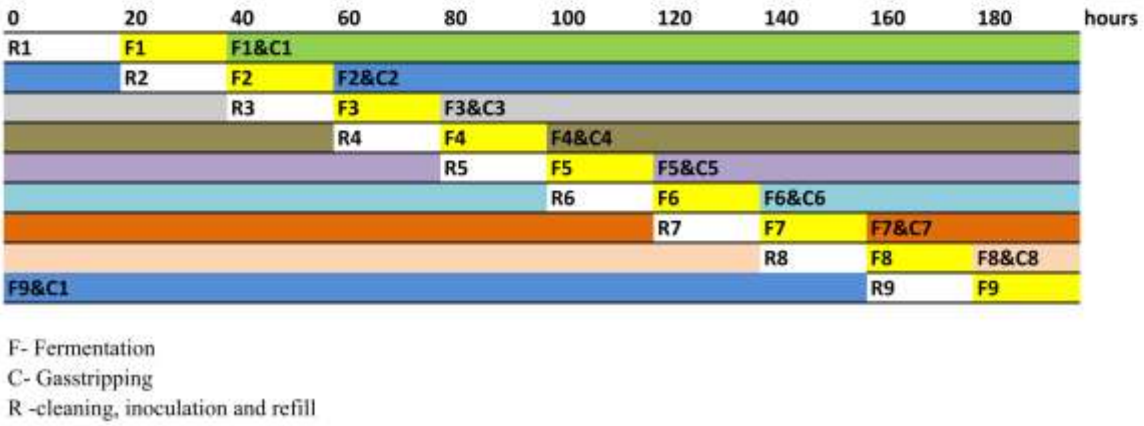


Figure 7 Sensitivity of butanol production costs to fermentation holding time.

The fermenter size used in the model is 750 m^3. Depending on the fermentation time the total volume is calculated and divided by the scheduling factor and then by the fermenter unit volume, i.e. 750 m^3, to estimate the number of fermenters to be operated in parallel. The scheduling factor is the factor resulted from the assumed schedule for continuous operation. In all the cases, 20 hrs is assumed for cleaning, refilling and inoculation and another 20 hrs before gas stripping is commenced, see Figure 8. Furthermore, the productivity is assumed to remain the same during the sensitivity analysis.



F- Fermentation
C- Gasstripping
R -cleaning, inoculation and refill

Figure 8 Schedule for continuous butanol production

4 THE SUCCINIC ACID PROCESS

Succinic acid has previously been produced as a specialty chemical by catalytic conversion of maleic acid or maleic anhydride from fossil sources. Succinic acid has however been identified as an important molecule in new green chemical processes as it can be produced by bacterial fermentation and has the potential to replace the widely used fossil maleic acid in many processes. The possibility to catalytically convert succinic acid to butanol is investigated to compare a traditional, catalytic process with the microbial process developed in the project.

Several national investigations on the future of the chemical industry have pointed out succinic acid as a cornerstone in future chemical engineering. One of the most interesting properties of the molecule is the potential it has for new polymers, both the acid itself and its derivatives [39, 40]. Succinic acid is an intermediate product in the citric acid cycle and thus a by-product in fermentation processes, but can also be produced separately as an end-product via anaerobic processes. Research on succinic acid production is vast and has been reviewed several times [40-43] but is not investigated in depth here. Firstly, a short presentation of the research on chemical conversion of succinic acid to different intermediaries and end-products is presented. Thereafter follows a section on conversion of succinic acid to butanol through an identified path via 1,4-butanediol and 3-buten-1-ol.

4.1 SUCCINIC ACID – A PLATFORM MOLECULE

Succinic acid is being promoted as a key compound for the future bio-based chemical industry as it can be converted to several useful chemical compounds. Among the derivatives suggested by several researchers are pyrrolidones which are important solvents, succinate salts which can be used as deicers, γ-butyrolactone (GBL) which is used in the pharmaceutical and agrichemical industry, tetrahydrofurane (THF) which is another important solvent and 1,4-butanediol (BDO) which is a useful intermediary for many processes [42, 44-47]. These are only a few of the possibilities to turn succinic acid into high value chemicals. Figure 9 shows some of the feasible production paths for these and other chemicals from bio-based succinic acid. The hydrogenation reactions producing GBL, THF and BDO, which may possibly be the most important path, will be further discussed later.

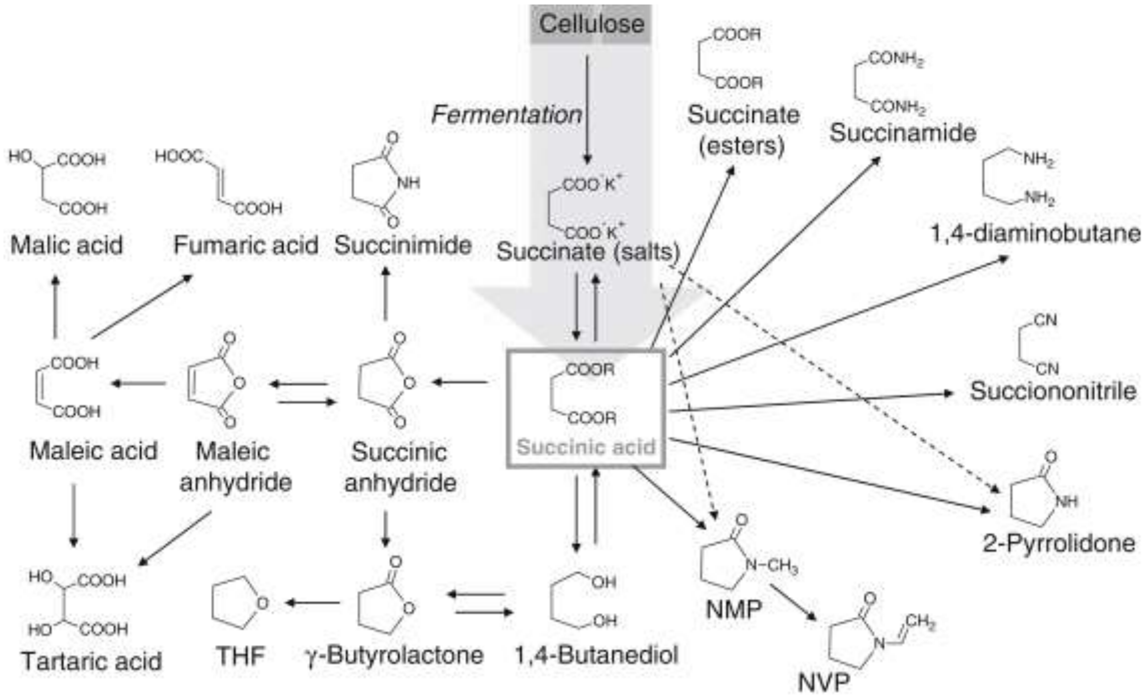


Figure 9 Suggested derivatives of succinic acid [45, 48].

However, apart from the products mentioned above, one of the most important aspects of succinic acid production is the possibility to use it for the production of biopolymers. New materials will be needed to substitute the many petroleum derived plastics which are used in vast volumes today. New, bio-based polymer processes thus have the possibility to be implemented in large scale if it can be shown that they are feasible. Succinic acid can be used to produce plastics which can compete with fossil polymers and is thus very interesting for this, potentially vast, market. The first commercial polymer based on succinic acid derived monomers is the Bionolle [49], which is a polyester of succinic acid and BDO, yielding poly(butylene succinate) (PBS). The polymer is yet produced from fossil derived succinic acid, but the production is intended to substitute this with bio-based feedstock in the future. PBS has good biodegradability and the interest for the material is increasing, several manufacturers are now producing PBS for applications such as plastic bags, packaging film and others. A thorough review of the possibilities for PBS is presented in [50]. Other possible polymerization paths are presented in [51]. Succinic acid and its derivatives can be used to produce polyamides such as polysuccinamide. Variations of common plastics such as PET can be produced from BDO, yielding instead polybutylene terephthalate [39, 50-52].

4.2 SUCCINIC ACID TO BUTANOL THE CATALYTIC CONVERSION POSSIBILITIES

A suggested reaction path to produce butanol from succinic acid is to hydrogenate the acid, which gives 1,4-butanediol. Subsequent dehydration forms 3-buten-1-ol which can be hydrogenated to butanol using standard methods for hydrogenation of unsaturated carbohydrates. This reaction path is shown in Figure 10. Below, each of the reactions will be described discussed.

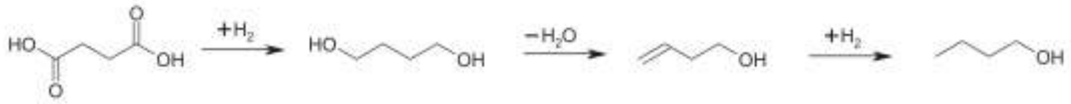


Figure 10 Catalytic conversion of succinic acid to butanol via 1,4-butanediol and 3-buten-1-ol.

4.2.1 *Hydrogenation of succinic acid*

As pointed out earlier, hydrogenation of succinic acid is one of the most important processes in the usage of bio-based succinic acid. The hydrogenated derivatives BDO, GBL and THF are all used in large quantities and will be cornerstones in the future downstream succinate industry [42]. The reaction network for the hydrogenation process of maleic and succinic acid is shown in Figure 11.

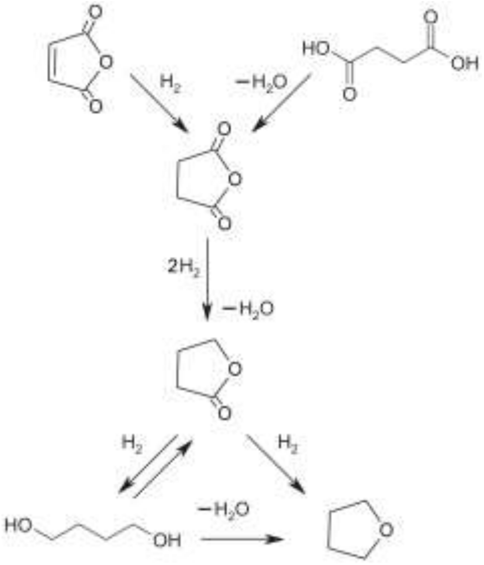


Figure 11 A simplified reaction network for maleic and succinic acid hydrogenation as described by [42].

Many patents have been published in the area of maleic acid and anhydride hydrogenation, covering process design and catalyst production to efficiently hydrogenate different feedstock mixes to the three compounds GBL, THF and BDO. However, the scientific literature presents only a few papers on the subject of hydrogenation of succinic acid, and no systematic research on catalyst materials for the process [45]. Since both GBL and THF are valuable products, coproduction of these compounds seems common. The compounds are used as solvents, pharmaceutical chemistry and for other applications and are more valuable than BDO, thus the processes are often not optimized for sole production of BDO.

Further, although there are many similarities between the traditional maleic acid and processes and the new ones based on succinic acid, there are several complications which will be necessary to handle. Whereas maleic acid is produced from petroleum based feedstock's and thus has been handled in organic solvent phase, succinic acid will be available in a water solution from the fermentation broth. The catalysts must therefore be tolerant not only to water, but ideally also to salts and other contaminants which will be present in the solution, to reduce the need for expensive high-grade purification of the succinic acid before conversion. Table 9 presents some of the more recent patents on catalysts for hydrogenation of maleic or succinic acid or anhydride to 1,4-butanediol.

Table 9 Some catalysts patented for hydrogenation of SAC/N or MAC/N to BDO.

Catalyst	Feedstock	Phase	BDO selectivity	Year	Ref.
Co	MAN		69 %	1991	[53]
ReO/CuO/ZnO	MAN/SAN	gas	94 %	1991	[54]
Ru/Ni/Co/ZnO	SAN in GBL		93 %	1993	[55]
Pd/Ag/Re on C	MAN		74 %	1995	[56]
Pd/Ag/Re on C	MAC	liq.	93 %	1997	[57]
Pd/Ag/Re/Fe on C	MAC	aq.	90 %	1999	[58]
Ru/Sn on TiO2	MAC/SAC	aq.	94 %	1999	[59]
Pt/Rh/Sn	MAC	aq.	91 % (BDO +THF)	2003	[60]
Pd/Ag/Re	MAC	aq.	>90 %	2006	[61]
CuO on ZnO/Al2O3	MAC/SAC	gas		2006	[62-64]
CuO on ZnO/Al2O3	MAC/SAC	gas	82 %	2008	[65]
Pd/Re on TiO2	SAC	gas	85 %	2011	[66]

Apart from the patent literature, Herrman and Emig investigated several commercial liquid phase hydrogenation catalysts based on copper and noble metals [67]. Succinic acid was hydrogenated to GBL and the same catalysts were used to hydrogenate the GBL further to BDO. The highest selectivity's for BDO production were found when using a Cu/Zn catalyst (G66).

The hydrogenation reaction yields equilibrium of the three products BDO, GBL and THF, but they are favoured at different thermodynamic conditions. Generally, BDO seems to be favoured at higher hydrogen pressures (4-10 MPa) and lower temperatures than what favours THF production [42, 44]. Roesch *et al*. describe how the product specification can be changed by varying the process conditions [65]. The product stream from the hydrogenation process will however always contain a relevant share of by-products. Apart from the three main hydrogenation products, by-products may be carboxyl acids and alcohols with lower carbon numbers. Fractional distillation to separate the hydrogenated products is thus suggested in several process descriptions [42].

4.2.2 *Dehydration of 1,4-butanediol to 3-buten-1-ol*

Dehydrating BDO 3-buten-1-ol has been investigated thoroughly by a research group in Japan. Among the catalysts investigated were CeO_2 [68, 69] and sodium modified ZrO_2 with selectivity of more than 70 % [70], although higher yields and selectivity's were reached when using rare earth oxides. Most suited were weakly basic, heavy rare earth oxide catalysts such as Dy_2O_3,Ho_2O_3, Er_2O_3,Tm_2O_3,Yb_2O_3,Lu_2O_3, and Y_2O_3 supported on ZrO_2 [71-73] with Yb_2O_3 standing out as the best catalyst for the reaction. This catalyst gave a selectivity for conversion of 1,4-BDO to 3B1O of about 85% at atmospheric pressure and 325 °C. By-products from the process are THF, 2-buten-1-ol and some other components.

4.2.3 *Hydrogenation of 3-buten-1-ol to butanol*

Selective hydrogenation of unsaturated compounds is a very common industrial process and thus catalysts for this purpose are widely available.

4.3 INPUT-OUTPUT STRUCTURE

The target in of succinic acid conversion to butanol is set to match the fermentation process; production level of 10 000 ton/year and 8000 operational hours per year. The starting point of modelling is a commensally available succinic acid (Biosuccinium™) produced by fermentation at Reverdia's plant in Cassano, Italy.

Table 10 Composition of Biosuccinium™ according to the producer

Parameter	Specification
Purity (dry basis)	≥ 99.5 w%
Water content	≤ 1.0 w%
Other organic acids	≤ 0.1 w% each
	≤ 0.5 w% total
Iron	≤ 5ppm

The input-output data are summarized in Table 11.

The schematics of the developed process are shown below in Figure 12. The model that was used for the techno-economic evaluation did however not include the initial succinic acid fermentation, but started with an input of pure succinic acid to the thermochemical process. The process was modelled using the software Aspen Plus.

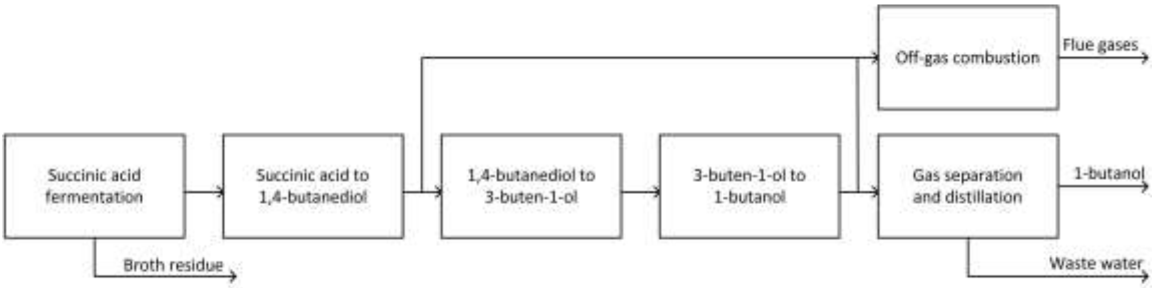


Figure 12 Schematics of the thermochemical production process for production of 1-butanol from succinic acid.

Table 11 Main input-output flows of the thermochemical production process.

Input	ton/h	ton/year
Succinic acid	2.955	23637
Water	8864	70913
Hydrogen	257.2	2057
Nitrogen	2720	21758
Oxygen	825.8	6606

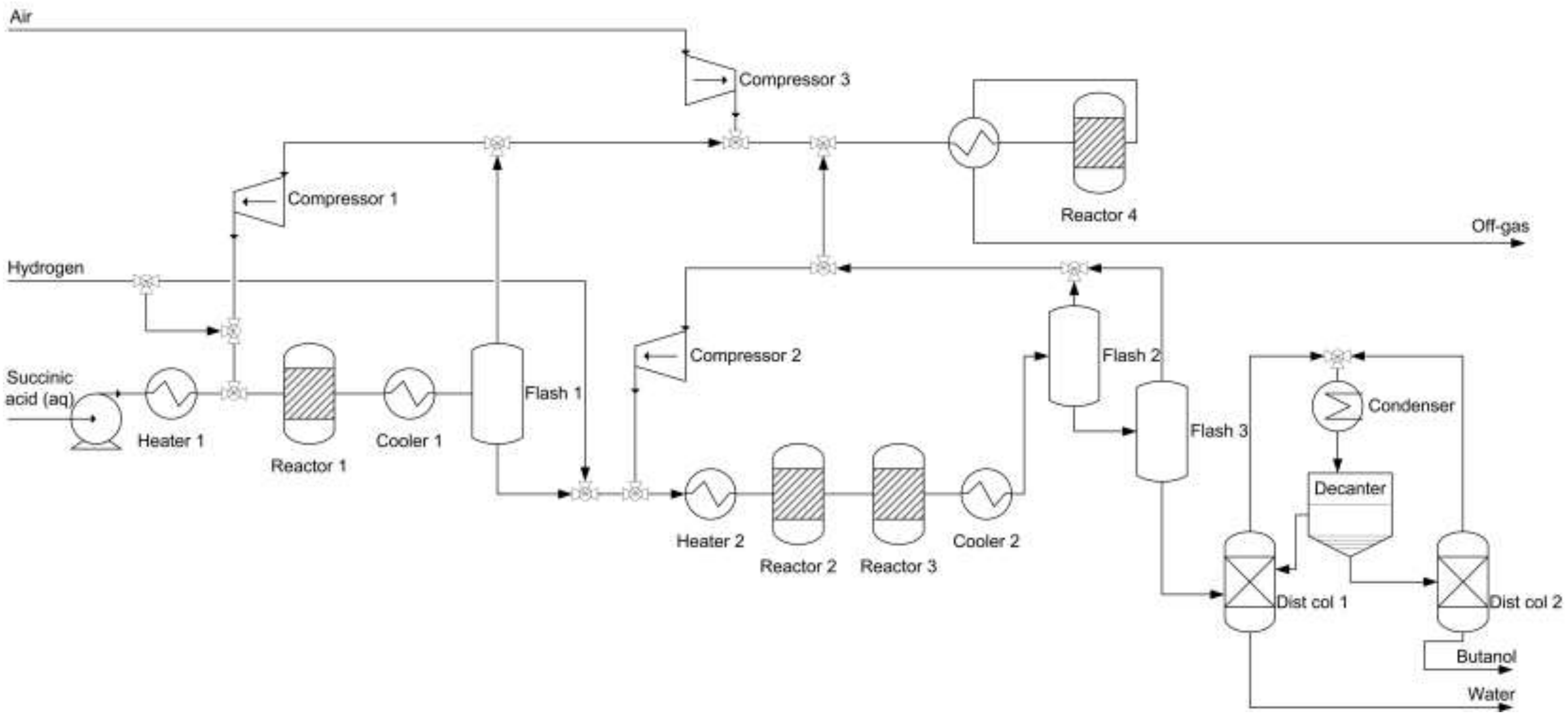


Figure 13 Process flow diagram schematically describing the catalytic conversion of succinic acid to butanol

4.4 TECHNO-ECONOMIC EVALUATION

In a similar fashion to the fermentation-based conversion, the production cost of the thermal route is determined. The heat and mass balance has been determined using the Aspen plus software and has been the basis for the detail dimensioning of the unit operations. The detailed information on the unit operations have been used for estimating the costs and the flow rates for determining the operational costs.

4.5 INVESTMENT COST

The investment cost has been determined using the detailed design of the equipment as per the simulations. The underlying data has been collected from the literature [37] and [74]. The major costs are summarised in Table 12 for a CEPCI of 586 and including the Hand factors given in Table 5.

Table 12 Equipment costs and overall initial capital cost.

Equipment type	**MUSD**
Electrolyser	11.13
Buildings	6. 63
Controls	8.10
Hydrogenation reactor 1	4.88
Dehydration reactor	4.21
Miscellaneous	2.91
Separation	1.16
Wastewater treatment	0.99
Compressors	0.62
Boiler	0.63
Hydrogenation reactor 2	0.60
Off-gas combustion	0.10
Total equipment cost	**41.97**
Start-up cost	4.20
Working capital	6.29
Overall initial capital cost	**52.46**

As may be viewed in the table the overall investment cost comes to about $52 million. Out of this, the electrolyser investment cost is the most expensive single item. This is followed by buildings and control system. The reactors for performing the reactions are also accounted amongst the most expensive, especially the dehydration reactor and first hydrogenation reactor. Assuming 13% interest rate of return and 15 years economic life time, the annuity becomes 8.11 MUSD. The investment costs, excluding start-up cost and working capital, are further illustrated in Figure 14.

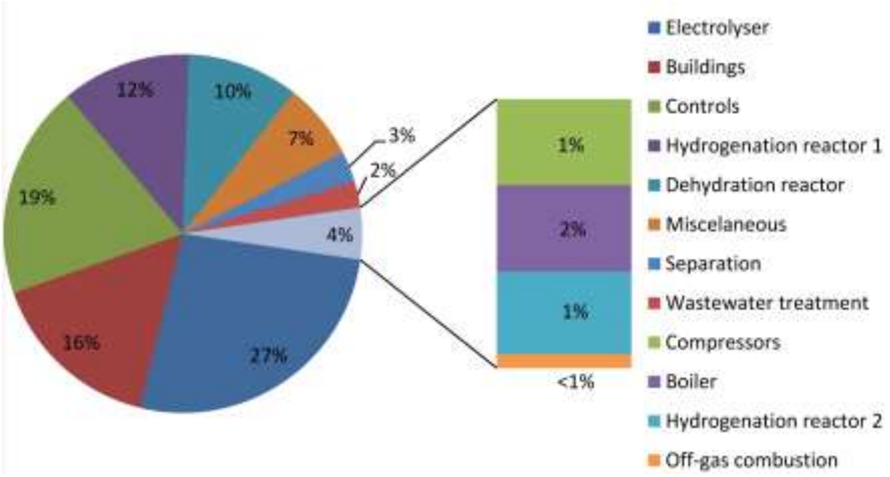


Figure 14 Breakdown of the investment cost of the thermochemical plant.

4.5.1 Production costs

The required number of personnel has been estimated using the data available in literature where fractions are assigned for personnel per unit operation per shift as previously described. These fractions are multiplied with the number of unit operations of each type and with the number shifts and summed up to obtain the total number of persons needed. Accordingly, there are 3 compressors (0.09 persons/shift/unit), 4 reactors (0.25 persons/shift /unit), 2 distillation towers (0.25 persons/shift/unit), 9 heat exchangers (0.05 persons/shift/unit), 1 decanter (0.1 persons/shift/unit) and 3 flash vessels (0.05 persons/shift /unit); for the electrolysers 1 persons/shift/unit. Assuming 5 shifts, about 20 personnel are required. This has been accounted in the production cost estimation by assigning USD 71 500 per person per year. The production cost is complemented with a production cost of succinic acid with $ 2000/tonne and summarized in Table 13 [75].

Table 13 Butanol production cost based on a succinic acid cost of $ 2000/tonne.

Input	**\$/m^3 butanol**
Succinic acid	$4 728
electricity	$623
water	$4
wastewater	$163
HP Steam	$377
MP Steam	$235
Personell cost	$143
Capital cost	$812
Production cost	**$7 083**

It can be inferred from the results that the production cost is largely affected by the raw material cost as this is the single largest factor affecting the production cost. The distribution of the production cost on raw materials, utilities, capital and labour is shown below in Figure 15.

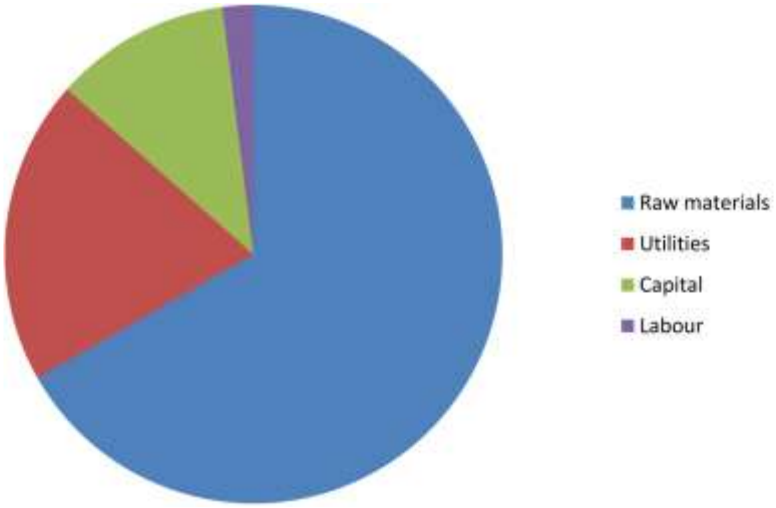


Figure 15 Distribution of the production cost of butanol from succinic acid.

4.5.2 Sensitivity Analysis

The most influential parameter by far is the cost of the succinic acid, as shown above. Varying the cost of succinic acid by ±50%, i.e. between 1250 and 3750 $/tonne, has a major impact on the total production cost. The Figure 16 shows this dependency of the butanol production price on the cost of succinic acid.

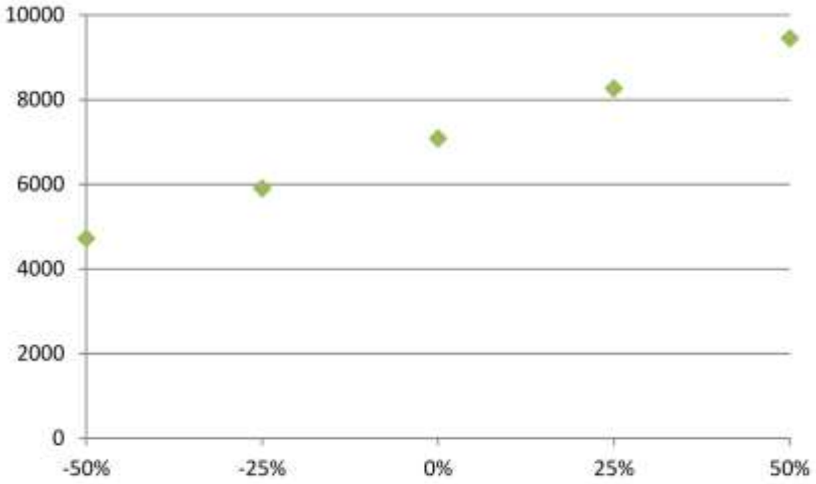


Figure 16 Butanol production cost as a function of the succinic acid cost centered at $ 2500/ton.

5 COMPLEMENTARY ANALYSIS

In order to compare the two models starting from sugar, a complementary analysis covering the succinic acid fermentation is necessary (Figure 17). This analysis includes expected yields using different raw materials, carbon dioxide balances and recovery of succinic acid.

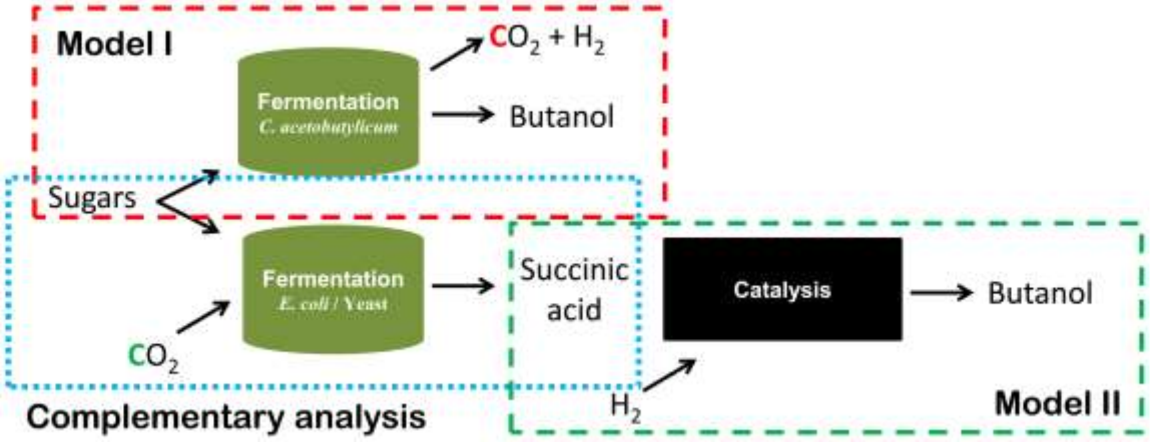


Figure 17 Overview of process models including the complementary analysis interconnecting the two models.

5.1 CARBON DIOXIDE FIXATION

The complex dual-phase fermentation used for succinic acid production with both an aerobic cell growth phase and an anaerobic production phase is difficult to implement in simulations. An inborn obstacle of capturing this process is the slow microbial growth occurring after the diauxic shift (in-between aerobic and anaerobic phase). At this stage the bacterial strain direct metabolism into maintenance and synthesis of product where no growth is detected. Yet with a holistic methodology using closed bioreactor systems key parameters regarding the overall mass balances can be calculated. In this way, data regarding the carbon dioxide fixation and yields were obtained [76]. Mentioned study is one of few covering the two-phase fermentation and has consequently been used to provide data for the scale up estimations. Fed-batch fermentation at pH 7.0 and 6.3 was evaluated resulting in different carbon dioxide fixations and yields Table 14.

Table 14. Overall two-stage yield and CO_2 requirement using glucose as substrate.

pH	**7.0**	**6.3**
Yield of succinic acid (g/g glu)	0.77	0.87
CO_2 required (g/g SA)	0.89	0.26

The yields obtained with glucose should be adjusted to wheat straw to justify comparison. The CO_2 fixation using pentoses as substrate should not deviate more than 6% from acquired glucose data based on current metabolic models [77]. The CO_2 fixation estimation on pentose (xylose) was calculated by flux variability analysis [78] assuming equal substrate uptake rate (weight adjusted), product formation rate and biomass formation. Scenario estimating CO_2 fixation is found in section sensitivity analysis below.

5.2 EFFICIENCY IN FERMENTATIVE PRODUCTION OF SUCCINIC ACID

Succinic acid production using various raw complex materials is summarized in Table 15. The succinic acid yield and productivity depend on the sugar, nutrient and inhibitor concentrations in the biomass derived media [15].

Table 15 Succinic acid production using various raw materials

Substrate	Yield (g/g sugar)	Productivity (g/L h)
Cane molasses	0.80	1.15
Corncob hydrolysate	0.58	0.49
Corn core	0.89	0.67
Corn straw	0.81	0.70
Corn stover hydrolysate	0.66	1.38
Crop stalk (corn stalk and cotton stalk)	1.23	0.62
Glucose with spent Brewer's yeast hydrolysate	0.69	0.98
Rapeseed meal	0.12	0.33
Rice straw	0.63	0.37
Straw hydrolysate	0.81	0.95
Flour hydrolysate and fungal autolysate	0.81	1.19
Wheat hydrolysate with seawater	0.94	1.12
Wheat straw	0.74	0.40
Wheat milling by-products hydrolysate	1.02	0.91

The yield of succinic acid after fermentation is high (Table 15) compared to butanol fermentation (< 0.3 g/g glucose, Table 1, 2) regardless of the substrate used. However the succinic acid needs to be recovered from the fermentation broth which contains by-products such as cell biomass and unconsumed substrates. Succinic acid recovery is traditionally performed by precipitation using ammonia and calcium hydroxide. Several new strategies have been investigated and a summary of some selected methods and their obtained recovery have been summarized in Table 16 [15, 48, 79, 80]. Information on recovery process used in current succinic acid industrial plant is not available.

Table 16 Summary of downstream processing methods for succinic acid recovery.

Recovery method	Yield (%)
Ammonia precipitation	93
Electrodialysis	60
Direct crystallization, ion-exchange	89
Reactive extraction	97-99

5.3 SENSITIVITY ANALYSIS

Starting with butanol fermentation and the yields used for modelling, it is assumed that the modeled fed-batch fermentation would require 43 500 ton of substrate (glucose, xylose and arabinose). This translates to an overall yield of 0.23 g butanol per g substrate. The catalytic conversion yield is predicted to 0.42 g butanol (including 2-butanol) per g SA and will therefor require a total fermentative succinic acid yield of at least 0.54 g SA/g substrate to start with equal amount of substrate (43 500 ton). This level of yield in the succinic acid fermentation can be achieved with most raw materials if the recovery is sufficient (Table 15, 16). To summarize, a plot of required substrate for production of 10 000 ton of butanol with the two approaches, Figure 18.

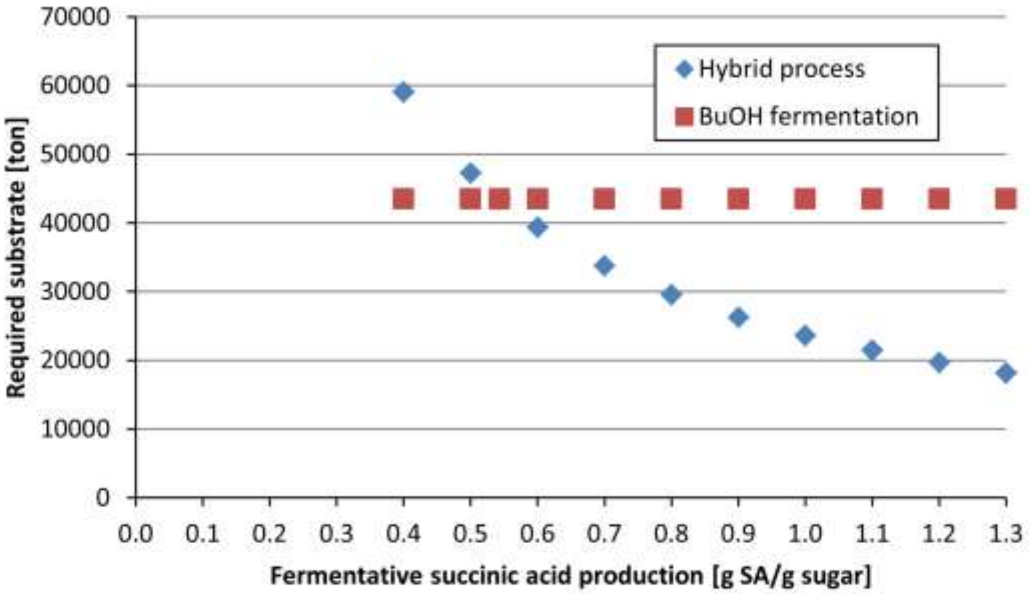


Figure 18 Substrate requirement for production of 10 000 ton of butanol as a function of SA yields.

Assuming a feasible overall succinic acid yield of 0.7 (g SA/g sugar) a raw material saving of 22% can be made. In this scenario the CO_2 fixation can be calculated from earlier described estimations (Table 17).

Table 17 Substrate requirement and carbon dioxide fixation at succinic acid yield of 0.7 (g SA/g sugar).

Model	Butanol fermentation	Hybrid process
Substrate (ton)	43 500	33 767
Succinic acid (ton)	0	23 637
CO_2 fixation during fermentation (ton)	- 24 211 (released)	6 000 - 20 000
Butanol (ton)	10 000	10 000

During succinic acid fermentation other by-product such as formic acid, acetic acid and pyruvic acid are also formed. The gas production during conventional butanol fermentation includes release of both carbon dioxide and hydrogen. From the Aspen model we get that 24 211 ton of carbon dioxide (Off-Gas, CO_2 and H_2, 3.12 ton/h * 8000 h * 0.97 wt%) is released during butanol fermentation.

6 CONCLUSIONS

The aim of this study was to investigate a novel route of butanol production. This new hybrid process would then be compared to the conventional fermentation process for production of butanol. We can conclude from our investigation of the conventional process that it is on the margin of being economically feasible. Based on current price on butanol produced by the petrochemical industry 1000-1650 $/ton [36], the cost of fermentative production cannot be performed as stand-alone plants. In a recent study aiming at utilizing the pentose sugars in an existing ethanol plant by ABE fermentation, profitability can be achieved [36]. The production level of butanol was calculated to be 7 to 12 thousand tonnes per year similar to our simulation. This study was using batch fermentation which is less productive than the fed-batch process we have modelled. To push the production cost even further some of the distillation columns can be replaced with a liquid–liquid extraction column used for product recovery [81]. In any fermentation process, product recovery is a major challenge. This is also affecting the current price of the succinic acid produced by fermentation. The production cost of butanol from succinic acid by the hybrid process is mainly attributed to the price of succinic acid. Almost 70% (Figure 15) of the production cost is raw material cost. To lower the production cost, the succinic acid recovery process would be directly linked to the catalytic conversion. The current study was though focused at the conversion of solid, purified succinic acid and shows an improved conservation of carbon from sugar to butanol. The catalytic conversion has a predicted carbon conservation of 67 mole %. If this yield can be improved by 5%, significant savings of required raw material can be made in addition to significant reduction of carbon dioxide.

Chemical intermediates in the catalytic provide various co-production possibilities. Since both GBL and THF are valuable products, coproduction of these compounds together with BDO is a reasonable option. This would decrease the productivity of butanol from succinic acid, but could have the possibility of increasing the total yield and total income from the process. The compounds are used as solvents, in the pharmaceutical chemistry and for other applications. Changing the process to enable the production of these other compounds as well would mean significant changes, mainly regarding separation and purification units – a more complex separation scheme would have to be implemented to allow THF and GBL to be extracted from the process after the first reactor. Thus, as the process would become more complex, the complexity and increased operating cost would have to be balanced by a significantly higher price for the new products than for butanol.

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