

Lappeenranta University of Technology

LUT School of Engineering Science

Chemical Engineering

Master's Thesis

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PROFITABILITY OF ETHANOL PRODUCTION BY GAS FERMENTATION FROM
STEEL MILL FLUE GASES

Supervisor and Examiner: Professor Tuomas Koiranen

Second Supervisor: Lic. Tech. Esko Lahdenperä

Abstract

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The aim of this master's thesis was to study processing of syngas by gas fermentation for the conversion of steel mill waste gases into ethanol. At first, the process was studied through literature review which involves in designing of preliminary process. Gas fermentation is the novel technology which can convert industrial waste gases into commodity chemicals and fuels. Microorganisms such as *Clostridium ljungdahlii* and *Clostridium autoethanogenum* have the capability to convert gases into ethanol and acetic acid as a major side product. The conversion through microorganisms depend on the selectivity, growth medium and configuration of the reactor. In the process evaluation, syngas composition was received from Outokumpu Steel Mills, Tornio which had 86% CO, 4% H₂, 5% CO₂ and 5% N₂ from three submerged arc furnace. The total flow rate was 32000 Nm³/hr which will generate 5667 kg/hr of ethanol. The gas was at 10 °C and it was compressed to 3 bar. The temperature in the airlift bioreactor was 39 °C as bacteria can withstand only in the range of 36 – 40°C. The nutrient media and bacteria was cultivated in the separate tank. The compressed stream of syngas and bacteria along with nutrient media was entered in the reactor. The mass transfer coefficient was adjusted to 36 hr⁻¹ and selectivity basis was also considered for reactions. The vent gases were exhausted in the atmosphere. The fermentation broth was then transferred to distillation column where 83% ethanol was separated from top and acetic acid with bacteria was separated from bottom. The waste stream includes acetic acid, bacteria and water. Acetic acid and bacteria was

sent to waste and water was reused again in the process. ASPEN Plus software was used for simulations. The results obtained from simulations were used for economic evaluation of the process. The production rate was achieved 6428 tons/year by keeping ethanol concentration less than 6% in recovered water stream. The revenue would be 3300 k€ at a price of 520 € per ton of ethanol. The payback period would be 6 years with return of investment at 11.8%. The total production cost was estimated 2480 k€ and annual gross profit would be 770 k€. In conclusions, the process is profitable but the changing prices of ethanol and emerging of new research for renewable fuels will highly effect it. The prices were taken keeping in consideration that higher production rate will reduce cost but on the other hand more production of ethanol globally will also have to effect market prices. The vent gas stream was high in this process but it can be used either to generate electricity or to reuse in the process.

List of Symbols and abbreviation

Symbols

a – gas-liquid interfacial area per unit volume, m^2/m^3

E – electricity power consumption, W

H – Henry's law constant

$H_{CO}^{39^\circ C}$ – Henry constant of carbonmonoxide at $39^\circ C$, $\text{mol}/\text{m}^3, \text{Pa}$

$H_{H_2}^{39^\circ C}$ – Henry constant of hydrogen at $39^\circ C$, $\text{mol}/\text{m}^3, \text{Pa}$

K_L – overall mass transfer coefficient, hr^{-1}

N_S^G – moles of substrate transported from the gas phase

P_S^G – partial pressure of the substrate in the bulk gas

P_S^L – partial pressure of the substrate in the liquid phase

ΔP – pressure drop/ pressure difference, Pa

Q – flow of cooling water, m^3/s

t – time, s or hr

V_L – volume of liquid, m^3

η – pump efficiency

Abbreviations

ATCC™ – American Type culture collection

ATP – Adenosine triphosphate

BOF – Basic oxygen furnace

BOS – Basic Oxygen Steelmaking

CODH/ACS – Carbon monoxide dehydrogenase/acetyl-CoA synthase complex

DSMZ™ – Deutsche Sammlung von Mikroorganismen und Zellkulturen

ISBL – Inside battery limit

LMTD – Log mean temperature difference

NADH – Nicotinamide adenine dinucleotide

NADPH – Nicotinamide adenine dinucleotide phosphate

NPV – Net present value

OSBL – Outside battery limit

Opt – Optimum

ROI – Return of investment

SLP – Substrate level phosphorylation

SAF – Submerged arc furnace

WLP – Wood Ljungdahl pathway

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1. INTRODUCTION

The scarcity of resources and political unstableness throughout the world is boosting the exploration of alternative fuel sources to substitute conventional fuel sources. Greenhouse gases (GHG) is also another clamant issue for prevailing society. The urge of latest technologies and methodologies to minimize the impact of GHG are in focus (Molitor et al., 2016). The escalated vulnerability of global warming and inconsistent prices of oil have also contributed in unearthing nascent technologies (Kennes et al., 2015). The 21st Conference of the Parties to the United Nations Framework Convention on Climate Change was held in December 2015 and 195 countries agreed on one agenda which is called Paris Agreement. The objective of this agreement to emphasize on the worldwide response of adversities of climate changes and furthermore, tries to control the expansion in worldwide average temperature to well beneath 2°C.

Industrial gases from steel mills, paper industry, oil refineries and power plants are usually used for combustion or flared which results in huge wastage of unused raw material (IBC Finland 2016). Carbon dioxide is being produced from many industries and it is poisonous waste gas which is emitting in enormous amounts. The usage of carbon monoxide as feedstock in gas fermentation will result in turning waste into beneficial products and also reduces environmental hazards (Nam, Jung, and Park, 2016).

1.2 Objective

The core objective of the Master's Thesis research work is the preliminary designing of ethanol production by gas fermentation and techno-economic analyses for the feasibility of the process by using ASPEN Plus V 8.6 software. To familiarize with the topic and to make advancement in process design, extensive literature review was done. The novelty and uniqueness of this process demands deep study of existing laboratory works and research which was done in this work. The main objective of this project is to reutilize the off gas from the Finnish steel mill industry and convert it into a valuable product such as ethanol through gas fermentation and make a techno economic analysis of preliminary design. However, such a task reveals several untackled technical issues that must be addressed. The most important of these issues is to design a bioreactor that is capable

of delivering enough mass transfer from the gas into the growth media (liquid) in an economical and energy effective manner at industrial scale. Also, the project design aims to come up with an original and efficient solution to gas pretreatment and latter separation issues.

2. GAS FERMENTATION

Gas fermentation is the biological process which utilize carbon monoxide CO and hydrogen H₂ as raw material to convert it ethanol, acetic acid, 2,3-butanediol in the presence of biocatalysts ([Griffin and Schultz, 2012](#)).

The advantages of producing fuels and chemicals by fermentation of syngas offers numerous pluses over conventional metal catalytic process. The features such as selectivity of biocatalyst, less cost of energy, higher resistance to catalyst poisoning and impartiality to the fixed H₂:CO ratio are revealed. From past two decades, many novel isolates and anaerobic microorganism were studied which have capabilities to cultivate with gaseous substrate of CO and H₂. ([Bredwell, Srivastava, and Worden, 1999](#))

Many strains exhibited the production of acetate, butyrate and formate along with ethanol and butanol. Other purple non-sulfur bacteria also showed the conversion of CO to H₂ in a similar reaction as water-gas shift reaction (WGS) ([Klasson et al., 1992](#)).

The process considered here converts carbon-containing input gas into ethanol. The fermentation process can accommodate a range of input gas compositions and is tolerant of typical gas contaminants such as sulfur, which minimizes pretreatment requirements. The microbes of LanzaTech consume CO for both energy and carbon. If present in input gas blend, H₂ can be utilized by the microorganisms as a supplemental energy source. In addition to the input carbon as gas, a fermentation media including macro- and micro-nutrients for the organism is fed into the bioreactor. The LanzaTech process is a continuous fermentation, meaning that media is continuously fed into the bioreactor while fermentation broth (containing ethanol, fermentation coproducts, and spent biomass) is removed at an equal rate. Trace amounts of other coproducts, besides ethanol, are also produced in the fermentation process. The ratio of ethanol to coproduct and identity of

the coproducts can be varied substantially by modifications to the process. (Handler et al., 2016)

In gas fermentation of syngas, CO plays a primary role as a carbon source to generate fuel and chemicals and displays high conversion rate in the process. The process can work on a wide range of hydrogen and carbon monoxide compositions excluding conditioning of syngas. The maximization of CO production is the target in gasifier, on the other hand high H₂ proportion should be higher in thermochemical processes. The conditioning of syngas generates required H₂:CO ratio. In figure 1, a block diagram is presented to see the differences between biomass generated syngas fermentation and flue gas from industries as syngas for gas fermentation.

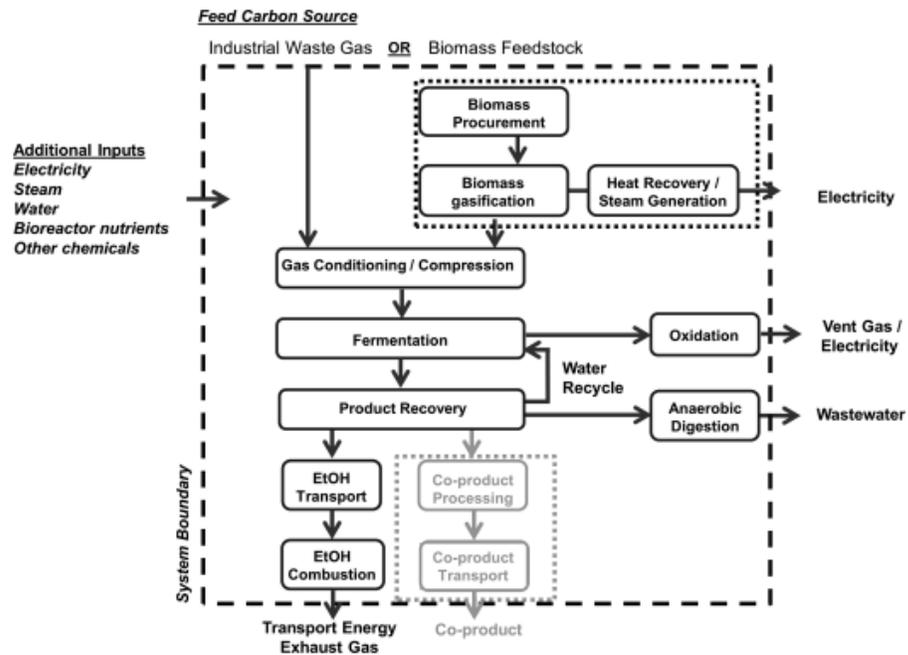


Figure 1. Overview of ethanol production from biomass from LanzaTech (Handler et al., 2016)

The tolerance to impurities in syngas fermentation is high and nothing else than vent gas scrubbing is required. This uses energy but it is better than other processes.

The process description from LanzaTech highlights that carbon from CO can be transformed to products completely as compared to conversion from metal catalyst methods.

Syngas fermentation, on high selectivity, can produce ethanol with less expensive separation costs as compared to catalytic production methods of alcohols. The low pressure and temperature requirement of syngas fermentation makes it an economically viable in comparison with conventional chemical methods ([Handler et al., 2016](#)).

3. ACETOGENIC MICROORGANISMS

Gas fermentation utilizes ability of certain type of bacteria to function also in low oxygen environment. Acetogenic bacteria have stirred interest in the past decades due to their ability to turn syngas compounds such as hydrogen or carbon monoxide into valuable products like ethanol or 2,3-butanediol in anaerobic conditions. Anaerobia allows for an oxygen free atmosphere, which eliminates inflammation risks when working with flammable gases and makes biological impurity less likely ([Liew et al., 2016](#)). What makes these bacteria strains so effective is their ability to undergo the Wood-Ljungdahl pathway, which is considered the most resourceful mechanism for carbon fixation ([Fast and Papoutsakis, 2012](#)).

Acetogenic bacteria are the type of anaerobes which follows acetyl-CoA pathway to reduce CO₂ to acetyl-CoA, conservation of energy and integration of CO₂. They are popular for their CO₂ fixing properties ([Drake, Gößner, and Daniel, 2008](#)).

3.1 Types of Acetogens

There are over a 100 different known species of acetogenic bacteria ([Imkamp and Müller, 2007](#)), but not all of them render the same products and not all of them are viable for their use in a process at an industrial scale. Acetogens are the type of microorganisms which are specialized and targeted in gas fermentation. Acetogens are anaerobic bacteria abundant in nature and highly important in global carbon cycle. Acetogens have been quarantined from different sources which include soil, sediments and intestinal tracts of animals ([Daniell, Köpke, and Simpson, 2012](#)).

Acetogens have potential to metabolize gaseous substrates which are rich in C1 compounds to valuable products such as ethanol and acetic acid by following Wood-Ljungdahl pathway. Some acetogens also produces 2,3-butanediol and butanol as products. Mostly these acetogens produce acid but some microbes such as *Clostridium ljungdahlii*, *Clostridium autoethanogenum* and *Clostridium coskatii* have tendency to yield alcohols. The

flexibility of these microorganisms allows to use syngas from biomass as well as industrial waste gases to formulate ethanol (Abubacker et al., 2016). Table 1 shows an overview of acetogenic bacteria strains capable of producing ethanol and their optimum growth conditions.

Table 1. Description of different microorganisms with their productivities and operating conditions (Liew et al., 2016)

Microorganisms	Substrates	Products	pH_{opt}	T_{opt} °C
<i>Acetobacterium woodii</i>	H ₂ /CO ₂ , CO	Acetate	30	6.8
<i>Acetoneema longum</i>	H ₂ /CO ₂	Acetate, butyrate	30–33	7.8
<i>Alkalibaculum bacchi</i>	H ₂ /CO ₂ , CO	Acetate, ethanol	37	8.0-8.5
<i>Butyribacterium methylotrophicum</i>	H ₂ /CO ₂ , CO	Acetate, ethanol, butyrate, butanol	37	6
<i>Clostridium aceticum</i>	H ₂ /CO ₂ , CO	Acetate	30	8.3
<i>Clostridium autoethanogenum</i>	H ₂ /CO ₂ , CO	Acetate, ethanol, 2,3-butanediol, lactate	37	5.8-6.0
<i>Clostridium carboxidivorans</i> or "P7"	H ₂ /CO ₂ , CO	Acetate, ethanol, butyrate, butanol, lactate	38	6.2
<i>Clostridium coskatii</i>	H ₂ /CO ₂ , CO	Acetate, ethanol	37	5.8-6.5
<i>Clostridium difficile</i>	H ₂ /CO ₂ , CO	Acetate, ethanol, butyrate	35-40	6.5-7.0

<i>Clostridium drakei</i>	H ₂ /CO ₂ , CO	Acetate, ethanol, butyrate	25-30	3.6-6.8
<i>Clostridium formicoaceticum</i>	CO	Acetate, formate	37	-
<i>Clostridium glycolicum</i>	H ₂ /CO ₂	Acetate	37-40	7.0-7.5
<i>Clostridium ljungdahlii</i>	H ₂ /CO ₂ , CO	Acetate, ethanol, 2,3-butanediol, lactate	37	6
<i>Clostridium magnum</i>	H ₂ /CO ₂	Acetate	30-32	7.0
<i>Clostridium mayombei</i>	H ₂ /CO ₂	Acetate	33	7.3
<i>Clostridium methoxybenzovorans</i>	H ₂ /CO ₂	Acetate, formate	37	7.4
<i>Clostridium ragsdalei</i> " or "P11"	H ₂ /CO ₂ , CO	Acetate, ethanol, 2,3-butanediol, lactate	37	6.3
<i>Clostridium scatologenes</i>	H ₂ /CO ₂ , CO	Acetate, ethanol, butyrate	37-40	5.4-7.5
<i>Eubacterium limosum</i>	H ₂ /CO ₂ , CO	Acetate, butyrate	38-39	7.0-7.2
<i>Oxobacter pfennigii</i>	H ₂ /CO ₂ , CO	Acetate, butyrate	36-38	7.3
<i>Blautia productus</i>	H ₂ /CO ₂ , CO	Acetate	37	7

Microorganism, which have abilities to convert syngas into ethanol and other byproducts through gas fermentation are, mostly mesophilic. The most promising pH limit for productive microbial growth is between 5.8-7.0 and temperature ranges from 36–40 °C depending on species. ([Munasinghe and Khanal, 2010](#))

3.2 Influence of pH and Temperature

Temperature and pH levels will thus be fixed in the fermenter to achieve high cell density under optimum growth conditions. In order to maintain these parameters constant, refrigeration is needed in the bioreactor as well as previous cooling of the incoming steel mill flue gas, while the pH can be controlled through an aqueous solution of ammonia (NH₃). On the other hand, it is also important to point out that temperature is a factor affecting the solubility of gases and thus has an influence on mass transfer resistance. In addition to that, the bacteria need a continuous feed of nutrients for them to undergo microbial metabolism. ([Molitor et al., 2016](#))

3.3 Clostridium autoethanogenum

Clostridium autoethanogenum is a gram positive anaerobic motile and spore forming bacteria. It was first discovered in rabbit feces. The importance of Clostridium autoethanogenum is due to its utilization of C1 gases carbon monoxide and carbon dioxide which exist in large quantities in industrial exhaust gases to convert them in alcohols and acetate. It is also characterized as significant biocatalyst for sugars ([Bruno-Barcena, Chinn, and Grunden, 2013](#)).

Clostridium autoethanogenum is being utilized in gas fermentation of syngas obtained from industrial off gases. It is close relative of Clostridium ljundahlii and Clostridium rag-sadalei. It can cultivate on both CO, CO₂ and H₂. When it grows on CO as the main carbon and energy source, it produces different products which includes ethanol and acetic acid as key products and 2-3-butanediol, lactic acid and small amount of H₂. Growth rate and production is lower when CO₂ and H₂ are used as source. The optimal pH range is from 5 - 5.5 and optimal temperature is 37 °C. ([Mock et al., 2015](#))

3.4 Clostridium ljungdahlii

Clostridium ljungdahlii is acetogenic microorganism which has capability to utilize synthesis gas for the production of ethanol. It was separated and obtained from chicken manure. Clostridium ljungdahlii is gram positive, spore forming and rod shaped acetogenic. It cultivates with syngas which includes carbon monoxide, carbon dioxide, hydrogen and also on ethanol, pyruvate, arabinose, xylose, fructose or glucose. (Tanner, Miller, and Yang, 1993)

4. WOOD-LJUNGDAHL PATHWAY

A considerable investment in biological processes to produce renewable products contributes in substrate analyses. The ideal microorganism should be workable with wide-ranging substrates of both gaseous and solid wastes and tolerant to impurities to synthesize products. Many factors are considered with cost of substrates such as source and obtainability, changeability in structure and pureness, requirement of pretreatment, flexibility in cells for effective operation, product separation and yield. (Fast and Papoutsakis, 2012) There are six natural carbon fixation pathways of different classes of microorganism which are mentioned in Table 2.

Table 2. Pathways for different species of microorganisms

Pathway	Microorganisms
Calvin-Benson-Bassham Cycle	Algae and Cyanobacteria
Reverse Tricarboxylic Acid Cycle	Phototrophic Green Sulfur bacteria, sulfur-reducing bacteria and Archaea
Wood-Ljungdahl Pathway	Acetogens and Methanogens
3-hydroxypropionate cycle	Non-sulfur bacteria
3-hydroxypropionate/4-hydroxybutyrate cycle	Hyperthermophilic, aerobic archaeon
dicarboxylate/4-hydroxybutyrate	Archaea of Thermoproteales and Desulfurococcales

Wood-Ljungdahl pathway is the most ancient pathway of CO₂ fixation. It has numerous advantages which make it startling. Figure 2 is explaining Wood-Ljungdahl pathway in which methyl and carbonyl branch are the two branches of WLP. These two branches supply reduced carbon molecules to form acetyl-CoA. The autotrophic growth of microbe on carbon dioxide, CO₂ and hydrogen, H₂ is firstly explained. The reduction of six electrons of CO₂ produces a methyl moiety whereas CO₂ is reduced to CO which is then attached to the carbon monoxide dehydrogenase/acetyl-CoA synthase complex (CODH/ACS). CODH/ACS bonds the two branches by reacting these resultant products with co enzyme to yield acetyl-CoA. Therefore, one ATP is required for formate fixation and for fixation of two molecules CO₂ requires eight electrons. H₂ is the only electron donor and hydrogenase reduces co-factor intermediates which are utilized afterwards for reduction of CO₂. In syngas, CO is present in plentiful amount and sometimes it is capable to withstand autotrophic growth as individual electron donor by Wood-Ljungdahl pathway. On the carbonyl branch, carbon monoxide is attached to CODH/ACS which means no reduction required. Therefore, only one ATP and four electrons are required to convert CO to acetyl-CoA. By substrate level phosphorylation (SLP), the conversion of acetate to acetyl-CoA produces one molecule of ATP. The Wood-Ljungdahl pathway produces zero ATP through SLP as a net result and four or eight electrons are required for the reduction to ferredoxin, NADH or NADPH for syngas fixation. Electrons are donated by CO or H₂ in the syngas fermentation. Though, the WL pathway is able of obtaining electrons from numerous compounds under heterotrophic conditions such as alcohols, sugars and organic acids (Latif et al., 2014)

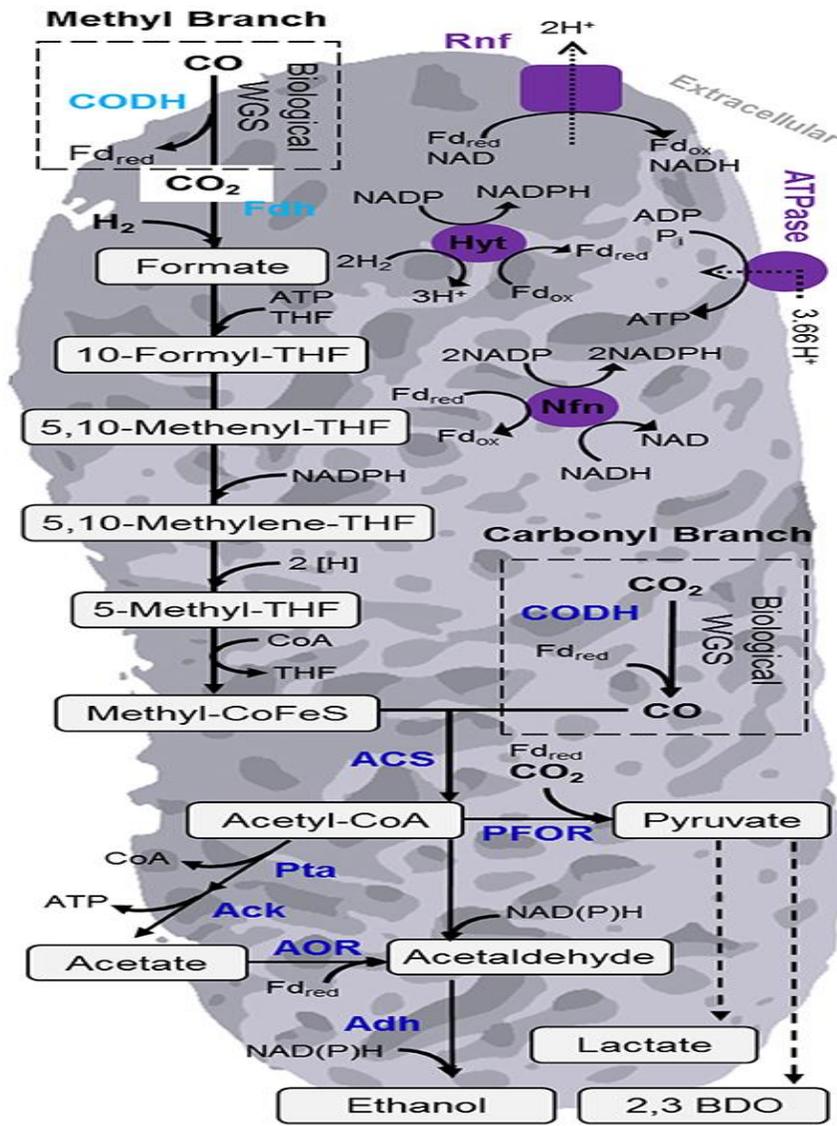


Figure 2. Wood-Ljungdahl pathway (Liew et al., 2016)

5. SYNGAS

Synthesis gas or syngas is a mixture of gases consisting of carbon monoxide, hydrogen and carbon dioxide in variable proportions. Syngas can be produced from any carbon-based feedstock hydrocarbons, coal, petroleum coke and biomass. Syngas can be formed from high carbon content raw materials such as coal, pet coke, biomass and organic waste. Organic waste and biomass are economical routes for syngas formation (Speight, 2008).

5.1. Syngas from biomass

Biomass is the most abundant raw material for renewable energy generation. The consumption of biomass for renewable products will not affect food production and also will not fulfill energy demand. Syngas from biomass is produced by gasification. In this process, carbon rich biomass is converted into H₂ and CO which are main gaseous energy content of syngas to use in gas fermentation. Gasification of biomass is a several step process. The reaction occurs at a temperature of 600-1000 °C in the presence of oxidizing agents which can be air, steam or oxygen. The whole process comprises of many steps which include dehydration, pyrolysis, combustion, partial oxidation, methanation, water gas shift and Boudouard reaction. The composition and quality of syngas depends on biomass and processing conditions (Griffin and Schultz, 2012b). A typical process diagram of syngas formation from biomass is shown in Figure.3.

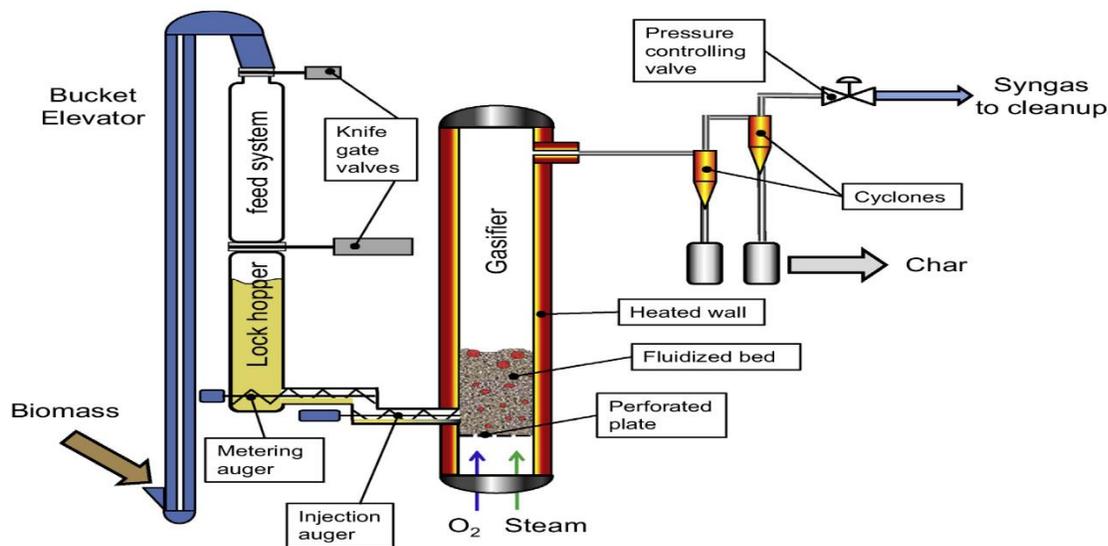


Figure 3. Biomass gasification to produce syngas (Broer et al., 2014)

5.2. Coal Gasification

Coal gasification is a process in which solid coal reacts with steam and oxygen at high temperature and pressure to produce syngas. Figure 4 is a typical coal gasification process with a gasifier and gas cleaning process and following reaction takes place for syngas:

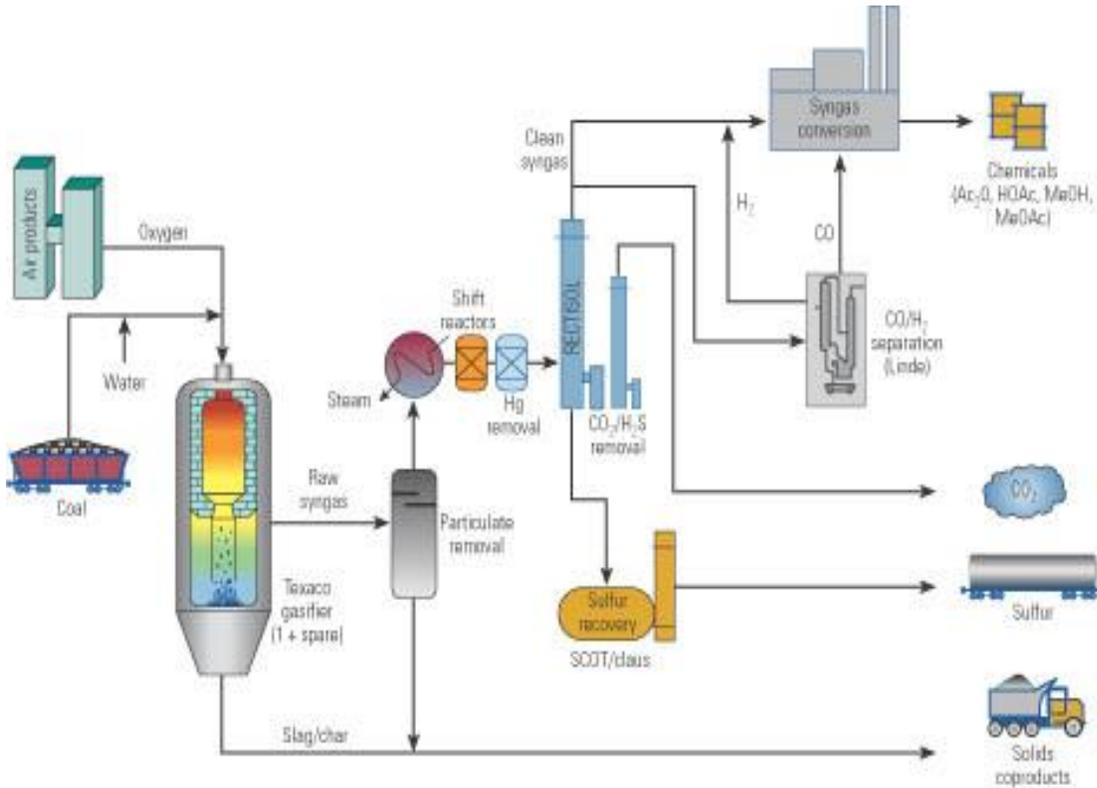


Figure 4. Coal gasification process (Platts, 2004)

5.3 Steel Mill Flue Gases

Global steel mill production was 1.5 billion tons/year in 2011. Around 60% industries use Basic Oxygen Steelmaking (BOS) process globally. Electric arc furnace is also being adopted by many industries and use of this technology is growing (Stubbles, 2016). Figure 5 is highlighting both processes.

In steel industry, iron ores are reduced into iron metal. In this process, coal, natural gas and oil is used for carbon source. The following reaction takes place:



The reaction takes place in the blast furnace where molten iron or pig iron is produced. They have high carbon content normally ranges 3.5–4.5%. The resulted iron is sent to basic oxygen furnace (BOF). BOF regulates the amount of carbon in the final steel product by blowing oxygen on the surface of hot molten metal. The reaction between oxygen

and carbon in pig iron forms a carbon rich waste gas which contains 50–60% CO, 10–20% CO₂, and 20–30% N₂. These gases are also utilized in the heat generation for process as heat recovery. The variation in the composition of syngas from different raw materials is summarized in Table 3.

Table 3. Components of different syngas sources

Component	Biomass	Coal	Steel Mill Off Gases
Carbon Monoxide, CO	43-52%	40-65%	50-70%
Hydrogen, H ₂	14-32%	25-35%	1-2%
Carbon dioxide, CO ₂	14-36%	1-20%	10-20%
Nitrogen, N ₂	-	-	15-30%

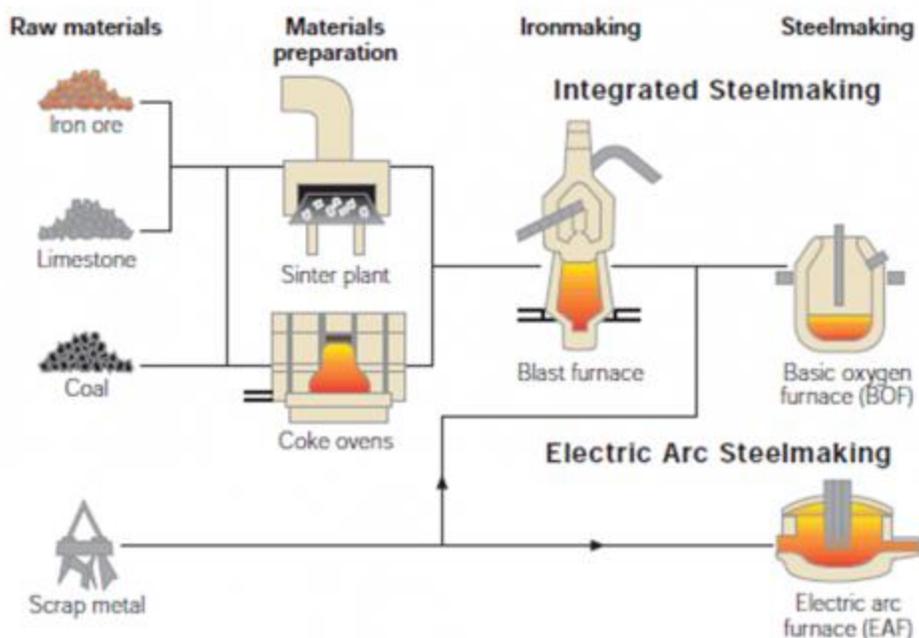


Figure 5. Steel production process by Basic Oxygen Furnace and Electric Arc Furnace (Steel Construction, 2016)

6. IMPURITIES OF SYNGAS

Syngas or “clean syngas” constitutes only of carbon monoxide, carbon dioxide and hydrogen but other contaminants are also present dependence on the source. Water, H₂O and Methane, CH₄ also exist as main gaseous compounds in syngas. Contaminants which are reported in biomass syngas, coal syngas and syngas from mixture of both are concluded in Table 4.

Table 4. Contaminants in biomass and coal derived syngas

Contaminant	Biomass (mol%)	Coal	Co-Feeding
Methane, C ₂ H ₄	15	7.4	7.5
Acetylene, C ₂ H ₂	0.69	0.13	-
Ethylene, C ₂ H ₄	5.3	01	0.8
Ethane, C ₂ H ₆	0.8	1.7	2.3
Benzene, C ₆ H ₆	0.3	-	-
Naphthalene, C ₁₀ H ₈	0.3	0.02	-

Nitrogen Compounds (NH ₃ and HCN)	0.28	0.4	-
Sulphur Compounds (H ₂ S and COS)	0.0004	1.0	-
Sulphur Dioxide, SO ₂	0.055	-	-
Mono Nitrogen Oxide, NO _x	0.123	-	-

Steel mill exhaust gases are comparatively clean in comparison with other industrial gases but presence of other trace impurities such as volatile organic compounds (benzene, toluene, methylbenzene, xylene and naphthalene is possible). (Molitor et al 2016)

6.1. Types of Impurities in Syngas

Syngas from biomass accounts 75% of total cost in biofuel production. Gas purification and gas conditioning are two main stages to use syngas for further processes. The primary products in syngas include CO, H₂, CH₄, CO₂, H₂O and N₂ when is used as oxidizing agent is used in gasification. Secondary products like tars, nitrogen, sulphur, chlorine compounds and solid particulates are problematic in further processing (Yohan et al 2012). High cost purification methods are required for syngas to avoid poisoning of metal catalysts but biocatalysts are more tolerant to these impurities. Therefore, these microbes are abundantly being used for the production of ethanol by many companies such as LanzaTech, INEOS Bio, and Coskata. (Kopke et al., 2010).

Nitrogen

Nitrogen occurs as an inert and non-toxic gas. Microorganisms have the capability to neutralize molecular nitrogen under nitrogen reducing conditions. When nitrogen is present in the form of ammonia, nitrate or in any liquid form, cell energy and some reducing equivalents may be sidetracked from products in order to fix molecular N₂ by nitrogenase. Inert nitrogen may slow down transfer rate of gaseous substrate CO and H₂ and eventually the rate of gas fermentation (Molitor et al., 2016).

Oxygen

Presence of oxygen is also alarming impurity for anaerobic bacteria. Oxygen is not present in steel mill flue gases but it may be entrained through leakages during gas transportation and conditioning process (Molitor et al 2016). Oxygen reduces metabolism rate of H₂ and CO and it also minimizes carbon requirement from CO in product formation (Whitham et al., 2015). However, these microbes have the ability to eliminate oxygen by rich culture of clostridia by enzymatic process or by oxidizing dead cells (Molitor et al., 2016).

Sulfur and Nitrogen Compounds

Sulfur compounds in gaseous state such as hydrogen sulfide (H₂S) and carbonyl sulfide (COS) also poses harmful impacts on microorganisms. However, sulfur acts as nutrient in fermentation but presence of high concentration of these compounds may negatively affect microbes. Hydrogen cyanide is not present in steel mill off gases but it is toxic to biocatalysts if present more than 1ppm. (Molitor et al., 2016)

Solid Particulates and Tar

Particulates and tars also have the tendency to disrupt process by choking filter or by lining up in the reactor (Molitor et al., 2016).

7. SYNGAS IMPURITY SEPARATION TECHNOLOGIES

The need of removing impurities from syngas depend on the effect of impurities on process and microorganisms along with the impact on environment. Several cleanup technologies can be employed which depend on process cost and product specification (Xu, Tree, and Lewis, 2011). Cleaning technology should be inexpensive and robust for smooth running of process over a period of time (Molitor et al 2016). A list of cleaning technologies which can be used are described in Table 5.

Table 5. Technologies for syngas cleaning (Woolcock and Brown, 2013)

Contaminant	Technology	Effect
Tar and Solid Particulates Removal	Tar cracking, Cyclones, filters, electrostatic precipitators, water scrubbers, rotating particle separator	Clogging and choking filters, layer formation in reactor
Oxygen Removal	Hot copper bed regenerated with H ₂ , Platinum and Pladinum catalyst on alumina	Toxic to certain microorganisms, production rate
Hydrogen Sulfide, H ₂ S and Carbonyl Sulfide, COS removal	Iron or zinc oxide bed, Zinc titanates sorbents, COS Hydrolysis	Toxic in higher concentrations
Removal of Nitrogenous impurities	Water wash system, selective and non-selective reduction, catalytic decomposition	Metabolism rate of microbes, cell growth, product distribution

8. REACTORS FOR GAS FERMENTATION

In gas fermentation, gas/liquid mass transfer is considered to be rate limiting step. Overall mass transfer coefficient K_La and driving force for mass transfer are labeled based on volumetric mass transfer rate. The reason is lower solubility of CO and H₂ in liquid phase and consumption of high amount of gas molecules required per carbon. (Bredwell, Srivastava, and Worden, 1999)

Cell concentration also effects the yield of product by limiting process kinetically. The industrial bioreactor should be able to tackle high cell concentrations, high volumetric mass transfer coefficient and effective mixing in processing (Ungerma and Heindel, 2008).

Compared to chemical reactors, a biochemical reactor is special because microorganisms are involved. In chemical reaction, the amount of product depends only on composition and process parameters. In biochemical reaction microorganisms have

different strains and different metabolic pathways, variation in products formation are considered. Microorganisms can also die and productivity may shift to undesirable product. Cell density, growing medium, aeration conditions and mass transfer also impact biosynthesis reaction. (Benz, 2009)

The difficulty in syngas fermentation is the formation of such culture conditions which prefer promising gas-liquid mass transfer rate. Multitude types of reactors are being used for gas fermentation which includes continuous stirred tank reactors, bubble column reactor, trickle bed reactors, membrane reactors and monolithic biofilm reactors (Chen et al., 2015).

8.1. Bioreactor design

Bioreactor design constitutes the most crucial step towards optimization of ethanol production through anaerobic fermentation. This is due to the low solubility of the substrate gases H_2 and CO into the liquid medium as shown in Appendix 1, which leads to a limiting step in the process, and which determines the capacity of ethanol production. This bottleneck problem requires both the understanding of mass transfer basics and the implementation of a feasible solution in the form of an energy efficient, commercial scale bioreactor design (IBC Finland, 2016). It has been found that for slightly soluble gases like the ones mentioned, the rate of mass transfer usually determines reactor size (Klasson et al., 1992). The suitable reactors for such processes will be the ones that attain both high mass transfer rates and high cell density with a low operation and maintenance cost and an easy scale-up.

The variables that increase mass transfer are:

- Pressure: according to Henry's law, increased partial pressure of the substrates can increase the rate of transport from the bulk gas, as shown in equation 3. However, at greater concentrations of gaseous substrates, particularly for CO , microbial growths are inhibited (Munhasinge and Khanal, 2010), which can lead to bioreactor failure. Possible measures to approach this issue are CO level feedback control and further adaptation to the bacterial strain to make it more robust to inhibitory substances (Bredwell, Srivastava, and Worden, 1999).

- Gaseous flow: an increase of superficial gas velocity is translated into higher turbulence and thus high transport rates substances ([Bredwell, Srivastava, and Worden, 1999](#)). However, the use of high gaseous flow rates also derives in a lower conversion, leading to the need of a recycle stream. Along this possibility, it is necessary to consider the cost of gas recycling, especially that of gas compression.
- Gas residence time.
- Bubble break-up: high bubble breakup leads to a higher interfacial area and thus higher transport rates. This is why bubble break-up constitutes one of the main research boundaries being pushed to tackle the mass transfer challenge. This aspect highly affects the type of bioreactor. For example, in a CSTR, the most common bioreactor used in fermentation, the agitation rate is a carefully chosen parameter to increase bubble break-up. Further study of these reactor configurations is conducted in the following pages.
- Temperature: Henry's law also dictates that a reduction in temperature increases the solubility of a gas. However, temperature is a well-fixed parameter in processes involving microbial species because it highly affects their growth and productivity. For the bacteria strain, Clostridium being considered for this process. The optimal temperature is from 30 to 40 °C. Thus, it is important to point out that refrigeration of the bioreactor unit will be needed to keep temperature at a constant level. ([Munhasinge and Khanal, 2010](#))

8.2. Types of Bioreactors

In order to choose the best suitable option for a reactor, several different types must be considered taking into account what has been mentioned above.

Continuous stirred tank reactor (CSTR)

This is the most common bioreactor used in syngas fermentation at a laboratory scale. In a CSTR, gas is continuously injected into the reactor with a high flow rate, while only a small liquid flow rate of culture media is added to nutrients supplements for bacterial

growth (Klasson et al., 1992). The outgoing product flow is drawn at the same rate than the feed, while the gaseous substrates that haven't reacted leave the tank from the top (probably to be compressed and recycled). While high cell densities and excellent mixing can be achieved in these reactors, the biggest concern is the rate of agitation. Increased agitation will translate in an increased mass transfer, as mentioned above. However, the strategy of increasing the impeller flow rate may not meet economical practicality for industrial syngas fermentation process (Liew et al., 2016).

Another option to consider is two CSTR in series. The reason behind this configuration is the fact that the selectivity of ethanol over other byproducts is increased by configuring two-step process. The acidogenesis, the production of acetic acid and bacterial growth will occur in first step and solventogenesis, the production of ethanol and partial cell growth will occur in second step. A 30-fold high was recorded in two reactor system in comparison to single reactor with *Clostridium ljungdahlii*. This process can also be achieved in order single reactor types and configurations with a dynamic regime that alters pH value. (Klasson et al., 1992)

Bubble column reactor

Highly suitable for commercial applications with huge operational volumes, the bubble column reactor offers a promising performance with high mass transfer rates and low operation and maintenance costs. Its main setbacks are coalescence and back-mixing (Datar et al., 2004). However, new research and technological advance is being made in these types of reactors to solve these problems, the main one being microbubble dispersions. Peclet numbers obtained in a study in a bubble column reactor showed that, with a value ranging from 42 – 400, axial mixing was considerably less with microbubble dispersion equipment (Bredwell and Worden, 1998).

Trickle bed reactor (TBR)

Packed bed gas-continuous reactor where the liquid streams descending while the gas stream can either go in descending (co-current) or in upward (counter-current) direction. Low liquid and gas flows are normally utilized in this kind of reactors, resulting in low pressure drops. On the other hand, the lack of mechanical agitation makes them more energy efficient than CSTR reactors. As for the culture medium, the TBR allows it to either be

suspended or fixed. The latter is an appealing option since it eliminates the need of expensive cell recycling equipment. Furthermore, under gas-continuous conditions, the mass transfer resistance is fairly low, allowing for high conversion rates ([Andrews and Noah, 1995](#)).

Monolithic biofilm reactor

Growth media builds up a biofilm through which gaseous substrates are allowed to pass through in this type of reactors, which are operated under atmospheric conditions, making the process more economically viable ([Munhasinge and Khanal, 2010](#)).

Airlift Reactor

A variety of gas-liquid and gas-liquid-solid pneumatically powered which specialized in circulation of fluid and airlifts are built to fulfill this requirement of process. The circulation of materials in reactor is achieved by pneumatically agitators for which an air stream or gas streams are used. The major difference in bubble column and airlift is the geometry of reactor. In bubble column, gas is fed from the bottom and rising bubbles perform arbitrary mixing but in airlift reactor riser and down comer channels are present which are connected in the bottom and top for the loop formation. ([Merchuk and Gluz, 2002](#))

Categories of Airlift reactor

Airlift reactors are classified in two main categories.

- 1) External Loop Reactor
- 2) Internal Loop Reactor

In external loop reactor, the circulation of the fluid is done in isolated and detached channels. And in internal loop reactor, baffles generate conduits for the circulation. Figure 6 illustrates categories of airlift reactor according to flow directions.

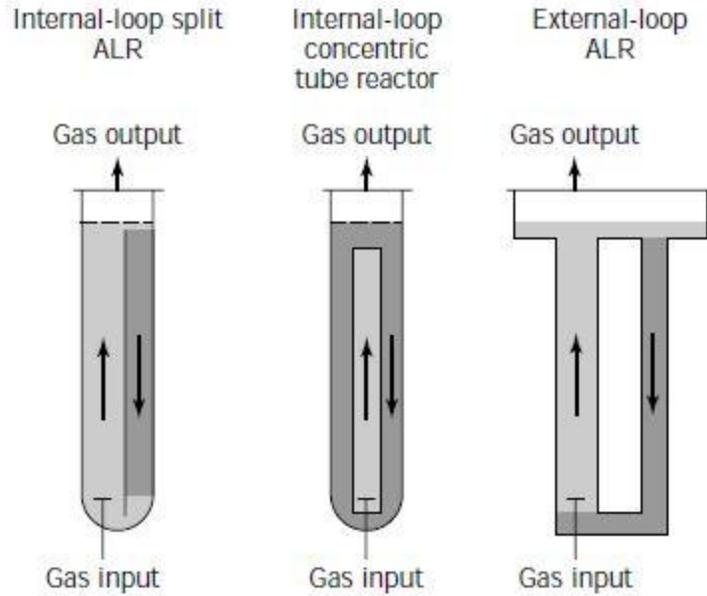


Figure 6. Different setups of airlift reactor (Merchuk and Gluz, 2002).

Every airlift reactor has following basic units in the reactor: riser, down comer, base, gas separator

Riser

In this section, injection of gas takes place and both liquid and gas moves in upward direction.

Down comer

In this section both liquid and gas move downwards. The down comer is connected to the riser. Density is the main driving force between riser and down comer which creates pressure gradient for effective circulation of liquid.

Base

Base is the lower part of the airlift reactor and it has no functionality in the reactor except its design can influence liquid velocity, gas hold ups and flow of solids.

Gas Separator

Gas separator is the top part of airlift reactor which aid recirculation of liquid and separating gas (Merchuk and Gluz, 2002).

9. FACTORS EFFECTING SYNGAS FERMENTATIONS

There are several factors which can influence the process of syngas fermentation. All of these factors will result in low production rate of final desired products.

9.1. Impurities

Several impurities are associated with syngas which depends on the source and process of syngas formation. These impurities are listed as methane (CH₄), hydrogen sulfide (H₂S), sulfur dioxide (SO₂), ammonia (NH₃), nitrogen (N₂), carbonyl sulfide (COS), oxygen (O₂), water (H₂O), and mono-nitrogen oxides (NO_x) as well as tars and ashes (Xu, Tree, and Lewis, 2011). These impurities of syngas hinder in cell growth and product yield by barring biocatalysts and potential scaling in pathways. Solid particulates, tar and ash inactivates cells but it can be prevented by introducing filter (Munasinghe and Khanal, 2010). Nitrous oxide inhibits hydrogenase enzyme activity and reduce the availability of carbon to form ethanol (Ahmed and Lewis, 2007). The introduction of potassium permanganate and sodium hydroxide solution is helpful in absorbing NO and also SO₂ for their removal (Chu, Chien, and Li, 2001).

9.2. Reactor Selection

The productivity of syngas fermentation can be enhanced by efficient design of reactor which allows high mass transfer rate between gas and liquid (Acharya, Roy, and Dutta, 2014). Batch and continuous reactors have been tested for gas fermentation. In batch reactor, fermentation of gaseous substrate occurs in a closed system by continuous supply of gas. The resulted samples are analyzed at different intervals. CSTR is the most used reactor in gas fermentation compared to bubble column reactor, trickle bed reactor, monolithic biofilm reactor and microbubble dispersion stirred tank reactor (Munasinghe and Khanal, 2010). Addition of separate growth reactor as a continuous part of main reactor reduces startup time and cost of process (Bell and Ko, 2012).

9.3. Temperature

Optimal temperature is very vital for gas fermentation. Temperature effects microbial growth and substrate availability as well as solubility rate of gases into liquid phase. The most feasible temperature range is between 37– 40 °C for mesophilic acetogens and 55 –80 °C for thermophilic microorganism (Munshange and Khanal, 2009).

9.4. pH

pH plays an important role in the optimal performance of biocatalysts. The ideal range of pH varies from 5.5 – 7.5 depends on the type of microorganism. Table 1 shows the performance of microorganisms and their operating pH (Munshange and Khanal ,2009). Temperature above these ranges will affect the cell growth and eventually results in lower production rate (Kundiayana, Huhnke, and Wilkins, 2010).

9.5. Growth Media

Growth media are selected to provide feed to microorganisms to grow. The growth media should include essential vitamins, minerals, trace elements and reducing agent for maximum development of these microorganisms. The selection of growth media depends on the species and desired products. Microorganisms grow on carbon and acquires energy from syngas but other nutrients are also required to keep up the level of metabolic activity (Abubackar, Veiga, and Kennes, 2011). For example, elimination of yeast extract and vitamin B increases ethanol to acetate ratio with small reduction in growth in *Clostridium ljungdahlii* (Philips et al., 1993) but addition of 0.01 g/L of yeast extract boosts the production of ethanol (Wu and Tu, 2010). Similarly, addition of cellobiose in growth media increases the cell concentration and ethanol- acetate ratios from 4:3 as compared to addition of yeast extract. Reducing agents are also useful in escalating concentration of ethanol and product yield. Cysteine-hydrochloride and aqueous sodium sulfide are acclaimed reducing agents by ATCC™ (American Type culture collection) and DSMZ™ (Deutsche Sammlung von Mikroorganismen und Zellkulturen) (Abubackar, Veiga, and Kennes, 2011).

9.6. Microorganism Selection

In the past decades, the acetogenic bacteria has been intensively researched and studied for syngas fermentation (Drake, Gößner, and Daniel, 2008). Naturally occurring fermentation products from the acetogenic bacteria *Clostridium ljungdahlii* and *Clostridium autoethanogenum* are mainly acetic acid, and 2,3-butanediol (2,3BD). The production of ethanol by gas fermentation depends on growth conditions. Two routes have been suggested for ethanol production either by aldehyde/alcohol dehydrogenases or by ferredoxin-dependent aldehyde oxidoreductase with the grouping of alcohol dehydrogenase. The second route is considered to improve overall energy production and significant for redox-cofactor which eventually maintain balance in the cells (Bertsch and Müller, 2015).

When it comes to deciding, which strain is the most suitable for the process, several issues must be addressed. First, performance parameters regarding ethanol production establish the economic feasibility of the fermentation process which is judged by volumetric rate of production and titers of ethanol. High ethanol titers and production rates are desired, and they can be achieved through high mass transfer rates and high selectivity of ethanol over other byproducts such as acetic acid. However, studies on ethanol fermentation offer results on performance that can't be compared due to a lack in standard procedure between experiments, consequential in very different process arrangements, fermentation constraints, and medium conditions (Molitor et al., 2016). On the other hand, when a specific strain is utilized for an industrial process like ethanol fermentation, it must first be adapted to meet specific requirements such as being robust and achieving desired performance. Therefore, there are inherent differences between the public data offered and the little-known specifications of those strains that have been developed for commercial use by companies such as LanzaTech.

In conclusion, given the unclear difference in performance parameters and the fair similarity between the strains considered (almost all of them belong to the *Clostridium* family), the amount of research drives the decision available, for which *Clostridium ljungdahlii* is the best suitable option. To support this choice, it has been consid-

ered that adaptation to the process specific requirements is a preliminary step, thus making this decision a more flexible one. Furthermore, it seems like performance can be managed more easily through correct bioreactor configurations to improve mass transfer (high ethanol production rates) and operation parameters to improve ethanol selectivity (high ethanol titers). (Phillips et al., 1993)

10. PRODUCTS

A brief description of resulted products is shown below:

10.1. Ethanol and acetic acid

The gas transfer rate determines the production of ethanol. Higher gas transfer rate results in higher titers of ethanol and additional side products such as acetic acid and 2,3-butanediol should be reduced. Different configuration of fermenters, changing fermentation parameters and alteration in growth medium results in higher production rate but no single ideal conditions have been defined yet (Molitor et al., 2016). The maximum documented ethanol concentration of 48 g/L in a peer-reviewed literature was stated for *Clostridium ljungdahlii* in 1993 (Phillips et al., 1993).

One patent described volumetric ethanol production rates of up to $10 \text{ gL}^{-1} \text{ h}^{-1}$ in a lab-scale CSTR with *Clostridium ljungdahlii*, and gas transfer rates of CO and H₂ to dissolve in water are enhanced by pressurizing. The LanzaTech in their laboratory experiment attained a steady production rate more than $8 \text{ gL}^{-1} \text{ h}^{-1}$ without pressurization in CSTRs with *Clostridium autoethanogenum* (Gaddy, 1999).

The gas transfer rate of CO and H₂ is one major obstacle in achieving high production rate of ethanol. The feasibility of stable economic evaluation of laboratory scale experiments with required mass transfer rate into commercial plant will be vital progress. Numerous approaches can be engaged to increase gas transfer rates. Many methodologies can be adopted to increase mass transfer rate such as high gas flow, breaking bubbles, optimized gas residence time, partial pressures of gaseous substrates and through agitation (Liew, Kopke, and Dennis, 2013).

The ratio of ethanol and acetic acid in the optimized configurations can rise up to 20 which means high selectivity of ethanol. The high production can be pushed towards ethanol by shifting several parameters which includes increasing of stress in microorganism culture and maximum supply of CO to the cell culture (Phillips et al., 1993).

10.2. Production of 2, 3-butanediol

2,3-butanediol is also obtained from acetogenic bacteria, but in lesser amounts. Some articles set the ethanol to butanediol ratio at 10 (Molitor et al. 2016). Butanediol is a solid example of a chemical that can add value to the overall fermentation process and there are several studies centered on driving production to this product alone (Köpke et al., 2011). However, given the low 2,3-butanediol titers obtained and its high boiling point (182 °C), separation methods like distillation will be energy-intensive and therefore potentially expensive. Extending the product portfolio with examples like 2,3-butanediol remains still a research boundary and it can be established that its reach is out of this project.

11. SEPARATION TECHNIQUES

11.1. Distillation

Distillation is the conventional technique of separating ethanol and other byproducts from fermentation broth. Ethanol has the boiling point of 78.5 °C. The difference in boiling point and vapor pressure of ethanol and water are the basis of distillation. When mixture of ethanol and water is heated ethanol being more volatile than water, it vaporizes easier than water. The vapors are then condensed which has higher concentration as compared to mixture. Rectification is also used to separate all ethanol from the system (Amara-sekara, 2013).

The maturity of the distillation process makes it favorable for separation of products from fermentation broth. But high energy usage goes into deficiency of distillation process. The microorganisms, which are used in syngas fermentation, have the tendency to tolerate ethanol to 6 w-% as compared to yeast which is used for sugar fermentation can tolerate

up to 15 w-%. The mixture of ethanol and water from syngas fermentation containing 2 to 6 w-% of ethanol demands high energy distillation. On the other hand, high energy cost can be minimized by producing higher titers of ethanol. The struggles for improving tolerance of ethanol by acetogens are under process and even little advancement in tolerance could reduce significantly energy consumption. (Molitor et al., 2016). The energy requirement for 2 w-% ethanol stream requires 12 MJ-fuel per kilograms of ethanol and 6 w-% demands 5 MJ-fuel per kilograms of ethanol for fractional distillation. (Vane, 2008).

11.2. Pervaporation

In pervaporation, a liquid stream of two or more miscible components is introduced to a side of non-permeable polymeric membrane or molecularly inorganic porous membrane and vacuum or gas purge is implied on opposite side. The miscible components are held on membrane surface and liquid passes as permeate through the membrane and vaporizes. The permeate in vapor phase is then condensed (Vane, 2005). The mechanism of pervaporation is clearly seen in the Figure 7 which is a good pictorial explanation.

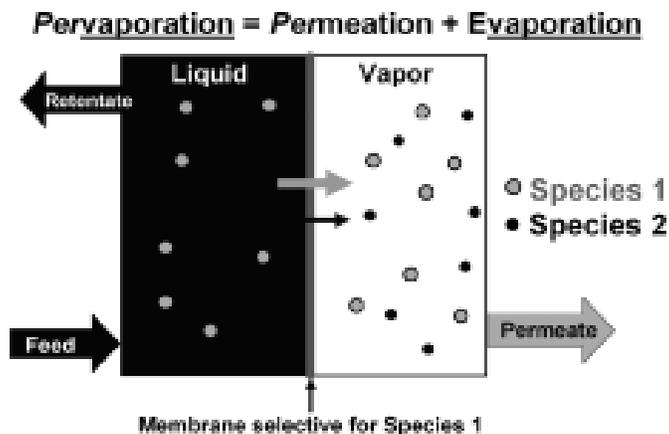


Figure 7. Mechanism of pervaporation (Vane, 2005)

The effectiveness of pervaporation depends on the qualities of membranes and operating conditions. In pervaporation, the advantage is to operate clearly below component boiling points by using low grade heat. Energy consumption of pervaporation is also less as it uses energy only for permeate evaporation. Modular and robust design of membrane units are easier to change operating capacity and easier in maintenance. Membranes also provide large surface area for phase contact. Slight modifications and development

in flux and selectivity can make pervaporation a cost-effective process for ethanol recovery in fermentation (Frolkova and Raeva, 2010).

11.3. Liquid/Liquid Extraction

Liquid-liquid extraction is a process in which water immiscible organic extractant is added to the fermentation broth. The higher solubility of solvent in organic phase than in aqueous phase leads to extract solvents from fermentation broth. As the extractant is insoluble in broth, the separation of extractant will be easy. Nutrients or water is not removed from this technique but removal of gaseous substrates might be possible due to higher solubilities of CO and H₂ in organic solvents. The selected extractant should be non-toxic, cheap and efficient, oleyl alcohol is considered to be best choice for this technique (Ezeji, Qureshi, and Blaschek, 2007 and Liew, Kopke, and Dennis, 2013).

11.4. Gas Stripping

Gas stripping is a startling technique for product retrieval in gas fermentation because the departing gaseous stream from the bioreactor can be utilized for in situ product recovery. In this technique, oxygen free nitrogen or carbon dioxide and hydrogen gases are bubbled through fermentation broth and cooled down by condensation along with product. After that gas is recycled back to fermenter and product is separated (Ezeji et al., 2010).

12. PATENT REVIEW

Review

A patent review has been done from 1992 to 2016. Patents of LanzaTech, Ineos Bio Sa and Coskata, University of Arkansas, Bioengineering resources Inc. have been reviewed and following information is generated. Applicants, main claim(s), what is protected, patent status and publication date are presented. The details can be found out in patents or patent applications. Most of new patents seem to be in A1-state.

Summary

A patent review has been done from 1992 to 2016. Patents are from: LanzaTech, Ineos Bio Sa, Coskata, University of Arkansas, Bioengineering resources Inc. 32 patents or

patent applications found. 10 granted patents have been found, and 9 microbe patents or applications have been found. Patented microbes have been: Clostridium ljungdahlii, Clostridium ragsdalei, Modified Escherichia coli, Bacillus smithii ERIH2. Oldest patent is Clostridium ljungdahlii from 1992 and the next one is Bacillus smithii ERIH2 from 1998.

Patent: WO2012015317

Applicant: LanzaTech

Inventors: B. Daniel Heijstra, E. Kern, M. Koepke, S. Segovia, F. Liew

Product: Clostridium autoethanogenum

Claim: Clostridium autoethanogenum, a bacterium which biological pure isolate has ability to produce ethanol and optionally acetate by anaerobic fermentation.

Protected: Clostridium autoethanogenum pure quarantined bacterium for anaerobic fermentation of CO substrate.

Patent Class: A1

Publication Date: Feb 2, 2012

Patent: WO2007117157

Applicant: LanzaTech

Inventors: S.D. Simpson, R. Llewellyn S. Forster, M. Rowe

Product: Efficiency enhancement of anaerobic gas fermentation

Claim: Process to produce ethanol and acetate. Conversion of acetate into H₂ and CO₂ to use as co-substrate in fermentation process.

Protected: Process of gas fermentation with following steps

i) Fermenting gases into alcohol and acetate **ii)** Converting acetate into H₂ and CO₂ gases **iii)** using resulted CO₂ and H₂ as co-substrate in fermentation process.

Patent Class: A1

Publication Date: Oct 18, 2007

Patent: US5173429

Applicant: University of Arkansas

Inventors: J.L. Gaddy, E.C. Clausen

Product: Clostridium ljungdahlii

Claim: Clostridium ljungdahlii bacteria can produce ethanol and acetate by fermentation of syngas.

Protected: Pure culture of Clostridium ljungdahlii microorganism with identical characteristics of ATCC™ No.49587.

Patent Class: B

Publication Date: Dec 22, 1992

Patent: US20130045517

Applicant: LanzaTech

Inventors: S. D.Oakley, J. A. Coombes, S. D. Simpson, B. D. Heijstra, M. A.Schultz, S. Molloy

Product: Microbial fermentation of biogas to produce products

Claim: Conversion of biogas to substrate contains CO and fermenting substrate in the presence of culture of microorganisms anaerobically to produce alcohols, acids and byproducts.

Protected: A method in which methane biogas is passed on conversion zone and a portion of it is converted into CO substrate and that substrate is passed to microbial culture to produce alcohols, acids and mixture by anaerobic fermentation.

Patent Class: A1

Publication Date: Feb 21, 2013

Patent: US136577

Applicant: Bioengineering Resources Inc.

Inventors: J.L. Gaddy

Product: Biological production of ethanol from waste gases with *Clostridium ljungdahlii*

Claim: A process for producing ethanol by anaerobic fermentation with CO using *Clostridium ljungdahlii* bacteria.

Protected: A process for producing ethanol by anaerobic fermentation with CO using *Clostridium ljungdahlii* strain O-52 ATCC™ No.55988 and No.55989.

Patent Class: B

Publication Date: Oct 24, 2000

Patent: US5807722

Applicant: Bioengineering Resources Inc.

Inventors: J.L. Gaddy

Product: Biologically conversion of waste gases to produce ethanol using *Clostridium ljungdahlii*.

Claim: A process for producing acetic acid by anaerobic fermentation with CO or CO₂ using *Clostridium lungdahlii* bacteria.

Protected: A process for producing acetic acid by anaerobic fermentation with CO or CO₂ and H₂ using *Clostridium ljungdahlii* No.55380.

Patent Class: B

Publication Date: Sept 15, 1998

Patent: US20130045517

Applicant: LanzaTech

Inventors: S. D. Oakley, J. A. Coombes, S. D. Simpson, B. D. Heijstra, M. A. Schultz, S. Molloy

Product: Microbial fermentation of biogas to produce products

Claim: Conversion of biogas to substrate contains CO and fermenting substrate in the presence of culture of microorganisms anaerobically to produce alcohols, acids and byproducts.

Protected: A method in which methane biogas is passed on conversion zone and a portion of it is converted into CO substrate and that substrate is passed to microbial culture to produce alcohols, acids and mixture by anaerobic fermentation.

Patent Class: A1

Publication Date: Feb 21, 2013

Patent: US6368819

Applicant: Bioengineering Resources, Inc., Celanese International Corporation

Inventors: James L. Gaddy, E.C. Clausen, C.W. Ko, L. E. Wade, C. V. Wikstrom

Product: Microbial process for the preparation of acetic acid: Modified water-immiscible solvent and increase in process efficiency of acetic acid recovery.

Claim: Solvent comprises of 50% by volume of a combination of isomers of extremely branched di-alkyl amines and 0.01% – 20% by volume of mono-alkyl amines with distribution coefficient value greater than 10. It extracts acetic acid from aqueous stream. An anaerobic bacterial fermentation route to produce acetic acid.

Protected: A water immiscible solvent for acetic acid extraction

Patent Class: B1

Publication Date: 9 Apr, 2002

Patent: US20130149693

Applicant: Ineos Bio Sa

Inventors: Ryan Senaratne, Song Liu

Product: Ethanol concentration management in syngas fermentation.

Claim: Contacting syngas with inoculated medium with at least 0.1 g/L cell density, removal and separation of cells and medium to provide concentrated cells and permeate, separation of ethanol from permeate to provide ethanol and reduced aqueous ethanol for fermentation.

Protected: Process of fermentation according to claim

Patent Class: A1

Publication Date: 13 Jun, 2013

Patent: WO2009151342

Applicant: LanzaTech

Inventors: S. D. Simpson, P. L. Tran, C. D. Mihalcea, J. M. Yee Fung, F. Liew

Product: Production of 2,3-butanediol by anaerobic fermentation

Claim: Microbial anaerobic fermentation of substrate consists of CO in a bioreactor by culture of microorganisms to produce 2,3-butanediol.

Protected: A method of producing 2,3-butanediol according to claim.

Patent Class: A1

Publication Date: Dec 17, 2009

Patent: WO2013002948

Applicant: Ineos Bio Sa

Inventors: P. S. Bell, Ching-Whan Ko

Product: A bioreactor design consists of main reactor and continuous growth reactor

Claim: **1.** A main reactor can be stirred tank reactor, unstirred tank reactor, trickle bed reactor, cocurrent contactor, moving bed bioreactor or a bubble column reactor and part of it is used as growth reactor. **2.** Continuous growth reactor is attached with main reactor which can also be from above mentioned types of reactors. Long list of bacteria mentioned.

Protected: A bioreactor with configuration such as growth reactor is continuous with main reactor.

Patent Class: A1

Publication Date: Jan 3, 2013

Patent: US2016115505

Applicant: LanzaTech

Inventors: S.R. Trevethick, J.C.Bromley, G. W. Waters, M. Koepke, L. P. Tran, R. J. Overgaard

Product: Multi stage biological processes and systems for C1 carbon conversion into desired end products.

Claim: A multi-stage processing of gaseous C1 carbon source to first bioreactor stage and resulted liquid product which contains C1 fixing microbes from first stage to second bioreactor stage to obtain desired end products.

Protected: A method of converting C1 carbon by multi-stage process.

Patent Class: A1

Publication Date: Apr 28, 2016

Patent: US20090275787

Applicant: LanzaTech

Inventors: R. Llewellyn S. Forster, S.D. Simpson, C.Collet

Product: Production of butanol by microbial fermentation from substrate comprises of glycerol and/or acetate.

Claim: An anaerobic fermentation method to produce butanol from by-product from industrial process containing glycerol in a bioreactor holding culture of one or more microorganisms and then capturing and recovery of butanol.

Protected: Butanol production from residue of glycerol from industries by fermentation.

Patent Class: A1

Publication Date: Nov 5, 2009

Patent: US20100323417

Applicant: LanzaTech

Inventors: S. D. Simpson, C. Collet, R.L.S. Forster, M. C. M.Cockrem, S.D. Oakley, M. Kopke

Product: Carbon capturing of substrate from CO by microbial gas fermentation

Claim: A method consists of waste gases or off gases containing CO from steel mills are entered bioreactor in the presence of culture of microorganisms to produce ethanol.

Protected: Method of capturing carbon by microbial fermentation and processing into products.

Patent Class: A1

Publication Date: Dec 23, 2010

Patent: US20160160223

Applicant: LanzaTech

Inventors: M.Koepke, P. A.Mueller, P.L. Tran

Product: Recombinant carboxydrotrophic clostridium bacteria comprising CO to produce alcohols, butanediols, fatty acids, biopolymers etc.

Claim: A recombinant carboxydrotrophic Clostridium bacteria consists of one or more enzymes from group which contains pyruvate:ferredoxin oxidoreductase, acetolactate synthase and cetolactate decarboxylase and each enzyme highly demonstrate endogenous enzyme, a mutated endogenous enzyme, or an exogenous enzyme.

Protected: Carboxydrotrophic clostridium bacteria: ferredoxin oxidoreductase (EC 1.2.7.1), acetolactate synthase (EC 2.2.1.6), and acetolactate decarboxylase (EC 4.1.1.5). And method of gas fermentation on gaseous substrate to produce alcohols, biopolymers and mixtures.

Patent Class: A1

Publication Date: Jun 9, 2016

Patent: US20160122787

Applicant: LanzaTech

Inventors: S. D. Simpson, S. M. Bernasek, D.K. Tuli

Product: Two stage fermentation process to produce lipids from gaseous substrate

Claim: The technique includes reception of gaseous substrate in first bioreactor which holds culture of microorganisms in aqueous nutrient medium and fermenting gaseous

substrate to produce acid product. The portion of resulted acid product is transferred to second bioreactor which contains culture of microalgae from group Scenedesmus, Thraustochytriu, Japonochytrium, Aplanochytrium, Elina, and Labyrinthula to produce lipid product by fermentation.

Protected: Lipid products from gaseous substrate by fermentation in presence of described microalgae as described in claim.

Patent Class: A1

Publication Date: May 5, 2016

Patent: US20160115517

Applicant: LanzaTech

Inventors: B. D. Heijstra, S. D. Simpson, N. Bourdakos, J. C. Bromley, Kai-Ming YAP

Product: Gas testing unit and method

Claim: A gas testing unit consists of first bioreactor to analyze composition of C1 carbon substrate and second bioreactor to estimate.

Protected: Gas testing unit with specific configuration as described in claims.

Patent Class: A1

Publication Date: April 4, 2016

Patent: WO2014047079

Applicant: Ineos Bio Sa

Inventors: Ryan Senaratne

Product: A method for reduction of carbon dioxide emissions as well as increasing production rate of ethanol by fermentation.

Claim: Treatment of resulted gas from CO fermentation

Protected: A process in which fermentation is done in zones and off-gas of first zone is provided to other adjoining zones.

Patent Class: A1

Publication Date: 27 Mar, 2014

Patent: US20150087037

Applicant: LanzaTech

Inventors: K.F.Smart, A. P. Mueller, M. J. H. Mawdsley, C. D. Mihalcea

Product: Increase in production of 2,3-butanediol

Claim: A fermentation process in which CO as gaseous substrate with acetogenic microorganisms in a bioreactor in presence of nutrient medium produces 2-3-butanediol from acetolactate and prevent flux of carbon to form branched chain amino acids.

Protected: The process to inhibit flux of carbon to branched chain amino acids.

Patent Class: A1

Publication Date: 26 Mar, 2016

Patent: US20150337343

Applicant: LanzaTech

Inventors: F. Benkwitz, C.D.Mihalcea, A.M.Havill

Product: Microbial Fermentation Process for alcohols

Claim: A microorganism culture with CO as gaseous substrate are introduced in a bioreactor where portion of broth is removed from bleed stream as permeate stream. The

product depleted stream is clarified and again introduced in the bioreactor. In this way, used fermentation broth is reused as treated permeate.

Protected: Introduction of bleed stream within the reactor for anaerobic fermentation.

Patent Class: A1

Publication Date: 26 Nov, 2016

Patent: US20160010116

Applicant: LanzaTech

Inventors: C.Collet, G.W.Waters, J.C.Bromley, J.Y.Yang, J.N.Wilson

Product: Process of microbial fermentation to produce ethanol and impact of process parameters on productivity, bacterial growth rate and time reduction in process.

Claim: A mixture of substrate comprises of CO and basic neutralizing agent with culture medium and microorganisms. The flow rate of neutralizing agent is regulated on properties of culture medium.

Protected: Process of microbial fermentation

Patent Class: A1

Publication Date: 01 Jan, 2014

Patent: US20160130610

Applicant: Coskata Inc.

Inventors: Shih Peng Tsai, Robert Hickey, Jianxin Du, Jian Xu, Joshua Schumacher

Product: Anaerobic bioconversion of syngas to for oxygenated compound and recovery and recycling of hydrogen sulfide from off-gas

Claim: A gas substrate and aqueous solvent in acidic anaerobic conditions with sulfur nutrient converts gas substrate to oxygenated organic compound and basic solvent solution is introduced to protect microorganisms from pH changes. A portion is also withdrawn at different intervals to protect microorganisms from concentration changes due to product formation. The exhausted gas is also removed continuously to reduce concentration of hydrogen sulfide.

Protected: Addition of sulfur nutrient for bioconversion of syngas to maintain pH of fermentation medium and to recover hydrogen sulfide as well.

Patent Class: A1

Publication Date: 12 May, 2016

Patent: US20150132815

Applicant: Coskata Inc.

Inventors: Robert Hickey

Product: Enhancing of performance in large scale anaerobic fermenter

Claim: A syngas containing CO, H₂ and CO₂ is introduced in a reactor which contains microorganisms to convert syngas into oxygenated organic compounds. Also, a stable gas-liquid mixture is formed at lower portion of aqueous solution and microbubble size is used to controlled rate of transfer of syngas in liquid to provide gas-in-liquid mass transfer and off gas is provided in head space.

Protected: A configuration of bioreactor and process conditions for maximum production of fermentation products.

Patent Class: A1

Publication Date: 14 May, 2014

Patent: US20120156747

Applicant: Coskata Inc.

Inventors: J.A.Zahn, J.Saxena

Product: Clostridium coskatii

Claim: A process to produce ethanol in which carbon and electron source are combined and Clostridium coskatii under operating conditions convert carbon source to ethanol.

Protected: Clostridium coskatii ATCC™ No. PTA-10522 under specific conditions to produce ethanol

Patent Class: A1

Publication Date: 21 June, 2016

Patent: US6136577A

Applicant: INEOS Bio Ltd.

Inventors: James L. Gaddy

Product: Ethanol from waste gases with Clostridium ljungdahlii

Claim: A biological process to produce ethanol from gas containing carbon monoxide in the presence of Clostridium ljungdahlii strain O-52 ATCC™ No. 55989 and Clostridium ljungdahlii strain C-01 ATCC™ No. 55988 with aqueous nutrient media in a bioreactor to result in a fermentation broth from which ethanol is separated continuously.

Protected: A gas fermentation process to produce ethanol from Clostridium ljungdahlii strain O-52 ATCC™ No. 55989 and Clostridium ljungdahlii strain C-01 ATCC™ No. 55988

Patent Class: A

Publication Date: 24 Oct, 2000

Patent: US7704723

Applicant: INEOS Bio Ltd.

Inventors: Raymond L. Huhnke, Randy S. Lewis, Ralph S. Tanner

Product: Ethanol from CO gas fermentation in the presence of Clostridium ragsdalei, ATCC™ BAA-622, "P11"

Claim: Clostridium ragsdalei which is biologically pure culture of microorganism and is similar to ATCC™ PTA-7826 with all identical specifications.

Protected: Clostridium ragsdalei, ATCC™ BAA-622, "P11" strain for producing ethanol from CO gas fermentation.

Patent Class: B2

Publication Date: 27 Apr, 2010

Patent: US5807722

Applicant: INEOS Bio Ltd.

Inventors: James L. Gaddy

Product: A process to transform industrial flue gases into useful products such as acetic acid and ethanol in the presence of Clostridium ljungdahlii ATCC™ No. 55380

Claim: A fermentation process to produce products such as acetic acid and salts by converting carbon monoxide in the presence of Clostridium ljungdahlii ATCC™ No. 55380 which is present in aqueous nutrient media and constantly removing and recovering of desired product from fermentation broth.

Protected: Process along with apparatus for the production of acetic acid and its salts from waste gas fermentation in the presence of microorganism Clostridium ljungdahlii.

Patent Class: A

Publication Date: 15 Sep, 1998

Patent: US7972824

Applicant: LanzaTech New Zealand Ltd

Inventors: Sean Dennis Simpson, Richard Liewellyn Sydney Forster, Matthew Rowe

Product: Production of ethanol along with acetate as additional side product

Claim: The production of one or more alcohols from gas which is mainly consists of carbon monoxide along with acetate anaerobically in the bioreactor and that acetate will be transformed into hydrogen and carbon dioxide which can be utilized as co-substrate in the fermentation

Protected: Process to produce ethanol and acetate from gas fermentation and converting resulted acetate into hydrogen and carbon dioxide to be used in further fermentation process

Patent Class: B2

Publication Date: 05 Aug, 2011

Patent: US20120309066

Applicant: LanzaTech New Zealand Ltd

Inventors: Sean Dennis Simpson, Richard Liewellyn Sydney Forster, Simon David Oakley, Michael Charles Milner Cockrem, Michael Koepke

Product: Production of ethanol with side products by syngas fermentation and also carbon dioxide capturing to increase overall carbon capture

Claim: A process in which firstly methane is passed to a conversion unit to obtain gaseous stream of carbon monoxide and then entering this stream into a bioreactor which also contains culture of microorganisms and produce alcohols, acids and mixture of products by anaerobic fermentation.

Protected: Method of producing ethanol from CO by microbial fermentation and natural gas reforming process to produce syngas and utilizing CO as gaseous substrate.

Patent Class: A1

Publication Date: 06 Dec, 2012

Patent: US8143037

Applicant: Coskata Inc

Inventors: James A. Zahn, Jyotisna Saxena

Product: Clostridium coskatii ATCC™ No. PTA-10522, “PS02”

Claim: Clostridium coskatii isolated bacterial species having the identical characteristics of ATCC™ No. PTA-10522 to produce ethanol from carbon monoxide, hydrogen and carbon dioxide or the mixture of them by anaerobic fermentation.

Protected: Bacterial strain of Clostridium coskatii under ATCC™ No. PTA-10522

Patent Class: B2

Publication Date: 27 Mar, 2012

Patent: US9347076

Applicant: LanzaTech New Zealand Ltd

Inventors: Fungmin Liew, Michael Koepke

Product: Modified carboxydrotrophic acetogenic bacteria to produce biodiesel and products from gaseous substrate mainly consists of carbon monoxide by fermentation.

Claim: A recombinant genetically modified carboxydrotrophic acetogenic bacteria with external or exogenous nucleic acid with an unidentified acetyltransferase

Protected: Modified strain of carboxydrotrophic acetogenic bacteria

Patent Class: B2

Publication Date: 24 May, 2016

Patent: US7803589

Applicant: Genomatica Inc.

Inventors: Mark J. Burk, Christophe H. Schilling, Anthony P. Burgard, John D. Trawick

Product: Modified unnatural occurring microorganism with exogenous nucleic acid and proteins to utilize syngas and methanol by acetyl-CoA pathway.

Claim: A genetically engineered Escherichia coli microorganism in which modified exogenous bacterial nucleic acid molecules encoding proteins cobalamide corrinoid, iron sulfur protein, methyltransferase, carbon monoxide dehydrogenase, acetyl-CoA synthase, acetyl-CoA synthase disulfide reductase and hydrogenase and these proteins will also enhance the productivity of generating acetyl-CoA from gaseous substrate of carbon monoxide, hydrogen, carbon dioxide or the mixture of them.

Protected: Modified strain of Escherichia coli microorganism

Patent Class: B2

Publication Date: 28 Sep, 2010

Patent: US5821111

Applicant: Bioengineering Resources Inc.

Inventors: James L. Gaddy, Guang Jiong Chen

Product: Production of ethanol, hydrogen and acetic acid from the biomass waste, solid municipal waste, sewage sludge, residual plastics, tires, agricultural waste and coal.

Claim: Bacillus smithii ERIH2, a pure culture of biological microorganism which has identical specifications to ATCC™ No. 55404.

Protected: Bacillus smithii ERIH2, a bacterial strain

Patent Class: A

Publication Date: 13 Oct, 1998

Patent: US8039239

Applicant: Coskata Inc.

Inventors: Andrew Reeves

Product: Production of ethanol, hydrogen and acetic acid from the biomass waste, solid municipal waste, sewage sludge, residual plastics, tires, agricultural waste and coal.

Claim: *Bacillus smithii* ERIH2, a pure culture of biological microorganism which has identical specifications to ATCC™ No. 55404.

Protected: *Bacillus smithii* ERIH2, a bacterial strain

Patent Class: B2

Publication Date: 13 Oct, 1998

13. MARKET SURVEY

13.1. Demand and supply of the product

EU is targeting the increment in use of renewable energy in transport to 10% by 2020. In other words, EU is targeting to reduce greenhouse gas emissions from transport and biofuels are the fastest and most cost-effective way. Finland is one step forward targeting 20% biofuels in transportation that includes biofuels from vegetable oils, fat, cellulose based ethanol, fuels from waste, etc. United States and Brazil dominate ethanol production worldwide producing from sugar cane, corn, wheat and potatoes. In Europe, largest producers are France, Germany and Spain from sugar beet and wheat. In Finland, ethanol production is based on collected household, commercial and industrial bio-waste and residues. Also, ethanol is produced from food and baking industry using decentralized production method from side-streams (Nylund et al., 2015).

Gasoline markets hold ethanol as a competent contributor for following reasons:

- The approximate demand of ethanol as a fuel globally is 75 million tons per year.

- US and Brazil are the biggest markets of ethanol (*Fueling a high Octane Future, 2016*).

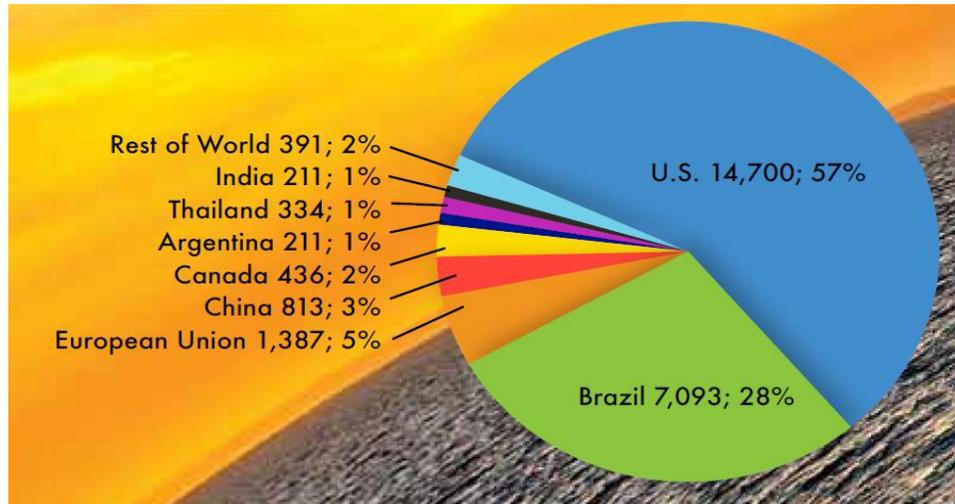


Figure 8. Global fuel ethanol production by Country in 2015 (*Fueling a high Octane Future, 2016*)

13.2. Potential markets

Finland has a distribution obligation that requires the part of biofuels in the total energy content of petrol, diesel oil and biofuels that must be at least

- 12% in 2017
- 15% in 2018
- 20% in 2020

This target is challenging and is possible only if more alternative fuel production plants run as quickly as possible. Substituting thus produced ethanol from still mill flue gas in the transportation area will provide the highest prospective market for ethanol. Ethanol is being used in transportation as follows.

- Fuel for vehicles

Gasoline in Finland is already mixed with ethanol, 95E10 has 10% ethanol while 98E5 has 5 % ethanol also fuel E85 with up to 85% ethanol blended with gasoline is available.

Hydrous ethanol (95% v/v) can also be used directly in vehicles with engine modification (Nylund et al., 2015).

- Fuel cell

Fuel cells convert chemical energy into electrical energy. Ethanol can be ideal fuel for fuel cell to convert into highly efficient energy source. Highly purified ethanol can overcome catalyst deactivation and membrane contamination in fuel cell (van Kasteren et al., 2005).

- E-diesel

It is a blend between ethanol and diesel consisting of 15% ethanol, diesel fuels and additives. This blend is greener compared to petro-diesel fuel as less particulate matter and toxic emission is achieved. Also, it improves cold flow properties.

A comparison of ethanol prices and variation within few years in Table 6. It is clearly seen that ethanol prices are fluctuating and decreasing gradually. The price which is used in economic analyses is 520 €/ton for 83% pure ethanol and estimated from global prices of ethanol. Figure 9 is also displaying deviations within 2015-2016 and 520 €/ton for 83% is also estimated based on these values.

Table 6. Global ethanol prices from two big producers (Fueling a high Octane Future, 2016).

Year	Brazilian Ethanol, \$/gallon	U.S. ethanol, \$/gallon
2010	2.82	1.83
2011	3.37	2.56
2012	2.40	2.24
2013	2.34	2.23
2014	2.28	2.04
2015	1.81	1.52

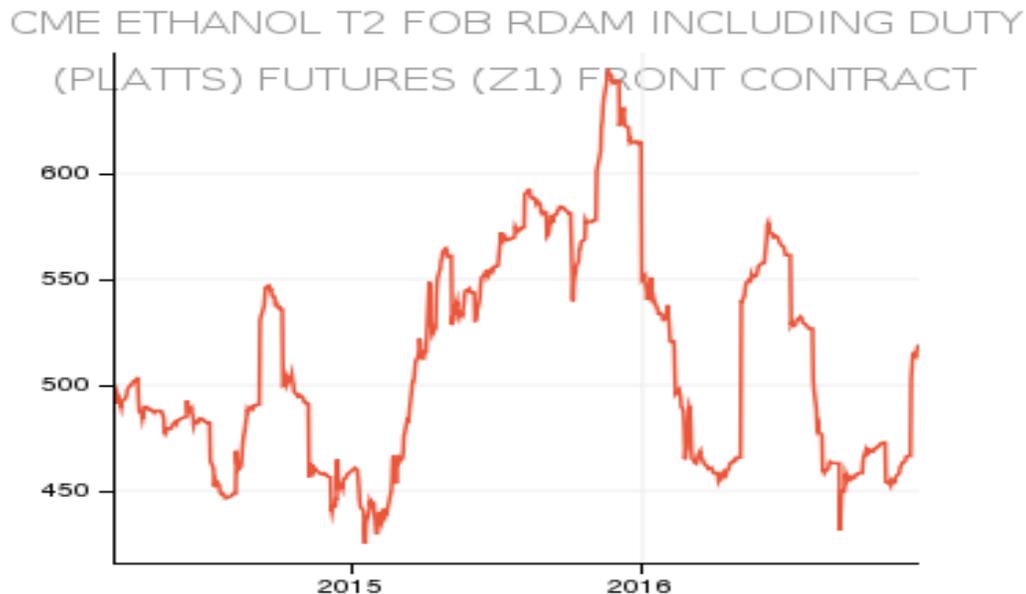


Figure 9. Price for European T2 ethanol (CME Ethanol, 2016)

13.3. Comparison of ethanol production technologies

Ethanol produced from fermentation of sugar and starch is currently dominating the market. These high value food crops have various food applications as world needs more food. Land usage for these crops compared to sugar is very low. Production costs can be reduced by using still mill flue gas for ethanol. Current ethanol conversion technologies:

- Ethanol production from straw or wood by acid hydrolysis

Besides, still being used in lab scale in many countries, Sweden has started using this technology for large-scale production of ethanol, mainly for Stockholm Transportation Agency. The main cost in this process is in the separation of acid before fermentation. Relatively low productivity adds up the extra cost to this process due to the lower efficiency in C5 sugar fermentation. (van Kasteren et al., 2005)

- Ethanol from Lignocellulosic enzymatic fermentation

This process uses enzymes instead of acid to hydrolyze the biomass. However, this is relatively expensive method and there are on-going researches on its technical and economical feasibilities by Abengoa Bioenergy, which is the leading European company producing ethanol (van Kasteren et al., 2005).

- Ethanol by fermentation of syngas from biomass

This process uses fermentation method with biomass generated syngas to produce ethanol. Currently, LanzaTech, Coskata and INEOS Bio are current players in commercialization of syngas fermentation for ethanol productions ([Liew, Kopke, and Dennis, 2013](#)). Coskata is US based company with its facility in Madison, USA, while INEOS is also US based company with its production facility in Vero Beach, USA. LanzaTech is a New Zealand based company having its ethanol production facilities in more than 5 countries.

- Ethanol by fermentation of steel mill flue gas

In this process, syngas from steel mill is used as a raw material for the production of ethanol by fermentation. LanzaTech is the leading company in this process with commercial facilities in ([Liew et al., 2016](#)):

- Blue Scope, New Zealand, Pilot, established in 2008, 15000 gal/year.
- Baosteel, China, Pre-commercial, est. 2012, 100,000 gal/year.
- CaptialSteel, China, Pre-commercial, est. 2013, 100,000 gal/year.
- ArcelorMittal, Belgium, 1st phase ready by mid-2017 and 2nd phase by 2018 producing in total 47,000 ton/year.

As a small note: Energy consumption of Outokumpu steel mill was 4.8 tW/h in 2008. Out of which 9% energy was produced from CO i.e. 0.432 tW/h ([Outokompu, 2008](#)). Let us assume that this share of energy comes from electricity. Taking the basic price of electricity in Finland i.e. 1 MW/h= 26.5 € ([Wanhatalo, 2012](#)), will put total energy cost acquired from CO to €11 million. In reality, the price of electricity for big companies will be much lower than that. Hence ethanol produced from Outokumpu steel mill syngas must also compete with the energy source, while considering in the environmental aspect that another source should replace the energy source, probably fossil-based.

13.4. Factors affecting the markets in future

In general sense, the factors that affect the ethanol price can be easily assumed to be food prices but in real world, things are different. Although, food prices affect the price but it is not the only factor and the price of ethanol is relatively stable.

- Food prices

Food price has also some effect on price of ethanol. It can be assumed that food-based ethanol can increase the food prices, while ethanol must compete with food for the use of corn that can increase the price of ethanol as well. So, food and ethanol are connected. If the use of corn or sugarcane was only for ethanol then it would be different scenario so alternative to pure corn, corn waste or other waste could be a good option. (Schill and Jessen, 2016)

- Weather

It has been seen that weather has affected the ethanol price in some months of year due to extremely harsh weather. Ethanol is mainly transported in tanks on trains or on trucks due to highly volatile nature. Only few pipelines have been designed for transportation of ethanol. (Knowledge, 2015)

- Ethanol Production

It has been seen historically that whenever there is an increase in production data of ethanol, the prices have gone down. This is due to the reason that the increase in ethanol production increases the production of crude oil derivatives, which reduces the price of gasoline. (Knowledge, 2015)

- Crude oil effect

This is an important factor that can affect ethanol price in future. It is expected that ethanol industry may overcome crude oil industry. If any slip in crude oil market occurs then, traders are more optimistic about the future of ethanol. But if we go to a bit depth study, increase of crude oil prices can also increase the price of ethanol. Increase in crude oil price shifts market towards ethanol and in return raises the value of ethanol and price too. (Knowledge, 2015)

- Gasoline Consumption

As ethanol is now added to gasoline, it is important in gasoline market. So, increase in gasoline consumption increases the demand for ethanol by raising the ethanol price.

- Tariffs and taxes

This is also important factor when ethanol is imported or exported. Tariffs and taxation on imported or exported ethanol might make it less competitive with the domestic producers. This type of schemes is designed to keep the domestic ethanol industry more competitive. But only in the case when you have enough domestic supply. ([Knowledge, 2015](#))

13.5. Outokumpu syngas

The storage facility of syngas storage for Outokumpu is claimed to have the total energy saving by using CO 324,000 GJ in 2008 ([Outokumpu, 2008](#)). That will bring the energy saving of €2.4 million.

As per the calculation based on flow rate of syngas, the net ethanol production will be around 22 million gal/year, using the price of ethanol as \$1.52 per gallon amounts to €33 million. So, ethanol produced from Outokumpu steel mill syngas presents a profit opportunity which far exceeds that from electricity generation. However, there is a down low in the environmental aspect, given the fact that energy must be replaced by another source, probably fossil-based.

Price of ethanol which is used in the cost estimation is 520 €/ton. The reason of this high price is that the yearly data of ethanol's prices is obtained for corn-based ethanol which is currently a mature process as compared to syngas fermentation. Another fact which is kept in mind during cost analysis is the behavior of microorganisms which may be different in real time processing on large scale. Recovery and reutilization of waste from the process such as bacteria recycling, separation of acetic acid and vent gases can decrease the ethanol price in syngas fermentation.

Gas fermentation process is much greener compared to power generation process from syngas. Gas fermentation process works with low energy and produces valuable products

with less waste. So, the carbon footprint is less for this process. However, power generation from syngas produces CO₂ in large amount and uses a lot of energy from pressurizing to heating. These should be taken into consideration in the comparison.

14. PROCESS DESIGN

14.1. Determination of process capacity

Flue gas from the steel mill industry varies in composition depending on many variables, most importantly the particular process where it is being generated and the steel mill itself. Outokumpu has provided data for the flue gas outcoming from their three-submerged arc furnace (SAF) units. An overview of the rate and the composition of the flue gas coming out of each unit as well as the total gas flow rate can be seen in Table 7:

Table 7. Flue gas rates and composition of the gas outcoming from the three-submerged arc furnace (SAF) units in Outokumpu's steel mill in Tornio. (Outokumpu, Tornio)

Furnace	Volume (Nm ³ /h)	CO%	H ₂ %	CO%	N ₂ %	Average Volume (Nm ³ /h)	CO%	H ₂ %	CO%	N ₂ %
SAF1	8000	88	3.6	1.7	6.7	8000				
SAF2	14000-16000	87	4.8	5.2	3	15000				
SAF3	22000-24000	84	3.9	6	6.1	23000				
Total						46000	86	4	5	5

However, under normal working conditions, only 70% of the rate comes out of the arc furnaces, according to Outokumpu. This leaves a flue gas rate of:

$$46000 * 0.7 = 32000 \text{ Nm}^3/\text{hr} = 1430 \text{ kmol}/\text{hr} \quad (3)$$

Nitrogen can be considered an inert gas for this process as long as the source of nitrogen in the liquid medium in the form of liquid ammonia isn't depleted, in which case the bacteria begin to fix it and thus reduce productivity (Köpke et al., 2010). This particular gas composition is highly advantageous for the process given its high amount of CO, which implies a high carbon recovery since bacteria can rely

solely on CO for ethanol production as it will be seen further on (Molitor et al., 2016), and its relatively low content in impurities, which according to Outokumpu consist mainly of dust particles of Zn and Cr, thus reducing the need for intense conditioning steps other than particle removing.

14.2. Reactions

The overall reactions of ethanol and acetate formation from CO and CO₂ /H₂ rich gases carried out by *Clostridium ljungdahlii* (Klasson et al., 1992) are:



As it was mentioned above, bacteria can rely entirely upon CO for producing ethanol, while in the case of CO₂ and H₂ both must be present. As a result, for reactions (4) and (6) the limiting compound is CO, given that water can be added in any desired quantity and that it is also being produced, whereas the reactions involving both carbon dioxide and hydrogen gas will be limited by either one of the reactants. Since more hydrogen is used in both reactions (3 times and 2 times more, for ethanol and acetate production respectively), and given that CO₂ is also being produced from CO in reactions (4) and (6), hydrogen will be the limiting reactant. A matrix of the stoichiometric coefficients of the whole process is shown in Table 8. Please note the reactions involving 2,3-butanediol formation have been neglected due to the low ethanol to butanediol molar ratio that is obtained. (Köpke et al., 2011) A more detailed explanation of the biochemical process carried out by *Clostridium ljungdahlii* is explained further on.

Table 8. matrix of stoichiometric coefficients. Limiting compounds to the reactions have been highlighted. Reactants have positive stoichiometric values and products have negative values.

Reaction	CO	H ₂ O	H ₂	CO ₂	C ₂ H ₅ OH	CH ₃ COOH
Eq.3	6	3	0	-4	-1	0
Eq.4	0	-3	6	2	-1	0
Eq.5	4	2	0	-2	0	-1
Eq.6	0	-2	4	2	0	-1

14.3. Mole balance

Appendix 1 contains detailed calculations for the mole balance. As it was mentioned before, the reactions involving CO₂ and H₂ have the latter as the limiting reactant, whereas for reactions (3) and (5) CO is the limiting reactant. In order to solve the balance, two important terms have been used: selectivity and conversion. Articles vary on the ethanol/acetic acid ratio from 0,05 (Phillips et al., 1993) to 20 (Molitor et al. 2016), so a conservative value of 3 found in the literature has been selected (Gaddy et al., 1995). Since no selectivity values have been found for the competitive reactions, the ethanol/acetic acid ratio given is the value used as the selectivity of the competitive reactions involving CO (eq. 3 and 5) as well as the competitive reactions involving CO₂ and H₂ (eq. 4 and 6). On the other hand, a conversion value for CO and H₂ of 70% has been used to correct theoretical values due to mass transfer factors. The assumptions thus made are the following:

For simplicity reasons, the calculations have been made considering an incoming flue gas rate of 1 kmol /hour and will be scaled up afterwards.

- All the off gas is being used for ethanol production, setting aside other uses such as electricity generation.
- CO is the limiting reactant for reactions (4) and (6), whereas H₂ is considered limiting to reactions (3) and (5).
- Selectivity values for the ethanol-yielding reactions (4 and 5) over acetic acid-yielding reactions are chosen at a conservative value of 3 moles ethanol per moles of acetic acid.

- Theoretically, it will be considered that all the CO and all the H₂ are consumed.
- Conversions for both CO and H₂ to correct the theoretical values obtained are 70%. Competitive reactions are (4) and (6) on one side and (3) and (5) on the other.

Table 9 represents the values in kmol/h for the different compounds present in the incoming and outgoing currents as obtained from the mass balance in Appendix 1 and already scaled up from 1 to 1430 kmol/h. According to these results, the total amount of ethanol that can be obtained is 123 kmol/h. **This is equivalent to 5667 kg/h or 49640 tons of ethanol per year which is same as 63 million liters a year.**

Table 9. Inlet and outlet values for the theoretical and real cases

Compound	Inlet (kmol/h)	Outlet (kmol/h)	
	Theoretical	Theoretical	Real
CO	1229.8	0	368.9
H ₂ O	715	130.1	306
H ₂	57.2	0	17.2
CO ₂	71.5	831.5	632
C ₂ H ₅ OH	0	175.1	123
CH ₃ COOH	0	58.3	40
N ₂	71.5	71.5	71.5

14.4. Comparison of electricity and ethanol production

The amount of ethanol produced in this process must compete in benefit with other possible uses for the off gas. At a value of the mean prize of US ethanol from the last five years, 2.1 \$ per gallon or what is the same 0.55 \$ per liter (0.5 €/l), the net profit in a year from the ethanol being produced is 41 million €. On the other hand, an incoming CO current of 1600 kmol/h can yield as much as 51 kWh per hour of electricity, as shown in equation 5 and according to the electric energy value of CO:

Effective energy value of CO = 31.4 kWh/kmol

Hourly production of electricity:

$$1600 \text{ kmol/h} \cdot 31.4 \text{ kWh/kmol} = 50.2 \text{ MWh/h}$$

In a year, the electricity produced from this current amounts to:

$$50.2 \text{ MWh/h} \cdot 24 \cdot 365 = 0.4 \frac{\text{TWh}}{\text{year}}$$

Which, at a value of 65 € per MWh, results in a profit of 26 million € per year. This does not mean that all of the CO from the flue gas should be employed for ethanol production, even though it is more profitable. The reason, some of the CO shall be employed for electricity production is due to other aspects such as environmental impact. It can be studied whether it is feasible that the process of ethanol production becomes self-sustainable in terms of energy by using some of the CO to produce the energy needed for ethanol production. Also, it must be taken into account the fact that the energy that is not produced by CO must be substituted by another source, probably fossil based. However, this study needs more development based upon energy requirements of the process which will be found out later.

15. DETERMINATION OF UNIT LOCATION

The main aspect to consider in this subject is the availability of the main raw material: the off gas from the Outokumpu steel mill industry in Tornio, Finland ([Outokumpu, 2016](#)). Thus, the plant location is fixed next to the steel mill considered for this particular project, where the cost of transport of the flue gases is minimized. Furthermore, other important aspects such as transport connections (it's located in the coast of the Gulf of Bothnia and has its own harbor), availability of labor and availability of utilities (water, steam, fuel, electricity...) are answered by the mere fact that the steel mill is already settled in this area. Finally, the possibility of choosing another plant location must be rejected due to the enormous cost of building a pipeline for gas transport.

16. PROCESS SELECTION

Metal industries flue gases containing CO, H₂, N₂, can be converted into ethanol by gas fermentation. The complete process can be generally distributed into following steps;

1. Generation of syngas
2. Gas cleaning
3. Gas fermentation in the fermenter.
4. Product separation.

A flow diagram of this whole process is given in Figure 10.

The syngas is generated and cleaned in Outokumpu, Tornio. The syngas coming out from the steel mill furnace has a temperature of 10 °C but after passing from compressor its temperature rises and needs to be cooled down because the gas fermentation is carried out around 39 °C. Therefore, it is required to lower down temperature of the gas to 39 °C before entering the fermenter. After cooling the gas, it will be fed into the fermenter along with water. A separate tank will be used to grow microorganism and the microorganism will be fed into the reactor directly from the growth media. After carrying out the reaction, the product ethanol will be separated by using distillation and the waste will be collected and send to waste water treatment plant.

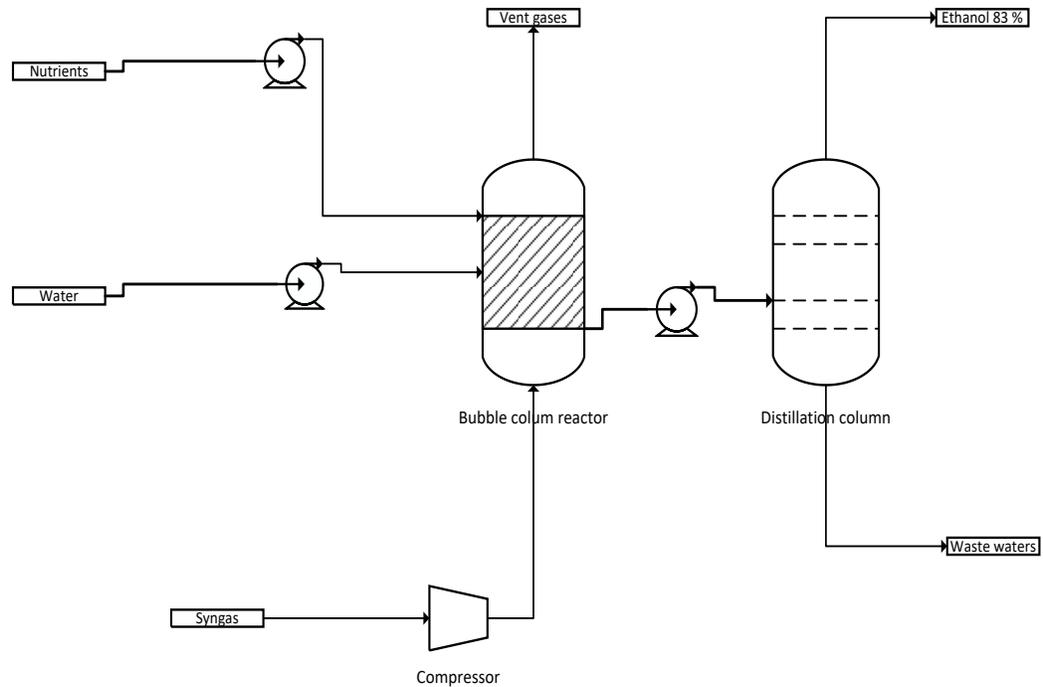


Figure 10. Preliminary process diagram for gas fermentation of metal industry flue gas

16.1. Process description

Flue gas at a temperature of 10 °C and atmospheric pressure is taken to compressor C-101 to raise its pressure from 1 to 3 bar. Temperature of the gas leaving compressor unit C-101 is 151.5 °C. Cooler E-101 reduces the gas temperature to 39 °C before entering airlift reactor R-101. The reactor is also fed by two more currents: first, 9,5m³/hr. at 39 °C by pump P-101. Second, the growth media containing 233.4 kg/hr. of bacteria in 1.5 m³/hr. of water at 39 °C pumped by pump P-102. The growth media is stored and monitored in vessel V-101, which is fed by 1.5 m³/hr of water, 23.4 kg/hr of bacteria, and 209.8 kg/hr of nutrients. Airlift reactor R-101 is kept at 39 °C. A stream of 40 ton/h of unreacted vent gases leaves the reactor at atmospheric pressure, while the fermentation broth containing the products is removed at a rate of 11.4m³/hr. The fermentation broth is fed to distillation column T-101. The distillate from T-101 is removed as product (83% in ethanol), while bottom product containing mostly water and bacteria is removed at 106.4 °C and 1.26 bar at a rate of 10.5 m³/hr. Bacteria is then removed in membrane filtration unit F-102 at a rate of 233.4 kg/hr. The permeate is recycled back to the distillation column after bleeding

20% of its flow and cooling to 39 °C in cooler E-102. This current is then combined with 1.5 m³/hr of fresh water and fed to reactor R-101.

In Figure 11 PID diagram of the process and Figure 12 is process flowsheet which are presented to picture process equipment, instrumentation and stream flows.

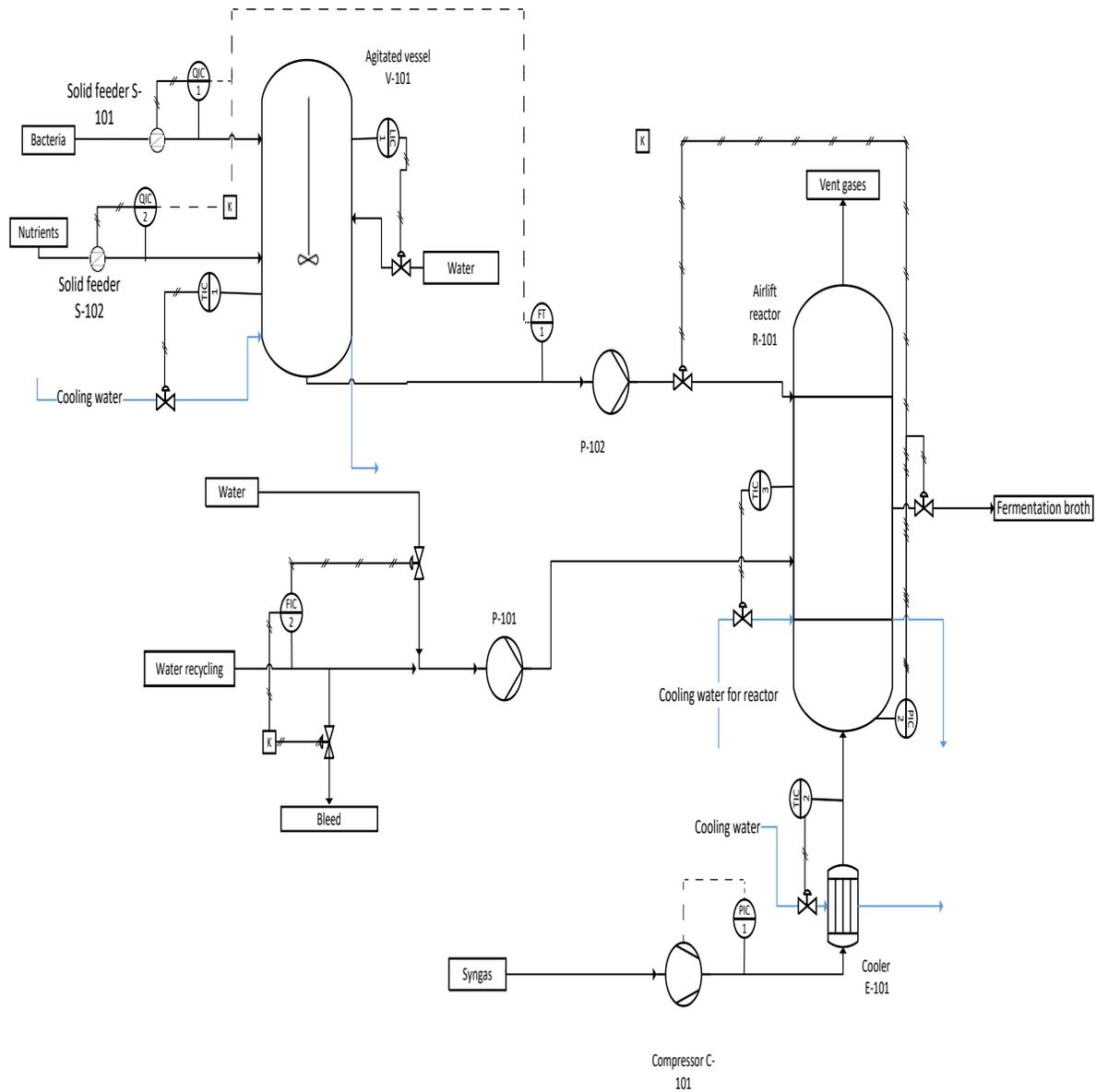


Figure 11. PID of process design (Reactor Part)

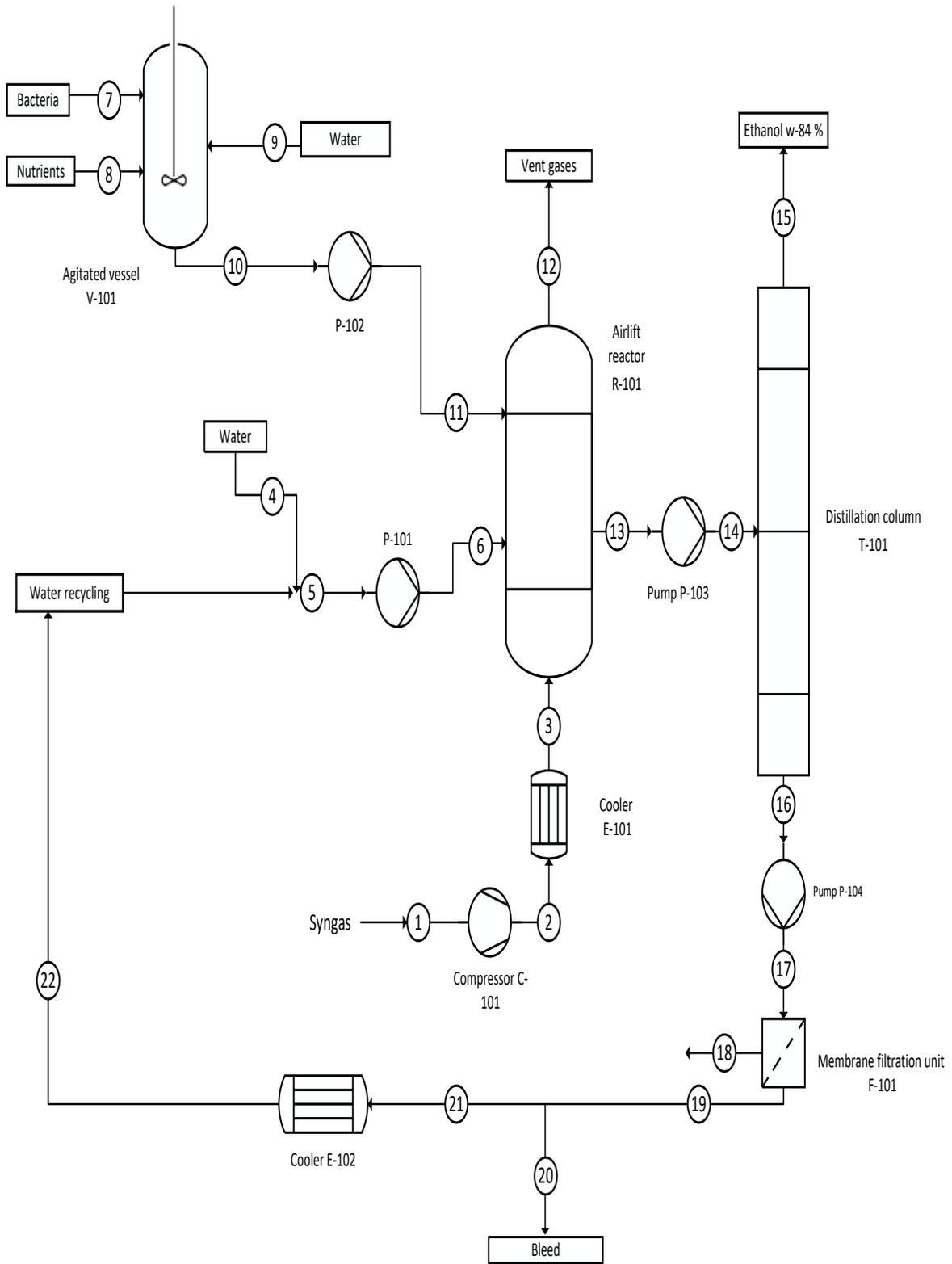


Figure 12. Process flowsheet diagram

17. ASPEN PLUS SIMULATION

Aspen Plus simulations are used to analyze the process behavior and flow rates which eventually helped in optimizing cost analysis and profitability of process.

17.1. Heat exchanger simulation

It's compulsory to cool down the gas after compressor before introducing into fermenter. The cooling process is designed by a counter-current cooler HEATX. Water is the cooling agent, which will change to steam. Due to the design specification that is defined by the fermentation unit the temperature of cooled syngas must be 39 °C.

Aspen was used for brief simulation of heat exchangers but most of the calculations were done manually. Area, heat duty and LMTD were all simulated and calculated. Table 10 below shows the simulated results of heat exchangers.

Calculations can be seen in Appendix 3. Floating head type heat exchangers were used for cooling syngas before entering the reactor. the compressed syngas from 1 bar to 3 bar was further cooled from 151.5°C to 39 °C. Shell and tube heat exchangers are efficient and very feasible with high temperature due to their configuration. Specification for these heat exchangers are on Appendix 4.

Table 10. Heat exchanger simulation

Name	Type / Position	Heat duty (kW)	Heat Exchange area(m ²)	LMTD (°C)
E101	Shell and tube / Horizontal	1087	275.8	43.7
E102	Shell and Tube / Horizontal	803	67.5	99.8

Table 11 shows the heat duties of heat exchanger. The total of 1890 kW heat duty is required for both heat exchangers.

Table 11. Heat duties values for heat exchangers and reboilers.

Units	Heat Duty [kW]
E101	1087
E102	803
Total	1890

17.2. Simulation of the reactor and distillation

For this process, both the reaction phase and the product separation as well as product recycling were simulated using Aspen Plus. The main objectives of the simulations are:

- To define a simple but solid mass-transfer model for the reactor and estimate the outcome.
- To check if the process selected allows for an energy-efficient product recovery.
- To determine the effects of recirculating valuable products e.g. water.
- To size equipment.
- To determine optimal process conditions such as temperature and pressure.
- To determine mass and energy balances.

To tackle this challenge, several assumptions were made:

1. Bacteria and other components from growth media (nutrients, buffer solutions) are not considered in the simulations.
2. NRTL method was selected as the property estimation model. Thus, along with the Hayden O'Connell (HOC) allows determination of activity coefficient (Corbetta et al., 2016).
3. Reactor selected for simulations is CSTR.

Reactor simulation

The reactor selected for the simulation is RCSTR. Through its rate selection option, this reactor allows modelling the bottleneck of this reaction: mass transfer from the bulk gas into the liquid. This means that the pace of the reaction is determined by the rate of

transfer from the gas to the liquid, which can be expressed through the following equation (Klasson et al., 1992):

$$\frac{1}{V_L} \frac{dN_S^G}{dt} = K_L a \cdot H (P_S^G - P_S^L) \quad (7)$$

Where N_S^G is moles of substrate transported from the gas phase, V_L is the volume of the liquid, t is time, K_L is the overall mass transfer coefficient, a is the gas-liquid interfacial area per unit volume, H is Henry's law constant, P_S^G is the partial pressure of the substrate in the bulk gas, P_S^L and in the partial pressure of the substrate in the liquid phase.

Of course, if the bottleneck of the reaction is within this mass-transfer phase, the concentration of the gas in the liquid will tend to zero, and equation 1 will be as follows:

$$\frac{dN_S^G}{V_L dt} = K_L a \cdot H \cdot P_S^G \quad (8)$$

The limiting compounds are hydrogen and carbon monoxide, for their corresponding reactions. As a result, these equations are referenced to each of these compounds. The Henry constant values at 39 °C for these compounds are (Sander, 2015):

$$H_{CO}^{39^\circ C} = 8,11 \cdot 10^{-6} \left(\frac{mol}{m^3 Pa} \right)$$

$$H_{H_2}^{39^\circ C} = 7,3 \cdot 10^{-6} \left(\frac{mol}{m^3 Pa} \right)$$

On the other hand, in order to take into consideration selectivity of competitive reactions (ethanol and acetic acid yielding-reactions), the calculated constant for the acetic acid acid-yielding reactions is divided by 10, given the fact that ethanol to acetic acid ratios are 10 to 1 (VTT, 2016). Finally, reactor conditions are set at 39 °C and 3 bar, which correspond to optimum working conditions for bacteria and allow efficient mass transfer rates for the bulk gas, respectively. Table 12 summarizes the values used for the reaction. The reactor volume is a design variable, given the fact that the reactor used is not CSTR and thus dimension will not be the same. Reactor volume was modified within a range from 150 to 700 m³ until a satisfactory amount of ethanol of 19 kmol/h was obtained.

Residence Time

In airlift reactor, liquid and gas residence time are specified separately because of multiple reactions. The liquid residence time is higher than the gas retention time. In this particular case, liquid residence time is estimated from literature which is 10-20 hours and gas residence time is 2-2.5min (Gaddy et al., 2013).

The dimensions of reactor cannot be calculated. The exact calculations of reactor dimensions require experimentation and practical work. The estimated reactor volume in Aspen Plus simulations seems reasonable when industrial scale is considered. The values of Henry constant H , mass transfer coefficient K_La , reactor volume and process parameters are combined in Table 12.

Table 12. Values used for reactor simulation.

Factor	Value
Reactor volume (m ³)	700
$H_{CO}^{39^{\circ}C} \left(\frac{mol}{m^3 Pa} \right)$	$9,37 \cdot 10^{-6}$
$H_{H_2}^{39^{\circ}C} \left(\frac{mol}{m^3 Pa} \right)$	$7,7 \cdot 10^{-6}$
K_La (h ⁻¹)	36
Temperature (°C)	39
Pressure (bar)	3

Figure 13 represents the main flowsheet of simulation of the process in ASPEN Plus V8.6:

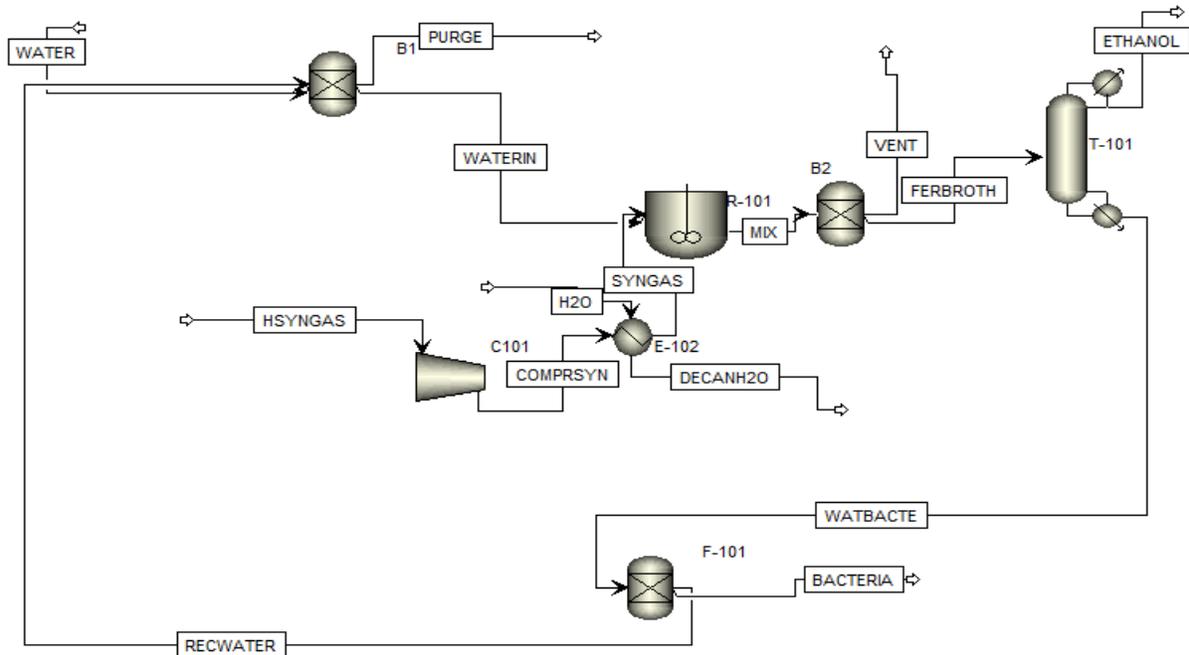


Figure 12. Main flowsheet for simulation (ASPEN V8.6)

The result of each stream and flow composition is shown in Appendix 2.

18. EQUIPMENT SIZING AND UTILITIES

Sizing of every equipment which is considered in process design is calculated which can be seen from *Appendix 3* to *Appendix 7*. Mass and energy balance are also calculated which can be seen in *Appendix 8* and these mass and energy balance are also used in cost calculations.

19. ECONOMIC EVALUATION

19.1. Estimation of Total Capital Investment

The total capital investment is approximated from the equipment cost. The way these costs have been estimated is explained in *Appendixes 9 to 13*. Then, the installation costs are obtained through percentage of purchased equipment cost, as explained in *Appendix 11*. Please note piping costs have been estimated separately. These costs add up to the

inside battery limits or ISBL investment, from which the rest of the capital investment terms (OSBL, engineering, contingency, start-up, and working) are obtained, as explained in Appendix 13. The values obtained are shown in Table 13.

Table 13. Estimation of total capital investment.

Fixed capital investment	Cost (k€)
<u>ISBL</u>	
<u>Purchased equipment</u>	
1. Agitated vessel V-101	67.5
2. Pump P-101	8
3. Pump P-102	8
4. Pump P-103	8
5. Pump P-104	8
7. Membrane filter F-101	112
8. Airlift reactor R-101	1400
9. Distillation column T-101	175
10. Cooler E-101	29
11. Cooler E-102	10
12. Compressor C-101	295
13. Storage tank	53
Total	2176
Installation costs	1163
<u>Piping</u>	311
Total ISBL cost	3650
<u>OSBL</u>	
Total	1095
<u>Engineering and supervision</u>	
Total	912
<u>Contingency</u>	
Total	547
Total Fixed capital investment	6206
Working capital	310
Total capital investment	6516

19.2. Estimation of operation cost

The operation cost is calculated as the addition of two terms: fixed and variable costs. Variable costs are determined by the cost of raw materials and utilities, as well as the waste water disposal. Also, the price of ethanol purification through an external service (e.g. ST1) has been included as a variable cost, and is estimated as 5% of the total

cost of the product. On the other hand, fixed costs have been estimated depending on labor and other factors explained in Appendix 13. Please note these costs have also been calculated on a cost per unit of product basis. On the other hand, a fully operational year is considered to be of 8000 hours, taking maintenance into account.

19.3. Variable cost estimation

19.3.1. Water for reactor

The reactor is being continuously fed with 3 m³/h of fresh water. The cost of the cubic meter is taken as 1.62 €/m³ (Lappeenrannan Energiaverkot oy, 2015).

19.3.2. Bacteria and nutrients

The cost of bacteria and nutrients is estimated altogether to be 100 € / ton.

19.3.3. Syngas

The cost of syngas is, for the moment, estimated to be free.

19.3.4. Electricity

The cost of the electricity in Finland for industrial purposes is considered to be 70 €/MWh. The calculations for the electricity consumed by each equipment are summarized in Table 14.

Table 14. Electricity consumption in the plant.

Equipment	Power (kW)	Electricity consumption on yearly basis (MWh/year)
Pump P-101	0.45	3.6
Pump P-102	0.22	1.76
Pump P-103	0.51	4.08
Pump P-104	0.22	1.76
Filtration unit F-101	20.6	164.8
Compressor C-101	781	6248
Total	803	6424

19.3.5. Electricity needed for pumping cooling water

It is considered that the plant counts already with a pumping station for the cooling water. The cooling water itself is free and can be taken from the river Torne. The electricity consumed by pumping the water is calculated as shown in equation 7:

$$E = \frac{Q \cdot \Delta P}{\eta} \quad (7)$$

Where E is the electricity power consumption, Q is the flow of cooling water, ΔP is the pressure drop, and η is the pumps efficiency. Both the pressure drop and the efficiency values are estimated as 100 kPa and 80%, respectively. These calculations are summarized in Table 15.

Table 15. Determination of the electricity needed for pumping cooling water.

Equipment	Flow rate of cooling water (m ³ /h)	Power consumption (kW)	Electricity consumption on a yearly basis (kWh/year)
E-101	20.94	0.7	5817
E-102	7.24	0.3	2011
Reactor	19.5	0.7	5417
Condenser	43.9	1.51	12125
Total	91.5	3.2	25370

19.3.6. Aqueous waste disposal

The waste water from process is considered qualified for municipal waste water treatment process. The cost of disposing of the water that is bled from the recirculation current is taken as 2.21 €/m³ (Lappeenrannan Energiaverkot oy, 2015).

19.3.7. Ethanol purification

The final product for which the price is considered is fuel ethanol. As a result, the purification of ethanol through an external service (e.g. ST1) must be considered. This cost is estimated as 5% of the retail price of fuel ethanol. This is purely an estimation, so that is the reason why this cost is analyzed in the sensitivity analysis.

Table 16. Summary of variable operation costs.

Variable Cost of Production						
Raw materials	Units	units/ton of ethanol	units/year	€/unit	k€/year	€/ton of ethanol
1. Fresh water for reactor	m ³	3.84	24000	1.62	39	6.2
2. Bacteria and nutrients	ton	0.3	1865.6	100	186	30
3. Syngas	m ³	41045	256452000	0	0	0
<u>Utilities</u>	Units	units/ ton of ethanol	units/year	€/unit	k€/year	€/ton of ethanol
Electricity	MWh	1.0	6424	70	449	72
Cooling water	kWh	4.6	28694.4	0.5	1.4	0.23
<u>Effluent disposal</u>	Units	units/ ton of ethanol	units/year	€/unit	k€/year	€/ ton of ethanol
Aqueous waste	m ³	2.6	16000	2.21	35	5.7
<u>Ethanol purification</u>					k€/year	€/ ton of ethanol
					162	26
Total variable cost of production					874	140

19.4. Fixed cost estimation

The given the size of the plant, a total of 2 operators per shift is sufficient. Being operational on a continuous basis, 6 shift positions of 8 hours each are considered. The annual wage for each operator is considered to be 41664 €. On the other hand, supervision costs are estimated as 5% of the operating labor, given the low supervision requirements in the plant. Side costs are set at 190% of the operating labor and supervision costs. Maintenance costs are 3% of the ISBL since the plant handles mostly fluids (Towler and

Sinnott, 2012). Land fees are not considered because the plant location is within the boundaries of Tornio's steel mill. Insurance is 1% of ISBL and OSBL investments (Towler and Sinnott, 2012), whereas depreciation is estimated to be 5% of the fixed capital investment, considering a life span for the plant of 20 years. Quality control is estimated as 0.5% of the sales revenues. License fees and interest are set to be 2% of the fixed capital investment. Finally, corporate overhead charges, which include administrative, marketing, and R&D costs, are estimated at 5% of labor, supervision and maintenance, 2% of total product costs, and again 2% of total product costs respectively. These costs are summarized in Table 17.

Table 17. Summary of fixed operation costs

Labor	2 operators/shift position		k€/year	€/ton of ethanol
Number of shift positions	6	41664 €/year each	250	40
Supervisions	5% of operating labor		12.5	2
Side costs and benefits	190% of operating labor and supervisions		498.7	79.8
Maintenance	3% of ISBL investment		109.4	17.5
Insurance	1% of ISBL and OSBL investment		47.5	7.6
Quality control	0.5% of sales revenues		16.2	2.6
Interest	2% of fixed capital investment		124.1	20
License fees	2% of fixed capital investment		124.1	20
Depreciation	5% of fixed capital investment		310.3	49.7
Administrative costs	5% of labor, supervision, and maintenance		18.6	3
Selling and marketing costs	2% of total product costs		47.7	7.6
Research and development costs	2 % of total product costs		47.7	7.6
Total fixed cost of production			1607	257

The total operation cost will be the addition of the variable and fix costs of operation, as shown in Equation 8:

$$\begin{aligned}
 \text{Total operation cost} &= \text{Variable cost of operation} + \text{Fixed cost of operation} \\
 &= 875 + 1599 = 2474 \text{ k€/year} \\
 &= 397 \text{ €/unit of product} \tag{8}
 \end{aligned}$$

19.5. Revenues and profitability analysis

The revenues are estimated from the price of the final product (fuel ethanol) and the production volume. The revenue expected from the consumption of CO₂ is not considered given the fact that CO₂ is being produced in the process and not consumed. Also, the tax from producing this CO₂ has not been considered in the costs. The total revenue from this operation is shown in Table 18.

Table 18. Total revenue from production of 83% ethanol.

Revenue					
	Units	units/ton of ethanol	units/year	€/ton of ethanol	k€/year
Fuel ethanol	tons	1	6248	520	3249

The estimated cost of operation and the revenue determine the profit of the operation, which then allows to determine the payback period, at which the initial investment is returned and profit is made. In order to analyze the profitability over the years, several assumptions have been made:

1. The plant's life span is considered to be 20 years.
2. Linear depreciation is considered the life span of the plant. This is, 5% of the fixed capital investment, resulting in a whole 100% in 20 years.
3. The working capital is included in the initial investment, and it is also returned at the end of the 20 years.

4. Taxes are not considered.
5. The plant is fully operational from its construction.

The estimation of profitability on a yearly basis is shown in Table 19, while the profitability analysis over the plant's life span is shown in Appendix 10 and in Figure 13.

Table 19. Estimation of profitability on a yearly basis

Profitability	k€/year	€/ton of ethanol
Variable cost of production	875	140
Fixed cost of production	1607	257
Total cost of production	2482	397
Revenue	3249	520
Annual gross profit	767	123

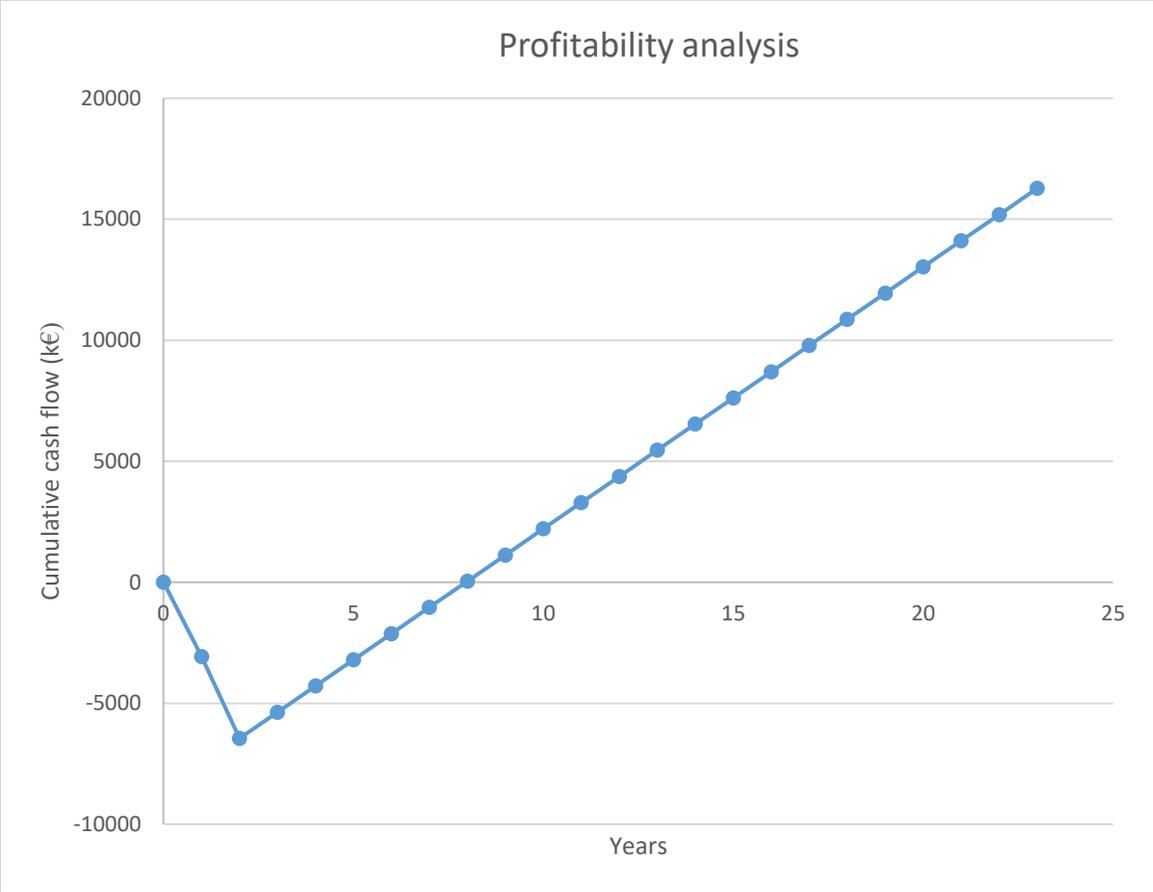


Figure 13. Profitability analysis.

The net present value or NPV can be calculated from the cash flow in each year and a set interest value. The NPV has been studied at different interest rates varying from 6 to 17%, as shown in Figure 14.

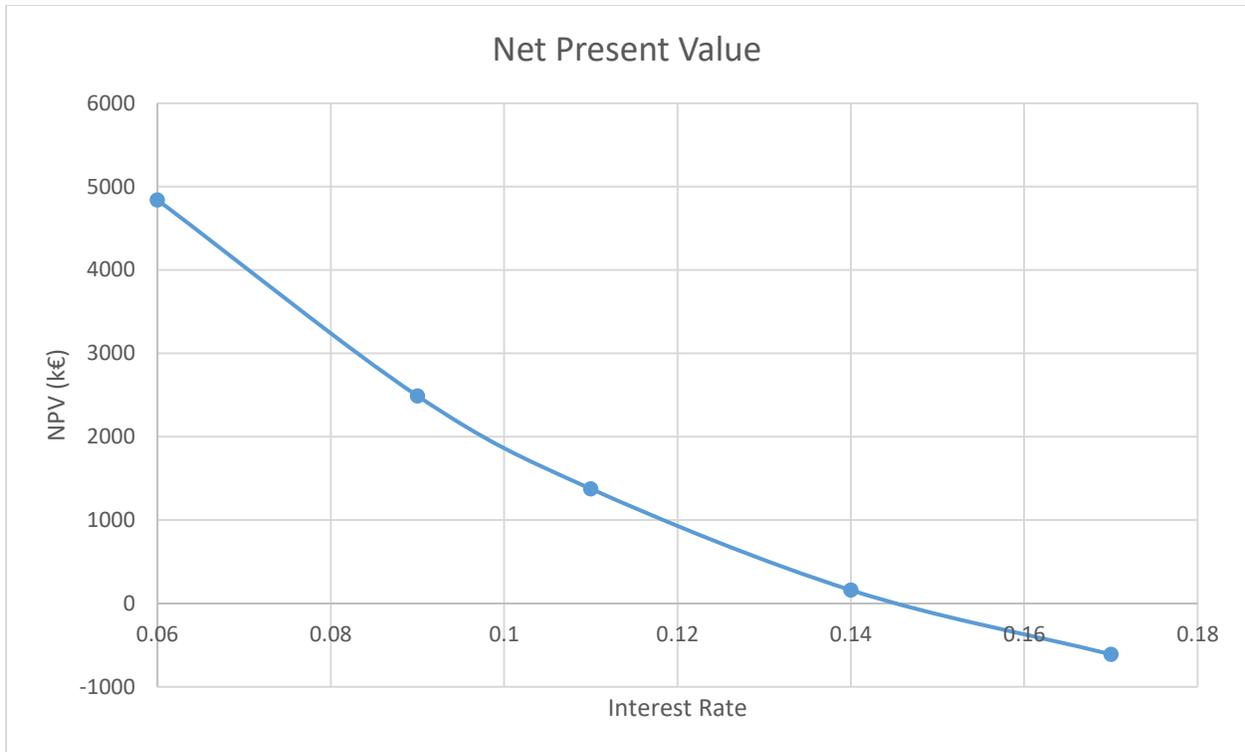


Figure 14. Net present value at different interest rates.

Also, the payback period and the return on investment can be calculated through simple formulas. Please note the payback period is determined setting as zero the year in which the plant starts operating.

- The return on investment (ROI):

$$\begin{aligned} \% ROI &= \frac{\text{Annual profit}}{\text{Total capital investment}} \cdot 100 \\ &= 11.8 \% \end{aligned} \quad (9)$$

- Payback period:

$$\begin{aligned} \text{Payout time (yr)} &= \frac{\text{Total capital investment}}{\text{Annual gross profit} + \text{depreciation}} \\ &= 6 \text{ years} \end{aligned} \quad (10)$$

19.6. Sensitivity Analysis

The best estimation of required investment and cash flows are the basis of any economic analysis. Many factors such as cost of raw materials and operating cost can affect the actual cash flows in any year. These are dependent on sales and prices. The uncertainties which can be foreseen are analyzed with sensitivity analysis for the capability of process.

Among all the variable costs, five parameters were considered. These parameters are:

- Cost of electricity: the cost of electricity, with a value of 72 €/ ton of ethanol, is the biggest contributor to the variable operation costs.
- Cost of ethanol purification: the cost of ethanol purification has been estimated to be 5% of the final retail price for fuel ethanol. However, this estimation lacks any reference, so it is important to study how the profitability will react to changes in this cost.
- Cost of bacteria: with a cost of 30 €/ ton of ethanol, the bacteria is the second biggest contributor to variable costs.
- Product price: the product price determines the revenue and its estimation and forecasting is essential to estimate the feasibility of this project.
- Fixed capital investment: the fixed capital investment is calculated through a series of assumptions that start at the estimation of the cost of equipment. Furthermore, many terms from the fixed costs are calculated as a percentage of the FCI. As a result, it is convenient to study the effects of the FCI in the project's profitability within the range of -10 to +25%.

Among these five parameters, cost of electricity has been varied within a range of $\pm 25\%$ of their original value and fixed capital investment and ethanol price were varied in a range of -10 to +25% and -40 to 40% respectively.

Figures 15 to 17 show the effect of these variations over the cumulative cash flow and the payback time for each case. Again, the same assumptions as with the profitability analysis have been made in order to plot the graphs (plant fully operational from the start, life span of 20 years). The sensitivity analysis graphs for the ethanol purification cost and

the cost of bacteria have been eliminated due to their low impact on the profitability of the project.

19.6.1. Electricity prices

Since electricity costs account for 25% of the operation costs, a fluctuation of 25% on its price has been studied. The price considered for electricity in Finland is 70 € per MWh. This value could vary depending on several factors, like the size of the Tornio steel mill to which the plant is attached (given that bigger productions mean bigger electricity consumption and thus lower price on electricity) or the recovery of part of this utility by electricity generation from the vent gases. Either way, the fluctuations on the price of the kWh do not affect much to the profitability of the whole project, as it can be seen in Figure 15.

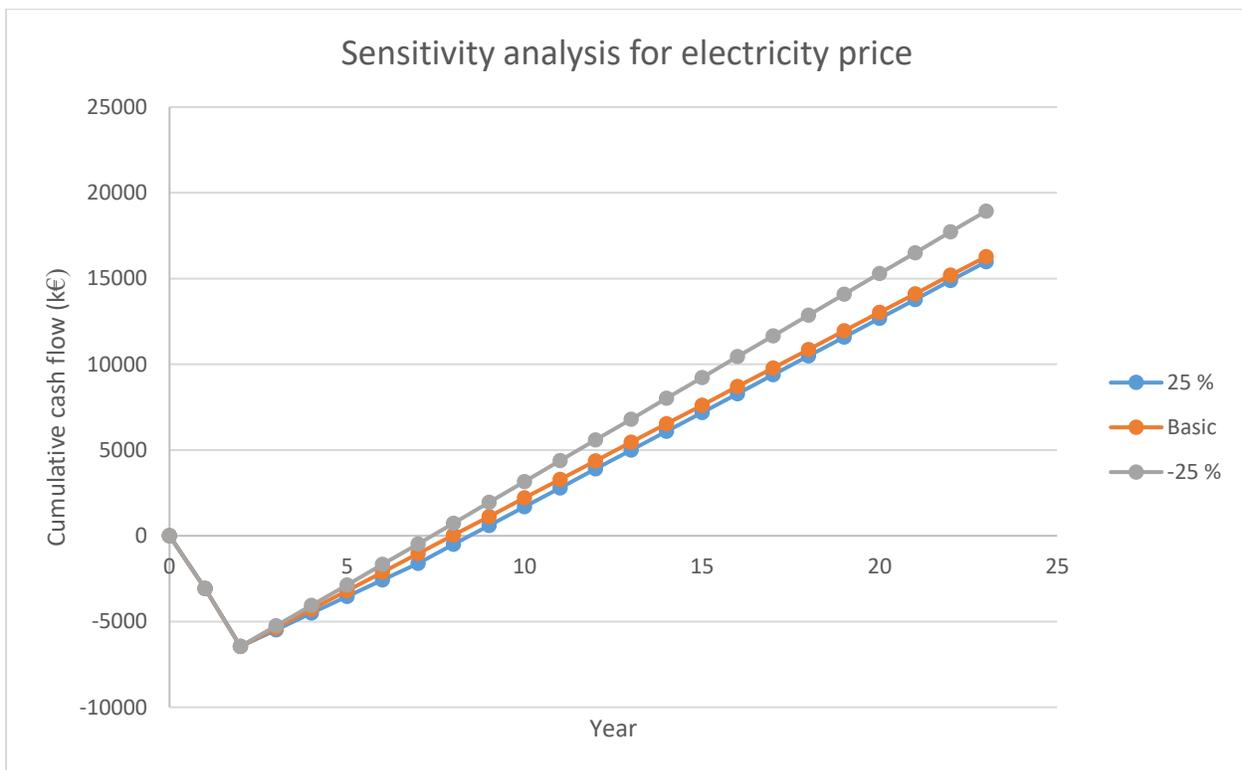


Figure 15. Sensitivity analysis for electricity price

19.6.2. Ethanol price

Ethanol prices have been considerably volatile during the past years, with a variation between $\pm 10\%$ in 2016 (Trading, 2016). The variation of ethanol price in sensitivity analysis is done in a range of $\pm 40\%$ because the prices in the start of 2015 were 550 euros

per ton of 99% ethanol which raised to 627 euros. The purity of product also makes variation in the prices. High pure ethanol has high price as compared to less pure ethanol. Keeping these scenarios in mind, $\pm 40\%$ range was selected. These variations could make the payback period to increase highly undesirably, as seen in Figure 16. The sensitivity analysis shows thus a potential threat if the prices of ethanol drop in the next few years. As a measure of caution, the possibility to increase the production capacity, which would not have a great impact on the overall design of the project and yet might eliminate the threat of changing prices in the market. Even if it increases operation costs (see from Figure 13), it does not have a great impact on profitability.

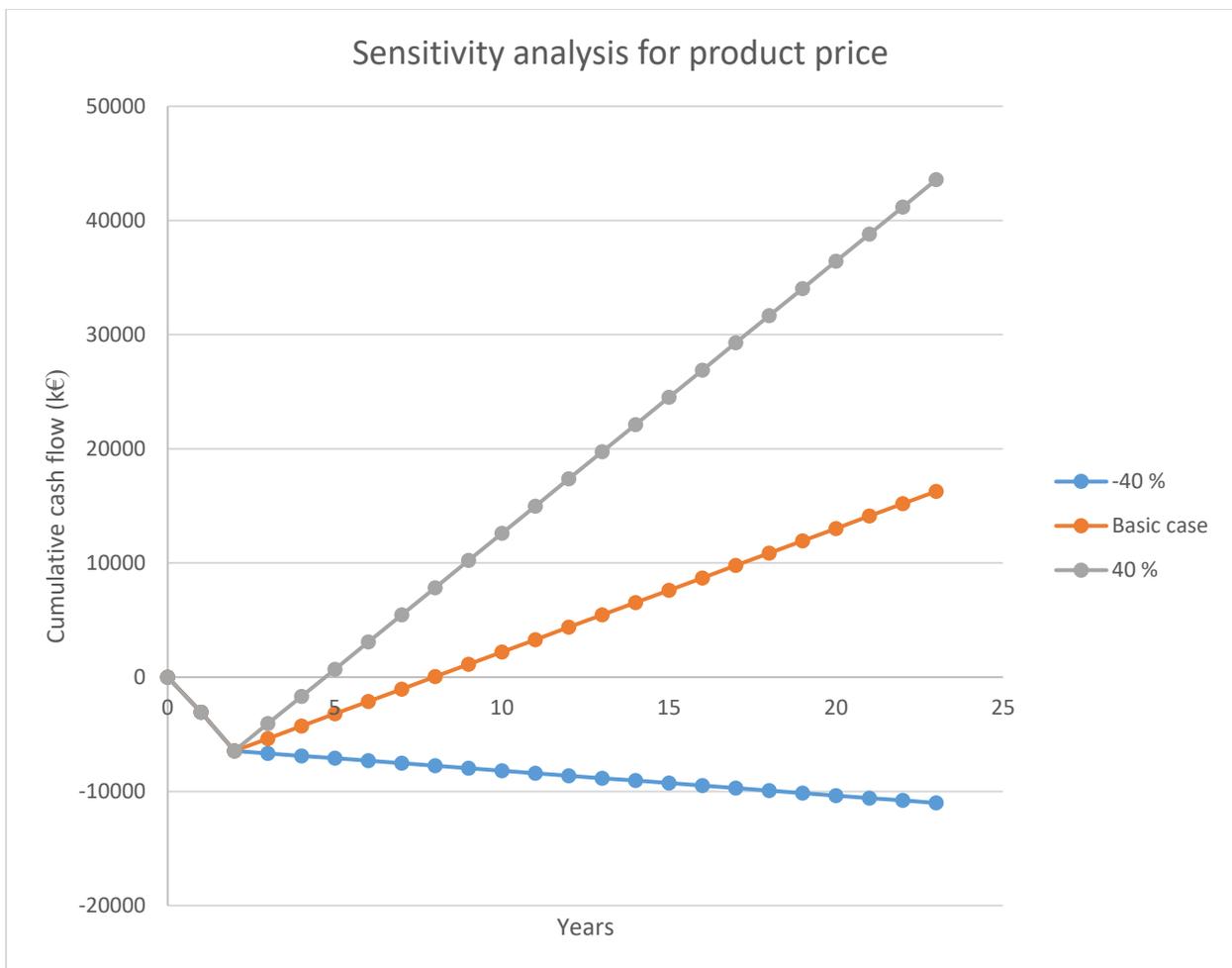


Figure 16. Sensitivity analysis for ethanol price

19.6.3. Fixed capital investment

The second greatest impact from the terms studied comes from the fixed capital investment, as seen in Figure 17. An optimistic fluctuation between +10 and -25% has been considered to take into account the possible shift of the fixed capital investment given variations in equipment prices and the installation costs, as well as changes in other costs like OSBL or contingency, which for this analysis have been calculated through percentages (see Appendix 13: Formulas).

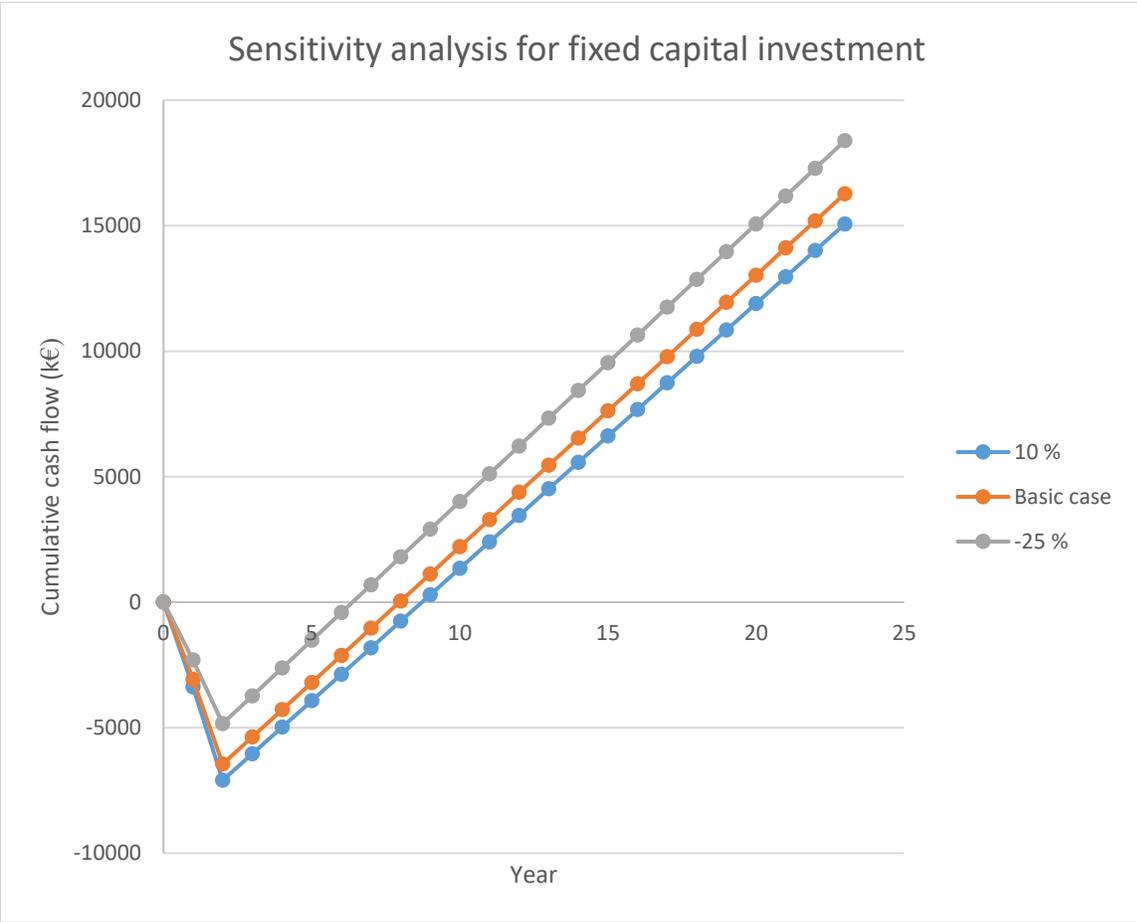


Figure 17.Sensitivity analysis for fixed capital investment

19.7. SWOT Analysis

SWOT analysis is the abbreviation of strengths, weaknesses, opportunities and threats. It's an analytical tool which predicts the future challenges for the company and narrow downs the potential markets. The key idea of SWOT analysis is to conclude the future prospects and complete mindfulness of the factors which can affect operations.

Figure 18 shows a summary of the different factors of the SWOT analysis.

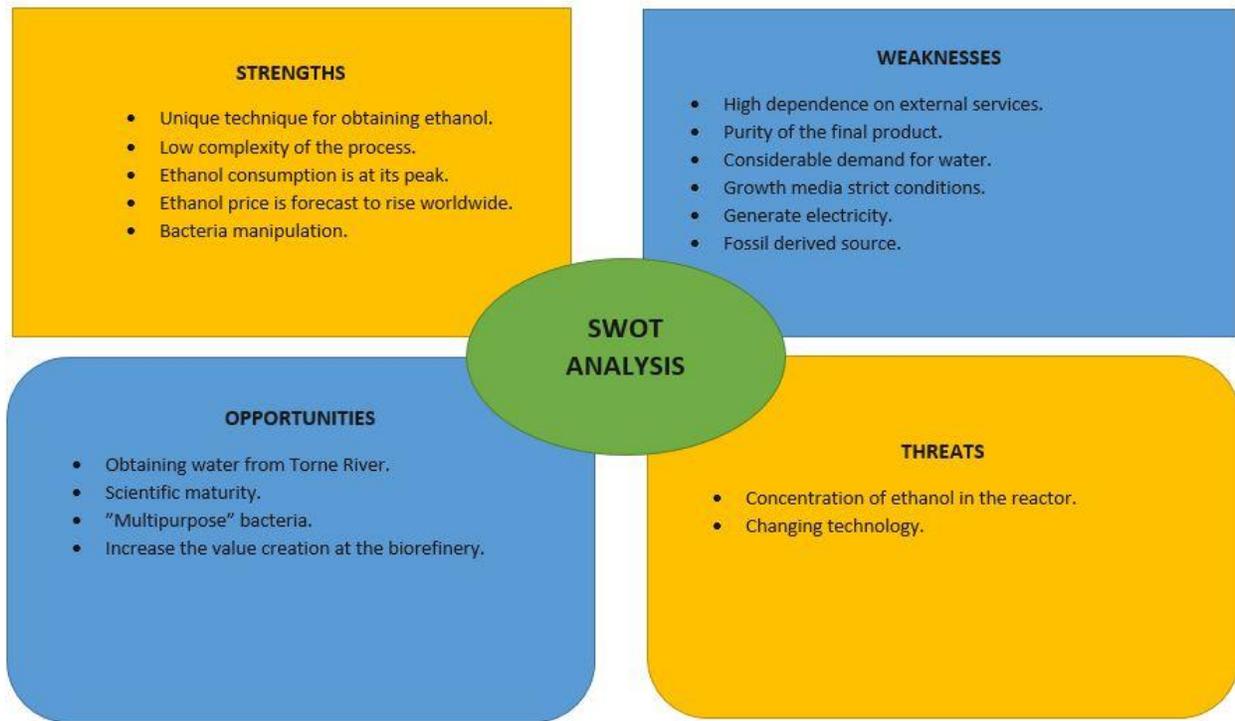


Figure 18. SWOT analysis

19.7.1. Strengths assessment

Following points are considered for strength assessments and their details are as follows:

Unique technique for obtaining ethanol

Although it is common to produce ethanol by fermentation, it is not common approach to obtain ethanol from steel mill flue gases which is further economically appealing than obtaining ethanol from fermentation of sugar. It is competitive edge.

Ethanol consumption is at its peak

Ethanol fulfills The Clean Air Act of United States which means ethanol is particulate free fuel which ignites with oxygen and emits less amount of carbon dioxide, carbon monoxide and aldehydes. Brazil is one of the biggest consumer of ethanol. Brazil has also applied an order to mix anhydrous ethanol in gasoline fuel in the ratio ranges from 4.5%-27% (Nuñez and Önal, 2016).

Ethanol price is forecast to rise worldwide

Analysts foresee demand from Brazil increasing in 2017, while the country's capacity use in the same year is projected to drop marginally. Additionally, investors expect some slight reductions in supply during the latter part of this summer. The U.S. Department of Agriculture also increased the demand scenario for corn, from which ethanol is produced. Lastly, the Energy Regulatory Commission of Mexico passed the first regulation on ethanol in the nation's history, which permits the blending and sale of up to 5.8% ethanol in the country's fuel supply, thus further supporting demand prospects.

19.7.2. Weaknesses assessment

Weaknesses of every process play a vital role in judging and controlling factors which can reduce process capabilities. Following considered weaknesses of this process are discussed

Purity of the ethanol and high dependence on external services

It is mandatory to purify the final product somehow. The outlet stream of the distillation column contains lower ethanol concentration than required. It would add some costs to the process before selling the ethanol.

Considerable demand for water

Although recycling of water is implemented in the process, a huge amount of water is necessary to use in different equipment.

Growth media strict conditions

As it was explained in previous reports, these microorganisms are very selective with their environment. That means the airlift reactor must be carefully managed to work properly without modifying growth media properties.

On the other hand, it also affects to ethanol titers which should be reduced as we decided in the previous stage.

Generate electricity

Electricity generation from biomass to use in charging for electric vehicles is much eco-friendlier as compared to produce ethanol. Researchers are working to open more ends in the development of cost effective processes for cellulosic ethanol and batteries for vehicles.

19.7.3. Opportunities assessment

Syngas fermentation has many uncovered areas and there are many opportunities which will decrease cost of process with high productivity. Opportunities analyses is as followed:

Increasing the volume of production

The team believes that the possibility of increasing the volume of production should be further studied and analyzed. The main facts that support this possibility are on one hand the low impact variable costs have on the profitability of the process, as seen in the sensitivity analysis, and on the other hand the fact that the design of the equipment and the overall plant would not vary significantly is the volume of production was to increase.

Obtaining water from Tornio River

Regardless of the amount of water that is needed, a key point is that it could possibly be obtained from Torne River. Due to the location of the plant, Outokumpu in Tornio, it is possible to get all the amount of water that is required for the process in an economically feasible manner.

There is a chance of getting permissions to treat this water. Therefore, the water would be acquired for free.

Scientific maturity

It is a new way for obtaining ethanol. None of the most popular companies is producing ethanol by using steel mill flue gases, which is a key point and a big advantage because it is very appealing for the market.

Significant advances in genetic engineering for acetogens has ensured advance products and pathways to raise production and yields. In future, more focus is required to attain genetic tools and methods to simplify the complexities of genetic engineering and classification. (Liew et al, 2016)

Multipurpose bacteria

Re-adapting the bacteria used in the process, it could be obtained a higher ethanol concentration or other quality products as 2,3-butanediol.

2,3-butanediol (23BD) is an important chemical in petrochemical industry but bacteria can also generate it. Pathogenic bacteria have found to produce 2,3-butanediol with high production rate by fermentation. Sugars are the carbon and energy source for them. It can also be produced by *Clostridium ljungdahlii*.

Increase the value creation at the biorefinery

The future fermentation plants to produce ethanol as a major product can also consider the production other commodity chemicals. The genetic modification of acetogens and more research this can be done easily. Otherwise bioreactors pairing with other platforms such as biotechnology platform with carboxylate platform can also be helpful in attaining multi range of products ([Molitor et. al, 2016](#)).

19.7.4. Threats assessment

Threats are always challenging and safe operations are always demanded. Threats which are expected in this process is as under:

Concentration of ethanol in the reactor

The maximum concentration of ethanol that the bacteria can survive on is 5%. Even though the team has designed a method to maintain the ethanol concentration lower than 5%, the fact that a higher value of concentration will affect to the functioning of the reactor should be taken into account. It is a big threat which must be carefully treated.

Changing technology

Technology is being developed continuously. The process which the team has made up is a new way for obtaining ethanol, it is possible to encounter a new technologically advanced method though. It is not a big deal, but it should be considered that it would be many competitors developing some improvements.

20. FEASIBILITY STUDIES

Feasibility analysis is the practice toward figuring out if a business idea is appropriate. It is the preparatory assessment of a business idea, led with the final goal of figuring out if the idea can be pursued after analyzing standards. There are four divisions for an appropriately led feasibility studies. They are;

1. Product/service feasibility
2. Industry/Target market feasibility
3. Organizational Feasibility
4. Financial feasibility

1. Product feasibility analysis

Product feasibility analysis is carried out for two different components as follows;

Product desirability: The main target is to produce ethanol from steel mill flue gas by fermentation process. This ethanol can be used as biofuel. Finland is targeting to have 20% biofuels in transportation by 2020 which is produced mainly from household, commercial and industrial bio-waste. Ethanol is also an environmental friendly fuel. Therefore, producing ethanol from flue gases is highly desirable.

Product demand: Ethanol is a major component of gasoline market which has a global demand of 75 million tons per year. Considering this huge market size, the product is highly demandable.

2. Target market feasibility analysis

Ethanol can be used as fuel for vehicles, in fuel cells as well as E-diesel. As mentioned above, Finland is targeting to have at least 20% of biofuel in the total energy content of petrol and diesel oil. This target is pretty challenging and therefore production of ethanol from alternative sources is of high interest. Sugar and starch fermented ethanol is currently dominating the market which is a threat for food security. Utilization of steel mill flue gas for ethanol production will decrease the demand of ethanol production from food.

Apart of food based ethanol production, it can be produced by acid hydrolysis of wood and straw, enzymatic fermentation of biomass. These are the competitors for syngas fermentation process. But the new venture has competitive advantages as the main raw material (syngas) is obtained free of cost.

3. Organizational feasibility

Organizational feasibility analysis has two components such as management prowess and resource sufficiency. As this new venture is an integrated plant with existing steel mill, it is considered that the firm has adequate passion and expertise in the management team to start this new venture.

Some example of non-financial resources are available office or lab space, local and state government support, class of the workers available, immediacy to main contractors and customers, readiness of high value workforces to join the organization and obtaining intellectual property protection in key areas. Considering a steel mill integrated new venture, our firm has availability of all the resources.

4. Financial feasibility

The main component of economic feasibility analysis is required start-up money, economic operation of related business and total financial desirability of the estimated project. Considering the existing and already established firm that are going to start the new venture, the firm has adequate start-up cash for budgeting the capital purchases and operating cost mention in the detail economic analysis in third stage.

21. FURTHER DISCUSSIONS

From the cost evaluation, we have seen that the price of ethanol is one of the important factor for the profitability of this venture. According to EU regulation, blending biofuel or ethanol with the fossil fuels is set to become 10% by 2020, while Finland has a target of 20% by the same timeframe. This gives significant opportunity for domestic ethanol market as ethanol has already been blended with petroleum products for transportation fuel. However, price for ethanol has been very volatile for years so depending only on the price of ethanol for venture profitability does not seem quite reliable.

The other important factor is the capital investment cost. This however cannot be lowered significantly but increasing the production rate can somehow increase the ROI but in return also increases the variable cost. Mass transfer in the fermenter has been a major limiting factor for ethanol production so further studies on increasing the mass transfer can surely benefit the process. Although energy cost did not directly affect the profitability of venture, it can always be considered as a contributor to product price hike due to the rise in energy price every year. As an alternative source of energy, energy from vent gas can also minimize the energy cost.

21.1. Future investigations and perspectives

The optimal production of ethanol from syngas relies on activity of microorganisms. The modification of different species of microorganisms and combination of different bacteria can result in higher production of ethanol. Genetic engineering and modification is needed to obtain optimized strain of microorganisms which can generate broad portfolio high value products ([Liew et al., 2016](#)).

Gas-liquid mass transfer is one of the biggest obstacle in commercialization of syngas fermentation process. In different designs of reactors, volumetric mass transfer coefficient can be analyzed and ideal value can be obtained. The progress in designs of impellers, fluid behavior, power effectiveness on aeration, mixing time, modified baffle designs and dispersers for microbubbles can be revolutionary to eliminate this limitation. ([Munsunghe and Khanal et al., 2009](#)).

Reactor in series is one productive option. In this way, maximum conversion of raw material can be achieved and high production of ethanol can be achieved. The vent gas stream can be added to feed stream of second reactor to convert into ethanol. The addition of parallel equipment placement especially membranes, to wash one when other one is working and vice versa. The proposed design has room to add more equipments and increase the capacity in order to maximize production.

Distillation is one the ideal and mature technology for the separation of ethanol from mixture in syngas fermentation rather it is costly in energy demand. But other technologies such as ultrasonic atomization, vapor reuse, vapor recompression, selective adsorption and vacuum distillation can also be tested in order to minimize ethanol recovery cost (Sato et al., 2001).

22. CONCLUSIONS

The preliminary design of syngas fermentation using steel mill waste gases is based on the literature review and cost analysis. The plant seems to be profitable but the variation in ethanol market is quite wavy which can alter the process both in positive and negative sides. The gas flow rate of 32000 Nm³/hr can generate 5667 kg/hr which is equal to 63 million liters in a year. But this study can produce only up to 903 kg/hr of 83% ethanol which is equal to 1 million liters a year. There are many factors which are studied. The main factor is the mass transfer coefficient, kLa. The kLa is chosen as 36 hr⁻¹ which is lower and many different values were tried and increase in ethanol titer was observed but at the same time it increased concentration of ethanol in the bacteria stream. The bacteria can withstand on 6 w-% of ethanol and more concentration will result in the death of cells.

Secondly, nutrient media is always a prime parameter for the growth of bacteria. As this study is simulation based but in laboratory experimentation different nutrient media can be tried which will increase production rate.

Based on economic analyses, the plant is profitable and feasible. The production cost is 2480 k€/year and revenue is calculated as 3300 k€/year with 770 k€/year of annual gross profit. But the price of ethanol is very high, 520 €/ton of ethanol. It is the main factor in economic analysis. The ethanol market prices are very wavy and an estimated value from previous years and future values is calculated. The price for 95% pure ethanol is around 460-560 k€/year. It highlights that the profitability is decreased a lot if purity will increase because distillation will be then azeotropic and high cost is required for it. The energy consumption will be higher and cost of distillation tower will be more.

The generation of vent gases is quite high which can be used for energy generation or to reuse as a raw material. The energy values of carbon monoxide and hydrogen are 315217

MJ/kg and 11939 MJ/kg respectively. These gases can be utilized in the process with high mass transfer rate which will reduce vent gases or they can be used for energy generation or reuse in process.

Acetic acid is considered as a waste in this study. The reason is less amount of production rate of acetic acid and if it is separated another distillation column will be needed which decrease the profitability of process.

Bacteria in this process can be used for multipurpose. These microorganisms can generate ethanol along with acetic acid and 2,3-Butanediol but selectivity of microorganism play an important role in producing product. An intensive amount of research is required to study the behavior of these microorganism's growth and their changing behaviors towards product formation.

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APPENDICES

Appendix 1

Mole balance

Composition of the gas:

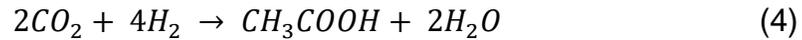
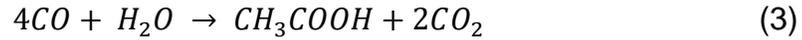
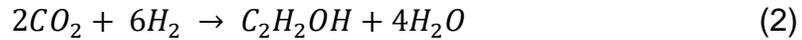
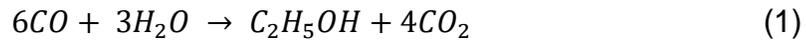
Table 1: Composition of the incoming off gas

Compound	Composition (mol%)
CO	86
CO ₂	5
H ₂	4
N ₂	5

Assumptions:

- For simplicity reasons, the calculations have been made considering an incoming flue gas rate of 1 kmol /hour and will be scaled up afterwards.
- All of the off gas is being used for ethanol production, setting aside other uses such as electricity generation.
- CO is the limiting reactant for reactions 1 and 3, whereas H₂ is considered limiting to reactions 21 and 4.
- Selectivity values for the ethanol-yielding reactions (1 and 2) over acetic acid-yielding reactions are chosen at a conservative value of 3 moles ethanol per moles of acetic acid.
- Theoretically, it will be considered that all CO and all H₂ are consumed.
- Conversions for both CO and H₂ to correct the theoretical values obtained are 70%. Competitive reactions are 1 and 3 on one side and 2 and 4 on the other.

Reactions involved:



Selectivities of competitive reactions:

$$S_{1/3} = S_{2/4} = 3 \frac{\text{mol ethanol}}{\text{mol acetic acid}}$$

Balance for the different species:

To determine the outlet components and their quantities, the advance of the different reactions should be used to represent the amounts being consumed and produced in each reaction, as shown in Table 2.

Table 2: Balance for incoming and outgoing currents

Compound	CO	H ₂ O	H ₂	CO ₂	C ₂ H ₅ OH	CH ₃ COOH
Initial	0,86	0,5	0,04	0,05	0	0
Final	$0,86 - 6\xi_1 - 4\xi_3$	$0,5 - 3\xi_1 + 3\xi_2 - 2\xi_3 + 2\xi_4$	$0,04 - 6\xi_2 - 4\xi_4$	$0,05 + 4\xi_1 - 2\xi_2 + 2\xi_3 - 2\xi_4$	$\xi_1 + \xi_2$	$\xi_3 + \xi_4$

Mass balance for the limiting reactant of reactions 1 and 3, CO:

$$In - Out + Generation - Consumption = 0$$

Considering the best-case scenario, all CO is consumed, so the outgoing value is zero. On the other hand, no CO is being generated in any of the reactions. Thus:

$$0.86 - 6\xi_1 - 4\xi_3 = 0 \quad (5)$$

On the other hand, the selectivity for the reactions involving CO can be expressed in terms of the advance of the reactions:

$$S_{1/3} = 3 = \frac{\xi_1}{\xi_3} \quad (6)$$

Solving equations 5 and 6:

$$\xi_1 = 0.117 \text{ kmol/h of CO}$$

$$\xi_3 = 0.039 \text{ kmol/h of CO}$$

The amount of ethanol produced in reaction 1 is, therefore:

$$\dot{n}_{ethanol(1)} = \xi_1 = 0.117 \text{ kmol/h}$$

And that of acetic acid in reaction 3:

$$\dot{n}_{acetic\ acid(3)} = \xi_3 = 0.039 \text{ kmol/h}$$

Mass balance for the limiting reactant of reactions 2 and 4, H₂:

$$In - Out + Generation - Consumption = 0$$

Again, the best-case scenario is the one where all hydrogen is consumed, so outgoing value is zero. Also, consumption can be expressed in terms of the advance of reactions 2 and 4 in moles of H₂:

$$0.04 - 6\xi_2 - 4\xi_4 = 0 \quad (7)$$

On the other hand, the selectivity for the reactions involving CO can be expressed in terms of the moles of CO reacted in both reactions:

$$S_{2/4} = 3 = \frac{\xi_2}{\xi_4} \quad (8)$$

Solving equations 7 and 8:

$$\xi_2 = 5.45 * 10^{-3} \text{ kmol / (h of H}_2\text{)}$$

$$\xi_4 = 1.8 * 10^{-3} \text{ kmol / (h of H}_2\text{)}$$

The amount of ethanol produced in reaction 2 is, therefore:

$$\dot{n}_{ethanol (2)} = \xi_2 = 5.45 * 10^{-3} \text{ kmol/h}$$

And that of acetic acid in reaction 4:

$$\dot{n}_{acetic acid (4)} = \xi_4 = 1.8 * 10^{-3} \text{ kmol/h}$$

In total, the amount of ethanol being produced from a flue gas with at a rate of 1 kmol/hour is:

$$\dot{n}_{ethanol} = \dot{n}_{ethanol (1)} + \dot{n}_{ethanol (2)} = \xi_2 = 0.117 + 5.45 * 10^{-3} = 0.122 \text{ kmol/h}$$

And for the rest of the components:

Table 3. Theoretical values for the mass balance.

Compound	CO	H ₂ O	H ₂	CO ₂	C ₂ H ₅ OH	CH ₃ COOH
Initial	0,86	0,4	0,04	0,05	0	0
Final	0	0,09	0	0,582	0,122	0,041

However, not all reactants are consumed, and therefore there is a yield to the reaction. This yield is expressed in the form of the conversion of the limiting reactants, which happen to be the least soluble ones also. The value of the conversion for both compounds is 0,7. Thus, outgoing values is the mass balances no longer equal zero, and equations 5 and 7 change to the following:

$$0.86 - 0.258 - 6\xi_1 - 4\xi_3 = 0 \tag{9}$$

$$0.04 - 0.012 - 6\xi_2 - 4\xi_4 = 0 \quad (10)$$

Recalculating, the values obtained for the advance of the reactions are the following:

$$\xi_1 = 0.082 \text{ mol}$$

$$\xi_2 = 3.81 \cdot 10^{-3} \text{ mol}$$

$$\xi_3 = 0.027 \text{ mol}$$

$$\xi_4 = 1.27 \cdot 10^{-3} \text{ mol}$$

And the new values are expressed in Table 4.

Table 4. Real values for the mass balance.

Com- pound	CO	H₂O	H₂	CO₂	C₂H₅OH	CH₃COOH
Initial	0,86	0,5	0,04	0,05	0	0
Final	0,258	0,214	0,012	0,442	0,086	0,028

Appendix 2

Flow composition in kg/hr

Table 5. Flow compositions and conditions for each current. Flow is expressed in kg/hr. Please note the bacteria are not considered.

Stream number	1	2	3	4	5	6	7	8	9	10	11
Stream component											
CO ₂	3146.7	3146.7	3146.7	0	0	0	0	0	0	0	0
CO	34452.8	34452.8	34452.8	0	0	0	0	0	0	0	0
H ₂	115.3	115.3	115.3	0	0	0	0	0	0	0	0
H ₂ O	0	0	0	1660	9149	9149	0	0	1514.4	1514.4	1514.4
N ₂	2003	2003	2003	0	0	0	0	0	0	0	0
Ethanol	0	0	0	0	0,2	0,2	0	0	0	0	0
Acetic acid	0	0	0	0	53.5	53.5	0	0	0	0	0
Bacteria	0	0	0	0	0	0	233.2	0	0	233.2	233.2
Nutrients	0	0	0	0	0	0	0	209.8	0	0	0
Total (kg/h)	39717.8	39717.8	39717.8	1660	9508.2	9508.2	233.2	209.8	1514.4	1747.6	1747.6
Pressure (bar)	1	1	3	1	1	1	1	1,1	N/A	N/A	1
Temperature (°C)	10	151.5	39	39	39	39	39	39	39	39	39

Table 1. (Continued)

Stream number	12	13	14	15	16	17	18	19	20	21	22
Stream component											
CO₂	6407.55	0	0	0	0	0	0	0	0	0	0
CO	31171.5	0	0	0	0	0	0	0	0	0	0
H₂	98.7	0	0	0	0	0	0	0	0	0	0
H₂O	0	9828	9828	186	9641	9461	491	9149	1829.8	7319.2	7319.2
N₂	2003	0	0	0	0	0	0	0	0	0	0
Ethanol	0	904	904	904	0,3	0,3	0,01	0,2	0,04	0.16	0.16
Acetic acid	0	167	167	0	167	167	100	67	13.2	52.8	52.8
Clostridium Ljungdhalii	0	233.2	233.2	233.2	233.2	233.2	233.2	0	0,0	0	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0
Total (kg/h)	39680.75	11132.2	11132.2	1323.2	9861.5	9861.5	824.2	9216.2	1843	7372.2	7372.2
Pressure (bar)	2	2	2	1	1,3	1,3	1,2	1,2	1,2	1,2	1
Temperature (°C)	39	39	39	78.5	106.3	106.4	106.4	106.4	106.4	106.4	39

Appendix 3

Calculation of the area of heat exchanger

Area of Heat Exchangers can be calculated as follows;

$$A = \frac{Q}{U\Delta T_{lm}} \quad (1)$$

$$\Delta T_{lm} = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\frac{\Delta T_1}{\Delta T_2}\right)} \quad (2)$$

Where,

$$\Delta T_1 = Th_2 - TC_1 \quad (3)$$

$$\Delta T_2 = Th_1 - TC_2 \quad (4)$$

The rate of heat transfer (Q) was obtained from Aspen Plus simulation using heater block. Th_2 , Th_1 , TC_1 , TC_2 are the output temperatures of hot stream, the inlet temperatures of hot stream, the inlet temperatures of cold stream and the outlet temperatures of cold stream respectively. ΔT_{lm} is the log mean temperature difference (LMTD).

For kettle type reboiler, where steam is introduced to heat the liquid media, the LMTD (ΔT_{lm}) is different,

$$\Delta T_{lm} = T - t \quad (5)$$

Where T is the condensing steam temperature while t is the boiling liquid temperature.

Steam flow rate (m_s) requirement for reboiler;

$$m_s = q/h_e \quad (6)$$

$$\Delta T_{lm} = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\frac{\Delta T_1}{\Delta T_2}\right)} = \frac{93,1 - 16}{\ln\left(\frac{93,1}{16}\right)} = 43,7$$

$$A = \frac{Q}{U\Delta T_{lm}} = \frac{1086}{90 * 43,7} = 275.8 \text{ m}^2$$

E102,

$$\Delta T_{lm} = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\frac{\Delta T_1}{\Delta T_2}\right)} = \frac{188.5 - 18.1}{\ln\left(\frac{188.5}{18.1}\right)} = 72.7$$

$$A = \frac{Q}{U\Delta T_{lm}} = \frac{4800}{977.4 * 72.7} = 67.53 \text{ m}^2$$

Appendix 4

Heat exchanger specification sheet

Table 6. E101 Specification sheet

HEAT EXCHANGER - SPECIFICATION SHEET			
EQUIPMENT NAME: E101		In Series	1
		In Parallel	None
GENERAL DATA			
Service	: Heat Exchanger		
Type	: Shell and Tube		
Position	: Horizontal		
Heat Duty	[KW]	: 1087	
Heat Exchange Area	[m ²]	: 275,8	
Overall Heat Transfer Coefficient	[W/m ² .C]	: 90	
LMTD	[C]	: 43,7	
Passes Tube Side	: 2		
Passes Shell Side	: 1		
LMTD Correction Factor (minimum 0,99)	: 1		
Corrected LMTD	: 43,7		
PROCESS CONDITIONS			
	Units	Shell Side	Tube Side
Medium		Flue gas	Cooling water
Stream flow	[Kmol/h]	1430,2	1163,4
Average Specific heat	[KJ/Kg.C]	-	3,85
Heat of Evap./Condensation	[KJ/Kg]	-	-
Temperature IN	[C]	189,6	20
Temperature OUT	[C]	36	96,5
Pressure	[bar]	3	1,1
Density	[Kg/m ³]	0,3	49,4
Material		CS	Brass
REMARKS			
CS: Carbon Steel LMTD: Log Mean Temperature Difference			

Table 7. E103 Specification sheet

HEAT EXCHANGER - SPECIFICATION SHEET			
EQUIPMENT NAME: E102		In Series	1
		In Parallel	None
GENERAL DATA			
Service	: Heat Exchanger		
Type	: Shell and Tube		
Position	: Horizontal		
Heat Duty	[KW]	: 803	
Heat Exchange Area	[m2]	: 18	
Overall Heat Transfer Coefficient	[W/m2.C]	: 850	
LMTD	[C]	: 51.95	
Number of shells		: 1	
LMTD Correction Factor (minimum 0,99)		: 1	
PROCESS CONDITIONS			
	Units	Shell Side	Tube Side
Medium		hot water	Cooling water
Stream flow	[m ³ /h]	9,78	7,24
Average Specific heat	[KJ/Kg.C]	-8,8	9,34
Heat of Evap./Condensation	[KJ/Kg]	-15633,3	15346,3
Temperature IN	[C]	106,35	5
Temperature OUT	[C]	36	95
Pressure	[bar]	1,26	1
Density	[Kg/m3]	909,68	992,59
Material		CS	Brass
REMARKS			
CS: Carbon Steel LMTD: Log Mean Temperature Difference			

Table 8. R101 Specification sheet

HEAT EXCHANGER - SPECIFICATION SHEET			
EQUIPMENT NAME: R101		In Series	1
		In Parallel	None
GENERAL DATA			
Service	: Reboiler		
Type	: Thermosiphon		
Position	: Horizontal		
Heat Duty	[KW]	: 4680	
Heat Exchange Area	[m2]	: 67,41	
Overall Heat Transfer Coefficient	[W/m2.C]	: 977,4	
LMTD	[C]	: 72,7	
Passes Tube Side	: 2		
Passes Shell Side	: 1		
PROCESS CONDITIONS			
	Units	Shell Side	Tube Side
Medium		ET/ACET/H2O	Steam
Stream flow	[Kmol/h]	390,74	359,5
Average Specific heat	[KJ/Kg.C]	-	2320
Heat of Evap./Condensation	[KJ/Kg]	-	2107,4
Temperature IN	[C]	77,17*	265,8
Temperature OUT	[C]	77,37*	95,2
Pressure	[bar]	1,32	4
Density	[Kg/m3]	17,8	1,62
Material		Brass	CS
REMARKS			
CS: Carbon Steel LMTD: Log Mean Temperature Difference *: In reality the inlet and outlet temperature are considered same			

Appendix 5

Purification of ethanol

Given the changes in the process that derive from the maximum concentrations of ethanol allowed in the fermentation broth, the team decided to study the possibility of purifying the ethanol instead of doing it centralized. In order to do this, azeotropic distillation was considered, using cyclohexane as an entrainer. The advantages and disadvantages of such a process are shown below in Table 1.

Table 9. Advantages and disadvantages of ethanol purification on-site.

Advantages	Disadvantages
Increased purity of the final product. The final product is obtained within the plant.	Higher capital investment and operation costs from a new distillation column
No need for external services	Addition of a new component to the process: the entrainer
	Increased complexity to the process

Although reducing dependence on external services is desirable, it is decided to undergo the ethanol purification in a centralized way given the time and resources available. However, a possible flowsheet configuration of an integrated ethanol purification process is shown in Figure 1.

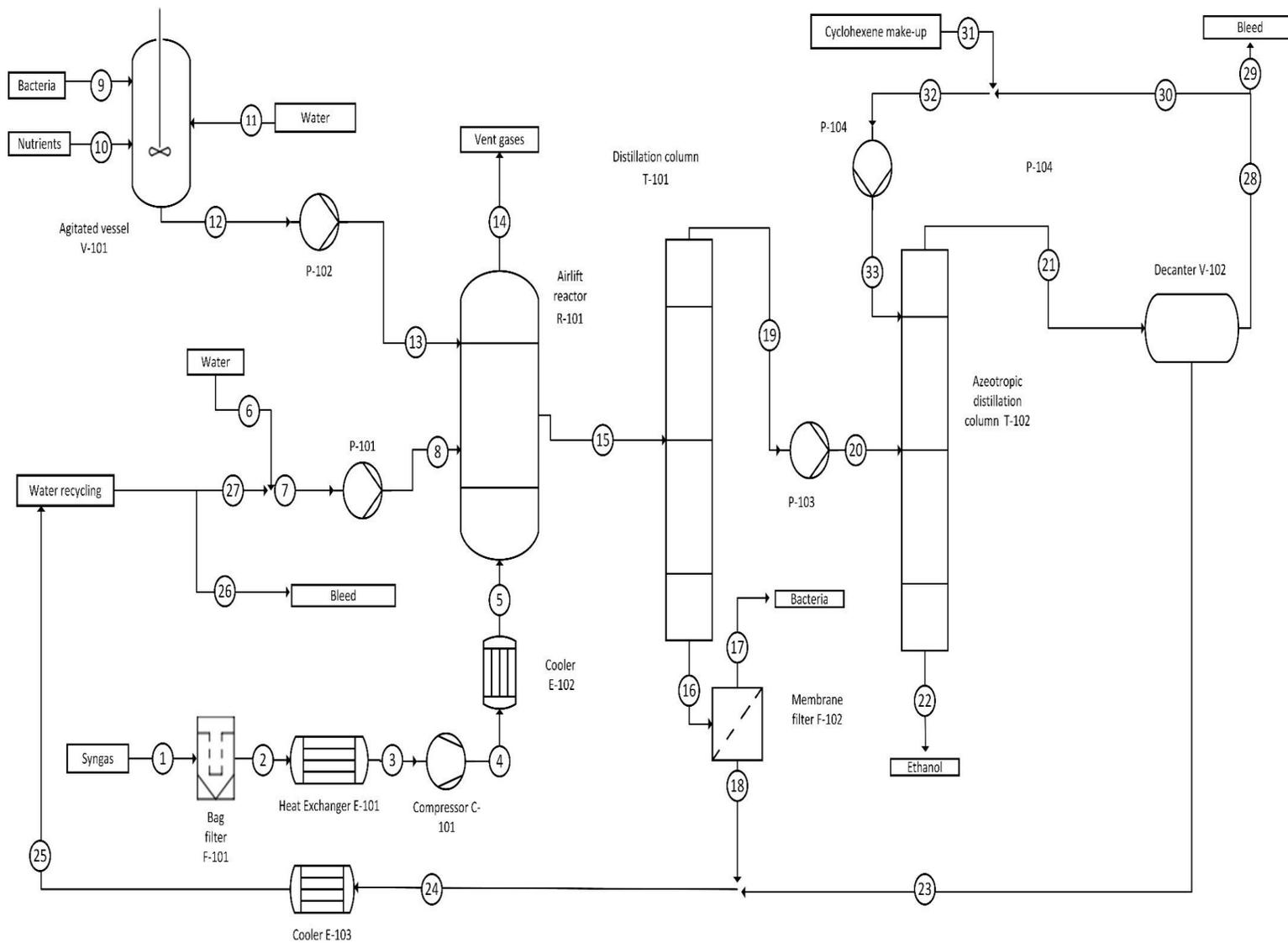


Figure 1. Possible process configuration with integrated ethanol purification.

Appendix 6

Removal of bacteria from water stream

Following equations are used to characterize membrane

$$J = \frac{Q_p}{A_m} \quad (1)$$

Flux, $J = \text{m}^3/\text{m}^2.\text{h}$

A_m = membrane surface area

Q_p = filtrate flow rate through membrane

Here,

$A_m = 14 \text{ m}^2$ (Capillary module is considered)

Flowrate of water $Q_f : 10.5 \text{ m}^3/\text{h}$

Considering 95% feed water pass through the filter.

$Q_p = 10 \text{ m}^3/\text{h}$

$J = 0.71 \text{ m}^3/\text{m}^2.\text{h}$

Removal of bacteria, R,

Characterized as the rate of sustained material to the membrane unit that passes through the membrane, i.e., the filtrate, and does not consider any acetic acid consumed in back pulse or chemical cleaning:



(2)

Where:

R = percentage recovery of a membrane unit

Q_f = Volumetric feed flow to the membrane unit = 10,5 m³/h

$$R = 0.95$$

Pressure difference across the membrane: $TMP = P_f - P_p$

Where:

TMP = transmembrane pressure, bar

P_f = pressure on the feed acetic acid side of the membrane, = 1.3 bar

P_p = Filtrate side pressure of membrane, = 1 bar

$$TMP = 1.3 - 1.00 = 0.3 \text{ bar}$$

Appendix 7

Gas Hold Up

Gas hold up is the volumetric fraction of gas in the total volume of gas in a total volume of gas-liquid-solid.

$$\varepsilon = \frac{V_g}{V_L + V_G + V_S} \quad (1)$$

where L, G and S are liquid, gas and solid.

Gas holdup is important because of two benefits

- It highlights tendency of mass transfer. Larger holdup defines larger gas-liquid interfacial area
- The substantial gradient between riser and down comer holdups produces liquid driving force

Gas holdups in riser and in down comer are calculated by following equations

$$\varepsilon_r = \frac{U_{Gr}}{0,24 + 1.35(U_{Gr} + U_{Lr})^{0.93}} \quad (2)$$

$$\varepsilon_d = k\varepsilon_r \quad (3)$$

The overall fractional gas holdup in the reactor, ε is calculated by following equation

$$\varepsilon = \frac{\varepsilon_r A_r + \varepsilon_d A_d}{A_r + A_d} \quad (4)$$

Following assumptions are made based on literature review. The value U_{Lr} is assumed to be 1 ms^{-1} and $U_{Lr} + U_{Gr} < 1.3 \text{ ms}^{-1}$. The value of k is taken from literature which is equal to 0.9. The values of A_r and A_d is assumed from the ratio of

$$\frac{A_d}{A_r} = 1 \text{ (Chishti and Merchuk).}$$

Pressure Difference

The injection of gas in airlift reactor is single point. The circulation of gas in airlift reactor is aided by the gas and liquid differences in holdups and generates a pressure difference which is related by following equation

$$\Delta P_b = \rho_L g (\varepsilon_r - \varepsilon_d) \quad (5)$$

Appendix 8

Mass and Energy Balance

Table 10(a). Mass and energy balance of all equipments

Equipment	Equip- ment number	Mole (kmol/hr)			Mass (kg/hr)		
		In	Out	Differ- ence	In	Out	Differ- ence
Airlift reac- tor	R-101	2031.1	1946.92	-84.2	50580.7	50580.7	0
Compressor	C-101	1430.2	1430,2	0	39717.7 6	39717.7 6	0
Cooler	E-102	944.7	944.7	0	17013	17013	0
Cooler	E-101	2759.8	2759.8	0	63671.6	63671.6	0
Membrane filter	F-101	575.62	575.62	0	10548.1	10548.1	0
Pump	P-101	603.2	603.2	0	9488.1	9488.1	0
Pump	P-102	84.1	84.1	0	1747.6	1747.6	0
Tray col- umn	T-101	567.9	567.9	0	10900	10900	0
Vessel	V-101	84.1	84.1	0	1770	1770	0
TOTAL	-	9081	8997	-84.2	205437	205437	0

Table 10(b). Energy balance of all equipments

Equipment	Equipment number	Enthalpy (kW)		
		In	Out	Difference
Airlift reactor	R-101	-93017.1	-94276.5	-1259.4
Compressor	C-101	-45453.9	-43629.3	1824.6
Cooler	E-102	-42671.9	-43474.5	-802.6
Cooler	E-101	-1253.5	1395.6	2649.1
Membrane filter	F-101	-44965.1	-44965.1	0
Pump	P-101	-48348.12	-48347.7	0.38
Pump	P-102	-23949.6	-23949.4	0.23
Tray column	T-101	-45057.5	-44250.8	806.7
Vessel	V-101	-6659.2	-6659.2	0
TOTAL	-	-499770	-499353	417

Power requirements calculations

1. Power requirement for pump

Required hydraulic power for pump $P_h = Q\rho gh/3.6 \times 10^6$ (1)

Pump 101:

Flow rate: = 10.99 m³/h

Density = 976,522 kg/m³

h = 5 meter

Pump efficiency = 0.9

Motor efficiency = 0.9

Suction area: 0.05 m²

Hydraulic static head = 5 [m-kgf/kg]

Head developed = 10.4[m-kgf/kg]

Fluid power = 0.31 [kW]

Electricity = 0.38 [kW]

Calculated discharge pressure [bar] = 2.2

Calculated pressure change [bar] = 1

Pump (P102) [For microorganism feeding]

Flowrate: 5436 kg/hour

Discharged pressure: 2.2 bar

Electricity [kW] = 0.228

Pumps for cooling water for heat exchangers

Total Flow [l/min] = 199.79

Density [gm/cc] = 0.99

Pump efficiency = 0.4

Driver efficiency = 0.4

Suction area [m²] = 0.05

Fluid Power [kW] = 0.99

Electricity [kW] = 2.23

Head developed [m-kgf/kg] = 30.62

Total Flow [l/min] = 299.79

Density [gm/cc] = 0.99

Pump efficiency = 0.5

Driver efficiency = 0.5

Suction area [m²] = 0.05

Fluid Power [KW] = 0.04

Electricity [kW] = 0.09

Head developed [m-kgf/kg] = 1.02

2. Power requirement for Compressor (C-101):

The requirement of power in adiabatic gas compression without heat transferring can be represented as

$$HP = [144 N P_1 V k / 33000 (k - 1)] [(P_2 / P_1) (k - 1) / N k - 1] \quad (2)$$

Where,

HP = horsepower

N = number of compression stages = 1

k = 1.41 = adiabatic expansion coefficient

P₁ = absolute initial atmospheric pressure (psi) = 1psi

P₂ = absolute final pressure after compression (psi) = 2psi

V = volume of air at atmospheric pressure (cfm) = 18540.199 ft³/min

Power required (Theoretical), = 893 HP = 657 kW

Due to Friction- in general add 10-20% to the power

Therefore, final power required : 657 * 0.2 + 657 = 788 kW

Appendix 9

Equipment cost estimation

Table 11: Source of cost estimation of different process equipments and utilities

Name of equipment	Price (k€)	Vendors/manufacturers/Reference
Heat exchanger (E101 and E102)	39.8	Matche
Membrane filtration (F102)	90.2	Microdyn-Nadir™ GmbH
Compressor (C101)	294	Matche
Airlift Reactor	1400	Outotec™
Bacteria	420	DSMZ™

Equipment cost summary

Table 12. Cost summary for all equipments.

<u>Purchased equipment</u>	Price (€)	Year	Index year	Index 2016	Price (€)
1. Agitated vessel V-101	48790	2000	394.1	544.9	67459.2
2. Pump P-101	8050.1	2010	532.9	544.9	8231.4
3. Pump P-102	8109.1	2010	532.9	544.9	8291.7
5. Membrane filter F-102	90150	2016	-	-	90.2
6. Airlift reactor R-101					1400000
7. Distillation column T-101					175595.4
7.1. Shell	126900	2002	395.6	544.9	174792.2
7.2. Trays	785.5	2010	532.9	544.9	803.2
9. Cooler E-101	27360.92	2016	156.1	168.2	29481.8
10. Cooler E-102	11720.58	2014	595.5	523.6	10305.1
Pump P-103					8337.2
Pump P-104					8290.8
Storage tank S-101					52845.8
11. Compressor C-101	287300	2014	941	966	294932.8
Total	2244631.6				

Pumps P-101 and P-102

The price determination for pumps P-101 and P-102 is done through cost curves.

Equation 4 shows the equation of the curve (Towler and Sinnott, 2012).

$$C_e = 8000 + 240 \cdot S^{0.9} \quad (1)$$

Where S is the flow in liters/second. The prices for both pumps are:

$$CP-101=8000+240 \cdot 2,6^{0,9}=8563,9 \text{ \$} \quad (2)$$

$$CP-101=8000+240 \cdot 0,4^{0,9}=8109,1 \text{ \$} \quad (3)$$

A summary of these results as well as the updated price is shown in Table 3.

Table 13. Cost summary for pumps P-101 and P-102.

Equipment	Cost (€)	Year	Cost index for the year (CEPCI)	Cost index for July 2016 (CEPCI)	Cost in 2016 (€)
P-101	8050,1	January 2010	532,9	544,9	8231,3
P-102	8109,1	January 2010	532,9	544,9	8109,1
Total					16340,4

Distillation column T-101

The specifications for distillation column T-101 are shown in Table 4. The values that are used to estimate the value of the column have been highlighted.

Table 14. Specifications of distillation column.

EQUIPMENT NR.: NAME:	T101 Distillation column
Temperature [°C]:	36 / 78.4 / 106.4
Pressure [bar]:	2 / 1 / 1.26
Height [m]:	16.8
Diameter [m]:	1.3

Internals:	
-Tray type:	Sieve Trays
-Tray number:	25
-Feed tray:	22
-Overall column efficiency (%):	39
Materials of construction:	Column: carbon steel Trays: SS316

The method selected for estimating the price of the column is through cost curves. Figure 2 is a graph showing the cost of the shell with two heads and edge, but without trays or connections (Peters, Timmerhaus and West 2013). The cost is determined according to these graphs from the column diameter and height, and linear interpolation is used between values. The final cost obtained from the graph is 135000 \$ (45000 \$ times 3 from the material adjustment factor) in January of 2002, a value which will be corrected for its present value through the cost indices. On the other hand, the value of the trays can be estimated from a different cost curve, for which the equation is shown in Equation 4 (Towler and Sinnott, 2012).

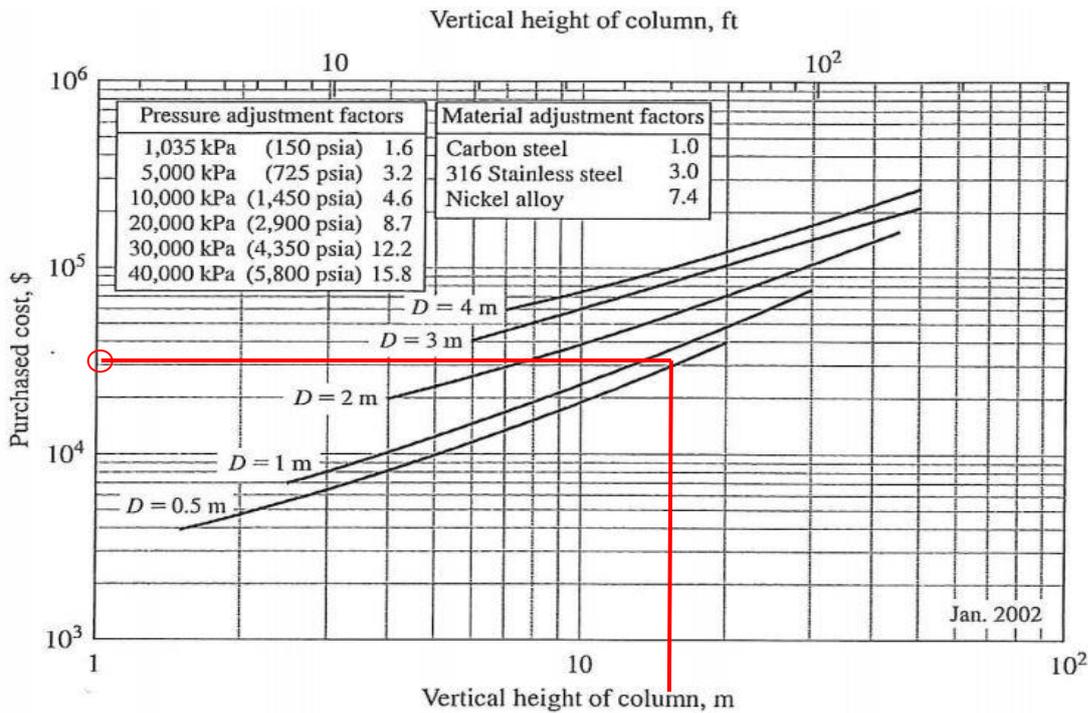


Figure 2. Cost of the shell with two heads and skirt, without trays or connections.

$$C_e = a + b \cdot S^n \quad (4)$$

Where C_e is the cost of the trays in dollars, a and b are the cost constants, S is the size parameter (tray diameter is this case) and n is an exponent factor specific for each equipment. Specifying for the case of 23 trays, equation 5 is:

$$C_e = 130 + 440 \cdot 1,3^{1,8} = 835,6 \text{ \$} \quad (5)$$

This cost is specified on a U.S. Gulf Coast basis in January of 2010, and must be corrected with the due cost indices. Table 15 shows a summary of the cost for distillation column T-101 as well as the correction with the due cost indices for each year and the conversion to euros €.

Table 15. Cost summary for distillation column T-101.

Component	Cost (\$)	Cost (€)	Year	Cost index for the year (CEPCI)	Cost index for July 2016 (CEPCI)	Cost in 2016 (€)
Shell	135000	126900	January 2002	395.6	544.9	174792.2

Trays	835.6	785.5	January 2010	532.9	544.9	803.2
Total						175595.4

Membrane Cost Calculation

Clostridium bacteria has various size depending on the species. The typical size is 0.6 micrometer across by 3 to 7 micrometers long. Therefore, a microfiltration will be suitable for separating the bacteria from acetic acid. The size range of the particles that can be retained is from 0.05 to 10 μm that means the suspensions and emulsions can be retained. The membrane MD200CV2N is the product of MICRODYN-NADIR™ GmbH which has a cost of 28111 euros including instrumentation and mechanical cost (Scott, 1995). The operating pressure of one module is 10.00 m^3/h and it is proposed to use four modules, two in series and two in parallel to ensure continuous operation of plant during washing of membranes.

The membrane selected for this process is MICRODYN MV200CV2N from Microdyn-Nadir™ GmbH. It is capillary module with the surface area of 14 m^2 . The membrane material is polypropylene with 1.8mm inner diameter and pore size is 0.2 μm . The shell of this module is made of polyvinylchloride (PVC). Surface regeneration can be achieved by altering feed flow, periodic backwashing and reverse flow chemical cleaning (Nadir, 2016).

Table 206: Basic design parameters of membrane for microorganism filtration

Characteristics	Value/comments
Flowrate of water	10.5 m^3/h
Flow rate of microorganism	255.6 kg/h
Temperature of acetic acid stream	106 $^{\circ}\text{C}$
Pressure	1.2 bar
Membrane material	PVC (ref: MICRODYN-NADIR™ GmbH)
Membrane surface area	14 m^2 (Capillary module) (ref: MICRODYN-NADIR™ GmbH)
Flux, J	0.71 $\text{m}^3/\text{m}^2.\text{h}$
Removal of bacteria, R (%)	0.95
Transmembrane pressure, TMP	0.3 bar
Amount of water	10.00 m^3/h

Agitated growth vessel V-101

The growth vessel in which the bacteria are grown has a volume of 54 m³ and must be insulated. Also, it must incorporate some kind of agitation, although this one has not been specified. Figure 3 shows the cost curve for what might be a suitable option of equipment for this purpose (Gerrard,2000). The total cost for the equipment is 41000 £. Table 16 shows a summary of this equipment cost together for the inflation correction through the cost index.

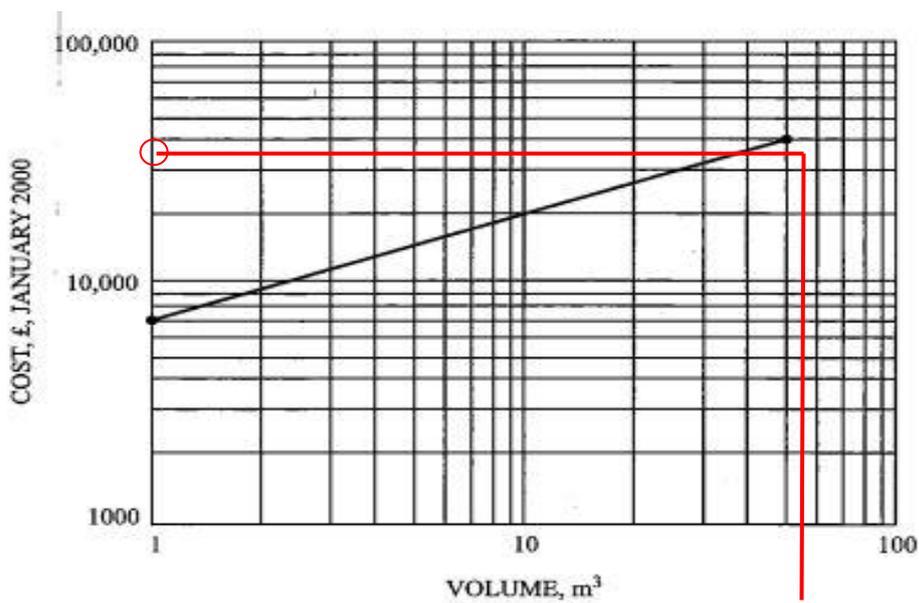


Figure 3. Cost curve for an agitated and insulated reactor vessel.

Table 17. Cost summary for growth vessel V-101.

Component	Cost (£)	Cost (€)	Year	Cost index for the year (CEPCI)	Cost index for July 2016 (CEPCI)	Cost in 2016 (€)
Growth vessel V-101	41000	48790	January 2000	394.1	544.9	67459.2

Cost calculation of Compressor (C101)

Cost of Compressor = 287300 euro (2014)

$$\text{Cost in year A} = \text{Cost in year B} \times \frac{\text{Cost index in year A}}{\text{Cost index in year B}} \quad (7)$$

Chemical engineering plant cost index (CEPCI) is used to calculate the cost in 2016

Cost in year 2014(B) = 287300

Cost index in year 2014(B) = 941

Cost index in year 2016 (A) = 966

Cost in year 2016 = 287300 * (966/941) = 294932.8 euro

Heat exchangers E101 and E102

E102

Base Cost of the Heat Exchanger, $C_B = \text{EXP}(8.202+0.01506+0.06811*(\ln A)^2) = 34118.59$, where A is the heat exchange area = 275.8 m²

Exchange type cost factor, $F_D = \text{EXP}(-0.7844+0.0830*\ln A) = 0.727627$, for 2 tube side pass

Design-pressure cost factor, $F_p = 1.2002+0.07140*\ln A = 1.175416$, for pressure range of 2 bar to 4.2 bar

Material of construction cost factor, $F_m = 0.0+(A/100)^{0.0} = 1$, ($F_m=a+(A/100)^b$) Carbon steel shell side and carbon steel tube side, a=0.0 and b=0.0. This is suitable for processes with temperature below 600 C and our process temperature is around 200 C.

Heat Exchanger Cost, $C_E = C_B * F_D * F_p * F_m = \text{€ } 27429.59$

Heat Exchanger Cost Updated, $C_{E(\text{Updated})} = (CI_{(2016)} / CI_{(2011)}) * C_E = (168.2/156.1) * \text{€}29180.41$

= € 29555.78

Cost calculation of Heat Exchanger (E103)

Cost of heat exchanger = 11720 euro (2014)

$$\text{Cost in year A} = \text{Cost in year B} \times \frac{\text{Cost index in year A}}{\text{Cost index in year B}} \quad (6)$$

Chemical engineering plant cost index (CEPCI) is used to calculate the cost in 2016

Cost in year 2014(B) = 11720

Cost index in year 2014(B) = 635.1

Cost index in year 2016 (A) = 558.4

Cost in year 2016 = 11720 * (558.4/635.1) = **10305.1 euro**

Appendix 10

Table 18. Profitability Evaluation

Year	Fixed capital investment	Working capital	Annual gross profit	Depreciation	Cumulative cash flow
0	0	0	0	0	0
1	3101.9				-3101.9
2	6203.9	310.2			-6514.1
3			768	310.2	-5435.9
4			768	310.2	-4357.7
5			768	310.2	-3279.5
6			768	310.2	-2201.3
7			768	310.2	-1123.1
8			768	310.2	-44.9
9			768	310.2	1033.3
10			768	310.2	2111.5
11			768	310.2	3189.7
12			768	310.2	4267.9
13			768	310.2	5346.1
14			768	310.2	6424.3
15			768	310.2	7502.5
16			768	310.2	8580.7
17			768	310.2	9658.9
18			768	310.2	10737.1
19			768	310.2	11815.3
20			768	310.2	12893.5
21			768	310.2	13971.7
22			768	310.2	15049.9
23			768	310.2	16128.1

Appendix 11

Estimation of installation costs

Percentage of purchased equipment cost determines the costs of installation. The installation cost of equipment comprises of labor, foundations, supports, platforms, cost of construction and all other factors which are relevant to the assembling of equipment. For this particular process, the phases are liquid and gas, depending on the equipment, whereas pressures are always under 3 bar and temperatures vary from 800 °C to 25 °C. Table 1 shows a summary of installation costs percentages for each respective equipment ([Peters and Timmerhaus, 1991](#)).

Table 19. Installation cost estimation.

Type of Equipment	Installation Cost, %	Cost of Equipment	Total Cost(k€)
Compressors C-101	20	294.9	88.5
Membrane Filter F-102	65	90.2	58.63
Agitated Vessel V-101	30	67.5	20.2
Airlift Reactor	60	1400	840
Pump-101	25	8.2	2.05
Pump P-102	25	8.3	2.07
Distillation Column	60	175.6	105.36
Cooler E-101	30	29.5	8.9
Cooler E-102	30	10.3	3.1

Appendix 12

Determination of piping costs

The cost of piping installation and materials can be calculated through the curves shown in Figure 4 and 5 (Gerrard,2000).

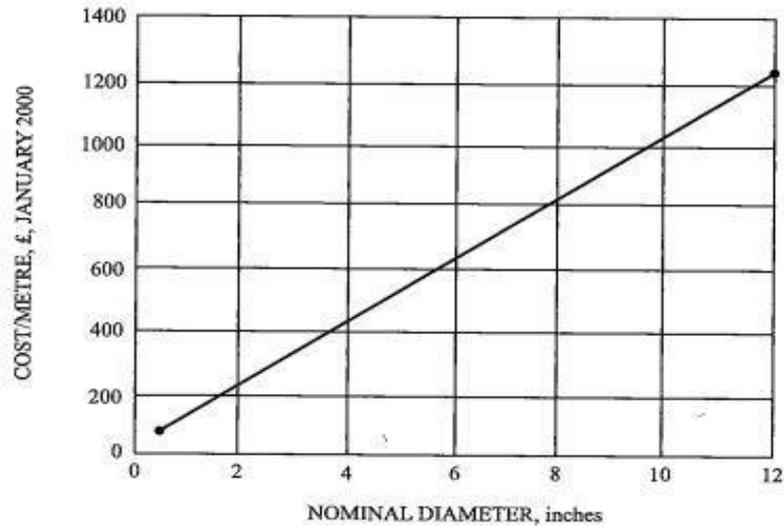


Figure 4. Installed piping cost.

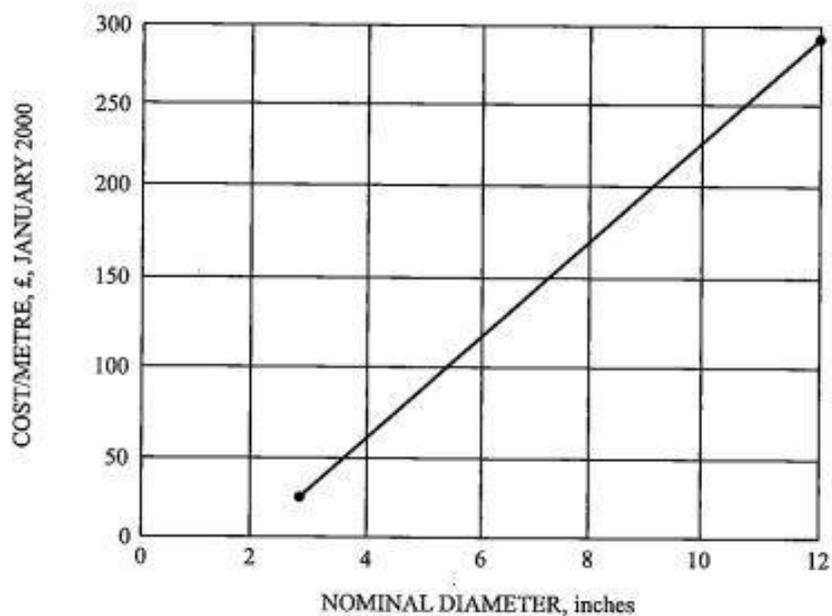


Figure 5. Cost of piping materials

The cost of piping will thus be influenced by the length of piping needed and the nominal diameter of the pipes. As a first approximation for the diameter, 6 inches (15 cm) will be considered for those pipes handling liquids and 12 inches (30 cm) for those

handling the gases. On the other hand, the plant layout will be used to approximate the length of the piping needed. Figure 6 shows the plant layout.

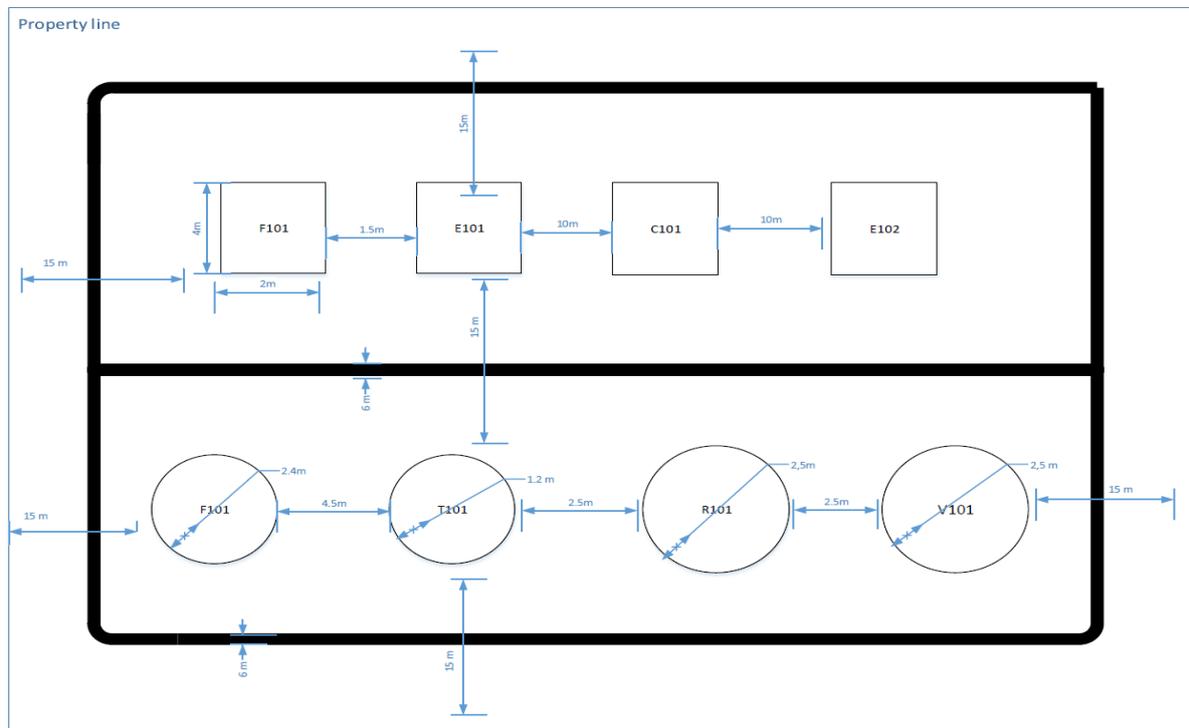


Figure 6. Plant layout. Gas pipes are marked as red dashed lines, while pipes handling liquids are marked as black dashed lines.

Table 1 shows a summary of the specifications for the piping for the plant. The material costs obtained from the graph are referred to plain carbon steel. As a correction factor for stainless steel 316, a value of 1.3 is selected (Towler and Sinnott,2012).

Table 20. Summary of piping specifications for the plant

Nominal diameter (inches)	Length (m)	Material	Installation cost (€)	Materials cost (€)	Total cost in 2000 (€)	Total cost in 2016 (€)
12	76.5	Carbon steel	112455	26163	138618	191659.3
6	50	Carbon steel	37500	6900	44400	61389.4
6	45.2	Stainless steel 316	33900	8108.9	42008.9	58083.4
Total					225026.9	311132.1

Appendix 13

Formulas

This appendix gathers all the equations used to estimate costs.

Investment costs

1. ISBL cost:

$$ISBL = \text{purchase of equipment} + \text{installation of equipment} + \text{piping cost} \quad (1)$$

2. OSBL cost:

$$OSBL = 0.35 \cdot ISBL \quad (2)$$

3. Engineering and supervision cost:

$$\text{Engineering and supervision} = 0.25 \cdot ISBL \quad (3)$$

4. Contingency cost:

$$\text{Contingency} = 0.1 \cdot ISBL \quad (4)$$

5. Total fixed capital investment:

$$TFCI = ISBL + OSBL + \text{Engineering and supervision} + \text{Contingency} \quad (5)$$

6. Start-up cost:

$$\text{Start up} = 0.1 \cdot TFCI \quad (6)$$

7. Total capital investment:

$$\text{Total Capital Investment} = TFCI + \text{Start up} \quad (7)$$

Operation costs

Operation costs are calculated as the addition of variable and fixed operation costs:

$$\text{Operation costs} = \text{Variable op. costs} + \text{Fixed op. costs} \quad (8)$$

Variable operation costs

8. Electricity consumption for pumping water:

$$\text{Electricity (kWh/year)} = \frac{Q \cdot \Delta P}{\eta \cdot 3600} \quad (9)$$

where Q is the flow rate of cooling water on a yearly basis (m³/year), ΔP in the pressure drop in kPa, η is the pump efficiency, and 3600 is the conversion factor from kJ/s to kWh. The values used for the pressure drop and the efficiency are 10 kPa and 80% each.

9. Price of ethanol purification through an external service:

$$\text{Ethanol purification cost} = 0.05 * \text{fuel ethanol market price} \quad (10)$$

Fixed operation costs

The fixed operation costs are mainly calculated as percentages of different factors and the cost of labor. The formulas used for each of its components are shown in Table 14.

Table 21. Fixed operating cost

Labor	2 operators/shift position	
Number of shit positions	6	41664 €/year each
Supervisions	15% of operating labor	
Side costs and benefits	1,9% of operating labor and supervisions	
Maintenance	3% of ISBL investment	
Insurance	1% of ISBL and OSBL investment	
Quality control	7% of sales revenues	
Interest	2% of total capital investment	
License fees	2% of total capital investment	
Depreciation	8% of fixed capital investment	
Administrative costs	8 % of labor, supervision, and maintenance	
Selling and marketing costs	2% of total product costs	
Research and development costs	5% of total product costs	

Profitability

10. Annual gross profit:

$$\text{Annual gross profit} = \text{Revenue} - \text{Total cost of production} \quad (11)$$

11. Return on investment:

$$\% ROI = \frac{\text{Annual profit}}{\text{Total capital investment}} \cdot 100 \quad (12)$$

12. Payout time:

$$\text{Payout time (yr)} = \frac{\text{Total capital investment}}{\text{Annual gross profit} + \text{depreciation}} \quad (13)$$