Process System Modeling of Large-Scale Energy Storage, CO_2 and Biomass Based Formic Acid Production Systems

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This thesis is the final part of my mechanical engineering master's degree. It has been a personal and academical progressive challenge. I would like to dedicate this part to people who I owe for their support.

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Abstract

Transition to renewable and alternative energy sources has become one of the most important subject of the decade. In The Netherlands today, 11.1% of the primary energy demand is obtained from renewable energy and the biomass accounts for 54% [1]. Another promising material for value added chemical synthesis is carbon dioxide. By utilization of CO_2, the production of valuable chemical materials such as methanol, formic acid that can be used as a fuel, heat or power source and reducing the greenhouse gas effect by lowering emission levels will provide industrial and environmental advantages at the same time.

Formic acid, used in the agriculture, pharmaceuticals and textile, is a key chemical that can also be used in energy conversion processes. In the current industrial practice, formic acid is produced by carbonylation of methanol with carbon monoxide. However, methanol is another value added chemical that is used in energy production, hence expensive for the process. Therefore, researchers started looking into alternative methods. Biomass and carbon dioxide utilization methods are two of them. In this thesis study, 10 kton and 100 kton annual production of 85 wt.% formic acid from wet oxidation of glucose and catalytic reduction of carbon dioxide, have been modeled and a techno-economic analysis is carried out. Additionally, the processes of obtaining glucose from lignocellulosic biomass and carbon dioxide from syngas by pre-combustion capture are also simulated. ASPEN Plus V8.8 process flowsheeting package program has been used for the simulations.

From the results, in energy analysis biomass based formic acid synthesis process showed higher efficiency than CO_2 based production. When the hydrogen peroxide and oxygen based biomass wet oxidation routes are compared, it is observed that oxygen based operation is more efficient than hydrogen peroxide based conversion because of lower utility requirements. It was determined that biomass based formic acid production can be economically profitable, but only for large scale wet oxidation via oxygen together with the sale of by-products obtained in pre-treatment process. On the contrary, no profit was obtained by the hydrogen peroxide route. In carbon dioxide utilization route, the breakeven selling price (BSP) of the formic acid was computed to be 7% more than the current market price. In order to improve the process, two case studies were created. In the first case, economically the most suitable reactor amount configuration is determined. However, the process was still not profitable. In the second case study, two times more active catalyst, Au/Al_2O_3, has been utilized. The process took half the residence time of the previous case and BSP value determined to be 2.6% lower than the current market price. Also, slight increase in efficiency is observed.

In conclusion, more research should be done and experiments regarding reaction and intermediate substance performances should be conducted, in order to simulate the process more in detail. However, despite the uncertainties, in this era where the transition to greener energy production through the use of biomass and the reduction of carbon dioxide emissions have been made a definite target by the governments, the synthesis methods studied, will gain importance as the purposes of formic acid use increase.

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Nomenclature

AA	Acetic Acid
AFEX	Ammonia Fiber Explosion
BIZ	Butylimidazole
BOD	Basis Of Design
BSP	Breakeven Selling Price
CCOP	Cash Cost of Production
CCS	Carbon Capture & Storage
DAC	Direct Air Capture
DEA	Diethanolamine
DMEPEG	Dimethyl Ether of Polyethylene Glycol
EoS	Equation of State
FA	Formic Acid
FCOP	Fixed Cost of Production
FPU	Filter Paper Unit
GP	Gross Profit
HHV	Higher Heating Value
HMF	5-hydroxymethylfurfural
HPA-5	Polyoxometalate
HY	Faujasite
IL	Ionic Liquid
LA	Lactic Acid
LeA	Levulinic Acid
MAE	Microwave Assisted Extraction
MDEA	Methyldiethanolamine
MEA	Monoethanolamine

MOF	Metal Organic Framework
MW	Megawatt
Net3	Triethylamine
NRTL	Non Random Two Liquids
OxFA	Oxidation of Biomass to Formic Acid
p-TSA	Toluenesulfonic Acid
PAN	Polyaniline
PC-SAFT	Perturbed-chain statistical associating fluid theory
PEM	Polymer Electrolyte Membrane
PPy	Polypyrrole
PR	Peng-Robinson
PZ	Piperazine
SRK	Soave-Redlich-Kwong
SRM	Steam Reforming of Methane
UNIFAC	Universal Quasi Chemical Functional-Group Activity Coefficients
UNIQUAC	Universal Quasi Chemical
VB	Valence Band
VCOP	Variable Cost of Production
WGS	Water Gas Shift

1 Introduction

1.1 Necessity of Sustainability

NASA satellites have projected that Greenland and Antarctica is melting six times faster than in the 1990s [16]. The scientific magazine National geographic [17] discloses that Arctic sea ice is shrinking more than 10% per decade for the past 40 years and its foreseen that they will extinct in 20-25 years or even sooner. Flue gases from cars, factory chimneys and many more sources emit 32.5 billion metric tons of carbon dioxide (CO_2) to the atmosphere [18]. Due to this harmful release, the average temperature of Earth is reported to be rising 1.5 °C in 2018 [19].

The concept of "Global Warming" was first discovered by Swedish scientist Svante Arrhenius in 1895 [20]. Stated that, the excessive use of fossil and coal-based resources emitting huge amounts of carbon dioxide, causing imbalance of the nature. Unfortunately, humanity did not take any constructive precautions at first. With the introduction of the internet in 1980s and 1990s, countries and big companies focused on growth. Hence, industrialization took the top priority. Therefore, environment suffered the most. Increasing amount of gas emissions to the atmosphere lead to an increase of temperature of the planet followed by acid rains and drought.

Our elders always say; "A fault confessed is half redressed". Thus in 2000s, global warming was defined as one of the biggest threat to humanity worldwide [20]. Related to the new awareness, "Renewable Energy" and "Sustainability" was born and became the most promising, important solution. Unfortunately, decades old habits of fossil fuel usage can not be abandoned at once. People and world economies had neither the sources nor the technology to replace fossil fuel as an energy source. Nevertheless, countries realised that the problem was global and therefore sought to unite their sources and goals under the "Climate Action" by the United Nations.

The biggest step was The Paris Agreement, which was signed on 2015. Countries came to an agreement for providing required logistical,financial and technical support to each other. In 2020, the European Union reached an agreement on reducing carbon dioxide emissions by 55% until 2030 [21]. Moreover, they raised their goals to wiping out the CO_2 emissions by 2050. This agreement indicates a vital milestone for battling against greenhouse gas emissions.

1.2 Renewable Energy Production in Netherlands

Renewable energy generation in the Netherlands gained great importance after the Paris Agreement. It is considered to be most natural way to produce energy from sun,wind, earth sub-surface and even from anaerobic bacteria [22]. The Netherlands is one of the top three countries in Europe in annually installed solar panel capacity [23]. According to the government records, Netherlands produced 3,000 MW of electricity, supplying 5% of the country's energy requirement with 2525 onshore wind turbines in 2015. In terms of geothermal energy, the goal is to reduce CO_2 emissions by supplying the 15% of heat energy requirement in 2030 and 25% by the year 2050 [24].

Renewable energy sources can be better for the environment but they are often intermittent. For example, the sun might not be seen for days in the Netherlands; therefore, reliability on solar power is an issue. For wind turbines, energy production per turbine is still not satisfactory; therefore more and more turbines are required. The inadequacy and unreliability in renewable power supply methods have forced scientists to look for alternative methods. The most developed ones are electrochemical cells and chemical treatment of biomass which are studied vastly. The alternative methods are academically accepted to be efficient and environmental friendly. Fuel cells are small sized electrochemical cells for power generation. However, the assembly is a very delicate process and large number of cells are required to produce a high amount of energy. On the other hand, large scale energy production from biomass is drawing great interest from the commercial companies due to its sustainability, because agricultural and industrial wastes are used as raw material. A lot of base chemicals such as methanol, hydrogen or formic acid can be produced via biomass processing. On the other hand, formic acid is one step ahead of chemicals such as hydrogen an methanol due to its wide range of use. It can be used in agriculture for silage or as pesticide for crops, in food industry as preservative or as an intermediate in pharmaceuticals. However, its production via methanol carbonylation is economically not feasible [7].

1.3 Research Objective

The aim of the ongoing master's thesis is to research and model renewable formic acid production processes. Then the thesis study will be followed by a technical and economical analysis.

Literature background of conventional formic acid production process; hydrolysis of methyl formate will be explained. For the scope of the project, alternative formic acid synthesis methods based on biomass and carbon dioxide will be investigated and compared.

One from each biomass and carbon dioxide based formic acid production routes will be selected for further modelling and investigation. The comparison of greener formic acid synthesis methods will be based on the following factors;

- Large scale applicability
- Catalyst variety
- Catalyst cost
- Temperature range
- Pressure range
- Formic acid yield

- FA synthesis reaction residence time

The selected processes will be modeled by ASPEN Plus process flowsheeting package, to obtain formic acid with 85 wt% purity. Besides production, the pre-treatment of biomass raw material and also the carbon dioxide capture will be simulated to cover the complete process from the very beginning. The production is divided into the following stages;

- Biomass pre-treatment / Carbon dioxide capture
- Formic acid synthesis
- Separation of unreacted compounds
- Purification

The temperature and pressure values of flash tanks to be used in the separation and distillation columns in purification processes will be optimized via ASPEN Plus sensitivity analysis. In the biomass pretreatment, carbon dioxide capture and formic acid production processes, either the experimental data or the values used during the experiment will be used, depending on the adequacy of the information obtained from the literature. Then, the energy and economy analysis will be carried out by simulating the production of the desired 85 wt.% pure formic acid. Moreover, in order to observe the effect of production capacity, 10 and 100 kilotons of annual formic acid production will be simulated separately. Then, the study will be conducted by comprehensive analyses to show the feasibility of the material pre-treatment and formic acid synthesis procedures, in terms of energy and economy. Comparison of the selected biomass and carbon dioxide routes will be carried out throughout the analysis.

In energy analysis following properties will be calculated and evaluated.

- Heating, cooling and electricity consumption per ton of formic acid produced. Pre-treatment and carbon capture process results will be summarized with the appropriate formic acid synthesis process.
- Overall energy efficiency of each individual process.

In economic analysis, the following terms will be calculated.

- Equipment cost
- Total capital cost
- Raw material cost
- Fixed and variable costs of production
- Breakeven selling price

- Gross and net profit

Thus, the investigation and modelling of a formic acid production plant is summarized in a general research question;

" What is the technically and economically optimal, circular CO_2 *and biomass based formic acid production route from a process operation's modelling perspective ? "*

The goal of this thesis is to provide an answer to the question above.

2 Literature Study

2.1 Biomass: Sustainable Resource

According to The Paris Agreement, the Netherlands aims to produce 14% of its total energy demand from renewable sources by 2020 [25]. By 2023, it is aimed to be 16% and almost totally renewable energy supply is targeted by 2050 [26] [27].
However, by 2020, the production levels are lower from targeted numbers as shown in Figure 1.

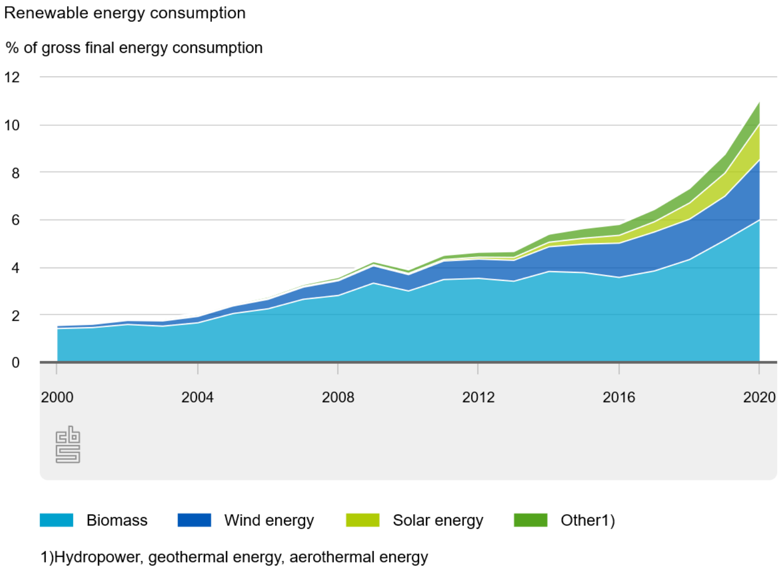


Figure 1: Renewable energy consumption in The Netherlands [1]

From Figure 1 [1] it can be seen that only 11.1% of the primary energy demand is supplied by renewable energy in 2020. In addition, 46 % of the energy is supplied from solar and wind energy. The remaining 54% is supplied via biomass route only. This distribution shows the great impact of biomass in the current numbers and no doubt that it will be significant in the future.

The biomass concept simply refers to obtaining energy from wastes. In industry, it is the production of value added chemicals and biofuels via waste materials as feedstock. These wastes are mainly agricultural or food-based which will be discussed later. Actually, biomass energy has always been in our life since the discovery of fire. Obviously it was not producing electricity but it was providing heat for people around the campfire. In 1800s, biomass was being used as lamp oil. In 1980s, biomass was first used in advanced heating systems in Sweden [28].

Another alternative energy generation is accomplished by polymer electrolyte membrane (PEM) fuel cells. A fuel cell is an electrochemical cell where electricity can be produced

by permeation of anions or cations through a selectively permeable membrane. However, voltage production per cell is low (maximum of 0.8 Volts) due to small surface area of the electrodes. Therefore, it is not possible to obtain high electricity power from a single cell. In addition, larger surface area design is impractical in terms of production and insulation of the cell. In order to produce a high amount of power, cells are assembled to make a stack. And unfortunately, producing electricity in order to supply domestic energy demands would require millions of cells. The implementation is not practical either. PEMFC for example, the cost of the delicate production and the expensive cell components such as Nafion membranes or titanium coated end plates.
Due to its reasonable - energy produced per money spent - property, biomass based energy production routes will be more beneficial. However, the technical and economical feasibility of the biomass route still needs improvement. Despite supplying the Netherlands' 5.06% of primary energy demand, the overall biomass process must be improved in terms of efficiency and production expenses. As the current studies continue to make progress, biomass is expected to take a bigger role in sustainable energy production.

2.1.1 Lignocellulosic Biomass

Lignocellulosic biomass is defined as non-edible secondary generation raw material. It is the most abundant and also the most available biomass source of all. Wood, straw, crop, crop-residues, agricultural and forest residues are some types of many. Wood pellets are the most common resource material with four million tons being traded worldwide every year [29]. In the Netherlands, consumption of wood based biomass is increasing rapidly.

The Dutch Platform BioEnergie reports that the woody biomass (except wood pellets) consumption was 1.2 Mton in 2014. The consumption increased approximately 40% in 2017, reaching 1.67 Mton in order to produce heat and power [27].
Lignocellulosic biomass consists of polysaccharides such as cellulose, hemicellulose and lignin. Besides the organic part they also include fats, proteins and micro elements such as potassium, magnesium, zinc, iron etc.[30] The organic content of lignocellulosic biomass is shown in Figure 2.

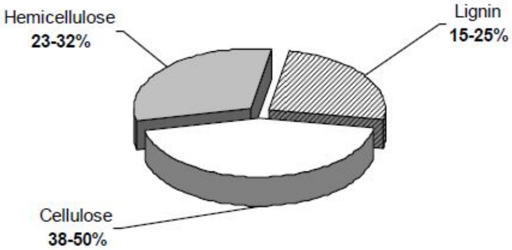


Figure 2: Fractions of organic material in lignocellulosic biomass [2]

Lignocellulosic biomass mainly consists of;

- 38-50 % [31] (45% [32]) of Cellulose; a C6 sugar constructed by multiple glucose based monosaccharides. [33]
- 23-32 % [31] (25% [3]) of Hemicellulose; a heteropolysaccharide made of multiple C5 and C6 monosaccharides. Acts as a wall for the organic structure. [33]
- 15-25 % [31] (20% [32]) Lignin; an amorphous polymer formed by heterogeneous aromatic structures. It is the substance giving toughness to the plant. [33]

The ingredients of lignocellulosic raw material tends to vary depending on the raw material. Substance fractions of some sources are given in Table 1.

Table 1: Composition of lignocellulosic feedstocks

Feedstock Type	Cellulose [%]	Hemicellulose [%]	Lignin [%]	Moisture [%]	Ash [%]
Dry Shavings [34]	51	25	18	7	0,4
Solid Wood Sawdust [34]	49	25	19	8	0,7
Engineered Wood Sawdust [34]	50	27	16	9	0,6
Green Wood Chips [34]	51	27	17	30	0,5
Rye Straw Pellet [35]	38	48		11	4
Buckwheat Straw Pellet [35]	32	52		10	6
Wheat Straw Pellet [35]	37	48		12	3
Rape Straw Pellet [35]	35	50		12	3
Triticale Straw Pellet [35]	38	45		10	8
Hay Pallet [35]	35	48		10	8
Kanlow [36]	31	30	19	-	2
Cave-in-Rock [36]	29	31	20	-	2
Pulped Cave-in-Rock [36]	34	32	23	-	3
Radiotis [36]	43	36	22	-	2
Madakadze [36]	44	31	24	-	5
Wheat Straw [37]	42	23	12	20	9
Rice Straw [37]	39	24	36	30	20
Corn Straw [37]	61	19	7	27	8

Additional information to Table 1, can be found on large variety of lignocellulosic biomass data in the ECN Phyllis classification databank, provided by TNO [38].

Depending on the type of chemical substance to be produced, the material to be chosen will also differ. The selection of an appropriate lignocellulosic biomass feedstock depends on experimental data of the synthesis methods available in the literature. However, these raw materials are not ready for direct production, physically or chemically. These materials must be subjected to some pretreatment before they can be converted into valuable chemicals.

2.1.2 Pre-treatment of Lignocellulosic Biomass

Raw materials collected from nature or waste materials of industry are not available in acceptable size. They are mostly centimeter-sized; as a result, the size must be reduced. The main purpose of the processes is to obtain carbohydrate in the end. In atomic levels, the cellulose component of lignocellulosic biomass has strong intermolecular forces such as hydrogen bonds [39]. These bonds are weaker than covalent or ionic bonds but still have a high energy threshold of 4-13 kJ/mol [40]. The explained chemical structures are demonstrated in Figure 3.

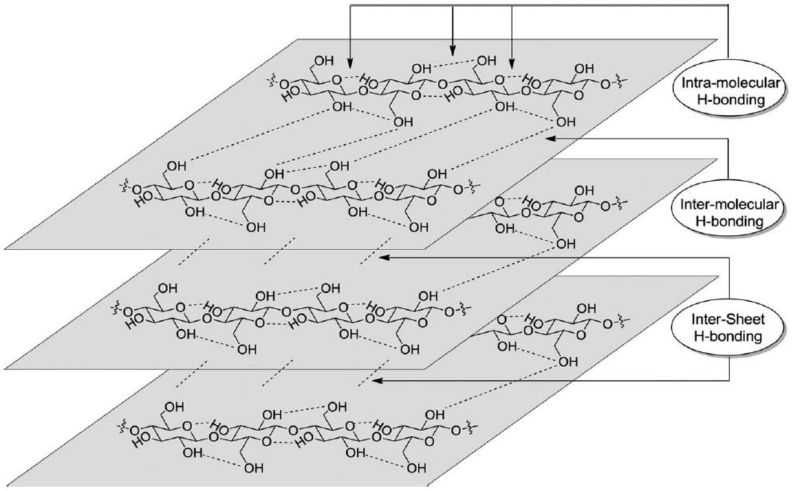


Figure 3: Hydrogen bonds in cellulose [3]

Breaking intermolecular forces put extra heat and pressure requirements for production processes. The increase in temperature and pressure would also require additional modifications for components. Consequently, making the process more complex and delicate is not favored for any scale of production plant. Therefore this incoming feedstock must be handled and well prepared in advance. These treatments can be divided into three groups; 1) Physical, 2) Physico-chemical and 3) Chemical [3]. Their purpose, operating and working conditions are explained in the following chapter.

2.1.2.1 Physical Treatment

During physical treatment, chemical reactions occur at molecular level but the raw material in the stock or storage does not match this size. Simple physical procedures can overcome this issue. Generally grinding, crushing or milling is used to decrease the material size from meters to millimeters. Another benefit of this process is to decrease cellulose crystallinity, in order to weaken its structure. This operation can be alternatively done by ultrasound treatment. In addition, next to the cellulose treatment lignin separation can be performed by microwave irradiation.

Basic physical treatment methods can accomplish the mentioned benefits without requiring too much energy, which may be favoured by engineers. However, some methods might be insufficient for cellulose treatment. Moreover, alternative methods require precise temperature distribution during the process in order to be effective. This makes a proper control mechanism necessary. Therefore in large scale productions, where massive amount of material is utilized, it is not practically possible to keep the whole process under control. Hence it can be neither effective, nor efficient.

2.1.2.2 Physico-Chemical Treatment

As its name signifies, it is the process in which physical and chemical applications are applied simultaneously or sequentially. The most common method is known as steam explosion [3]. Saturated steam at 6.9-48.3 bar (10-35 bar [41]) and 160-260 °C (180 to 240 °C [41]) enters the reactor after the biomass is loaded. After few minutes or seconds pressure is reduced directly to atmospheric pressure. This causes an explosive decompression which leads to breaking of hydrogen bonds hence, breaking the fiber structure of the biomass. By steam explosion, hemicellulose is removed and the lignin matrix is altered. There are almost no chemicals used since only steam is added. The mixture is in gaseous state, and this makes it easy to recover almost all of the biomass in liquid or in solid state (depending on their phase change temperatures) from an outlet stream of the reactor. Therefore no additional recovery or recycle step is necessary. Addition of alkaline medium or mineral acid is reported to be shortening the process duration [3].

Ammonia fiber explosion (AFEX) is developed next to the conventional method. This process occurs in the same way but at lower temperature (60-100 °C [41]) and lower pressure range (17-21 bar [41]), with liquid ammonia ($\mathrm{NH_3}$). By the improvement, the pretreatment process lasts for only half an hour [42]. Generally, 1-2 kg ammonia is used per kilogram of dry biomass. This method is reported to be working fine for raw material with low lignin content [43]. The amount of NH_3 being used in the system, therefore the cost of the operation, mostly depends on the recycling of the ammonia.

2.1.2.2.1 Chemical Treatment

Acid pretreatment method is also one of the most common methods. Hemicellulose is separated from cellulose by rupturing its polymer bonds. Unfortunately, acid treatment is not effective against lignin. It is practically advantageous, as it can be applied for both continuous and batch production methods for removing hemicellulose. For continuous operation it can be accomplished at temperatures higher than 160 °C, with low biomass loading and with exactly opposite properties in batch processing. Sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and phosphoric acid (H_3PO_4) are some of the acids used [44]. However, acid concentration should be paid attention to because concentrated acid is reported to be effective but it causes corrosion in components which leads to extra maintenance and capital costs. Moreover, high acid use becomes expensive due to their price. Therefore acid must be recovered after the process. Hence, dilute acid (less than 4 wt.%) is preferred and resembling results have been obtained.

Alkali salt and sodium hydroxide (NaOH) are utilized in the alkaline pretreatment method to decrease crystallinity of lignocellulosic biomass. Processes at 55 °C with 4-8 % NaOH have been demonstrated for 24 hours process. It is observed that, treatment can be improved with increasing salt concentration [45].

In organosolv pretreatment, lignocellulosic biomass is exposed to (aqueous) organic solvent (methanol, ethanol etc.) with acid catalysts at elevated temperatures [3]. Via this method, lignin is obtained in a water mixture and easily removed from the system. However, the solvent and catalyst costs are high, making this method inappropriate for large scale production.

Although having options that do not require too much energy, pretreatment methods fall short in removing unwanted substances. To progress towards the goal of reducing particle size and obtaining cellulose from lignocellulosic biomass physically or chemically or both the same time; hemicellulose and lignin must be separated or removed. In pretreatment methods, either lignin or hemicellulose can be removed and separated. This inadequacy has made it necessary for researchers to develop additional processing methods aimed at direct sugar synthesis in addition to these methods.

2.1.3 Sugar Synthesis

In literature, experiments are carried out at laboratory scale to illustrate formic acid production steps or to demonstrate the expected reactions within the reactors. In great majority of the experiments, sufficient results were obtained via glucose (see Section 2.2). Lignocellulosic biomass does not usually contain free glucose. The ones containing glucose or any other type of C6 sugars are mostly edible and not preferred, due to ethical reasons. Therefore, methods regarding glucose synthesis need to be developed. These process development efforts are also getting attention from companies because of the insufficiency of the pretreatment methods and because of the aim to promote glucose formation.

2.1.3.1 Homogeneous Catalyzed Synthesis

A homogeneous catalyst is defined as the intermediate substance which is in the same physical state within the reactants [7]. This physical compatibility gives larger contact area between the material and the catalyst, resulting in higher selectivity and yield than heterogeneous equivalents. Highly active interaction between these chemicals complicates the separation of the end product. In addition, having all chemical substances in the same state makes the necessity of complex separation processes such as, extractive, vacuum or reactive [11] distillation units and energy intensive stripping columns inevitable.

2.1.3.1.1 Acid Catalyzed

Mineral acids such as sulfuric acid, hydrogen chloride and carbonic acid are fed into a reactor with lignocellulosic biomass. The operating conditions are at elevated pressures and within a temperature range of 100-260 °C. Antonoplis et al. [46] set up a pretreatment process followed by hydrolysis, in which wood chips were used as raw material. In both systems, gaseous HCl was used as catalyst. High yields of glucose (80%) and xylose (95%) were obtained in products. These high yields are due to high activity of the homogeneous nature of the catalysts.

Heteropolyacids have also been given a shot instead of mineral acids. (Section 2.1.3.2.1). Cellulose hydrolysis experiments run with phosphotungstic acid ($H_3PW_{12}O_{40}$) and $H_3BW_{12}O_{40}$ reported 18-77% glucose yields along other sugar yields [47].
Together with later studies, it has been found that parameters such as temperature, density and cellulose structure affect the functionality of acidic catalysts [48]. For example, in the experiments conducted with different acid concentrations (0.5-40 wt%), concentrated acid solutions caused glucose degradation at high temperatures. This has been noticed by obtaining side products such as 5-hydroxymethylfurfural (HMF), levulinic and formic acid along with glucose [3].
Aforementioned developments and studies exhibit the possible issues of homogeneous acid catalysts. Due to high temperature requirements of the cellulose hydrolysis process, use of concentrated acids might provide better acidity thus good yield but it leaves the system vulnerable for degradation which could damper the synthesis. This product loss can be avoided by utilizing dilute acids, however then a portion of quality has to be compromised but catalyst recovery and recyclability is still a concern. Also use of concentrated catalysts is quite corrosive therefore harm the equipment. Unfortunately, despite the degradation, high costs and low recovery, homogeneous acid catalysts are being used in the industry until their alternative equivalents take place.

2.1.3.1.2 Alkali Catalyzed

Cellulose can be converted to C6 sugars using alkali catalysts via endwise degradation and hydrolysis of glycosidic bonds, respectively . Endwise degradation, also known as peeling, is the removal of monomers from the ends of cellulose within a temperature range of 100-140 °C. However, the process was really slow and hard to sustain [48] [49].

Researchers managed to accelerate and control the process via oxidising the reducing ends of cellulose chain by alkali solvents. However, formed glucose was exposed to isomerization, which lead to the degradation of glucose into other C6 sugars with different structure such as fructose and mannose, decreasing the yield. Moreover, alkali based intermediates were also utilized in oxidation reactions. The intermediate gained an another purpose by catalyzing the conversion of cellulose into oxycelluloses, carbon dioxide and water depending on the operation conditions [3].

2.1.3.1.3 Enzyme Catalyzed

Enzymes work by ‘inversion’ and ‘retention’ mechanisms [3]. Cellulose crystallinity dissolution and glucose molecule formation is achieved by these mechanisms. In order to achieve hydrolysis, enzymes have to be put in a mixture due to each of their specific capabilities. For example, in enzymatic hydrolysis of lignocellulosic biomass, three enzymes were used; Endoglucanases and exoglucanases for the hydrolysis of cellulose into cellobiose and β-1,4-glucosidases for the conversion of cellobiose to glucose. Generally, operations are carried out in a temperature range of 40-55 °C and pH range of 4.5 to 5.5. Kadam et al. [50] investigated the narrow temperature range and observed enzyme degradation. They concluded that it was due to deactivation of the hydrolytic enzymes.

Compared to other catalysts, enzymes have been produced for prices in the range of $ 0.1-0.2 by the industries in Denmark and United States since 2004 [51]. This improvement has increased the interest in enzymatic methods. On the other hand, enzymes are prone to degrade at high mixing speeds and temperatures. Recent studies by Qing et al. demonstrated the opposite, achieving glucose yields up to 71% in the presence of xylose and glucan enzyme at 50 °C and at pH of 4.8 [52], overcame the possible drawbacks of the sugar synthesis.

2.1.3.1.4 Ionic Liquid (IL) Catalyzed

Ionic liquids are organic salt based catalysts, which are in liquid state, at relatively low temperatures ($<$100 °C) [23]. First studies of cellulose hydrolysis via ILs were carried on with the presence of mineral acid (sulfuric acid). Cellulose crystallinity reduction was provided by ILs and H_2SO_4 was utilised for hydrolysis. Based on these researches, experiments performed with cellulose, via $[C_4mim]Cl$ and H_2SO_4 resulted with 50 % glucose yield [53]. Different ILs were also developed and utilized. It is reported that yield levels were enhanced via usage of $[BMIM]Cl$ with HCl for the same process [54]. Currently, ILs are unlikely to be applied industrially due to high manufacturing costs and lack of recyclability, despite their good thermal stability [55].

2.1.3.2 Heterogeneous Catalyzed Synthesis

Heterogeneous catalysts are quite the opposite of the homogeneous equivalents. They are chemical accelerators that are in a different physical state than the product. The practical drawbacks of the conventional catalysts forced the industry to select the use of solid catalysts. The superiority of solid catalysts is quite noticeable in the classification of reactor types (see Section 2.2.4) .

In the creation of homogeneous catalysts, use of expensive organic or acidic components increases the cost of the material vastly and makes the cost of catalyst losses even higher due to the use of energy intensive recovery equipments. On the other hand, utilizing heteropolyacid based heterogeneous catalysts costs less. Additionally, the phase difference of the intermediate substance facilitates the separation process. This also allows ease of control and reuse of the catalyst, which provides benefits for lower capital costs, hence lower operational costs [56] [4].

2.1.3.2.1 Solid Acid Catalyzed

Solid acids are basically solid catalysts with either Bronsted acid sites or Lewis acid sites, or both. Zeolites, ion exchanged resins and heteropolyacids are some of many types of solid acid catalysts used for hydrolysis of polysaccharides into sugars.

Zeolites are crystallized, porous aluminosilicates consisting of AlO_4 and SiO_4 [57] [58]. Zeolites provide high surface area, thus higher catalyst activity. Faujasite (HY) zeolites with varying Si/Al ratio have been experimented to investigate their effect. Depending on the natural material, when disaccharides, maltose and cellobiose were treated with HY having a Si/Al ratio of 15 at 150 °C; 83% and 88% glucose yields were achieved, respectively. Another type of zeolite, H-form of mordenite (HMOR) was also used for glucose synthesis from cellulose. Earlier experiments were not promising in terms of selectivity. Later, the cellulose was physically pre-treated by ball milling to reduce particle size and cellulose crystallinity. As a result, only 13% glucose yield was obtained from cellulose treatment via HMOR with a Si/Al ratio of 75 at 150 °C [59]. In conclusion, zeolites show low hydrothermal stability and leaching of Si and Al is reported to be decreasing the hydrolysis of cellulose drastically.

Acidity of ion-exchanged resins is ensured by the presence of $-SO_3H$ groups. Despite showing low catalyst activity, Amberlite based resins performed well when applied to maltose. Sugar yields up to 95% were obtained via Amberlite-200 at 80 °C [60]. Same results were also obtained with Dowex 50x2-100 resin, at higher temperatures of 120 °C [61]. Contrarily, the intermediate was insufficient for cellulose hydrolysis due to high temperature requirements, because ion-exchange resins are not thermally stable at moderate temperatures (150 °C). Ionic liquid supported zeolites were developed for this drawback, reaching yields up to only 39%, by using NKC-9 resin with $[C_4min]Cl$ ionic liquid [62].

Heteropolyacids are solid acid catalysts containing oxoacids. Keggin and Dawson type HPAs are the most common types [63]. Keggin types have given better glucose yields when tested cellulose. In one study, microcrystalline (pre-treated) cellulose yielded 52% glucose at 180 °C via usage of $H_3PW_{12}O_{40}$. The catalyst was used six times, without showing any signs of degradation [47].

2.1.3.2.2 Supported Metal Catalyzed

Hydrolysis reactions of cellulose in order to synthesize glucose were achieved by supported ruthenium hydrogenolysis, homogeneous acid catalysts. Balandin et al. obtained a yield of 80%, by introducing Ru/C to 1-2 wt% sulfuric acid, at 70 bar hydrogen pressure [64]. The same group replaced H_2SO_4 with phosphoric acid. Increasing the acidity increased the yield up to 90%. Recent methods demonstrated platinum (Pt/Al_2O_3) based catalysts.

With the studies in recent years, the use of heterogeneous catalysts is increasing in industrial processes gradually. The reason is totally practical. Because heterogeneous catalysts exhibit better behaviour over homogeneous catalysts in terms of selectivity, stability, corrosiveness, catalyst recovery and lifespan. Hence, along with the minimum catalyst loss, heterogeneous intermediates provide functional and economical convenience by making the process easier to control.

2.1.3.3 Extraction

In the system where a solid-liquid mixture (depending on the temperature and pressure requirements) is present, development of extraction methods is not something unexpected.

Determining the appropriate extraction route depends on the chemical properties of the substances present in the mixture and the component to be separated. Liquid-liquid and liquid-solid extractions are the conventional choices [65]. Recently, alternative routes have been developed in order to overcome the energy barriers. Available methods are;

- Liquid-Liquid Extraction: Accomplished by using two solvents, first one always being water. Dichloromethane-water and hexane-water are few examples. Conventional methods suffer from toxicity and flammability [66] [67].
- Liquid-Solid Extraction: It is the removal of the solid component from a liquid-solid mixture via a solvent. Soxhlet extraction, maceration and percolation are few examples of conventional methods for solid phase separation. Despite being applied in the industry, these methods include of hazardous substances and the process takes too much time [65] [7].
- Supercritical Fluid Extraction: As its name signifies, the mixture is separated by using a supercritical liquid solvent. Currently it is mainly used in pharmaceutical and food industries due to its effectiveness in extraction of high quality, essential oils. However, preparation and handling of the supercritical fluid requires high capital costs. [65] [68]
- Ultrasound Assisted Solvent Extraction: Sonic waves created by ultrasound waves cause cavitation in the liquid environment. Cavitation creates negative pressured bubbles, which implode. Implosion then creates micro-scaled systems at high temperature and pressure, achieving the extraction via a solvent. These bubbles can be created both in liquid and aqueous solid mixtures, offering a wide range of applications. Solid based operations can be problematic due to possible decomposition. But only limited number of large scale implementations of the process exist [69] [70].
- Microwave Assisted Extraction (MAE): Combination of microwaves and solvent provide the extraction process. Energy of the microwave radiation is used in order to create an available environment for extraction to take place. Then separation is carried on via a solvent. MAE offers controllability of the system, high purity and stability [65].

Using pretreatment steps or sugar synthesis alone is not favored [71]. Pretreatment methods, as explained above, do not meet the glucose conversion requirements (selectivity, yield). Sugar synthesis routes on the other hand, would require high amount of energy to reduce cellulose crystallinity to remove lignin and hemicellulose in addition to existing high temperature and pressure specifications. Therefore, in recent studies, a compatible combination of the two procedures is sought and investigated.

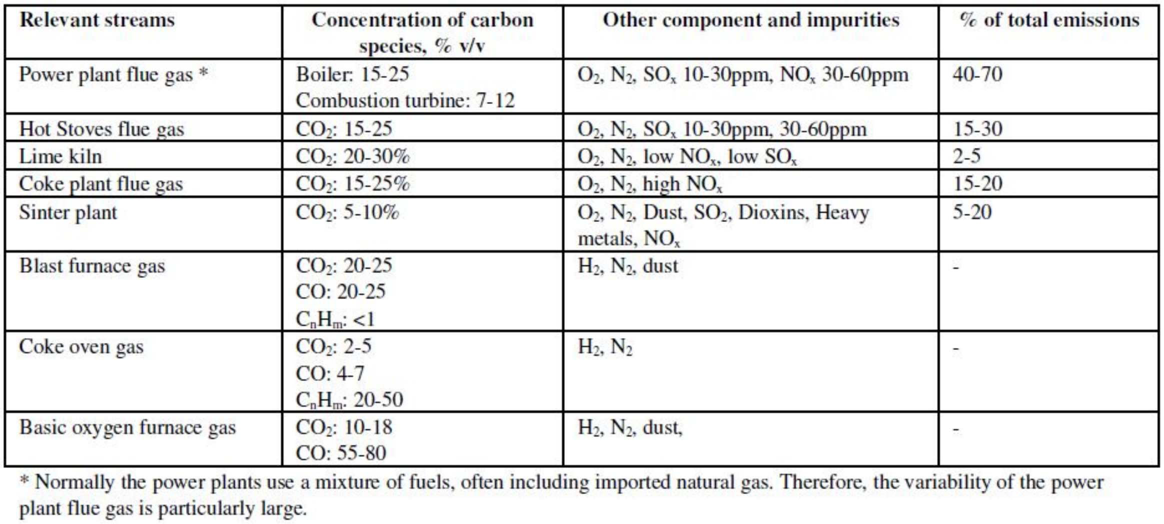
2.1.4 Carbon Dioxide Capture

Air and flue gas contain carbon dioxide, inferring that carbon dioxide does not exist in pure state. Therefore any of the preferred gases should be captured and the carbon dioxide contained in those should be collected and stored. There are many methods being investigated and still being developed, in the literature. However, the capture methods differ from source to source.

2.1.4.1 CO_2 Capture from Stationary Sources

Basically, stationary sources refer to chimneys. Gases released from plants and furnaces contain carbon dioxide. Capturing processes are advantageous if the carbon dioxide is going to be utilized in a plant nearby. The source for the gas must be determined before designing the carbon capture unit, to assure that enough carbon dioxide is available which can be retrieved from. Cement plants have a big part in emissions. A Dutch cement company ENCI B.V. owns a factory located in Velsen-Noord, which produces 1.4 million tons of cement every year [72]. Iron & Steel industry is another important source of carbon emission. The gas emission characteristics of an integrated steel mill is given in Table 2. The figure exhibits the percentage of CO_2 concentration in the gases emitted by different sources on site [73] [74].

Table 2: Gas characteristics of iron & steel industry [13]



Relevant streams	Concentration of carbon species, % v/v	Other component and impurities	% of total emissions
Power plant flue gas *	Boiler: 15-25 Combustion turbine: 7-12	O_2, N_2, SO_x 10-30ppm, NO_x 30-60ppm	40-70
Hot Stoves flue gas	CO_2: 15-25	O_2, N_2, SO_x 10-30ppm, 30-60ppm	15-30
Lime kiln	CO_2: 20-30%	O_2, N_2, low NO_x, low SO_x	2-5
Coke plant flue gas	CO_2: 15-25%	O_2, N_2, high NO_x	15-20
Sinter plant	CO_2: 5-10%	O_2, N_2, Dust, SO_2, Dioxins, Heavy metals, NO_x	5-20
Blast furnace gas	CO_2: 20-25 CO: 20-25 C_nH_m: <1	H_2, N_2, dust	-
Coke oven gas	CO_2: 2-5 CO: 4-7 C_nH_m: 20-50	H_2, N_2	-
Basic oxygen furnace gas	CO_2: 10-18 CO: 55-80	H_2, N_2, dust,	-

* Normally the power plants use a mixture of fuels, often including imported natural gas. Therefore, the variability of the power plant flue gas is particularly large.

Amount of carbon dioxide captured from plants vary. Yavini et al. estimated that cement industry emits 900 kilograms of CO_2 per ton of cement produced [6]. On the other hand, according to Alvarez et al. carbon dioxide content in cement and steel production derived gas is 20-30 % of the overall volume [75]. Additionally, Romano et al. state that cement plants emit gasses with 15-30 % CO_2 content [13].

After estimating the possible carbon dioxide amount that can be captured from an industrial plant, the next decision point is whether the carbon will be captured before or after the combustion occurs. Sequence schemes are demonstrated in Figure 4.

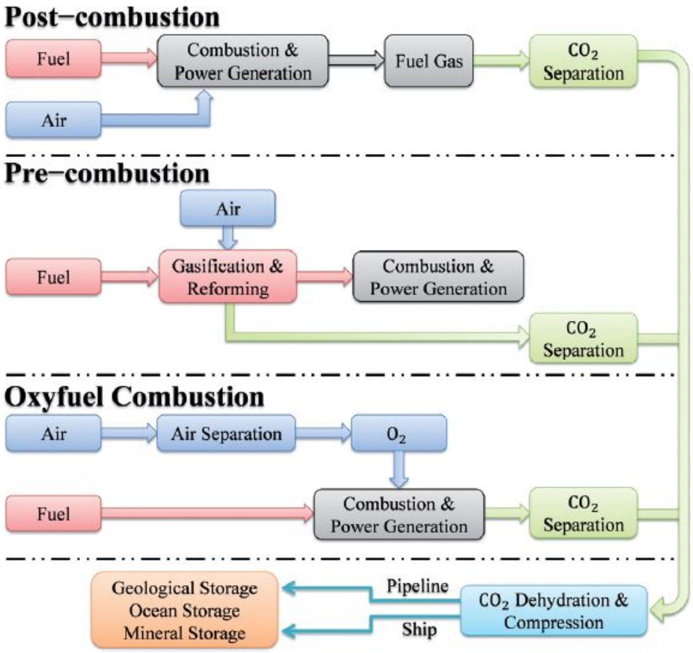


Figure 4: Carbon capture sequence flowchart [4]

- Post-combustion: Capturing carbon dioxide from the products of combustion currently dominates the industry. Basically, the CO_2 is separated and obtained after the fuel is burned. Since the fuel is already used for furnaces and ovens, the post-combustion method is quite convenient for the industry. Producing chemicals is considered to be practical, by using some of the harmful gases formed after the fuel is burned. In addition, since the system does not have many preconditions, it can be integrated into the end of any existing production plant. However, SOx and NOx and dust removal would require additional gas cleaning before the capture unit [13] [76].

- Pre Combustion: Separating carbon dioxide prior to the combustion is recently being investigated. Removal of the CO_2 leaves H_2 as the only fuel substance [77]. Preventing normal combustion has environmental benefits. Altered fuel is more eco-friendly because it will not have the familiar harmful emissions. Also the hydrogen can be used in its own energy production routes via fuel cells or gas turbines. These routes are recently acknowledged and seem promising. In the contrary, pre-combustion method is not applied in the industry as much as post-combustion. This is related to the addition of carbon capture processes to an existing production plant. Implementation of new setup with its own equipment brings extra complexity and capital costs.

- Oxy Combustion: It is the recovery of carbon dioxide from flue gas containing only carbon dioxide and water. The difference is that, pure oxygen is being used as oxidizer for the combustion. The setup costs as much as post-combustion at small scale operations. The content of the flue gas is simple, making the separation process easier. However, the maintenance, storage, transportation and the handling of pure oxygen adds complexity and safety concerns [78].

Carbon dioxide is captured via absorption, adsorption and membrane separation. These methods are modified according to the desired capture sequence. Therefore these modifications will be explained next along with the capture methods.

2.1.4.1.1 Absorption Capture

Gas absorption is the separation process of gas (or gas containing) mixtures by washing via a liquid substance [79]. The desired gaseous component is absorbed into the liquid and therefore separated. Absorption method is frequently applied in the industry due to its simplicity and reasonable cost. These liquids, referred as solvents, are divided according to the absorption mechanism [57].

Chemical absorption is achieved by reaction of gaseous components with a solvent, in order to form a chemical mixture. Later, the solvent is regenerated and removed. Amine based substances are the most mature intermediates in the industry for post-combustion operations.
Three types of amines are used in the industry. These are;

1. Primary amine, monoethanolamine (MEA),
2. Secondary amine, diethanolamine (DEA),
3. Tertiary amine, methyldiethanolamine (MDEA).

Theoretically, carbon dioxide can be captured at 85-95% selectivity and yields higher than 99.95% via aqueous amine solutions [5].

Primary amines show good selectivity properties at moderate concentrations. On the other hand, MEA requires high temperatures for regeneration and it is more corrosive than other amine solutions. Secondary amines can be also used for sulfur (e.g. H_2S) removal. DEA is reported to be working well at low pressures. However, it requires regeneration at pressures lower than atmospheric levels, which is challenging to maintain. MDEA is also thermally and chemically stable, has high solution capacity and it is non-corrosive [80] [81].

In addition to using amines individually, amine mixtures have also been tried. Piperazine (PZ) showed no signs of degradation while working effectively at high temperatures of 150 °C [57]. However, its solubility was not satisfactory despite its costly production.

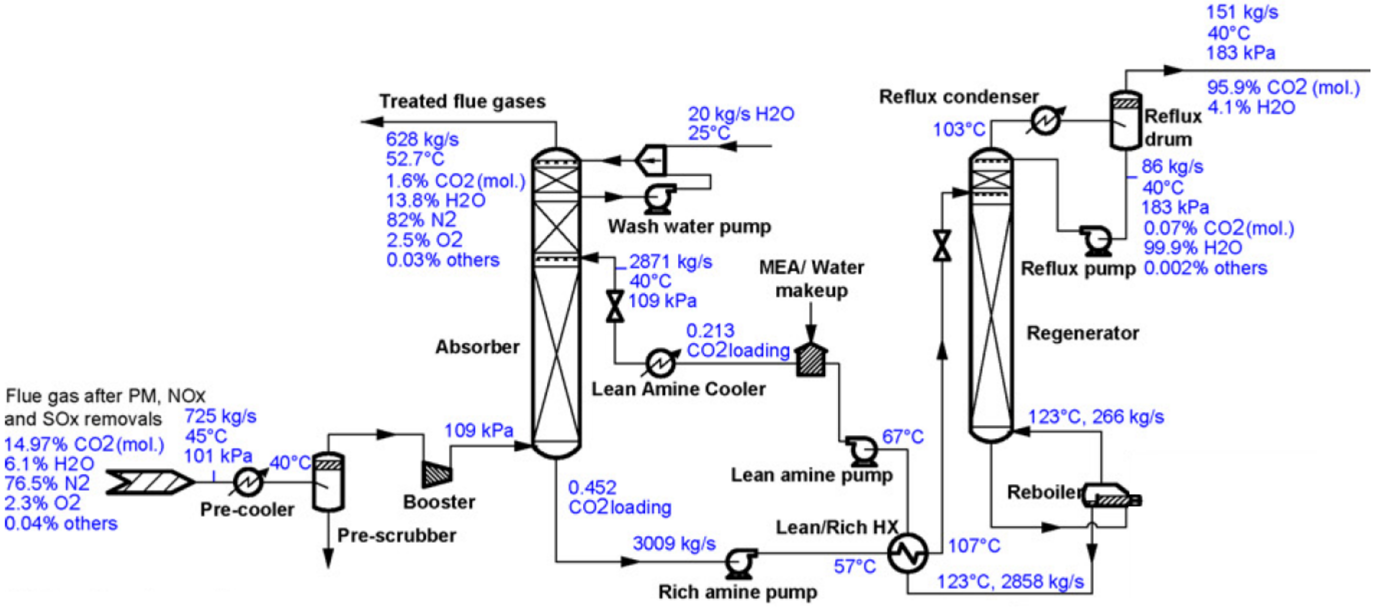


Figure 5: Solvent based CO_2 capture [5]

Solvent based carbon dioxide capture (see Figure 5) can be simply explained via the following procedure;

- A gas mixture is treated with the solvent inside an absorber column at low temperatures of 15-60 °C.
- CO_2-rich solvent mixture is fed into a desorption column, carbon dioxide is obtained by stripping at high temperatures.
- Solvent is recycled back to the absorption column.

Physical absorption is run by the differences in physical parameters such as temperature and pressure between the components and solvents. Compared to chemical equivalents, physical sorbents can be used for both post and pre-combustion configurations [82]. This is because of solvent capacity dependency on the carbon dioxide partial pressure [57].

Commercially known sorbents are Selexol, Rectisol, Fluor and Purisol. However, only Selexol (also known as polyethylene glycol [6]) manufacture is reasonably affordable [81]. Additionally, Selexol provides high solubility and it does not cause any reaction to take place, since it is run by physical differences. Processes including Selexol can operate at lower temperatures between 0-5 °C but at higher pressures compared to chemical sorbents.

In the Figure 6, a Selexol-based, post-combustion carbon dioxide process flowsheet is shown. Tsunatu et al. achieved 98% purity from 97% of the CO_2 emitted by a cement plant. They have also estimated the operational and capital costs; Carbon dioxide captured only at a value of 58$ per ton, which is almost the same as conventional amine based methods [6].

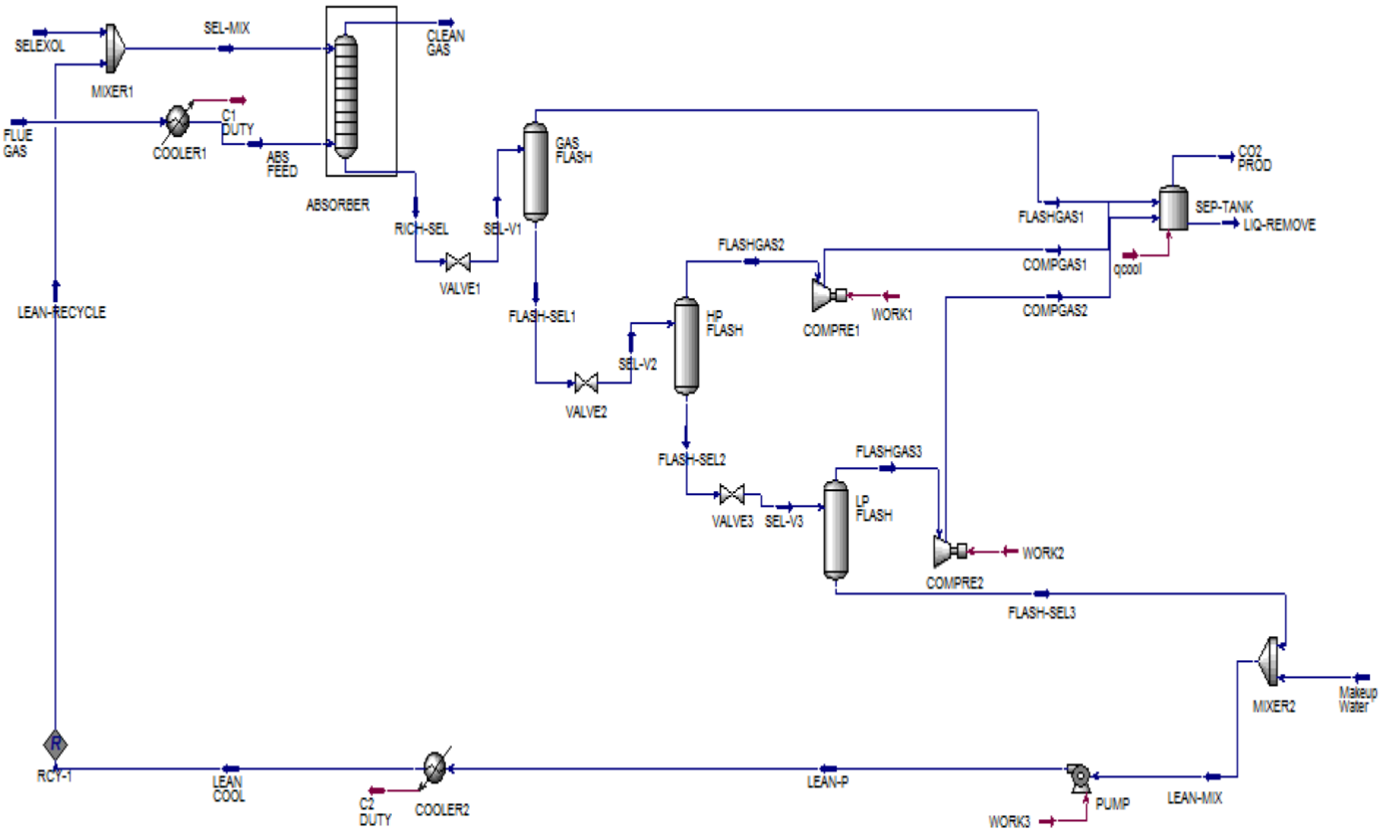


Figure 6: CO_2 capture via Selexol based physical solvent [6]

Recently, ionic liquids (ILs) are being studied due to their high thermal stability, low volatility and non-flammability. Their high production cost is preventing them from being used in industrial applications [13].

2.1.4.1.2 Adsorption Capture

Gas adsorption is the adhesion of gas molecules to a solid surface. In this case, carbon dioxide is collected and separated via solid molecules. Then, sorbent removal is done via pressure, temperature or vacuum swing adsorption cycles. Intermediates used within these columns currently include amines, metal organic frameworks (MOF), zeolites and activated carbons. CO_2 capacity, selectivity, stability and regenerability are the targeted properties for solid adsorbents [57].

Amine-based solid materials gained importance since they were utilized in NASA's space shuttles and submarines. They were used due to effective operation with water vapor, which is approximately 10-15% of flue gas [83]. Solid amine integrated aqueous solutions are water resistant and have high CO_2 capacity at low temperatures [84]. They are well suited for temperature swing adsorption. Pressure swing adsorption also has been tried but, it required an extra step of rinsing to obtain desired CO_2 purity. However, the sorbent showed signs of unstability after multiple cycles [57].

Zeolites are crystallized, porous aluminosilicates that are effective at temperatures lower than 100 °C. For example, X and Y Faujasite zeolites such as 4A and 13X have been utilized for carbon dioxide capture. High CO_2 capacities were achieved at room temperatures and at very low pressures. However, the presence of moisture and impurities have been shown to weaken the substances [85] [86].

Compared to zeolites, metal organic frame works are reported to be working well at elevated pressures. MOFs are less favored due to their uncertain regenerability, despite high surface area and more controllable chemical properties. Since these tailorable configurations come at high costs, loss of the substances cannot be taken granted.

Activated carbons are applied to pre-combustion pressure swing adsorption of CO_2. Their performance is stable at high temperatures and low pressures, with large adsorption capacity [87]. However, they are not suitable for post-combustion applications due to low CO_2 capacity and selectivity at mild conditions. They are also vulnerable in the presence of SOx and NOx [57].

2.1.4.1.3 Membrane Capture

Membrane technologies are advantageous over conventional methods because they do not require additional sorbent regeneration steps. By their selective permeability, membranes can separate the demanded molecules with the appropriate diffusion mechanisms. Inorganic, polymeric, mixed matrix and transportation membranes have been demonstrated in laboratory scales, in the literature.

Practically, large scale applications of CO_2 capture via membranes are not likely. Fabrication, the assembly and installation of this innovative component is quite delicate, despite improved affordable production routes. The long term stability, impurity resistance and reliability are still an issue for the current studies.

Recently, physical solvent based carbon dioxide absorption processes have gained importance. Damaging equipments due to corrosion, the difficulty of separability and recyclability are the most significant reasons in the preference of innovative materials such as Selexol, over conventional solvents. Selexol can operate at temperatures between 0 and 25 °C [88] and pre-combustion method is more suitable compared to other methods because of this operating range. The high temperature of the flue gas in other methods requires additional cooling duty, which would correspond to the addition of equipment and energy.

2.2 Production of Formic Acid

In this report, large scale production of formic acid is studied. Conventional and renewable production routes will be explained below. But first, the product must be acknowledged.

2.2.1 Formic Acid

Hydrogen (H_2) is gaining more reputation every year. Hydrogen driven fuel cells will be providing various services in the upcoming future, in addition to the vehicle Mirai manufactured by Toyota. However hydrogen is an odorless, transparent and highly explosive gas. Also hydrogen has low density and low compressibility, which makes hydrogen to be stored at very high pressures, i.e. around 300 bars. These high pressure requirements come with high operational costs in storage. The same challenges are faced during the transportation of the gas. These drawbacks pushed scientists to look for substances with safer mobility and storage possibilities.

The future must rely on sustainable and environmentally friendly substances. In this vital task Formic acid (FA) -also known as methanoic acid)- steps forward among other substances, produced for energy purposes in the industry. It is one of the simplest, colorless, transparent carboxylic acids. It was discovered in 1670 inside ants, getting its name from the red ant "Formica Rufa" [7]. It also has low toxicity. Therefore it is being used in food industry as an additive. However, it must be noted that concentrated formic acid is corrosive, toxic and can harm humans [89].

Formic acid is a versatile chemical which is used in a variety of sectors such as textile, leather and pharmaceuticals [7]. For example, in Europe it is mainly used in agriculture, for acidification at silage. Having a pH of 4, it acts as an anti-bacterial to extent the durability of stored, freshly mown plants.

Properties of formic acid are given in table 3 for 25 °C and atmospheric pressure [7].

Table 3: Properties of Formic Acid

Property	Value	Unit
Chemical Formula	HCOOH	-
Molecular Weight	46.03	kg/kmol
Melting Point	8.3	°C
Boiling Point	100.8	°C
Corrosive	Very	-
Color	None	-
Smell	Pungent	-
pKa (Acid Strength)	3.739	-
Density	1.220	g/cm^3
Vapor Pressure (25 °C)	5.866	kPa
Specific Heat Capacity	2.1745	J/g.K
Heat of Fusion	276	J/g
Heat of Vaporisation	483	J/g
Heat of Formation Liquid	-425	kJ/mol
Heat of Formation	-378.57	kJ/mol

It must be noted in Table 3 that the boiling point of formic acid at atmospheric pressure is 100.8 °C, which is very close to water's boiling point (100 °C). This means that their mixture forms an azeotrope which will be discussed later on.

Formic acid has been produced on industrial level for the last half-century. The ambition for a brighter future and the increasing implementation of biomass will provide a smooth transition to climate friendly process.

2.2.2 Conventional Production Methods

In the past decades, formic acid was produced in small amounts, due to its insignificance. First, it was being obtained as a by-product in the production of acetic acid, which was being produced by oxidation of hydrocarbons. Later on, formic acid was produced via hydrolysis of formamide, i.e. amide originated from formic acid. It was the most common method in Europe in the 1970s. After the process improved scientifically, companies worked on particular methods, to produce formic acid as the only product.

Formic acid had already been produced at various industrial levels for the last half century. Ullmann et al. stated 260 ktons in 1987 and 390 ktons of formic acid in 1995 were produced worldwide. The production capacity increased rapidly, since then. The capacity has reached approximately 850 ktons per year, in 2014 [90].
Currently in Europe, Germany is leading the production levels with 60% of the 350 ktons of annual production. Therefore, understanding of this process is crucial to identify and avoid its drawbacks in the new biomass route [91].

Presently, 90% of the total formic acid production in the world is realized via hydrolysis of methyl formate. Generally, the procedure consists of two steps; First reaction is the carbonylation reaction of methanol (CH_3OH) with carbon monoxide (CO) forming methyl formate ($HCOOCH_3$) [92].
The reaction occurs as follows;

$$CH_3OH + CO \longleftrightarrow HCOOCH_3 \tag{1}$$

Second reaction is the production step which is the hydrolysis of methyl formate, which yields methanol and formic acid. It is demonstrated as;

$$HCOOCH_3 \longleftrightarrow HCOOH + CH_3OH \tag{2}$$

One major advantage of this production method compared to previous routes can be deduced from the process equations. As shown in equation 1 and 2, in the beginning methanol is the reactant, then it comes out with the main product, formic acid. This means that one of the reactants can be recovered and recycled to the process, after some separation steps. This may seem to be increasing the first investment costs but for mass production, recovering the materials at this point is far more beneficial.
According to the literature, there are three most widely known systems carrying out this process industrially. In chronological order, they are BASF, Kemira-Leonard and USSR processes.

2.2.2.1 BASF Process

It is the first plant including the carbonylation and hydrolysis technologies, built by the German chemical company BASF in 1981, in Ludwigshafen. Here formic acid production techniques are used including the carbonylation and hydrolysis technologies. The plant has the largest production capacity in the world with 100,000 tons of formic acid per year [7]. To give an idea about the size of the plant; In 2014, the production capacity in Germany was estimated to be 210,000 tons [93], meaning that the capacity was so big that it could be doubled only after thirty years. The flowsheet for the BASF process is given in the Figure 7.

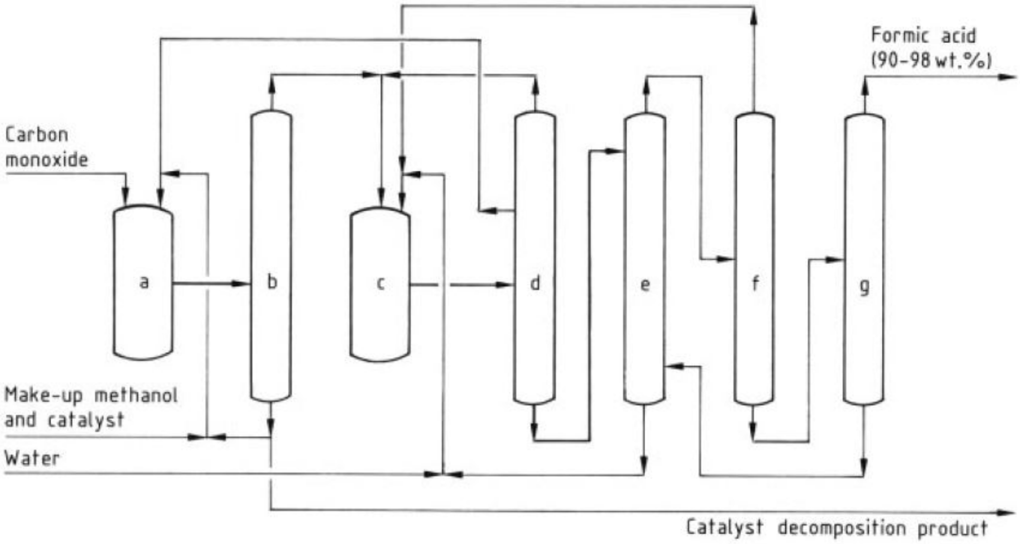


Figure 7: The BASF Process [7]

The production occurs as follows;

- Methanol and carbon monoxide enter the first reactor (a), with a certain amount of catalyst/reagent, for the carbonylation reaction.
- The products of the first reactor is fed to distillation column (b), where methyl formate is recovered from the top and sent for formic acid production. Unreacted methanol and the catalyst are covered from the bottoms and recycled back to the first reactor.
- The methyl formate enters to the second reactor (c) for the hydrolysis reaction.
- The products are fed into the second distillation unit (d)
- The more volatile component of this mixture, methyl formate, is obtained from the distillate stream.
- Since its boiling temperature is much lower than water and formic acid, the unreacted methanol is also obtained from the upper half section of the column.
- Water-formic acid here forms an azeotrope. Therefore, the mixture is sent to an extraction column (e). Solvent is added from a separate stream.
- Formic acid is the heavier substance, hence it is obtained from the bottom stream.

- The water is retrieved from the distillate stream with a fraction of solvent and formic acid included. The mixture is sent to an dehydration column (f). The water then is taken back to the second reactor.
- The formic acid is purified in acid column (g) to meet the desired specifications.

2.2.2.2 Kemira Leonard Process

The plant was built by Leonard Process Company, which started operation in 1982. It is located in Finland which has an annual capacity of 20,000 tons. Kemira-Leonard process has also been applied in different countries, like India and Korea [7]. The flowsheet of the plant in Finland is shown in Figure 8.

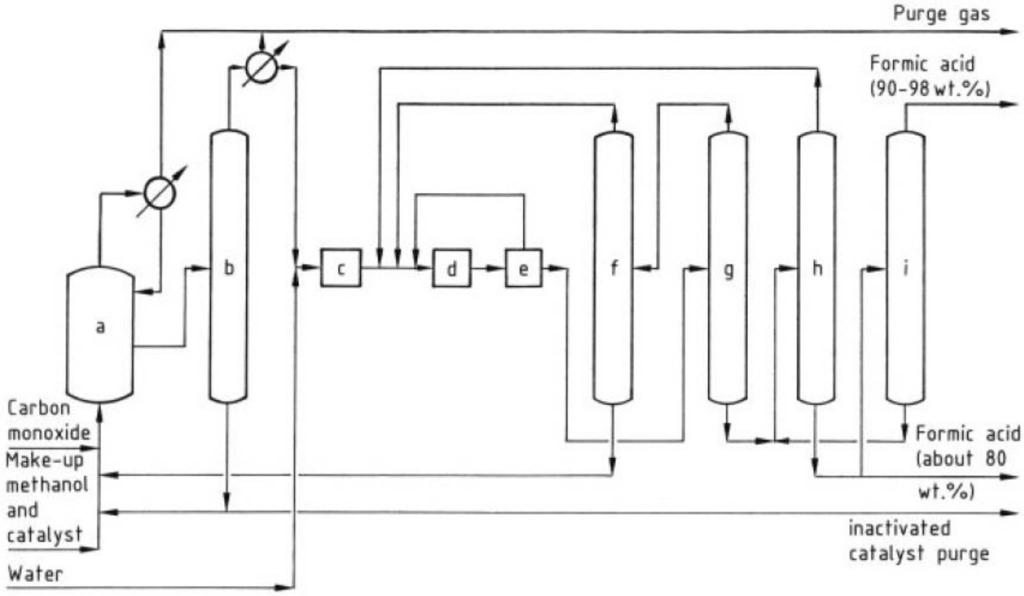


Figure 8: The KL Process [7]

The formic acid production process is carried out as described below;

- Methanol and carbon monoxide enter the first reactor (a) for the carbonylation reaction, with the presence of catalyst.
- Methyl formate and other substances are fed into column (b). Methyl formate with higher saturation pressure is obtained from the distillate stream. The rest of the mixture consists of methanol and catalyst, which are sent back to the first reactor.
- Methyl formate and water are first sent to a preliminary reactor (c). The outlet stream is sent to the main reactor (d).

- The products of the hydrolysis reaction are sent to a flash tank (e) working at atmospheric pressure. Methanol and methyl formate are separated from the mixture. However, a small amount of formic acid is present in this stream
- Methanol and methyl formate are then separated via vacuum distillation column (g). They are also obtained from different streams in column (f).
- The main product formic acid is finally purified in columns (h) and (i) with an outcome of 98 wt.% [91].

2.2.2.3 USSR Process

Another formic acid production plant is built in Saratov, Ukraine. It started operation in 1989. Its reported production capacity is 40,000 tons per year. In this plant, the hydrolysis process differs from other plants, as it occurs at a temperature of 80 °C and at a pressure of 6 bars. The process flowsheet is shown in Figure 9.

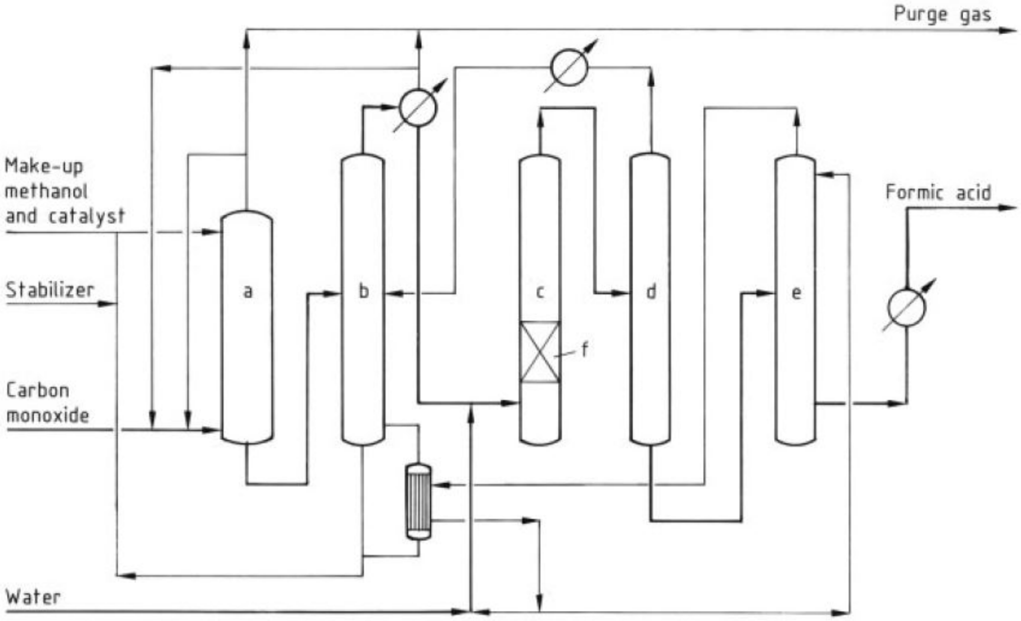


Figure 9: The USSR Process [7]

The process occurs in following steps;

- Methanol and carbon monoxide enter a reactive distillation (a) for the first reaction, with the proper catalyst and stabilizer. The reaction takes place at a high pressure of 30 bars.
- The products of the reactive column are distillated in column (b). The distillate stream containing methyl formate are fed to the formic acid process.

- Water and methyl formate first pass through the packed catalyst section (f) of the reactive column (c), where the hydrolysis reaction occurs.
- All products of the second reaction are sent to the second distillation column (d). Here, the formic acid-water mixture is obtained from the bottoms outlet. The methanol and methyl formate mixture is distilled, recycled and sent to the first distillation column (b).
- The formic acid is finally retrieved via column (e) with 85% purity.

The aforementioned methods have been applied for the last decades. Their different production capacities and improved properties have been demonstrated in different parts of the world. But despite being actively chosen in the industry, the conventional method has its drawbacks; First, the use of carbon monoxide can not be considered a renewable method. Moreover, CO utilization possess an environmental safety issue. Inhaling this gas even in small amounts can cause serious health problems for humans. Using in large scale, recycling processes would require delicate piping, maintenance and more precautions to prevent hazardous results.

Secondly, large amount of methanol is being used as reactant in the BASF process. From literature, it is known that methanol can be obtained by a sustainable process via air and solar power. Latest research shows that methanol also can be used as fuel in future transportation. Therefore, it is becoming more valuable, and hence more expensive everyday. By fourth quarter of 2020, one metric ton of methanol cost approximately 320 euros in Europe [94]. This improving value of methanol is a major trade-off for production plant operations.

The third drawback is operational. The separation process simply has too many steps. For example, in the first column of the KL process, formic acid still exists within the recycle stream. It can be neglected. However, in the long run the ignored amount of formic acid disfavors the process economically. On the other side, the additional separation and purification steps increase the investment cost, and hence the operational costs.

2.2.3 Renewable Formic Acid Production

Today, formic acid synthesis can be achieved in a sustainable way through the use of biomass and carbon dioxide. Traditional methods based on petrol and coal are gradually losing their importance, due to their irreversible environmental damages and with the significant reduction in the petrol and gas resources compared to the past. Recently, the development of processes where valuable chemicals can be produced out of waste or unwanted raw materials, has become the focus of all researchers. The same trend is true for engineering companies and thus countries, in this age of renewable energy transition.

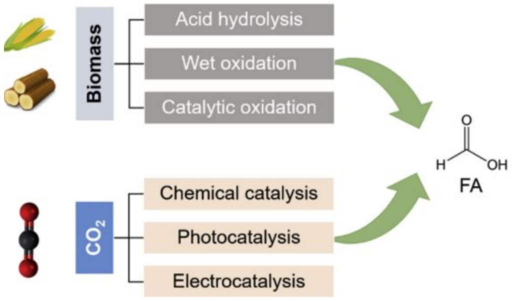


Figure 10: Renewable FA production routes [8]

As depicted in Figure 10 formic acid can be produced by biomass utilization. As explained in previous chapters, because of their chemical side gains (O/C ratio), cellulose-based lignocellulosic biomass is the preferred, for this route. Biomass raw material can be processed via acid hydrolysis, wet oxidation or catalytic oxidation

2.2.3.1 Formic Acid Production via Biomass

2.2.3.1.1 Acid Hydrolysis

By definition, hydrolysis is a type of chemical interaction in which water is added to the reactant to either form a new chemical or split the reactant into two or more new substances. To be precise, acid hydrolysis is hydrolysis reaction being run in the presence of acidic catalysts [8]. Mainly, levulinic acid is aimed to be produced.
Formic acid formation is achieved via acidic hydrolysis of carbohydrates (e.g. glucose), which occurs as in the following two reaction steps;

- First, dehydration of sugar to its soluble intermediate, 5-hydroxymethylfurfural (HMF) takes place.

  $$C_6H_{12}O_6 + H_2SO_4 \longrightarrow C_6H_6O_3 + 3\,H_2O \tag{3}$$

  This reaction takes place in harsh conditions; within a temperature range of 180-240 °C and 25 bar pressure [95].

  Operation conditions are varied according to the catalyst loading. Concentrated acid catalyst requires lower temperatures (100 °C), on the contrary high temperatures are (160 °C) required for dilute solutions [96].

- The second reaction is the hydrolysis of HMF to levulinic acid (LeA, $C_5H_8O_3$) and formic acid. .

  $$C_6H_6O_3 + 3\,H_2O \longrightarrow C_5H_8O_3 + HCOOH + H_2O \tag{4}$$

  Reaction takes place in another reactor, and lasts for approximately 20 minutes [95]. The process can be optimized to fit in a single reactor.

A similiar process can be applied for cellulose, since it has one water molecule less in its chemical formula; the stoichiometric number of water will be one less compared to the reactions 3 and 4. Formic acid and acetic acids are obtained from aqueous hemicellulose solutions. An other difference is the formation of furfural ($C_5H_4O_2$) in the primary reaction [97].

Sulfuric acid is the most common of many catalysts used in reactions explained above due to its abundance and good performance. Formic acid with 4.2% and 52.5 % levulinic acid purities were obtained from hydrolysis of glucose with 0.1M H_2SO_4 [98]. Yoshida et al. realized decreasing formic acid yield in higher pH values, when fructose was used as the source substance. His experiments proved that formic acid formation was enhanced in higher acidic environments. He reported 8.5% yield when using HCl and 1.5% with maleic acid [99].

As their advantages were explained (see Section 2.1.3.2), solid (or heterogeneous in this case) catalysts are tried for better production conditions. Joshi et al. used zirconium dioxide (ZrO_2) at 180 °C and reached a higher purity of 45% than zeolite based catalysts [100]. Ahlkvist et al. used a macroporous acidic ion-exchange resin, Amberlyst-70. He obtained the highest theoretical yields reported, with 59 and 68 mol % for formic acid and levulinic acid, respectively, in a single reactor at varying temperatures of 180-200 °C [101]. Mentioned materials made catalyst separation and recovery easy, however they offered less selectivity and activity.

Acid hydrolysis method works fine for LA, practically. Therefore, the method was studied and applied in the industry. But the method does not sound good for formic acid prioritized production; since it is just a by-product. This is because levulinic acid is a versatile material. Various derivatives of levulinic acid are used in many different fields. Carboxylic acids obtained from LA can be used as fuel source for gas turbines [102]. Also, diphenolic acid, formed from the carbonyl group of LA, is involved in polymers [103], lubricants [104], fire-proof materials [105] and paints [106] production. Finally, its methyl group used in pharmaceuticals [107].

In current studies and even industrial applications run with acid hydrolysis, formic acid is obtained in low amounts compared to main product LA and it is not separated properly [108]. Possible profitability of formic acid purification is being questioned and investigated operationally [109]. Elsewise, the extra expenses of additional equipment could be disadvantageous for a large scale plant where the economical feasibility is questioned.

2.2.3.1.2 Wet Oxidation

Conversion of organic biomass materials into organic acids [110] such as formic acid, acetic acid (AA) and lactic acid (LA) accomplished by oxidation reactions. Use of aqueous solutions (i.e. subcritical or supercritical water) in order to form cations and hydroxide anions gives method the "wet" definition. Wet oxidation of glucose occurs as in the following reaction [9];

$$C_6H_{12}O_6 + 6\,H_2O_2 \longrightarrow 6\,HCOOH + 6\,H_2O \qquad (5)$$

Instead of hydrogen peroxide, oxygen can also be utilized. The reaction equation is given below.

$$C_6H_{12}O_6 + 3\,O_2 \longrightarrow 6\,HCOOH \tag{6}$$

The above chemical processes takes places at temperatures 150-230 °C and high pressure 10-50 bar [9]. Wood biomass (wood pellets, straw pellets, agricultural and industrial residues) [111], bio-oil, lignin and therefore carbohydrates can be used for the production. Depending on the used raw material's chemical structure, utilization conditions differ. General description of the processes are shown in the Figure 11.

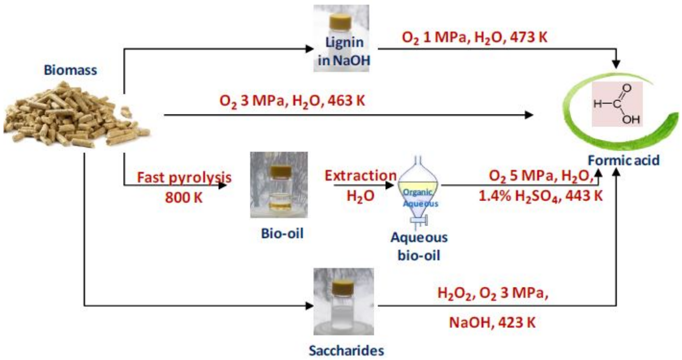


Figure 11: Wet oxidation alternatives for biomass [9]

Lignin (4 g/L) is converted into formic acid and succinic acid mixture at 170-225 °C with 5-15 bar oxygen, without the presence of a catalyst. Low concentrations (4 g/L) gave better yield of 44% , where high concentrations only result with 16% purity [112].

Bio-oils contain significant amount of water and oxygen, as discussed in Section 2.1.1, The oxygen content must be lowered, in order to reduce O/C, with the excess amount of water [113]. Therefore, the raw material is subjected to intermediate extraction processing. Then, bio-oil is utilized in a two step process with sulfuric acid as catalyst and high pressurized oxygen at 170 °C, forming no other products but formic acid with 56% yield [114].

Major results were obtained via the wet oxidation of glucose. Jin et al. tested the oxidation of glucose into formate salts with high yield of 75%, in the presence of alkali catalysts and excess amount of H2O2 at 250 °C inside a batch reactor. In fact, at these conditions hydrogen peroxide converts to oxygen and water. The importance of an alkali was also investigated. Only 24% purity could be achieved in the absence of an alkali [115].

Recently, improved studies on wet glucose oxidation gave very couraging results. Common bases such as lithium hydroxide (LiOH), sodium hydroxide (NaOH) and potassium hydroxide (KOH), with hydrogen peroxide as oxidant at room temperature and atmospheric pressure were used. The carbohydrate transformed into 91.3% pure formic acid with approximately 90% selectivity [10]. This experiment reached a record not only in terms of purity levels, but also in temperature and pressure values. Demonstration of the reaction mechanism is given in the Figure 12.

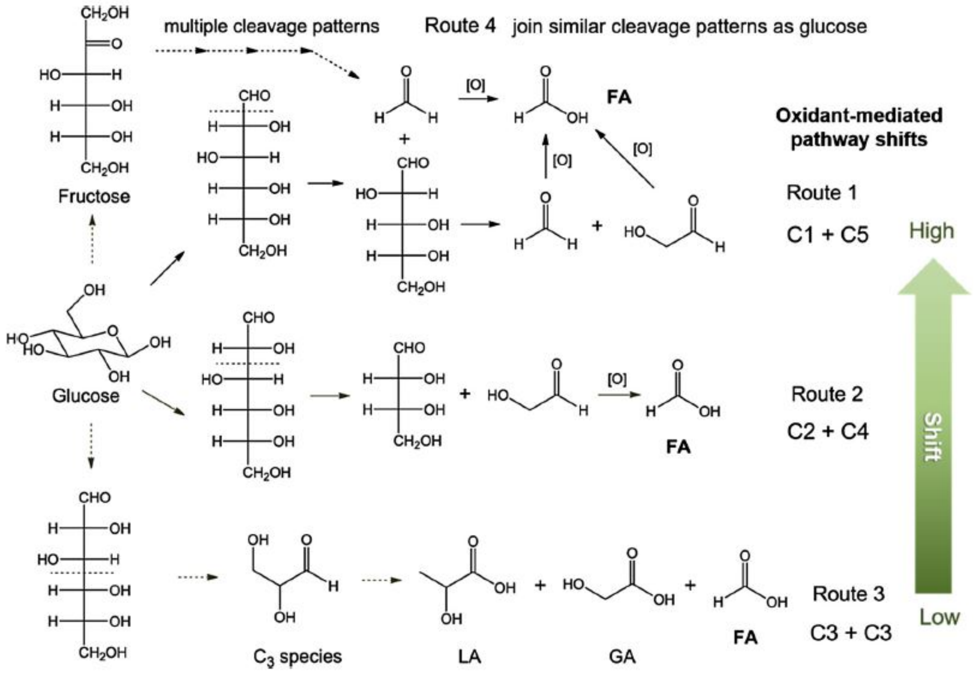


Figure 12: Wet oxidation reaction of glucose in room temperature [10]

Despite the seminal works, it must be noted that the excessive use of pressure and temperature in this oxidation process may cause deterioration of formic acid. For example, Calvo et al. acquired almost less than 15% formic acid yield at 300 bar and 400 °C conditions, although preparing a good quality hydrogen peroxide oxidant. The reaction lasted five minutes, however the oxidant strength and temperature caused formic acid degradation [116]. Demesa et al. also reported formic acid loss at temperatures higher than 200 °C when treating lignin without any intermediate substances [117]. Hence, the choice of resource material and catalyst limits the production. Therefore, great care must be taken to avoid undermining the production.

2.2.3.1.3 Catalytic Oxidation

Catalytic oxidation of biomass is achieved via a preferably acidic catalyst, solvent (mainly H_2O) and with a preferably oxygen oxidant at high pressures and moderate temperatures. Next to the lignocellulosic biomass, red and green algae [118], animal fats, starch and vegetable oils [119] have been used as raw material. By the reaction, six moles of formic acid can be obtained from a single mole of glucose [120]. The chemical relation is;

$$C_6H_{12}O_6 + 3\,O_2 \longrightarrow 6\,HCOOH \tag{7}$$

Because of formic acid formation via this process, the method is frequently referred as "Oxidation of biomass to formic acid" (OxFA), in the literature. By OxFA processes, not only glucose but also lignin, hemicellulose and cellulose have been reported to be oxidized with the presence of an intermediate. The catalysts used are classified under two main types; heteropolyacid (HPA) and vanadium based acids.

Heteropolyacids are strong acidic substances that exhibit redox properties [121]. In major studies run by Wasserscheid et al., Keggin type polyoxometalate catalysts ($H_5PV_2Mo_{10}O_{40}$) have been experimented for the oxidation of cellulose and glucose, at temperatures less than 100 °C with oxygen at 30 bars. Formic acid with 1% and 50 % yields were formed at the end of day-long procedures. The same group also converted lignin and hemicellulose with 14% and 33% yields, respectively. In order to enhance formic acid conversions, they introduced para-Toluenesulfonic Acid (p-TSA) based solvents at 90 °C and 30 bars. It paid off well as the results, oxidation of lignocellulosic biomass showed the doubling of formic acid yield levels and raising as high as 31% [122].

Later, Li et al. conducted the same experiments at higher temperatures (170 °C) and obtained 35% yield from cellulose [123]. Zhang et al. achieved 68% formic acid yield from cellulose at a higher temperature of 180 °C and relatively low pressure of 6 bar, with the presence of phosphovanadomolybdic acid ($H_4PVMo_{11}O_{40}$) [124] [125] .

Highest FA yield was obtained by Reichert et al., by using polyoxometalate (HPA-5, $H_8PV_5Mo_7O_{40}$) as a catalyst in the treatment of glucose, at 90 °C under 20 bar oxygen gas. 85% FA purity was achieved in a biphasic system [126].

Vanadyl sulfate ($VOSO_4$), Sodium metavanadate ($NaVO_3$) are two common types of vanadium based catalysts. Having a high melting point (630 °C [127]) assures that the substance remains in solid state, throughout the process. In this case, it can be defined as a heterogeneous catalyst, where the product(s) and the reactants are in liquid state.
In the literature, combination of $NaVO_3$ and H_2SO_4 have been reported to be increasing the performance of the process. Wang et al. demonstrated this positive aspect by introducing 0.7 wt% sulfuric acid at 160 °C and 30 bar oxygen. Relatively high 68.2 % FA yield was formed after an hour process [128].

Formic acid yield was increased even more by adding methanol or ethanol into the vanadyl sulfate based catalyzed system, which inhibited side formation of CO_2. With the addition of methanol, the FA yield from glucose increased to 75.0% at 140 °C and under 20 bar oxygen, with a reaction time of 3 hours. The same group obtained 70% yield when ethanol was used at 160 °C and 20 bar, for five hours [129].

Dorothea et al. state that OxFA systems suffer from limited FA yields below 70%, in monophasic aqueous systems [130]. From many studies in the literature, it is observed that purity and residence time are affiliated with each other in this method. Although the improvements explained above have been obtained, high formic acid yields are only achieved by long duration processes. For large scale operations, day(s) lasting processes are not feasible due to requirement of large volume reactors. Intuitively, in order to meet the production targets, reactor size is expected to be multiple times larger than processes which use less time for production to produce the same amount of material. Recently, vanadium based systems became promising. However, they suffer from high material costs.

2.2.3.2 Formic Acid Production via CO_2 Utilization

Another way of producing formic acid is through the reduction reactions of carbon dioxide. Reducing carbon dioxide levels and converting it to valuable chemicals with an environmentally friendly method is more desirable than industrial solutions.

2.2.3.2.1 Catalytic Hydrogenation

Catalytic reduction (also known as chemical reduction) of carbon dioxide is the most promising operation studied among other carbon dioxide utilization methods. Hydrogenation of carbon dioxide has already been used for methanol production. Therefore, theoretical information was already available.
Basically, direct hydrogenation of carbon dioxide with hydrogen at 50-130 °C and high pressures [131], depending on the catalyst, results in formic acid formation according to the reaction below;

$$CO_2 + H_2 \longleftrightarrow HCOOH \tag{8}$$

The reaction is exothermic. Hence, according to the Le Chatelier's principle, increasing the reaction temperature would move the reaction to the reactants side [132]. Then, heat is only required to achieve activation energy. High pressure is required to maintain reactions with both gaseous reactants.

In order to enhance yield and selectivity of the production, homogeneous and heterogeneous catalysts have been used, along side with the reaction. Inoue et al. demonstrated the first homogeneous hydrogenation reaction via Wilkinson Rhodium based catalyst, $RhCl(PPh_3)_3$, in 1976 [56]. Currently, experiments are being run mainly on ruthenium and rhodium based homogeneous catalysts [131], after trying other materials. This particular type of intermediate has often being modeled in the literature. An example process demonstrated by Perez-Fortes et al. has been shown in Figure 13.

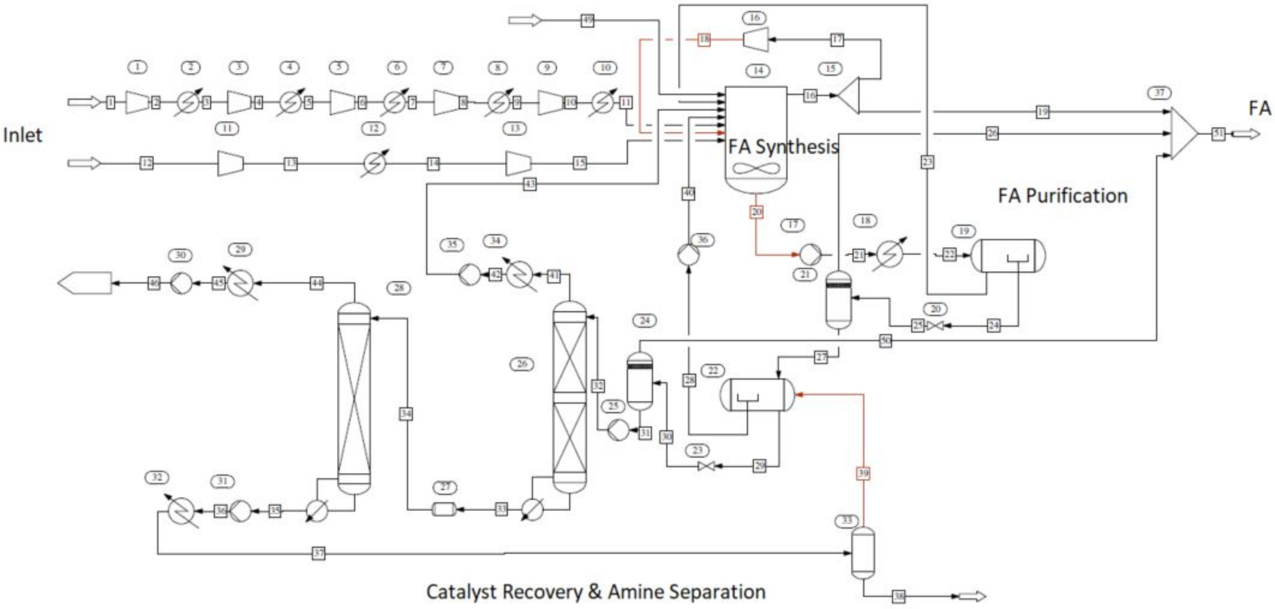


Figure 13: CO_2 hydrogenation via homogeneous catalyst [11]

However, ruthenium and rhodium based catalysts suffer from high costs and separation difficulties (see Figure 13). Using Triethylamine (NEt_3) as a solvent next to the catalyst results in formic acid-amine adduct as the product. Catalyst's high activity advantage turns into a practical disadvantage because the necessity for adduct separation and catalyst recovery. Additional separation steps such as extraction, distillation or reactive distillation are required to gain back the valuable intermediate. But still some is lost along the procedure. These energy intensive steps add up to the operational and capital cost.

In 1935, Farlow and Adkins conducted the first experiment with a heterogeneous raney nickel catalyst. They operated at 80 °C accomplishing 55% yield after one hour [131]. Preti et al. used gold/titanium oxide (Au/TiO_2) with triethylamine base at 130 bar and 40 °C obtaining 83% yield. The catalyst was reported to be stable for 37 days. However, gold particles observed to be losing their activity when not supported. Similarly, many experiments have been run with different support materials. Among them, gold/aluminum oxide (Au/Al_2O_3) showed the best performance with high hydrogen dissociation. Ruthenium based catalysts (Ru/TiO_2) supported with alkali salts ($NaHCO_3$, $NaOH$, KOH) utilized at 100 °C, under 20 bar H_2 and supported palladium (Pd) catalysts (Pd/TiO_2) showed good activity [8].

Heterogeneous catalysts are favored due to their many advantages. Firstly, they can be handled easier, as they are thermally stable. This also ensures their longevity which can be understood from the number of experiments run with a single batch of catalysts in the literature. By definition, heterogeneous catalysts are in different physical state than the reactants. This difference allows the catalysts to be separated straightforwardly; for example by filtration [133], since they are in solid form [134]. This practicality makes them the first candidates to be widely used in the industry.

Unfortunately, heterogeneous catalysts come with a drawback. Their active area is limited to the surface only and once it is saturated with the reactant molecules the process cannot proceed, causing limited molecule interaction with the reactants. Therefore, heterogeneous catalysts suffer from mass transfer limitations, preventing higher selectivity and yield.

2.2.3.2.2 Photocatalytic Reduction of CO_2

Photocatalysis reaction occurs by the absorption of light into the surface of the photocatalyst which is usually a semiconductor. Photocatalyst provides the required activation energy for the electrochemical cells inside. The electrons absorbed from the light source are transported from low energy valence band (VB) of the semiconductor to the high energy conductive band of the electrochemical cell through band gap [8]. The demonstration of the photoelectrochemical cell is shown in Figure 14.

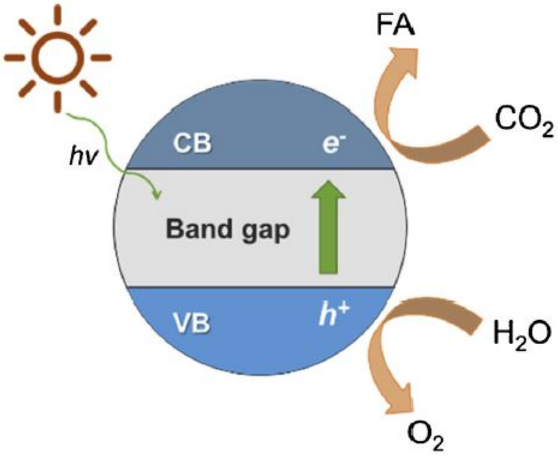


Figure 14: Photocatalysis of CO_2 [8]

Various materials such as GaP, InP, CdTe, Si have been used as p-type semiconductors. Ruthenium based homogeneous catalysts are also implemented to increase selectivity and faradaic efficiency. Currently, Cu and TiO_2 based catalysts and their combinations show promising results, in addition to their abundance and cheapness [135]. Despite the improvements over the years, this method has not been selected for industrial applications due to low selectivity in water. The practical feasibility of the method is also challenging.

2.2.3.2.3 Electrochemical Catalysis

An electrochemical cell consists of two electrodes, anode and cathode, separated by an electrolyte layer, material that allows only charged molecules to permeate [136]. The cell structure can be seen in Figure 15.

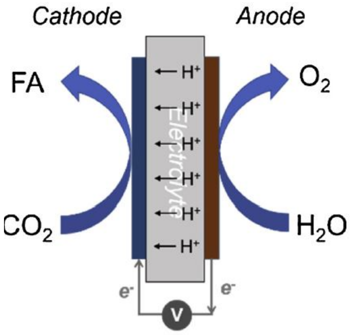


Figure 15: Electrochemical reduction of CO_2 [8]

Half-cell equations [90] are;

- Anode Side ;

$$2\,OH^- \longrightarrow \frac{1}{2}\,O_2 + H_2O + 2\,e^- \tag{9}$$

- Cathode Side ;

$$CO_2 + 2\,H^+ + 2\,e^- \longrightarrow HCOOH \tag{10}$$

For electrodes; rhodium based $Rh(diphos)_2Cl$, was the first developed homogeneous, metal complex catalyst [137]. Approximately 42% current efficiency was obtained. Iridium was also utilized as catalyst. However, ruthenium performed better at efficiency, catalytic activity and selectivity [4].
Metal catalysts containing palladium (Pd) [138], tin (Sn), mercury(Hg), indium (In), cadmium (Cd) have been tested. Moreover, Pd and Pb elements gave almost 100% faradaic (current) efficiency [139]. In and Hg were also used, 80% efficiency was obtained [140] [141]. Combined configurations of heterogeneous metal electrode catalysts and electrolytes is shown in Figure 16 below.

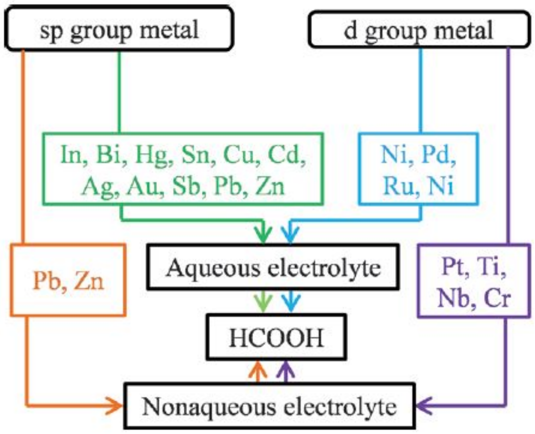


Figure 16: Metal electrodes and electrolytes used in electrochemical reduction of CO_2 [4]

Despite being highly common, metal catalysts require large electric potentials to prevent formation of unwanted CO_2^- anion [4]. Different materials have been searched for lower requirements. Aydin et al. prepared metal-free (heterogenous) catalyst with two carbon based polymers, called as polypyrrole (PPy) and polyaniline (PAN), to promote electrochemical reduction of CO_2 into formic acid at room temperatures and varying pressures. PPy electrodes showed the best conversion at 20 bars, with 0.249 mM formic acid after five hours [142].

Electrolytes are classified whether they are formed as a solution (see Figure 16). Aqueous electrolyte solutions, reported to be increasing formic acid production by dissolving HCO_3^- and CO_3^{2-} ions and supply stable ion conductivity [143] [144][145]. Potassium bicarbonate ($KHCO_3$) electrolyte with copper [146][147] and palladium [148] based electrodes are few examples. On the other hand, nonaqueous electrolytes, such as potassium hydroxide are used for increasing CO_2 solubility and decreasing hydrogen formation. New electrolytes consist of ionic liquids [149] and liquid salts additionally reported high conductivity. Therefore, they seem to be promising for future development.

Compared to biomass, there are no by-products reported in carbon dioxide route, besides the substances formed from catalyst or other intermediate degradation. Therefore, only formic acid (or formic acid adduct) is obtained from the process, in use of heterogeneous catalysts and does not require complex separation steps. Conventional purification and catalyst (or solvent) recovery steps would be sufficient. However, the current intermediates are derived from expensive elements. Economical feasibility of this route becomes worse in large production capacities due to material requirements and complexity in production. Additionally, there are still uncertainties in operational (temperature and pressure) cost requirements due to limited practical work in this method.

2.2.4 Reactor Types

The reactor is a vital component of the plant where controlled chemical reaction(s) take place. In every reactor hosting a reaction, a catalyst is present to boost the reaction in all manners, therefore they are also called as catalytic reactors. There are several factors in the classification of reactors. Those are;

- Size
- Operation scenario, continuous or batch, under steady state or transient (dynamic) condition
- The physical state of the substances within.

Depending on size, laboratory reactors are small scaled catalytic reactors, used for experimenting and monitoring reaction kinetics, yield, selectivity or any other desired outputs. On the other hand, industrial reactors, as its name signifies, are built for chemical processes on plant sites.

In this project, formic acid production will be demonstrated on industrial levels. Therefore only industrial reactors are taken into account for the present literature survey. Classification of industrial reactors are given in Figure 17.

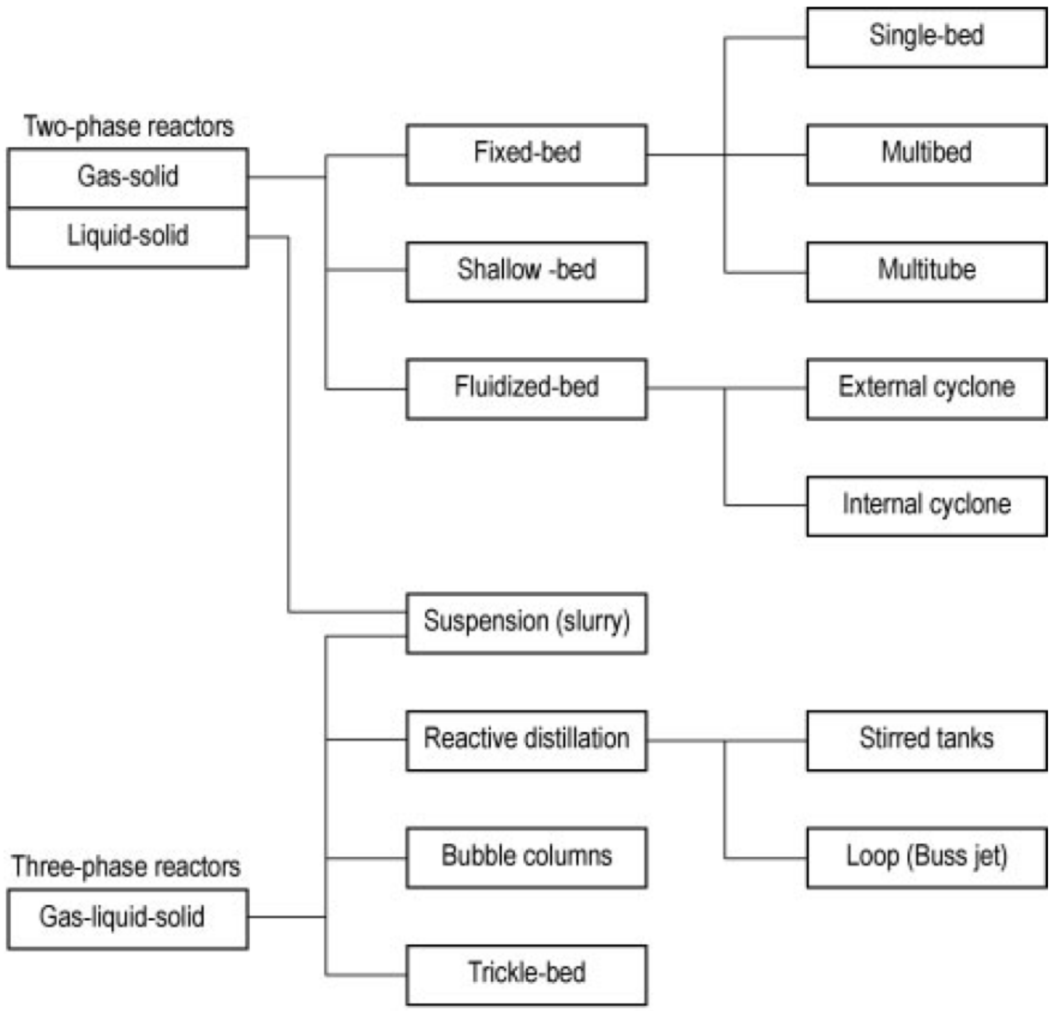


Figure 17: Classification of industrial catalytic reactors [7]

Physical state dependency on reactor selection is quite simple as seen from Figure 17. In industrial processes, existence of liquid-vapor mixture is inevitable, since homogeneous catalysts are in the same phase with the mixture content. Nonetheless, heterogeneous catalysts are employed as well, because of their practical superiority. Therefore, solid state catalysts must be considered.

2.2.4.1 Fixed Bed Reactor

Fixed bed reactors are suited for heterogeneous catalyst supported gaseous phase reactions.

The shape of the catalysts determine the catalyst bed configuration. The shape of catalysts are determined by the heat source, mass transfer limitations and pressure distribution along the system. However, if various shaped (sphere, cylinder etc.) catalysts are present, then randomly packed beds can be equipped. Different types of catalyst bed configurations are illustrated in Figure 18.

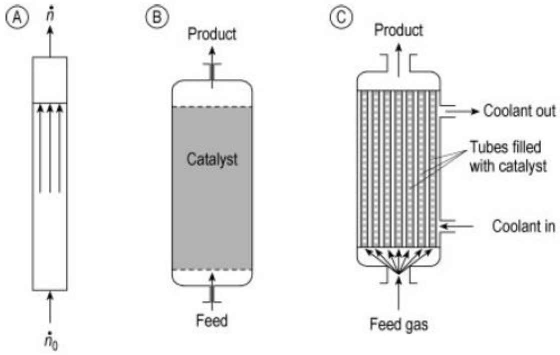


Figure 18: Fixed bed reactor schemes: A) Tubular fixed bed reactor, B) Adiabatic fixed-bed reactor, C) Multitube fixed-bed reactor [7]

Heat source of the reactor is an important parameter for the configuration of the reactor. Exothermic reactions allow the options for adiabatic operation where the heat dissipation of the exothermic reaction runs the fixed bed reactor. This selection is applicable for operations at high temperatures and low residence times. For this choice, a short but wide shallow bed can be mounted. However, the heat amounts, temperature levels, limit the activity of the production. In order to overcome thermal limitations, multistage reactors with interstage heat exchangers have been introduced to demonstrate equal heating and cooling for the reactor equipment.

In non-adiabatic reactors, heating and cooling is supplied externally through the reactor walls. In isothermal reactors, heat is provided regularly and temperature distribution along the reactor volume is satisfactory. For example, multitubular reactor (shown in Figure 18C) allows easy catalyst loading. Therefore, multitubular configuration can be used for temperature sensitive and highly exothermic applications.

2.2.4.2 Fluidized Bed Reactor

Fluidized bed reactors are equipped for operations where gaseous explosions take place or catalyst degrades quickly. Catalyst beds can be located inside the reactor or can be mounted side (so called integrated cyclones) of the reactor as seen in Figure 19.

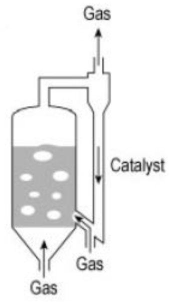


Figure 19: Fluidized-bed reactor with catalyst recirculation [7]

Catalyst particles are fed and carried along the equipment in a fluidized state by an upstream of reactants which are in liquid or gaseous state. The process is dictated by flow rates of the fluids which is a limitation in this case. On the other hand, the direct contact between the inlet stream and accelerator substance provide good contact, thus high chemical activity. The fluid flow distribution in fluidized bed reactor is accomplished by perforated plates, nozzles or bubble caps placed at the bottom of reactor equipment.

Fluidized bed reactors suffer from expensive catalyst separation and purification processes because of additional cyclone and filter requirements, despite the good quality in heat and mass transfer mechanisms. The catalyst still remains inside the product flow must be separated right before reactor outlet and returned to the catalyst bed for the next batch. Moreover, the high flow velocities must be avoided for possible erosion of the physical structure.

2.2.4.3 Slurry Reactor

Slurry reactors equipped to achieve chemical interactions between solid catalyst and gas particles which are dissolved in a liquid. Hence, the catalyst particles must be small ($<200\mu m$). Slurry reactors are divided into fixed bed or suspension reactors, depending on the catalyst bed configuration.

Fixed bed reactors have trickle bed and bubble flow configurations, based on reactant flow direction [150]. In trickle bed arrangement, the gas containing liquid flows downwards through the catalyst bed. Catalyst contact is assured by countercurrent or concurrent flows.
Trickle bed configuration shows no signs of difficulty in catalyst separation. Therefore, intermediate recovery is satisfactory. Moreover, chemical interactions can be carried out quickly, without requiring much energy due to the natural downflow of the materials. However, this speed may not be favored throughout the reactor and in some cases it may be partially insufficient.

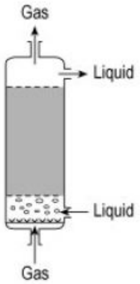


Figure 20: Packed bubble column or slurry reactor [7]

Bubble-flow reactors are fed from the bottom section. Inlet stream proceeds through reactor via an upstream flow, as shown in Figure 20. Bubble flow configuration is preferred over fixed bed, due to high heat and mass transfers and ability to work at low flow speeds. The flow pattern can be set by perforated plates, tubes or nozzles. The catalyst can be supplied either internally with a catalyst bed built inside or externally by ventury jet tubes.

Slurry reactors provide good and homogeneous chemical activity, temperature control at reasonable operational and costs, therefore being used in numerous industrial applications.

2.2.4.4 Reactive Distillation

The combination of reactor and distillation column allows reaction and separation processes simultaneously. The chemical conversion occurs inside the non-conventional equipment volume. Then the product substance with the higher tendency to evaporate is removed from the top of the reactor by fractional distillation.

Any possible unwanted side reactions due to excess amount of product or reactant can be avoided due to quick separation. The process suffers from mass and heat transfer limitations due to different types of chemical mechanisms present. Therefore, their combined kinetics must be investigated together [151].

2.2.5 Thermodynamic Models

First two steps in modelling chemical process by a simulation package program are component and method definition. Components can be easily selected from the databank. On the other hand, method has to be chosen according to multiple factors and it is a crucial step for an engineer. Method selection is the determination of the most suitable thermodynamic model for the simulation. Selection relies on chemical classification and structure of the components, operation temperature, operation pressure and whether the process is assumed as ideal. Simulation results close to the real-life experiments can only be achieved by implementing the correct thermodynamic properties.

Determination of thermodynamic properties consists of [152];

- Equation of state (EOS),

- Activity coefficient model (non-ideal, multi-component liquid phase),
- Enthalpy model.

Additional parameters, K-value and vapor pressure, are calculated through these properties. In present study, only non-ideal mixture/component properties will be focused and explained. Assumption reason is to construct a realistic system.

2.2.5.1 Equation of State

Equation of state is the combination of thermodynamical and mathematical relation between temperature, pressure and volume (or specific volume) for substances also for mixtures.

- Cubic EoS;
  - Peng-Robinson (PR) : Applied for non-ideal, two phase (vapor-liquid), mixtures with non-polar substances. It is suitable for all temperatures and pressures for mixtures containing hydrocarbons [153].
  - Soave-Redlich-Kwong (SRK): First Redlich and Kwong derived an equation of state working great for non-ideal liquid mixtures, Soave introduced a new parameter "accentric factor", making vapor phase predictions of hydrocarbons far more accurate. It can be used for non ideal vapor-liquid mixtures which contain non-polar components [153].
- Viral EoS; Valid for gases at low density and low pressure [152].
  - Hayden-O'Connell : It is well developed for both ideal and non-ideal, vapor mixtures at low pressure.

2.2.5.2 Activity Coefficient

Activity coefficient is factor for liquid mixtures to measure their deviation from ideal conditions.

- Non-Random Two Liquids (NRTL) : It is an improvement over Wilson and Van Laar activity coefficients. It can be used both for liquid-liquid and vapor-liquid mixtures. Solves azeotropic mixtures (for example, formic acid-water) very well.
- Universal Quasi Chemical (UNIQUAC) : It is widely applied for non-ideal liquid solutions containing non-polar and/or polar components. Two parameters (q and r) must be entered before calculations.
- UNIQUAC Functional-group Activity Coefficients (UNIFAC) : Improved version of UNIQUAC. It is practically advantageous to use if the binary interaction parameters are not available for aqueous mixtures with no polar compounds.

2.2.5.3 Enthalpy Model

Required for energy balance calculations. Excess enthalpy models are coupled to the EoS to demonstrate enthalpy values as excess functions for non-ideal systems [152].

The next step after completing the literature review is to establish a formic acid production system with the information obtained.

3 Basis of Design of Renewable Formic Acid Production Plant

Research and evaluation of the current or developing technologies is followed by definition of limits,goals, methods and logistical decisions prior the modelling of the plant.

3.1 Basis of Design

Basis of design (BOD) sheet is an instruction manual prepared by engineers alongside the customer's requests. It shows how the process will be handled [154]. The fundamentals that should be involved in the document are explained one by one below

3.1.1 Capacity & Operation Scenario

According to Douglas [155], first step of the design procedure is to determine the operation scenario based on production capacity which can be done continuously or in batches. Two different annual formic acid production capacity levels, 10 kton and 100 kton are set, in order to measure and observe the effect of capacity on operational capability.

This capacity will be the designated target of the plant, whose effects will be investigated further. The capacity amount is set equal to the BASF plant, the largest plant built for the formic acid synthesis, capacity can be satisfied.

The operation scenario depends on capacity as it follows;

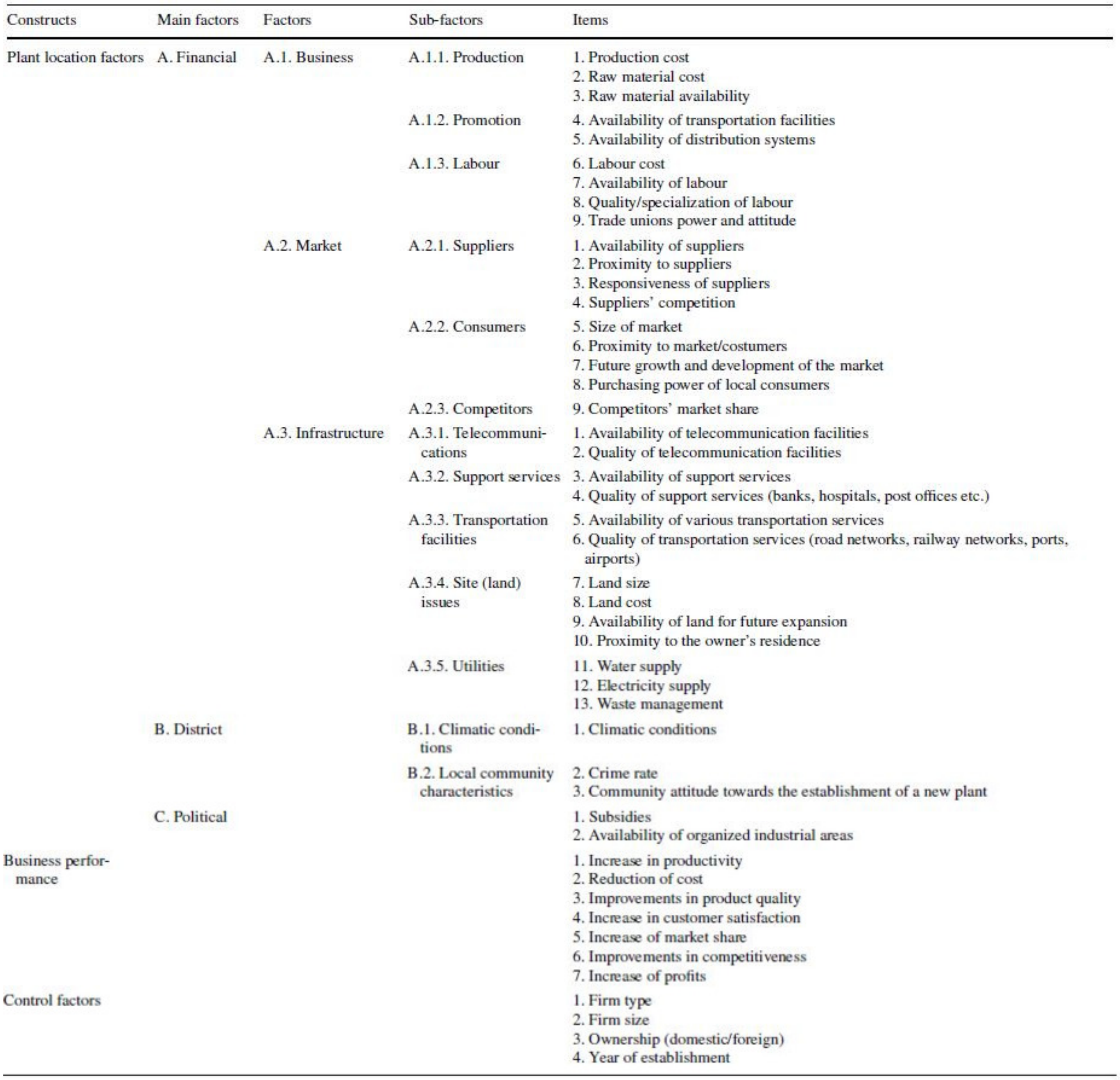
- For production rates higher than 5,000 tons per year, batch production scenario is not feasible operationally in order to reach production targets [155]. Also for large scale operations, plant start and stop process get cumbersome (immediate start is not possible) and takes more energy to start-up components working at high temperatures.
- In addition, the requirement of the plant is neither season nor specification dependent. Therefore, a batch process would not be advisable.

Therefore the plant will operate continuously. It is assumed that the plant will operate 360 days per year, remaining 5 days and 0.25 hours are left for maintenance and repairs. Meaning that, 8640 hours of operation every year.

3.1.2 Plant Location

After deciding on the plant capacity, it must be decided where the production will take place. The selection can be gathered around on three main factors; 1) Financial, 2) District and 3) Political [14]. All factors and their parameters are given in Table 4. In this study, only financial parameters will be taken into account.

Table 4: Location factors [14]



Constructs	Main factors	Factors	Sub-factors	Items
Plant location factors	A. Financial	A.1. Business	A.1.1. Production	1. Production cost 2. Raw material cost 3. Raw material availability
			A.1.2. Promotion	4. Availability of transportation facilities 5. Availability of distribution systems
			A.1.3. Labour	6. Labour cost 7. Availability of labour 8. Quality/specialization of labour 9. Trade unions power and attitude
		A.2. Market	A.2.1. Suppliers	1. Availability of suppliers 2. Proximity to suppliers 3. Responsiveness of suppliers 4. Suppliers' competition
			A.2.2. Consumers	5. Size of market 6. Proximity to market/costumers 7. Future growth and development of the market 8. Purchasing power of local consumers
			A.2.3. Competitors	9. Competitors' market share
		A.3. Infrastructure	A.3.1. Telecommunications	1. Availability of telecommunication facilities 2. Quality of telecommunication facilities
			A.3.2. Support services	3. Availability of support services 4. Quality of support services (banks, hospitals, post offices etc.)
			A.3.3. Transportation facilities	5. Availability of various transportation services 6. Quality of transportation services (road networks, railway networks, ports, airports)
			A.3.4. Site (land) issues	7. Land size 8. Land cost 9. Availability of land for future expansion 10. Proximity to the owner's residence
			A.3.5. Utilities	11. Water supply 12. Electricity supply 13. Waste management
	B. District		B.1. Climatic conditions	1. Climatic conditions
			B.2. Local community characteristics	2. Crime rate 3. Community attitude towards the establishment of a new plant
	C. Political			1. Subsidies 2. Availability of organized industrial areas
Business performance				1. Increase in productivity 2. Reduction of cost 3. Improvements in product quality 4. Increase in customer satisfaction 5. Increase of market share 6. Improvements in competitiveness 7. Increase of profits
Control factors				1. Firm type 2. Firm size 3. Ownership (domestic/foreign) 4. Year of establishment

By the list on Table 4, Rotterdam Port is selected for the formic acid production plant because of its satisfaction on transportation facilities, distribution systems, labour availability and quality, the most important is the market availability and proximity. The study is aimed for Europe currently so, Rotterdam port, the largest and the smartest port in the continent [156], can provide the best resources for the parameters taken into consideration.

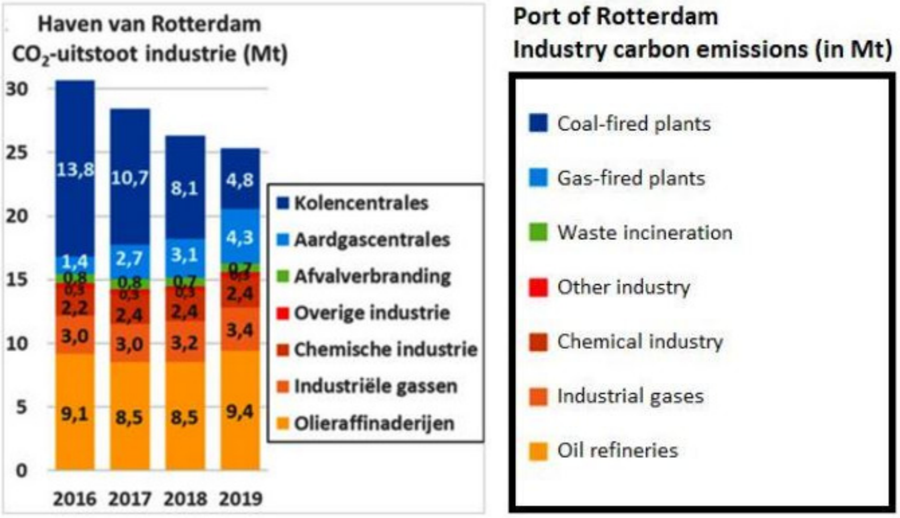


Figure 21: Rotterdam port carbon levels [12]

Another positive aspect of Rotterdam port is the carbon dioxide emission levels, as a matter of fact it is harmful for the environment indeed but it is a good resource. A press release from the Port states that, Rotterdam's industry have lowered their carbon emissions by 3.8 % but the refineries increased theirs [12]. From the Figure 21, the carbon emission levels of the industry is still high with approximately 25 million tonnes in 2019. Hence, these stationary sources will be a great source for the formic acid production via carbon dioxide.

3.1.3 Final Product Quality & Purpose

The quality of a chemical product varies according to the production stages and conditions. Likewise, this difference in quality plays a vital role in determining the processes in which the product can be used, and therefore the buyer range. The production capacity is shaped in line with this supply and demand. For this purpose, formic acid is available in the market with a purity of 85, 90, 95, 98, >99 percent. Highest purities are used in laboratories and chemical applications. The most common is stated to be 85% which can be used as fuel for power and transportation [93].

Since it has a wider range of customers, 85% pure formic acid is decided to be produced. The purity level chosen has economic benefits due to lower operation costs because of less energy intensive separation processes compared to higher purities.

The selected purity level is still sufficient for industrial use as fuel. Therefore, syngas production is the chosen purpose for the formic acid. Syngas is normally produced with a combination of endothermic steam reforming of methane (SRM) and exothermic water gas shift (WGS) reactions. By formic acid being fed to the SRM process, WGS reaction can be unnecessary. That is because formic acid decomposes into H_2 and CO_2 and required hydrogen:carbon monoxide ratio is satisfied within the SRM reaction. Where this ratio was

conventionally accomplished by WGS reaction. It is a promising feature due to high temperature requirements of water gas shift process [157].
After determining the production targets, quality and plant location, facilities have to be modeled and simulated in the process flowsheeting package program.

4 Model Design

Various methods by which formic acid can be produced from biomass and carbon dioxide are available in the literature. Among the methods, wet oxidation of glucose has been picked for the biomass route and catalytic hydrogenation is picked for carbon dioxide route. The reasoning is explained in Appendix 10

4.1 Process Design

Flowsheet design and simulation of the formic acid production methods chosen will be explained below. ASPEN Plus V8.8 process flowsheeting package program have been used for the simulations.

4.1.1 Targets & Assumptions

Designed flowsheets include, pre-treatment and glucose synthesis of lignocellulosic biomass, conversion of glucose to formic acid by wet oxidation, carbon dioxide capture from syngas by pre-combustion method and conversion of carbon dioxide to formic acid by hydrogenation. Formic acid storage and further processing of the product for fuel based purposes is not in the scope of the present thesis. Therefore, these have not been considered. Before starting to modelling some assumptions have made;

- Process is steady state.
- All vapor liquid mixtures are assumed to be non-ideal, this selection affects the choice of thermodynamic model in ASPEN method selection.
- All catalysts and other intermediate substances are ready for utilization, catalyst preparation procedures are neglected.
- Syngas for CO_2 supply is assumed to have a constant composition.
- Pre-treatment and carbon dioxide capture flowsheets are set up separately but outlet conditions of these processes have been entered to the formic acid synthesis flowsheets.
- All pumps and compressors have an isentropic efficiency of 0.75, assumption based on previous modellings in literature [93].

- After completing process modelling and obtaining the initial energy results, ASPEN Energy Analyzer suggested solutions to increase energy savings. The energy analyzer program offered usage of heat exchangers to transfer the excess heat of cooling processes to the process streams where heating is required. Therefore, excess heat within the systems is used to decrease energy consumption in every process. Instead of going through tedious design procedure of a heat exchanger for every two stream (one cold and one hot), two equipments and a heat stream is defined. A heater or cooler is placed where temperature change is required and a heat stream is used to transfer heat between equipments. Both types of equipment are designed separately, their cost and the cost of heat stream is also included in economic calculations.

4.1.2 Biomass Pre-Treatment & Glucose Synthesis in Present Study

In feedstock treatment, lignocellulosic biomass is processed through pre-treatment. Followed by glucose synthesis. The glucose formed then is purified by removing the solid content. A glucose water mixture is obtained and sent to formic acid synthesis process.

The first and the most important step of the modelling is the implementation of lignocellulosic biomass into ASPEN. Unfortunately, the organic content of the lignocellulosic structure is not available in the package program. Since it can not be defined from chemicals present in program's databanks, biomass raw feedstock is modelled as a non-conventional substance. It's enthalpy and specific heat values are calculated by HCOALGEN and DCOALIGT property methods in ASPEN Plus, respectively [158].

As stated in Section 2.1.1, lignocellulosic biomass mainly consists of cellulose, hemicellulose and lignin, which are also not defined specifically in ASPEN databanks. In standard conditions all three substances are in solid state [159]. Therefore, their type have to be defined as "Solid" in component definition tab. Hemicellulose is defined as Xylan, which is the main component of hemicellulose [159]. Lignin and cellulose are defined as themselves. However, in order to balance mass and energy, ASPEN needs several properties entered by hand in pure component properties tab. Manually defined properties are given below.

- Molecular weight, number of elements
- Solid enthalpy of formation
- Solid molar volume
- Solid heat capacity

After the component definition, the thermodynamic model has to be defined. Peng-Robinson thermodynamic model is selected due to its applicability for non-ideal mixtures and non-polar components. Also the chosen method is compatible for organic matter processing [33]. Simulation model can now be built. The flowsheet of the simulation can be seen in Figure 22

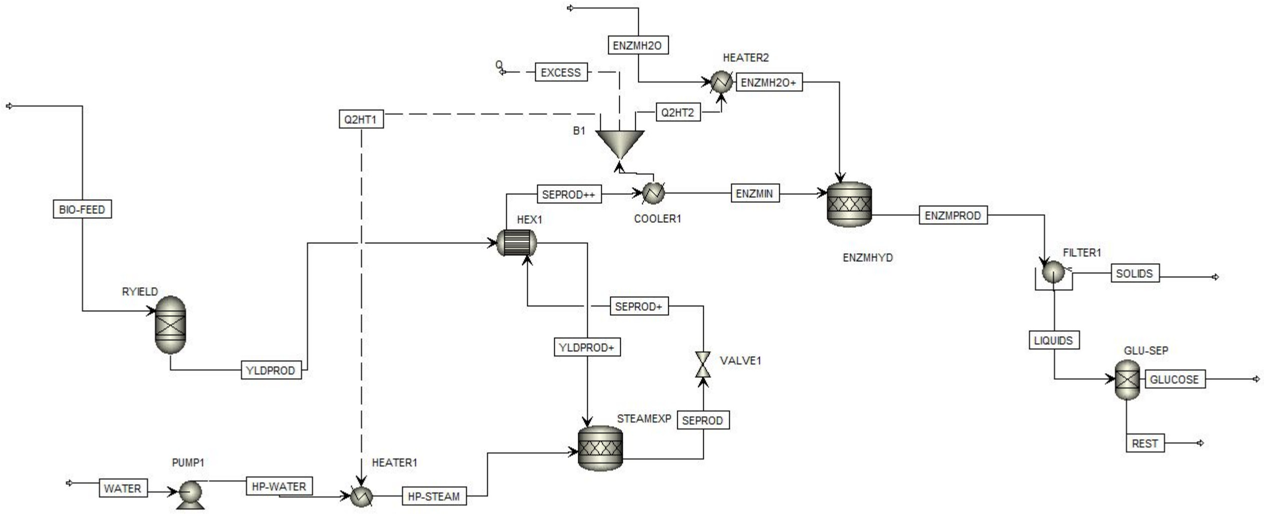


Figure 22: Process simulation of biomass pre-treatment and glucose synthesis

The pre-treatment flowsheet begins with the definition of lignocellulosic biomass into the simulation. For processing the raw material along the flowsheet, element composition of the biomass material is entered by hand to the BIO-FEED stream as non-conventional solid. ASPEN estimates its content by proximate and ultimate analysis. The explained process is only for defining the biomass raw material into the simulation environment. Compositions of cellulose and other organic content still must be defined into the flowsheet. RYIELD reactor is the only available equipment for this purpose. However, the wood pellet also contains ash. Since it does not react with any substance, it is assumed as an inert component therefore it has not been defined in the product stream.

After defining the raw feedstock, lignocellulosic biomass is heated up to 165 °C through a shell and tube heat exchanger (HEX1) in order to pre-heat the biomass material. The process is followed by the steam explosion via a pressure reactor. Biomass material with high pressure steam (160 °C, 6.5 bar), is exposed to 24 bar pressure at 224 °C. Pressure is then reduced back to the atmospheric levels. By the process, lignin matrix is ruptured and hemicellulose is liquefied. Due to selected temperature and pressure levels, cellulose and hemicellulose (xylan) are hydrolyzed to glucose and xylose [160], with conversion fractions of 4.4% and 84.6% [161], respectively.

The products of the steam explosion, then sent to the enzyme hydrolysis. Cellulase enzyme from Trichoderma reesei, is used as catalyst for the process. It includes three enzymes; endo-1,4-β-D-glucanase, exo-1,4-β-D-glucanase β-glucosidase for cellulose to glucose conversion [162]. Enzyme loading of 15 Filter Paper Unit (FPU) per gram of cellulose is a commonly used to achieve economically reasonable sugar yields from pre-treated biomass feedstock [163]. Here, cellulose is hydrolyzed, forming glucose at 60 °C. A fixed bed reactor is chosen for the process in order to ensure the contact between the solid cellulose and solid enzyme surfaces in an aqueous environment with water, resulting in a 75.8% glucose

yield. Under the reaction conditions indicated, the enzyme hydrolysis process takes 4 hours [161]. In order to satisfy the production rates (both 10 kton and 100 kton) and to achieve the most economically beneficial outcome, an economical analysis has been run. It is determined that, the configuration with 4 enzyme hydrolysis reactors is the most beneficial.
The temperature level is set by the performance of enzyme intermediate. Viikari et al. states that the FPU activity of the enzyme showed the highest activity and better thermal stability at 60 °C [164]. At higher temperatures, same group noticed inactivation of enzyme.

After the hydrolysis reaction, solid content is separated by a vacuum drum filter. Finally, xylose is removed from the rest of the stream by a separator tank. By the above process, a slurry mixture of glucose and water is obtained.

4.1.3 Conversion of Glucose to Formic Acid

Glucose from the pre-treatment flowsheet is converted to formic acid by wet oxidation. Glucose oxidation occurs by two separate ways via hydrogen peroxide or oxygen. After the formic acid synthesis, unreacted substances are recovered. Finally, the formic acid is distillated until the purity target is reached. In both designs Peng-Robinson thermodynamic model is selected. However, for non-ideal formic acid and water mixture, which forms an azeotrope, Non-Random Two Liquid - Hayden O'Connell (NRTL-HOC) method [91] is used for distillation columns.
Flowsheet of formic acid production with hydrogen peroxide is shown in Figure 23.

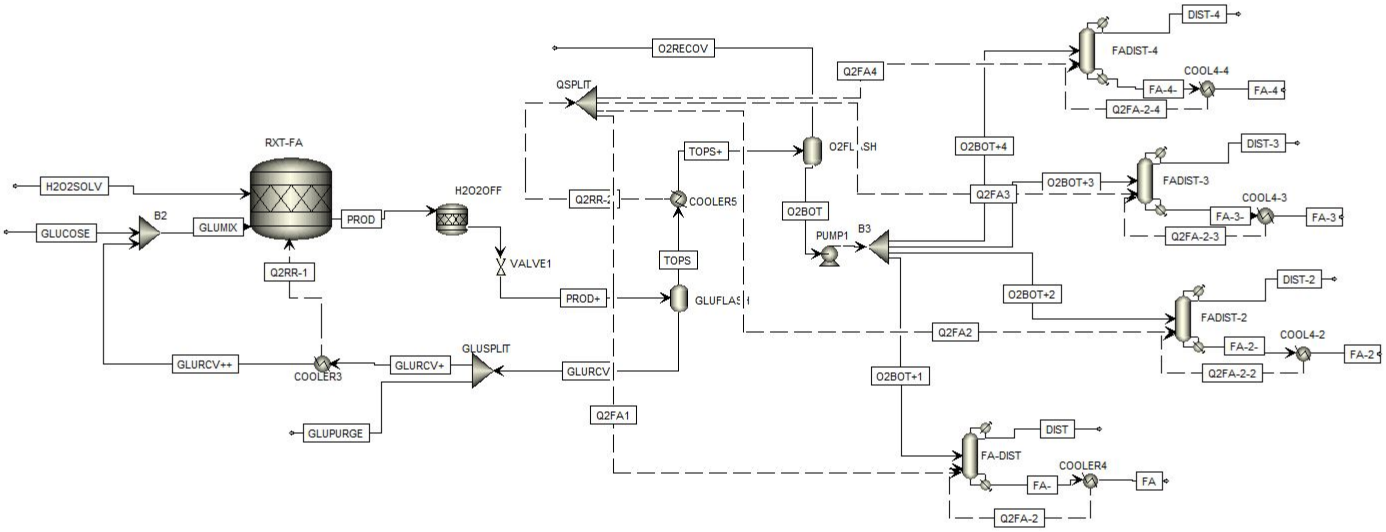


Figure 23: Process simulation of wet oxidation of glucose with hydrogen peroxide

The process directly begins with the oxidation of slurry glucose. Glucose is not pre-heated to reaction temperature in order to prevent glucose decomposition into hydroxymethylfurfural at temperatures above 200 °C [165]. Hydrogen peroxide used is a 30 wt.% water solution. Oxidation occurs at 250 °C and 31 bars within a slurry reactor. The specified reactor was chosen to provide homogeneous heat distribution and to ensure the contact between liquid and aqueous reactants and solid intermediates, KOH and NaOH. Excess amount of hydrogen peroxide is given to the reactor, which means that more than the stoichiometric requirement, in order to prevent dehydration of glucose, which may result in formation of 5-hydroxymethyl-2-furaldehyde (HMF) that easily forms acetic acid via oxidation. Glucose oxidation without hydrogen peroxide resulted only 24% formic acid yield [166]. By 120% hydrogen peroxide loading also with addition of 1.25M alkali catalysts such as KOH and NaOH, the yield is increased up to 69% [166]. Addition of NaOH prevents the decomposition of formic acid into carbon dioxide due to presence of hydrogen peroxide. It must be noted that, at the given reaction conditions, hydrogen peroxide decomposes. Normally, hydrogen peroxide decomposes into water and oxygen when reaching its boiling point at 150 °C. However, the effect of temperature greatly affects the reaction. An increase of 10 °C in temperature increases the rate of the decomposition 2.3 times [167]. Therefore, the remaining hydrogen peroxide is assumed to be converted into water and oxygen.

After the products exiting the reactor, un-reacted glucose is separated from the mixture. Due to high vaporization temperature, first, glucose is separated from rest of the product mix at 200 °C and atmospheric pressure by GLU-FLASH liquid outlet. Next, oxygen is separated with another flash tank operating at 20 °C. Finally, the remaining stream containing formic acid is sent to a configuration of 4 fractional distillation columns. The ideal number of distillation towers is determined by simulating the process with ASPEN Economic Analyzer, in order to obtain optimum economic result by increasing the equipment costs and reducing operation costs. Moreover, because the formic acid weight fraction is higher than 20%, extractive distillation or pressure swing adsorption is not necessary. In the end, formic acid with 85% purity is obtained as the final product.

The second method of wet oxidation of glucose, via oxygen, is shown in Figure 24

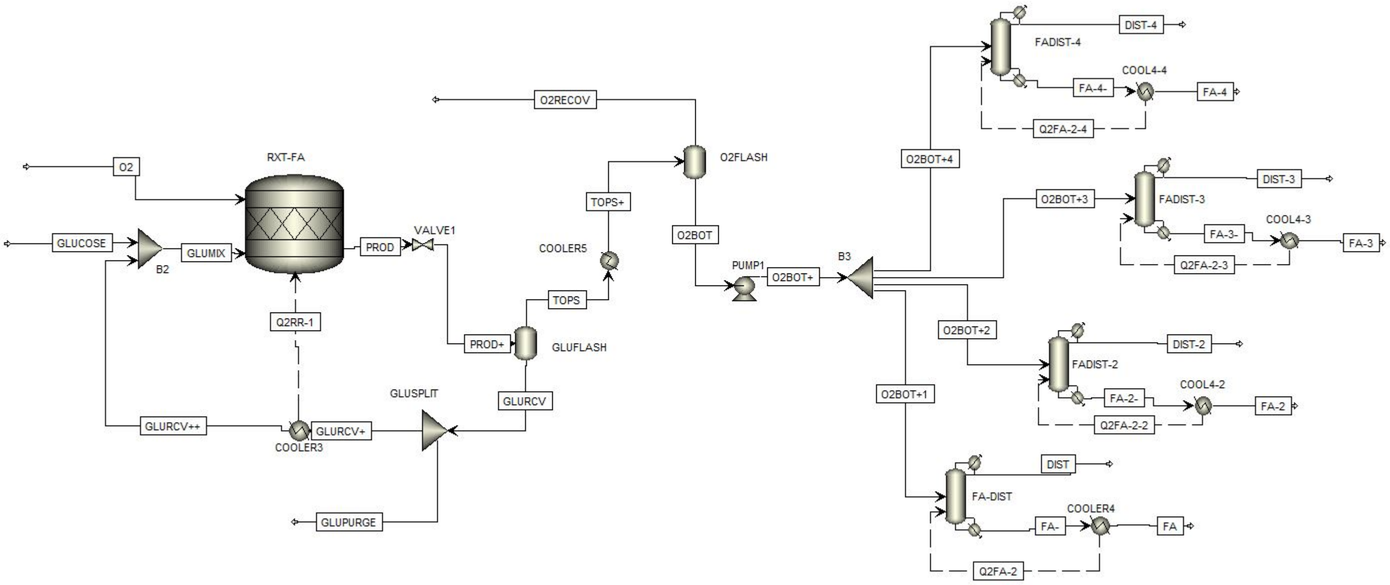


Figure 24: Process simulation of wet oxidation of glucose with oxygen

In the second wet oxidation process oxygen gas enters the reactor and reacts with slurry glucose at 200 °C and 33 bars [168]. Again, the glucose is not pre-treated to prevent glucose decomposition into HMF. [165]. By the addition of 0.67% ferric sulfate, 30wt.% yield level is obtained.

After the reaction, glucose is separated at 220 °C and 1 bar. Followed by oxygen separation at 25 °and 1 bar. After the oxygen separated, the remaining stream enters the fractional distillation columns. Finally, formic acid with 85 wt.% is obtained as the end product.

4.1.4 Carbon Dioxide Capture from Syngas with Pre-Combustion Method

The carbon dioxide to be used in hydrogenation reaction is acquired via absorption mechanism. Amines are frequently used in conventional applications. However, chemical solvents reacting with the source gas require additional separation processes. Since no perfect separation is possible, some amount of valuable intermediate is always lost. These technical and practical aspects can be avoided by utilization of physical solvents at high pressure and low temperature.

Selexol is a commonly used physical solvent in carbon dioxide absorption. However, Selexol is the commercial name of the glycol based solvent. Dimethyl ether of polyethylene glycol (DMEPEG) is used in the simulation as chemical equivalent [75].
DMEPEG has advantages over conventional chemical solvents such as;

- Working compatibility with H_2S and CO_2,
- Lower gas desorption duty

- Less corrosion
- Lower power consumption for solvent recovery and circulation

DMEPEG consists of polymer chain lengths of glycol ethers which make them a polar molecule and functions properly at a temperature range of 0-25 $^{\circ}C$ [88]. The structural affinity of DMEPEG with H_2S and CO_2 shows improved absorption which is important and one of the main reasons why physical solvents are drawing attention.

In order to represent the thermodynamical behavior of the physical solvent and taking the literature studies [169] into consideration, perturbed-chain statistical associating fluid theory (PC-SAFT) [169] has been selected in the program . DMEPEG data for vapor pressure, liquid density, heat capacity, viscosity, thermal conductivity is provided by Coastal Chemical [170]. Solubility data including binary interaction parameters between DMEPEG and selected components is provided by the studies of Xu et al [171]. Which showed similar results to the experimental carbon dioxide and hydrogen sulfide solubility data in physical solvent in various temperatures. Carbon capture flowsheet is shown below in Figure 25

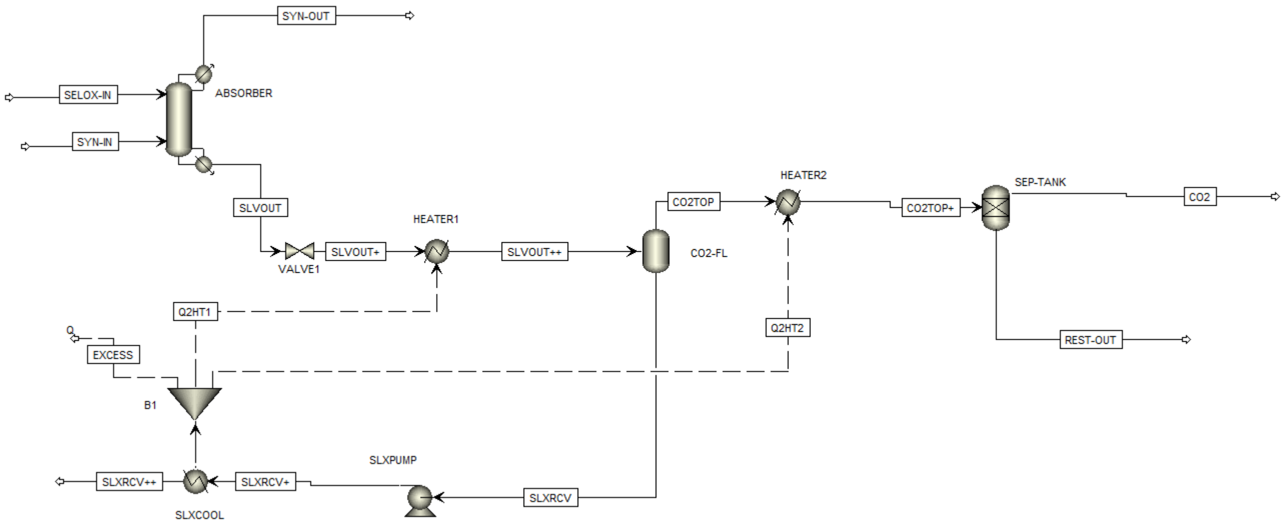


Figure 25: Process simulation of carbon capture via DMEPEG

The syngas from the gasification plant enters bottom of the absorber column. Since the syngas is received from an another source plant, its storage conditions are unknown. Therefore, it is assumed to be entering the absorber at 20 °C and 31.9 bar. The physical solvent at -1.2 $^{\circ}C$ and 31.9 bar enters from the top stage.

The absorber column, which consists of 4 stages, works at 31.9 bar. The CO_2 rich DMEPEG mixture from the bottom of the absorber column is sent to a flash tank, CO2-FL, separated at 6.75 $^{\circ}C$ and 1 bar. The CO_2 is then purified at SEP-TANK. As a result, 99.67 wt.% pure carbon dioxide is obtained.

4.1.5 Hydrogenation of Carbon Dioxide to Formic Acid

Conversion of the captured carbon dioxide into formic acid via hydrogenation, is shown in Figure 26

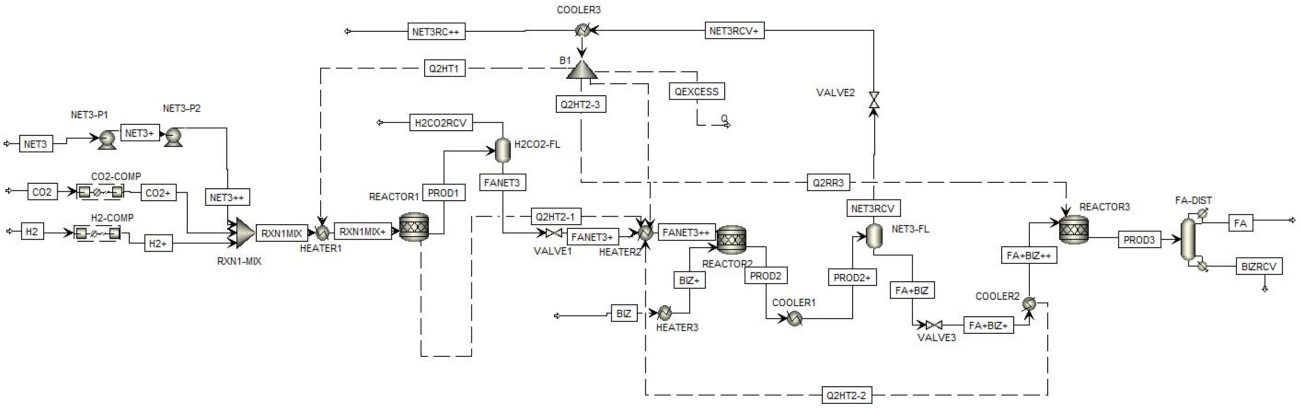


Figure 26: Process simulation of carbon dioxide hydrogenation

PC-scalar method is used in the simulation due to presence of non-ideal mixtures, both polar and non-polar substances and high pressure applications.
Carbon dioxide is pressurized up to 180 bars with a six stage compressor. Hydrogen in storage conditions is also pressurized to reaction conditions via three stage compressor. Triethylamine, which is an intermediate substance favoring the thermally endergonic and chemically unreactive hydrogenation reaction [131], reaches to 180 bar with two pumps. These streams are mixed, again heated to the reaction temperature and enter the first reactor. Hydrogenation of carbon dioxide occurs at 40 °C and 180 bars. High temperature and pressure is required to function the heterogeneous Au/TiO_2 (commercially known as AUROlite) catalyst. Use of homogeneous catalyst is avoided because of the separation drawbacks and possible decomposition to CO_2, H_2 and Net_3 [172]. The reaction lasts for 72 hours and to ensure the annual production requirements, in the reference article, a system with 74 catalytic reactors is designed [173]. Therefore, in the initial design of this study, 72 catalytic reactors are equipped. Since all three phases are present, bubble column suspended bed reactors are preferred because of high pressure and continuous operation [174].

After the REACTOR1, the un-reacted hydrogen and carbon dioxide gases are recovered by flash tank $H2CO2-FL$ at 175 bar and 40 °C. Formic acid - amine adduct is the main product of the hydrogenation reaction. Adduct is a molecular combination of two separate compounds forming a new chemical structure, which is not defined in ASPEN Plus. Moreover, formed adduct has different structure therefore different properties and no specific experimental data can be found in the literature. Hence, those properties have to be numerically estimated. This is done by group contribution methods.

In the literature, group contribution methods are defined as package of equations calculating thermal properties of a substance according to its chemical structural groups. Each method has different set of structural group. Because of its simplicity and compatibility of structural groups to the used chemicals in the flowsheet, Joback method is used. Via Joback method the following properties are estimated;

- Critical temperature, pressure, volume
- Boiling and freezing temperatures
- Enthalpy of formation
- Gibbs energy of formation
- Enthalpy of vaporization
- Enthalpy of fusion
- Molecular weight
- Viscosity

Amine adduct forms an azeotrope, hence a satisfactory separation is energy intensive. In reference article, amine adduct is decomposed and separated via reactive distillation and Butylimidazole (BIZ) used as solvent. However there is no T-x or x-y data of the amine adduct and BIZ mixture is available but the reaction equation is known. Therefore, in order to define the process, RSTOIC reactor is used. The second reactor runs at 178 $°C$ and 1 bar, BIZ decomposes the amine adduct with an amine shift reaction, forming butylimidazole - formic acid adduct. Properties of BIZ and BIZ-formic acid adduct are also estimated with the same group contribution method. After the second reactor, Net_3 is separated by NET3-FL flash tank at 110 °C and 5.6 bar. The remaining BIZ adduct decomposed to formic acid and BIZ in third and the last reactor at 97 °C and 0.2 bar. Formic acid and BIZ mixture does not form an azeotrope. Hence, it is separated with a vacuum distillation column at 0.2 bar. In the end, 85 wt.% pure formic acid is obtained.

4.2 Stoichiometric Calculations of the Above Method

The required inlet amounts must be determined for the initial input estimation. Calculation is basically done by balancing the reaction equations and implementing yield values of the selected production routes.

Mass calculations have been advanced from the end to the beginning. Since the annual product amount from the 360 days of operation is known, hourly formic acid production rates can be calculated by simple unit conversion.

4.2.1 Biomass to Formic Acid Conversion Calculations

In wet oxidation of glucose with hydrogen peroxide, one glucose molecule and six molecules of hydrogen peroxide produce six formic acid and six water molecules (Section 2.2.3.1.2), as shown in Equation 5

An alternative route is the wet oxidation of biomass via oxygen gas, one molecule of glucose with 3 oxygen molecules result in six formic acid molecules (Section 2.2.3.1.2), the reaction is given in Equation 6. By the chemical reaction equations, theoretical amount of glucose requirement is calculated. However, glucose is planned to be obtained via pre-treatment processes. From the glucose amount, biomass inlet is estimated.

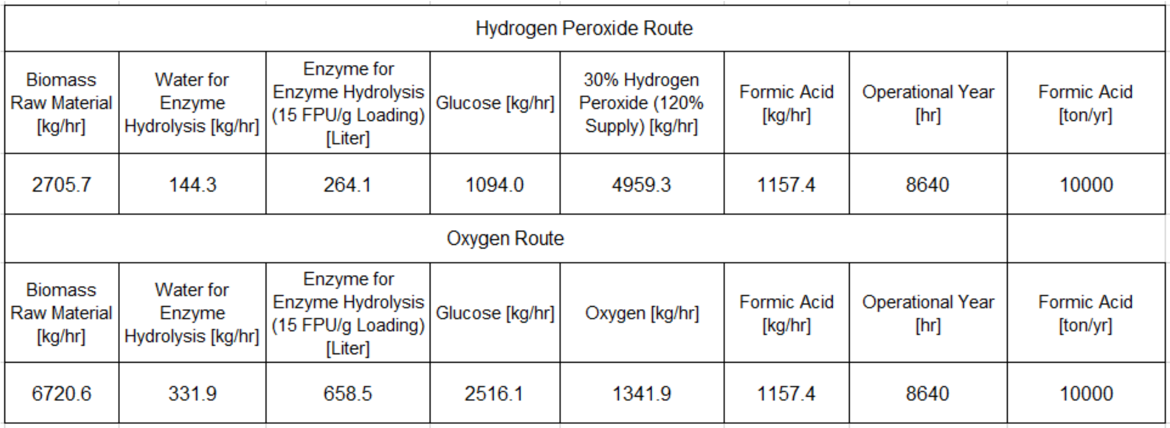
In the last pre-treatment operation, enzyme hydrolysis, 75.8% of the organic content of the lignocellulosic biomass is converted into glucose. By this estimation, required cellulose amount is estimated. Steam explosion selectivity is taken as 1, as the whole batch of organic material is exposed to high pressure and temperature.

However, the raw material entering to the very beginning of the formic acid synthesis process is wood based products. The required amount of raw feedstock is simply calculated by their cellulose content. Pure pine based wood pellet [175] is chosen for supply due to its high cellulose content and abundance.

The enzyme amount is calculated based on its loading rate and volumetric activity. Cellulase enzyme has activity of 65 FPU/mL [176], with 15 FPU/g-Cellulose loading, 15/65=0.23 mL-Cellulase/g-Cellulose has to be used in the processes. The total amount required is computed according to the cellulose inlet amounts in oxygen and hydrogen peroxide methods.

Finally, all the required raw material amounts are calculated. The estimated values for both oxygen and hydrogen peroxide routes together with their pre-treatment and formic acid synthesis are shown in Table 5

Table 5: Inlet mass flow rate for biomass to formic acid production



Hydrogen Peroxide Route

Biomass Raw Material [kg/hr]	Water for Enzyme Hydrolysis [kg/hr]	Enzyme for Enzyme Hydrolysis (15 FPU/g Loading) [Liter]	Glucose [kg/hr]	30% Hydrogen Peroxide (120% Supply) [kg/hr]	Formic Acid [kg/hr]	Operational Year [hr]	Formic Acid [ton/yr]
2705.7	144.3	264.1	1094.0	4959.3	1157.4	8640	10000

Oxygen Route

Biomass Raw Material [kg/hr]	Water for Enzyme Hydrolysis [kg/hr]	Enzyme for Enzyme Hydrolysis (15 FPU/g Loading) [Liter]	Glucose [kg/hr]	Oxygen [kg/hr]	Formic Acid [kg/hr]	Operational Year [hr]	Formic Acid [ton/yr]
6720.6	331.9	658.5	2516.1	1341.9	1157.4	8640	10000

From Table 5 it can be observed that, the oxygen route consumes more biomass material than the hydrogen peroxide route. The reason is the difference in the yield values of the reactions. Yield levels of wet oxidation of glucose oxidation are 30% and 69% in oxygen and hydrogen peroxide routes, respectively.

4.2.2 Carbon Dioxide to Formic Acid Conversion Calculations

Calculation of the total required amount of carbon dioxide begins with the formic acid production.
CO_2 is converted into formic acid by the hydrogenation [173] . The reaction equation is given below.

$$CO_2 + H_2 + C_6H_{15}N \longrightarrow HCOOH - C_6H_{15}N$$

The product is called formic acid amine adduct and has to be chemically decomposed, hence Butylimidazole is used in process known as amine shift reaction. The chemical equation is;

$$HCOOH - C_6H_{15}N + C_7H_{12}N_2 \longrightarrow HCOOH - C_7H_{12}N_2 + C_6H_{15}N$$

By the explained reaction, triethylamine is recovered. The butylimidazole formic acid adduct does not form an azeotrope, separation reaction occurs in a reactor at 97 °and 0.2 bar;

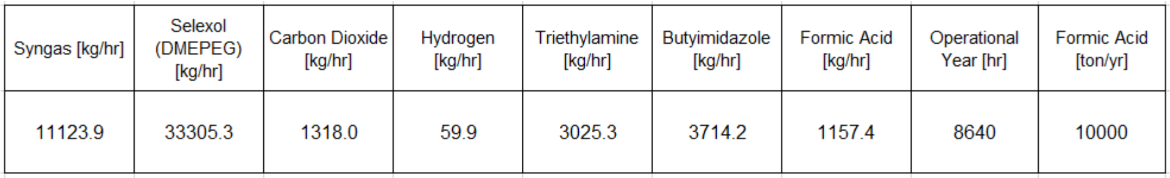
$$HCOOH - C_7H_{12}N_2 \longrightarrow HCOOH + C_7H_{12}N_2$$

Theoretical estimation of carbon dioxide and other intermediate substance quantities is basically done by mass balance of the production reactions. Actual produced amounts can be calculated by multiplying theoretical amounts with yield.
How much CO_2 is required is known. However, it is found with a proportion inside the syngas. In order model, its mass amount and content have to be entered to ASPEN. Several documents from the literature have been taken as reference for the gas content. However, it must be stated that by assumption no prior pre-treatment for the syngas is taken into consideration. The syngas content with mass percentages [82] [177] [178] , is given below;

- CO_2: 85.59%
- H_2: 5.34%
- N_2: 6.65%
- H_2O: 0.06%
- H_2S: 0.32%
- CH_4: 0.02%
- CO: 1.08%
- Ar: 0.94%

As a result, all the compound inlet mass flow rates are known. The estimated values for both carbon capture and carbon dioxide hydrogenation are given in Table 6.

Table 6: Inlet mass flow rate for carbon dioxide to formic acid production



Syngas [kg/hr]	Selexol (DMEPEG) [kg/hr]	Carbon Dioxide [kg/hr]	Hydrogen [kg/hr]	Triethylamine [kg/hr]	Butyimidazole [kg/hr]	Formic Acid [kg/hr]	Operational Year [hr]	Formic Acid [ton/yr]
11123.9	33305.3	1318.0	59.9	3025.3	3714.2	1157.4	8640	10000

After the explanation of the designed raw material acquisition and formic acid production processes, in the next section, the energy and economical viability of the value added chemical synthesis will be examined.

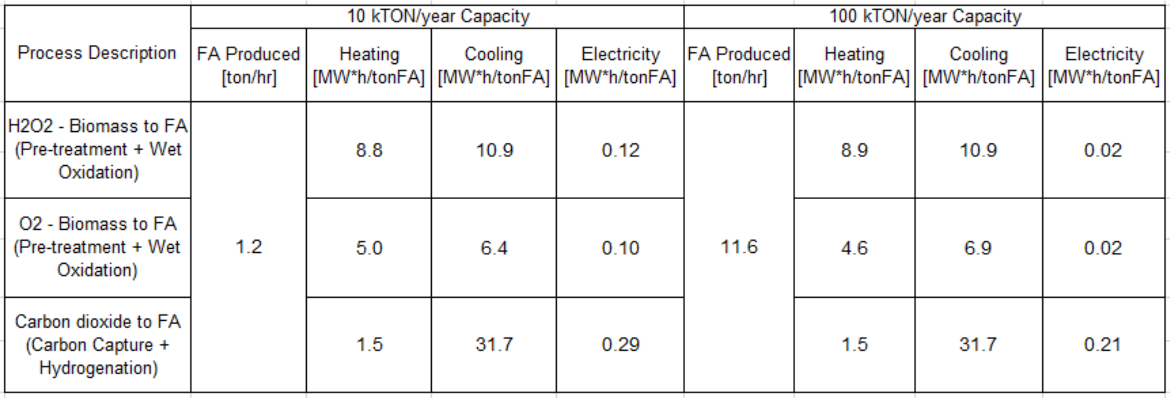
5 Results: Energy & Economical Feasibility of Formic Acid Production

Energy and economical analysis results of the flowsheets will be performed in the following part of the thesis report. Carbon dioxide and biomass routes will be evaluated and compared, also effect of production capacity will be investigated whether it is advantageous to produce in large amounts. Therefore, production capacity scenarios of 10 kilo tons and 100 kilo tons of annual production have been taken into account.

5.1 Energy Analysis of Formic Acid Production

Utility consumption and overall energy efficiency is calculated in energy analysis.
Heating, cooling and electricity consumption per ton of formic acid (FA) produced is estimated and shown in Table 7 in order to view the energy intensity of the processes.

Table 7: Utility consumption per ton FA produced



Process Description	10 kTON/year Capacity				100 kTON/year Capacity			
	FA Produced [ton/hr]	Heating [MW*h/tonFA]	Cooling [MW*h/tonFA]	Electricity [MW*h/tonFA]	FA Produced [ton/hr]	Heating [MW*h/tonFA]	Cooling [MW*h/tonFA]	Electricity [MW*h/tonFA]
H2O2 - Biomass to FA (Pre-treatment + Wet Oxidation)	1.2	8.8	10.9	0.12	11.6	8.9	10.9	0.02
O2 - Biomass to FA (Pre-treatment + Wet Oxidation)		5.0	6.4	0.10		4.6	6.9	0.02
Carbon dioxide to FA (Carbon Capture + Hydrogenation)		1.5	31.7	0.29		1.5	31.7	0.21

From Table 7, it is seen that;

- Wet oxidation requires significantly higher heating and cooling energy requirements than hydrogenation because of higher reaction temperature conditions.
- Hydrogen peroxide method requires more heating in oxidation reactor and glucose separation due to higher inlet material flow rates. Moreover, the cooling duty difference between the wet oxidation routes is higher than heating. The reason is the low temperature oxygen separation.
- Due to 180 bar operation, electric power requirement of the carbon dioxide process surpasses the biomass route. In addition, the reason why the cooling usage is much higher than any other consumption values is that the hydrogenation reaction. Because the presence of triethylamine, the reaction becomes exergonic [131]. Therefore,

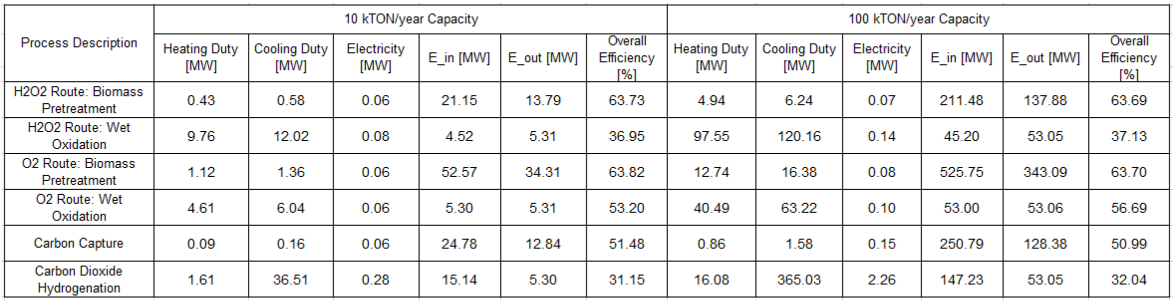
based on the total number of reactors used in the initial design, the process of synthesizing formic acid from carbon dioxide requires a significant amount of cooling.

Additionally, energy efficiency of the methods are also investigated by creating an overall energy balance. Biomass route have been considered together with pre-treatment and carbon dioxide route with carbon capture model. Efficiency evaluation is done by the following relation;

$$\eta = \frac{\sum E_{out}}{\sum E_{in}} 100 = \frac{E_{HHV_{product}}}{\sum E_{HHV_{inlet}} + E_{electric} + E_{heat}} 100 \tag{11}$$

In equation 11, $\sum E_{in}$ is the total inlet energy [MW], which includes the sum of higher heating values (HHV) of the entering materials [MW], the required energies; heat and electricity. $\sum E_{out}$ is the sum of the higher heating values of the product(s) obtained. The energy efficiency of the biomass and carbon dioxide routes have been calculated and shown in Table 8

Table 8: Overall efficiency results



Process Description	10 kTON/year Capacity						100 kTON/year Capacity					
	Heating Duty [MW]	Cooling Duty [MW]	Electricity [MW]	E_in [MW]	E_out [MW]	Overall Efficiency [%]	Heating Duty [MW]	Cooling Duty [MW]	Electricity [MW]	E_in [MW]	E_out [MW]	Overall Efficiency [%]
H2O2 Route: Biomass Pretreatment	0.43	0.58	0.06	21.15	13.79	63.73	4.94	6.24	0.07	211.48	137.88	63.69
H2O2 Route: Wet Oxidation	9.76	12.02	0.08	4.52	5.31	36.95	97.55	120.16	0.14	45.20	53.05	37.13
O2 Route: Biomass Pretreatment	1.12	1.36	0.06	52.57	34.31	63.82	12.74	16.38	0.08	525.75	343.09	63.70
O2 Route: Wet Oxidation	4.61	6.04	0.06	5.30	5.31	53.20	40.49	63.22	0.10	53.00	53.06	56.69
Carbon Capture	0.09	0.16	0.06	24.78	12.84	51.48	0.86	1.58	0.15	250.79	128.38	50.99
Carbon Dioxide Hydrogenation	1.61	36.51	0.28	15.14	5.30	31.15	16.08	365.03	2.26	147.23	53.05	32.04

From Table 8 it can be seen that;

- In biomass pre-treatment, HHV of the lignin, hemicellulose and xylose are also included next to the glucose. In oxygen route pre-treatment process, more lignocellulosic biomass feedstock is fed into the system due to difference in required glucose amounts between the methods because of the formic acid yields. Thus, more heating and cooling is needed for the glucose synthesis.

- In wet oxidation, both required heating and cooling energies are higher in hydrogen peroxide utilization. The excess amount of 30 wt.% hydrogen peroxide solution is the main reason in energy consumption.

- Despite the glucose amount used in the oxygen method is higher, it has been observed that the energy efficiency in the hydrogen peroxide method is lower. The reason for this difference is, again, the hydrogen peroxide used. Despite its low HHV (0.9 MJ/kg), the amount used has increased $\sum E_{in}$ considerably.

- Because of its lower reaction temperature requirements, in carbon dioxide hydrogenation, less amount of heating is required when compared to the other formic acid synthesis methods. In contrast, the use of electricity is more due to the high pressure requirement of hydrogenation and the following carbon dioxide and hydrogen separation processes.

That sums up the energy analysis of the formic acid synthesis. In the next section, economical aspects are discussed.

5.2 Economic Feasibility of the Formic Acid Production Plant

The economic feasibility of the formic acid synthesis is measured by calculating the minimum selling price per ton of formic acid and net profit. Thus, fixed and variable costs have to be calculated. Each cost of the formic acid production plant is explained in detail in the sections below.

5.2.1 Equipment & Capital Cost

Equipment costs are partially estimated via Aspen Economic Analyzer. There are predefined types of equipment in the cost calculator in ASPEN Plus and every equipment has physical limitations such as size, capacity, power etc. However, all equipments do not match the system requirements and therefore the program gives calculation errors. Hence, another sort of equipment must be chosen.
In case, where equipment cost data is not available or can not be estimated via ASPEN Plus, the correlations given in Table 33 and 34 in Appendix 13 are used to calculate equipment cost by Equation 12 [15];

$$Cost_{purchase_{component}} = a_{component} + b_{component}\, S_{component}^{n_{component}} \tag{12}$$

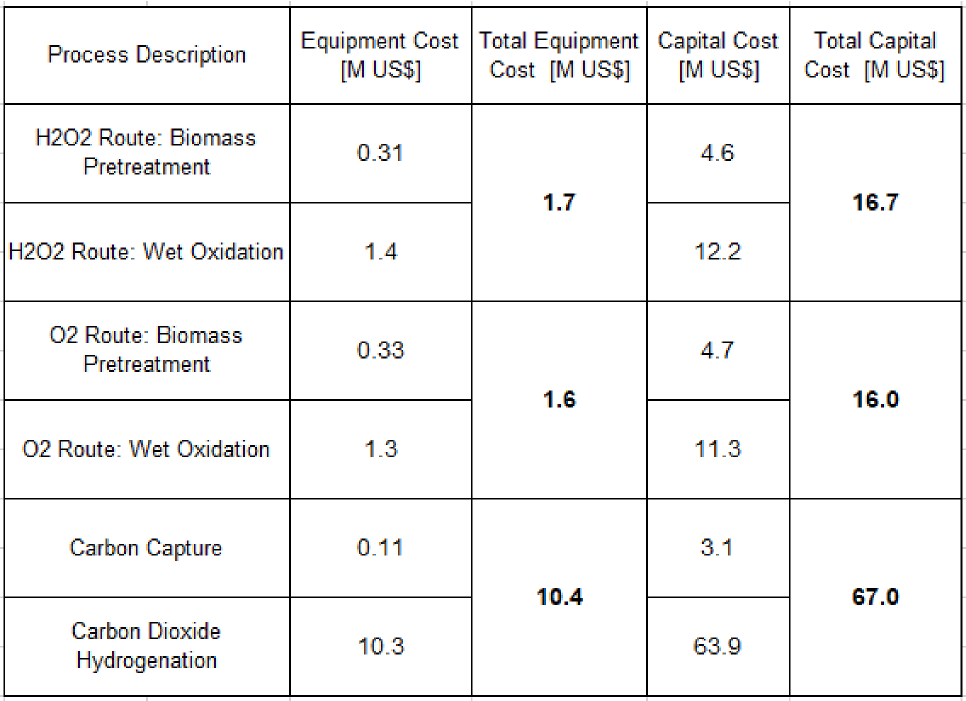
Capital cost is the total cost of the equipments in a production plant. In addition of price of the equipment, costs such as delivery, installation, piping and electrical systems contribute to the cost estimation. The capital cost of small scale production is calculated via ASPEN economic analyzer and Equation 12. In order to calculate the capital cost of the large scale production, cost curve method [15] is used. Capital cost of a plant can be related to capacity by the following relation;

$$C_2 = C_1 \left(\frac{S_2}{S_1}\right)^n \tag{13}$$

Where;

- C_2: Inside battery limits (ISBL) capital cost of the plant with capacity S_2,
- C_1: Inside battery limits (ISBL) capital cost of the plant with capacity S_1,
- Exponent n depends on the type of the process but in the chemical industry in general, taken as 0.6 [15],

Table 9: Equipment & Capital cost of 10kTON annual formic acid production



Process Description	Equipment Cost [M US$]	Total Equipment Cost [M US$]	Capital Cost [M US$]	Total Capital Cost [M US$]
H2O2 Route: Biomass Pretreatment	0.31	**1.7**	4.6	**16.7**
H2O2 Route: Wet Oxidation	1.4		12.2	
O2 Route: Biomass Pretreatment	0.33	**1.6**	4.7	**16.0**
O2 Route: Wet Oxidation	1.3		11.3	
Carbon Capture	0.11	**10.4**	3.1	**67.0**
Carbon Dioxide Hydrogenation	10.3		63.9	

From Table 9 it is seen that;

- In wet oxidation, H_2O_2 method has higher equipment cost. This is because increased reactor volume. Total amount of material entering, mainly determines the size of the reactor. Inlet material rates in oxygen method is 5583.23 kg/hr (1341.92 kg/hr oxygen and 4241.31 kg/hr slurry glucose mix, can be found in Table 26 in Appendix 11) and 5813 kg/hr (4500 kg/hr hydrogen peroxide and 1313 kg/hr slurry glucose mix, can be found in Table 25 in Appendix 11) in hydrogen peroxide utilized method. In addition to the inlet mass flow rate differences, H_2O_2 decomposition into water and oxygen inside the reactor also contributes to larger reactor volume. Also due to the generated oxygen, a flash tank is necessary to remove unwanted O_2 gas.

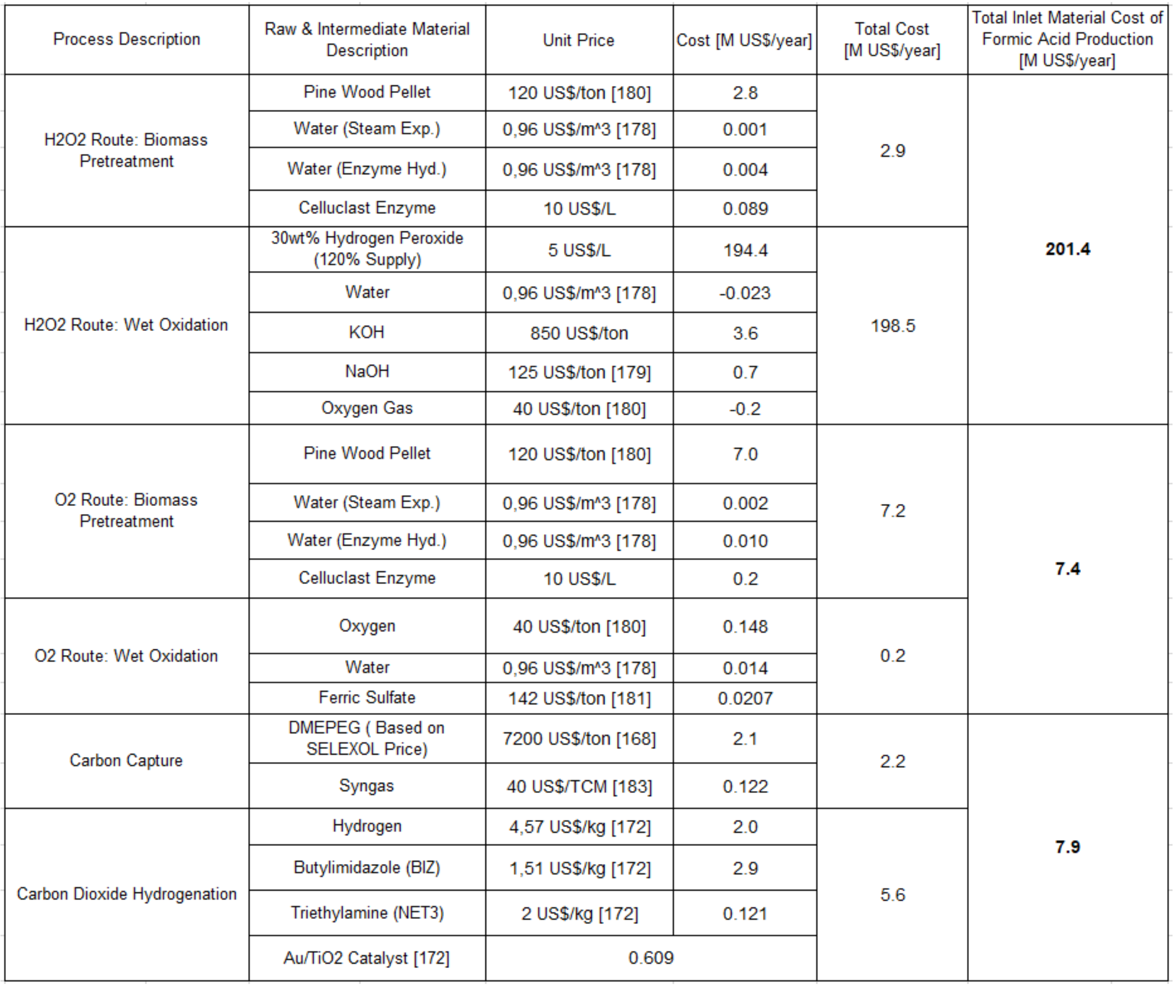
- The equipment cost of carbon dioxide hydrogenation is the highest of all. That is because of the number of reactors required for the hydrogenation reaction due to residence time of 72 hours. Based on work [173], where 74 catalytic reactors are implemented, the configuration of 72 reactors is economically not realistic. Therefore, reactor quantity must be dropped (Section 5.3.0.1 and 5.3.0.2).

5.2.2 Raw Material & Intermediate Costs

Raw material costs are the major expense of a production plant. In other words reactant and intermediate substance costs are considered as the bottleneck of the plant economics.

Practically, total price of the inlet material must be lower than product revenues for an investment to make profit to pay for equipment and capital costs. The quantities of materials required for synthesis and their corresponding costs are given below in Table 10

Table 10: Material cost of 10kTON annual formic acid production



Process Description	Raw & Intermediate Material Description	Unit Price	Cost [M US$/year]	Total Cost [M US$/year]	Total Inlet Material Cost of Formic Acid Production [M US$/year]
H2O2 Route: Biomass Pretreatment	Pine Wood Pellet	120 US$/ton [180]	2.8	2.9	**201.4**
	Water (Steam Exp.)	0,96 US$/m^3 [178]	0.001		
	Water (Enzyme Hyd.)	0,96 US$/m^3 [178]	0.004		
	Celluclast Enzyme	10 US$/L	0.089		
H2O2 Route: Wet Oxidation	30wt% Hydrogen Peroxide (120% Supply)	5 US$/L	194.4	198.5	
	Water	0,96 US$/m^3 [178]	-0.023		
	KOH	850 US$/ton	3.6		
	NaOH	125 US$/ton [179]	0.7		
	Oxygen Gas	40 US$/ton [180]	-0.2		
O2 Route: Biomass Pretreatment	Pine Wood Pellet	120 US$/ton [180]	7.0	7.2	**7.4**
	Water (Steam Exp.)	0,96 US$/m^3 [178]	0.002		
	Water (Enzyme Hyd.)	0,96 US$/m^3 [178]	0.010		
	Celluclast Enzyme	10 US$/L	0.2		
O2 Route: Wet Oxidation	Oxygen	40 US$/ton [180]	0.148	0.2	
	Water	0,96 US$/m^3 [178]	0.014		
	Ferric Sulfate	142 US$/ton [181]	0.0207		
Carbon Capture	DMEPEG (Based on SELEXOL Price)	7200 US$/ton [168]	2.1	2.2	**7.9**
	Syngas	40 US$/TCM [183]	0.122		
Carbon Dioxide Hydrogenation	Hydrogen	4,57 US$/kg [172]	2.0	5.6	
	Butylimidazole (BIZ)	1,51 US$/kg [172]	2.9		
	Triethylamine (NET3)	2 US$/kg [172]	0.121		
	Au/TiO2 Catalyst [172]	0.609			

During the material cost computation, simulation problems were encountered in carbon dioxide hydrogenation process due to recycle streams, which are explained in detail in Section 6.1. Therefore in material cost estimations, results are calculated by assuming that the materials have been recycled and only 1% is lost after each recycle stream. Fortunately, this manual calculation does not have an impact on the outcome.
From Table 10 it is understood that;

- Between the biomass utilization methods, pine wood pellet expenses are much lower in hydrogen peroxide route because of lower biomass material requirement. The reason is the relatively higher yields (69%) compared to the oxygen route, which is 30% [168]. As the yield decreases, by definition, more material has to be actually put into the system in order to satisfy formic acid production requirements.

- In both pre-treatment configurations, the amount of enzyme added to the system is calculated considering the enzyme degradation. An aqueous environment is required for the enzyme to be functional, and the solid molecules found cause its degradation. Lignin and cellulose are the substances that cause degradation the most [179]. As a result, the amount of enzyme to be replaced is determined based on the ratio of these solid molecules to the whole solution. Additionally, all four enzyme hydrolysis reactors were taken into account when calculating the amount of enzyme introduced. The cost of enzyme is calculated by assuming this implantation is required to be done monthly.

- In wet oxidation of glucose with oxygen, [168] et al. states that 0.67% ferric sulfate addition increases the yield of wet oxidation of pine wood from 14% to 30%. However, there is no literature available for parameters of degradation of the intermediate. Therefore, it is assumed that the complete amount ferric sulfate required is put into the reactor for every wet oxidation reaction and its price is calculated based on these assumptions.

- In hydrogen peroxide route, an assumption has been made in calculation of amount of KOH and NaOH that has to be resupplied to the system. Since there is no information available on degradation of both intermediates, it is assumed that the half of the required KOH and NaOH amounts are refilled to the reactor every month. In addition, the reason why oxygen and water costs are negative is that when hydrogen peroxide decomposes, more oxygen and water is obtained than supplied.

- Intuitively, it can be understood that the hydrogen peroxide utilization in formic acid production is not affordable at all. Complete decomposition of H_2O_2 under the reaction conditions (Section 4.1.3) eliminate the possibility of recycling the valuable reactant material. Therefore, it is assumed that the entire required amount must be put into the system for each reaction. Supplying more hydrogen peroxide than its stoichiometric requirement to the system prevents the glucose dehydration [166]. Even if this issue is not taken into consideration, in 100% supply, the annual cost of H_2O_2 is 162 million dollars.

- In carbon capture, despite being recycled to the system, Selexol is one of the most expensive intermediates. In this estimation, only 0.1% amount the compound is purged, there are no leaks or additional losses taken into account due. Additionally, there is no information on degradation of Selexol. In a real application, there would be losses and some portion of degradation of the intermediates. If that is considered, it can be expected that the raw material costs for carbon dioxide capture and hydrogenation can exceed the main product revenues.

The above explanations, summarize the evaluation and comparison raw material and intermediate costs. Next, breakeven selling price and profitability is estimated.

5.2.3 Breakeven Selling Price & Profitability

5.2.3.1 Breakeven Selling Price

Breakeven selling price (BSP) is the minimum price of the product that can be sold and still cover expenses. It is based on varying or fixed quantities of production, which is calculated by;

$$BSP = \frac{CCOP}{Volume\,of\,Production}\ [US\$/unit] \tag{14}$$

Cash cost of the production (CCOP) is the cost of making product and it is the sum of fixed (FCOP) and variable (VCOP) production costs [15].

$$CCOP = VCOP + FCOP\ [US\$/yr] \tag{15}$$

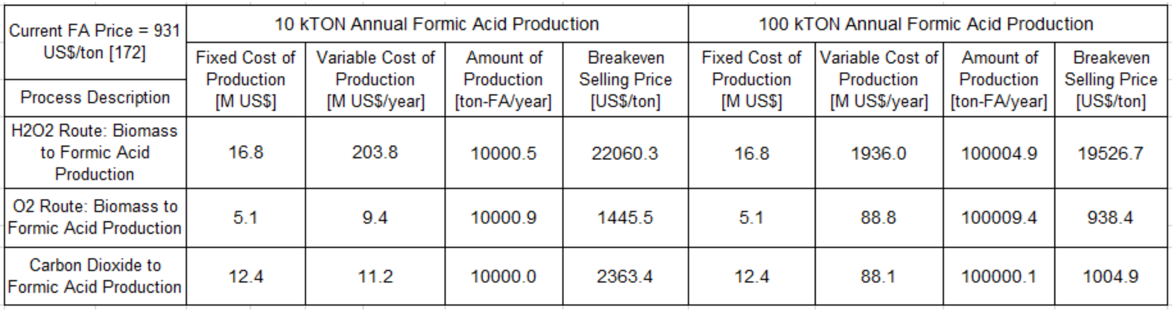
By definition, fixed costs of production [15] are costs that do not change despite changing plant operation rate or output. These expenses [180] are;

- Operating labor: 10 labors/shift, 3 shift/day, 50000 $/labor/year,
- Supervision: 20% of operating labor,
- Maintenance & Repairs: 6% of fixed capital investment,
- Operating Supplies: 15% of maintenance and repairs,
- Laboratory Charges: 15% of operating labor,
- Patents & Royalties: 1% of total production cost,
- Local Taxes & Insurance: 3% of fixed capital investment,
- Plant Overhead: 60% of sum of operating labor, supervision and maintenance costs,
- General expenses: Administration (20% of sum of operating labor, supervision and maintenance costs) , Distribution & Selling (5% of total production cost).

On the other hand, variable costs of production corresponds to [15] expenses varying due to change in production rate, which are;

- Raw material: Due to economy of scale, in large scale production, 5% bulk purchase discount has been assumed and included.
- Utilities,
- Depreciation cost: Equipment with 20 years life span and 5% salvage value.

Table 11: Breakeven selling price results



Current FA Price = 931 US$/ton [172]	10 kTON Annual Formic Acid Production				100 kTON Annual Formic Acid Production			
Process Description	Fixed Cost of Production [M US$]	Variable Cost of Production [M US$/year]	Amount of Production [ton-FA/year]	Breakeven Selling Price [US$/ton]	Fixed Cost of Production [M US$]	Variable Cost of Production [M US$/year]	Amount of Production [ton-FA/year]	Breakeven Selling Price [US$/ton]
H2O2 Route: Biomass to Formic Acid Production	16.8	203.8	10000.5	22060.3	16.8	1936.0	100004.9	19526.7
O2 Route: Biomass to Formic Acid Production	5.1	9.4	10000.9	1445.5	5.1	88.8	100009.4	938.4
Carbon Dioxide to Formic Acid Production	12.4	11.2	10000.0	2363.4	12.4	88.1	100000.1	1004.9

Table 11 shows the breakeven selling prices. From Table 11 it is seen that;

- Price of the hydrogen peroxide it the main issue with its utilization for formic acid synthesis. As explained in Section 5.2.2, hydrogen peroxide can not be recovered due to its decomposition. In wet oxidation of glucose via oxygen, the BSP value is lower than H_2O_2 route but higher than the market value.
- In the exact same production methods, when the effect of production capacity is looked at, it is realized that the breakeven selling price is lower in large capacity of production. Fixed fees play a key role in this case. Because fixed production costs remain constant even if the operation scale changes. Therefore, as the volume of production is increased fixed costs per unit drops.
- Formic acid obtained via carbon dioxide hydrogenation in small scale is well above the market price (931 \$/ton [173]). In large scale scenario, it is 1.08 times higher than the current sale price. The reason is the cost of the equipment, mentioned in Section 5.2.1, high reactor costs increase the capital costs, hence, the fixed fees dependent on capital costs account for a large proportion when determining the breakeven selling price.

5.2.3.2 Profitability: Gross & Net Profit

Another aspect of expressing the economic viability of the production is the calculation of possible profit. Capital costs and raw material fees will be the decisive parameters in examining the profitability of this processes.

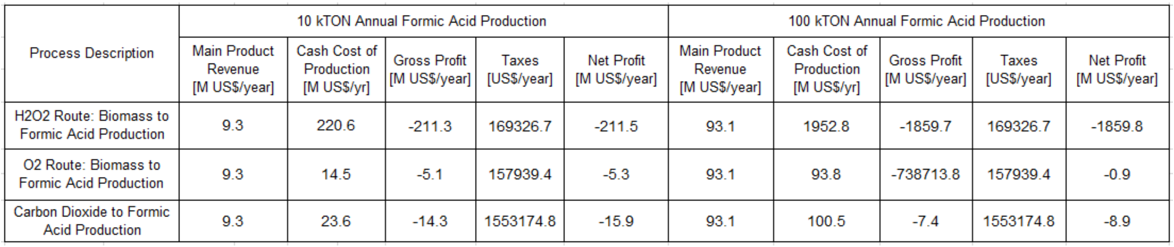
The money gained from the process after the tax cuts which will be a return on the initial investments, is referred as net profit. It is calculated by;

$$NetProfit = GrossProfit - Taxes \tag{16}$$

Local taxes and insurance account for 3% of the fixed capital investment [180]. Gross profit (GP) is estimated by subtracting cash cost of production from the money earned by the sales of the product. Table 12 shows both gross and net profit.

$$GP = Main\ Product\ Revenue - CCOP \tag{17}$$

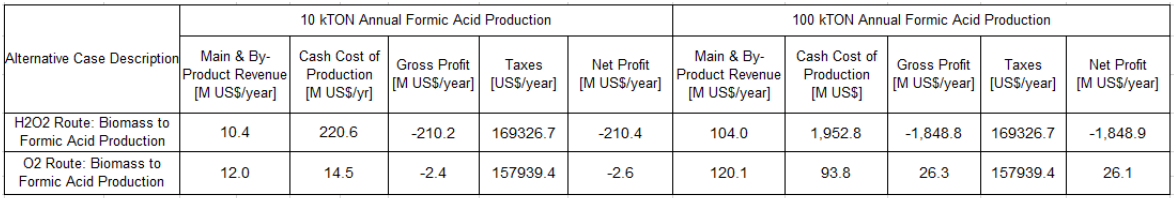
Table 12: Profit results



Process Description	10 kTON Annual Formic Acid Production					100 kTON Annual Formic Acid Production				
	Main Product Revenue [M US$/year]	Cash Cost of Production [M US$/yr]	Gross Profit [M US$/year]	Taxes [US$/year]	Net Profit [M US$/year]	Main Product Revenue [M US$/year]	Cash Cost of Production [M US$/yr]	Gross Profit [M US$/year]	Taxes [US$/year]	Net Profit [M US$/year]
H2O2 Route: Biomass to Formic Acid Production	9.3	220.6	-211.3	169326.7	-211.5	93.1	1952.8	-1859.7	169326.7	-1859.8
O2 Route: Biomass to Formic Acid Production	9.3	14.5	-5.1	157939.4	-5.3	93.1	93.8	-738713.8	157939.4	-0.9
Carbon Dioxide to Formic Acid Production	9.3	23.6	-14.3	1553174.8	-15.9	93.1	100.5	-7.4	1553174.8	-8.9

From Table 12 it is understood that, none of the operations are profitable. Unlike the carbon dioxide method, hemicellulose, lignin and xylose are obtained as by-products in the biomass pretreatment process which can be sold. The most important of these is lignin, and it is priced between \$ 70 and \$ 150 for use in energy production [181], assuming an average 110\$ sale price per ton in this case . The rest is assumed to be sold from 50 \$/ton. As a result, next to the formic acid revenues, by-product sales can be very financially beneficial. Their contribution to the plant economics are shown in Table 13.

Table 13: Biomass method profit values including the income of by-products



Alternative Case Description	10 kTON Annual Formic Acid Production					100 kTON Annual Formic Acid Production				
	Main & By-Product Revenue [M US$/year]	Cash Cost of Production [M US$/yr]	Gross Profit [M US$/year]	Taxes [US$/year]	Net Profit [M US$/year]	Main & By-Product Revenue [M US$/year]	Cash Cost of Production [M US$]	Gross Profit [M US$/year]	Taxes [US$/year]	Net Profit [M US$/year]
H2O2 Route: Biomass to Formic Acid Production	10.4	220.6	-210.2	169326.7	-210.4	104.0	1,952.8	-1,848.8	169326.7	-1,848.9
O2 Route: Biomass to Formic Acid Production	12.0	14.5	-2.4	157939.4	-2.6	120.1	93.8	26.3	157939.4	26.1

From the results at Table 13, the additional sales of by-products make no difference for hydrogen peroxide method. In 100 kton oxygen method, 26.1M US\$ profit is obtained. This result shows that a system consisting of the designed biomass pre-treatment and the wet oxidation of glucose with oxygen can be economically feasible.
From the energy and economic analysis, it can be seen that;

- O_2 route seems to be applicable only in large scale. In small scale, the fixed cost productions account for the majority of the money earned from the sales of the formic acid.
- H_2O_2 route is economically not practical for formic acid production. Despite higher formic acid yield results for wet oxidation process, the requirement for new batch of hydrogen peroxide for every hour of production makes the process economically impossible even for the large scale production.

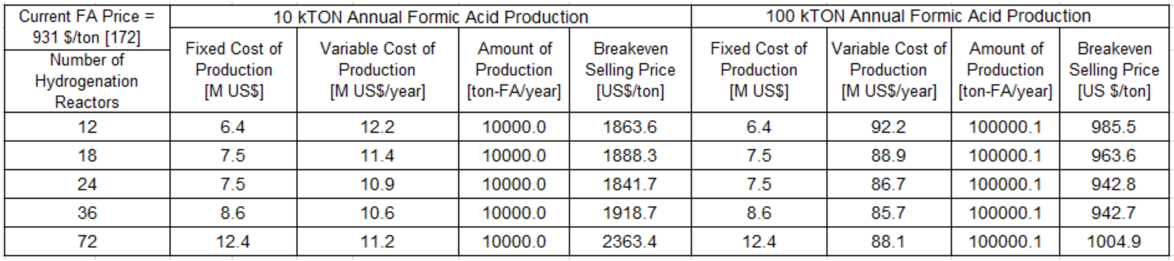
- In terms of reducing intermediate substance cost for H_2O_2 method, a process without KOH can be built. However, $NaOH$ has to be present in the mixture to prevent formic acid decomposition. This configuration effects the wet oxidation yield. With KOH present, 69% formic acid yield is obtained for 120% hydrogen peroxide supply. If KOH is not used, 64% yield is reached with NaOH only [166]. However, the cost of the hydrogen peroxide is still an issue.
- Unlike the oxygenated biomass method, the carbon dioxide method is not a profitable method due to equipment costs. Changes should be made in the operation in order to obtain feasible results. Therefore adjustments have been made particularly for hydrogenation process, which is the bottleneck of the plant. These adjustments are explained in detail as two case studies in the next two sections.

5.3 Case Study I & II: Carbon Dioxide Hydrogenation Improvement

5.3.0.1 Case Study I: Reactor Quantity Configuration

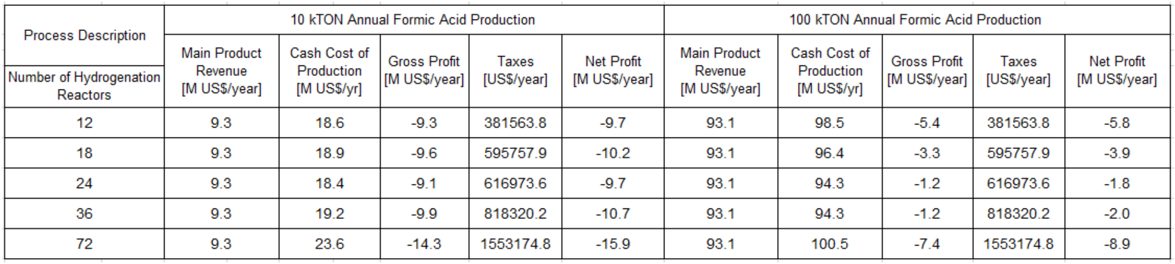
In Section 5.2.3 it was shown that the formic acid production from carbon dioxide hydrogenation is not profitable. The reference article [173] states that the carbon dioxide to formic acid conversion process with Au/TiO_2 heterogeneous catalyst requires a residence time of 72 hours. In the initial design, a system with 72 reactors was modeled by considering the system with 74 catalytic reactors mentioned in the reference article [173]. However, the total capital cost of the first catalytic reactor (REACTOR1) of the process resulted to be the main reason for over priced product. Therefore the amount of reactors can not be taken granted. In this case study, the appropriate number of reactors determined by varying the quantity of hydrogenation reactors and the corresponding mass flow rate. When the number of reactors is reduced, the amount of product to be obtained from each reactor increases, after 72 hours of residence time. This corresponds to an increase in the inlet mass flow rates. The economical result of varying reactor quantities, breakeven selling prices are shown in Table 14 and profit values are shown in Table 15.

Table 14: Case Study I: Breakeven selling price results



Current FA Price = 931 $/ton [172]	10 kTON Annual Formic Acid Production				100 kTON Annual Formic Acid Production			
Number of Hydrogenation Reactors	Fixed Cost of Production [M US$]	Variable Cost of Production [M US$/year]	Amount of Production [ton-FA/year]	Breakeven Selling Price [US$/ton]	Fixed Cost of Production [M US$]	Variable Cost of Production [M US$/year]	Amount of Production [ton-FA/year]	Breakeven Selling Price [US $/ton]
12	6.4	12.2	10000.0	1863.6	6.4	92.2	100000.1	985.5
18	7.5	11.4	10000.0	1888.3	7.5	88.9	100000.1	963.6
24	7.5	10.9	10000.0	1841.7	7.5	86.7	100000.1	942.8
36	8.6	10.6	10000.0	1918.7	8.6	85.7	100000.1	942.7
72	12.4	11.2	10000.0	2363.4	12.4	88.1	100000.1	1004.9

Table 15: Case Study I: Gross and net profit results



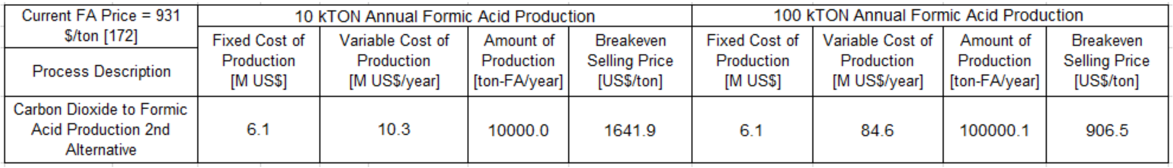
Process Description	10 kTON Annual Formic Acid Production					100 kTON Annual Formic Acid Production				
Number of Hydrogenation Reactors	Main Product Revenue [M US$/year]	Cash Cost of Production [M US$/yr]	Gross Profit [M US$/year]	Taxes [US$/year]	Net Profit [M US$/year]	Main Product Revenue [M US$/year]	Cash Cost of Production [M US$/yr]	Gross Profit [M US$/year]	Taxes [US$/year]	Net Profit [M US$/year]
12	9.3	18.6	-9.3	381563.8	-9.7	93.1	98.5	-5.4	381563.8	-5.8
18	9.3	18.9	-9.6	595757.9	-10.2	93.1	96.4	-3.3	595757.9	-3.9
24	9.3	18.4	-9.1	616973.6	-9.7	93.1	94.3	-1.2	616973.6	-1.8
36	9.3	19.2	-9.9	818320.2	-10.7	93.1	94.3	-1.2	818320.2	-2.0
72	9.3	23.6	-14.3	1553174.8	-15.9	93.1	100.5	-7.4	1553174.8	-8.9

From tables above, it is realized, the formic acid synthesis process is still not profitable for the current residence time and hydrogenation reactor amount configurations. Hence, the catalyst change is mandatory. In order to see the best effect of the change, 24 reactor configuration is the most appropriate. When less reactors are used, the material put increases. Thus, the size of the equipments and utility costs rise. On the other hand, when more than 24 reactors are used, the capital cost of the reactors increases the minimum selling price and significantly increases the economic loss. The effect of another catalyst is calculated in the second case study.

5.3.0.2 Case Study II: Heterogeneous Catalyst Change

In the reference article [173], titanium supported gold catalyst ($AuTiO_2$) is used in the hydrogenation reaction. Also stated in the referenced article, it is still not possible to make a profit in the carbon dioxide method, although the hydrogenation reactor quantity is altered. Therefore, another catalytic intermediate is used from another article in the literature. In this case, the economic effect of different catalyst utilization is investigated. The same operating conditions are accepted as in the previous case study. An aluminium oxide based gold catalyst (Au/Al_2O_3) is chosen. Sun et al. [176] stated that the aluminium catalyst showed twice the activity of the titanium equivalent (TONs of 215 and 111 s^{-1}, respectively) when used in exact reaction conditions for equal experiment duration. Therefore, the hydrogenation reaction was considered to be twice as fast. Hence, half the 24 reactor system chosen in the previous case study is sufficient.
The breakeven selling price of the different catalyst configuration is shown in Table 16.

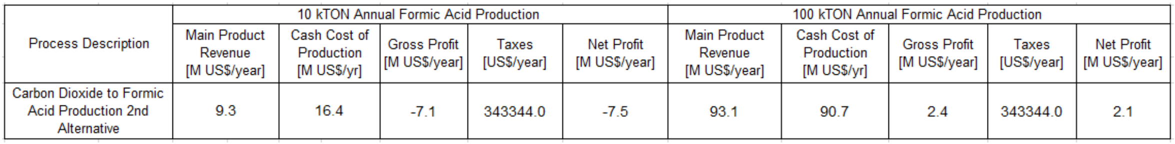
Table 16: Case Study II: Breakeven selling price results



Current FA Price = 931 $/ton [172]	10 kTON Annual Formic Acid Production				100 kTON Annual Formic Acid Production			
Process Description	Fixed Cost of Production [M US$]	Variable Cost of Production [M US$/year]	Amount of Production [ton-FA/year]	Breakeven Selling Price [US$/ton]	Fixed Cost of Production [M US$]	Variable Cost of Production [M US$/year]	Amount of Production [ton-FA/year]	Breakeven Selling Price [US$/ton]
Carbon Dioxide to Formic Acid Production 2nd Alternative	6.1	10.3	10000.0	1641.9	6.1	84.6	100000.1	906.5

The profit made in the second case study is shown in Table 17.

Table 17: Case Study II: Gross and net profit results

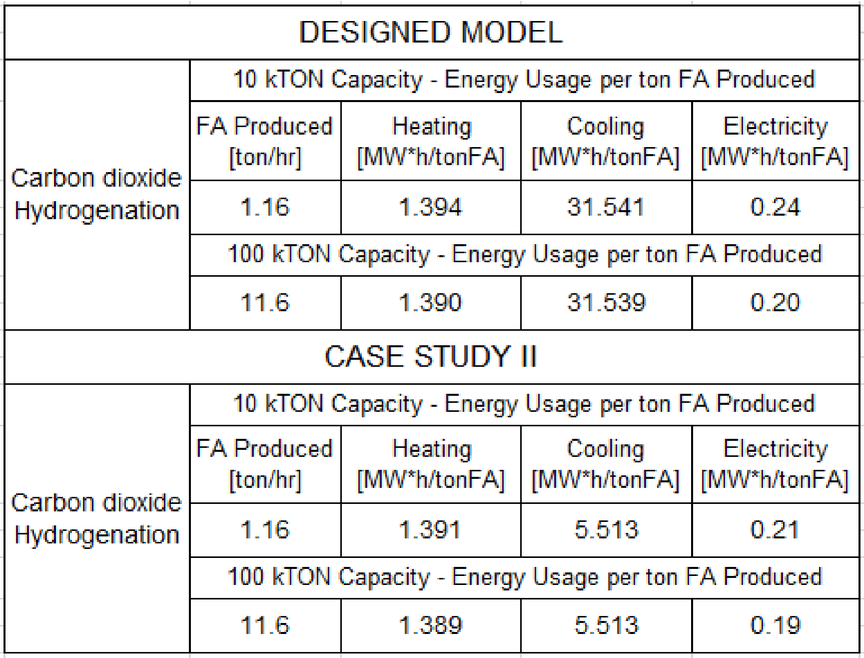


Process Description	10 kTON Annual Formic Acid Production					100 kTON Annual Formic Acid Production				
	Main Product Revenue [M US$/year]	Cash Cost of Production [M US$/yr]	Gross Profit [M US$/year]	Taxes [US$/year]	Net Profit [M US$/year]	Main Product Revenue [M US$/year]	Cash Cost of Production [M US$/yr]	Gross Profit [M US$/year]	Taxes [US$/year]	Net Profit [M US$/year]
Carbon Dioxide to Formic Acid Production 2nd Alternative	9.3	16.4	-7.1	343344.0	-7.5	93.1	90.7	2.4	343344.0	2.1

According to Table 16 and 17, with the transition to a more active catalyst material, the number of reactors have been reduced to 12. Compared to the very first configuration, this great reduction in equipment cost has made the carbon dioxide utilization process profitable by reducing the product unit price below the current market price.

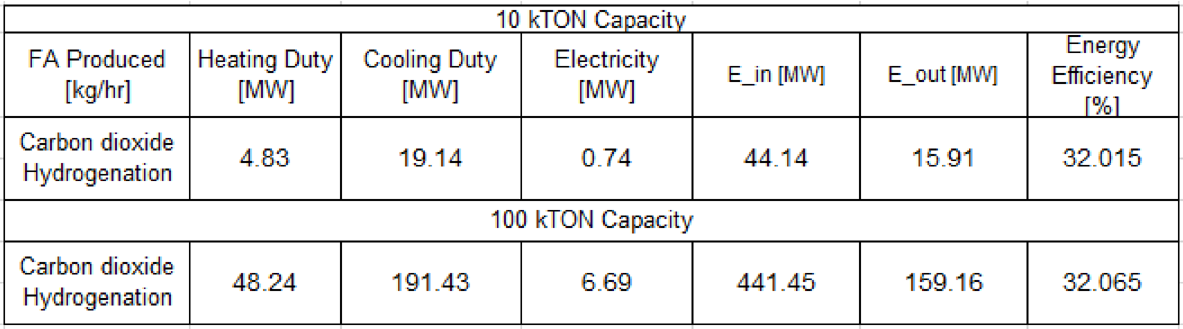
After making a profit, the energy analysis of the improved configuration has been made. Energy usage per ton of formic acid produced and overall energy efficiency results are shown in Table 18 and 19

Table 18: Energy consumption of case study II



DESIGNED MODEL				
Carbon dioxide Hydrogenation	10 kTON Capacity - Energy Usage per ton FA Produced			
	FA Produced [ton/hr]	Heating [MW*h/tonFA]	Cooling [MW*h/tonFA]	Electricity [MW*h/tonFA]
	1.16	1.394	31.541	0.24
	100 kTON Capacity - Energy Usage per ton FA Produced			
	11.6	1.390	31.539	0.20
CASE STUDY II				
Carbon dioxide Hydrogenation	10 kTON Capacity - Energy Usage per ton FA Produced			
	FA Produced [ton/hr]	Heating [MW*h/tonFA]	Cooling [MW*h/tonFA]	Electricity [MW*h/tonFA]
	1.16	1.391	5.513	0.21
	100 kTON Capacity - Energy Usage per ton FA Produced			
	11.6	1.389	5.513	0.19

Table 19: Energy balance of case study II



10 kTON Capacity						
FA Produced [kg/hr]	Heating Duty [MW]	Cooling Duty [MW]	Electricity [MW]	E_in [MW]	E_out [MW]	Energy Efficiency [%]
Carbon dioxide Hydrogenation	4.83	19.14	0.74	44.14	15.91	32.015
100 kTON Capacity						
Carbon dioxide Hydrogenation	48.24	191.43	6.69	441.45	159.16	32.065

By Table 19, there is an slight increase in the process overall efficiency for both capacity scenarios. The reason is shown in Table 18, which is the slightly lower electricity and heating utility consumption per ton of formic acid produced by the aluminium based catalyst utilization. Another important issue that needs to be mentioned is that, as a result of two case studies, the required hydrogenation reactor number is reduced from 72 to 12 and a direct proportional decrease in cooling load consumption is observed.

The energy and economical analysis results of formic acid production have been investigated. Several assumptions have been made in the modelling and analysis of wet oxidation of lignocellulosic biomass and catalytic reduction of carbon dioxide. The factors that have been encountered in the thesis study and that may be encountered in future studies and practical applications are explained in discussion.

6 Discussion

Innovative processes for formic acid production via biomass feedstock and carbon dioxide have been studied. In the final chapter of the thesis report, problems and difficulties encountered, recommendations for future work and summary of results will be explained.

6.1 Problems and Difficulties Encountered

Several issues were encountered during the study. It is thought that it will be informative to indicate these problems, in order to overcome when the studies on the methods and materials used increase.

- According to the studies of Grous et al. [161] the operating condition and duration of the steam explosion affects the glucose yield in enzymatic hydrolysis of lignocellulosic biomass [161]. The yield value also varies with the duration of the enzymatic hydrolysis process itself. The data is provided by an article [161] and an equation can be obtained by data correlation, to describe the relationship between these parameters and the yield. Therefore, in ASPEN Plus, a calculator block was used to enter the data via a FORTRAN subroutine. However, despite not giving any code errors, the program did not work. The problem was realised after looked at the internet. It is that, ASPEN Plus requires an additional and user defined FORTRAN compiler program. The versions of the program that published after 2015 have to be installed and defined to the simulation program manually by writing command codes to the operating system of the computer, which requires the attention of an experienced computer technician. Therefore, the subroutine code could not be run because the FORTRAN compiler can not be defined and can not be run. Achieving the execution of the code will be important in modelling the correlation to be estimated from existing and future data.
- In carbon dioxide hydrogenation, properties of BIZ, BIZ-FA and Amine-FA adducts are calculated via Joback group contribution method. The reason is that, the Joback method has the highest affinity of group increments to the butylimidazole and amine adduct structures. However there are other methods present, giving more accurate results in particular properties. For example, Gani method gives critical pressure value with 2.89% average relative error where Joback method has 5.2 % [182]. However, the group increments have to be defined in simulation program and only Joback method's fit the compounds used. Calculating the material properties with the least error-prone method will logically provide more realistic results for the compounds and for the process.
- In carbon dioxide method, since BIZ-FA or other manually defined substances do not have T-x or x-y data with any compound used in the process, the decomposition processes of formic acid adducts in distillation columns given in the reference article, could not be performed. Instead, RSTOIC, one of the reactors available in the program, was used and the reaction equation and conditions were defined. Fractional

distillation is only used to separate formic acid from BIZ. Because the distillation process can be set according to the known properties of formic acid. It is certain that the difference in equipment used differed in expenses and energy.

- Recycling is an inevitable concept in the production methods specified in the thesis report and takes part a major role in the decrease in raw material costs, which is one of the most important items in economic calculations. While recycling is included in economic calculations, a number of problems were encountered in model simulation. Recycle streams were created in ASPEN Plus, in carbon dioxide hydrogenation flowsheet simulation. However, despite the change in the convergence method of the program and a higher tolerance in the mass balance, realistic results could not be obtained. The recycled material accumulated across the whole flowsheet. This varying amount of substances cause thermodynamic equilibrium in flash tanks to give erroneous results. Therefore, the valuable material separation fails. In the end, fractional distillation columns in both formic acid synthesis methods become insufficient to extract formic acid. Moreover, sensitivity analysis can not be converged, for example during the sensitivity analysis of flash tanks, the appropriate operating conditions can not be estimated due to changes in mass fractions of components. In order to observe more realistic effect of recycling material, other simulation programs such as DWSIM or ASPEN HYSYS should be used.

6.2 Recommendations for Future Work

Several practical and technical aspects of the project requiring further attention are explained below. Further reflection on the following points will shed light on future evaluations of the processes.

- The pre-treatment and carbon capture processes are carried out at full capacity, regardless of material recycling, due to the problems encountered in simulating the recycle streams in formic acid production. By recycling unreacted glucose or carbon dioxide into the reactor, the raw material to be fed into the system can be saved. However, in the raw material production facility, production can be made at full capacity for precautionary purposes. By producing raw materials in quantities specified in stoichiometric calculations, they can be stored for use in case of any interruption in production or when formic acid production needs to be resumed after a planned maintenance. It is possible, albeit unlikely, to be sold at an industrial quality price. It can even be burned to power the system, like lignin obtained from biomass pretreatment. It can be configured in order to the get the best of the produced compounds.

- According to the literature [162], commercial enzymes have a maximum activity at 60 °C, but when the components of the same enzyme have been obtained separately and prepared as a mixture, 25% higher enzyme activity was observed at 65 °C. Therefore, if the enzyme is produced and prepared on site, higher enzyme activity can be reached than the industrial products. By this higher activity, the required enzyme quantity, residence time and as a result, required number of reactors will decrease. However, the enzyme production methods should be investigated and simulated. Their economical and energy analysis should be

- In carbon capture, Selexol costs depend on assumption of no losses and no degradation (Section 5.2.2). In reality, they are expected to be present. Hence, the cost of the Selexol, therefore raw material costs of formic acid production with carbon dioxide can be more than the earning of the product sales. On site production of Selexol must be developed for the future use of the compound. Because if its production costs decrease, the price of the Selexol will decline. Hence, making the physical solvent more preferable over conventional amine compounds.

- In carbon dioxide capture, water gas shift process can be installed to the plant. Hydrogen can be synthesized by converting carbon monoxide inside the gas source with steam. From high temperature or low temperature shift methods, it should be analyzed which will work most compatible with the carbon dioxide capture process. Recovery of hydrogen on site may have decrease the raw material costs of carbon dioxide hydrogenation process. As shown in Section 5.2.2, hydrogen has one of the highest unit price in formic acid synthesis. Besides the economic evaluation, utility consumption and energy efficiency of the possible configuration should be investigated.

- In order to find solutions to make profit from the CO_2 method, two case studies have been done. In the second case study however, to improve the number of reactors, in order to reduce the equipment cost, the improvement is based on the catalytic activity difference between the two catalyst materials, where Au/Al_2O_3 is measured to be twice as Au/TiO_2 [176]. The reason is that there are not enough sources about the production of formic acid as a result of carbon hydrogenation with heterogeneous catalysts. It is considered certain that these intermediates will be preferred as more studies have been accomplished and the current activity values are exceeded.

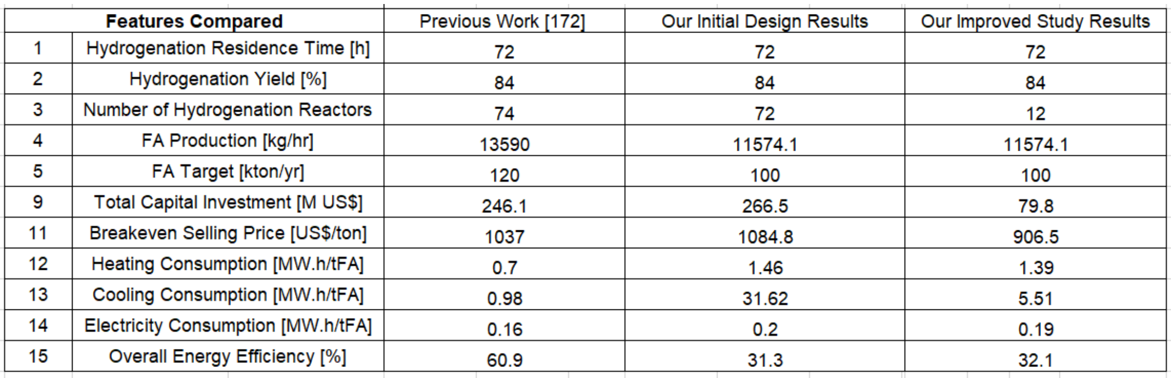
- In the literature, there is a lack of experimental information on reaction kinetics and conversion rates for enzyme hydrolysis, wet oxidation and carbon dioxide hydrogenation with a heterogeneous catalyst. When proper data is obtained, more precise processes can be simulated by observing the effect of reaction parameters.

After explaining the obstacles encountered and the points should be paid attention, the report must be concluded.

7 Conclusion

First, comparison of the results obtained in this thesis with literature is shown below.

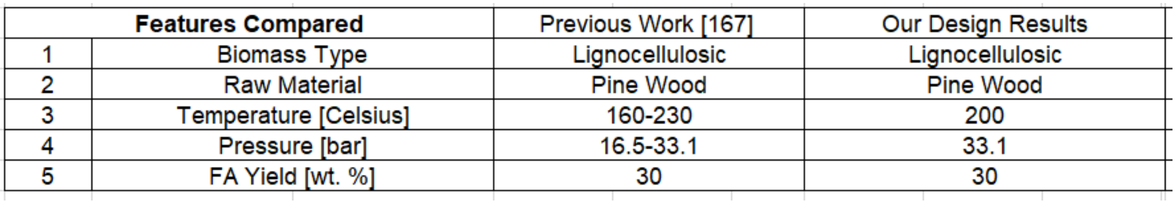
Table 20: Comparison of the results obtained in CO_2 method with literature



	Features Compared	Previous Work [172]	Our Initial Design Results	Our Improved Study Results
1	Hydrogenation Residence Time [h]	72	72	72
2	Hydrogenation Yield [%]	84	84	84
3	Number of Hydrogenation Reactors	74	72	12
4	FA Production [kg/hr]	13590	11574.1	11574.1
5	FA Target [kton/yr]	120	100	100
9	Total Capital Investment [M US$]	246.1	266.5	79.8
11	Breakeven Selling Price [US$/ton]	1037	1084.8	906.5
12	Heating Consumption [MW.h/tFA]	0.7	1.46	1.39
13	Cooling Consumption [MW.h/tFA]	0.98	31.62	5.51
14	Electricity Consumption [MW.h/tFA]	0.16	0.2	0.19
15	Overall Energy Efficiency [%]	60.9	31.3	32.1

Table 20 shows the comparison of CO_2 hydrogenation method used in our design and work [173]. In the table, there is both our initial and improved design results. The most important improvement in our work is the number of reactors used. Work [173] reports 74 reactors used in their CO_2 hydrogenation method. Although we started with 72, change of reactor number and change of catalyst and later economical analysis helped to improve our method by reducing the number of reactors down to 12. Another superiority of our method reveals itself in the breakeven selling price (BSP), due to the reduction in the number of reactors. The BSP has been reduced to 906.5 US $/ton in our improved method, compared to the 1037 $/ton of work [173]. Our BSP is below the current market price of one ton of formic acid. A critical feature is the Total Capital Investment (TCI) of the system. Our TCI is is initally higher, then it is better than work [173] with 79.8 $MUS\$$ compared to 246.1 $MUS\$$. However, overall energy efficiency in our method is almost half of the method in work [173]. Although we used the same energy efficiency equation given in work [173], for unbiased comparison purposes, the HHV values of inlet and outlet materials are not defined or declared in work [173]. Lack of detailed HHV values did not help us to find out the reason of our inferior performance in some features. Our method's heating, cooling and electricity consumption [MW.h/tFA] appear to be higher, even though 12 reactors are used, compared to 74 of work [173]. The utility consumption per ton of formic acid given by the authors does not seem realistic for 74 reactors and the remaining heavy equipment use.

Table 21: Comparison of the results obtained in biomass method with literature



Features Compared		Previous Work [167]	Our Design Results
1	Biomass Type	Lignocellulosic	Lignocellulosic
2	Raw Material	Pine Wood	Pine Wood
3	Temperature [Celsius]	160-230	200
4	Pressure [bar]	16.5-33.1	33.1
5	FA Yield [wt. %]	30	30

Table 21 shows the comparison of wet oxidation method used in our design and work [168]. Since the process modelling of glucose wet oxidation is not available in literature, process conditions in laboratory experiments from literature have been used.
A brief summary of the energy and economical analysis of the designed formic acid production is explained below.

- In energy analysis in Section 5.1, biomass utilization showed higher efficiency in both pre-treatment and formic acid synthesis processes. Although more heating and cooling was used in the pre-treatment compared to carbon capture, higher efficiency is obtained due to the higher energy output. In terms of formic acid production, wet oxidation has outpaced the carbon hydrogenation process. More heating and cooling loads were used in both oxidation processes because of the operating temperatures above 200 °C, followed by glucose separation at 200 °C. The difference in electricity usages is low, therefore its comparison is neglected. However, the difference in the total energy of the incoming substances, considering the higher HHV values of BIZ, Net_3 and hydrogen, is greater in CO_2 method. Thus, lower efficiency is calculated.

- When the wet oxidation routes are compared, it is observed that more efficiency is obtained via oxygen. Despite more glucose is used in oxygen method, heating and cooling duties are higher in hydrogen peroxide method. The reason is that the total reactants entering the wet oxidation reactor are more and due to hydrogen peroxide decomposition into water and oxygen, more material has to be separated in flash tanks and in distillation columns.

- Lignocellulosic biomass can be theoretically utilized to synthesize formic acid but only for wet oxidation via oxygen in large scale, when the formic acid produced is sold together with the by-products from the biomass pre-treatment process. On the other hand, the applicability of the biomass pre-treatment process may not be practically possible. The industrial grade price of the enzyme, which is accepted as 10 dollars per liter, is not known exactly. In addition, the amount of degradation of the enzyme, which there is no certain information available, is taken as the ratio of solid particles entering the enzyme hydrolysis to the entire mixture entering the reactor, considering that it occurs due to contact with solid particles, may not give a definite result. Therefore, the exact amount that has to be replaced and exact cost of replacement can not be estimated precisely. In other words, if the enzyme price exceeds the revenue from the sale of the product, no profit can be expected from the transaction.

- In carbon dioxide route, despite the harsh conditions of 180 bar and 40 C [173], the titanium based heterogeneous catalyst showed lower activity, compared to the aluminium equivalent [176]. The reaction could be completed only in 72 hours. The slow reaction is a major drawback for meeting the production rates. In first designed model, 72 catalytic reactors used to satisfy the production targets. Unfortunately, the selected solution is calculated to be not applicable for the process, in terms of economics. Because the increase in equipment costs results in very high capital costs, increasing the fixed costs of production. As a result, the calculated minimum selling price is 7% more than the current market price. In order to improve the process, two case studies were created. In the first case, a solution is sought by varying the amount of hydrogenation reactor. In addition, the amount of raw material to be put into each reactor, which directly affects equipment sizing and utility costs are examined. No profit was obtained from the case study. It was concluded that the use of platinum catalyst was not economically beneficial for the process. In the second case study, the Au/Al_2O_3 catalyst has been utilized as it has twice the activity value of the platinum supported catalyst with TONs of 215 and 111 s^{-1}, respectively. As a result, the process took half the time of the previous case and as outcome of improvement, the minimum selling price is obtained to be 2.6% below the current market value. Moreover, a small increase in energy efficiency is observed in both capacity scenarios in the second case study, which is due to slightly lower utility consumption per ton of formic acid produced.

To conclude, uncertainties are present in both production methods. More research and experiment should be done regarding reaction kinetics and intermediate substance performances in both biomass and carbon dioxide to formic acid conversion processes, in order to simulate the reactions, therefore the process, more in detail. However, despite the uncertainties, in this era where the transition to greener energy production through the use of biomass and the reduction of carbon dioxide emissions have been made a definite target by the governments, the synthesis methods studied, will gain importance as the purposes of formic acid use and therefore the consumption levels rise.

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8 Appendix A: Biomass Classification

8.1 Identification of Biomass as Raw Material

Producing energy from natural or discarded sources is more advantageous compared to fossil fuel and coal-based conventional processes. Its most significant advantage is sustainability. Secondly, since all people consume food or non-edible natural sources, these materials are abundant and available almost in every country. However, it must be noted that in this study, edible sources or food based wastes are not taken into consideration because those resources can be recycled back to the food chain. Therefore feedstock supply must not harm the natural ongoing nutrient cycle. Biomass feedstock mainly consists of carbohydrates (polysaccharides, sugar and starch), lipids and proteins. Classification of these resources are still being questioned by the scientist and authorities. However, Sanchez et al. makes this classification by four groups [183].
These groups are;

- Physical Condition; Biomass resources can be sorted according to their natural water content. They are basically defined as "wet" or "dry" biomass. Algae with 90% and wood with 8-25% water fraction are examples of these types, respectively.
- Origin; Biomass resources can be separated by their geographical locations or by industry of production. They are sorted as;
  - Aquatic biomass = Recognizing the importance of that three-quarters of the world being water, researchers have become interested in resources that can be obtained from the sea such as micro- or macro- algae.
  - Agricultural biomass = Provides sources such as energy crops, by-product of crops or farming wastes [183].
  - Forest biomass = As it is named, they are wood-based waste collected from legally defined forests.
  - Waste streams = They are mainly solid-organic wastes [184].

    They are also called as the "Biodegradable Fraction" of discarded textiles, metals and plastics in municipal solid waste [108]. As well as recovery of other sources such as paper, glass and copper, recycling itself is a great source of income for cities.
- Chemical Composition; The weight or molar fractions of the chemical content vary for each source, therefore biomass can also be divided into groups according to their majority content as;
  - Lignocellulosic biomass = From general perspective, it is the biomass feedstock that can be obtained from the whole biological plant kingdom. Theoretically, all plants can be used but practically not preferred. For example, herbal sources are not preferred because of their alternative benefits. Also herbal lifespan is not

  long enough to preserve their content for long transportation and storage periods. Herbs are mainly composed of organic polymers such as cellulose, hemicellulose and lignin.

  Lignocellulosic biomass is a crucial concept and it will be explained in detail in the following chapter.

  - Sugar-rich biomass = They are simply plants high in sugar content. In their chemical structure, glucose and fructose formations are dominant. Sugar cane and sugar beet are the most common feedstock.
  - Starch-rich biomass = They are found in plants such as barley, wheat and rye, which are known as the raw materials of foods that we consume as carbohydrates in our daily lives.
  - Oil-rich biomass = The most known aquatic biomass, algae, contains high proportions of lipid, which makes them oily and waxy [183].
  - Protein-rich biomass = Both animals and plant biomass such as beans contain a high amount of protein. Since they are consumed as food and protein-based resources are expensive, therefore they are not preferred for biorefinery, .

- Purpose of Use [183]; Unfortunately, a single biomass resource cannot be used in all applications. Their biological structure, hence chemical orientation is different. Raw materials can be sorted based on their use as;

  - Heat & Power = Wood-based biomass types have high heating values, therefore they can provide sufficient heat energy or they can supply the required heat for power cycles.
  - Transportation = Liquid or gaseous biomass resources such as bioethanol and biomethanol can be used to supply the necessary energy for combustion.
  - Biorefinery = Lignocellulosic biomass, starch- and oil-rich biomass can be used for producing energy or producing value-added chemicals. Especially lignocellulosic biomass provides versatile production possibilities, because of their wide availability and variety of content .

9 Appendix B: Carbon Dioxide Capture Classification

9.1 CO_2 Capture from Ambient Air

People breathe and exhale by nature. As oxygen enters a person's respiratory system, carbon dioxide is released. On the other hand, plants contain chloroplasts to produce oxygen during the day and carbon dioxide at night. Thus, plants are a source of oxygen, but the amount of natural carbon dioxide emission to the air cannot be ignored. Moreover, the increasing vehicle manufacture poses a serious problem for the environment Therefore capturing CO_2 directly from air has become a vital concept.

Direct Air Capture (DAC) is the recovery of carbon dioxide in the atmosphere from the environment. Ambient air is collected physically and treated via a sorbent. Dissolved mixture is then regenerated to obtain CO_2. Alkaline solutions, solid sorbents, amine-grafted oxides and amine-grafted metal organic frameworks (MOF) have been utilized for DAC [185].

Sodium hydroxide (NaOH) and potassium hydroxide (KOH) based direct capture, combined with chemical caustic recovery is commonly applied in the literature [186]. Alkaline solutions are quite cheap and offer great CO_2 selectivity. However, they suffer from high regeneration energy requirements.

Amine grafted oxides consisting of silica [187], alumina [188] and carbon [189] supported polyethylamine compositions [190] have been tried for CO_2 capture from air. These materials showed high capacity and selectivity. No degradation was noticed, even after multiple cycles. On the other hand, they require a few hours to begin operating, due to their slow adsorption kinetics [57].

Ethylenediamine has been analyzed for amine-grafted MOF based carbon capture which exhibited fast capture kinetics and high carbon dioxide capacity. On the other hand, this Mg-MOF-74 iso-structure with N,N-dimethylethylenediamine showed uncertainties, in stability and moisture sensitivity [191]. Moreover, this process proved to be an expensive production.

However, the amount of carbon dioxide in the air is only 0.04 wt% [192], which forces these methods to require high amount of energy to obtain a small ratio of CO_2. Going for higher capture capacities to satisfy large scale production demands, this process becomes the most expensive which is economically unfeasible. Long term DAC systems cost a lot; 115€ /tCO_2 +/− 40€ /tCO_2 [193], which is more than twice the stationary resources.

10 Appendix C: Formic Acid Production Method Selection

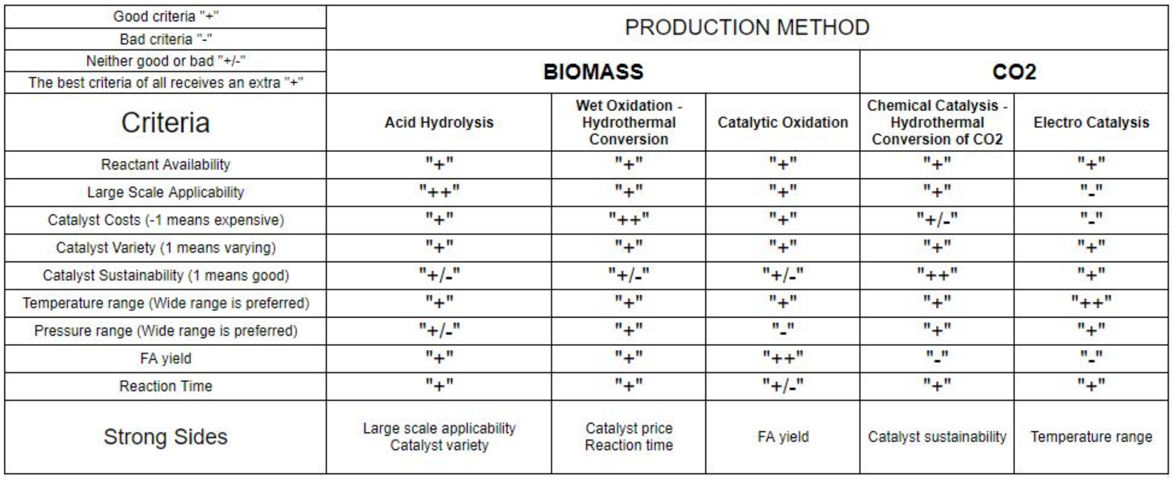
10.1 Method Selection

As explained in Section 2.2.3, there are six formic acid production routes. However it is not possible to optimize operating costs and conditions completely because the determination of the best case scenario in each way takes quite some time. Therefore, it is decided to choose 2 out of 5 because photocatalysis method was eliminated from the beginning. The reason was the lack of experimental results and lack of improvement on intermediate substances for increasing selectivity and product purity [194] compared to other options.
Then an elimination must be done by setting parameters. Which are;

1. Reactant Availability = A variety of polysaccharide types for the selected method.
2. Industrial Applicability = Whether there are any examples of practical information in the industry.
3. Catalyst Variety = The multiplicity of materials to accelerate the reaction is important for the applicability of the method.
4. Catalyst Cost = The economic liabilities of the catalyst must be taken into account for large scale productions.
5. Temperature & Pressure Range = Wide range of options is preferred to avoid strict control of the process and enabling room for improvements.
6. Formic Acid Yield = The formic acid purity obtained from the reaction itself can have important impacts on ease of separation.
7. Reaction Time = Required time for production has to be known to determine the production rate.

The criteria matrix is formed with the parameters above. Each method is then graded accordingly. Positive properties for the criteria are given plus, negative properties took minus. Properties with both pros and cons took both signs. The method with the best parameter condition took an extra plus. The criteria matrix is given in Table 22.

Table 22: Evaluation of formic acid production methods



Good criteria "+" Bad criteria "-" Neither good or bad "+/-" The best criteria of all receives an extra "+"	PRODUCTION METHOD				
	BIOMASS			**CO2**	
Criteria	**Acid Hydrolysis**	**Wet Oxidation - Hydrothermal Conversion**	**Catalytic Oxidation**	**Chemical Catalysis - Hydrothermal Conversion of CO2**	**Electro Catalysis**
Reactant Availability	"+"	"+"	"+"	"+"	"+"
Large Scale Applicability	"++"	"+"	"+"	"+"	"-"
Catalyst Costs (-1 means expensive)	"+"	"++"	"+"	"+/-"	"-"
Catalyst Variety (1 means varying)	"+"	"+"	"+"	"+"	"+"
Catalyst Sustainability (1 means good)	"+/-"	"+/-"	"+/-"	"++"	"+"
Temperature range (Wide range is preferred)	"+"	"+"	"+"	"+"	"++"
Pressure range (Wide range is preferred)	"+/-"	"+"	"-"	"+"	"+"
FA yield	"+"	"+"	"++"	"-"	"-"
Reaction Time	"+"	"+"	"+/-"	"+"	"+"
Strong Sides	Large scale applicability Catalyst variety	Catalyst price Reaction time	FA yield	Catalyst sustainability	Temperature range

The explanation for the criteria matrix is given below;

- Acid hydrolysis;
  - Cellulose and glucose have been reported as reactants frequently in the literature. Agricultural residues [8], paper sludge [184], and organic municipal waste [108] have been reported to be used as raw material.
  - The biomass route is applied in industrial scales for large scale production of levulinic acid [109] [108]
  - Some of the catalysts used; H_2SO_4, HCl, zirconium oxide (ZrO_2) [98], phosphoric acid [64], oxalic acid, citric acid and maleic acid.
  - Most of the catalysts are in acceptable price range, except ZrO_2 which costs 180 \$ per kilogram which is expensive [195].
  - Process has temperature range between 150 °C and 240 °C [109] [8]. Process have reported to be working with various pressures such as 8.6 [109] and 25 bar [95].
  - In acid hydrolysis, formic acid is the by-product and levulinic acid is the main product
  - Highest FA purity of 95 wt.% by hydrolysis of sugarcane bagasse, catalyzed by H_2SO_4 reported in single experiment process [109].
  - Reaction times of 20 minutes have been reported [95].
- Wet Oxidation;
  - Organic lignocellulosic biomass content had been used separately for production. Usage of wood biomass, bio oil, plastic waste (monomers) even fish waste had been reported [8] [9].

  - Wet oxidation has been developed recently. Therefore, it is not applied industrially frequently. However, some studies were found [166].
  - Acids (H_2SO_4) and alkalis (Iron(II)Sulfate-$FeSO_4$) are considered as catalysts [8] [166]. Hydrogen peroxide reported to be an efficient oxidant.
  - $FeSO_4$ is quite affordable, it is priced 51 \$ per ton and H_2O_2 costs around 217 \$ per metric ton [196].
  - Wet oxidation experiments reported to have wide temperature and pressure range. Temperature variations from 170 °C to 600 °C and pressures from 5 bars to 50 bars [9] [8].
  - Formic acid is the main product; acetic acid, lactic acid and succinic acid are reported by-products [8] [9].
  - In experiments, glucose treated with H_2O_2 resulted on purities up to 85 wt% [8]. When common bases NaOH and KOH are used in presence of hydrogen peroxide at room temperature, 91.3% yield and 90% selectivity was obtained [10].
  - Residence times such as thirty seconds or two minutes have been reported [166].

- Catalytic Oxidation
  - Glucose and all organic components of lignocellulosic biomass have been utilized. Beech wood, waste paper are some of the examples [8] [9].
  - Oxidation of biomass to formic acid (OxFA) is frequently studied for large scale biorefinery in literature [159] [130].
  - H_2SO_4 and HPA based [197] catalysts are common ones. $NaVO_3$ [128], polyoxometalate , iron are also tried in experiments.
  - Price of H_2SO_4 is acceptable. Keggin type polyoxometalate is preferred because of its low cost [198]. However, $NaVO_3$ costs 378 \$ per kilogram [199] which is too expensive.
  - Catalytic oxidation method reported to be accomplished at various temperatures; from 80 °C to 250 °C and with pressure levels varying from 20 to 60 bars [8] [159].
  - It is observed that purity and residence time are affiliated with each other for this method. Catalytic oxidation is reported to give better selectivity and yield for reactions which last longer. For example, glucose utilized under catalytic oxidation while sodium metavanadate ($NaVO_3$) acts as the catalyst at 160 °C under 30 bars of oxygen gas used as oxidant, FA yield of 68.2 % [128] was obtained. The process took 1 hour. On the other hand, when glucose treated with a Keggin type $H_8PV_5Mo_7O_{40}$ (polyoxometalate HPA-5) catalyst, in a biphasic system for 48 hours at 90 °C under 20 bar O_2. High FA yield of 85% was reported [126], which is quite an extreme process duration, to be applied in the industry. In contrary, quick processes also has been found. In which, wheat straw treated with $NaVO_3$ for 5 minutes under 160 °C and 20 bar O_2 and the process

resulted with low yield of 47 % [200]. It seems this purity-residence time trade-off is against the process engineer for this production option.

- Catalytic Reduction of Carbon Dioxide
  - CO_2 is the only reactant for this process.
  - Production of formic acid via carbon dioxide captured from plants is studied both economically and technically [11] [201].
  - Ruthenium based catalysts, $AuTiO_2$, Ni, Fe, Cu are commonly used catalysts [194].
  - All catalysts except ruthenium based one are affordable. Ruthenium is an expensive material (8.7 $ per gram). Its alternatives are searched by scientists.
  - Carbon dioxide can be chemically reduced to formic acid at 50-130 °C temperature and 20-60 bars pressure range.
  - In case homogeneous catalyst is used, formic acid amine adduct is obtained. Then, adduct must be removed, so does the catalyst. These separation procedures would require complex methods such as reactive distillation, vacuum distillation and stripping [11]. Heterogeneous catalysts are easier to separate. Therefore, heterogeneous intermediates should be utilized for simpler and cheaper operation.
  - CO_2 treated with Hexanehexol as reductant and $NaHCO_3$ as additive, giving formic acid yield of 80 % purity after an hour process [202].
  - Experiments lasting 1 to 8 hours have been run [8].
- Electrochemical Reduction of Carbon Dioxide
  - CO_2 is reported to be the only reactant for this process.
  - There are no reports found regarding to large scale formic acid production via electrochemical cells. Laboratory scales are used in experiments [90].
  - Iridium oxide (IrO_2), phosphine and carbon supported platinum catalysts (Pt-c) are some of the intermediates to speed up the process [203].
  - Currently, most of the catalyst materials are expensive. IrO_2 costs about 471 $/kg , Pt-c catalyst is around 18.8€ /g. Few exceptions, Pb and Cd which are around 2.5 $/kg [90], is affordable.
  - Electrochemical reactions were accomplished at room temperatures and with varying pressures from atmospheric pressure to 50 bars [136].
  - Electrochemical reduction of carbon dioxide gives low yields, such as 8-20 wt.% [203].

A decision is made by comparing and evaluating methods. One from biomass and one from carbon dioxide has been selected. Among biomass routes, wet oxidation is preferred due to negative aspects of other methods. Acid hydrolysis was eliminated mainly because of

formic acid is the secondary product. Large quantities of levulinic acid is produced but the formic acid levels are low.
Catalytic oxidation is eliminated due to high operating pressures and long residence times. Achieving higher conversion in the wet oxidation process compared to catalytic oxidation for the same amount of reaction time and the cost of catalysts used, are the most important reasons for choosing wet oxidation over catalytic oxidation. However, combining the two methods and taking advantage of the strengths of the two methods can have significant results.

For the CO_2 method, catalytic conversion is selected over electrochemical reduction because of its possible large scale applications and lower catalyst costs per production.

10.2 Simplified Flowsheet

To demonstrate formic acid synthesis, method(s) have to be determined. From renewable formic acid production methods (Section 2.2.3), wet oxidation of lignocellulosic biomass and catalytic carbon dioxide reduction methods were selected. Comparison of methods and reasons for preference are available in Appendix C.

Production methods to be developed by evaluating the information obtained from the literature were determined. The simplified flowsheets drawn and shown below are the general description of how formic acid production will be produced.
The simplified flowsheet for the wet oxidation is given in Figure 27. Pre-treatment is included to reveal the complete system.

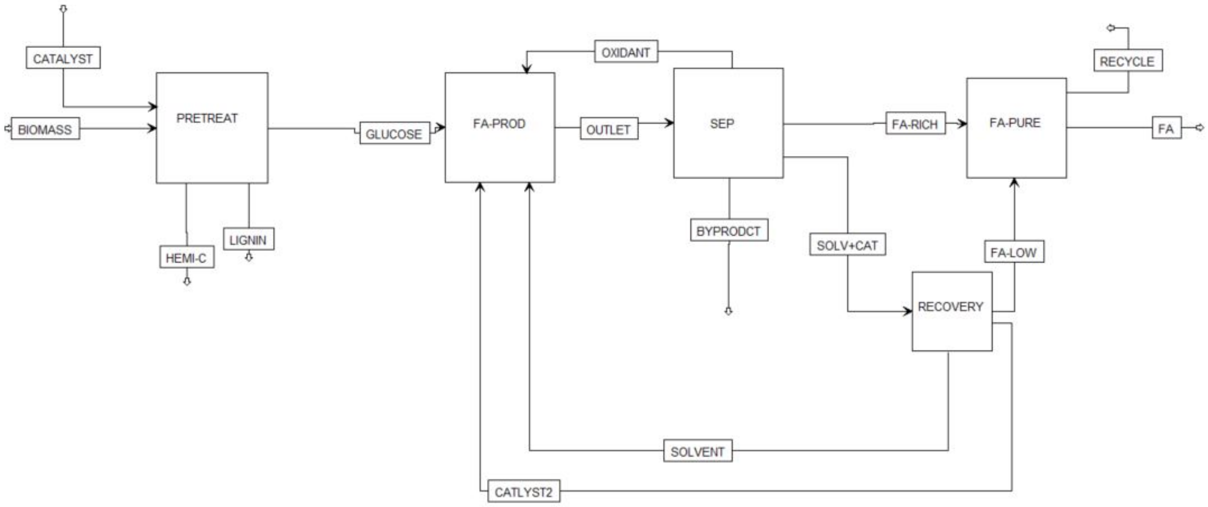


Figure 27: Simplified flowsheet for formic acid production via lignocellulosic biomass

The simplified flowsheet for the catalytic hydrogenation of carbon dioxide route with carbon capture and storage (CCS) is given in Figure 28.

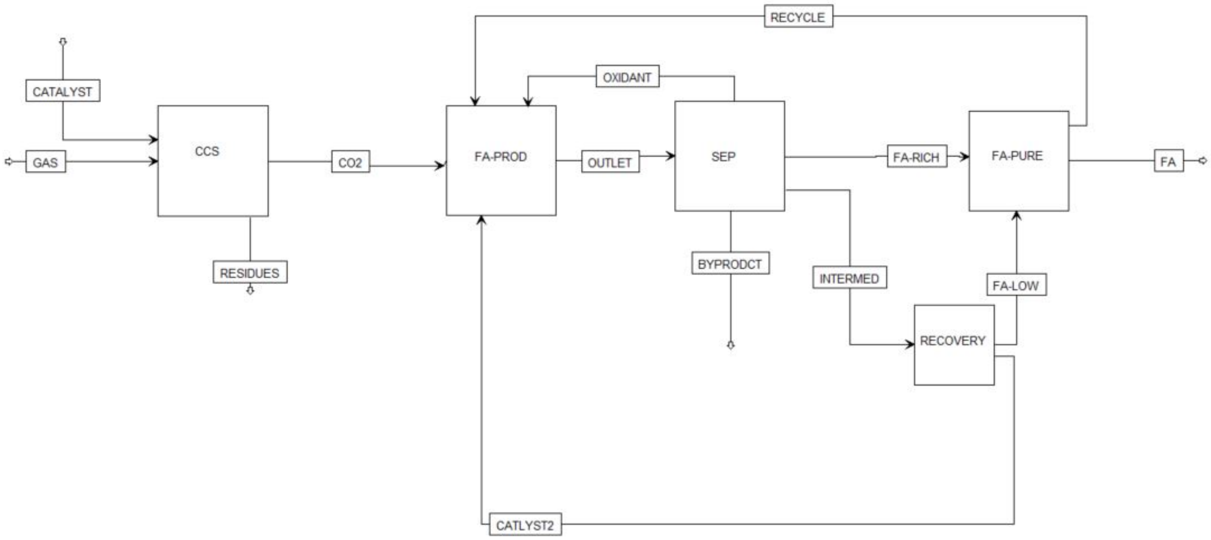
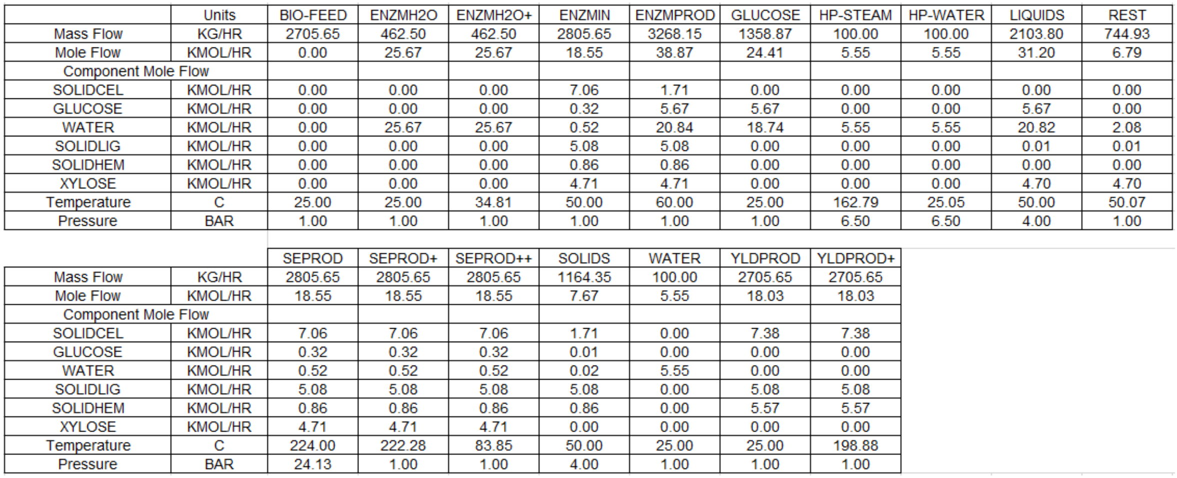


Figure 28: Simplified flowsheet for formic acid production via carbon dioxide

11 Appendix D: Stream Results

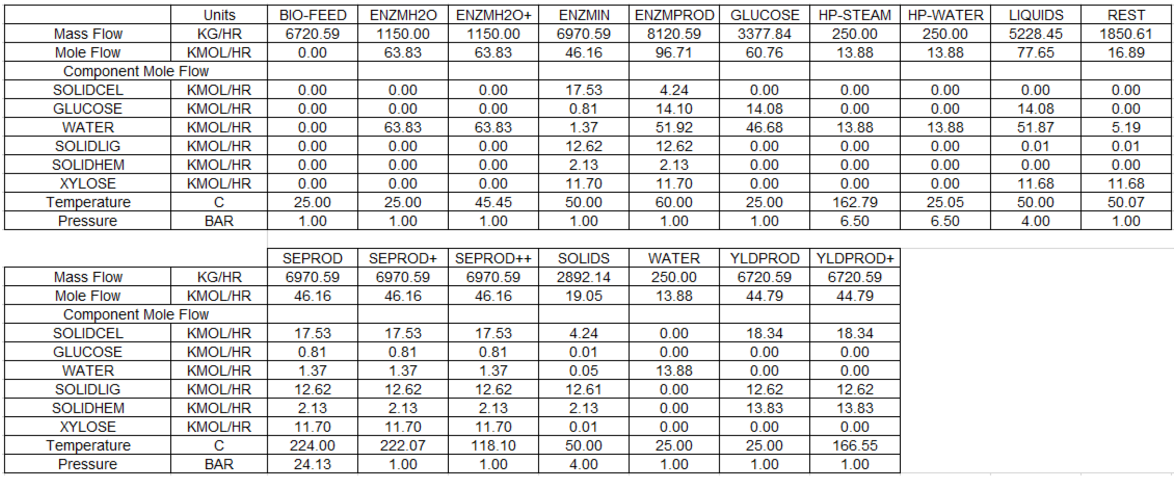
The stream results of biomass pre-treatment, carbon capture and formic acid production processes are given below. The results taken from a 10 kton annual production capacity scenario.

Table 23: Hydrogen peroxide method biomass pre-treatment simulation, stream results



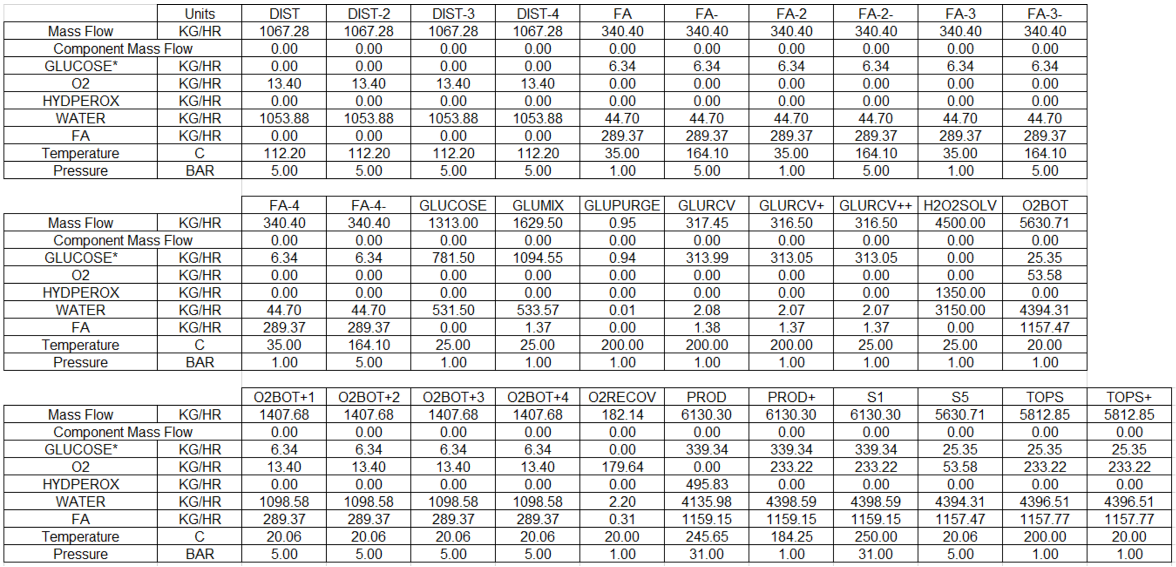
	Units	BIO-FEED	ENZMH2O	ENZMH2O+	ENZMIN	ENZMPROD	GLUCOSE	HP-STEAM	HP-WATER	LIQUIDS	REST	SEPROD	SEPROD+	SEPROD++	SOLIDS	WATER	YLDPROD	YLDPROD+
Mass Flow	KG/HR	2705.65	462.50	462.50	2805.65	3268.15	1358.87	100.00	100.00	2103.80	744.93	2805.65	2805.65	2805.65	1164.35	100.00	2705.65	2705.65
Mole Flow	KMOL/HR	0.00	25.67	25.67	18.55	38.87	24.41	5.55	5.55	31.20	6.79	18.55	18.55	18.55	7.67	5.55	18.03	18.03
Component Mole Flow																		
SOLIDCEL	KMOL/HR	0.00	0.00	0.00	7.06	1.71	0.00	0.00	0.00	0.00	0.00	7.06	7.06	7.06	1.71	0.00	7.38	7.38
GLUCOSE	KMOL/HR	0.00	0.00	0.00	0.32	5.67	5.67	0.00	0.00	5.67	0.00	0.32	0.32	0.32	0.01	0.00	0.00	0.00
WATER	KMOL/HR	0.00	25.67	25.67	0.52	20.84	18.74	5.55	5.55	20.82	2.08	0.52	0.52	0.52	0.02	5.55	0.00	0.00
SOLIDLIG	KMOL/HR	0.00	0.00	0.00	5.08	5.08	0.00	0.00	0.00	0.01	0.01	5.08	5.08	5.08	5.08	0.00	5.08	5.08
SOLIDHEM	KMOL/HR	0.00	0.00	0.00	0.86	0.86	0.00	0.00	0.00	0.00	0.00	0.86	0.86	0.86	0.86	0.00	5.57	5.57
XYLOSE	KMOL/HR	0.00	0.00	0.00	4.71	4.71	0.00	0.00	0.00	4.70	4.70	4.71	4.71	4.71	0.00	0.00	0.00	0.00
Temperature	C	25.00	25.00	34.81	50.00	60.00	25.00	162.79	25.05	50.00	50.07	224.00	222.28	83.85	50.00	25.00	25.00	198.88
Pressure	BAR	1.00	1.00	1.00	1.00	1.00	1.00	6.50	6.50	4.00	1.00	24.13	1.00	1.00	4.00	1.00	1.00	1.00

Table 24: Oxygen method biomass pre-treatment simulation, stream results



	Units	BIO-FEED	ENZMH2O	ENZMH2O+	ENZMIN	ENZMPROD	GLUCOSE	HP-STEAM	HP-WATER	LIQUIDS	REST	SEPROD	SEPROD+	SEPROD++	SOLIDS	WATER	YLDPROD	YLDPROD+
Mass Flow	KG/HR	6720.59	1150.00	1150.00	6970.59	8120.59	3377.84	250.00	250.00	5228.45	1850.61	6970.59	6970.59	6970.59	2892.14	250.00	6720.59	6720.59
Mole Flow	KMOL/HR	0.00	63.83	63.83	46.16	96.71	60.76	13.88	13.88	77.65	16.89	46.16	46.16	46.16	19.05	13.88	44.79	44.79
Component Mole Flow																		
SOLIDCEL	KMOL/HR	0.00	0.00	0.00	17.53	4.24	0.00	0.00	0.00	0.00	0.00	17.53	17.53	17.53	4.24	0.00	18.34	18.34
GLUCOSE	KMOL/HR	0.00	0.00	0.00	0.81	14.10	14.08	0.00	0.00	14.08	0.00	0.81	0.81	0.81	0.01	0.00	0.00	0.00
WATER	KMOL/HR	0.00	63.83	63.83	1.37	51.92	46.68	13.88	13.88	51.87	5.19	1.37	1.37	1.37	0.05	13.88	0.00	0.00
SOLIDLIG	KMOL/HR	0.00	0.00	0.00	12.62	12.62	0.00	0.00	0.00	0.01	0.01	12.62	12.62	12.62	12.61	0.00	12.62	12.62
SOLIDHEM	KMOL/HR	0.00	0.00	0.00	2.13	2.13	0.00	0.00	0.00	0.00	0.00	2.13	2.13	2.13	2.13	0.00	13.83	13.83
XYLOSE	KMOL/HR	0.00	0.00	0.00	11.70	11.70	0.00	0.00	0.00	11.68	11.68	11.70	11.70	11.70	0.01	0.00	0.00	0.00
Temperature	C	25.00	25.00	45.45	50.00	60.00	25.00	162.79	25.05	50.00	50.07	224.00	222.07	118.10	50.00	25.00	25.00	166.55
Pressure	BAR	1.00	1.00	1.00	1.00	1.00	1.00	6.50	6.50	4.00	1.00	24.13	1.00	1.00	4.00	1.00	1.00	1.00

Table 25: Hydrogen peroxide method wet oxidation simulation, stream results

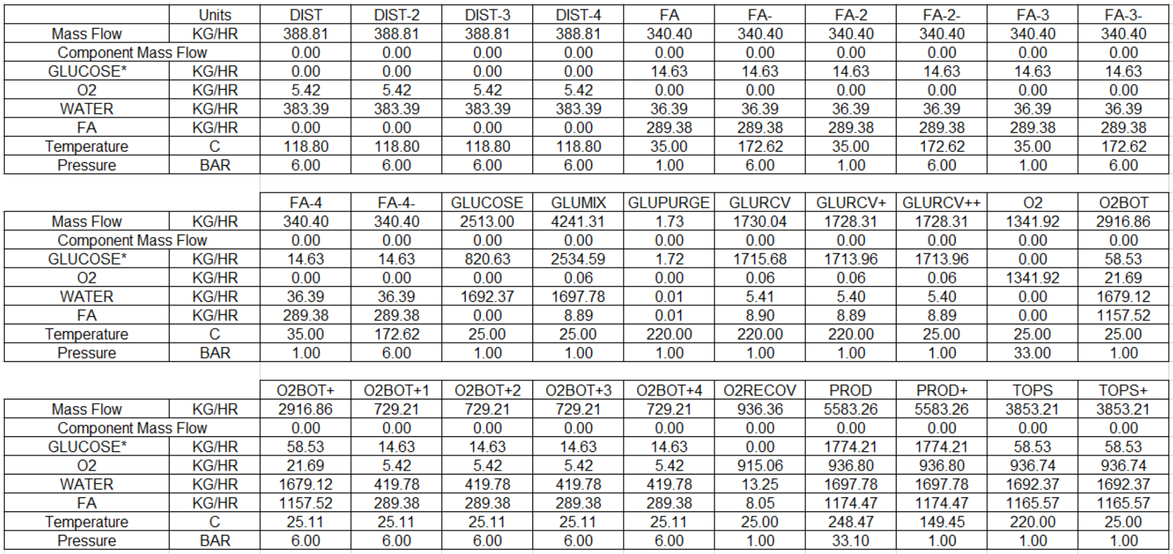


	Units	DIST	DIST-2	DIST-3	DIST-4	FA	FA-	FA-2	FA-2-	FA-3	FA-3-
Mass Flow	KG/HR	1067.28	1067.28	1067.28	1067.28	340.40	340.40	340.40	340.40	340.40	340.40
Component Mass Flow		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GLUCOSE*	KG/HR	0.00	0.00	0.00	0.00	6.34	6.34	6.34	6.34	6.34	6.34
O2	KG/HR	13.40	13.40	13.40	13.40	0.00	0.00	0.00	0.00	0.00	0.00
HYDPEROX	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
WATER	KG/HR	1053.88	1053.88	1053.88	1053.88	44.70	44.70	44.70	44.70	44.70	44.70
FA	KG/HR	0.00	0.00	0.00	0.00	289.37	289.37	289.37	289.37	289.37	289.37
Temperature	C	112.20	112.20	112.20	112.20	35.00	164.10	35.00	164.10	35.00	164.10
Pressure	BAR	5.00	5.00	5.00	5.00	1.00	5.00	1.00	5.00	1.00	5.00

		FA-4	FA-4-	GLUCOSE	GLUMIX	GLUPURGE	GLURCV	GLURCV+	GLURCV++	H2O2SOLV	O2BOT
Mass Flow	KG/HR	340.40	340.40	1313.00	1629.50	0.95	317.45	316.50	316.50	4500.00	5630.71
Component Mass Flow		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GLUCOSE*	KG/HR	6.34	6.34	781.50	1094.55	0.94	313.99	313.05	313.05	0.00	25.35
O2	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	53.58
HYDPEROX	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1350.00	0.00
WATER	KG/HR	44.70	44.70	531.50	533.57	0.01	2.08	2.07	2.07	3150.00	4394.31
FA	KG/HR	289.37	289.37	0.00	1.37	0.00	1.38	1.37	1.37	0.00	1157.47
Temperature	C	35.00	164.10	25.00	25.00	200.00	200.00	200.00	25.00	25.00	20.00
Pressure	BAR	1.00	5.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

		O2BOT+1	O2BOT+2	O2BOT+3	O2BOT+4	O2RECOV	PROD	PROD+	S1	S5	TOPS	TOPS+
Mass Flow	KG/HR	1407.68	1407.68	1407.68	1407.68	182.14	6130.30	6130.30	6130.30	5630.71	5812.85	5812.85
Component Mass Flow		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GLUCOSE*	KG/HR	6.34	6.34	6.34	6.34	0.00	339.34	339.34	339.34	25.35	25.35	25.35
O2	KG/HR	13.40	13.40	13.40	13.40	179.64	0.00	233.22	233.22	53.58	233.22	233.22
HYDPEROX	KG/HR	0.00	0.00	0.00	0.00	0.00	495.83	0.00	0.00	0.00	0.00	0.00
WATER	KG/HR	1098.58	1098.58	1098.58	1098.58	2.20	4135.98	4398.59	4398.59	4394.31	4396.51	4396.51
FA	KG/HR	289.37	289.37	289.37	289.37	0.31	1159.15	1159.15	1159.15	1157.47	1157.77	1157.77
Temperature	C	20.06	20.06	20.06	20.06	20.00	245.65	184.25	250.00	20.06	200.00	20.00
Pressure	BAR	5.00	5.00	5.00	5.00	1.00	31.00	1.00	31.00	5.00	1.00	1.00

Table 26: Oxygen method wet oxidation simulation, stream results

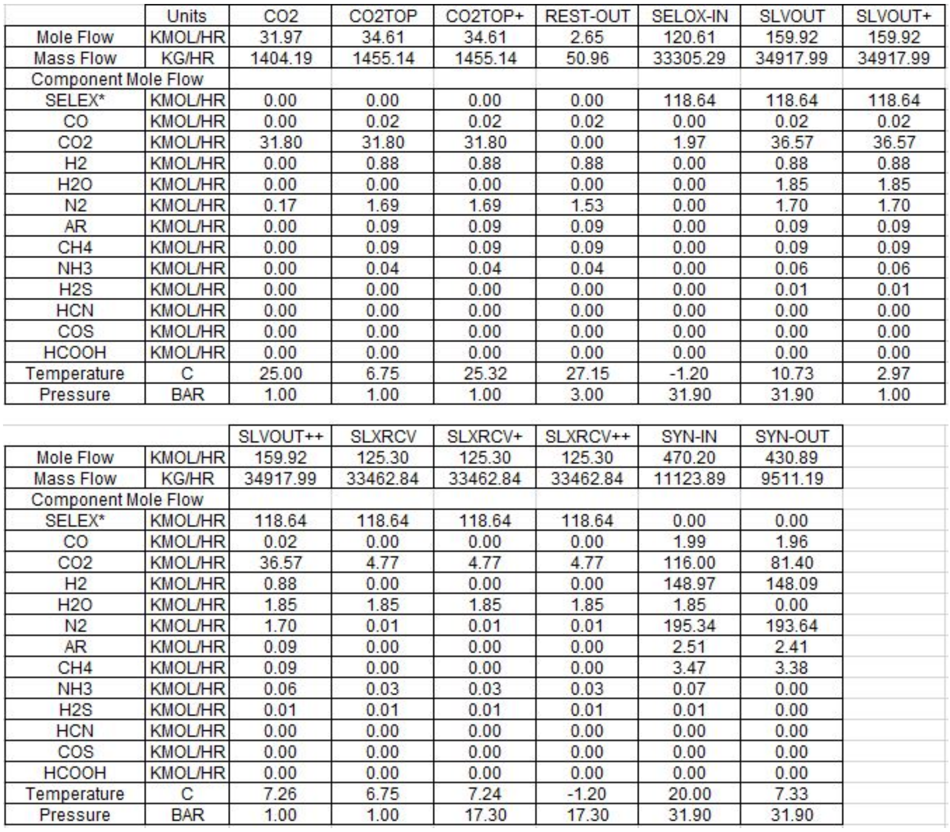


	Units	DIST	DIST-2	DIST-3	DIST-4	FA	FA-	FA-2	FA-2-	FA-3	FA-3-
Mass Flow	KG/HR	388.81	388.81	388.81	388.81	340.40	340.40	340.40	340.40	340.40	340.40
Component Mass Flow		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GLUCOSE*	KG/HR	0.00	0.00	0.00	0.00	14.63	14.63	14.63	14.63	14.63	14.63
O2	KG/HR	5.42	5.42	5.42	5.42	0.00	0.00	0.00	0.00	0.00	0.00
WATER	KG/HR	383.39	383.39	383.39	383.39	36.39	36.39	36.39	36.39	36.39	36.39
FA	KG/HR	0.00	0.00	0.00	0.00	289.38	289.38	289.38	289.38	289.38	289.38
Temperature	C	118.80	118.80	118.80	118.80	35.00	172.62	35.00	172.62	35.00	172.62
Pressure	BAR	6.00	6.00	6.00	6.00	1.00	6.00	1.00	6.00	1.00	6.00

		FA-4	FA-4-	GLUCOSE	GLUMIX	GLUPURGE	GLURCV	GLURCV+	GLURCV++	O2	O2BOT
Mass Flow	KG/HR	340.40	340.40	2513.00	4241.31	1.73	1730.04	1728.31	1728.31	1341.92	2916.86
Component Mass Flow		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GLUCOSE*	KG/HR	14.63	14.63	820.63	2534.59	1.72	1715.68	1713.96	1713.96	0.00	58.53
O2	KG/HR	0.00	0.00	0.00	0.06	0.00	0.06	0.06	0.06	1341.92	21.69
WATER	KG/HR	36.39	36.39	1692.37	1697.78	0.01	5.41	5.40	5.40	0.00	1679.12
FA	KG/HR	289.38	289.38	0.00	8.89	0.01	8.90	8.89	8.89	0.00	1157.52
Temperature	C	35.00	172.62	25.00	25.00	220.00	220.00	220.00	25.00	25.00	25.00
Pressure	BAR	1.00	6.00	1.00	1.00	1.00	1.00	1.00	1.00	33.00	1.00

		O2BOT+	O2BOT+1	O2BOT+2	O2BOT+3	O2BOT+4	O2RECOV	PROD	PROD+	TOPS	TOPS+
Mass Flow	KG/HR	2916.86	729.21	729.21	729.21	729.21	936.36	5583.26	5583.26	3853.21	3853.21
Component Mass Flow		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GLUCOSE*	KG/HR	58.53	14.63	14.63	14.63	14.63	0.00	1774.21	1774.21	58.53	58.53
O2	KG/HR	21.69	5.42	5.42	5.42	5.42	915.06	936.80	936.80	936.74	936.74
WATER	KG/HR	1679.12	419.78	419.78	419.78	419.78	13.25	1697.78	1697.78	1692.37	1692.37
FA	KG/HR	1157.52	289.38	289.38	289.38	289.38	8.05	1174.47	1174.47	1165.57	1165.57
Temperature	C	25.11	25.11	25.11	25.11	25.11	25.00	248.47	149.45	220.00	25.00
Pressure	BAR	6.00	6.00	6.00	6.00	6.00	1.00	33.10	1.00	1.00	1.00

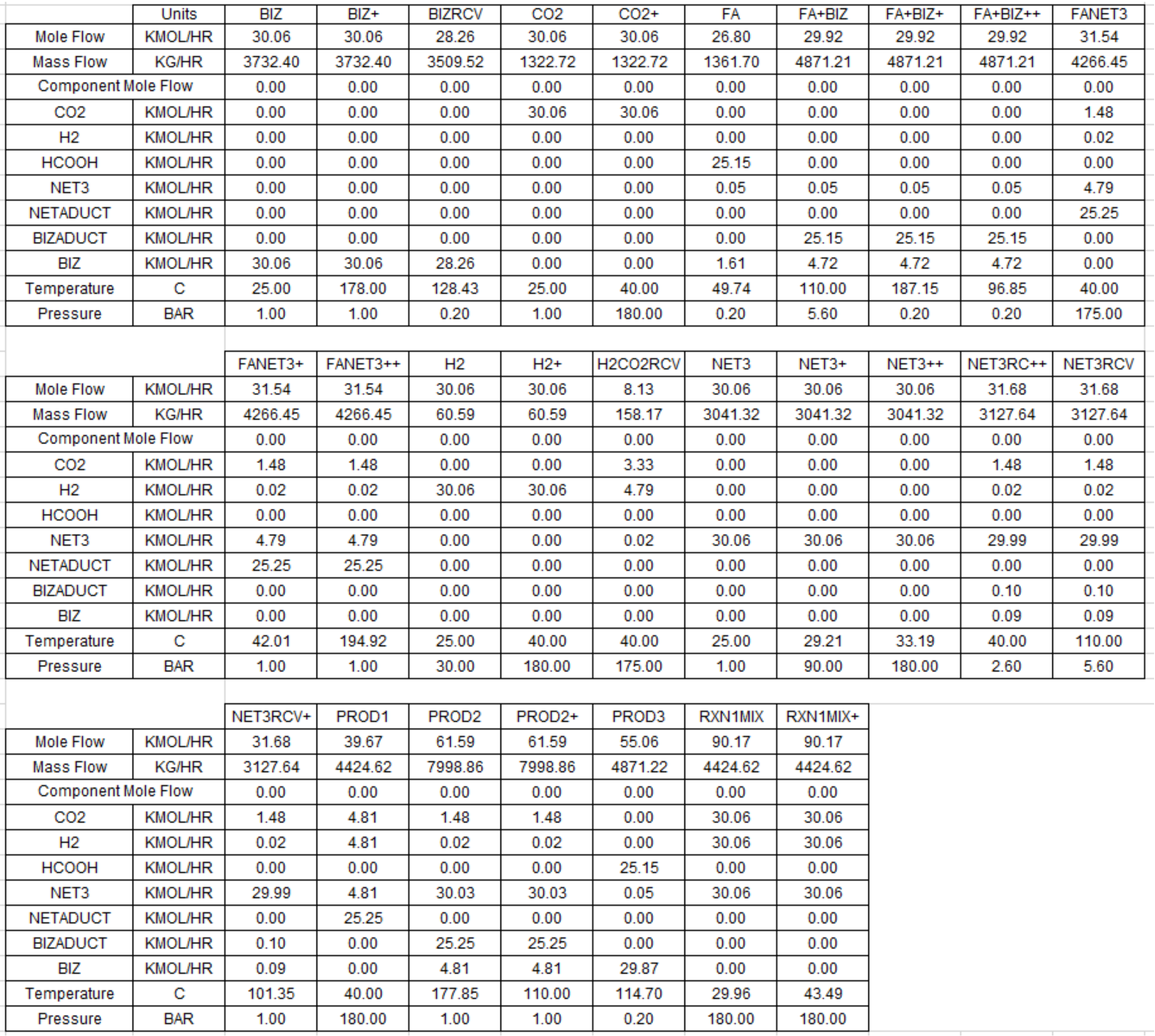
Table 27: Carbon dioxide capture simulation, stream results



	Units	CO2	CO2TOP	CO2TOP+	REST-OUT	SELOX-IN	SLVOUT	SLVOUT+
Mole Flow	KMOL/HR	31.97	34.61	34.61	2.65	120.61	159.92	159.92
Mass Flow	KG/HR	1404.19	1455.14	1455.14	50.96	33305.29	34917.99	34917.99
Component Mole Flow								
SELEX*	KMOL/HR	0.00	0.00	0.00	0.00	118.64	118.64	118.64
CO	KMOL/HR	0.00	0.02	0.02	0.02	0.00	0.02	0.02
CO2	KMOL/HR	31.80	31.80	31.80	0.00	1.97	36.57	36.57
H2	KMOL/HR	0.00	0.88	0.88	0.88	0.00	0.88	0.88
H2O	KMOL/HR	0.00	0.00	0.00	0.00	0.00	1.85	1.85
N2	KMOL/HR	0.17	1.69	1.69	1.53	0.00	1.70	1.70
AR	KMOL/HR	0.00	0.09	0.09	0.09	0.00	0.09	0.09
CH4	KMOL/HR	0.00	0.09	0.09	0.09	0.00	0.09	0.09
NH3	KMOL/HR	0.00	0.04	0.04	0.04	0.00	0.06	0.06
H2S	KMOL/HR	0.00	0.00	0.00	0.00	0.00	0.01	0.01
HCN	KMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00
COS	KMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HCOOH	KMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Temperature	C	25.00	6.75	25.32	27.15	-1.20	10.73	2.97
Pressure	BAR	1.00	1.00	1.00	3.00	31.90	31.90	1.00

		SLVOUT++	SLXRCV	SLXRCV+	SLXRCV++	SYN-IN	SYN-OUT
Mole Flow	KMOL/HR	159.92	125.30	125.30	125.30	470.20	430.89
Mass Flow	KG/HR	34917.99	33462.84	33462.84	33462.84	11123.89	9511.19
Component Mole Flow							
SELEX*	KMOL/HR	118.64	118.64	118.64	118.64	0.00	0.00
CO	KMOL/HR	0.02	0.00	0.00	0.00	1.99	1.96
CO2	KMOL/HR	36.57	4.77	4.77	4.77	116.00	81.40
H2	KMOL/HR	0.88	0.00	0.00	0.00	148.97	148.09
H2O	KMOL/HR	1.85	1.85	1.85	1.85	1.85	0.00
N2	KMOL/HR	1.70	0.01	0.01	0.01	195.34	193.64
AR	KMOL/HR	0.09	0.00	0.00	0.00	2.51	2.41
CH4	KMOL/HR	0.09	0.00	0.00	0.00	3.47	3.38
NH3	KMOL/HR	0.06	0.03	0.03	0.03	0.07	0.00
H2S	KMOL/HR	0.01	0.01	0.01	0.01	0.01	0.00
HCN	KMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00
COS	KMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00
HCOOH	KMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00
Temperature	C	7.26	6.75	7.24	-1.20	20.00	7.33
Pressure	BAR	1.00	1.00	17.30	17.30	31.90	31.90

Table 28: Carbon dioxide hydrogenation simulation, stream results



	Units	BIZ	BIZ+	BIZRCV	CO2	CO2+	FA	FA+BIZ	FA+BIZ+	FA+BIZ++	FANET3
Mole Flow	KMOL/HR	30.06	30.06	28.26	30.06	30.06	26.80	29.92	29.92	29.92	31.54
Mass Flow	KG/HR	3732.40	3732.40	3509.52	1322.72	1322.72	1361.70	4871.21	4871.21	4871.21	4266.45
Component Mole Flow		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO2	KMOL/HR	0.00	0.00	0.00	30.06	30.06	0.00	0.00	0.00	0.00	1.48
H2	KMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
HCOOH	KMOL/HR	0.00	0.00	0.00	0.00	0.00	25.15	0.00	0.00	0.00	0.00
NET3	KMOL/HR	0.00	0.00	0.00	0.00	0.00	0.05	0.05	0.05	0.05	4.79
NETADUCT	KMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	25.25
BIZADUCT	KMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00	25.15	25.15	25.15	0.00
BIZ	KMOL/HR	30.06	30.06	28.26	0.00	0.00	1.61	4.72	4.72	4.72	0.00
Temperature	C	25.00	178.00	128.43	25.00	40.00	49.74	110.00	187.15	96.85	40.00
Pressure	BAR	1.00	1.00	0.20	1.00	180.00	0.20	5.60	0.20	0.20	175.00

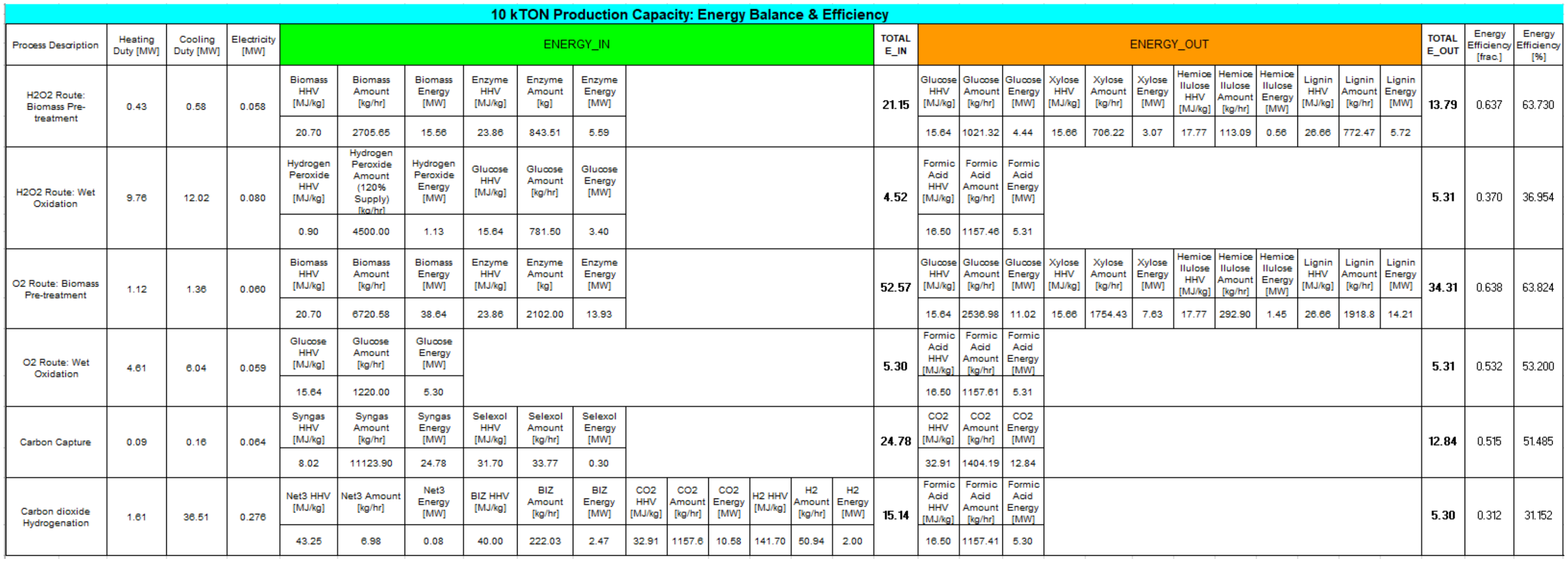
		FANET3+	FANET3++	H2	H2+	H2CO2RCV	NET3	NET3+	NET3++	NET3RC++	NET3RCV
Mole Flow	KMOL/HR	31.54	31.54	30.06	30.06	8.13	30.06	30.06	30.06	31.68	31.68
Mass Flow	KG/HR	4266.45	4266.45	60.59	60.59	158.17	3041.32	3041.32	3041.32	3127.64	3127.64
Component Mole Flow		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO2	KMOL/HR	1.48	1.48	0.00	0.00	3.33	0.00	0.00	0.00	1.48	1.48
H2	KMOL/HR	0.02	0.02	30.06	30.06	4.79	0.00	0.00	0.00	0.02	0.02
HCOOH	KMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NET3	KMOL/HR	4.79	4.79	0.00	0.00	0.02	30.06	30.06	30.06	29.99	29.99
NETADUCT	KMOL/HR	25.25	25.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BIZADUCT	KMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10
BIZ	KMOL/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.09
Temperature	C	42.01	194.92	25.00	40.00	40.00	25.00	29.21	33.19	40.00	110.00
Pressure	BAR	1.00	1.00	30.00	180.00	175.00	1.00	90.00	180.00	2.60	5.60

		NET3RCV+	PROD1	PROD2	PROD2+	PROD3	RXN1MIX	RXN1MIX+
Mole Flow	KMOL/HR	31.68	39.67	61.59	61.59	55.06	90.17	90.17
Mass Flow	KG/HR	3127.64	4424.62	7998.86	7998.86	4871.22	4424.62	4424.62
Component Mole Flow		0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO2	KMOL/HR	1.48	4.81	1.48	1.48	0.00	30.06	30.06
H2	KMOL/HR	0.02	4.81	0.02	0.02	0.00	30.06	30.06
HCOOH	KMOL/HR	0.00	0.00	0.00	0.00	25.15	0.00	0.00
NET3	KMOL/HR	29.99	4.81	30.03	30.03	0.05	30.06	30.06
NETADUCT	KMOL/HR	0.00	25.25	0.00	0.00	0.00	0.00	0.00
BIZADUCT	KMOL/HR	0.10	0.00	25.25	25.25	0.00	0.00	0.00
BIZ	KMOL/HR	0.09	0.00	4.81	4.81	29.87	0.00	0.00
Temperature	C	101.35	40.00	177.85	110.00	114.70	29.96	43.49
Pressure	BAR	1.00	180.00	1.00	1.00	0.20	180.00	180.00

12 Appendix E: Energy Balance Calculations

Total energy balance calculations for all biomass pre-treatment, carbon capture and formic acid processes separately are shown below. Energy analysis is done for both capacity scenarios. The energy balance of the Case Study I is also included because of the differences in hydrogenation reaction conditions.

Table 29: 10 kton formic acid production scenario, energy balance results

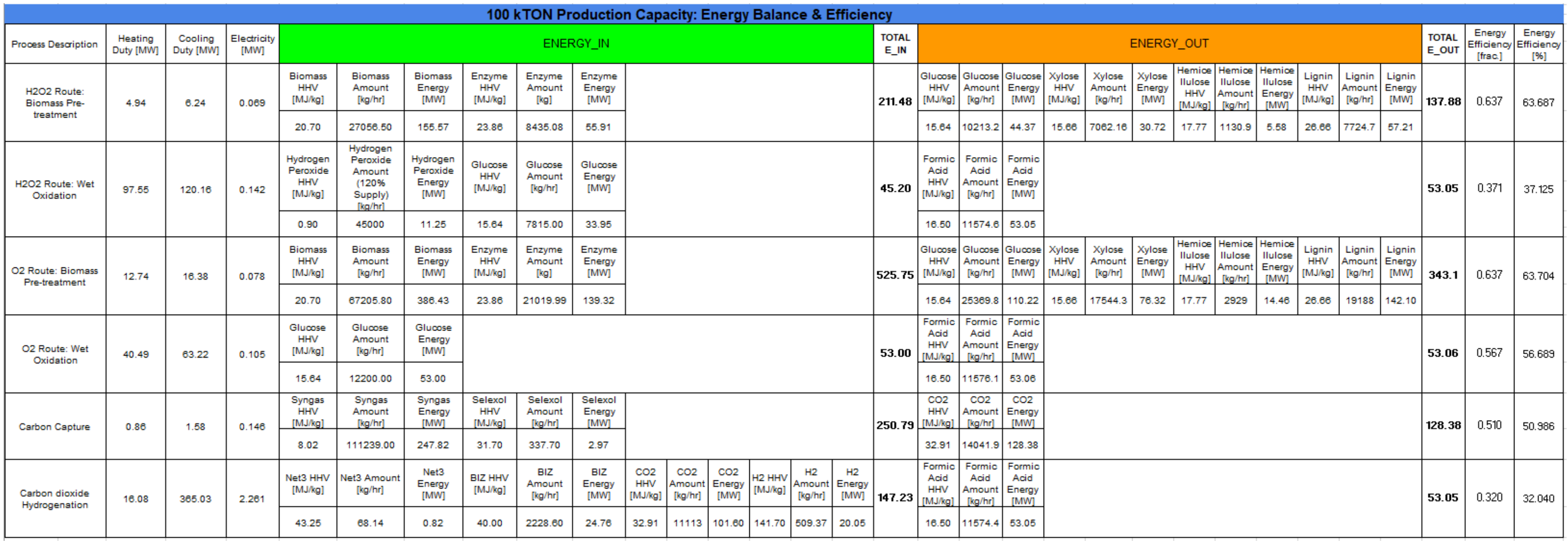


10 kTON Production Capacity: Energy Balance & Efficiency

Process Description	Heating Duty [MW]	Cooling Duty [MW]	Electricity [MW]	ENERGY_IN												TOTAL E_IN
H2O2 Route: Biomass Pre-treatment	0.43	0.58	0.058	Biomass HHV [MJ/kg]	Biomass Amount [kg/hr]	Biomass Energy [MW]	Enzyme HHV [MJ/kg]	Enzyme Amount [kg]	Enzyme Energy [MW]							**21.15**
				20.70	2705.65	15.56	23.86	843.51	5.59							
H2O2 Route: Wet Oxidation	9.76	12.02	0.080	Hydrogen Peroxide HHV [MJ/kg]	Hydrogen Peroxide Amount (120% Supply) [kg/hr]	Hydrogen Peroxide Energy [MW]	Glucose HHV [MJ/kg]	Glucose Amount [kg/hr]	Glucose Energy [MW]							**4.52**
				0.90	4500.00	1.13	15.64	781.50	3.40							
O2 Route: Biomass Pre-treatment	1.12	1.36	0.060	Biomass HHV [MJ/kg]	Biomass Amount [kg/hr]	Biomass Energy [MW]	Enzyme HHV [MJ/kg]	Enzyme Amount [kg]	Enzyme Energy [MW]							**52.57**
				20.70	6720.58	38.64	23.86	2102.00	13.93							
O2 Route: Wet Oxidation	4.61	6.04	0.059	Glucose HHV [MJ/kg]	Glucose Amount [kg/hr]	Glucose Energy [MW]										**5.30**
				15.64	1220.00	5.30										
Carbon Capture	0.09	0.16	0.064	Syngas HHV [MJ/kg]	Syngas Amount [kg/hr]	Syngas Energy [MW]	Selexol HHV [MJ/kg]	Selexol Amount [kg/hr]	Selexol Energy [MW]							**24.78**
				8.02	11123.90	24.78	31.70	33.77	0.30							
Carbon dioxide Hydrogenation	1.61	36.51	0.276	Net3 HHV [MJ/kg]	Net3 Amount [kg/hr]	Net3 Energy [MW]	BIZ HHV [MJ/kg]	BIZ Amount [kg/hr]	BIZ Energy [MW]	CO2 HHV [MJ/kg]	CO2 Amount [kg/hr]	CO2 Energy [MW]	H2 HHV [MJ/kg]	H2 Amount [kg/hr]	H2 Energy [MW]	**15.14**
				43.25	6.98	0.08	40.00	222.03	2.47	32.91	1157.6	10.58	141.70	50.94	2.00	

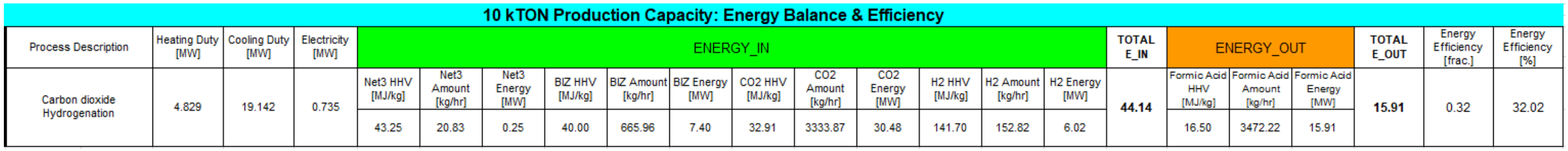
Process Description	ENERGY_OUT												TOTAL E_OUT	Energy Efficiency [frac.]	Energy Efficiency [%]
H2O2 Route: Biomass Pre-treatment	Glucose HHV [MJ/kg]	Glucose Amount [kg/hr]	Glucose Energy [MW]	Xylose HHV [MJ/kg]	Xylose Amount [kg/hr]	Xylose Energy [MW]	Hemicellulose HHV [MJ/kg]	Hemicellulose Amount [kg/hr]	Hemicellulose Energy [MW]	Lignin HHV [MJ/kg]	Lignin Amount [kg/hr]	Lignin Energy [MW]	**13.79**	0.637	63.730
	15.64	1021.32	4.44	15.66	706.22	3.07	17.77	113.09	0.56	26.66	772.47	5.72			
H2O2 Route: Wet Oxidation	Formic Acid HHV [MJ/kg]	Formic Acid Amount [kg/hr]	Formic Acid Energy [MW]										**5.31**	0.370	36.954
	16.50	1157.46	5.31												
O2 Route: Biomass Pre-treatment	Glucose HHV [MJ/kg]	Glucose Amount [kg/hr]	Glucose Energy [MW]	Xylose HHV [MJ/kg]	Xylose Amount [kg/hr]	Xylose Energy [MW]	Hemicellulose HHV [MJ/kg]	Hemicellulose Amount [kg/hr]	Hemicellulose Energy [MW]	Lignin HHV [MJ/kg]	Lignin Amount [kg/hr]	Lignin Energy [MW]	**34.31**	0.638	63.824
	15.64	2536.98	11.02	15.66	1754.43	7.63	17.77	292.90	1.45	26.66	1918.8	14.21			
O2 Route: Wet Oxidation	Formic Acid HHV [MJ/kg]	Formic Acid Amount [kg/hr]	Formic Acid Energy [MW]										**5.31**	0.532	53.200
	16.50	1157.61	5.31												
Carbon Capture	CO2 HHV [MJ/kg]	CO2 Amount [kg/hr]	CO2 Energy [MW]										**12.84**	0.515	51.485
	32.91	1404.19	12.84												
Carbon dioxide Hydrogenation	Formic Acid HHV [MJ/kg]	Formic Acid Amount [kg/hr]	Formic Acid Energy [MW]										**5.30**	0.312	31.152
	16.50	1157.41	5.30												

Table 30: 100 kton formic acid production scenario, energy balance results



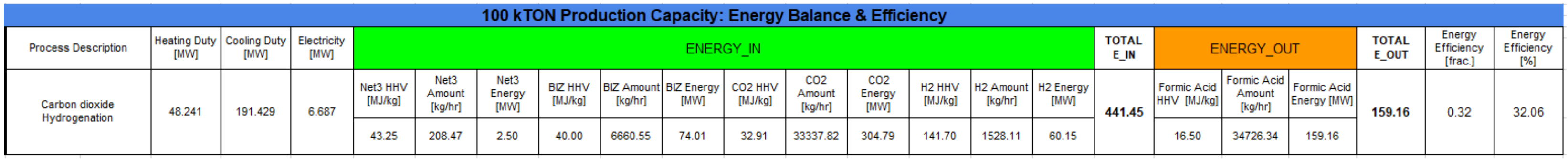
<table>
<tr><th colspan="32">100 kTON Production Capacity: Energy Balance & Efficiency</th></tr>
<tr><th>Process Description</th><th>Heating Duty [MW]</th><th>Cooling Duty [MW]</th><th>Electricity [MW]</th><th colspan="12">ENERGY_IN</th><th>TOTAL E_IN</th><th colspan="12">ENERGY_OUT</th><th>TOTAL E_OUT</th><th>Energy Efficiency [frac.]</th><th>Energy Efficiency [%]</th></tr>
<tr><td rowspan="2">H2O2 Route: Biomass Pre-treatment</td><td rowspan="2">4.94</td><td rowspan="2">6.24</td><td rowspan="2">0.069</td><td>Biomass HHV [MJ/kg]</td><td>Biomass Amount [kg/hr]</td><td>Biomass Energy [MW]</td><td>Enzyme HHV [MJ/kg]</td><td>Enzyme Amount [kg]</td><td>Enzyme Energy [MW]</td><td colspan="6" rowspan="2"></td><td rowspan="2">211.48</td><td>Glucose HHV [MJ/kg]</td><td>Glucose Amount [kg/hr]</td><td>Glucose Energy [MW]</td><td>Xylose HHV [MJ/kg]</td><td>Xylose Amount [kg/hr]</td><td>Xylose Energy [MW]</td><td>Hemicellulose HHV [MJ/kg]</td><td>Hemicellulose Amount [kg/hr]</td><td>Hemicellulose Energy [MW]</td><td>Lignin HHV [MJ/kg]</td><td>Lignin Amount [kg/hr]</td><td>Lignin Energy [MW]</td><td rowspan="2">137.88</td><td rowspan="2">0.637</td><td rowspan="2">63.687</td></tr>
<tr><td>20.70</td><td>27056.50</td><td>155.57</td><td>23.86</td><td>8435.08</td><td>55.91</td><td>15.64</td><td>10213.2</td><td>44.37</td><td>15.66</td><td>7062.16</td><td>30.72</td><td>17.77</td><td>1130.9</td><td>5.58</td><td>26.66</td><td>7724.7</td><td>57.21</td></tr>
<tr><td rowspan="2">H2O2 Route: Wet Oxidation</td><td rowspan="2">97.55</td><td rowspan="2">120.16</td><td rowspan="2">0.142</td><td>Hydrogen Peroxide HHV [MJ/kg]</td><td>Hydrogen Peroxide Amount (120% Supply) [kg/hr]</td><td>Hydrogen Peroxide Energy [MW]</td><td>Glucose HHV [MJ/kg]</td><td>Glucose Amount [kg/hr]</td><td>Glucose Energy [MW]</td><td colspan="6" rowspan="2"></td><td rowspan="2">45.20</td><td>Formic Acid HHV [MJ/kg]</td><td>Formic Acid Amount [kg/hr]</td><td>Formic Acid Energy [MW]</td><td colspan="9" rowspan="2"></td><td rowspan="2">53.05</td><td rowspan="2">0.371</td><td rowspan="2">37.125</td></tr>
<tr><td>0.90</td><td>45000</td><td>11.25</td><td>15.64</td><td>7815.00</td><td>33.95</td><td>16.50</td><td>11574.6</td><td>53.05</td></tr>
<tr><td rowspan="2">O2 Route: Biomass Pre-treatment</td><td rowspan="2">12.74</td><td rowspan="2">16.38</td><td rowspan="2">0.078</td><td>Biomass HHV [MJ/kg]</td><td>Biomass Amount [kg/hr]</td><td>Biomass Energy [MW]</td><td>Enzyme HHV [MJ/kg]</td><td>Enzyme Amount [kg]</td><td>Enzyme Energy [MW]</td><td colspan="6" rowspan="2"></td><td rowspan="2">525.75</td><td>Glucose HHV [MJ/kg]</td><td>Glucose Amount [kg/hr]</td><td>Glucose Energy [MW]</td><td>Xylose HHV [MJ/kg]</td><td>Xylose Amount [kg/hr]</td><td>Xylose Energy [MW]</td><td>Hemicellulose HHV [MJ/kg]</td><td>Hemicellulose Amount [kg/hr]</td><td>Hemicellulose Energy [MW]</td><td>Lignin HHV [MJ/kg]</td><td>Lignin Amount [kg/hr]</td><td>Lignin Energy [MW]</td><td rowspan="2">343.1</td><td rowspan="2">0.637</td><td rowspan="2">63.704</td></tr>
<tr><td>20.70</td><td>67205.80</td><td>386.43</td><td>23.86</td><td>21019.99</td><td>139.32</td><td>15.64</td><td>25369.8</td><td>110.22</td><td>15.66</td><td>17544.3</td><td>76.32</td><td>17.77</td><td>2929</td><td>14.46</td><td>26.66</td><td>19188</td><td>142.10</td></tr>
<tr><td rowspan="2">O2 Route: Wet Oxidation</td><td rowspan="2">40.49</td><td rowspan="2">63.22</td><td rowspan="2">0.105</td><td>Glucose HHV [MJ/kg]</td><td>Glucose Amount [kg/hr]</td><td>Glucose Energy [MW]</td><td colspan="9" rowspan="2"></td><td rowspan="2">53.00</td><td>Formic Acid HHV [MJ/kg]</td><td>Formic Acid Amount [kg/hr]</td><td>Formic Acid Energy [MW]</td><td colspan="9" rowspan="2"></td><td rowspan="2">53.06</td><td rowspan="2">0.567</td><td rowspan="2">56.689</td></tr>
<tr><td>15.64</td><td>12200.00</td><td>53.00</td><td>16.50</td><td>11576.1</td><td>53.06</td></tr>
<tr><td rowspan="2">Carbon Capture</td><td rowspan="2">0.86</td><td rowspan="2">1.58</td><td rowspan="2">0.146</td><td>Syngas HHV [MJ/kg]</td><td>Syngas Amount [kg/hr]</td><td>Syngas Energy [MW]</td><td>Selexol HHV [MJ/kg]</td><td>Selexol Amount [kg/hr]</td><td>Selexol Energy [MW]</td><td colspan="6" rowspan="2"></td><td rowspan="2">250.79</td><td>CO2 HHV [MJ/kg]</td><td>CO2 Amount [kg/hr]</td><td>CO2 Energy [MW]</td><td colspan="9" rowspan="2"></td><td rowspan="2">128.38</td><td rowspan="2">0.510</td><td rowspan="2">50.986</td></tr>
<tr><td>8.02</td><td>111239.00</td><td>247.82</td><td>31.70</td><td>337.70</td><td>2.97</td><td>32.91</td><td>14041.9</td><td>128.38</td></tr>
<tr><td rowspan="2">Carbon dioxide Hydrogenation</td><td rowspan="2">16.08</td><td rowspan="2">365.03</td><td rowspan="2">2.261</td><td>Net3 HHV [MJ/kg]</td><td>Net3 Amount [kg/hr]</td><td>Net3 Energy [MW]</td><td>BIZ HHV [MJ/kg]</td><td>BIZ Amount [kg/hr]</td><td>BIZ Energy [MW]</td><td>CO2 HHV [MJ/kg]</td><td>CO2 Amount [kg/hr]</td><td>CO2 Energy [MW]</td><td>H2 HHV [MJ/kg]</td><td>H2 Amount [kg/hr]</td><td>H2 Energy [MW]</td><td rowspan="2">147.23</td><td>Formic Acid HHV [MJ/kg]</td><td>Formic Acid Amount [kg/hr]</td><td>Formic Acid Energy [MW]</td><td colspan="9" rowspan="2"></td><td rowspan="2">53.05</td><td rowspan="2">0.320</td><td rowspan="2">32.040</td></tr>
<tr><td>43.25</td><td>68.14</td><td>0.82</td><td>40.00</td><td>2228.60</td><td>24.76</td><td>32.91</td><td>11113</td><td>101.60</td><td>141.70</td><td>509.37</td><td>20.05</td><td>16.50</td><td>11574.4</td><td>53.05</td></tr>
</table>

Table 31: Case Study II: 10 kton formic acid production scenario, energy balance results



10 kTON Production Capacity: Energy Balance & Efficiency																						
Process Description	Heating Duty [MW]	Cooling Duty [MW]	Electricity [MW]	ENERGY_IN												**TOTAL E_IN**	ENERGY_OUT			**TOTAL E_OUT**	Energy Efficiency [frac.]	Energy Efficiency [%]
				Net3 HHV [MJ/kg]	Net3 Amount [kg/hr]	Net3 Energy [MW]	BIZ HHV [MJ/kg]	BIZ Amount [kg/hr]	BIZ Energy [MW]	CO2 HHV [MJ/kg]	CO2 Amount [kg/hr]	CO2 Energy [MW]	H2 HHV [MJ/kg]	H2 Amount [kg/hr]	H2 Energy [MW]		Formic Acid HHV [MJ/kg]	Formic Acid Amount [kg/hr]	Formic Acid Energy [MW]			
Carbon dioxide Hydrogenation	4.829	19.142	0.735	43.25	20.83	0.25	40.00	665.96	7.40	32.91	3333.87	30.48	141.70	152.82	6.02	**44.14**	16.50	3472.22	15.91	**15.91**	0.32	32.02

Table 32: Case Study II: 100 kton formic acid production scenario, energy balance results

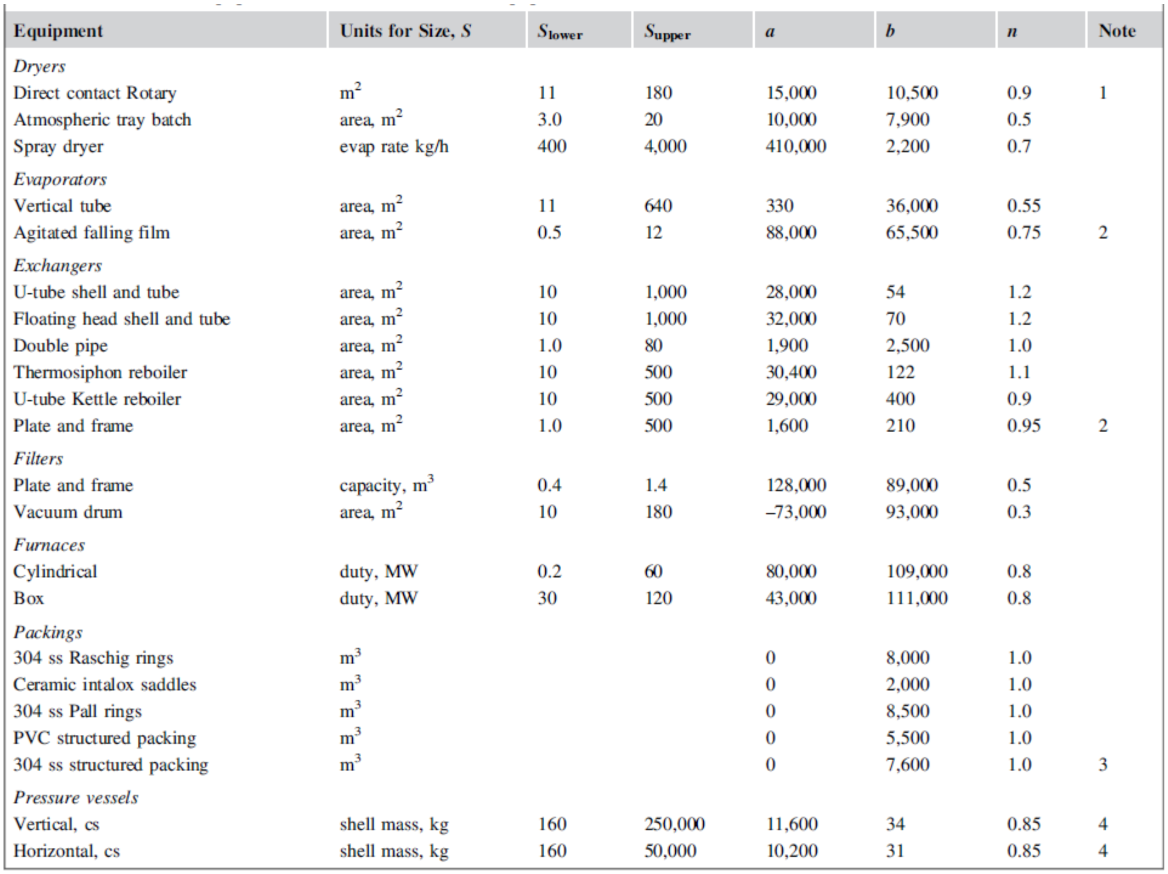


100 kTON Production Capacity: Energy Balance & Efficiency																						
Process Description	Heating Duty [MW]	Cooling Duty [MW]	Electricity [MW]	ENERGY_IN												**TOTAL E_IN**	ENERGY_OUT			**TOTAL E_OUT**	Energy Efficiency [frac.]	Energy Efficiency [%]
				Net3 HHV [MJ/kg]	Net3 Amount [kg/hr]	Net3 Energy [MW]	BIZ HHV [MJ/kg]	BIZ Amount [kg/hr]	BIZ Energy [MW]	CO2 HHV [MJ/kg]	CO2 Amount [kg/hr]	CO2 Energy [MW]	H2 HHV [MJ/kg]	H2 Amount [kg/hr]	H2 Energy [MW]		Formic Acid HHV [MJ/kg]	Formic Acid Amount [kg/hr]	Formic Acid Energy [MW]			
Carbon dioxide Hydrogenation	48.241	191.429	6.687	43.25	208.47	2.50	40.00	6660.55	74.01	32.91	33337.82	304.79	141.70	1528.11	60.15	**441.45**	16.50	34726.34	159.16	**159.16**	0.32	32.06

13 Appendix F: Equipment Lists

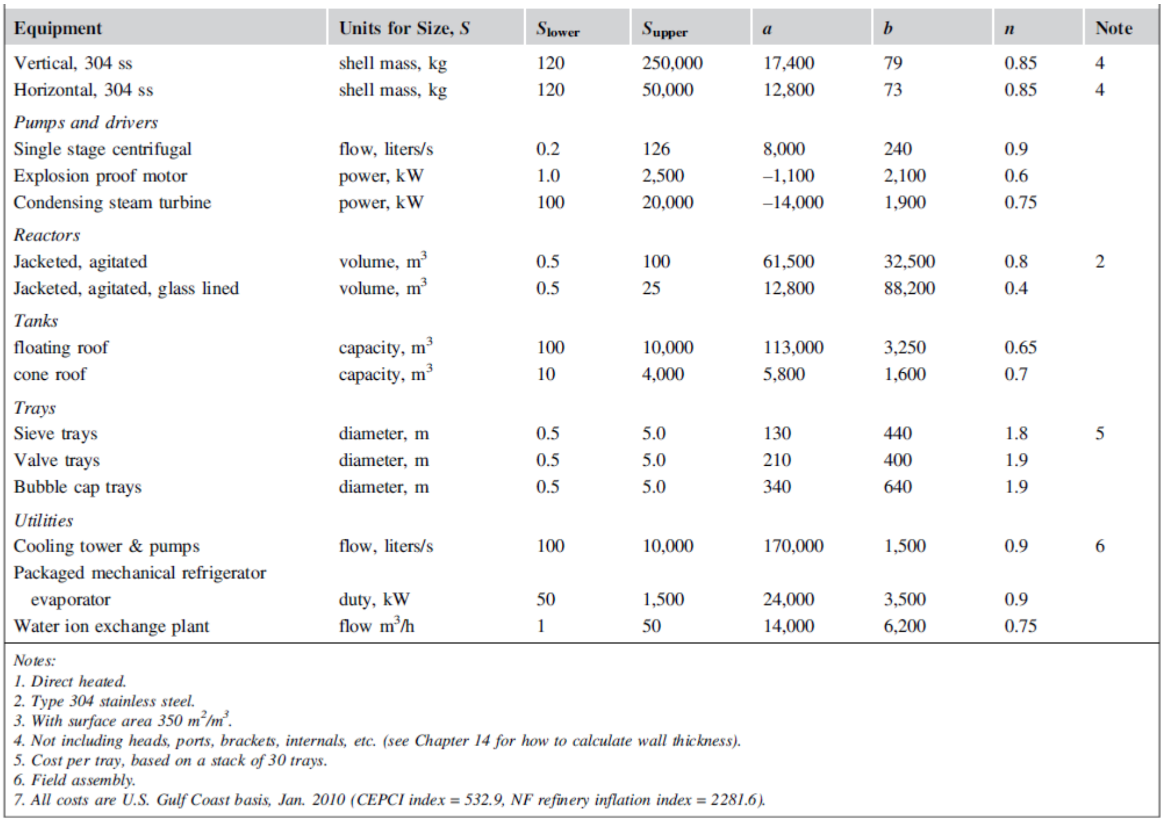
The purchased equipment cost calculation constants based on type and sizing [15] are shown in Table 33 and 34.

Table 33: Equipment selection with sizing limits and units [15]



Equipment	Units for Size, S	S_{lower}	S_{upper}	a	b	n	Note
Dryers							
Direct contact Rotary	m^2	11	180	15,000	10,500	0.9	1
Atmospheric tray batch	area, m^2	3.0	20	10,000	7,900	0.5	
Spray dryer	evap rate kg/h	400	4,000	410,000	2,200	0.7	
Evaporators							
Vertical tube	area, m^2	11	640	330	36,000	0.55	
Agitated falling film	area, m^2	0.5	12	88,000	65,500	0.75	2
Exchangers							
U-tube shell and tube	area, m^2	10	1,000	28,000	54	1.2	
Floating head shell and tube	area, m^2	10	1,000	32,000	70	1.2	
Double pipe	area, m^2	1.0	80	1,900	2,500	1.0	
Thermosiphon reboiler	area, m^2	10	500	30,400	122	1.1	
U-tube Kettle reboiler	area, m^2	10	500	29,000	400	0.9	
Plate and frame	area, m^2	1.0	500	1,600	210	0.95	2
Filters							
Plate and frame	capacity, m^3	0.4	1.4	128,000	89,000	0.5	
Vacuum drum	area, m^2	10	180	–73,000	93,000	0.3	
Furnaces							
Cylindrical	duty, MW	0.2	60	80,000	109,000	0.8	
Box	duty, MW	30	120	43,000	111,000	0.8	
Packings							
304 ss Raschig rings	m^3			0	8,000	1.0	
Ceramic intalox saddles	m^3			0	2,000	1.0	
304 ss Pall rings	m^3			0	8,500	1.0	
PVC structured packing	m^3			0	5,500	1.0	
304 ss structured packing	m^3			0	7,600	1.0	3
Pressure vessels							
Vertical, cs	shell mass, kg	160	250,000	11,600	34	0.85	4
Horizontal, cs	shell mass, kg	160	50,000	10,200	31	0.85	4

Table 34: Continued: Equipment selection with sizing limits and units [15]

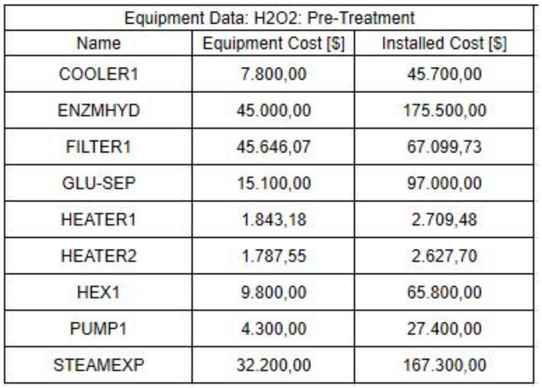


Equipment	Units for Size, *S*	S_{lower}	S_{upper}	*a*	*b*	*n*	Note
Vertical, 304 ss	shell mass, kg	120	250,000	17,400	79	0.85	4
Horizontal, 304 ss	shell mass, kg	120	50,000	12,800	73	0.85	4
Pumps and drivers							
Single stage centrifugal	flow, liters/s	0.2	126	8,000	240	0.9	
Explosion proof motor	power, kW	1.0	2,500	–1,100	2,100	0.6	
Condensing steam turbine	power, kW	100	20,000	–14,000	1,900	0.75	
Reactors							
Jacketed, agitated	volume, m^3	0.5	100	61,500	32,500	0.8	2
Jacketed, agitated, glass lined	volume, m^3	0.5	25	12,800	88,200	0.4	
Tanks							
floating roof	capacity, m^3	100	10,000	113,000	3,250	0.65	
cone roof	capacity, m^3	10	4,000	5,800	1,600	0.7	
Trays							
Sieve trays	diameter, m	0.5	5.0	130	440	1.8	5
Valve trays	diameter, m	0.5	5.0	210	400	1.9	
Bubble cap trays	diameter, m	0.5	5.0	340	640	1.9	
Utilities							
Cooling tower & pumps	flow, liters/s	100	10,000	170,000	1,500	0.9	6
Packaged mechanical refrigerator evaporator	duty, kW	50	1,500	24,000	3,500	0.9	
Water ion exchange plant	flow m^3/h	1	50	14,000	6,200	0.75	

Notes:
1. Direct heated.
2. Type 304 stainless steel.
3. With surface area 350 m^2/m^3.
4. Not including heads, ports, brackets, internals, etc. (see Chapter 14 for how to calculate wall thickness).
5. Cost per tray, based on a stack of 30 trays.
6. Field assembly.
7. All costs are U.S. Gulf Coast basis, Jan. 2010 (CEPCI index = 532.9, NF refinery inflation index = 2281.6).

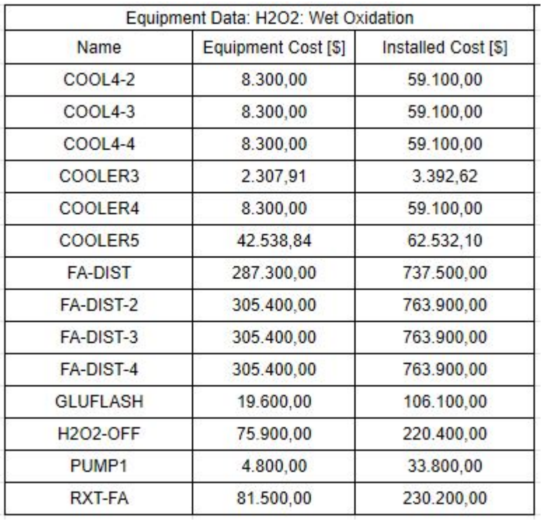
The lists of the used equipments are given below. In addition, purchased and installed cost of each equipment is shown. The results taken from a 10 kton annual production capacity scenario.

Table 35: Biomass, hydrogen peroxide method, pre-treatment simulation, equipments list



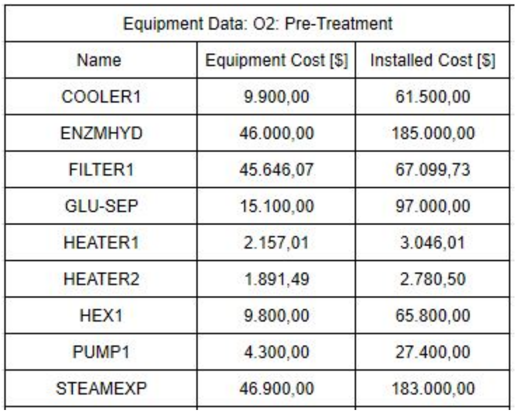
Equipment Data: H2O2: Pre-Treatment		
Name	Equipment Cost [$]	Installed Cost [$]
COOLER1	7.800,00	45.700,00
ENZMHYD	45.000,00	175.500,00
FILTER1	45.646,07	67.099,73
GLU-SEP	15.100,00	97.000,00
HEATER1	1.843,18	2.709,48
HEATER2	1.787,55	2.627,70
HEX1	9.800,00	65.800,00
PUMP1	4.300,00	27.400,00
STEAMEXP	32.200,00	167.300,00

Table 36: Biomass, hydrogen peroxide method, wet oxidation simulation, equipments list



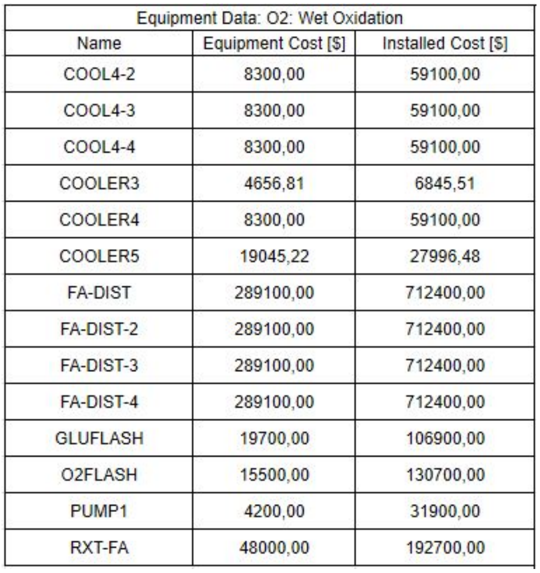
Equipment Data: H2O2: Wet Oxidation		
Name	Equipment Cost [$]	Installed Cost [$]
COOL4-2	8.300,00	59.100,00
COOL4-3	8.300,00	59.100,00
COOL4-4	8.300,00	59.100,00
COOLER3	2.307,91	3.392,62
COOLER4	8.300,00	59.100,00
COOLER5	42.538,84	62.532,10
FA-DIST	287.300,00	737.500,00
FA-DIST-2	305.400,00	763.900,00
FA-DIST-3	305.400,00	763.900,00
FA-DIST-4	305.400,00	763.900,00
GLUFLASH	19.600,00	106.100,00
H2O2-OFF	75.900,00	220.400,00
PUMP1	4.800,00	33.800,00
RXT-FA	81.500,00	230.200,00

Table 37: Biomass, oxygen method, pre-treatment simulation, equipments list



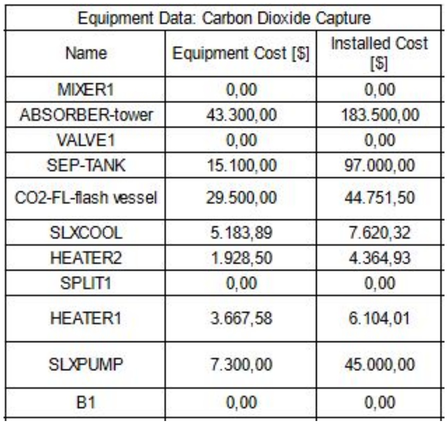
Equipment Data: O2: Pre-Treatment		
Name	Equipment Cost [$]	Installed Cost [$]
COOLER1	9.900,00	61.500,00
ENZMHYD	46.000,00	185.000,00
FILTER1	45.646,07	67.099,73
GLU-SEP	15.100,00	97.000,00
HEATER1	2.157,01	3.046,01
HEATER2	1.891,49	2.780,50
HEX1	9.800,00	65.800,00
PUMP1	4.300,00	27.400,00
STEAMEXP	46.900,00	183.000,00

Table 38: Biomass, oxygen method, wet oxidation simulation, equipments list



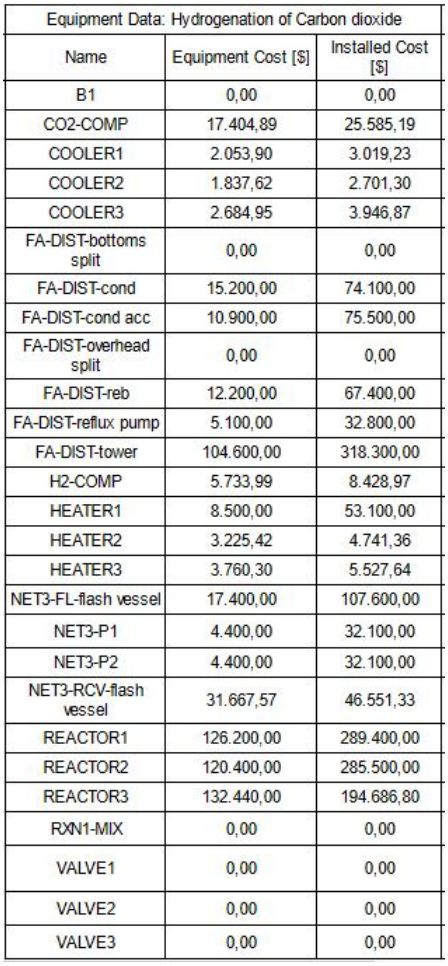
Equipment Data: O2: Wet Oxidation		
Name	Equipment Cost [$]	Installed Cost [$]
COOL4-2	8300,00	59100,00
COOL4-3	8300,00	59100,00
COOL4-4	8300,00	59100,00
COOLER3	4656,81	6845,51
COOLER4	8300,00	59100,00
COOLER5	19045,22	27996,48
FA-DIST	289100,00	712400,00
FA-DIST-2	289100,00	712400,00
FA-DIST-3	289100,00	712400,00
FA-DIST-4	289100,00	712400,00
GLUFLASH	19700,00	106900,00
O2FLASH	15500,00	130700,00
PUMP1	4200,00	31900,00
RXT-FA	48000,00	192700,00

Table 39: CO_2, carbon capture simulation, equipments list



Equipment Data: Carbon Dioxide Capture		
Name	Equipment Cost [$]	Installed Cost [$]
MIXER1	0,00	0,00
ABSORBER-tower	43.300,00	183.500,00
VALVE1	0,00	0,00
SEP-TANK	15.100,00	97.000,00
CO2-FL-flash vessel	29.500,00	44.751,50
SLXCOOL	5.183,89	7.620,32
HEATER2	1.928,50	4.364,93
SPLIT1	0,00	0,00
HEATER1	3.667,58	6.104,01
SLXPUMP	7.300,00	45.000,00
B1	0,00	0,00

Table 40: CO_2, hydrogenation simulation, equipments list

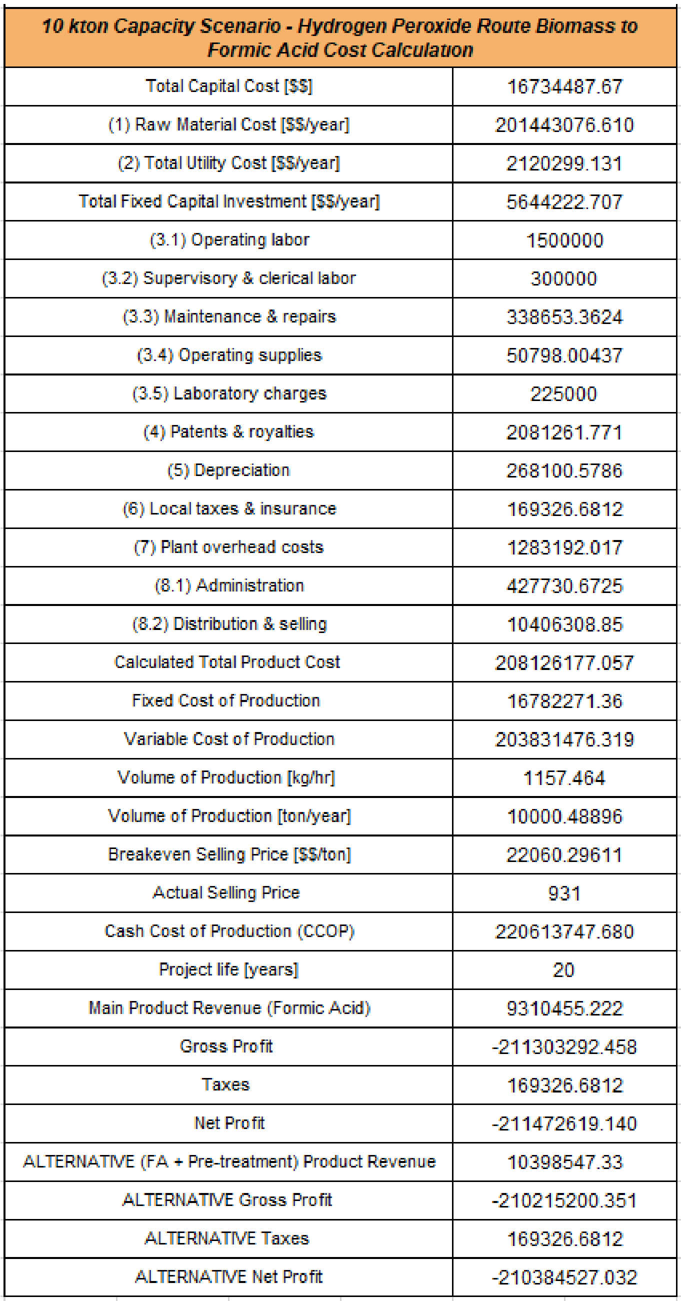


Equipment Data: Hydrogenation of Carbon dioxide		
Name	Equipment Cost [$]	Installed Cost [$]
B1	0,00	0,00
CO2-COMP	17.404,89	25.585,19
COOLER1	2.053,90	3.019,23
COOLER2	1.837,62	2.701,30
COOLER3	2.684,95	3.946,87
FA-DIST-bottoms split	0,00	0,00
FA-DIST-cond	15.200,00	74.100,00
FA-DIST-cond acc	10.900,00	75.500,00
FA-DIST-overhead split	0,00	0,00
FA-DIST-reb	12.200,00	67.400,00
FA-DIST-reflux pump	5.100,00	32.800,00
FA-DIST-tower	104.600,00	318.300,00
H2-COMP	5.733,99	8.428,97
HEATER1	8.500,00	53.100,00
HEATER2	3.225,42	4.741,36
HEATER3	3.760,30	5.527,64
NET3-FL-flash vessel	17.400,00	107.600,00
NET3-P1	4.400,00	32.100,00
NET3-P2	4.400,00	32.100,00
NET3-RCV-flash vessel	31.667,57	46.551,33
REACTOR1	126.200,00	289.400,00
REACTOR2	120.400,00	285.500,00
REACTOR3	132.440,00	194.686,80
RXN1-MIX	0,00	0,00
VALVE1	0,00	0,00
VALVE2	0,00	0,00
VALVE3	0,00	0,00

14 Appendix G: Total Cost Lists

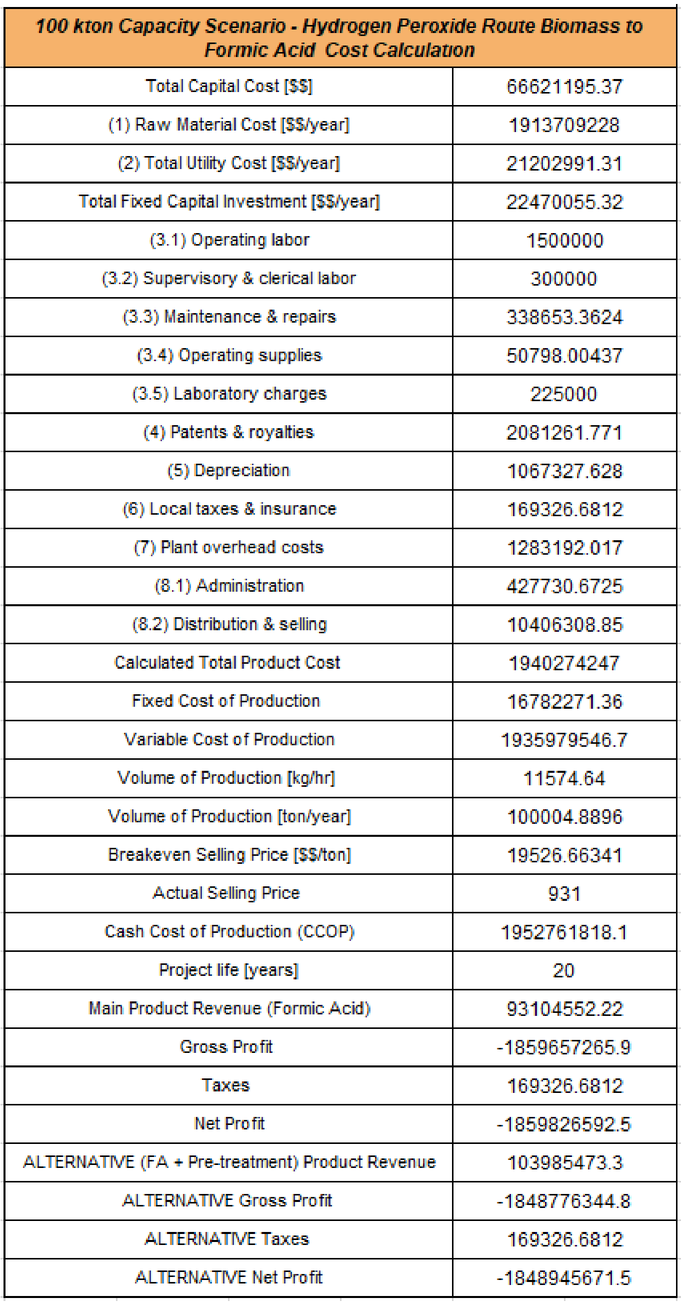
The complete result of the cost calculations for hydrogen peroxide, oxygen and carbon dioxide processes, both 10 kton and 100 kton operating scenarios.

Table 41: Biomass route, hydrogen peroxide method, economic calculation results for 10 kton operating scenario



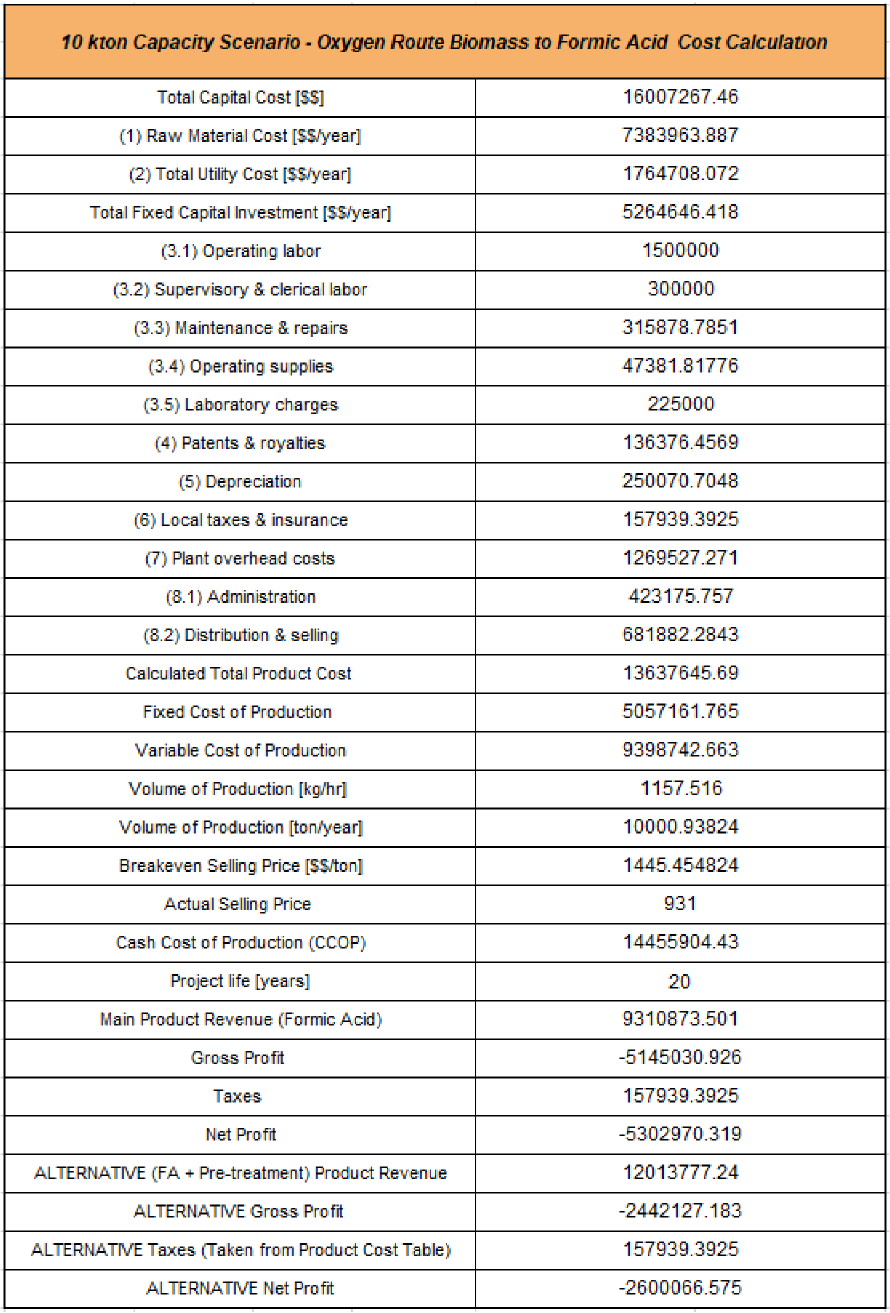
10 kton Capacity Scenario - Hydrogen Peroxide Route Biomass to Formic Acid Cost Calculation	
Total Capital Cost [S$]	16734487.67
(1) Raw Material Cost [S$/year]	201443076.610
(2) Total Utility Cost [S$/year]	2120299.131
Total Fixed Capital Investment [S$/year]	5644222.707
(3.1) Operating labor	1500000
(3.2) Supervisory & clerical labor	300000
(3.3) Maintenance & repairs	338653.3624
(3.4) Operating supplies	50798.00437
(3.5) Laboratory charges	225000
(4) Patents & royalties	2081261.771
(5) Depreciation	268100.5786
(6) Local taxes & insurance	169326.6812
(7) Plant overhead costs	1283192.017
(8.1) Administration	427730.6725
(8.2) Distribution & selling	10406308.85
Calculated Total Product Cost	208126177.057
Fixed Cost of Production	16782271.36
Variable Cost of Production	203831476.319
Volume of Production [kg/hr]	1157.464
Volume of Production [ton/year]	10000.48896
Breakeven Selling Price [S$/ton]	22060.29611
Actual Selling Price	931
Cash Cost of Production (CCOP)	220613747.680
Project life [years]	20
Main Product Revenue (Formic Acid)	9310455.222
Gross Profit	-211303292.458
Taxes	169326.6812
Net Profit	-211472619.140
ALTERNATIVE (FA + Pre-treatment) Product Revenue	10398547.33
ALTERNATIVE Gross Profit	-210215200.351
ALTERNATIVE Taxes	169326.6812
ALTERNATIVE Net Profit	-210384527.032

Table 42: Biomass route, hydrogen peroxide method, economic calculation results for 100 kton operating scenario



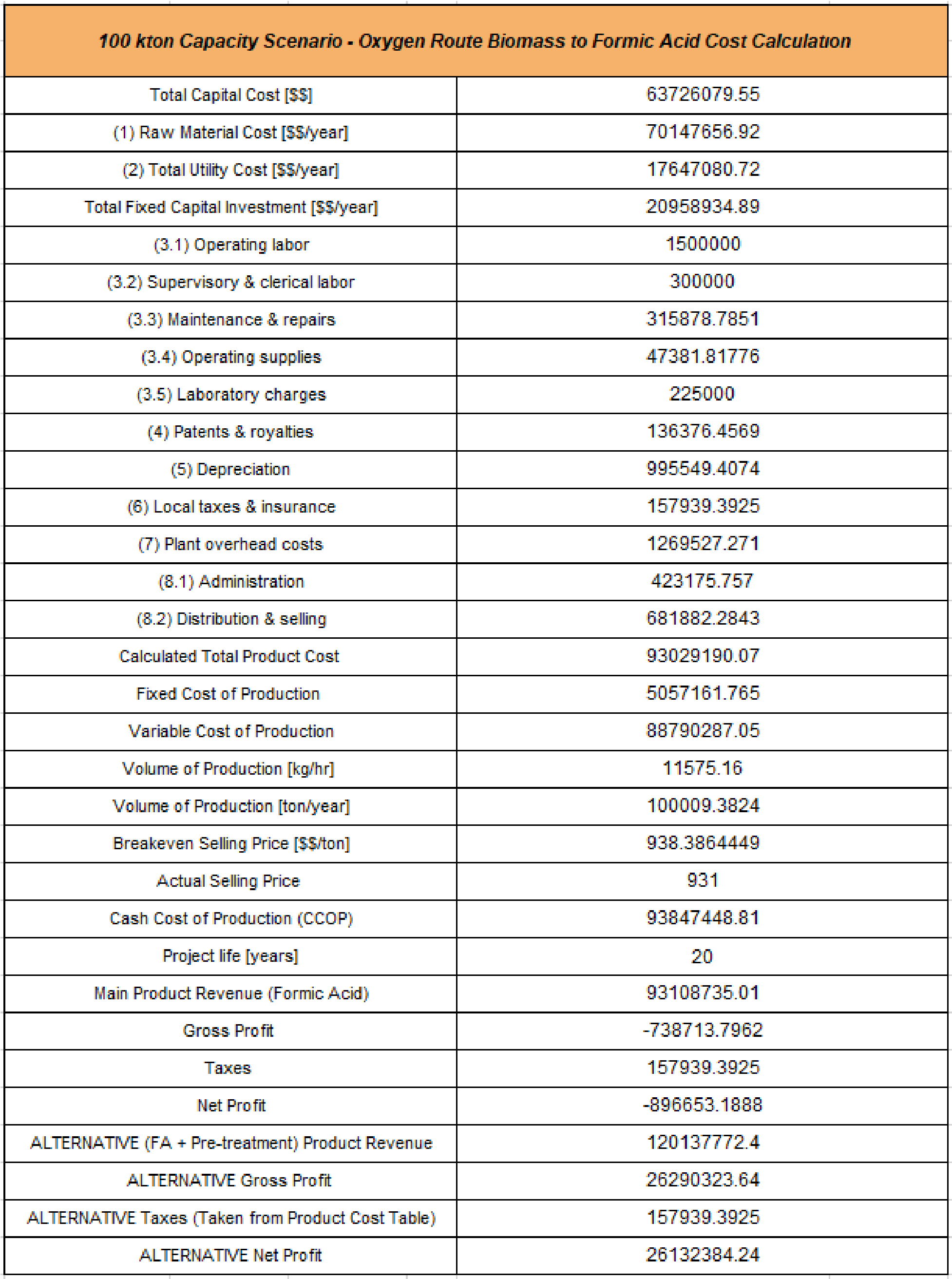
100 kton Capacity Scenario - Hydrogen Peroxide Route Biomass to Formic Acid Cost Calculation	
Total Capital Cost [S$]	66621195.37
(1) Raw Material Cost [S$/year]	1913709228
(2) Total Utility Cost [S$/year]	21202991.31
Total Fixed Capital Investment [S$/year]	22470055.32
(3.1) Operating labor	1500000
(3.2) Supervisory & clerical labor	300000
(3.3) Maintenance & repairs	338653.3624
(3.4) Operating supplies	50798.00437
(3.5) Laboratory charges	225000
(4) Patents & royalties	2081261.771
(5) Depreciation	1067327.628
(6) Local taxes & insurance	169326.6812
(7) Plant overhead costs	1283192.017
(8.1) Administration	427730.6725
(8.2) Distribution & selling	10406308.85
Calculated Total Product Cost	1940274247
Fixed Cost of Production	16782271.36
Variable Cost of Production	1935979546.7
Volume of Production [kg/hr]	11574.64
Volume of Production [ton/year]	100004.8896
Breakeven Selling Price [S$/ton]	19526.66341
Actual Selling Price	931
Cash Cost of Production (CCOP)	1952761818.1
Project life [years]	20
Main Product Revenue (Formic Acid)	93104552.22
Gross Profit	-1859657265.9
Taxes	169326.6812
Net Profit	-1859826592.5
ALTERNATIVE (FA + Pre-treatment) Product Revenue	103985473.3
ALTERNATIVE Gross Profit	-1848776344.8
ALTERNATIVE Taxes	169326.6812
ALTERNATIVE Net Profit	-1848945671.5

Table 43: Biomass route, oxygen method, economic calculation results for 10 kton operating scenario



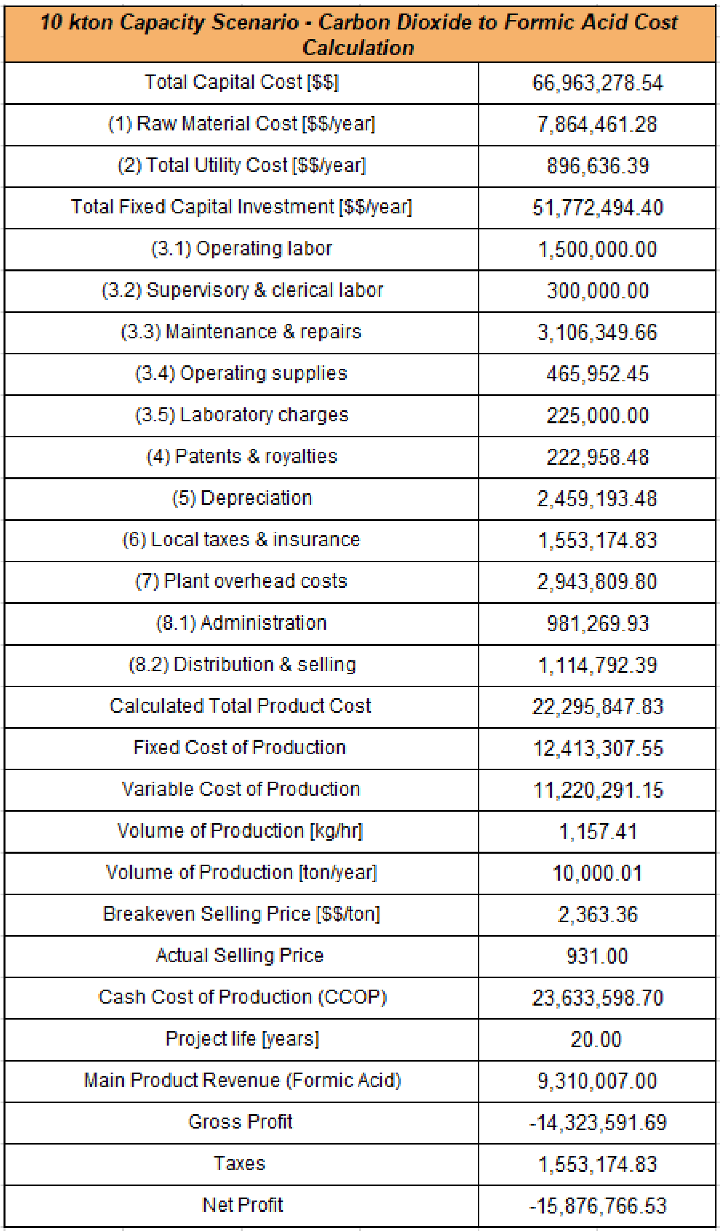
10 kton Capacity Scenario - Oxygen Route Biomass to Formic Acid Cost Calculation	
Total Capital Cost [S$]	16007267.46
(1) Raw Material Cost [S$/year]	7383963.887
(2) Total Utility Cost [S$/year]	1764708.072
Total Fixed Capital Investment [S$/year]	5264646.418
(3.1) Operating labor	1500000
(3.2) Supervisory & clerical labor	300000
(3.3) Maintenance & repairs	315878.7851
(3.4) Operating supplies	47381.81776
(3.5) Laboratory charges	225000
(4) Patents & royalties	136376.4569
(5) Depreciation	250070.7048
(6) Local taxes & insurance	157939.3925
(7) Plant overhead costs	1269527.271
(8.1) Administration	423175.757
(8.2) Distribution & selling	681882.2843
Calculated Total Product Cost	13637645.69
Fixed Cost of Production	5057161.765
Variable Cost of Production	9398742.663
Volume of Production [kg/hr]	1157.516
Volume of Production [ton/year]	10000.93824
Breakeven Selling Price [S$/ton]	1445.454824
Actual Selling Price	931
Cash Cost of Production (CCOP)	14455904.43
Project life [years]	20
Main Product Revenue (Formic Acid)	9310873.501
Gross Profit	-5145030.926
Taxes	157939.3925
Net Profit	-5302970.319
ALTERNATIVE (FA + Pre-treatment) Product Revenue	12013777.24
ALTERNATIVE Gross Profit	-2442127.183
ALTERNATIVE Taxes (Taken from Product Cost Table)	157939.3925
ALTERNATIVE Net Profit	-2600066.575

Table 44: Biomass route, oxygen method, economic calculation results for 100 kton operating scenario



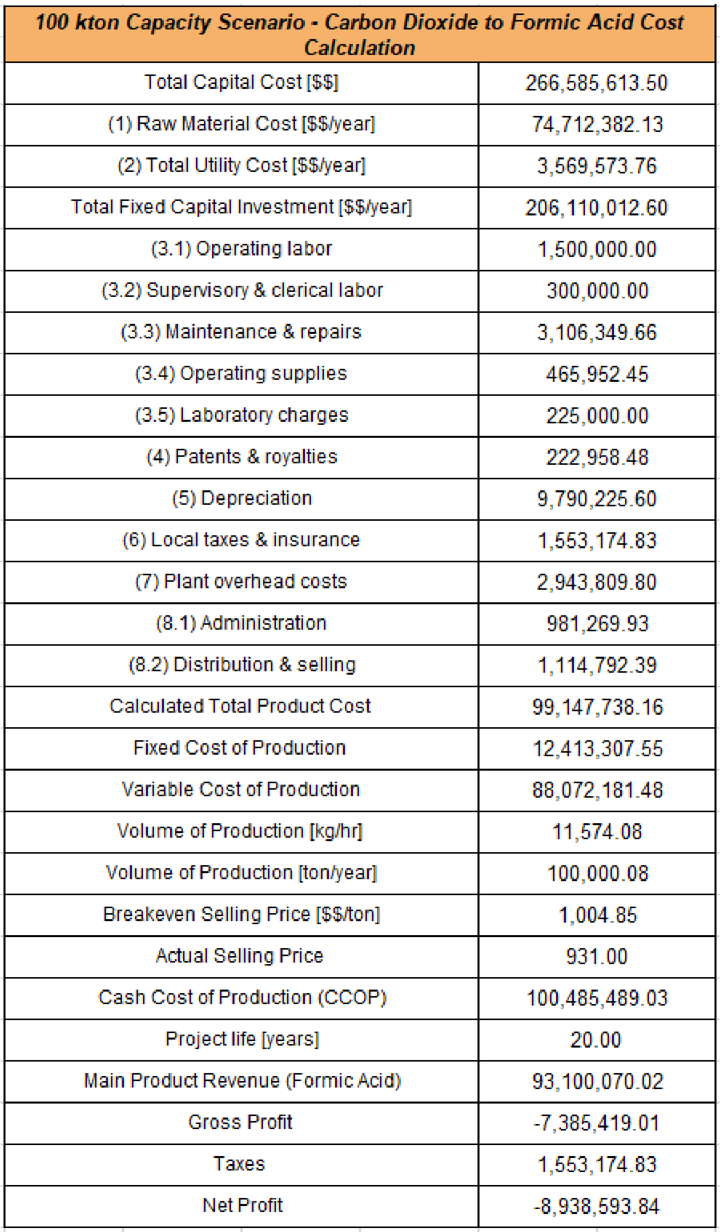
100 kton Capacity Scenario - Oxygen Route Biomass to Formic Acid Cost Calculation	
Total Capital Cost [$$]	63726079.55
(1) Raw Material Cost [$$/year]	70147656.92
(2) Total Utility Cost [$$/year]	17647080.72
Total Fixed Capital Investment [$$/year]	20958934.89
(3.1) Operating labor	1500000
(3.2) Supervisory & clerical labor	300000
(3.3) Maintenance & repairs	315878.7851
(3.4) Operating supplies	47381.81776
(3.5) Laboratory charges	225000
(4) Patents & royalties	136376.4569
(5) Depreciation	995549.4074
(6) Local taxes & insurance	157939.3925
(7) Plant overhead costs	1269527.271
(8.1) Administration	423175.757
(8.2) Distribution & selling	681882.2843
Calculated Total Product Cost	93029190.07
Fixed Cost of Production	5057161.765
Variable Cost of Production	88790287.05
Volume of Production [kg/hr]	11575.16
Volume of Production [ton/year]	100009.3824
Breakeven Selling Price [$$/ton]	938.3864449
Actual Selling Price	931
Cash Cost of Production (CCOP)	93847448.81
Project life [years]	20
Main Product Revenue (Formic Acid)	93108735.01
Gross Profit	-738713.7962
Taxes	157939.3925
Net Profit	-896653.1888
ALTERNATIVE (FA + Pre-treatment) Product Revenue	120137772.4
ALTERNATIVE Gross Profit	26290323.64
ALTERNATIVE Taxes (Taken from Product Cost Table)	157939.3925
ALTERNATIVE Net Profit	26132384.24

Table 45: Carbon dioxide route, economic calculation results for 10 kton operating scenario



10 kton Capacity Scenario - Carbon Dioxide to Formic Acid Cost Calculation	
Total Capital Cost [$$]	66,963,278.54
(1) Raw Material Cost [$$/year]	7,864,461.28
(2) Total Utility Cost [$$/year]	896,636.39
Total Fixed Capital Investment [$$/year]	51,772,494.40
(3.1) Operating labor	1,500,000.00
(3.2) Supervisory & clerical labor	300,000.00
(3.3) Maintenance & repairs	3,106,349.66
(3.4) Operating supplies	465,952.45
(3.5) Laboratory charges	225,000.00
(4) Patents & royalties	222,958.48
(5) Depreciation	2,459,193.48
(6) Local taxes & insurance	1,553,174.83
(7) Plant overhead costs	2,943,809.80
(8.1) Administration	981,269.93
(8.2) Distribution & selling	1,114,792.39
Calculated Total Product Cost	22,295,847.83
Fixed Cost of Production	12,413,307.55
Variable Cost of Production	11,220,291.15
Volume of Production [kg/hr]	1,157.41
Volume of Production [ton/year]	10,000.01
Breakeven Selling Price [$$/ton]	2,363.36
Actual Selling Price	931.00
Cash Cost of Production (CCOP)	23,633,598.70
Project life [years]	20.00
Main Product Revenue (Formic Acid)	9,310,007.00
Gross Profit	-14,323,591.69
Taxes	1,553,174.83
Net Profit	-15,876,766.53

Table 46: Carbon dioxide route, economic calculation results for 100 kton operating scenario



100 kton Capacity Scenario - Carbon Dioxide to Formic Acid Cost Calculation	
Total Capital Cost [$$]	266,585,613.50
(1) Raw Material Cost [$$/year]	74,712,382.13
(2) Total Utility Cost [$$/year]	3,569,573.76
Total Fixed Capital Investment [$$/year]	206,110,012.60
(3.1) Operating labor	1,500,000.00
(3.2) Supervisory & clerical labor	300,000.00
(3.3) Maintenance & repairs	3,106,349.66
(3.4) Operating supplies	465,952.45
(3.5) Laboratory charges	225,000.00
(4) Patents & royalties	222,958.48
(5) Depreciation	9,790,225.60
(6) Local taxes & insurance	1,553,174.83
(7) Plant overhead costs	2,943,809.80
(8.1) Administration	981,269.93
(8.2) Distribution & selling	1,114,792.39
Calculated Total Product Cost	99,147,738.16
Fixed Cost of Production	12,413,307.55
Variable Cost of Production	88,072,181.48
Volume of Production [kg/hr]	11,574.08
Volume of Production [ton/year]	100,000.08
Breakeven Selling Price [$$/ton]	1,004.85
Actual Selling Price	931.00
Cash Cost of Production (CCOP)	100,485,489.03
Project life [years]	20.00
Main Product Revenue (Formic Acid)	93,100,070.02
Gross Profit	-7,385,419.01
Taxes	1,553,174.83
Net Profit	-8,938,593.84

15 Appendix H: Joback Group Contribution Method Calculations

Joback group contribution method is used to define the required properties of BIZ, $Net_3 - FA$ and BIZ-FA adducts. The group increments and calculation results are shown below.

Table 47: Joback method BIZ results

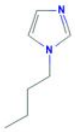
	**Formula:** $C_7H_{12}N_2$	**Molecule:** Butylimidazole												
	Property	T_c	P_c	V_c	T_b	T_f	$\Delta H^\circ_{f,298}$	$\Delta G^\circ_{f,298}$	ΔH_{vb}	ΔH_f	n_A	*MW*	*Cp (@298 K)*	*Liquid Viscosity*
	Units	K	bar	cm^3 mol^{-1}	K	K	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	-	g mol^{-1}	J/mol^{-1} K^{-1}	N s m^{-2}
	Estimated value	641	107.4	417	439.9	293	115.05	312.17	40.41	19.5	21	124	158.2	0.000421

Table 48: Group increments of BIZ used in Joback Method

Increment Type	Group	Number of each group in molecule	T_c	P_c	V_c	T_b	T_f	$\Delta H^\circ_{f,298}$	$\Delta G^\circ_{f,298}$	Ideal Gas Heat Capacity				ΔH_{vb}	ΔH_f	Liquid Viscosity		n_A	*MW*
										(a)	(b)	(c)	(d)			(η_A)	(η_B)		
Non-ring increments	−CH3	1	0.0141	-0.0012	65	23.58	-5.1	-76.45	-43.96	19.5	-0.00808	0.000153	-9.7E-08	2.373	0.908	548.29	-1.719	4	15
	−CH2−	3	0.0567	0	168	68.64	33.81	-61.92	25.26	-2.727	0.285	-0.00016	3.57E-08	6.678	7.77	282.48	-0.597	9	42
	>CH−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>C<	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=CH2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=CH−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=C<	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=C=	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=CH−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	≡C−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ring increments	−CH2−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>CH−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>C<	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=CH−	3	0.0246	0.0033	123	80.19	24.39	6.27	33.9	-6.42	0.1722	-4.9E-06	-4.8E-08	7.632	3.303	778.95	-2.106	6	39
	=C<	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Halogen Incrememts	−F	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−Cl	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−Br	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−I	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Oxygen increments	−OH (alcohol)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−OH (phenol)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−O− (non-ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−O− (ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>C=O (non-ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>C=O (ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	O=CH−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−COOH (acid)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−COO− (ester)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=O (except as above)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Nitrogen increments	−NH2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>NH (non-ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>NH (ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>N− (non-ring)	1	0.0169	0.074	9	11.74	48.84	123.34	163.16	-31.1	0.227	-0.00032	1.46E-07	1.896	4.703	0	0	1	14
	−N= (non-ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−N= (ring)	1	0.0085	0.0076	34	57.55	68.4	55.52	79.93	8.83	-0.00384	4.35E-05	-2.6E-08	6.528	3.649	0	0	1	14
	=NH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−CN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−NO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table 50: Group increments of $Net_3 - FA$ adduct used in Joback Method

Increment Type	Group	Number of each group in molecule	T_c	P_c	V_c	T_b	T_f	$\Delta H^{\circ}_{f,298}$	$\Delta G^{\circ}_{f,298}$	Ideal Gas Heat Capacity				ΔH_{vb}	ΔH_f	Liquid Viscosity		n_A	MW
										(a)	(b)	(c)	(d)			(η_A)	(η_B)		
Non-ring increments	−CH3	3	0.0423	-0.0036	195	70.74	-15.3	-229.35	-131.88	58.5	-0.02424	0.000459	-2.9E-07	7.119	2.724	1644.87	-5.157	12	45
	−CH2−	3	0.0567	0	168	68.64	33.81	-61.92	25.26	-2.727	0.285	-0.00016	3.57E-08	6.678	7.77	282.48	-0.597	9	42
	>CH−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>C<	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=CH2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=CH−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=C<	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=C=	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=CH−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	≡C−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ring increments	−CH2−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>CH−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>C<	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=CH−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=C<	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Halogen Incrememts	−F	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−Cl	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−Br	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−I	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Oxygen increments	−OH (alcohol)	1	0.0741	0.0112	28	92.88	44.45	-208.04	-189.2	25.7	-0.0691	0.000177	-9.9E-08	16.826	2.406	2173.72	-5.057	2	17
	−OH (phenol)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−O− (non-ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−O− (ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>C=O (non-ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>C=O (ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	O=CH−	1	0.0379	0.003	82	72.24	36.9	-162.03	-143.48	30.9	-0.0336	0.00016	-9.9E-08	9.093	3.197	740.92	-1.713	3	29
	−COOH (acid)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−COO− (ester)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=O (except as above)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Nitrogen increments	−NH2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>NH (non-ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>NH (ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>N− (non-ring)	1	0.0169	0.074	9	11.74	48.84	123.34	163.16	-31.1	0.227	-0.00032	1.46E-07	1.896	4.703	0	0	1	14
	−N= (non-ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−N= (ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=NH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−CN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−NO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table 49: Joback method $Net_3 - FA$ adduct results

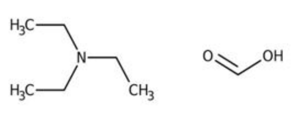
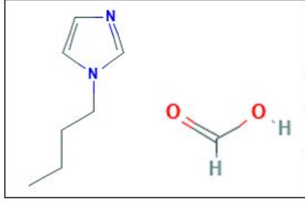
	Formula: C_6H_{15}N-HCOOH	**Molecule:** Amine-Formic Acid Adduct												
	**Property**	T_c	P_c	V_c	T_b	T_f	$\Delta H^{\circ}_{f,298}$	$\Delta G^{\circ}_{f,298}$	ΔH_{vb}	ΔH_f	n_A	MW	C_p (@298 K)	Liquid Viscosity
	Units	K	bar	$cm^3\ mol^{-1}$	K	K	$kJ\ mol^{-1}$	$kJ\ mol^{-1}$	$kJ\ mol^{-1}$	$kJ\ mol^{-1}$	-	$g\ mol^{-1}$	$J/mol^{-1}\ K^{-1}$	$N\ s\ m^{-2}$
	Estimated value	684	75.9	500	514.4	271	-469.71	-222.26	56.91	19.9	27	124	211.1	0.00243

Table 52: Group increments of BIZ-FA adduct used in Joback Method

Increment Type	Group	Number of each group in molecule	T_c	P_c	V_c	T_b	T_f	$\Delta H^{\circ}_{f,298}$	$\Delta G^{\circ}_{f,298}$	Ideal Gas Heat Capacity				ΔH_{vb}	ΔH_f	Liquid Viscosity		n_A	MW
										(a)	(b)	(c)	(d)			(η_A)	(η_B)		
Non-ring increments	−CH3	1	0.0141	-0.0012	65	23.58	-5.1	-76.45	-43.96	19.5	-0.00808	0.000153	-9.7E-08	2.373	0.908	548.29	-1.719	4	15
	−CH2−	3	0.0567	0	168	68.64	33.81	-61.92	25.26	-2.727	0.285	-0.00016	3.57E-08	6.678	7.77	282.48	-0.597	9	42
	>CH−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>C<	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=CH2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=CH−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=C<	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=C=	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	≡CH−	1	0.0027	-0.0008	46	9.2	-11.18	79.3	77.71	24.5	-0.0271	0.000111	-6.8E-08	1.155	2.322	0	0	2	13
	≡C−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ring increments	−CH2−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>CH−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>C<	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=CH−	3	0.0246	0.0033	123	80.19	24.39	6.27	33.9	-6.42	0.1722	-4.9E-06	-4.8E-08	7.632	3.303	778.95	-2.106	6	39
	=C<	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Halogen Incremements	−F	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−Cl	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−Br	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−I	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Oxygen increments	−OH (alcohol)	1	0.0741	0.0112	28	92.88	44.45	-208.04	-189.2	25.7	-0.0691	0.000177	-9.9E-08	16.826	2.406	2173.72	-5.057	2	17
	−OH (phenol)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−O− (non-ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−O− (ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>C=O (non-ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>C=O (ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	O=CH−	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−COOH (acid)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−COO− (ester)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	=O (except as above)	1	0.0143	0.0101	36	-10.5	2.08	-247.61	-250.83	6.82	0.0196	1.27E-05	-1.8E-08	5.909	3.624	675.24	-1.34	1	16
Nitrogen increments	−NH2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>NH (non-ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>NH (ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	>N− (non-ring)	1	0.0169	0.074	9	11.74	48.84	123.34	163.16	-31.1	0.227	-0.00032	1.46E-07	1.896	4.703	0	0	1	14
	−N= (non-ring)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−N= (ring)	1	0.0085	0.0076	34	57.55	68.4	55.52	79.93	8.83	-0.00384	4.35E-05	-2.6E-08	6.528	3.649	0	0	1	14
	=NH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−CN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−NO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table 51: Joback method BIZ-FA adduct results

	**Formula:** $C_7H_{12}N_2$-HCOOH	**Molecule:** Butylimidazole-Formic Acid Adduct												
	Property	T_c	P_c	V_c	T_b	T_f	$\Delta H^{\circ}_{f,298}$	$\Delta G^{\circ}_{f,298}$	ΔH_{vb}	ΔH_f	n_A	MW	*Cp (@298 K)*	*Liquid Viscosity*
	Units	K	bar	$cm^3\ mol^{-1}$	K	K	$kJ\ mol^{-1}$	$kJ\ mol^{-1}$	$kJ\ mol^{-1}$	$kJ\ mol^{-1}$	-	$g\ mol^{-1}$	$J/mol^{-1}\ K^{-1}$	$N\ s\ m^{-2}$
	Estimated value	715	118.1	527	531.5	328	-261.30	50.15	64.30	27.8	26	170	214.2	0.000490