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CONCEPTUAL DESIGN AND ECONOMIC EVALUATION OF A LIGNOCELLULOSIC-BASED BIOREFINERY FOR BIOETHANOL PRODUCTION

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ABSTRACT

Biofuels represent a sustainable alternative to fossil fuels, but much research is still required to make them economically competitive. In this sense, the design of novel plants that complement biofuel production with other bioproducts of higher value constitutes a challenging alternative. Much research is being pursued on the use of lignocellulosic biomass as an attractive feedstock for future supplies of ethanol as it does not compete for land and agricultural market resources with food crops. Dunnett et al. (2008) propose a mathematical modeling framework for the assessment of the lignocellulosic ethanol supply chain to provide insights into the optimal configuration of multiple plant systems. Martin and Grossmann (2011) determine optimal biorefinery schemes for ethanol production from lignocellulosic feedstocks through the application of mathematical programming techniques. Gasification of switchgrass combined with steam reforming and high alcohols synthesis catalytic processes is the technology yielding minimum energy consumption. Moreno et al. (2013) propose parameter estimation within a biochemical technology for ethanol production from lignocellulosic raw materials.

In this work, we address the design of a lignocellulosic ethanol biorefinery through a hybrid process that consists of biomass gasification and syngas fermentation. The combined gasification-fermentation process can use a wide variety of lignocellulosic biomass feedstock, such as prairie grasses, wood chips, paper wastes and solid municipal wastes. In this paper we consider switchgrass. The fermentation process shows tolerance to inhibitors and impurities of the syngas. We consider five main process sections; biomass pretreatment (washing, drying, size reduction), biomass gasification (fluidized-bed gasifier), gas cleaning (PSA and MEA system) and composition adjustment (steam reforming and H2-PSA removal), syngas fermentation (continuous bioreactor) and bioethanol purification (distillation and molecular sieves).

The process is modeled by formulating rigorous mass and energy balances for process units, short-cut models for the purification section, empirical correlations for the gasifier and the fermenter, and experimental data from the literature. The

problem is implemented in the GAMS modeling system and the NLP problem is solved with CONOPT3. Some of results were compared and justified with the use of the process simulator Aspen HYSYS.

The goal is to analyze results in order to estimate the hybrid process profitability, considering hydrogen as co-product. The mains factors that affect process profitability are: raw materials price and availability, the selling price of hydrogen, ethanol concentration in the fermenter and the composition of the gas generated in the gasifier.

PREFACE

Questo lavoro nasce dalla collaborazione tra il Politecnico di Milano e PLAPIQUI (Planta Piloto de Ingenieria Quimica), un istituto argentino dedicato alla didattica, ricerca e sviluppo delle tecnologie inerenti all' ingegneria chimica. É sostenuto dal Consiglio Nazionale delle Ricerche Argentine (CONICET) e dall' Università Nazionale di Bahía Blanca (UNS), con sede nella città di Bahía Blanca, situata a sud della provincia di Buenos Aires.

La realizzazione di questa opportunità è stata possibile grazie alla disponibilità e alla professionalità del Prof. Flavio Manenti e della Prof.ssa. Maria Soledad Diaz, i quali, attraverso la loro fattiva collaborazione didattica, ci hanno permesso di svolgere la nostra attività di tesi presso PLAPIQUI, per la durata di sette mesi, da aprile 2013 a ottobre 2013.

La decisione di iniziare un percorso didattico all'estero è maturata dopo interessanti e stimolanti colloqui con il Professor Manenti e successivamente, con la Professoressa Diaz, durante una sua visita al Politecnico. L'opportunità di studiare ed approfondire nuove tematiche relative alla bio-engineering, ci è servita come forte motivazione ad intraprendere una significativa esperienza didattica, culturale ed umana, in Argentina.

Il progetto che ne è nato, è stato seguito e diretto da entrambi i Professori, dall'inizio alla fine. La possibilità di lavorare quotidianamente presso PLAPIQUI, collaborando direttamente con il gruppo di ricercatori e dottorandi della Prof.ssa Diaz, ci ha permesso di mettere in pratica e migliorare tutte le competenze apprese nel periodo di studi universitari, oltre che acquisire nuove conoscenze sulla realtà bio e su differenti tecniche di programmazione.

Ci sono state messe a disposizione tutte le risorse necessarie, quali spazio, tempo e materiale didattico, affinchè potessimo affrontare e portare a termine nel migliore dei modi, il nostro progetto.

La tesi riguarda lo studio e la modellazione di una bioraffineria per la produzione di etanolo di seconda generazione, attraverso un processo ibrido, composto da una gassificazione della biomassa vergine e dalla successiva fermentazione del syngas prodotto. Il processo combinato di gassificazione-fermentazione può utilizzare un'ampia varietà di biomassa lignocellulosica come materia prima: scarti agricoli, forestali e rifiuti solidi urbani.

In questo lavoro prendiamo in considerazione la panico verga (*Panicum virgatum*, in inglese *switchgrass*) come feedstock della bioraffineria indagata. Il processo è diviso in cinque sezioni principali: PRETRATTAMENTI (lavaggio, asciugatura, riduzione delle dimensioni), GASSIFICAZIONE (a letto fluido), PURIFICAZIONE SYNGAS (PSA e sistema di MEA) e REGOLAZIONE DEL RAPPORTO H_2/CO (steam reforming e la rimozione H2-PSA), FERMENTAZIONE SYNGAS (bioreattore continuo) e PURIFICAZIONE BIOETANOLO (distillazione e setacci molecolari).

Il lavoro è stato suddiviso in più parti:

- Ricerca bibliografica: fondamentale per informarsi e conoscere l'argomento, già frutto di una ricerca iniziata al Politecnico prima della partenza per l'Argentina. Un paper, in particolare, ci è stato di sicuro aiuto in quanto è alla base della nostra tesi. L'articolo dal quale abbiamo preso spunto è: "M. Martín, I. E. Grossmann. Energy Optimization of Bioethanol Production via Gasification of Switchgrass. Department of Chemical Engineering, Carnegie Mellon University Pittsburgh, PA 15213". Abbiamo avuto l'onore di conoscere il Prof. Grossman e di partecipare ad un brain strorming, durante il quale gli abbiamo presentato il nostro progetto.
- Stesura del modello: la parte più impegnativa ed importante del nostro lavoro è stata, senza dubbio, la scrittura di un modello matematico che rappresenti l'impianto. Come linguaggio di programmazione è stato utilizzato GAMS. Abbiamo avuto modo di imparare ad usarlo proprio in Argentina.
- Analisi economica: è stata affrontata al Politecnico di Milano.

Non vi è dubbio ritenere che l'esperienza di tesi in Argentina abbia prodotto un lavoro significativo ed interessante. La forte motivazione a svolgere un'esperienza didattica così lontano, ci è servita come importante integrazione al serio lavoro svolto al Politecnico. Ci si è messi alla prova in un ambito professionale e di studio che ha favorito un arricchimento delle competenze e ha permesso di acquisire la capacità di utilizzarle proficuamente per la realizzazione del progetto.

1. INTRODUCTION

1.1 Biomass

Biomass is a term for all organic material that stems from plants (including algae, trees and crops). Biomass is produced by green plants converting sunlight into plant material through photosynthesis and includes all land and water based vegetation, as well as all organic wastes. The biomass resource can be considered as organic matter, in which the energy of sunlight is stored in chemical bonds. When bonds between adjacent carbon, hydrogen and oxygen atoms are broken by digestion, combustion, or decomposition, these substances release their stored chemical energy. Biomass has been always a major source of energy for mankind and it is presently estimated to contribute in the order of 10-14% for the world's energy supply.[1] The conversion of biomass into energy can be achieved in a number of ways. To provide a fuel suitable for direct use in spark ignition gas engines (s.i.g.e.), the fuel must be provided in either a gaseous, or a liquid form. Production of a gaseous fuel from biomass can be achieved by the application of a number of technologies, each with its specific requirements, advantages and dis-advantages. If biomass is processed efficiently, either chemically or biologically, by extracting the energy stored in the chemical bonds and the subsequent 'energy' product combined with oxygen, the carbon is oxidised to produce CO_2 and water. The process is cyclical, as the CO_2 is then available to produce new biomass. The value of a particular type of biomass depends on the chemical and physical properties of the large molecules from which it is made. Man for millennia has exploited the energy stored in these chemical bonds, by burning biomass as a fuel and by eating plants for the nutritional content of their sugar and starch. More recently, fossilised biomass has been exploited as coal and oil. However, since it takes millions of years to convert biomass into fossil fuels, these are not renewable within a time-scale mankind can use. Burning fossil fuels uses ''old'' biomass and converts it into ''new'' CO_2; which contributes to the ''greenhouse'' effect and depletes a non-renewable resource. Burning new biomass contributes no new carbon dioxide to the atmosphere, because replanting harvested biomass ensures that CO_2 is absorbed and returned for a cycle of new growth. One important factor, which is often overlooked when considering the use of biomass to assist alleviate global warming, is the time lag between the instantaneous release of CO_2 from burning fossil fuels and its eventual uptake as biomass, which can take many years. One of the dilemmas facing the developed world is the need to recognize this time delay and take appropriate actions to mitigate against the lag period. An equal dilemma faces the developing world as it consumes its biomass resources for fuel production but does not implement programmes of planting replacement. Numerous crops have been proposed or are being tested for commercial energy farming. Potential energy crops include woody crops and grasses/herbaceous plants (all perennial crops), starch and sugar crops and oilseeds.[1]

In general, the characteristics of the ideal energy crop are:

- high yield (maximum production of dry matter per hectare),
- low energy input to produce,
- low cost,
- composition with the least contaminants, low nutrient requirements.

1.1.1 Drivers for biomass

In the past 10 years, there has been renewed interest, world wide, in biomass as an energy source. There are several reasons for this situation:

- The agricultural sector in Western Europe and in the US, which is producing food surpluses. This situation has led to a policy in which land is set aside in order to reduce surpluses. Related problems, such as the de-population of rural areas and payment of significant subsidies to keep land fallow, makes the introduction of alternative, non-food crops desirable. Demand for energy will provide an almost infinite market for energy crops grown on such (potentially) surplus land.[1]

- The potential threat posed by climate change, due to high emission levels of greenhouse gases (CO_2 being the most important one), has become a major stimulus for renewable energy sources in general. When produced by sustainable means, biomass emits roughly the same amount of carbon during conversion as it is taken up during plant growth. The use of biomass therefore does not contribute to a build up of CO_2 in the atmosphere. But these two main issues are not the only chance: biomass is also an indigenous energy source, available in most countries and its application may diversify the fuel-supply in many situations, which in turn may lead to a more secure energy supply. Biomass production can generate employment and if intensive agriculture is replaced by less intensively managed energy crops, there are likely to be environmental benefits, such as reduced leaching of fertilisers and reduced use of pesticides. Moreover, if appropriate crops are selected, restoration of degraded lands may be possible. Depending on the crops used and the way the biomass is cultivated, increased biodiversity can be obtained, compared to current agricultural practice. Biomass is available on a renewable basis, either through natural processes, or it can be made available as a by-product of human activities (i.e. organic wastes). The potential of biomass energy derived from forest and agricultural residues world wide, is estimated at about 30 EJ/yr, compared to an annual world wide energy demand of over 400 EJ.[1] If biomass is to contribute to a larger extent to the world’s energy supply, then energy farming, the cultivation of dedicated crops for energy purposes, will be required, using fallow and marginal lands, the latter being largely unsuited for food crops. When energy crops are considered as a source of biomass, the total energy potential of biomass for energy production may be considerably larger than the energy potential of biomass residues.

1.1.2 Biomass types

Researchers characterise the various types of biomass in different ways but one simple method is to define four main types, namely;[1]

- woody plants,
- herbaceous plants/grasses,
- aquatic plants,
- manures.

Within this categorisation, herbaceous plants can be further subdivided into those with high and low moisture contents. Apart from specific applications or needs, most commercial activities has been directed towards the lower moisture-content types, woody plants and herbaceous species. Aquatic plants and manures are intrinsically high-moisture materials and as such, are more suited to ‘wet’ processing techniques. Based primarily upon the biomass moisture content, the type of biomass selected subsequently dictates the most likely form of energy conversion process. High moisture content biomass, such as the herbaceous plant sugarcane, lends itself to a ‘wet aqueous’ conversion process, involving biologically mediated reactions, such as fermentation, while a ‘dry’ biomass such as wood chips, is more economically suited to gasification, pyrolysis or combustion. Aqueous processing is used when the moisture content of the material is such that the energy required for drying would be inordinately large compared to the energy content of the product formed. However, there are other factors which must be taken into consideration in determining the selection of the conversion process, apart from simply moisture content, especially in relation to those forms of biomass which lie midway between the two extremes of ‘wet’ and ‘dry’. Examples of such factors are the ash, alkali and trace component contents, which impact adversely on thermal conversion processes and the cellulose content, which influences biochemical fermentation processes.

1.1.3 Plant characteristics

Biomass contains different amounts of cellulose, hemicellulose and lignin, and a small amount of other extractives. Woody plant species are typically characterised by slow growth and are composed of tightly bound fibres, giving a hard external surface, while herbaceous plants are usually perennial, with more loosely bound fibres, indicating a lower proportion of lignin, which binds together the cellulosic fibres. The relative proportions of cellulose and lignin is one of the determining factors in identifying the suitability of plant species for subsequent processing as energy crops.

- *Cellulose:* is a glucose polymer, consisting of linear chains of (1,4)-D-glucopyranose units, in which the units are linked 1-4 in the b-configuration, with an average molecular weight of around 100.[1]

- *Hemicellulose:* is a mixture of polysaccharides, composed almost entirely of sugars such as glucose, mannose, xylose and arabinose and methylglucuronic and galaturonic acids, with an average molecular weight of < 30. In contrast to cellulose, hemicellulose is a heterogeneous branched polysaccharide that binds tightly, but non-covalently, to the surface of each cellulose microfibril. Hemicellulose differs from cellulose, in consisting primarily of xylose and other five carbon monosaccharides.[1]

- *Lignin:* can be regarded as a group of amorphous, high molecular weight, chemically related compounds. The building blocks of lignin are believed to be a three carbon chain attached to rings of six carbon atoms, called phenyl-propanes. These may have zero, one or two methoxyl groups attached to the rings, giving rise to three structures, termed I, II and III, respectively. The proportions of each structure depend on the source of the polymer i.e. structure I is found in plants such as grasses; structure II in the wood of conifers; while structure III is found in deciduous wood.[1]

Cellulose is generally the largest fraction, representing about 40-50% of the biomass by weight; the hemi-cellulose portion represents 20-40% of the material by weight.[1]

Both woody and herbaceous plant species have specific growing conditions, based on the soil type, soil moisture, nutrient balances and sunlight, which will determine their suitability and productive growth rates for specific, geographic locations. Many types of perennial grasses, such as sugarcane and cereals like wheat and maize, have widely different yields, depending on the growing conditions: thus wheat can be grown in both hot and temperate climates with a wide range of rainfall, whereas sugarcane can be grown successfully only in warm, moist climatic conditions.

1.1.4 Plant species

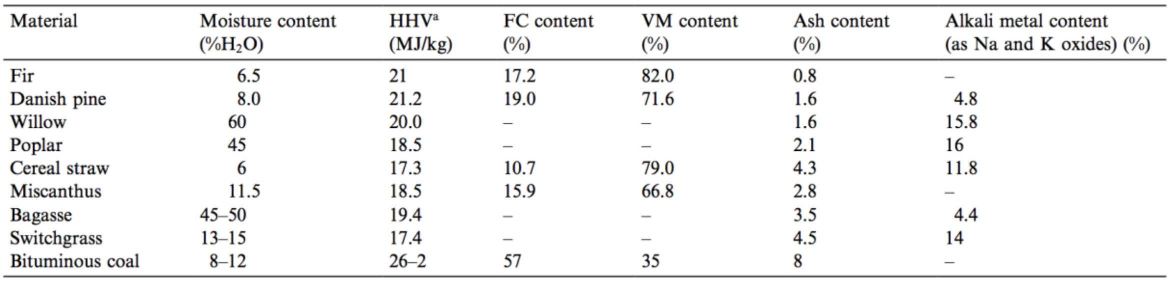
The choice of plant species depends upon the end-use and bioconversion option of interest (e.g. combustion, gasification, pyrolysis, fermentation or mechanical extraction of oils). Some plant species are amenable to nearly all of the potential conversion technologies: e.g. oil seed rape can be processed via combustion, gasification, pyrolysis or mechanical extraction, while others such as wood and cereal crops, are suitable for combustion, gasification, pyrolysis and fermentation. It is important to note that, while particular plant species may have specific benefits for subsequent processing technologies, the amount of energy potentially available from a given biomass source is the same, irrespective of the conversion technology used. What will vary between conversion technologies is the actual amount of energy recovered from the biomass source and the form of that energy.

1.1.5 Biomass Properties

It is the inherent properties of the biomass source that determines both the choice of conversion process and any subsequent processing difficulties that may arise. Equally, the choice of biomass source is influenced by the form in which the energy is required and it is the interplay between these two aspects that enables flexibility to be introduced into the use of biomass as an energy source.

Dependent on the energy conversion process selected, particular material properties become important during subsequent processing.

The main material properties of interest, during subsequent processing as an energy source, relate to:



Material	Moisture content (%H_2O)	HHV^a (MJ/kg)	FC content (%)	VM content (%)	Ash content (%)	Alkali metal content (as Na and K oxides) (%)
Fir	6.5	21	17.2	82.0	0.8	–
Danish pine	8.0	21.2	19.0	71.6	1.6	4.8
Willow	60	20.0	–	–	1.6	15.8
Poplar	45	18.5	–	–	2.1	16
Cereal straw	6	17.3	10.7	79.0	4.3	11.8
Miscanthus	11.5	18.5	15.9	66.8	2.8	–
Bagasse	45–50	19.4	–	–	3.5	4.4
Switchgrass	13–15	17.4	–	–	4.5	14
Bituminous coal	8–12	26–2	57	35	8	–

Figure 1: Properties of selected biomass materials (wt%).[1]

• *Moisture Content* (intrinsic and extrinsic): two forms of moisture content are of interest in biomass:

- intrinsic moisture: the moisture content of the material without the influence of weather effects,
- extrinsic moisture: the influence of prevailing weather conditions during harvesting on the overall biomass moisture content.

In practical terms, it is the extrinsic moisture content that is of concern, as the intrinsic moisture content is usually only achieved, or applicable, under laboratory conditions. Also of importance in respect of the prevailing weather conditions at the time of harvesting, is the potential contamination of the harvested biomass by soil and other detritus, which can in turn have a significant deleterious impact on other ‘material’ properties during subsequent treatment or processing. Other factors aside, such as the conversion to alcohol or gas/oil, the relationship between biomass moisture content and appropriate bioconversion technology is essentially straightforward, in that thermal conversion requires low moisture content feedstock (typically <50%),[1] while bioconversion can utilise high moisture content feedstocks. Thermal conversion technologies can also use feedstocks with high moisture content but the overall energy balance for the conversion process is adversely impacted. On this basis, woody and low moisture content herbaceous plant species are the most efficient biomass sources for thermal conversion to liquid fuels, such as methanol. For the production of ethanol by biochemical (fermentation) conversion, high moisture herbaceous plant species, such as sugarcane, are more convenient.

- *Calorific value.*

- *Proportions of fixed carbon and volatiles.*

- *Ash/residue content.*

- *Alkali metal content.*

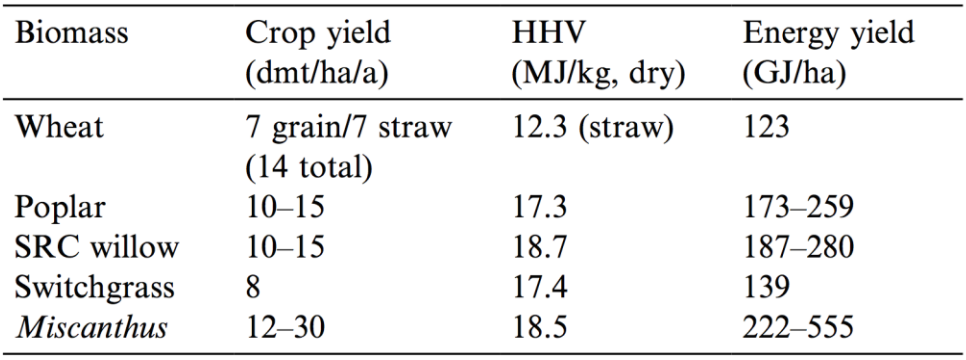
- *Cellulose/lignin ratio:* the proportions of cellulose and lignin in biomass are important only in biochemical conversion processes. The biodegradability of cellulose is greater than that of lignin, hence the overall conversion of the carbon containing plant material present as cellulose is greater than for plants with a higher proportion of lignin, a determining factor when selecting biomass plant species for biochemical processing. Figure 2 gives the proportions of cellulose/hemicellulose/lignin for selected biomass. For the production of ethanol, a biomass feedstock with a high, cellulose/hemicellulose content is needed to provide a high yield.[1] While the lignin content represents a potentially large energy source, current techniques involving enzymatic hydrolysis systems cannot convert the lignin to syngas. To illustrate the effect of cellulose content on ethanol yield, up to 280 l/t[1] of ethanol can be produced from switchgrass, compared with 205 l/t[1] from wood; an effect largely due to the increased proportion of lignin in wood. For dry biomass conversion processes, the first five properties are of interest, while for wet biomass conversion processes, the first and last properties are of prime concern.

Biomass or waste	Cellulose	Hemicellulose	Lignin
Trees			
Poplar	45-50	17-19	18-26
Eucalyptus	50	13	28
Pine (spruce)	44	23	28
Salix (hardwood)	43	22	26
Grasses			
Switchgrass	31-45	20-30	12-18
Bermuda grass	25	36	6
Rye grasses	25-40	35-50	10-30
Paper			
Office paper	69-99	0-12	0-15
Newspaper	40-55	25-40	18-30
Paper pulp	60-70	10-20	5-10
Food/agriculture wastes			
Corn cobs	45	35	15
Corn stover	38-40	22-28	18-23
Corn fibre	14	17	8
Wheat straw	30-38	21-50	15-23
Rice husk	24	27	13
Bagasse	38	27	20
Nut shells	25-30	25-30	30-40
Leaves	15-30	80-85	0
Cattle manure	1.6-4.7	1.4-3.3	2.7-5.7
Other wastes			
Sorted refuse	60	20	20
Primary	8-15	NA	24-29
wastewater			
solids	33	9	17
Municipal solid			
Waste (MSW)	62	5	11
MSW paper pulp			

Figure 2: Cellulose/hemicellulose/lignin content of selected biomass (Dry_wt%).[142]

1.1.6 Yields

The quantity of dry matter produced by a biomass species per unit area of production, determines the potential energy production capacity, or yield, of the available land area. Production is measured in DMt/ha (Dry Matter tons/hectare) and combined with the heating value (HHV) of biomass, allows to determine the energy yield of the cultivated crop. Figure 3 indicates the range of energy yields for a number of types of biomass. The development of dedicated plantations to grow biomass energy plants is likely to take two main forms: species with a high DMt/ha, grown ideally on good quality agricultural land e.g. set aside and species capable of reasonably high DMt/ha yields, grown on marginal land.



Biomass	Crop yield (dmt/ha/a)	HHV (MJ/kg, dry)	Energy yield (GJ/ha)
Wheat	7 grain/7 straw (14 total)	12.3 (straw)	123
Poplar	10–15	17.3	173–259
SRC willow	10–15	18.7	187–280
Switchgrass	8	17.4	139
Miscanthus	12–30	18.5	222–555

Figure 3: Energy yields from selected biomass.[1]

1.2 Biofuel

The production of biofuels has become a short and medium term solution to reduce our dependency on fossil fuels for the transportation sector due to their compatibility with the supply chain of the crude-based fuels as well as with the current automobiles, which can use biodiesel, bioethanol, or a blend with crude-based fuels. However, there are also concerns on the actual sustainability of the production process of biofuels mainly due to the consumption of energy and water. While energy consumption has always been a top priority in any production process as a result of its direct impact on production costs, water consumption has also become a major concern due to its increasing shortage in certain parts of the world.

Currently, the fossil resources are not regarded as sustainable and questionable from the economic, ecology and environmental point of views.[7] The burning of fossil fuels is a big contributor to increasing the level of CO_2 in the atmosphere which is directly associated with global warming observed in recent decades.[8] The adverse effects of greenhouse gas (GHG) emissions on the environment, together with declining petroleum reserves, have been realized. Therefore, the quest for sustainable and environmentally benign sources of energy for our industrial economies and consumer societies has become urgent in recent years.[9] Consequently, there is renewed interest in the production and use of fuels from plants or organic wastes. Biofuels produced from renewable resources could help to minimize the fossil fuel burning and CO_2 production. Biofuels produced from biomass, such as plants or organic wastes, could help to reduce both the world's dependence on oil and CO_2 production. These biofuels have the potential to cut CO_2 emission because the plants they are made from use CO_2 as they grow.[10] 21st Century is looking for a shift to alternate industrial feedstock and green processes to produce these chemicals from renewable biomass resources.[11]

1.2.1 Biofuels types

The range of biofuels that can be produced is listed below and includes biofuels that are being used at present and others which are still at the development stage. Biological based fuels can be solid, liquid and gaseous, and the physical state of the fuel greatly influences the way it is used. It is the developmental stage that has been used to divide biofuels into first, second and third generation biofuels (Figure 4). Those biofuels currently used and produced in large quantities are the first generation biofuels. Second generation biofuels have been produced but technical difficulties and high costs have delayed their application on a large scale. Third generation biofuels are those which are still at the research and development stage.

- *Solid fuels:*
    - Biomass
    - Wastes
- *Gaseous fuels:*
    - Methane (from biogas)
    - Hydrogen
    - Dimethyl ether (DME)
- *Liquid fuels:*
    - Methanol (from gasification)
    - Ethanol
    - Biobutanol
    - Synthetic petrol (FT origin)
    - Synthetic diesel (FT origin)
    - Biodiesel (Fatty-Acids-Methyl-Esters, i.e. FAME)
    - Biodiesel (pyrolysis bio-oil)
    - Green diesel (plant and microalgal hydrocarbons)
    - Green diesel (HDO microalgal oils)

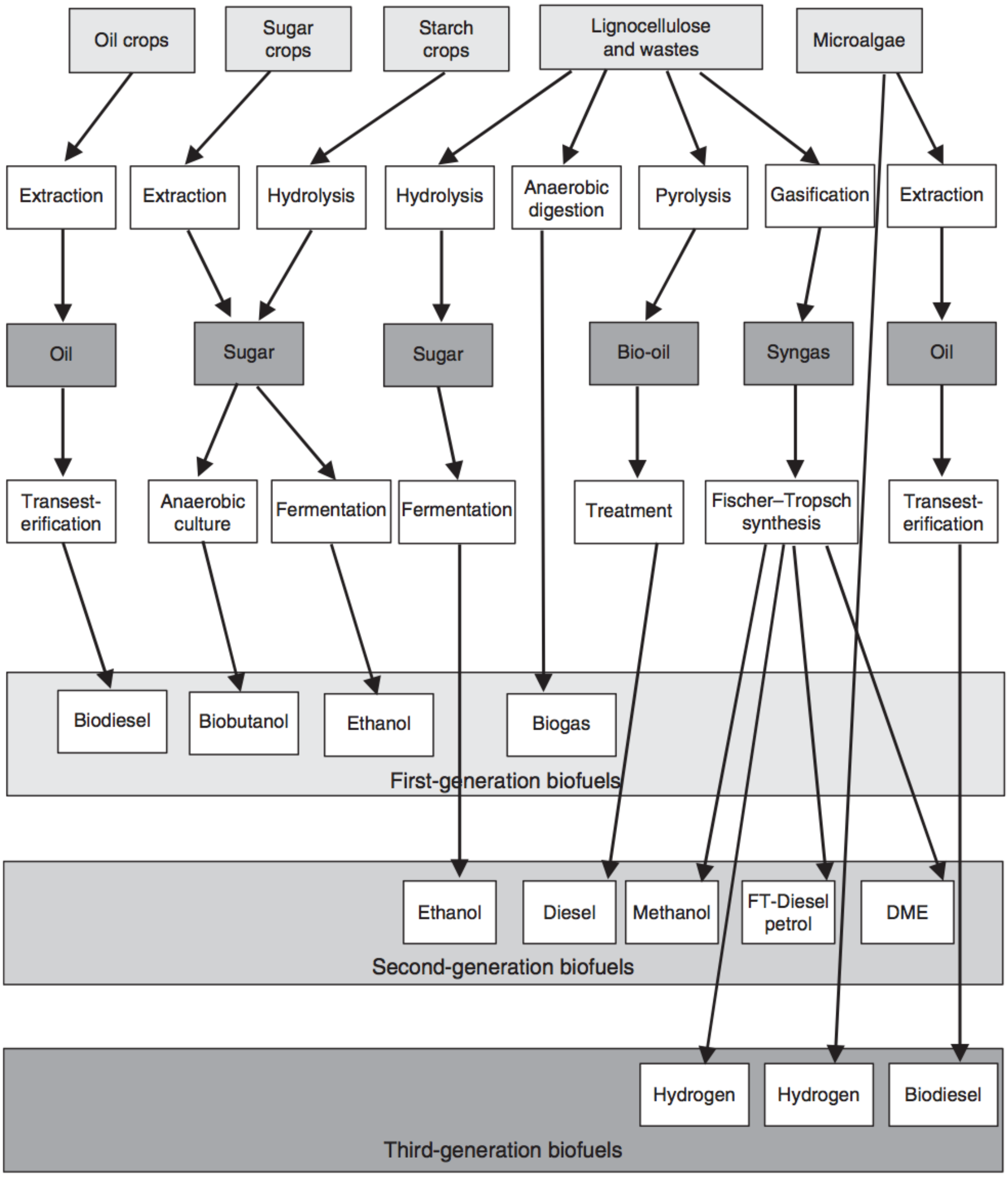


Figure 4: The sources and processes for the production of first, second and third generation biofuels.[16]

1.2.2 First generation

The first generation biofuels are produced from energy crops such sugarcane, sugarbeet, maize, wheat, rapeseed, soybean and sunflower. However, to completely replace the fossil fuels gas, petrol and diesel, large areas of land will be required. Hence, there is not enough land to grow sufficient energy crops without competing with food crops. For these reasons second and third generation biofuels are under development.[16]

The first generation biofuels can offer some CO_2 benefits and can help to improve domestic energy security. But concerns exist about the sourcing of feedstocks, including the impact it may have on biodiversity and Land Use and Competition (LUC) with food crops. A first generation biofuel (i.e. biodiesel (FAME), bio-ethanol, and biogas) is characterized either by its ability to be blended with petroleum-based fuels, combusted in existing internal combustion engines, and distributed through existing infrastructure, or by the use in existing alternative vehicle technology like FFVs (Flexible Fuel Vehicle) or natural gas vehicles. The production of 1st generation biofuels is commercial today, with almost 50 billion liters produced annually.[4] There are also other niche biofuels, such as biogas which have been derived by anaerobic treatment of manure and other biomass materials. However, the volumes of biogas used for transportation are relatively small today.

First generation biofuels seems to create some skepticism to scientists. There are concerns about environmental impacts and carbon balances, which sets limits in the increasing production of biofuels of first generation. The main disadvantage of first generation biofuels is the food-versus-fuel debate, one of the reasons for rising food prices is due to the increase in the production of these fuels.[17] Additionally it is claimed that biodiesel is not a cost efficient emission abatement technology.

The dramatic rise in oil prices seen in the last decade has also enabled liquid biofuels to become costcompetitive with petroleum based transportation fuels, and this has led to a surge in research and production around the world. The three main types of first generation biofuels used commercially are biodiesel, ethanol, and biogas.

1.2.3 Second generation

The second generation biofuels will be produced from lignocellulose biomass and wastes which have much better yields per hectare as the whole of the harvested plant will be used. The higher yields will mean that second generation biofuel production will compete less with food crops. Lignocellulosic feedstock can offer the potential to provide advanced biofuels.[20]

Therefore, it is essential that second and third generation biofuels are developed as first generation biofuels can only realistically supply 5% of the fuels required.

Second generation biofuels produced from ‘plant biomass’ refers largely to lignocellulosic materials, as this makes up the majority of the cheap and abundant non-food materials available from plants. Plant biomass represents one of the most abundant and underutilized biological resources on the planet, and is seen as a promising source of material for fuels and raw materials. However, there is great potential in the use of plant biomass to produce liquid biofuels. But, at present, the production of such fuels is not cost effective because there are a number of technical barriers that need to be overcome before their potential can be realized.[21] This has generated great interest in making use of dedicated biomass crops as feedstock for biofuel production.[22]

Lignocellulosic materials are a collection of feedstocks for advanced biofuels and can be obtained either through hydrolysis and fermentation (i.e. bioethanol) or through gasification (i.e. Fischer-Tropsch bio-diesel, bio-DME and bio-SNG). Advanced biofuels, also referred to as 2nd generation biofuels, are carbon-based fuels that are produced by innovative processes mainly using lignocellulosic materials for which commercial utilization is still under development.

The production of 2nd generation biofuels is non-commercial at this time, although pilot and demonstration facilities (REF) are being developed. Therefore it is anticipated that, these 2nd generation biofuels could significantly reduce CO_2 production, do not compete with food crops and some types can offer better engine performance. When commercialized, the cost of second generation biofuels has the potential to be more comparable with standard petrol, diesel, and would be most cost effective route to renewable, low carbon energy for road transport.[8]

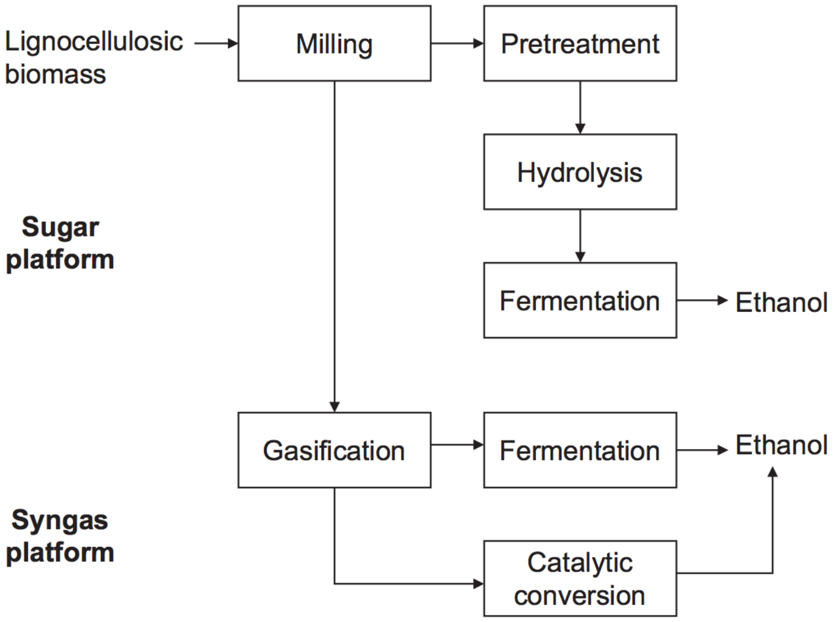


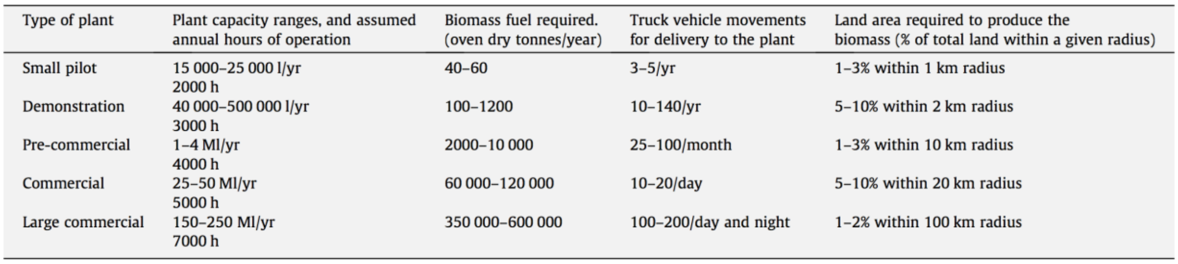
Figure 5: Second generation biofuel production from biomass.[26]

1.2.3.1 Biofuels conversion routes

The production of biofuels from ligno-cellulosic feedstocks can be achieved through two very different processing routes:[27]

- biochemical: in which enzymes and other micro-organisms are used to convert cellulose and hemicellulose components of the feedstocks to sugars prior to their fermentation to produce ethanol;

- thermo-chemical (also known as biomass-to-liquids, BTL): where pyrolysis/gasification technologies produce a synthesis gas (CO + H_2) from which a wide range of long carbon chain biofuels, such as synthetic diesel, aviation fuel, or ethanol, can be reformed, based on the Fischer-Tropsch conversion or fermentation.



Type of plant	Plant capacity ranges, and assumed annual hours of operation	Biomass fuel required. (oven dry tonnes/year)	Truck vehicle movements for delivery to the plant	Land area required to produce the biomass (% of total land within a given radius)
Small pilot	15 000–25 000 l/yr 2000 h	40–60	3–5/yr	1–3% within 1 km radius
Demonstration	40 000–500 000 l/yr 3000 h	100–1200	10–140/yr	5–10% within 2 km radius
Pre-commercial	1–4 Ml/yr 4000 h	2000–10 000	25–100/month	1–3% within 10 km radius
Commercial	25–50 Ml/yr 5000 h	60 000–120 000	10–20/day	5–10% within 20 km radius
Large commercial	150–250 Ml/yr 7000 h	350 000–600 000	100–200/day and night	1–2% within 100 km radius

Figure 6: Typical scale of operation for various 2nd-generation biofuel plants using energy crop-based ligno-cellulosic feedstocks.[27]

There is currently no clear commercial or technical advantage between the biochemical and thermochemical pathways, even after many years of RD&D and the development of near commercial demonstrations. Both technologies remain unproven at the fully commercial scale, are under continual development and evaluation, and have significant technical and environmental barriers yet to be overcome.

For the biochemical route, much remains to be done in terms of improving feedstock characteristics:

- reducing the costs by perfecting the pretreatment process;[28]

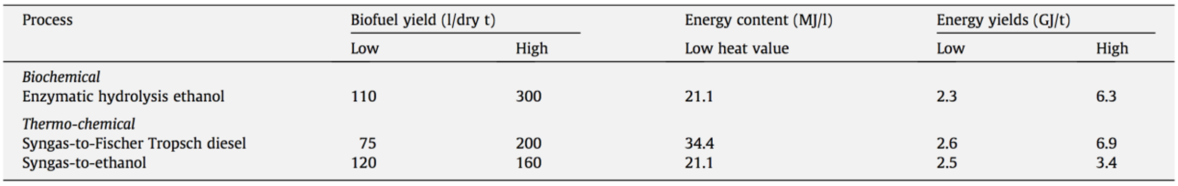
- improving the efficacity of enzymes;[29]
- lowering production costs;[30]
- improving overall process integration;[31]

The pretreatment process to expose the cellulose and hemicellulose for subsequent enzymatic hydrolysis is a critical process step. Options can be classified into biological, physical, chemical or a combination, each with variations having different temperatures and reaction times.[32] The pretreatment process is a major cost component of the overall process. The potential advantage of the biochemical route is that cost reductions have proved reasonably successful to date (such as enzyme recycling),[33] so the option could possibly provide cheaper biofuels in the longer term than via the thermo-chemical route.

Conversely, as a broad generalisation, there are less technical hurdles to the BTL route since many of the technological components of the system are already proven and have been in operation for decades, focusing on Coal-to-Liquids and more recently natural Gas-to-Liquids. Therefore, with this more mature technology, perhaps there is less opportunity for cost reductions. One specific problem concerns securing a large enough quantity of feedstock for a reasonable delivered cost at the plant gate in order to meet the demands of a large commercial scale plant that is required for BTL to become economic.

One key difference between the biochemical and BTL routes is that the lignin component of the biomass is a residue of the biochemical enzymatic hydrolysis process and hence can be used for heat and power generation or for bio-based chemicals production. In the BTL process the lignin is converted into synthesis gas along with the cellulose and hemicellulose biomass components. In spite of this difference, both processes can potentially convert 1 dry tonne of biomass (20 GJ/t) to around 6.5 GJ/t of energy carrier in the form of biofuels, there by giving an overall biomass to biofuel conversion efficiency of around 35%.[34] The similar overall yield in energy terms (around 6.5 GJ/t biofuels being the top of the range), is because synthetic diesel has a higher energy density by volume than ethanol. Although this efficiency appears relatively low, overall efficiencies of the process can be improved when surplus heat, power and co-product generation are included in the total system. Improving efficiency is vital to the extent that it reduces the final product cost and improves environmental performance, but it should not be a goal in itself.

Although both routes have similar potential yields in energy terms, different yields, in terms of litres per tonne of feedstock, occur in practice. Major variations between the various processes under development, together with variations between biofuel yields from different feedstocks, give a complex picture with wide ranges being quoted in the literature. Typically the enzyme hydrolysis process could be expected to produce up to 300 l ethanol (6 GJ)/dry tonne of biomass whereas the BTL route could yield up to 200 l (4 GJ) of synthetic diesel per dry tonne (Figure 7).[27]



Process	Biofuel yield (l/dry t)		Energy content (MJ/l)	Energy yields (GJ/t)	
	Low	High	Low heat value	Low	High
Biochemical					
Enzymatic hydrolysis ethanol	110	300	21.1	2.3	6.3
Thermo-chemical					
Syngas-to-Fischer Tropsch diesel	75	200	34.4	2.6	6.9
Syngas-to-ethanol	120	160	21.1	2.5	3.4

Figure 7: Indicative biofuel yield ranges per dry tonne of feedstock from biochemical and thermo-chemical process route.[27]

A second major difference between the two conversion paths is that the various biochemical routes produce ethanol, and others products, whereas the thermo-chemical routes can be employed to produce a range of longer-chain hydrocarbons from the synthesis gas. These include biofuels better suited for aviation and marine purposes.

The first fully commercial-scale plant could possibly be seen operating as early as 2012,[37] although the successful demonstration of a conversion technology will be required first in order to meet this target. Therefore given the complexity of the technical and economic challenges involved in the current demonstration plants, it could be argued that in reality, the first commercial plants are unlikely to be widely deployed before 2015 or 2020.[38]

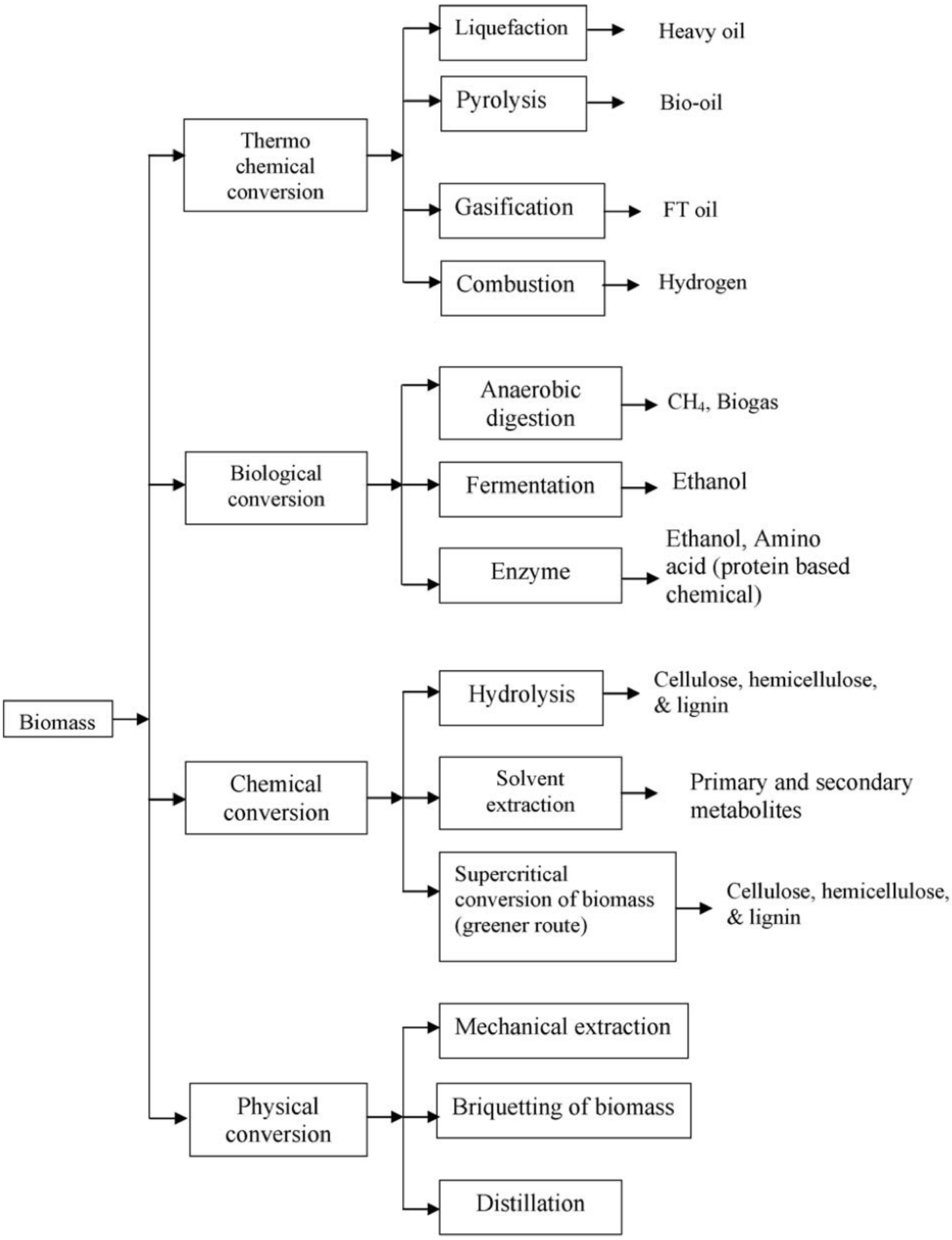


Figura 8: Biomass conversion processes.[26]

1.3 Biorafinery

The term Biorefinery was initially established by NREL during 1990, for the utilization of biomass for production of fuels and other bioproducts. This term refers to a facility (or group of facilities) which combines the production of materials, chemicals, or fuel products with energy production.[39] The biorefinery system includes biomass production, biomass transformation processing, and end use. The total biomass production on earth is approximately 100 billion tones organic dry matter of land biomass per annum and 50 billion tones of aquatic biomass.[40] The part of it is used as food, feed, energy and industrial raw materials, where food use is only 1.25 % of the entire land biomass. The rest of the biomass is unused or recycled in to the earth system, which can be used as raw material for chemical production. Currently, starches, sugar, oils and fats, cellulose, rubbers have been used industrially as well. [40]

Fuels such as ethanol, methane, and hydrogen are characterized as biofuels because they can be produced by the activity of biological organisms.

Which of these fuels will play a major role in our future? The answer is not clear, as factors such as land availability, future technical innovation, environmental policy regulating greenhouse gas emissions, governmental subsidies for fossil fuel extraction processing, implementation of net metering, and public support for alternative fuels will all affect the outcome. A critical point is that as research and development continue to improve the efficiency of biofuel production processes, economic feasibility will continue to improve.

Biofuel production is best evaluated in the context of a biorefinery (Figure 9). In a biorefinery, agricultural feedstocks and by-products are processed through a series of biological, chemical, and physical processes to recover biofuels, biomaterials, nutraceuticals, polymers, and specialty chemical compounds.[41]

This concept can be compared to a petroleum refinery in which oil is processed to produce fuels, plastics, and petrochemicals. Early proponents of the biorefinery concept emphasized the *zero emissions* goal inherent in the plan waste streams, water, and heat from one process are utilized as feed streams or energy to another, to fully recover all possible products and reduce waste with maximized efficiency.[41] Ethanol and biodiesel production can be linked effectively in this way.

In ethanol fermentation, 0.96 kg of CO_2 is produced per kilogram of ethanol formed.[46] The CO_2 can be fed to algal bioreactors to produce oils used for biodiesel production. Approximately 1.3 kg CO_2 is consumed per kilogram of algae grown, or 0.5 kg algal oil produced by oleaginous strains.[46]

Also encompassed in a sustainable biorefinery is the use of “green” processing technologies to replace traditional chemical processing. Ethanol can be used in biodiesel production from biological oils in place of toxic petroleum based methanol traditionally used. Widespread application of biorefinerie would allow for replacement of petroleum derived products with sustainable, carbon neutral, low-polluting alternatives. In addition to environmental benefits of biorefining, there are economic benefits as new industries grow in response to need.[41] A thorough economic analysis, including ecosystem and environmental impact, harvesting, transportation, processing, and storage costs must be considered.

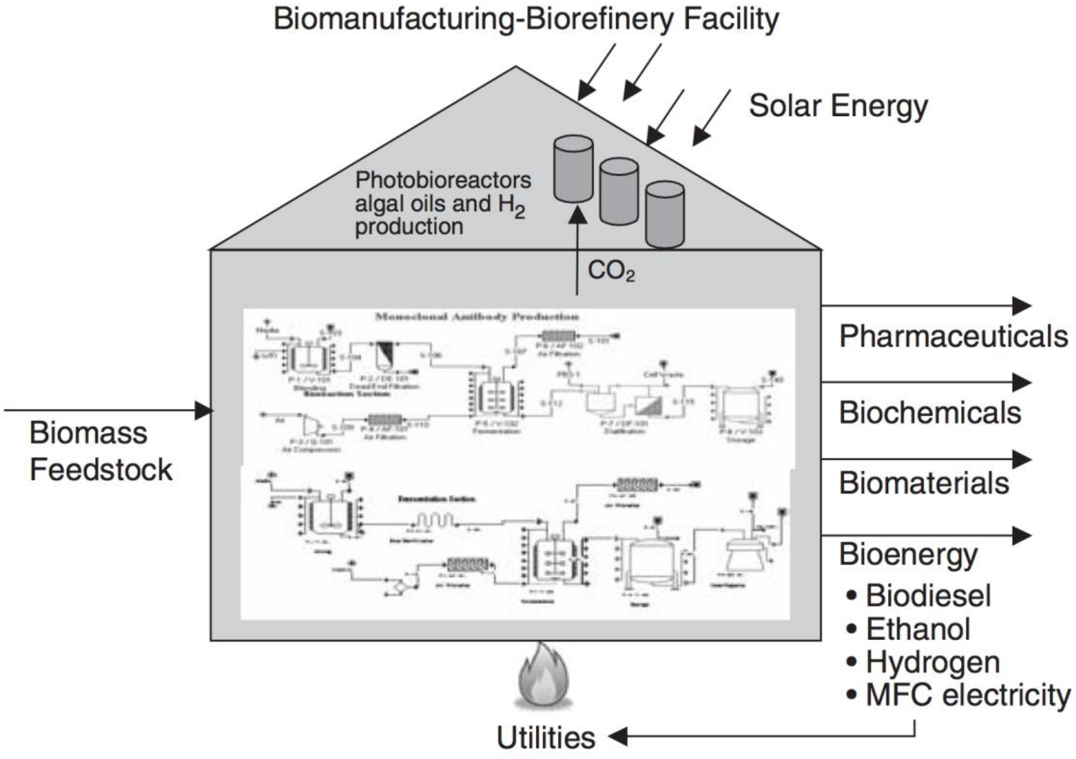


Figure 9: Integrated biorefinery showing example bioprocesses of monoclonal antibody and ethanol production.[46]

1.3.1 Biorafinery concept

The concept of producing products from agricultural commodities (i.e., biomass) is not new. However, using biomass as an input to produce multiple products using complex processing methods, an approach similar to a petroleum refinery where fossil fuels are used as input, is relatively new. Biomass consists of carbohydrates, lignin, proteins, fats, and to a lesser extent, various other chemicals, such as vitamins, dyes, and flavors.[54] The goal of a biorefinery is to transform such plentiful biological materials into useful products using a combination of technologies and processes. Figure 10 describes the elements of a biorefinery in which biomass feedstocks are used to produce various useful products such as fuel, power, and chemicals using biological and chemical conversion processes.

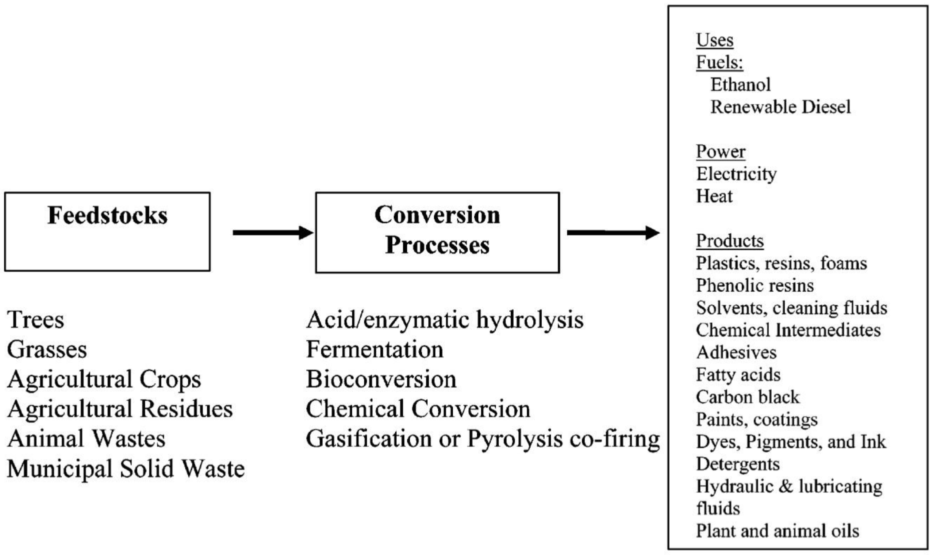


Figure 10: Simple three-step biomass-process-products procedure.[47]

The main goal of a biorefinery is to produce high value low volume (HVLV) and low value high volume (LVHV) products using a series of unit operations. The operations are designed to maximize the valued extractibles while minimizing the waste streams by converting LVHV intermediates into energy. The high value products enhance the profitability, while the high volume fuels help to meet the global energy demand. The power produced from a biorefinery also helps to reduce the overall cost. In contrast to a petroleum refinery, a biorefinery uses renewable resources and produces fuels and chemicals that contribute less to environmental pollution.

The development of comparable biorefineries, however, not in the sense of a direct copy of petroleum refinery, it is necessary to produce a broad variety of biobased products in an efficient construction set system.[48] Each biorefinery refines and converts its corresponding biological raw materials into a multitude of valuable products. The product types of a biorefinery includes not only the products produced in the petroleum refinery, but also in particular products that are not accessible in petroleum refineries.[49] Therefore it is necessary to develop new technologies such as:

- lignocellulosic feedstock biorefinery, including LCF pretreatment and effective separation in lignin, cellulose, and hemicellulose,
- further development of thermal, chemical, and mechanical processes,
- development of biological processes,
- combination of substantial conversions, such as biotechnological and chemical processes.[50]

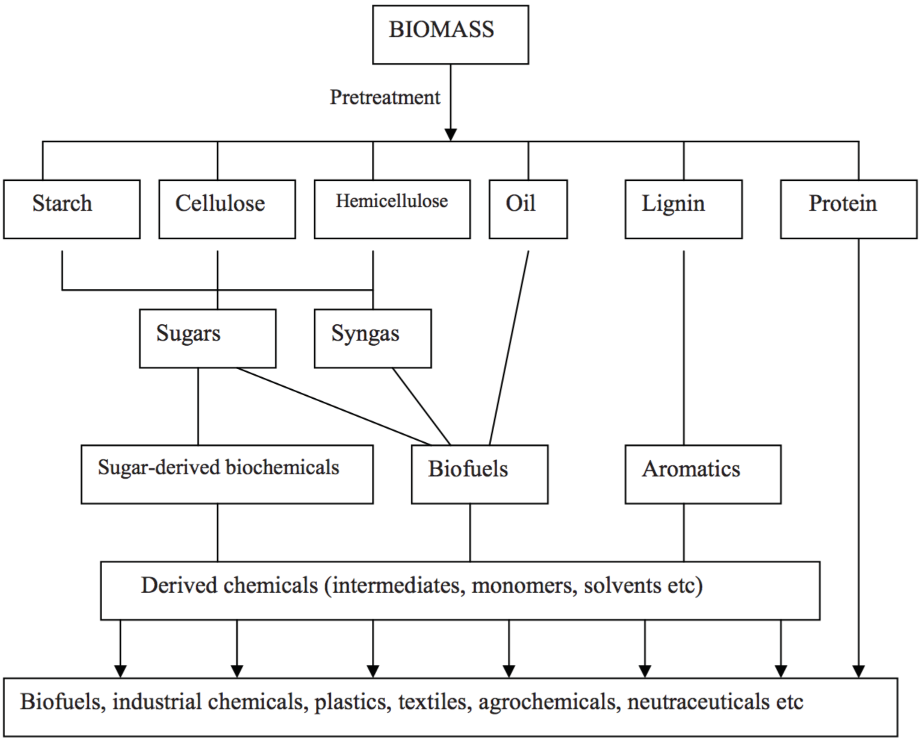


Figure 11: Flow diagram of a generalised biorefiner.[47]

1.3.2 Biorafineries types

Currently three biorefinery systems are pursued in research and development.[51]

- The 'Whole Crop Biorefinery': using raw material such as cereals or maize.
- The 'Green Biorefinery': using ‘nature-wet’ biomasses such as green grass, lucerne, clover, or immature cereal.
- The 'Lignocellulose Feedstock Biorefinery': using 'nature dry' raw material, such as cellulose containing biomass and wastes.

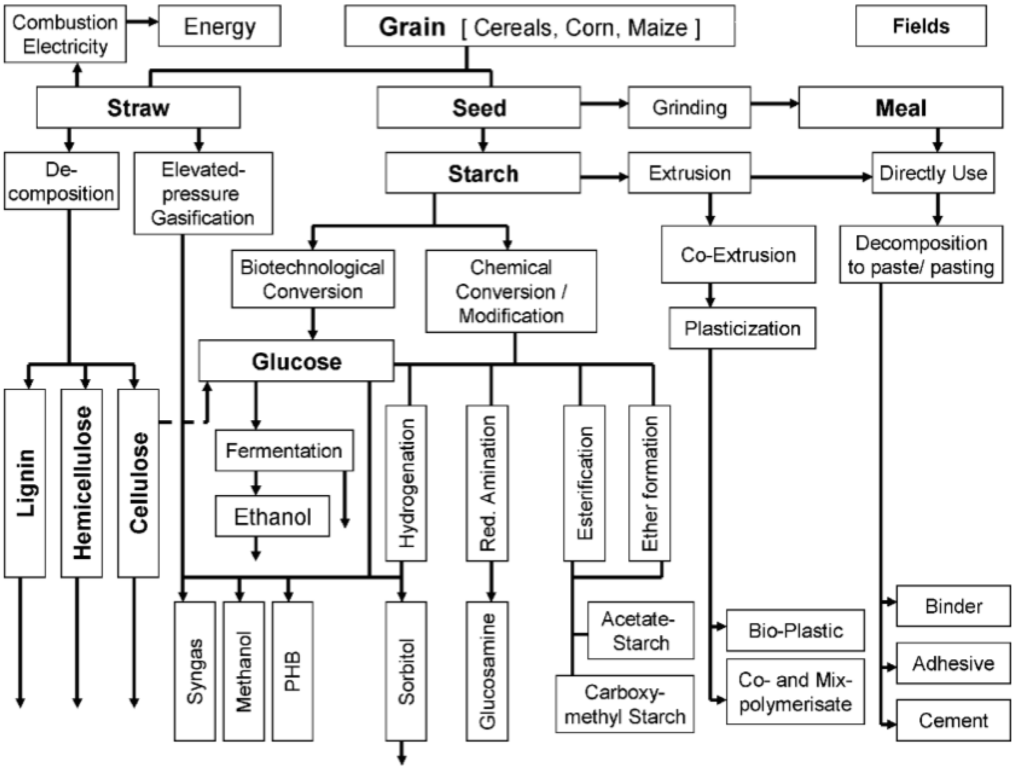


Figure 12: The whole crop biorefinery. Raw material: cereals, maize etc.[51]

<u>*The Lignocellulose Feedstock (LCF) Biorefinery*</u>: Among the potential large-scale industrial biorefineries the Lignocellulose Feedstock (LCF) Biorefinery will most probably be pushed through with highest success. On the one side the raw material situation is optimal (straw, reed, grass, wood, paper waste etc.), on the other side, conversion products have a good position, both, on the traditional petrochemical as well as on the future biobased product market. Lignocellulose materials consist of three primary chemical fractions or precursors:

- hemicellulose/polyoses, a sugar-polymer of pentoses predominantly
- cellulose, a glucose-polymer
- lignin, a polymer of phenols (Figure 13)

$$\text{Lignocellulose} + H_2O \rightarrow \text{Lignin} + \text{Cellulose} + \text{Hemicellulose}$$
$$\text{Hemicellulose} + H_2O \rightarrow \text{Xylose}$$
$$\text{Xylose } (C_5H_{10}O_5) + \text{acid Catalyst} \rightarrow \text{Furfural } (C_5H_4O_2) + 3H_20$$
$$\text{Cellulose}(C_6H_{10}O_5) + H_2O \rightarrow \text{Glucose } (C_6H_{12}O_6)$$

Figure 13: The general LCF-Biorefinery equation of conversion [51]

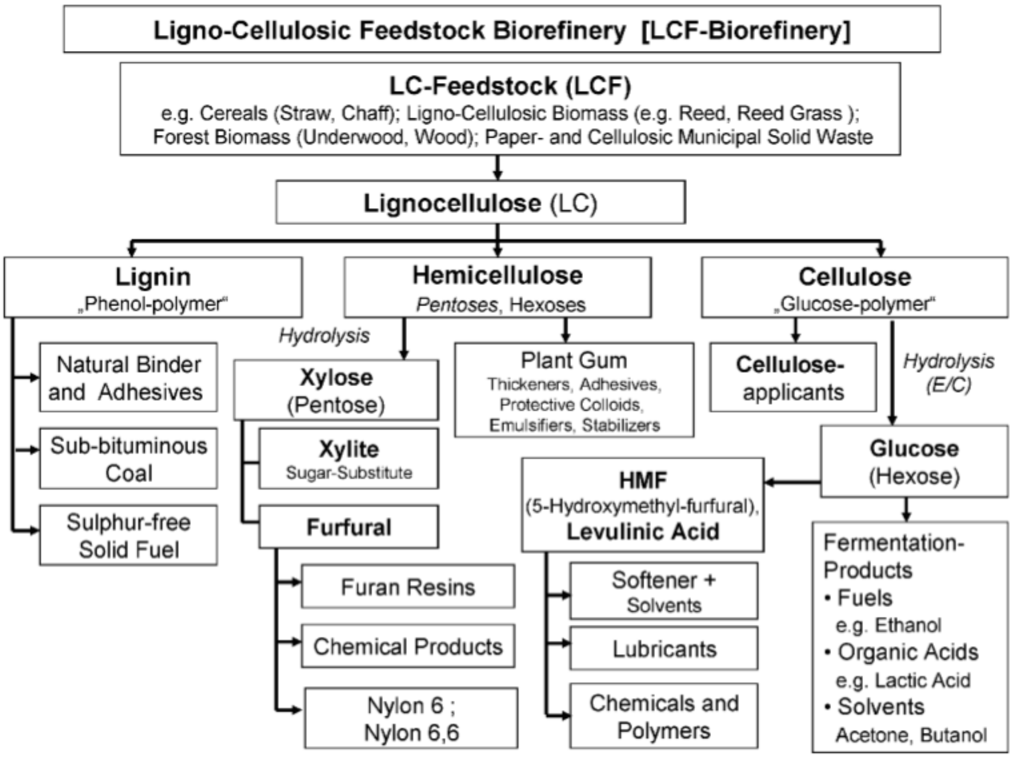


Figure 14: Ligno-cellulosic feedstock biorefinery (LCF-Biorefinery).[51]

However, there are still some unsatisfactory parts within the LCF, such as utilization of lignin as fuel, adhesive or binder. Unsatisfactory because the lignin structure contains considerable amounts of mono-aromatic hydrocarbons, which, if isolated in an economically efficient way, could add a significant value increase to the primary processes. It should be noticed that there are obviously no natural enzymes to split the naturally formed lignin into basic monomers as easy as this is possible for the also naturally formed polymeric carbohydrates or proteins.

An attractive process is already hydrolysis of the cellulose to glucose and the production of ethanol. Certain yeasts give a disproportionation of the glucose molecule during their generation of ethanol to glucose, which practically shifts its entire reduction ability into the ethanol and makes it obtainable in 90 % yield (w/w). Optimal profitability can be reached with a daily consumption of about 4360 tons of feedstock. Annually the plant produces 213.75 million L (47.5 million gallon) of ethanol and 323 000 tons of furfural.[53]

1.4 Ethanol

1.4.1 Historical Background

Ethanol and ethanol-petrol blends are not new as fuels for the internal combustion engine, since these fuels were proposed in the late 1800s by early car manufacturers. Henry Ford once described ethanol as the ‘fuel for the future’. During the First and Second World Wars, ethanol was mixed with petrol in order to preserve oil stocks. After the First World War, petrol dominated the fuel market although ethanol still continued to be used as an octane enhancer (anti-knock) in the 1920s but this was superseded by tetra-ethyl lead. The use of ethanol as a fuel re-emerged in the 1930s in the USA, where ethanol produced from maize was sufficiently cheap to be used in blends. It was used in concentrations of 5-17.5% to produce a blend called ‘gasohol’ and marketed as ‘Agrol’. In the UK, gasohol was marketed by the Cleveland Oil Company under the name of ‘Discol’ in the 1930s, a blend which continued to be sold until the 1960s. In the USA, gasohol was dropped by 1945 due to the availability of cheaper petrol.

In 1975 Brazil introduced the ‘Proalcool’ Programme to produce ethanol from sugarcane as a fuel to replace petrol as a response to oil price rises from 1973. The rise in oil prices was due to an Organization of the Petroleum Exporting Countries (OPEC) oil embargo as a consequence of the Arab-Israeli War in 1973. The reasons for the development of ethanol as a fuel in Brazil were to reduce the imports of petrol as Brazil had few oil fields, to open up areas of the country for cultivation, to provide employment, to increase the industrial base, and to develop ethanol exports of plant and expertise. In addition, Brazil is one of the largest producers of sugar from sugarcane so that a good substrate for ethanol production was readily available which did not require processing. The production of ethanol was encouraged by grants and subsidies to make ethanol cheaper than petrol. By the late 1980s about 50% of the cars used 95% (E95) ethanol as a fuel. However, price rises and a sugar shortage have reduced ethanol use to about 20% of vehicles, although 40% of the total fuel used is ethanol. One unforeseen outcome of the development of a large ethanol industry in Brazil producing, in 2006, 4.49 billion gallons is a flourishing export market for ethanol. In 2005 Brazil exported 100 million gallons to India, USA and Europe. [16]

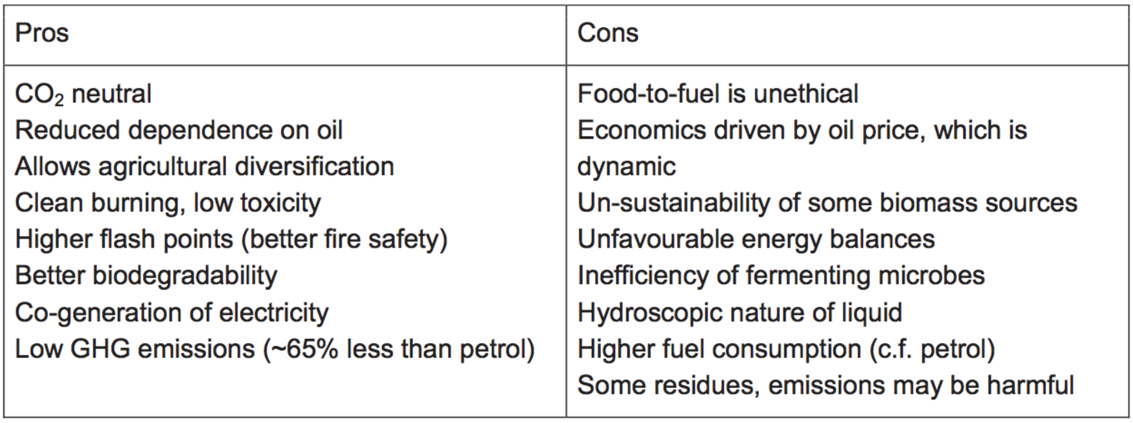
The USA initiated the production of fuel ethanol in 1978 with an Energy Tax Act where gasohol was defined as a blend of petrol containing more than 10% ethanol. The Act exempted ethanol from the US$0.40/gallon[16] tax on petrol. Apart from the tax changes, support for the ethanol industry was in the form of agricultural subsidies and tax credits awarded to blenders. The driving factors for the development of an ethanol industry were similar to those in Brazil. In the case of the USA, ethanol was produced from maize starch rather than from sugarcane. In addition, the price of chemically produced ethanol in the USA increased which made biologically produced ethanol more economic. In the 1970s chemically produced ethanol was selling at US$0.145/l [16] but in the 1980s the rise in the feedstock increased ethanol prices to US$0.53/l,[16] which was the same price as biologically produced ethanol. The tax exemption rose to US$0.60/gallon in the mid 1980s but was reduced in 2005 to US$0.51/gallon. An additional reason for the production of alcohol as a fuel was the low prices that the farmers were getting for their maize. At present, fuel ethanol accounts for 7% of the maize crop, boosting farm incomes by US$4.5 billion and is responsible for 200,000 jobs. In the 1980s, lead in petrol was removed and ethanol was of interest to increase the octane value.

1.4.2 Advantages and disadvantages

Bioethanol is an example of a renewable transportation fuel, the other major one being biodiesel from plant oils.

Figure 15 outlines the pros and cons of ethanol as a biofuel.

Bioethanol represents the largest volumetric production of any microbially produced biofuel, with current annual worldwide production around 100 billion litres (Renewable Fuel Association). The global leaders in bioethanol are USA with current production approaching ~50 billion litres (from maize) and Brazil with ~35 billion litres (from sugarcane).



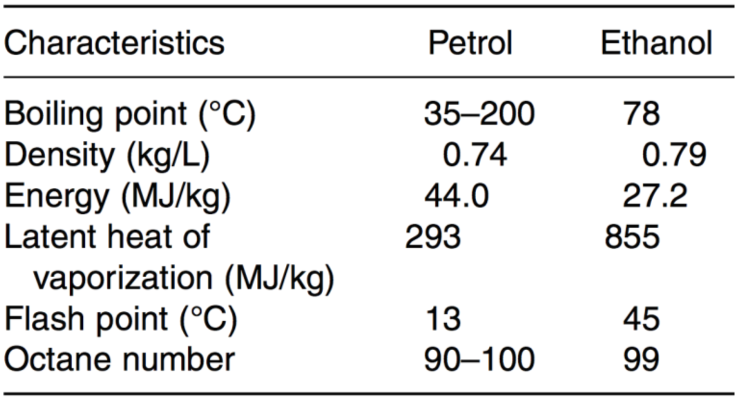
Pros	Cons
CO_2 neutral Reduced dependence on oil Allows agricultural diversification Clean burning, low toxicity Higher flash points (better fire safety) Better biodegradability Co-generation of electricity Low GHG emissions (~65% less than petrol)	Food-to-fuel is unethical Economics driven by oil price, which is dynamic Un-sustainability of some biomass sources Unfavourable energy balances Inefficiency of fermenting microbes Hydroscopic nature of liquid Higher fuel consumption (c.f. petrol) Some residues, emissions may be harmful

Figure 15: Some pros and cons of ethanol as a biofuel.

Drawbacks include the fact that agricultural land may be used for biomass production for biofuel and this may impact adversely on food security. In addition, the use of genetically-modified organisms has a perceived detrimental environmental impact from the general publics' perspective. However these disadvantages can be ameliorated by using "second generation" feedstocks (eg. from waste lignocellulosic material) together with modern chemical technology and biotechnology.

1.4.3 Ethanol properties

Petrol engines will run on ethanol as the properties of ethanol are similar to petrol in many aspects (Figure 16).



Characteristics	Petrol	Ethanol
Boiling point (°C)	35–200	78
Density (kg/L)	0.74	0.79
Energy (MJ/kg)	44.0	27.2
Latent heat of vaporization (MJ/kg)	293	855
Flash point (°C)	13	45
Octane number	90–100	99

Figure 16: The characteristics of petrol, bioethanol and butanol.[46]

The higher heat of vaporization of ethanol means that as the fuel is vaporized in the carburettor, the mixture is cooled to a lower temperature than for petrol. This means that more fuel enters the engine, in part compensating for the lower energy content, but the fuel inlet may need heating. Ethanol has a higher octane number and higher oxygen content than petrol. The heat of combustion (or gross energy) is lower than petrol, which leads to some reduction in performance and a 15-25% increase in fuel consumption.

To avoid separation of an aqueous layer in cold weather the ethanol needs to be anhydrous as ethanol normally contains 4.5% water. At 95.6% of ethanol, the mixture presents an azeotrope, so it is not possible to reach fuel grade ethanol purity with a simple distillation.

1.4.4 Ethanol conversion processes (1st generation)

A wide variety of carbohydrates containing raw materials have been used for production of ethanol by fermentation process. These raw materials are classified under three major categories:

- Sugar containing crops: sugar cane, wheat, beet root, fruits, palm juice, etc;
- Starch containing crops: grain such as wheat, barely, rice, sweet sorgum, corn, etc. and root plants like potato, cassava;

Chemical structure of starch consists of long chain polymer of glucose. The macromolecular starch cannot be directly fermented to ethanol by conventional fermentation technology. The macro-molecular structure first broke down in to simpler and smaller glucose. In this process, starch feedstocks are grounded and mixed with water to produce a mash typically contained 15-20% starch.

Ethanol production is usually obtained via enzymatic hydrolysis of starch containing crops like corn wheat. Corn ethanol production facilities can be classified into two groups i.e. wet & dry mill processes.[55] Dry mills are usually smaller in size (capacity) and are built primarily to manufacture ethanol only.

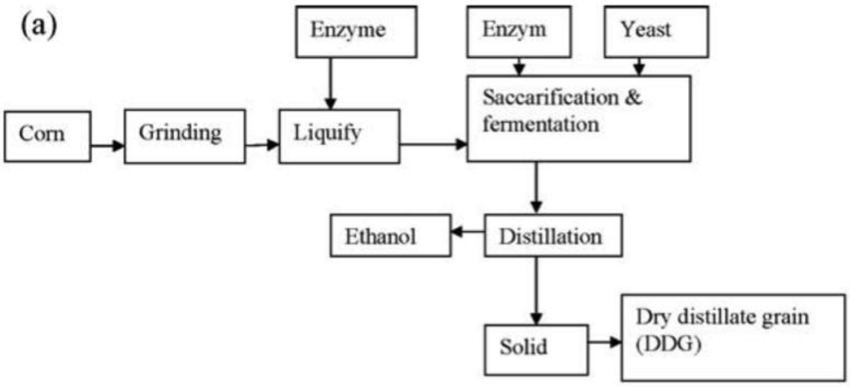


Figure 17: a) Dry mill process.[26]

1.4.5 Ethanol conversion processes (2^{st} generation)

There are two main routes available for producing liquid biofuels from biomass; one involves thermochemical processing and the other biochemical processing. Thermochemical processing defines the conversion of biomass into a range of products, by thermal decay and chemical reformation, and essentially involves heating biomass in the presence of different concentrations of oxygen. The clear advantage of thermochemical processing is that it can essentially convert all the organic components of the biomass compared with biochemical processing which focuses mostly on the polysaccharides.[22]

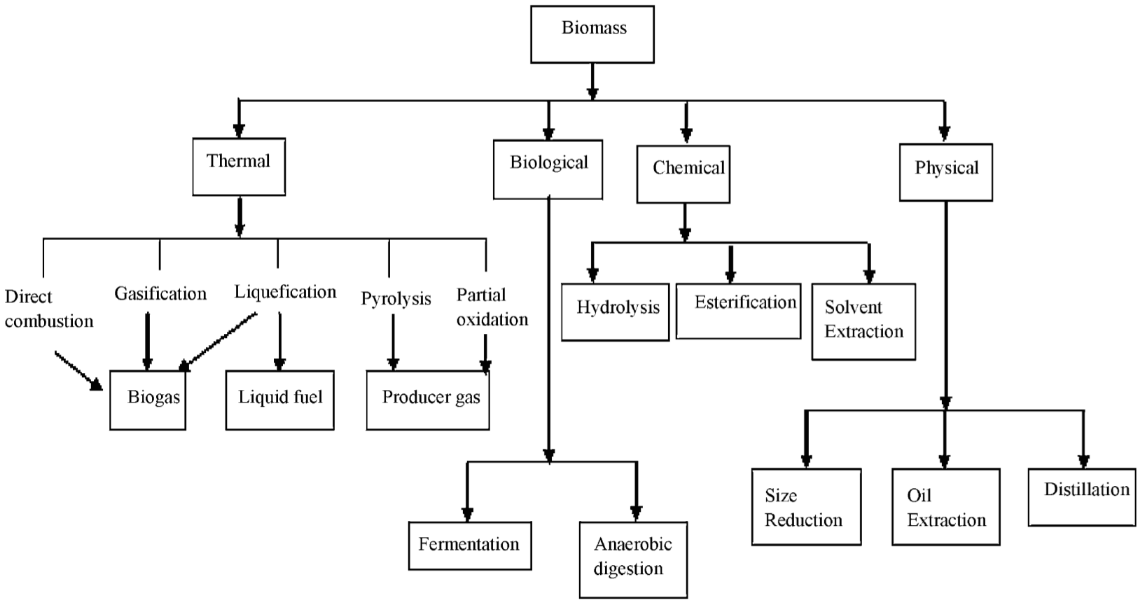


Figure 18: Conversion routes processes.[26]

Thermo-chemical conversion: Biomass can be converted to energy by mainly two processes. They are either thermo-chemical or biological. The thermo-chemical conversion process includes direct combustion, gasification, liquefaction, and pyrolysis as shown in Figure 18.

When biomass is heated under oxygen deficient conditions, it generates synthesis gas, or syngas, which consists primarily of hydrogen and carbon monoxide. This syngas can be directly burned or further processed for other gaseous or liquid products.

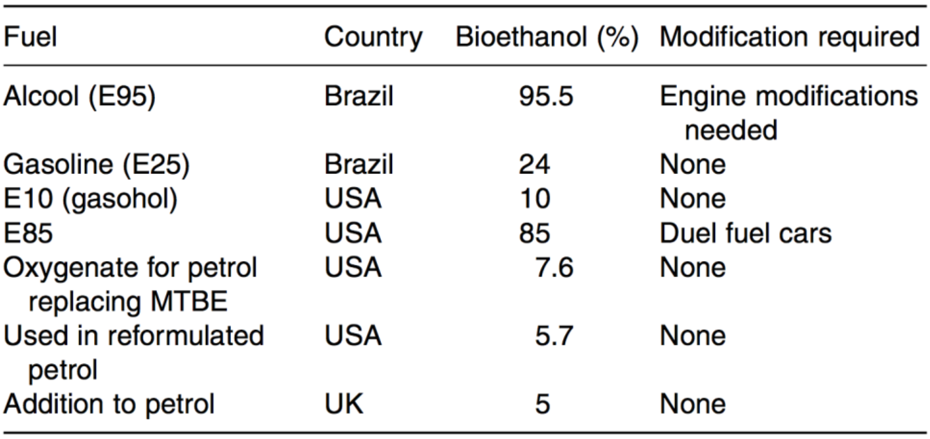
Biological conversion: are based on microbial and enzymatic process for producing sugars from biomass such as lignocellulosic, starch, cellulosic. The sugars later can be converted into alcohol and other solvents of interest to fuel and chemicals. For example, yeast based fermentation has shown good yield for ethanol from sugar or starch crops. Solid waste has been used to produce methane through anaerobic digestion in fabricated digesters or landfill. The production of ethanol from corn, sugarcane by biochemical means has already been commercially established. It is essential to hydrolyze lignocellulose for biological conversion. Enzymatic hydrolysis of lignocellulosic biomass required some research and developmental work to increase the yield of alcohol.

The conversion of biomass feed stocks to liquid fuels such as ethanol requires a number of basic unit operations including pretreatment, enzyme production, hydrolysis, fermentation and ethanol recovery. Biomass to ethanol research emphases on reduced costs which requires improved cellulose and hemicellulose conversion to sugar, combined xylose and glucose fermentation, lower pretreatment energy requirements, conversion of lignin to value added products, and efficient separation process for alcohol.[55,56]

Agricultural residues, forest residue, post harvest processing of industrial food crops generate enormous amounts of carbohydrate containing lignocellulosic waste.[58] The conversion of complex lignocellulosic biomass to alcohol is more difficult as compared to starch based feedstocks. The conversion of lignocellulosic biomass to alcohol requires three step process i.e. pretreatment of biomass, acid or enzymatic hydrolysis and fermentation/distillation.

1.4.6 Ethanol use in Vehicles

The concentration of ethanol used in petrol differs greatly from country to country. Hydrous ethanol which contains 4.5% water (alcool) has been used in all-ethanol vehicles in Brazil, but sales of these vehicles stopped in the 1990s to be replaced with a blend containing 24% ethanol (Figure 19).



Fuel	Country	Bioethanol (%)	Modification required
Alcool (E95)	Brazil	95.5	Engine modifications needed
Gasoline (E25)	Brazil	24	None
E10 (gasohol)	USA	10	None
E85	USA	85	Duel fuel cars
Oxygenate for petrol replacing MTBE	USA	7.6	None
Used in reformulated petrol	USA	5.7	None
Addition to petrol	UK	5	None

Figure 19: Ethanol petrol blends used in vehicles.[46]

This change was probably introduced in order to avoid the modification of car engines to use 95.5% (E95) ethanol allowing the unmodified engines to use both petrol and the 24% blend. The modifications to run on E95 were a heated inlet manifold due to the cooling effect of ethanol, changes to the carburetor, the fuel tank and fuel line replaced by one in tin and cadmium brass.

In the USA, the initial blend contained 10% ethanol (Gasohol) but more recently a blend containing 85% ethanol (E85) has been introduced and flexible fuel engines have been developed which can use either E85 or petrol. Ethanol is also used in the USA to increase the oxygen levels in petrol with an addition of 7.6% and as a replacement for MTBE in reformulated petrol. Ethanol contains 35% oxygen which increases combustion and therefore reduces particulate and NOx emissions.

1.4.7 Large scale Ethanol production

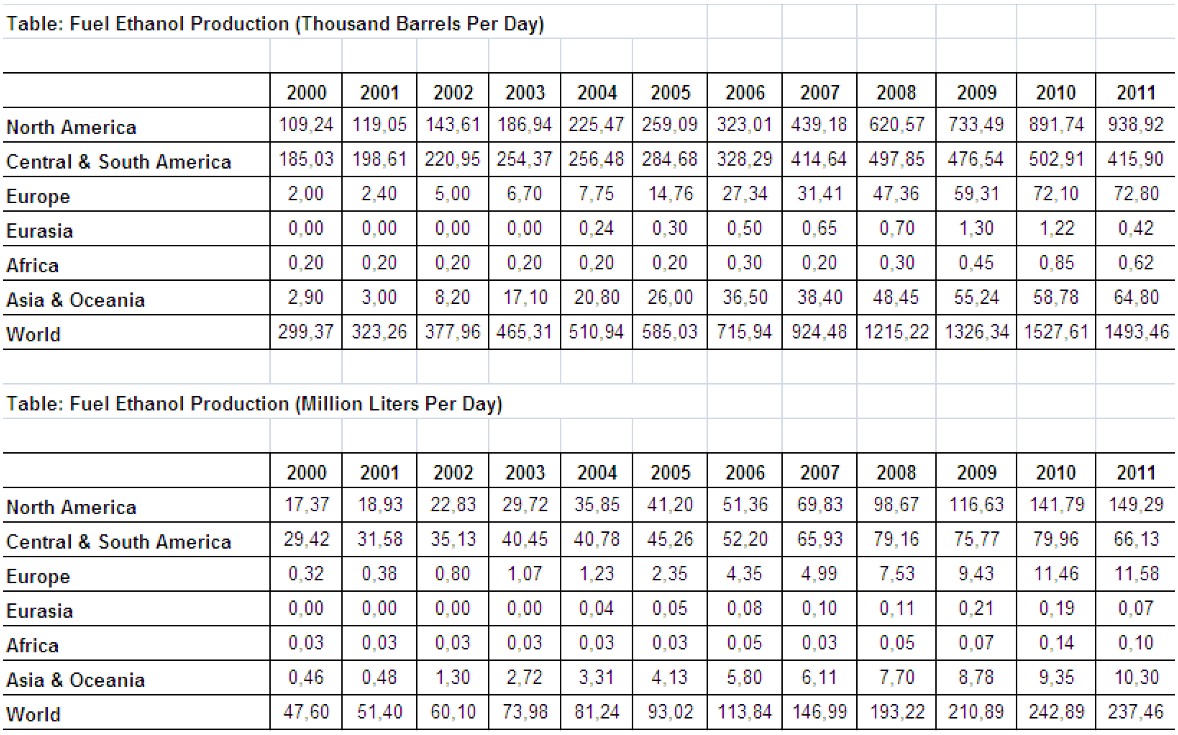


Table: Fuel Ethanol Production (Thousand Barrels Per Day)

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
North America	109,24	119,05	143,61	186,94	225,47	259,09	323,01	439,18	620,57	733,49	891,74	938,92
Central & South America	185,03	198,61	220,95	254,37	256,48	284,68	328,29	414,64	497,85	476,54	502,91	415,90
Europe	2,00	2,40	5,00	6,70	7,75	14,76	27,34	31,41	47,36	59,31	72,10	72,80
Eurasia	0,00	0,00	0,00	0,00	0,24	0,30	0,50	0,65	0,70	1,30	1,22	0,42
Africa	0,20	0,20	0,20	0,20	0,20	0,20	0,30	0,20	0,30	0,45	0,85	0,62
Asia & Oceania	2,90	3,00	8,20	17,10	20,80	26,00	36,50	38,40	48,45	55,24	58,78	64,80
World	299,37	323,26	377,96	465,31	510,94	585,03	715,94	924,48	1215,22	1326,34	1527,61	1493,46

Table: Fuel Ethanol Production (Million Liters Per Day)

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
North America	17,37	18,93	22,83	29,72	35,85	41,20	51,36	69,83	98,67	116,63	141,79	149,29
Central & South America	29,42	31,58	35,13	40,45	40,78	45,26	52,20	65,93	79,16	75,77	79,96	66,13
Europe	0,32	0,38	0,80	1,07	1,23	2,35	4,35	4,99	7,53	9,43	11,46	11,58
Eurasia	0,00	0,00	0,00	0,00	0,04	0,05	0,08	0,10	0,11	0,21	0,19	0,07
Africa	0,03	0,03	0,03	0,03	0,03	0,03	0,05	0,03	0,05	0,07	0,14	0,10
Asia & Oceania	0,46	0,48	1,30	2,72	3,31	4,13	5,80	6,11	7,70	8,78	9,35	10,30
World	47,60	51,40	60,10	73,98	81,24	93,02	113,84	146,99	193,22	210,89	242,89	237,46

Figure 20a: Ethanol Production.[59]

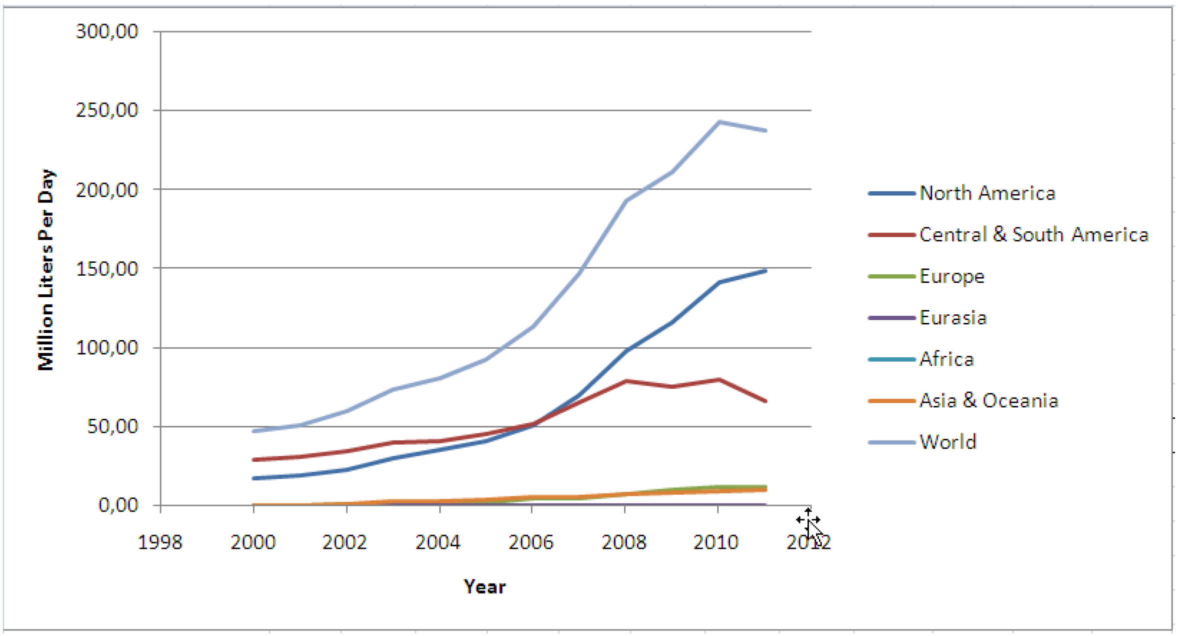


Figure 20b: Ethanol Production.[59]

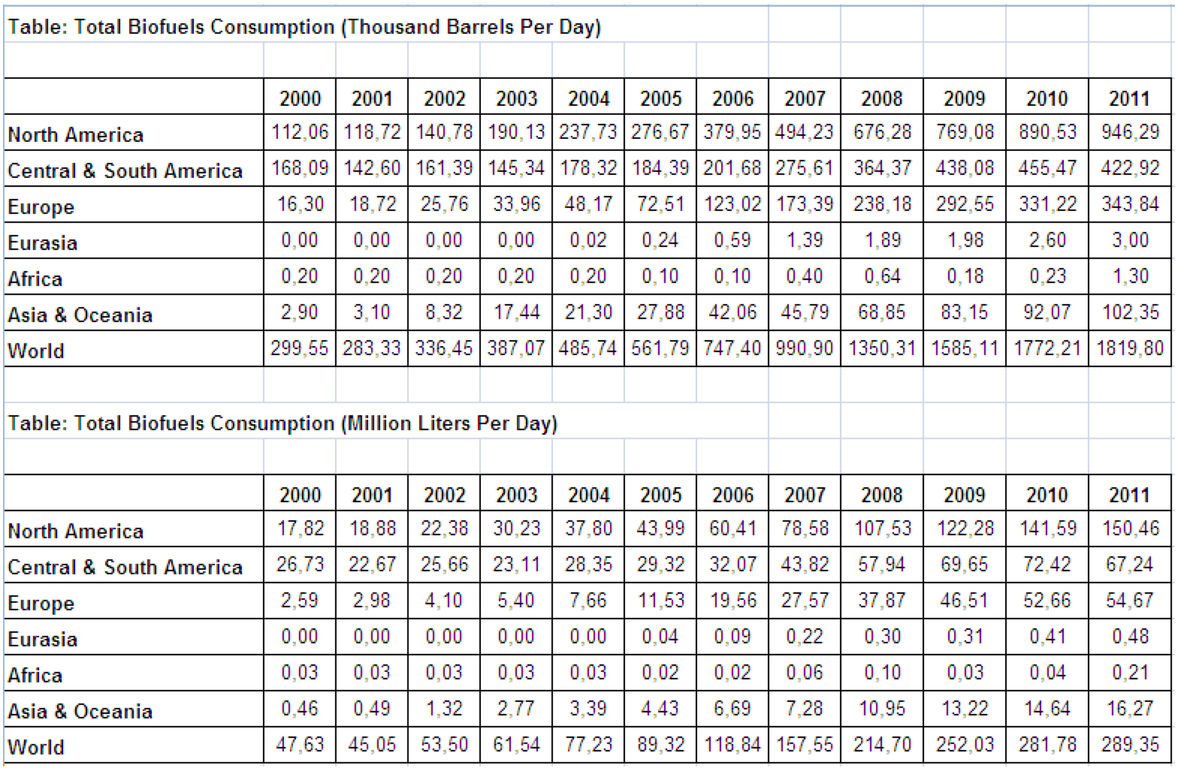


Table: Total Biofuels Consumption (Thousand Barrels Per Day)

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
North America	112,06	118,72	140,78	190,13	237,73	276,67	379,95	494,23	676,28	769,08	890,53	946,29
Central & South America	168,09	142,60	161,39	145,34	178,32	184,39	201,68	275,61	364,37	438,08	455,47	422,92
Europe	16,30	18,72	25,76	33,96	48,17	72,51	123,02	173,39	238,18	292,55	331,22	343,84
Eurasia	0,00	0,00	0,00	0,00	0,02	0,24	0,59	1,39	1,89	1,98	2,60	3,00
Africa	0,20	0,20	0,20	0,20	0,20	0,10	0,10	0,40	0,64	0,18	0,23	1,30
Asia & Oceania	2,90	3,10	8,32	17,44	21,30	27,88	42,06	45,79	68,85	83,15	92,07	102,35
World	299,55	283,33	336,45	387,07	485,74	561,79	747,40	990,90	1350,31	1585,11	1772,21	1819,80

Table: Total Biofuels Consumption (Million Liters Per Day)

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
North America	17,82	18,88	22,38	30,23	37,80	43,99	60,41	78,58	107,53	122,28	141,59	150,46
Central & South America	26,73	22,67	25,66	23,11	28,35	29,32	32,07	43,82	57,94	69,65	72,42	67,24
Europe	2,59	2,98	4,10	5,40	7,66	11,53	19,56	27,57	37,87	46,51	52,66	54,67
Eurasia	0,00	0,00	0,00	0,00	0,00	0,04	0,09	0,22	0,30	0,31	0,41	0,48
Africa	0,03	0,03	0,03	0,03	0,03	0,02	0,02	0,06	0,10	0,03	0,04	0,21
Asia & Oceania	0,46	0,49	1,32	2,77	3,39	4,43	6,69	7,28	10,95	13,22	14,64	16,27
World	47,63	45,05	53,50	61,54	77,23	89,32	118,84	157,55	214,70	252,03	281,78	289,35

Figure 21a: Ethanol Consumption.[59]

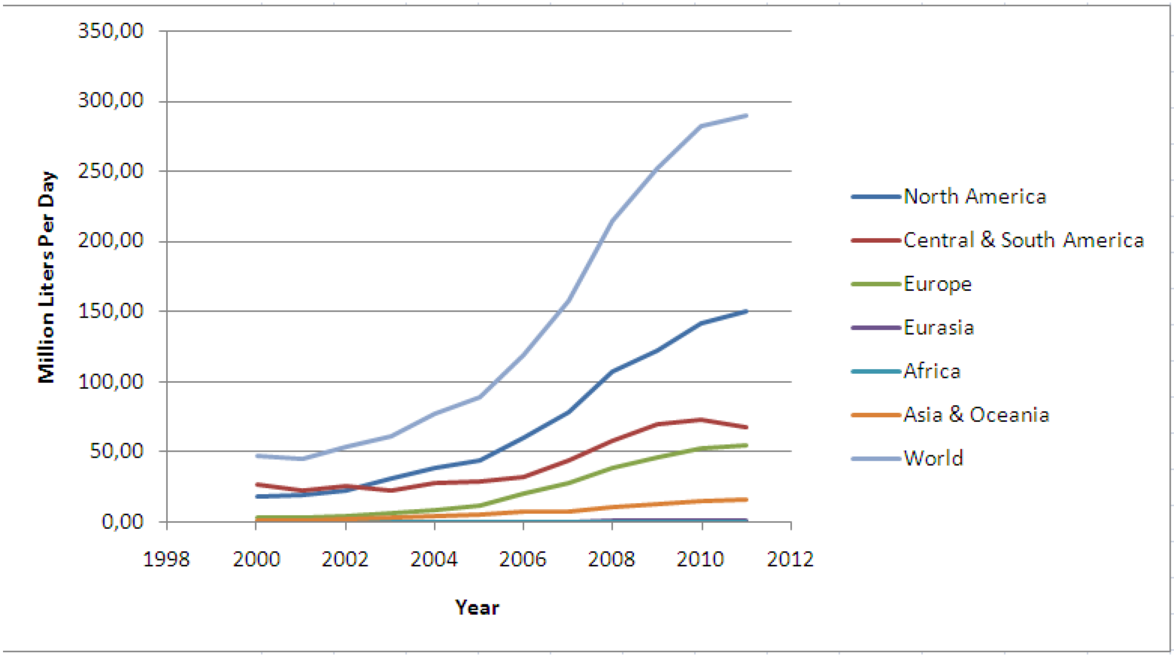


Figure 21b: Ethanol Consumption.[59]

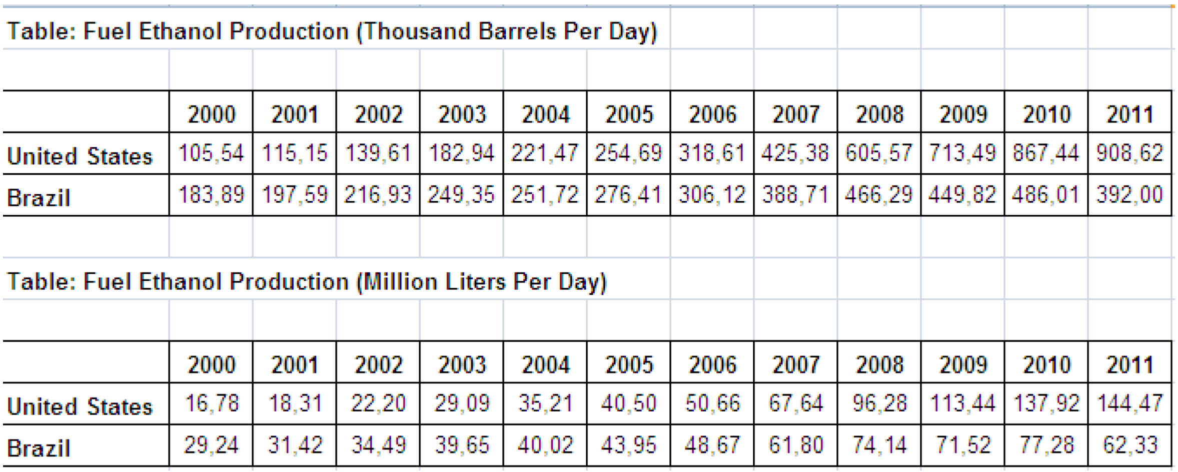


Table: Fuel Ethanol Production (Thousand Barrels Per Day)

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
United States	105,54	115,15	139,61	182,94	221,47	254,69	318,61	425,38	605,57	713,49	867,44	908,62
Brazil	183,89	197,59	216,93	249,35	251,72	276,41	306,12	388,71	466,29	449,82	486,01	392,00

Table: Fuel Ethanol Production (Million Liters Per Day)

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
United States	16,78	18,31	22,20	29,09	35,21	40,50	50,66	67,64	96,28	113,44	137,92	144,47
Brazil	29,24	31,42	34,49	39,65	40,02	43,95	48,67	61,80	74,14	71,52	77,28	62,33

Figure 22a: Ethanol Production in the main country.[59]

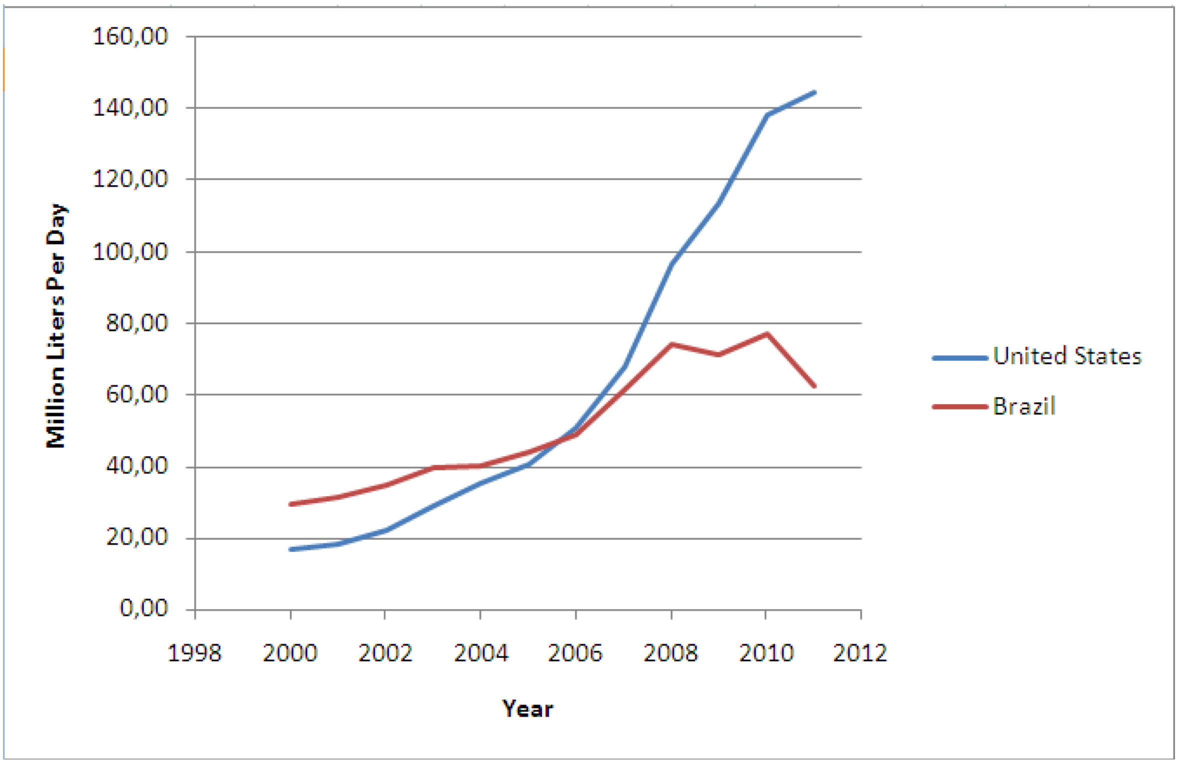


Figure 22b: Ethanol Production in the main country.[59]

2. HYBRID LIGNOCELLULOSIC BASED BIOREFINERY

One of the possibility for high fiber plant materials is, however, thermochemical processing into a uniform intermediate product that can be biologically converted into a biobased product. This route to biobased products is known as hybrid thermochemical biological processing or simply hybrid processing of biomass. It consists on gasification followed by fermentation of the resulting gaseous mixture of carbon monoxide (CO), hydrogen (H_2) and carbon dioxide (CO_2).[148]

Gaddy and co-workers at the University of Arkansas published a series of papers detailing how a variety of products, including methane, acetic acid, and ethanol, might be fermented from syngas.[148] Because of the US Department of Energy's interest in developing alternative transportation fuels from biomass, much of the early work in syngas fermentation focused on alcohol production.

Elmore and co-workers at Louisiana Tech University isolated three unidentified rod-shaped, gram-positive cultures that used mixtures of CO, CO_2, and H_2 (that is, simulated syngas) as their primary carbon source to produce acetate, ethanol, methanol, and smaller quantities of other alcohols and organic acids.[149,150,151,152,153]

Maness and Weaver at the National Renewable Energy Laboratory (1994)[156] opened up new opportunities for syngas fermentation by exploring the conversion of CO and H_2 into poly(3-hydroxybutyrate) by photosynthetic bacteria.[148] More recently, a team at the University of Oklahoma[154] has demonstrated the production of ethanol from clean syngas derived from a biomass gasifier and Iowa State University[155] is exploring the production of both hydrogen and polyesters from the purple non-sulfur bacteria Rhodospirillus rubrum under dark reaction conditions.

Syngas fermentation, is a second generation biofuel technology, one of three major approaches to the production of second generation biofuels from lignocellulosic biomass. The other two technologies are thermochemical (like Fischer-Tropsch (FT)) and biochemical (like Lignocellulosic Fermentation). In the context of syngas fermentation, lignocellulosic biomass such as forestry crops, perennial grasses and agricultural residues can be gasified to carbon monoxide

(CO) and hydrogen (H_2) rich synthesis gas (syngas), which is then fermented by acetogenic organisms to produce hydrocarbons that can be used as a fuel or chemical feedstock.[110]

Syngas fermentation offers numerous process advantages compared with other second generation approaches in terms of feedstock flexibility and production economics. Syngas fermentation has tremendous feedstock flexibility and high rates of energy and carbon capture. In addition, the selectivity, process robustness, catalyst flexibility, and development potential are high.[146,147]

INEOS Bio, Coskata and LanzaTech are three companies exploring the commercialisation of syngas fermentation for the production of liquid fuels.

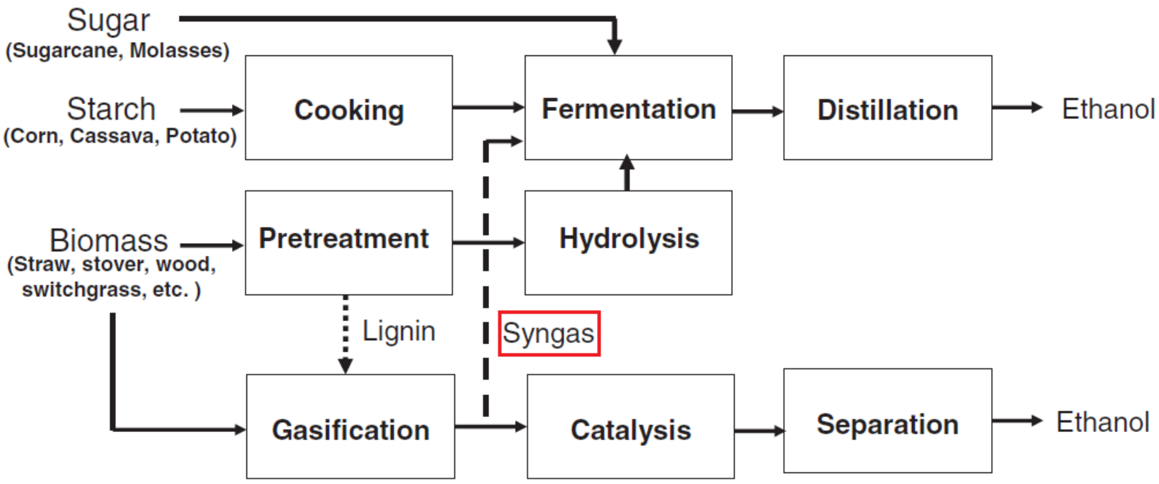


Figure 23: Hybrid Process Tecnology (Biomass Gasification & Syngas Fermentation).

2.1 Process description

The process structure consists of five different parts: pretreatment, gasification, gas cleaning, fermentation of syngas and bioethanol purification.

The first part, after biomass pretreatment, inviolves an indirect low pressure gasification (allothermal gasification) with steam, where the combustion of char in a parallel equipment (combustor) provides the energy for the gasification of the biomass by heating sand, which is fed back to the gasifier.

The second part comprises technologies to remove solids from the gas as well as other compounds like hydrocarbons, NH_3, CO_2 or H_2S and to adjust the gas composition. The hydrocarbons are partially removed in the tar reformer where they are either reformed with steam. Solids are removed together with NH_3 in a wet scrubber and compressed. In both cases traces of hydrocarbons (HBC) are removed in a Pressure Swing Adsorption (PSA) system with a bed of silica gel. Next, the composition of the gas is adjusted to a $CO:H_2$ molar ratio of 1. In order to realize that, a PSA is adopted for removal of H_2 (with a bed of oxides). Furthermore, it is more profitable to sell any excess of hydrogen. Sour gases such as CO_2 and H_2S are removed next. Fermentation with bacteria can handle up to 2.5% in volume of H_2S.

The two technologies are used for removing the sour gases are:

- the PSA system.
- the absorption of the sour gases in monoethanolamine (MEA).

The synthetic path is based on biological conversion, where the syngas is fermented in a bioreactor. The unreacted gases are fed in a steam boiler to recover energy. Finally, water is removed from the ethanol-water solution to obtain fuel quality ethanol using a beer column, a rectification column and molecular sieves.

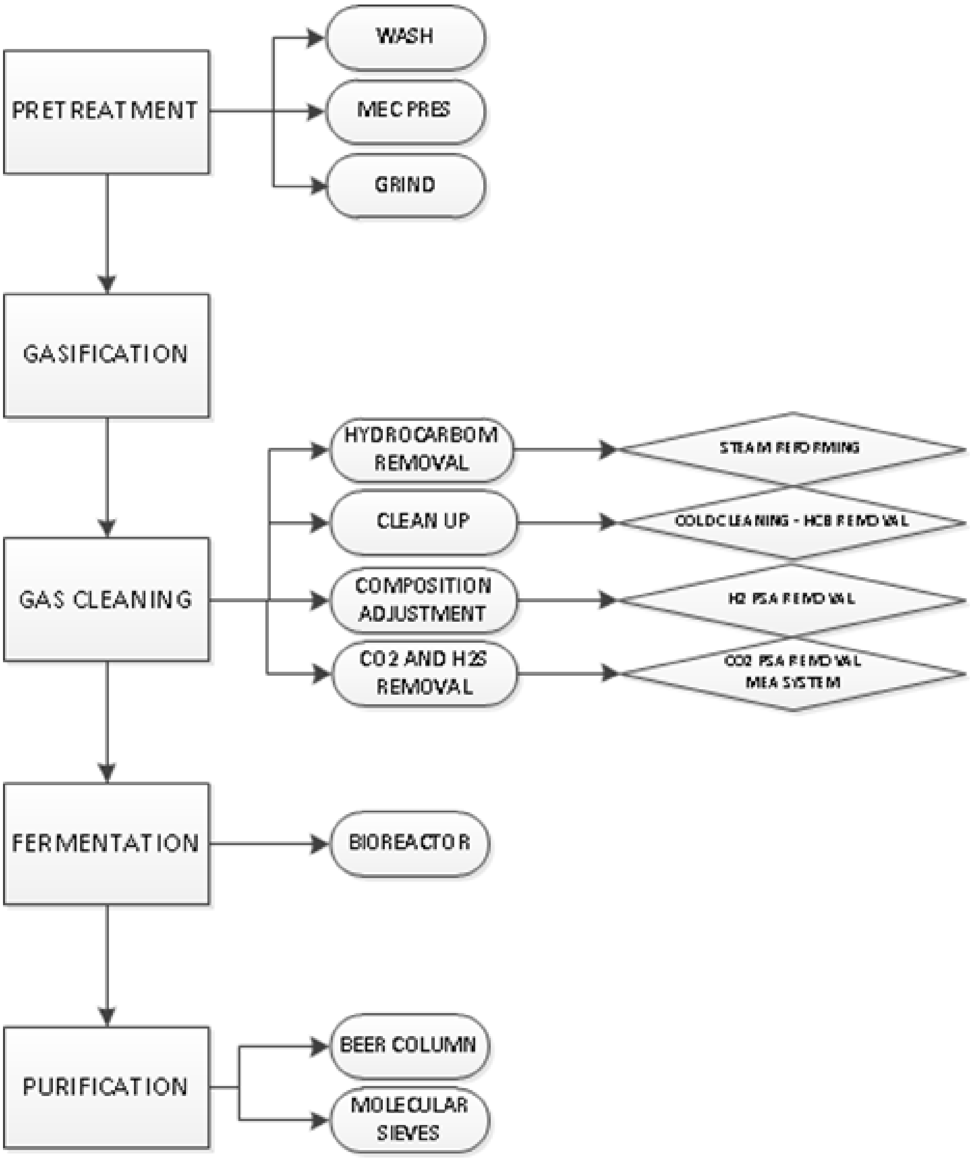


Figura 24: Process layout.

2.2 Pretreatment

In biomass to ethanol processes, pre-treatment basically refers to the mechanical and physical actions to clean and size the biomass, and destroy its cell structure to make it more accessible to further treatment. Each type of feedstock requires a particular pre-treatment method to minimize the degradation of the substrate, and to maximize the sugar yield.

The biomass is pretreated before gasification. Three unit operations are considered (Figure 25):

- washing;
- drying;
- size reduction.

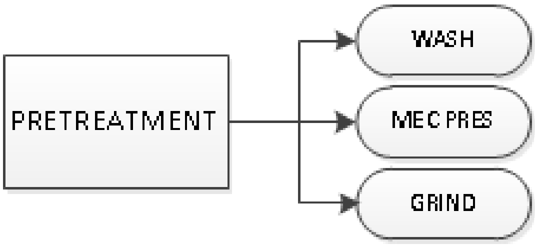


Figure 25: Pretreatment.

It may be necessary to clean the raw material by washing. This step removes dirt and dust from the grass. The washing step does not consume any heat because it takes place at ambient temperature. Clean feedstock, like production wood, will in general not need this step. Later, the grass is partially dried by means of a mechanical press accompanying the grass. Subsequently, raw material is sent to a size reduction unit. The switchgrass is chopped using grinding or milling processes in order to reduce size and to eliminate heat transfer limitations during the gasifying process. This tipe of configuration ensures correct operation of the fluid bed. Industry experts would typically agree that a feedstock size of 2.0-2.5” minus is ideal for this technology. At the end of the process, biomass pellets are ready to send into the gasifier.

2.3 Gasification

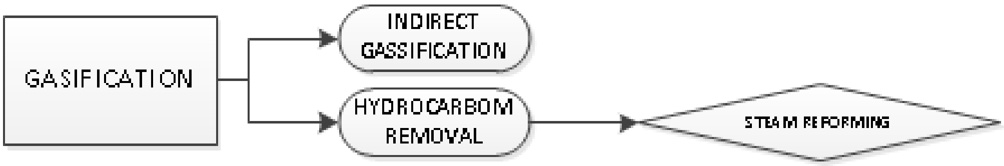


Figure 26: Gasification.

The gasifier technology consists of an atmospheric, indirectly heated biomass gasifier system capable of producing a syngas. The gasifier system is an allothermal gasifier (Figure 27), meaning the energy used for heating and maintaining the gasification reaction temperature is applied indirectly by heating the bed material from the combustion of the char in the combustion reactor. The bad material si olivine, a sand used as a thermal vector. Saturated low to medium pressure steam is required and added to the gasifier for bed fluidization. Note that oxygen is not added to the gasifier reactor because the gasification reactions are driven by indirect heating. (No air or oxygen is added to the gasifier).[73]

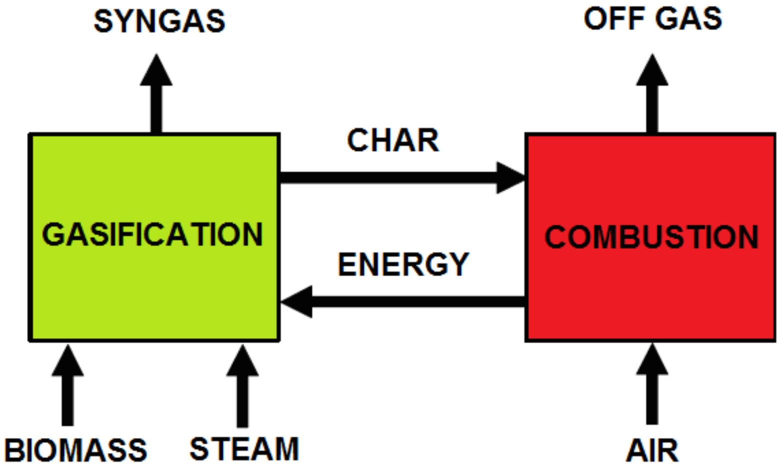


Figure 27: Gasifier Configuration.

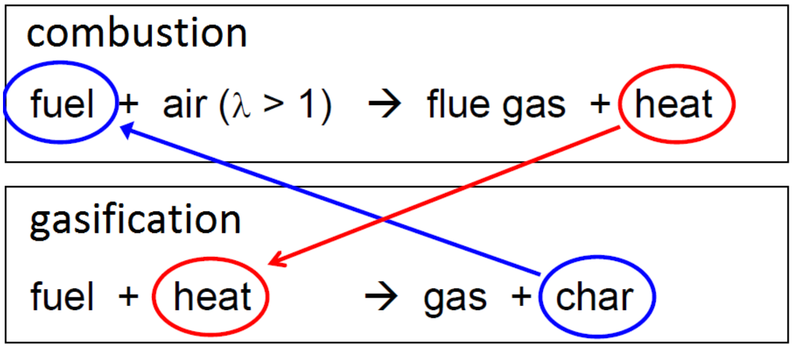


Figure 28: Theoretical Reactions.

Typically an allothermal (indirect) gasification system will produce syngas with a higher H_2 to CO ratio than an autothermal (direct with air or oxygen) system. In an allothermal system there is no need for the incomplete combustion or partial oxidation (volatile products and some of the char reacts with O_2 to form CO_2 and CO) step to take place because the heat required to volatilize the organic (biomass) material is added indirectly. As a result, most of the biomass reacts with CO_2 and water vapor to produce CO and H_2 in the gasification/steam reforming reactions.

The main advantages of indirect gasification are:

- N2 free syngas.
- Elevated carbon conversion (theoretically 100%).
- More scalable and applicable for large installations.
- Wider range of acceptable feedstock particle sizes, density, moisture and ash content.

Gasifier: The gasifier vessel is constructed with a refractory lining to protect the integrity of the steel shell. Reheated bed material is introduced into the bottom portion of the gasifier to provide heat and help form the fluidized bed. The circulating fluid bed gasification reactor is a non-coded vessel operating at atmospheric pressure. Due to the fast fluidization and the high gas velocities, the biomass material becomes thoroughly mixed with the bed material to enhance the heat and mass transfer. The biomass is rapidly converted into syngas at a temperature of approximately 890 °C. No bed material is removed or purged from the gasifier, rather a portion of the bed media is carried out with the syngas to the gasifier cyclones. Therefore, a bad material make-up must also be injected in the combustor. Syngas is discharged at the top of the gasifier vessel and is routed to the cyclone for char and particulate removal.

Combustor: the circulating fluid bed combustion reactor is a non-coded vessel operating at atmospheric pressure. The fluid bed reactor is a refractory lined pressure vessel with a distributor located at the bottom of the vessel to facilitate fluidization. Air is feed through a preheater, where the air is indirectly heated to approximately 300 °C with the flue gas produced by the combustion reactor. The heated combustion air is then injected beneath the distributor to achieve fluidization. The combustion process consumes the char and reheats the bed material to approximately 1,000 °C. The remaining carbon is consumed in the combustion reactor, resulting in a carbon-free ash. The flue gas stream from the combustion reactor is cleaned of any remaining ash and particulate matter by the ash cyclone and a electrostatic precipitator before exiting the system. After cleaning, the hot flue gas at approximately 1,000 °C is then used to heat combustion air for the combustion reactor.[73] The cooled flue gas exits the air heater is vented to the atmosphere. Note that there is sufficient heat remaining in the flue gas that it could be used for further heat recovery prior to venting.

Tars Reformer (steam reforming): Is necessary decomposing the hydrocarbons generated during the gasification process. Tar reforming occurs when water vapor in the incoming syngas is heated to a sufficient temperature to cause steam reforming in the gas conditioning reactor, converting condensable hydrocarbons (tars) to non-condensable lower molecular weight molecules. Moreover H_2/CO is increased; it's very useful because produces H_2 surplus, which has a great economical value. Typically, syngas is routed through heat exchange equipment to cool the syngas and transfer heat to a steam generator or water heating system. Cleanup of the cooled syngas usually follows the heat exchange operation. Because of the significant reduction in condensable material that occurred in the gas conditioning reactor, the syngas can be cooled to low temperatures to increases the heat recovery potential without the fear of buildup or fouling of the heat exchange surfaces.[73]

2.3.1 Hydrocarbon removal

There is a possibility to decomposing the hydrocarbons generated during the gasification process, producing hydrogen:

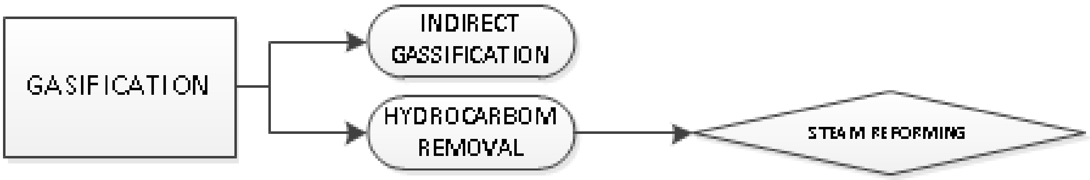


Figure 29: Gasification.

Steam reforming: The gas coming from the gasifiers is fed to the reformer at the same temperature as the outlet from the previous equipment.The tar reformer works at lower pressures.[74] For steam reforming, the chemical reactions taking place are of the form given by:

$$C_nH_m + nH_2O \longrightarrow nCO + \left(\frac{m}{2} + n\right)H_2$$

Figure 30: Tars Reformer Reactions.[65]

2.4 Gas Cleaning

2.4.1 Separation and purification processes

As discussed earlier, in each of the multitude of lignocellulose based biorefinery applications, in addition to the biomass conversion processes, separation and purification of the biomass components and the products streams and their full integration with the overall process is of utmost importance. In many instances this can be the single biggest factor influencing the overall success and commercialization of biorefineries. Given the significance and importance of this area, separation and purifications technologies and their applications in biorefineries is the focus of this work.

The following part presents a brief introduction and outlines the challenges and opportunities in many of the plausible separation and purification technologies in biorefineries.[75]

2.4.1.1 Absorption

Absorption is often used for separation of particles or desired gas components from a gas mixture into a liquid solvent phase. In biorefineries, absorption is commonly used for removal of acid gases such as H_2S and CO_2 from syngas prior to synthesis of syngas into methanol and diesel. There are two major type of absorption: physical and chemical absorption. Physical absorption is commercially used to remove acid gases such as CO_2 and H_2S from syngas in the production of hydrogen, ammonia and methanol.

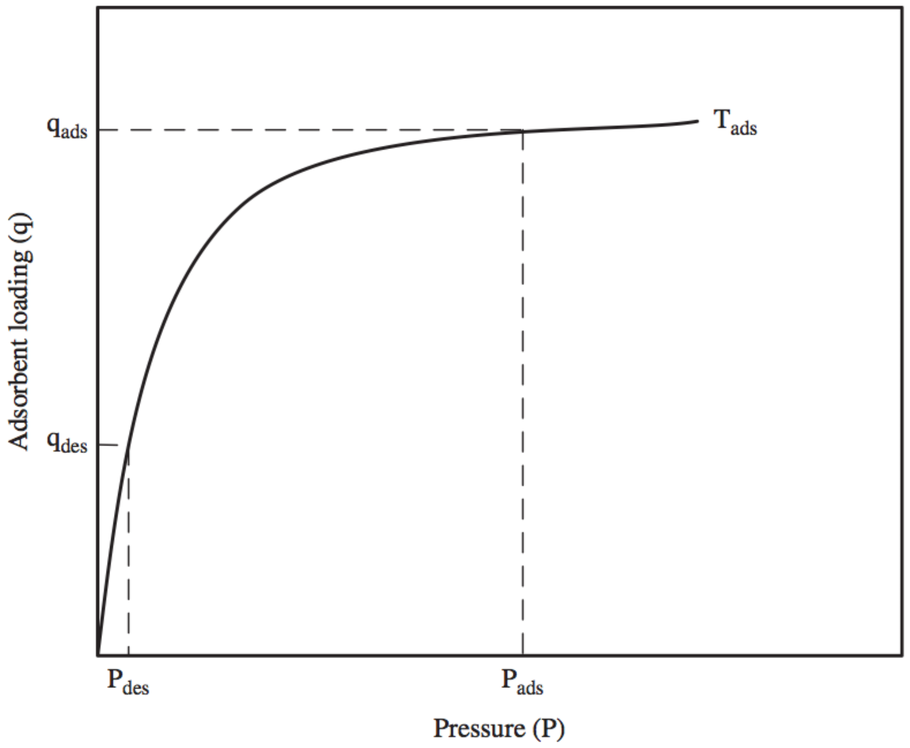
Currently, both the chemical absorption based on aqueous methanolamine (MEA) and the Selexol process are selected in commercial IGCC (Integrated Gasification Combined Cycle) facilities for removal of acid gases. Pressure Swing Adsorption (PSA) can be used for hydrogen purification[77] and for capturing CO_2.[76] One of the primary applications of PSA is for removal of CO_2 as the final step in the production and purification of hydrogen for use in biorefineries and in the production of ammonia, or the separation of CO_2 from biogas to increase the methane content.

2.4.1.2 PSA (Pressure Swing Adsorption)

PSA operates as a cyclic batch. The regeneration of the adsorbent bed is achieved by reducing the total pressure and purging the bed at low pressure with a small fraction of the product stream.

Figure 31 shows the effect of partial pressure on adsorbent equilibrium loading for a type I isotherm at adsorption temperature of T_{ads}. As the partial pressure is reduced from P_{ads} to P_{des}, the equilibrium loading is also reduced from q_{ads} to q_{des}. As pressure changes can be effected much faster than temperature changes, the PSA process allows a much faster cycling. Thus it can remove large quantities of impurities. For strongly adsorbed species, PSA would require a very low pressure for desorption, which can increase the operating cost. Pressure swing adsorption processes are often operated at low adsorbent loadings because selectivity between gaseous components is often greatest in the Henry’s law region. It is desirable to operate PSA processes close to ambient temperature to take advantage of the fact that, for a given partial pressure, the loading is increased as the temperature is decreased. The basic PSA process uses the two-bed system although multiple beds also can be operated in a staggered sequence. A typical PSA cycle consists of the following basic steps:

- Adsorption.
- Co-current depressurization.
- Counter-current depressurization.
- Purge at low pressure.
- Repressurization.



Fugure 31: Operating principle of a PSA system.[75]

These steps are illustrated in Figure 32.

<u>Adsorption (1→2)</u> The gas mixture is fed into an adsorber bed under high pressure. The impurities are adsorbed and the purified product is withdrawn. Flow is normally in the upward direction. When the adsorber reaches its adsorption capacity, it is taken off-line, and the feed is automatically switched to a fresh adsorber bed. This keeps the feed and product flows continuously.

<u>Cocurrent depressurization (2→3)</u> The gas mixture trapped in the void spaces of the adsorber is recovered by partly depressuring the bed from the product side in the same direction as the feed flow (co-current). This moves the impurity fronts migrating to the top of the adsorbent bed. Thus the cocurrent depressurization step can increase the concentration of the adsorbate recovered during the regeneration step.

Countercurrent depressurization (3→4) The saturated adsorber is then partly regenerated by depressurizing towards the feed end (counter-current), and the desorbed impurities are rejected to the PSA offgas.

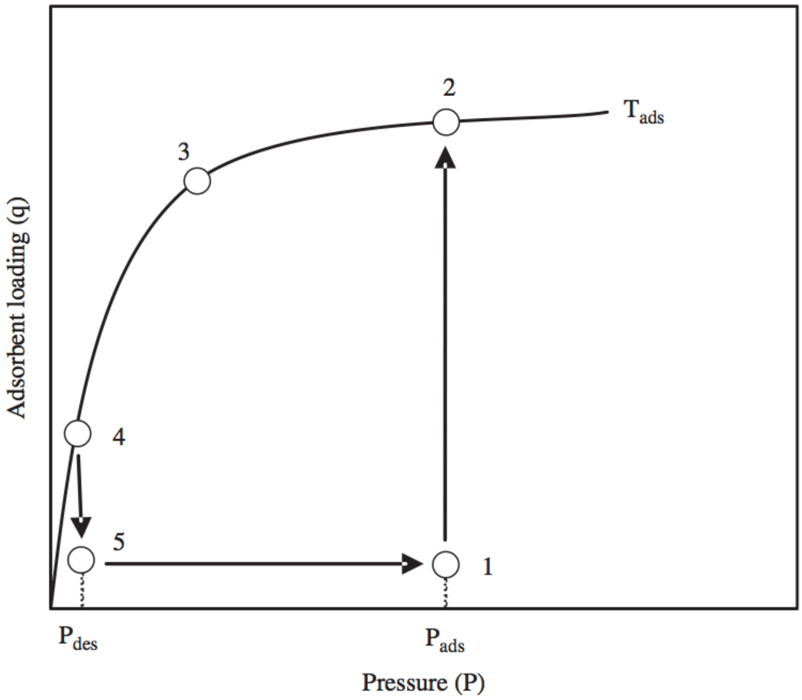


Figure 32: PSA cycle steps.[75]

Purge at low pressure (4→5) The adsorbent is then purged with purified product (taken from another adsorber during concurrent depressurization) at constant offgas pressure to further regenerate the bed.

Repressurization (5→1) The adsorber is then repressurized with product gas coming from the co-current depressurization, and with a slipstream from the product stream. When the adsorber has reached the adsorption pressure, the cycle has been completed, and the adsorber is ready for the next adsorption step.

2.4.1.3 H_2S and CO_2 absorbing

Figure 33 illustrates the general configuration of an amine based biogas scrubber. It consists of an absorption column, a desorption column and a water wash scrubber. Initially, raw biogas enters the absorption column where the amine solution removes H_2S and CO_2 (in a chemical reaction between the sour gas and the amine). Then, the biogas passes through the water wash scrubber where amines traces are removed and the saturated amine passes through the desorption column where it is regenerated. A heat exchanger is used to cool the regenerated amine before it re-enters the absorption column.

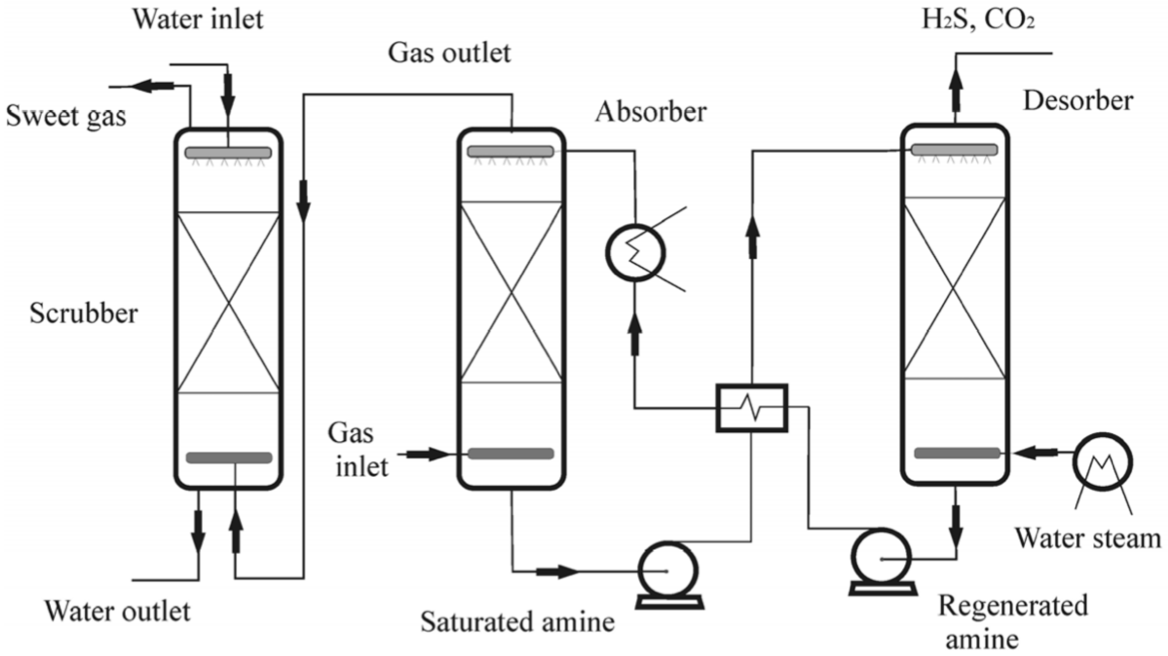


Figure 33: Illustration of the amine based biogas H2S and CO2 scrubber.[91]

<u>Absorption column</u>: It is a counter flow column where amine solution fall down due to gravity and raw biogas flows from the bottom towards the top of the column due to pressure difference. The column is fully packed to enhance the contact area between the gas and liquid phases. In addition several disks are incorporated to ensure the uniform distribution of both flows through the column.

The length of the column is designed to obtain the specified final H_2S and CO_2 concentration and the diameter is designed to meet a minimum pressure drop with the specified gas flow. This procedure is well established and reported in references.[87] The absorption column was instrumented with temperature and pressure sensors at the inlet and outlet. Flow meters were used for both the biogas and the liquid phase absorbing substance.

Regenerative column: amines desorb H_2S and CO_2 when they are heated up to 120°C at atmospheric pressure.[89] For the present application, this heat addition can be obtained in a counter-flow heat exchanger between the amine and the engine exhaust gases. Alternatively, exhaust gases can be used to generate saturated steam and then heat the amines by direct mixing with this steam in a desorbing column.

A desorbing column was designed, manufactured and tested to regenerate amines solutions by mixing with steam. Preheated saturated amine solution fall down through the desorption column due to gravity while steam moves in counterflow due to pressure difference. Under steady-state conditions the energy requirements for the desorption column are the heats of desorption, sensible and latent for the amine solution and for the steam. They are influenced by pressure and flow rates.[90] For larger scale applications the CO_2 and H_2S rich vapor stream that leaves the desorption column can be passed through a reflux condenser where H_2O is partially condensed, CO_2 sequestrated and H_2S recovered for industrial applications.

On the other side, regenerated amine solutions should be cooled before reentering the absorption column because temperature reduces the amine absorbing capacity. For this purpose it is used a heat exchanger between regenerated amine and saturated amine coming out of the absorption column. The regenerative is fully packed with stainless steel rashing rings to increase the contact area between the amine solution and the steam.

Fully saturated amines solutions were passed through the desorption column and collected at the bottom. Then they were cooled and used again in the absorption column under the same conditions as they were initially saturated It shows that the H_2S removing efficiencies change from 98% to 95% when the amine is regenerated. Similarly, it changes from 87% to 50% for the case of CO_2. Literature reports that amines can be regenerated 25 times before being degraded.

2.4.2 Solids removal – Cold cleaning

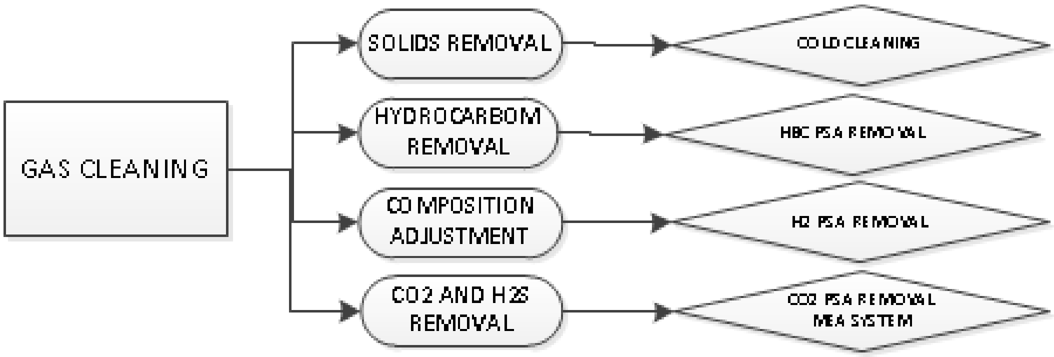


Figure 34: Gas Cleaning.

The syngas is sent to the Syngas Venturi Scrubber, to remove any remaining ammonia, particulates, metals, halides, or alkali remaining in the system. The water circulation rate to the scrubber is adjusted such that the exiting syngas is quenched to the appropriate temperature for feed to the first stage of the compressor.[103]

2.4.3 Hydrocarbon removal – HBC PSA

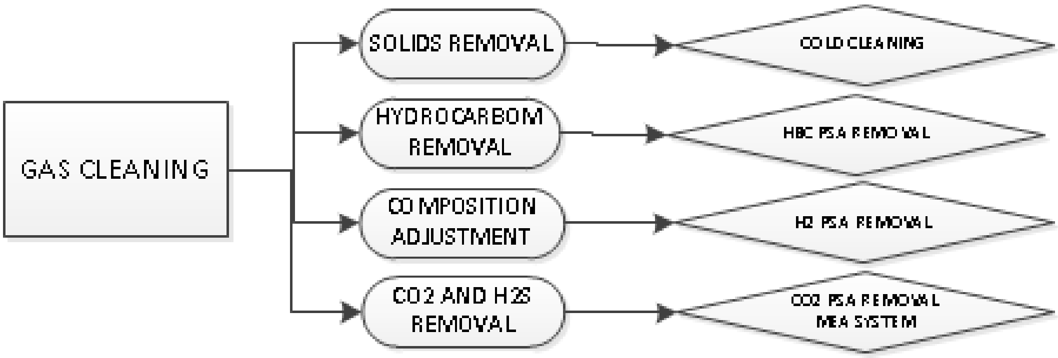


Figure 35: Gas Cleaning.

The trace of hydrocarbons that has not been eliminated in the reformer are withdrawn from the gas stream using a PSA system. Typically, a bed of silica gel is the most appropriate for the removal of hydrocarbons (HBC).

2.4.4 Composition adjustment – H2 PSA

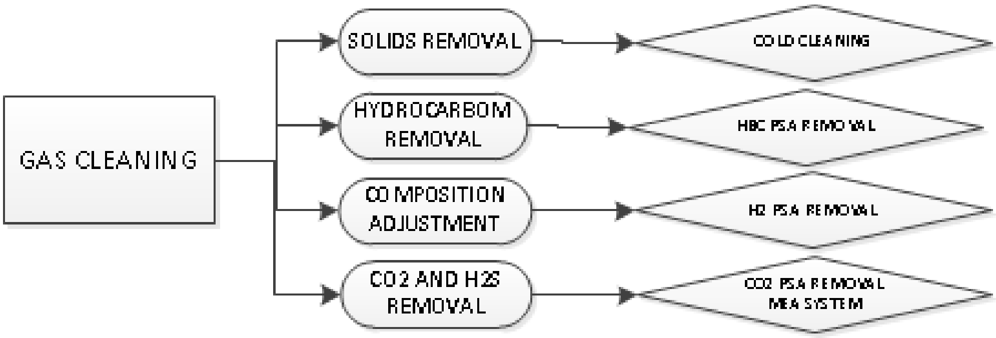


Figure 36: Gas Cleaning.

Once the main contaminants are eliminated, the composition of the gas must be adjusted so that the molar ratio between CO and H_2 is 1. In the case of syngas fermentation, a fixed molar ratio is not necessary for the process. However, given the economics of the co-products, it is desirable to separate the excess of hydrogen. A technology that consists of a hybrid membrane/PSA system (with a bed of Zeolite 13X) is here adopted to remove hydrogen. This surplus of hydrogen can be sold to increase the profitability of the process [94,95].

2.4.5 CO2 and H2S removal

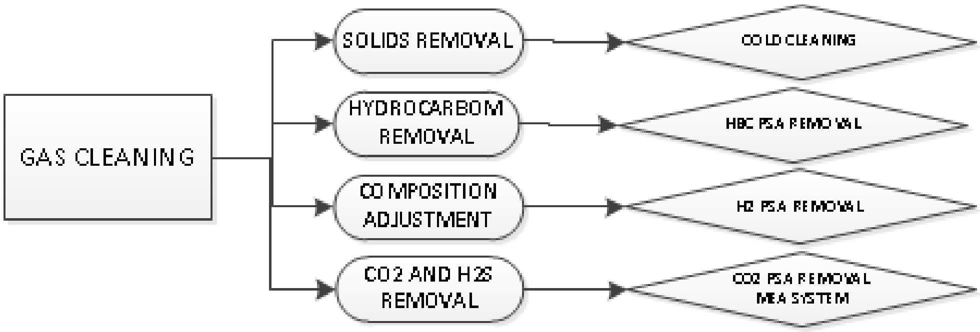


Figure 37: Gas Cleaning.

The removal of CO_2 and H_2S is the last cleaning stage for the preparation of syngas. The first stage is the use of a PSA system using a bed of Zeolite 5A capable of removing CO_2 from the stream.[98] However, the H_2S does not adsorb as it requires special coating,[99] but is useful because it separates most of the CO_2, greatly reducing the use of MEA and saving costs. The second stage is the absorption of CO_2 and H_2S in monoethanolamine (MEA).[97]

2.5 Fermentation

Bioethanol is predominantly produced through the fermentation of easily degradable carbohydrate substrates, such as corn starch and sugar cane. Alternatively, fermentable sugars can be obtained through the acid or enzymatic pretreatment of insoluble cellulosic biomass.[104,105] However, most biomass sources like straw and wood contain a large proportion of material that cannot be converted to ethanol by microorganisms. An alternative might be to gasify organic biomass and to use the produced synthesis gas (or syngas) as a feed stock for the synthesis of ethanol and other valuable compounds. Syngas, formed by the gasification or reforming of coal, natural gas or biomass, is a key intermediate in the production of synthetic fuels.[106] As syngas can be produced from both fossil fuels and renewable resources, it also enables a gradual transition to more sustainable energy and chemical production. Carbon monoxide and molecular hydrogen are the essential components of syngas and are used as building blocks in processes like Fischer-Tropsch synthesis to form linear alkanes.[106] Pure hydrogen is produced from syngas through the steam reforming.

The CO and H_2 present in syngas are substrates for microbial metabolism, which can be exploited for the synthesis of various interesting products. It is expected that syngas fermentation will play a role in the conversion of biomass, wastes and residues that form poor substrates for direct fermentation.[104,105,107,108] As gasification results in gas with a high temperature, thermophilic microbial processes might be most applicable for the biotechnological production of chemicals from syngas.[109]

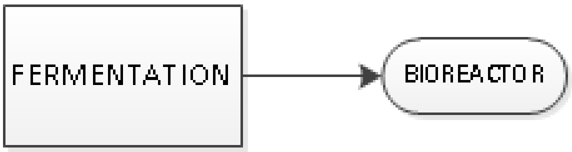
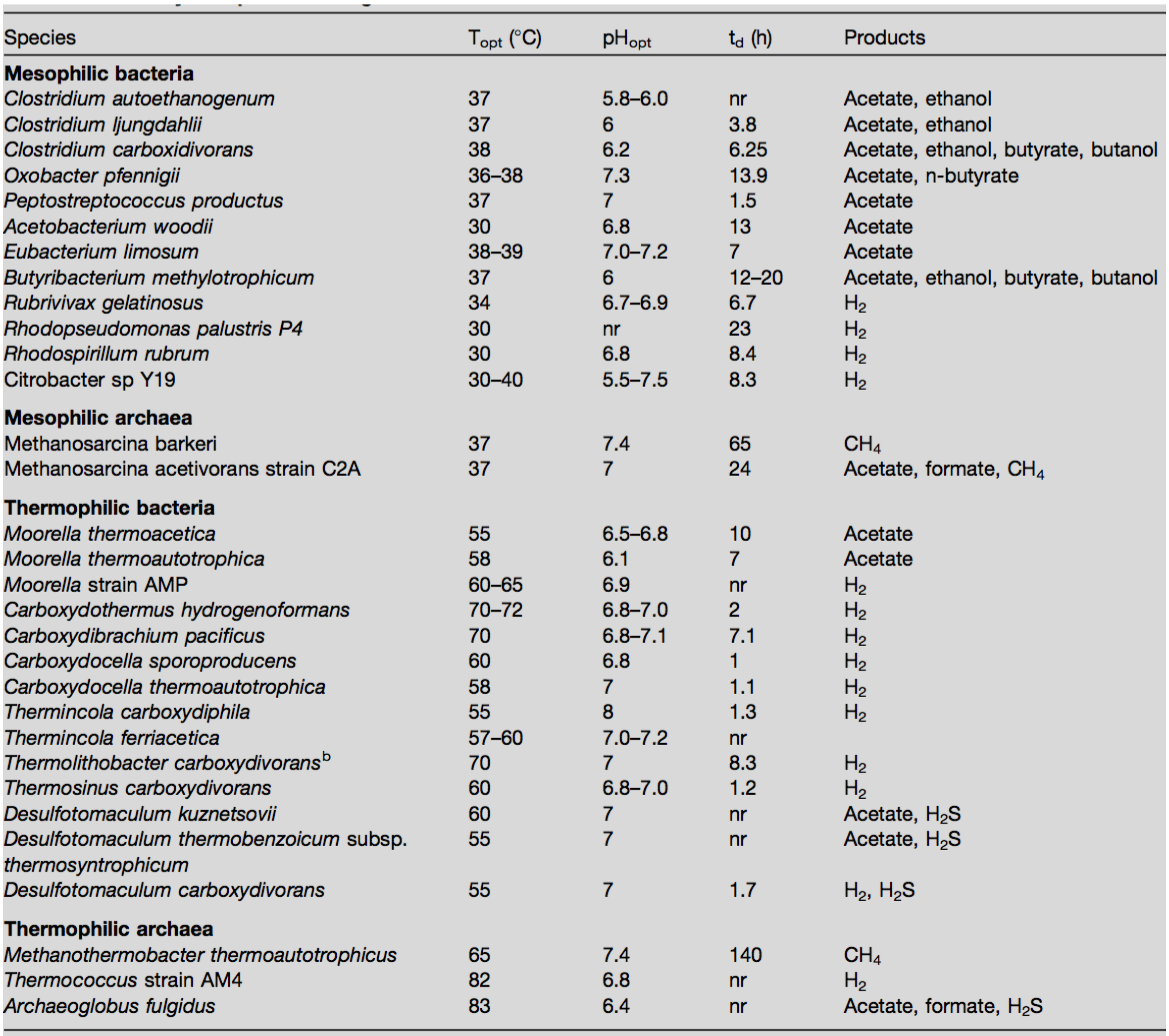


Figure 38: Fermentation.

2.5.1 Fundamental aspects of syngas fermentation

The production of fuels and chemicals through syngas fermentation offers several advantages over metal catalytic conversion processes. The higher specificity of the biocatalyst, lower energy costs, greater resistance to catalyst poisoning, and independence of a fixed H_2:CO ratio. In the past two decades, new isolates and some known anaerobic microorganisms were shown capable of growth with CO and H_2 as substrates (Figure 39). Although most strains showed the formation of acetate, formate and butyrate, ethanol and butanol were also reported as products.



Species	T_{opt} (°C)	pH_{opt}	t_d (h)	Products
Mesophilic bacteria				
Clostridium autoethanogenum	37	5.8–6.0	nr	Acetate, ethanol
Clostridium ljungdahlii	37	6	3.8	Acetate, ethanol
Clostridium carboxidivorans	38	6.2	6.25	Acetate, ethanol, butyrate, butanol
Oxobacter pfennigii	36–38	7.3	13.9	Acetate, n-butyrate
Peptostreptococcus productus	37	7	1.5	Acetate
Acetobacterium woodii	30	6.8	13	Acetate
Eubacterium limosum	38–39	7.0–7.2	7	Acetate
Butyribacterium methylotrophicum	37	6	12–20	Acetate, ethanol, butyrate, butanol
Rubrivivax gelatinosus	34	6.7–6.9	6.7	H_2
Rhodopseudomonas palustris P4	30	nr	23	H_2
Rhodospirillum rubrum	30	6.8	8.4	H_2
Citrobacter sp Y19	30–40	5.5–7.5	8.3	H_2
Mesophilic archaea				
Methanosarcina barkeri	37	7.4	65	CH_4
Methanosarcina acetivorans strain C2A	37	7	24	Acetate, formate, CH_4
Thermophilic bacteria				
Moorella thermoacetica	55	6.5–6.8	10	Acetate
Moorella thermoautotrophica	58	6.1	7	Acetate
Moorella strain AMP	60–65	6.9	nr	H_2
Carboxydothermus hydrogenoformans	70–72	6.8–7.0	2	H_2
Carboxydibrachium pacificus	70	6.8–7.1	7.1	H_2
Carboxydocella sporoproducens	60	6.8	1	H_2
Carboxydocella thermoautotrophica	58	7	1.1	H_2
Thermincola carboxydiphila	55	8	1.3	H_2
Thermincola ferriacetica	57–60	7.0–7.2	nr	
Thermolithobacter carboxydivorans[b]	70	7	8.3	H_2
Thermosinus carboxydivorans	60	6.8–7.0	1.2	H_2
Desulfotomaculum kuznetsovii	60	7	nr	Acetate, H_2S
Desulfotomaculum thermobenzoicum subsp. *thermosyntrophicum*	55	7	nr	Acetate, H_2S
Desulfotomaculum carboxydivorans	55	7	1.7	H_2, H_2S
Thermophilic archaea				
Methanothermobacter thermoautotrophicus	65	7.4	140	CH_4
Thermococcus strain AM4	82	6.8	nr	H_2
Archaeoglobus fulgidus	83	6.4	nr	Acetate, formate, H_2S

Figure 39: Anaerobic carboxydotrophic microorganisms.[109]

The fermentation of syngas to ethanol by Clostridium ljungdahlii was developed into a commercial process that combines biomass gasification, syngas fermentation and distillation of ethanol from the reactor effluent. Syngas is cooled before it can be introduced into the bioreactor.

Generally, gas/liquid mass transfer limits conversion rates in bioprocesses that use sparingly soluble gases.[112] High gas and liquid flow rates, large specific gas–liquid interfacial areas, and increased gas solubility (through the use of increased pressure or solvents), stimulate gas/liquid mass transfer rates. Continuous stirred tank reactors (CSTR) offer high gas/liquid mass transfer coefficients (K_{La}) at high impeller speeds, thus high power consumption.[111] High impeller speeds effectively break up large bubbles into smaller bubbles with more beneficial surface/volume ratios. Small bubbles additionally have lower rise velocities, thus longer liquid contact time. In micro-bubble dispersion, extremely small, surfactant-stabilised bubbles are created in a high shear zone, providing a more energy efficient method to increase K_{La} values.[111] In a study that addressed CO conversion in three types of reactors, it was found that a biotrickling filter gave higher efficiencies than CSTR and bubble column reactors. This was attributed to operational conditions that approach plug flow.[112] Furthermore, in biotrickling filters the K_{La} is relatively independent of the gas flow rate for sparingly soluble gasses.[111] Additionally, a low pressure drop is associated with trickle-bed reactors, ensuring relatively low power consumption. Novel bioreactor types designed to handle gases might be of interest for syngas fermentations. Monolith biofilm reactors resemble trickle-bed reactors in that the biomass is present as a biofilm attached to a carrier material and gas is led along the biofilm surface. In monoliths the pressure drop is lower than in randomly packed beds, owing to the large open frontal area.[113] In a membrane biofilm reactor (MBR) a biofilm is directly attached to a membrane through which gases used by the biomass diffuse.[114]

2.5.2 The acetyl-CoA pathway

Syngas-fermenting microorganisms use acetyl-CoA pathway to produce ethanol, acetic acid and other byproducts such as butanol and butyrate from syngas. The electrons required for the conversion is supplied by H_2 and CO, via the hydrogenase and carbon monoxide dehydrogenase enzymes, respectively. In addition, bifunctional carbon monoxide dehydrogenase enzyme produces CO_2 from CO which serves as a carbonyl group to produce acetyl-CoA.

Acetyl-CoA serves as a precursor for cell macromolecules as well as an adenosine triphosphate (ATP) source. The overall reductive acetyl-CoA pathway is an irreversible, non cyclic pathway which occurs under a strict anaerobic environment. There are two major steps involve in the production of acetyl-CoA. During the first step, CO or CO_2 is reduced to a methyl group through a series of reductive reactions in the presence of hydrofolate dependent enzymes and in the expense of ATP. Secondly, the methyl, carbonyl and the CoA groups are combined by the enzymes acetyl-CoA synthase (ACS) and carbon monoxide dehydrogenase complex (CODH) to produce acetyl-CoA. Acetyl-CoA is further reduced to acetate, ethanol and other byproducts during the later stages of the pathway. The overall biochemical reactions that take place in the reductive acetyl-CoA pathway are shown in Eqs. (1)–(4).

$$6CO + 3H_2O \rightarrow C_2H_5OH + 4CO_2 \qquad (1)$$

$$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O \qquad (2)$$

$$4CO + 2H_2O \rightarrow CH_3COOH + 2CO_2 \qquad (3)$$

$$2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O \qquad (4)$$

Figure 40: theoretical reactions.[15]

According to Eq. (1), one-third of the carbon from carbon monoxide is converted to ethanol and the combination of the two reactions in Eqs. (1) and (2) indicates that two-third of the carbon from CO can theoretically be converted to ethanol. Similarly, 50% of the carbon from CO can theoretically be converted into acetic acid (Eq. (3)). The overall yield of the fermentation is dependent on the composition of the syngas, where H_2 plays an important role. In this case, H_2 supplies H^+ ions and electrons required in the conversion of syngas into ethanol under the enzymatic activity of the hydrogenase enzyme. If the hydrogenase enzyme is inhibited, the microbes cannot utilize H_2 to produce electrons. Therefore, all the electrons necessary for the conversion should come from CO.[15]

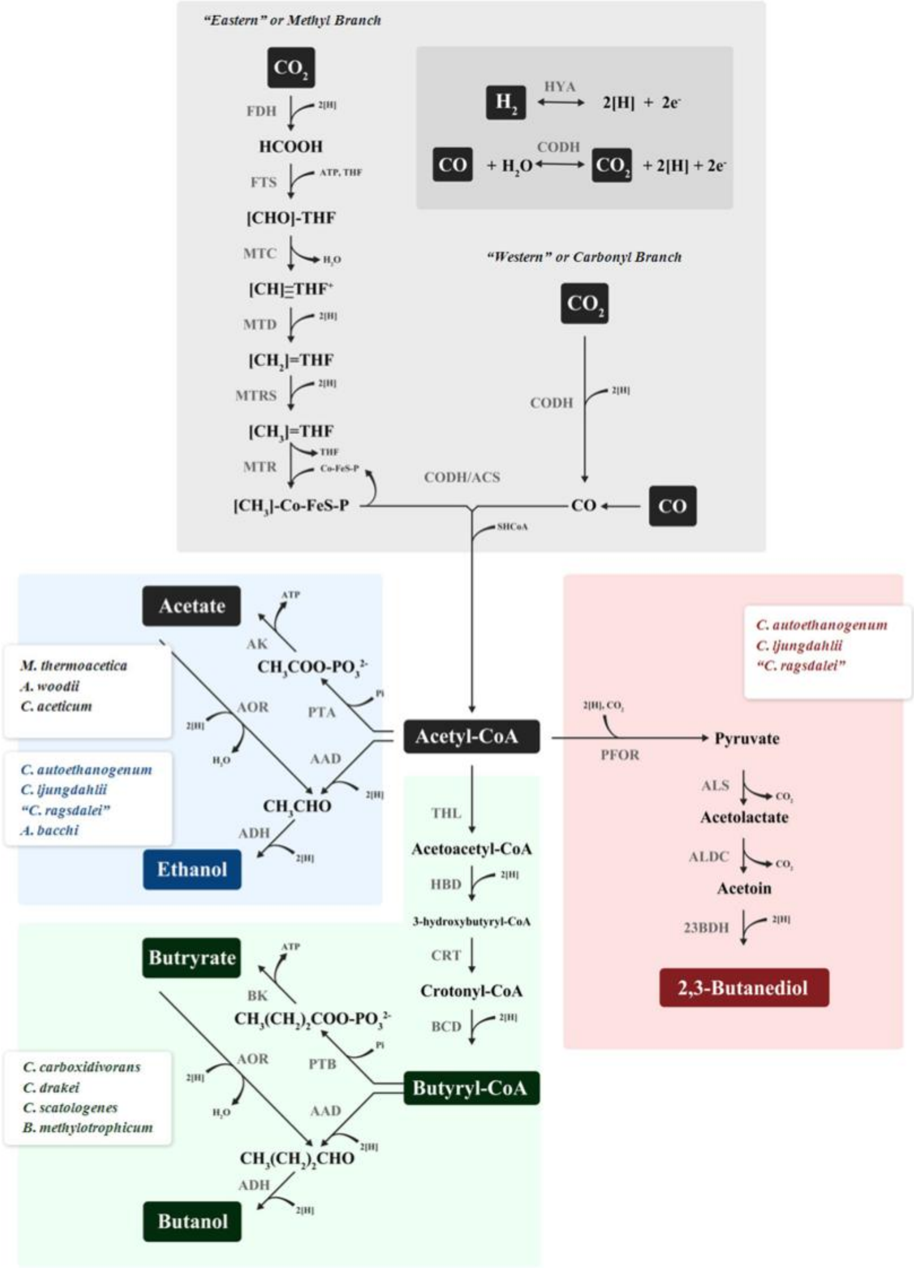


Figure 41: Schematic representation of the reductive acetyl-CoA pathway of bacteria and the pathway for the formation of organic acids and alcohols from acetyl-CoA.[109]

2.6 Purification

2.6.1 Distillation

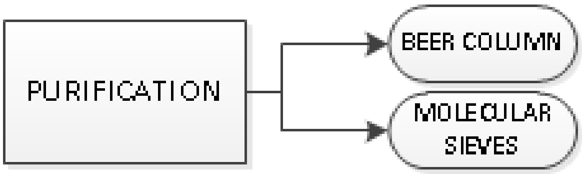


Figure 42: Purification.

In recent years, the distillation has been extended from its original field of chemical engineering to fields such as biotechnology, bioengineering, environmental engineering, biofuel and bioenergy engineering. This means that distillation technology will face new issues and challenges.

Distillation is a commonly used separation method in chemical and biochemical industries. There are different distillation processes for liquid mixture separation: ordinary distillation, azeotropic distillation, extractive distillation.

In a typical ethanol fermentation (first generation), broth containing dilute aqueous solution of about 5-12 wt% ethanol is produced. Separation of ethanol from this dilute solution accounts for a large fraction of the total production cost. Ethanol–water solution forms a minimum-boiling azeotrope at composition of 95.6 mol% ethanol at 78.15°C and at standard atmospheric pressure. Distillation is found to be an effective separation process to concentrate the dilute solution up to 85 wt%.[129] To go above this concentration, distillation becomes expensive requiring high reflux ratios and additional equipment.

Separation challenges in the ethanol production process can be divided into two categories: energy-demanding separations and technically difficult separations. The main energy-demanding process steps in lignocellulosic ethanol production are distillation to concentrate the ethanol, adsorption to remove the final content of water, and, optionally, evaporation either of the sugar solution before fermentation or of the stillage stream, as an option to anaerobic digestion, and drying of the solid residue (mainly lignin) if this is required. In these cases the main challenge is to reduce the energy demand. Figure 43 shows the energy demand levels in a process for production of ethanol from spruce based on a yearly capacity of 200

000 ton spruce as dry matter (DM). The overall energy demand is about 25.7 MJ l^{-1} of ethanol, of which 74% is for the separation processes. The net energy demand, after recovery of the secondary steam, is about 15.2 MJ l^{-1} ethanol.

Distillation: The distillation unit comprises several columns, for example one or more strippers to concentrate the fermentation broth from a typical 4–6 wt % to above 20 wt % and a rectifier to concentrate the ethanol to near azeotropic concentrations (93–94 wt %). There could also be other columns to purify the ethanol further, for example for removal of small amounts of aldehydes and methanol. The main columns are usually run in an energy-integrated way, with the various columns working at different pressures so that the overhead vapor from one column is used to provide heat in the reboiler of the next column when the vapor is condensed. Figure 44 shows the energy demand for a distillation unit comprising two stripper columns and a rectifier working in series as function of the

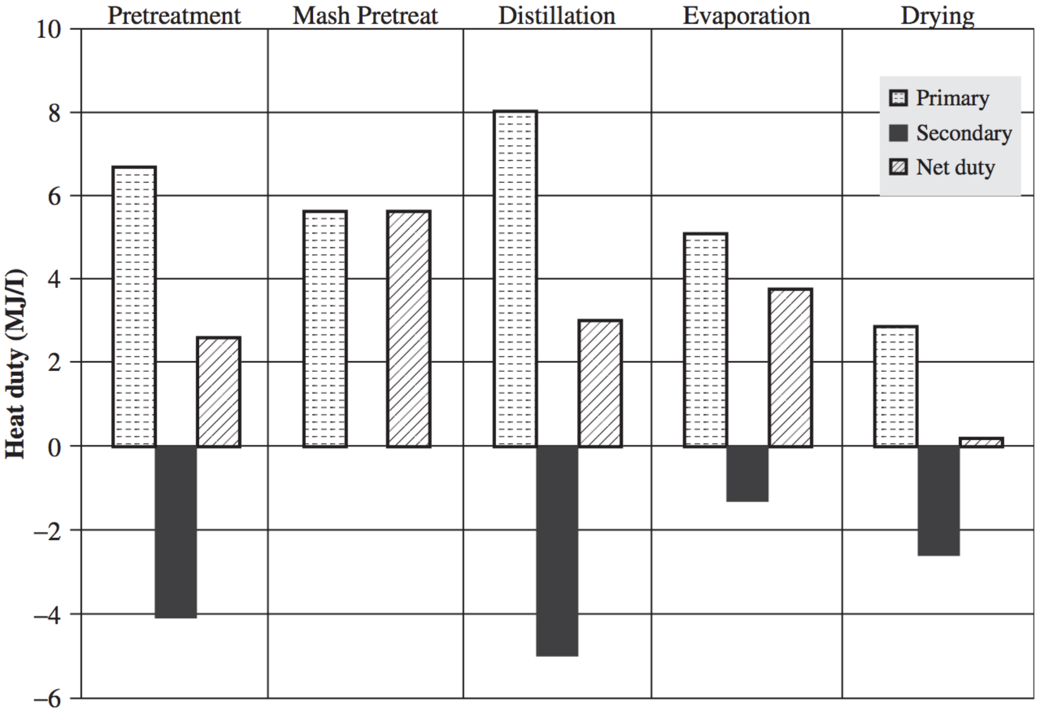


Figure 43: Heat duty of the energy-demanding process steps in the proposed ethanol production process. The dotted bars represent the primary steam demand while the black bars represent the amount of secondary steam that is generated. The striped bars are the difference between the primary steam demand and the generated secondary steam.[75]

ethanol concentration in the feed.[135] This shows the importance of reaching ethanol concentration in the fermentation at least above 4 wt %.

In process configurations where SSF is applied, the whole slurry after SSF is fed to the stripper units to avoid ethanol losses or dilution, which would occur in case the solid material is removed by filtration. This means that stripper columns must be capable of handling solid material, which requires special type of plates, for example, disc-and-donut trays, in order not to clog. This is an additional cost as the open structure of these trays usually has lower efficiency than normal trays, like valve trays. Further research on the development of more efficient equipment for stripping high solid containing streams may improve this.

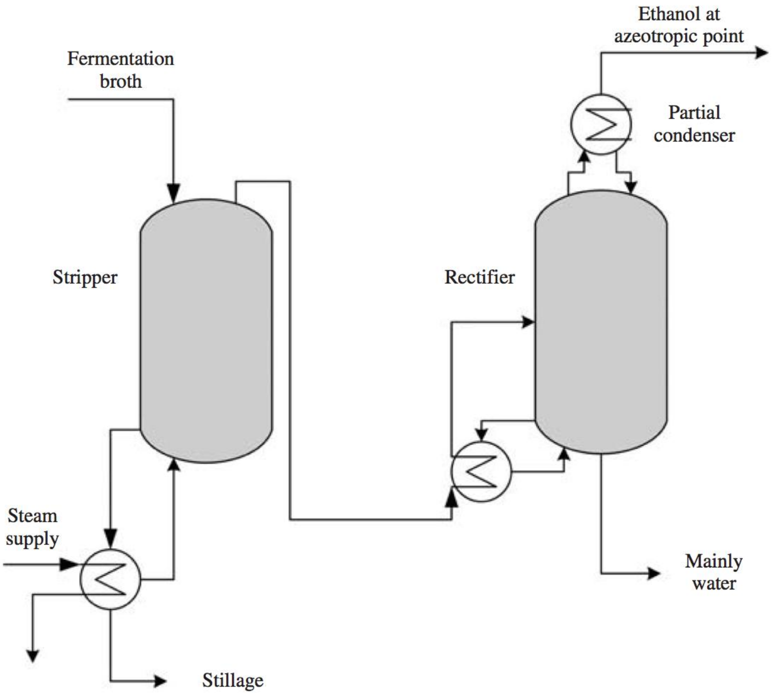


Figure 44: Distillation using one stripper and a rectifier.[75]

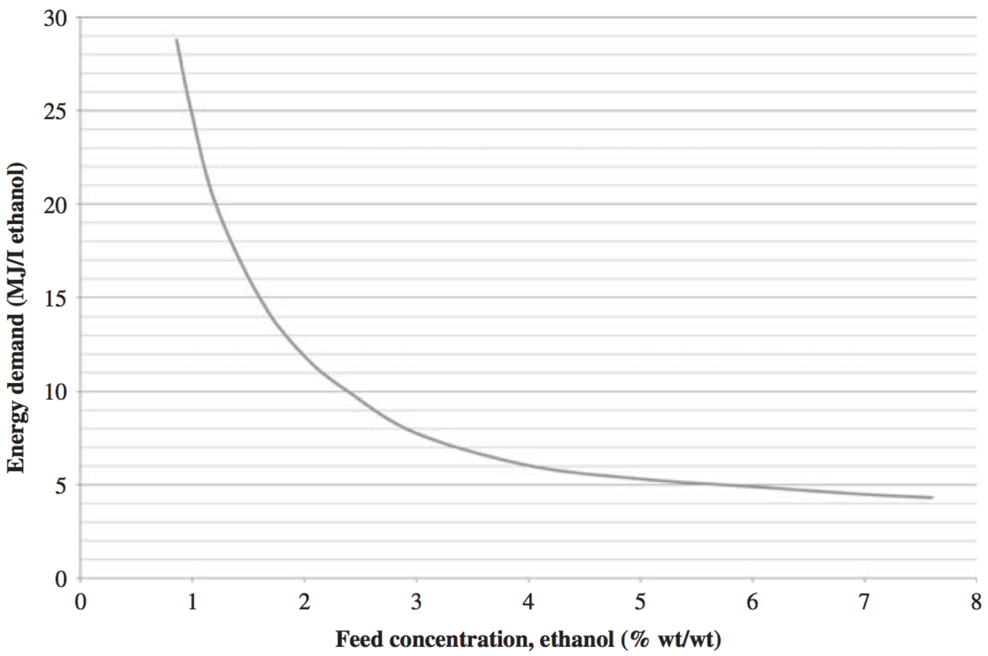


Figure 45: Energy demand in the distillation step, where ethanol is concentrated to 94 wt%, as a function of the ethanol feed concentration. The step was assumed to consist of two stripper columns (25 trays each) and a rectification column (35 trays) heat integrated by operating at different pressures. The inlet feed temperature was increased from 80◦C to the boiling temperature before entering each stripper column.[75]

2.6.1.1 Application in biorefineries

When conventional tray or packing columns cannot meet separation requirements in biorefineries, a process intensification approach to the existing distillation internals is needed. The special bioethanol distillation internals are not complicated in geometric structure and can be manufactured easily and cheaply. The investment in technology is therefore small and may be used for solving the following separation problems encountered in biorefineries:

- Separation of aqueous organic solutions with low concentration, such as in biomass-to-ethanol biorefineries, where the ethanol stream coming from the fermentor is at a low concentration of about 5–10 wt %. In this case the ratio of liquid to vapor flowrates along the distillation column will be high and thus the multi-overflow (double flow) slant-hole tray is suitable for the separation to obtain approximately 92.5 wt % ethanol.

2.6.2 Dehydration of ethanol

Dehydration of ethanol, from a ethanol–water mixture with approximately 92.4 wt % of ethanol, is imposible with an ordinary distillation column because ethanol forms an azeotropic mixtureat 95.6 % w/w with water (at temperature 78.15°C). Various techniques, such as adsorption, chemical dehydration, dehydration by vacuum distillation, azeotropic distillation, extractive distillation, membrane processes and diffusion distillation processes have been developed to break the azeotrope and produce anhydrous ethanol.[129,130] Among these techniques, adsorption is particularly attractive because of its low energy consumption.[131,132]

2.6.2.1 Molecular sieves

Molecular sieves are a very common technology that is used to selectively adsorb water from an ethanol-water mixture and obtain near 100 % pure ethanol, which is fuel quality. The inlet molecular sieves stream comes from the distillation columns in a near-azeotropic composition. Molecular sieves selectively adsorb water on the basis of difference in molecular size between water and ethanol. The Zeolite molecular sieve, which has anominal pore size of 3A, is most commonly used for dehydration of ethanol. Water molecules, with an approximate molecular diameter of 2.8 A, can easily penetrate the pores of the molecular sieve adsorbent, while ethanol, with an approximate molecular diameter of 4.4 A is retained.[134] Molecular sieves are found to adsorb water up to 22 % of their own weight. The molecular sieve operates in semi-continuous mode. The bed is saturated with water after a period of time and is then regenerated. They are generally regenerated using temperature swing with hot carrier gas. Bed temperatures in the 175–260 °C range are usually employed for type 3A zeolites whereas for 4A, 5A and 13X sieves require temperatures in the 200–315 °C range. An alternative to this energy-intensive regeneration is to use desorbing agents such as methanol or acetone.[130]

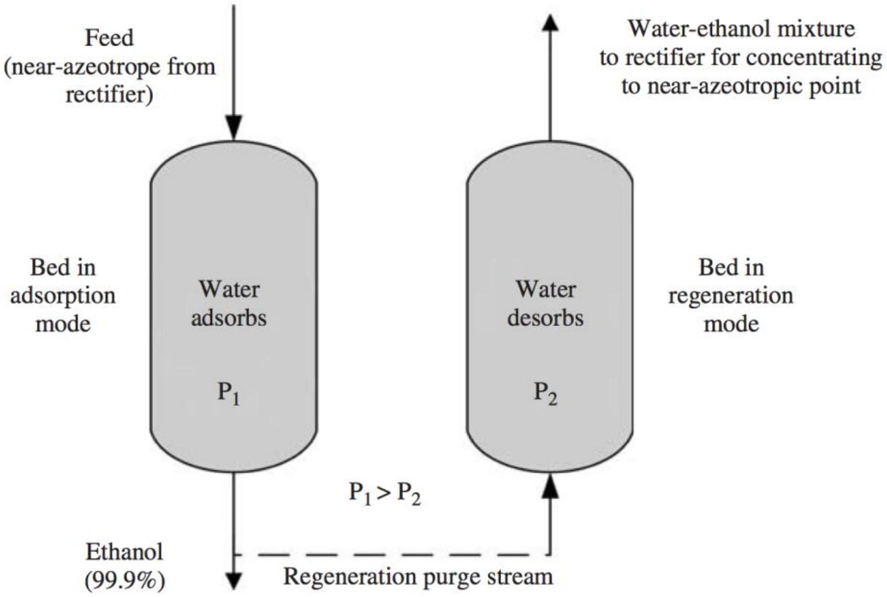


Figure 46: Molecular Sieves.[75]

3. MATHEMATICAL MODEL

In this work, we consider the conceptual design of the production of ethanol from the gasification of lignocellulosic raw material, with an ethanol production of 125 Ml/year. The goal is to analize and improve the energy consumption in the ethanol production process. Using as a basis short-cut models, empirical correlations and experimental data reported in literature, the model involves a set of constraints representing mass and energy balances and design equations for all the units of the system. The problem is implemented in GAMS software. The General Algebraic Modeling System (GAMS) is a high-level modeling system for mathematical programming and optimization. It consists of a language compiler and a stable of integrated high-performance solvers. GAMS is tailored for complex, large scale modeling applications, and allows you to build large maintainable models that can be adapted quickly to new situations.

In the following sections we describe the main ideas and considerations for each of the units as well as the main assumptions for their modeling. The model is written in terms of total mass flows, component mass flows and temperatures of the streams in the network.

All results related to the separations (columns, reboilers, condensers and absorbers), exchangers and compressors were compared and justified with the use of the process simulator Aspen HYSYS.

Finally, the process economic evaluation indicates the potential for achieving a producing cost of ethanol and analyzes the factors that determine the final cost when accounting for the sale of hydrogen as a co-product.[69]

3.1 Modeling aspects

All the units operations in the ethanol production process are modeled using as basis short-cut models, empirical correlations and experimental data reported in literature. The model involves a set of constraints representing mass and energy balances and these equations are implemented in the GAMS modelling system.
The modeling of a whole industrial process is significantly complex. It’s necessary a detailed analysis to identify a preliminary effective and efficient method for the equations and for variables characterization.

Our method is characterized by two key aspects:

- realize a series of standar process units, specifying type and interconnections, which automatically solve the mass balance (even with reactions) and energy (if required). This will not absolutely limit the ability to add and/or remove equations, allowing the realization of the most suitable model for each equipment. The greatest advantage is the possibility to create new process units already operating (before saturating the degrees of freedom), avoiding unnecessary repetitions and errors.
- set and define the process streams as connections between the different process units. These connections are identified as binary parameters (1 exist, 0 does not exist). In this way, the connections can be created without modifying or adding equations or variables. With these settings it is possible to define and divide all the variables related to the process unit, to the connections and to all the individual components of each of these.

3.2 Modeling characteristics

All connections between the process units, which represent the stream process, are characterized by the following variables:

- Total Mass Flow (f(e,u))
- Specific Mass Flow (fc(c,e,u))
- Molecular Weight (PM_mix(e,u))
- Total Molar Flow (f_mol(e,u))
- Specific Molar Flow (fc_mol(c,e,u))
- Temperature (T(e,u))
- Pressure (P(e,u))
- Mass Heat Capacity of ideal gas (Cp_mix_mass(e,u))
- Molar Heat Capacity of ideal gas (Cp_mol(c,e,u))
- Mix Heat Capacity of ideal gas (Cp_mass(c,e,u))

We have intentionally chosen to use the massive flow as a variable. It describes the composition of the streams and it greatly simplifies the degree of non-linearity of the system. On the contrary, if we had used the massive fractions, we would have significantly increased the degree of non-linearity, complicating the resolution of the problem NLP (Non-Linear Programming). For example, the resolution of mass balances in steady state conditions, using the specific flow, allows to remain in the field of solving linear problems.

Units used as products and by-products battery limits (inlet and oulet) are named:

- Snk (battery limit outgoing)
- Src (battery limit incoming)

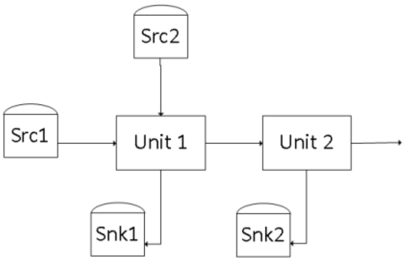


Figure 47: Battery Limits

3.2.1 Sets

It is possible to realize the proposed method, for the process variables, thanks to the section SETS of GAMS. This section allows to create indices that facilitate the writing and understanding of equations and variables.

The main SETS are:

- ‘c’: *<u>components index</u>*: is a vector which contains all the components. (H_2O, C, H, O, S, N, ash, H_2, CO, CO_2, CH_4, NH_3, H_2S, C_2H_2, C_2H_4, C_2H_6, C_6H_6, Tars, O_2, N_2, SO_2, MEA, EtOH);
- ‘e’: *<u>process units index</u>*: for example (Bioreactor, src10, compressor6, snk_ric_CO_2, MecSep2, HX20, beercolumn, etc. ..);
- ‘h’: *<u>process units index:</u>* only for units where material balance is performed. It is a subset of the index ‘e’;
- ‘r’: *<u>chemical reactions index</u>*: (C_comb, S_comb, ref_CH_4, etc. ..).

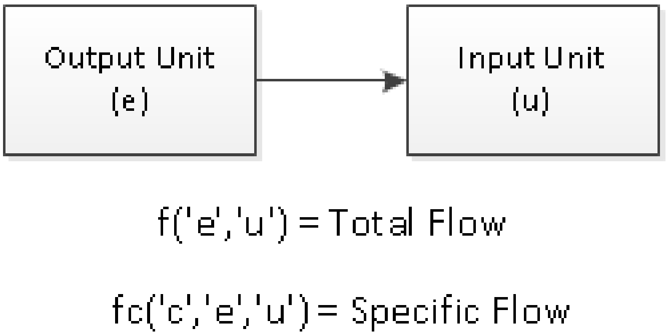


Figure 48: GAMS legend.

3.2.2 Material Balances

Each unit process is characterized by a generalized material balance:

- The sum of the specific material flows is equal to the total flow:
  f (e, u) = sum (c, fc (c, e, u)).

- Conservation of the material between the incoming and outgoing streams in the process unit, even with of chemical reaction:
  sum (fc (c, e, h)) + sum (r $ (stech (c, r) = sum (fc (c, h, e)).

- What is the level of advancement for all possible reactions:
  react (h, r) = conv (h, r, c) / stech (c, r) * sum (fc (c, e, h)).

3.2.3 Energy Balances

The thermodynamic parameters used in the model were taken from TERMOINT SOFTWARE PACKAGE: PHYSICAL PROPERTIES OF PURE COMPOUNDS AND MIXTURES. TERMOINT is a software package under development at the Group of Process Thermodynamics of PLAPIQUI. TERMOINT is a friendly interface that makes it possible to access a large database of physical properties. This database provides constant and temperature-dependent physical properties for hundreds of pure compounds. For instance, available properties are: liquid and vapor densities, vapor pressures, critical constants and vaporization enthalpies.

TERMOINT was used to calculate:

- P_{sat} (Saturation pressur with Antoine law)
- C_p (Mass heat capacity for ideal gas and liquid)
- H_{mol} (Entalphy of formation)
- Q_{vap} (Heat of vaporization)
- T_b (Normal boiling temperature)

The energy balance is obviously used only for those units that require it. It is not always the same because energy balance depends on the stream phase. The model, indeed, used the energy balances both for vapor streams, assuming ideal gas, and for two-phase currents.

3.2.3.1 Heat Exchangers

Heat exchangers are units that solve the overall material balance and energy balance (with differences whether they treat gas streams or biphasic streams). For gas streams it is assumed ideal gas behavior. It is used a value for heat capacity (Cp) which is the same as for perfect gas. For those heat exchangers that treat biphasic mixtures or in which phase changes are present, a specific model for each heat exchanger is provided. In this way it is possible to take into account the thermal capacity of each component of the liquid phase (and gas if present) and also their vaporization and condensation heats (all thermodynamic data taken from TERMOINT). Duty must be supplied (positive) or subtracted (negative) to ensure the specifications required by the process, usually to reach a desired temperature, and it is calculated with the resolution of an energy balance.

$$Q_{heat\ exchanger} = Q_{sens} + Q_{cond}$$

$$Q_{cond} = \Delta H_{ev}(\bar{T}) * fc(c,e,u)$$

$$Q_{sens} = \sum_{c=0}^{nc} \left(fc(c,e,u) \int_{T_{in}}^{T_{out}} Cp(c,e,h_{hx},u)\, dT \right)$$

where the Cp (of ideal gas) is in a polynomial form:

$$Cp_{gas,id}(T) = A + B\left(\frac{\frac{C}{T}}{sinh\left(\frac{C}{T}\right)}\right)^2 + D\left(\frac{\frac{E}{T}}{sinh\left(\frac{E}{T}\right)}\right)^2$$

and the Cp (of liquid phase) is in a polynomial form:

$$Cp_{liq}(T) = A + BT^2 + CT^3 + DT^4$$

and the Cp (of olivine)[157] is in a polynomial form:

$$Cp_{olivine}(T) = A + BT + CT^{-2} + DT^{-0,5} + ET^2$$

3.2.3.2 Compressors

Compressors are units that solve the overall material balance and energy balance. Power (W_{comp}) and temperature after each compressors are calculated assuming polytropic behavior; it has to be taken into account that, for intercooled compressors only, the pressure ratio is the same at each compression stage. Polytropic efficency (η_{pol}) and exponent (α) are taken from Aspen HYSYS.

$$\mathrm{Coeff}_{\mathrm{Wpol}} = \beta^{\left(\frac{(\alpha-1)}{\alpha}\right)}$$

$$\mathrm{W}_{\mathrm{pol}} = \frac{\mathrm{T} * \mathrm{R} * \ \mathrm{Coeff}_{\mathrm{Wpol}}}{\mathrm{MW}_{\mathrm{mix}} * \left(\frac{(\alpha-1)}{\alpha}\right)}$$

$$\mathrm{W}_{\mathrm{comp}} = \frac{\mathrm{fc(c,e,u)} * \ \mathrm{W}_{\mathrm{pol}}}{\eta_{\mathrm{pol}}}$$

$$\mathrm{W}_{\mathrm{comp}} = \sum_{i=1}^{nc} \mathrm{fc(c,e,u)} * \int_{Tin}^{Tout} Cp\, dT$$

Pumps, necessary for the system, are not included in the flowsheet and are not considered their values and energy costs.

3.3 *__Pretreatment__*

The elementary composition of the biomass is:

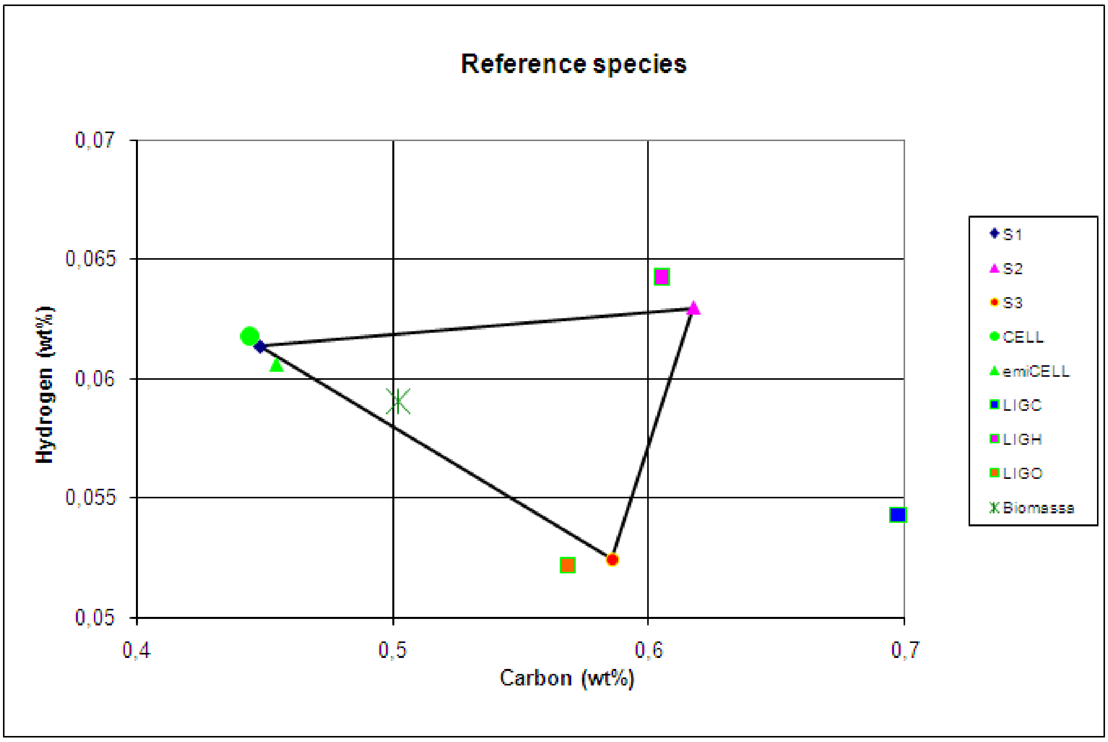
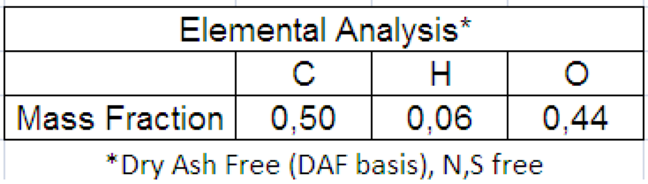


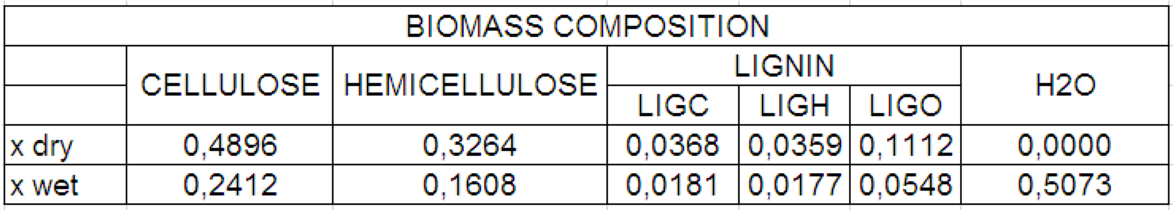
Figure 49: Biomass Type.



Elemental Analysis*			
	C	H	O
Mass Fraction	0,50	0,06	0,44

*Dry Ash Free (DAF basis), N,S free

Figure 50: Elemental Analysis.



BIOMASS COMPOSITION						
	CELLULOSE	HEMICELLULOSE	LIGNIN			H2O
			LIGC	LIGH	LIGO	
x dry	0,4896	0,3264	0,0368	0,0359	0,1112	0,0000
x wet	0,2412	0,1608	0,0181	0,0177	0,0548	0,5073

Figure 51: Biomass Biochemical Analysis.

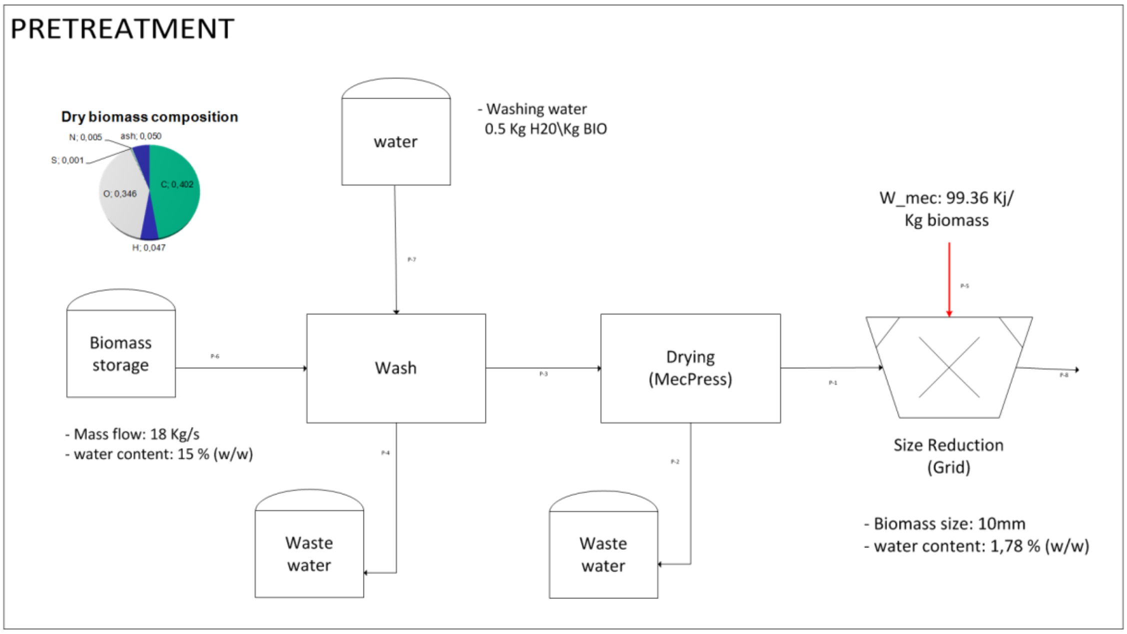


Figure 52: Pretreatment Block Flow Diagram.

Three unit operations are considered:

- *WASHING:*

  It is assumed that 0.5 kg of washing water is needed to wash 1 kg of switchgrass.

- *DRYING:*

  The grass is partially dried by means of a mechanical press that removes 90% of the water accompanying the grass.

- *SIZE REDUCTION*

  The particle size required is around 10 mm. The energy required is 99.36 kj/kg biomass.

All these units work at atmospheric pressure and temperature.

The equations used are:

$$f('Water','Wash') = f('BiomassStorage','Wash') * WWr$$

$$f('Water','Snk1') = f('Water','Wash') * (1 - WWr)$$

$$f('MecPres','Snk2') = f('H2O','Wash','MecPres') * \eta_{MecPres}$$

$$W_{Grind} = E_{Grind} * \ f('MecPre','Grind')$$

$$fc('H2O','Grind','Gasifier') = f(\ 'Grind','Gasifier') * U_r$$

Datas:

- WWr = washing water ratio [kg H_20\kg BIO] /0.5/ minwash = minimum amount of washing water required per kg of grass
- $\eta_{MecPres}$ = mechanical press efficency [-] /0.9/
- WWs = washing water in output flow [-] /0.01/
- E_{Grind} = energy consumption to grinding switchgrass = 27.6 [kWh\t biomass]

3.4 <u>Gassification</u>

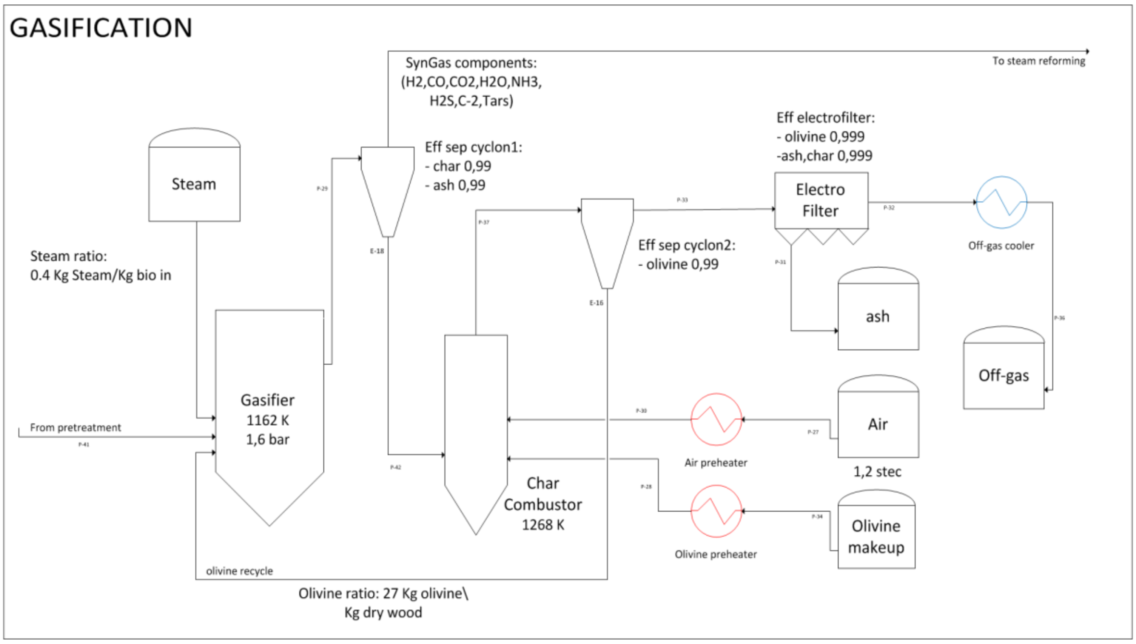


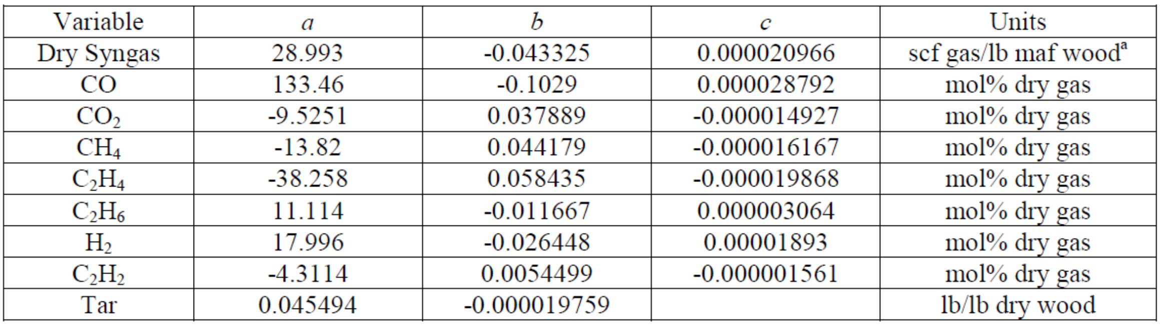
Figure 53: Gasification Block Flow Diagram.

3.4.1 Gasifier

The gasifier was modeled using correlations based on data from BCL[143,144] 9 tonne/day test facility. The temperature range for the data is 966 K to 1287 K and the pressure range is 0,16 to 1 bar; the majority of the data are in the range of 1089 K to 1184 K. The BCL test facility’s gas production data was correlated to gasifier temperature with a quadratic function in the form:

$$X = a + bT + cT^2$$

where the temperature, T, in units of °F.



Variable	a	b	c	Units
Dry Syngas	28.993	-0.043325	0.000020966	scf gas/lb maf wood[a]
CO	133.46	-0.1029	0.000028792	mol% dry gas
CO_2	-9.5251	0.037889	-0.000014927	mol% dry gas
CH_4	-13.82	0.044179	-0.000016167	mol% dry gas
C_2H_4	-38.258	0.058435	-0.000019868	mol% dry gas
C_2H_6	11.114	-0.011667	0.000003064	mol% dry gas
H_2	17.996	-0.026448	0.00001893	mol% dry gas
C_2H_2	-4.3114	0.0054499	-0.000001561	mol% dry gas
Tar	0.045494	-0.000019759		lb/lb dry wood

Figure 54: Gasifier correlations.[65]

The following main assumptions are used for the gasification production:

- The syngas amount and composition will be dependent from the biomass composition and the gasifier temperature.
- Gasifier temperature T is assumed to be 1162 K.
- The mass and molar amounts of carbon, hydrogen, oxygen, sulfur, nitrogen, and ash (as a pseudo-element($C_{10}H_8$)) are determined from the biomass ultimate analysis.
- The amount of carbon in the syngas and tar is determined. Residual carbon remains in the char.
- The amount of oxygen in the syngas is determined (4% of biomass oxygen). If there is a deficit of oxygen, then the associated water is decomposed to make sure that this amount of oxygen is parsed to the char;

if there is oxygen in excess, then it is parsed to the char without decomposing hydrogen.

- H_2S and NH_3 are generated proportionally to the amount of S and N in the biomass. A small percentage of both elements (8.3% and 6.6%, respectively) remain in the char.
- The amount of hydrogen in the syngas (including tar, H_2S, NH_3, and decomposed water) is determined. All remaining hydrogen is parsed to the char.
- All ash is parsed to the char.
- There is no benzene in our model
- Steam and olivine ratios are taken from the literature.[65]

$$Steam\ Ratio = \frac{\text{Kg/s Steam feed}}{\text{Kg/s Dry Biomass feed}}$$

$$Olivine\ Ratio = \frac{\text{Kg/s of Olivine}}{\text{Kg/s Dry Biomass feed}}$$

As an example, the resulting syngas composition for the woody biomass used in this design report can be seen in figure 48. Note from this figure that the amount of char decreases with increasing temperature and that water does not start to decompose until high temperatures (here at 900 K and higher).

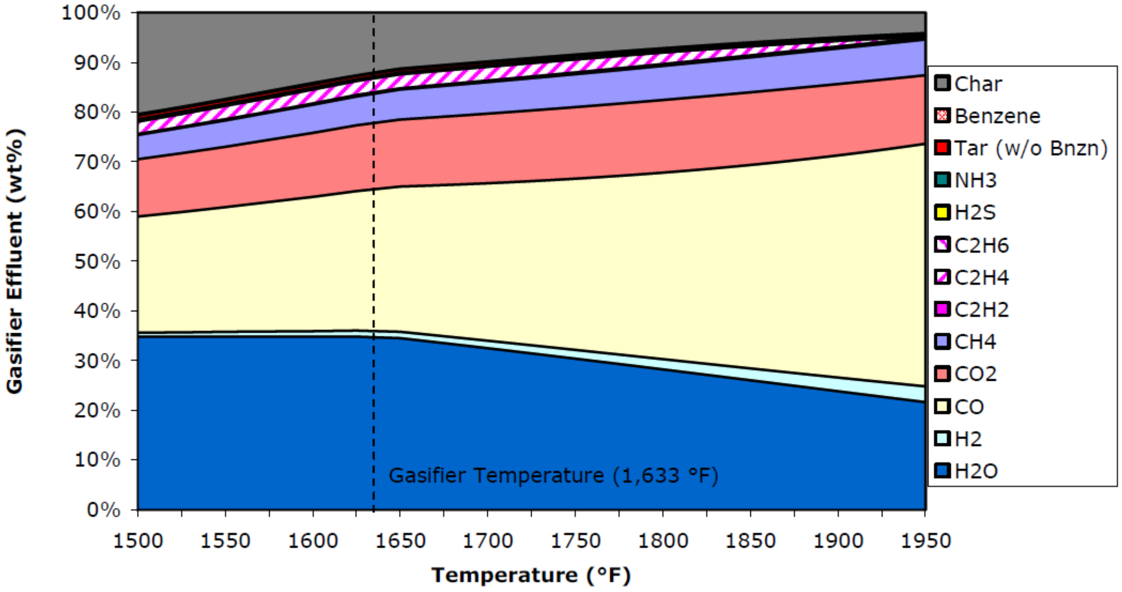


Figure 55: Syngas compositions.[65]

In this unit, the material balance is not solved automatically, but it is replaced by an atomic balance that follows the conservation law for atomic elementary components that exist in the biomass.

Syngas composition, obtained from experimental empirical correlations, have been normalized in order to respect material balances.

The mass balance of the gasifier si given by these equations:

$$n_{C,biomass} = n_{C,CO} + n_{C,CO2} + n_{C,CH4} + n_{C,C2H2} + n_{C,C2H4} + n_{C,C2H6} + n_{C,TARS} + n_{C,CHAR}$$

$$n_{O,biomass} = n_{O,CO} + n_{O,CO2} + n_{O,CHAR} + n_{O,water\ decomp}$$

$$n_{H,biomass} = n_{H,H2} + n_{H,CH4} + n_{H,NH3} + n_{H,H2S} + n_{H,C2H2} + n_{H,C2H4} + n_{H,C2H6} + n_{H,TARS} + n_{H,water\ decomp}$$

$$n_{H2O,in} = n_{H2O,out} - n_{H2O,water\ decomp}$$

$$n_{S,biomass} = n_{S,H2S} + n_{S,CHAR}$$

$$n_{N,biomass} = n_{N,NH3} + n_{N,CHAR}$$

$$n_{CHAR} = n_{ASH,CHAR} + n_{C,CHAR} + n_{O,CHAR} + n_{N,CHAR} + n_{S,CHAR}$$

3.4.2 Cyclons

The model for the cyclone 1(cyc1) is given by equations:

$$\mathrm{fc(j, cyc1, reformer)} = \left(1 - \mathrm{eff_{cyc1}}\right) * \mathrm{fc(j, gasifier, cyc1)}; \qquad j = char, olivine, ash$$

$$\mathrm{fc(c \neq j, cyc1, reformer)} = \mathrm{fc(c \neq j, gasifier, cyc1)};$$

Separation efficiency of cyclon 1 is 0,99 for j components

The model for the cyclone 2(cyc2) is given by equations:

$$\mathrm{fc(j, cyc2, electrofilter)} = \left(1 - \mathrm{eff_{cyc2}}\right) * \mathrm{fc(j, combustor, cyc2)}$$
$$\mathrm{j = char, olivine, ash}$$

$$\mathrm{fc(c \neq j, cyc2, electrofilter)} = \mathrm{fc(c \neq j, combustor, cyc2)};$$

Separation efficiency of cyclon 2 is 0,99 for j components

3.4.3 Electrostatic precipitator

$$\mathrm{fc(j, electrofilter, HX3)} = \left(1 - \mathrm{eff_{cyc1}}\right) * \mathrm{fc(j, cyc2, electrofilter)};$$
$$j = char, olivine, ash$$

$$\mathrm{fc(c \neq j, electrofilter, HX3)} = \mathrm{fc(c \neq j, cyc2, electrofilter)};$$

Separation efficiency of elecrostatic precipitator (elecrofilter) is 0,999 for j components

3.4.4 Combustor

Char and olivine are fed from cyclone 1 to the combustor. Air is also fed to burn the char and is heated up to 200ºC in heat exchanger 11 (HX11) before it is fed to the combustor. The amount of air injected is 20% in excess compared to the stoichiometric quantity to secure the combustion of the char. The air humidity is calculated to be 70% using the necessary equations (look at cold cleaning). Olivine is heated up again in the combustor while the make-up of olivine is heated up in HX2. The ash is liberated and the S and C oxidized. Nitrogen is also generated from the nitrogen in the char.

Mass balances with reaction are solved automatically, introducing the conversions of char (look at paragraph 3.3.2).

The reactions are:

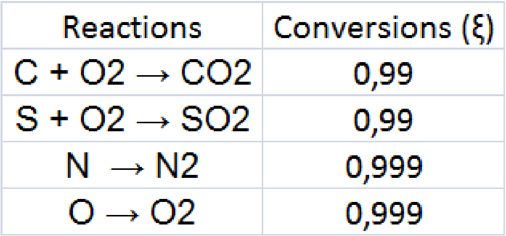
$$C + O_2 \rightarrow CO_2$$

$$S + O_2 \rightarrow SO_2$$

$$N_{char} \rightarrow N_2$$

$$O_{char} \rightarrow O_2$$

The convercions are:



Reactions	Conversions (ξ)
C + O2 → CO2	0,99
S + O2 → SO2	0,99
N → N2	0,999
O → O2	0,999

Figure 56: Conversions.

3.4.5 Hydrocarbon removal

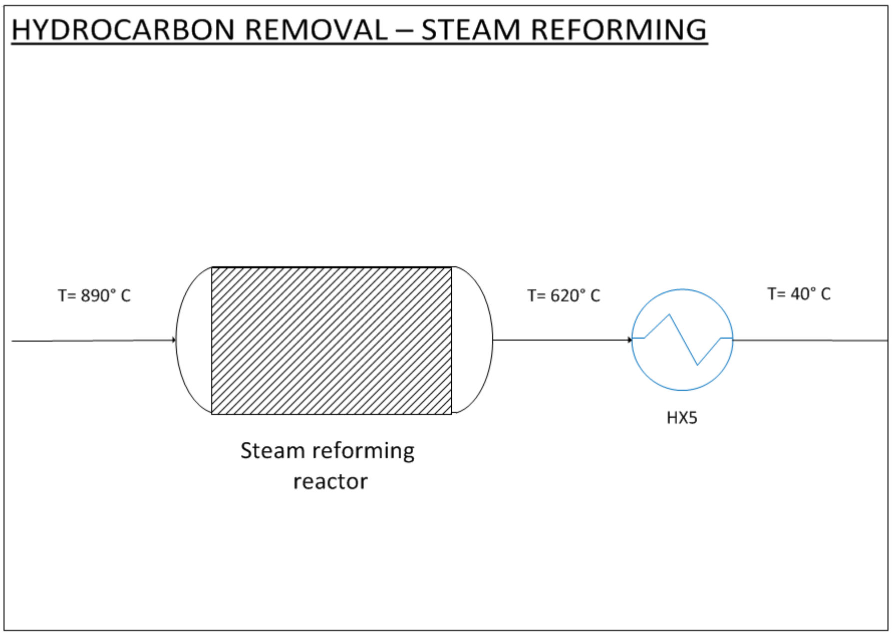


Figure 57: Hydrocarbon Removal – Steam reforming.

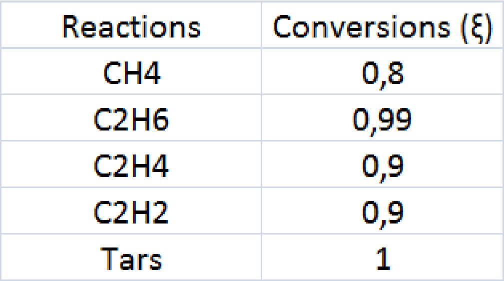
The stream coming from the gasifiers is fed to the reformer at the same temperature. For steam reforming the chemical reactions taking place are of the form:

$$C_nH_m + nH2O_n \rightarrow nCO + \left(\frac{m}{2} + n\right)H2$$

$$NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$$

Mass balances with reactions are solved automatically introducing conversions of char (view at paragraf 3.3.2).

Hydrocarbons conversions[65] are:



Reactions	Conversions (ξ)
CH4	0,8
C2H6	0,99
C2H4	0,9
C2H2	0,9
Tars	1

Figure 58: Reactions.

Reactions are endothermic. We consider that the reactor operates adiabatically and then the final temperature is reduced to account for the energy absorbed by the reactions. This approximation is needed because of the complexity of providing energy directly to the catalytic bed. [65]

The energy balance used to calcolate the outlet temperature is:

$$\sum_{c=1}^{nc}\left(fc_{c,in}\int_{T_{in}}^{T_{out}} Cp_c(T)\,dT\right) = -\sum_{r=1}^{nr}\lambda_r * \Delta H^0_{R,r}(T)$$

$$\Delta H^0_{R,r}(T) = \sum_{c=1}^{nc}\nu_{cr} * \Delta h^0_{f,c}(T)$$

$$\Delta h^0_{f,c}(T) = \Delta h^0_{f,c}(T_{rif}) + \int_{T_{rif}}^{T} Cp_c(T)\,dT$$

3.5 Gas Cleaning

3.5.1 Solids removal – Cold cleaning

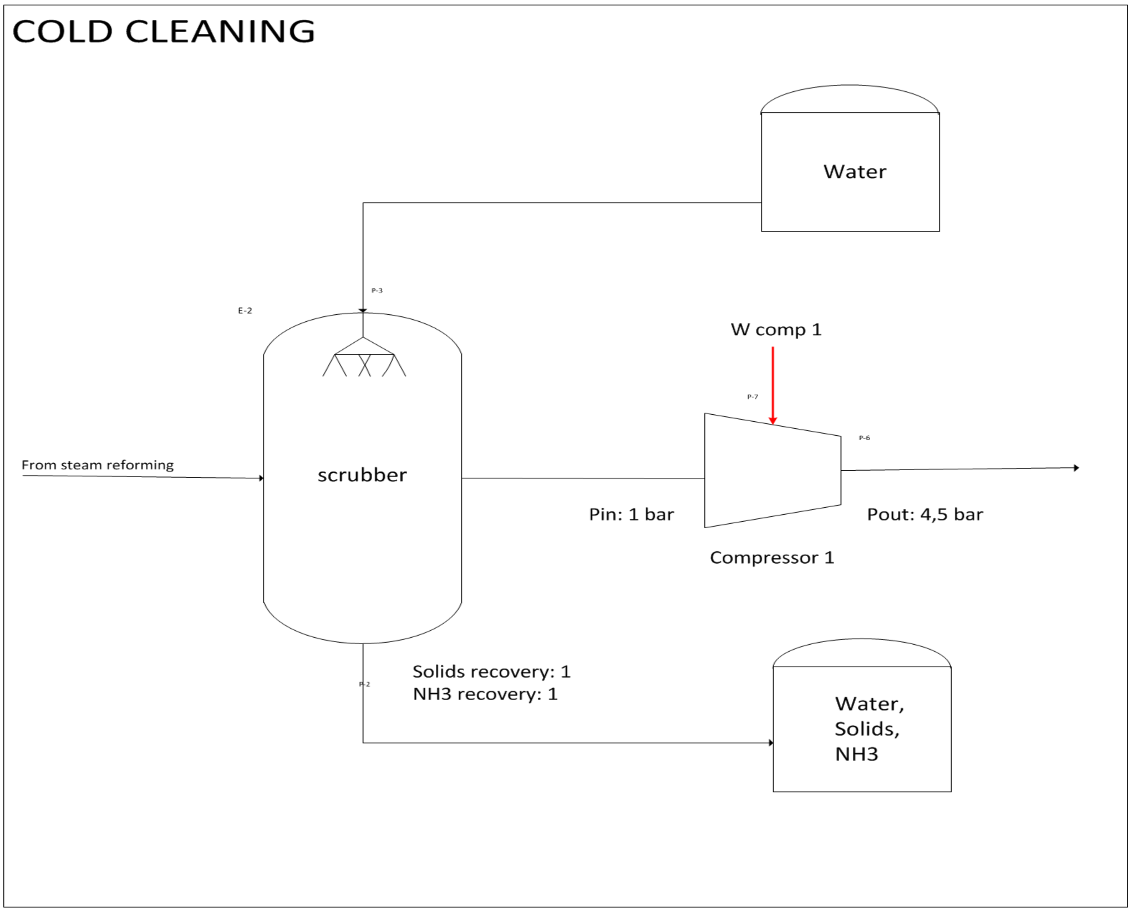


Figure 59: Cold Cleaning Block Flow Diagram.

The stream, coming from the indirect gasifier, is cleaned at low pressure. Then, the gas is cooled down in heat exchanger, and as a result, water condenses. The amount of condensed water is calculated based on the saturation moisture. Then, the stream is fed to the scrubber.

The goal is to remove the solids (Ash, Char, Olivine). The unit parameters are:

- The gas is cooled down to 40°C, and water condenses.
- The condensed water is calculated based on the saturation moisture at 40°C and 1.2 bar.
- The amount of water needed for the scrubber is calculated using L/G = 0.25 kg/m^3 of gas.

- Water is fed to the scrubber at room temperature 20°C.
- In the scrubber, solids (Ash, Char, Olivine) and NH_3 are eliminated, while the gas exits the scrubber with a humidity calculated based on saturated conditions.
- The temperatures of the streams exiting the scrubber are determined by an energy balance considering that the equipment operates adiabatically.

The equations used are:

$$\mathrm{P_{sat}} = \exp\left(\mathrm{A} + \frac{\mathrm{B}}{\mathrm{T}} + \mathrm{C}\log(\mathrm{T}) + \mathrm{D\,T^{E}}\right)$$

$$\mathrm{P_{vap}} = \mathrm{P_{sat}} * \mathrm{U_r}$$

$$\mathrm{U_s} = \frac{\mathrm{MW_{H2O}}}{\mathrm{MW_{gas}}} * \frac{\mathrm{P_{vap}}}{\mathrm{P} - \mathrm{P_{vap}}}$$

$$\mathrm{U} = \frac{\mathrm{MW_{H2O}}}{\mathrm{MW_{gas}}} * \frac{\mathrm{P_{sat}}}{\mathrm{P} - \mathrm{P_{sat}}}$$

$$fc^{L}('H2O','HX5','Scrubber') = fc('H2O','HX5','Scrubber') * \mathrm{U}_s \sum_{i=1}^{nc} \big(c, fc(c,'HX5','Scrubber')\big)$$

$$fc('H2O','Scrubber','\,Compressor1') = \sum_{i=1}^{nc} \mathrm{U} * fc(c,'HX5','Scrubber')$$

$$fc('H2O','Water','Scrubber') = \frac{L}{G} * \frac{1}{\rho_{gas}} * \sum_{i=1}^{nc} (1 + \mathrm{U}_s) * \big(c, fc(c,'HX5','Scrubber')\big)$$

$$fc('Solids','Scrubber','\,Snk8') = \eta_{sep} * fc('Solids','HX5','Scrubber')$$

The stream coming out of the scrubber is saturated with water and is compressed to the working conditions of the following PSA system, 4.5 bar,[93] in a compressor.

3.5.2 Hydrocarbon removal – HBC PSA

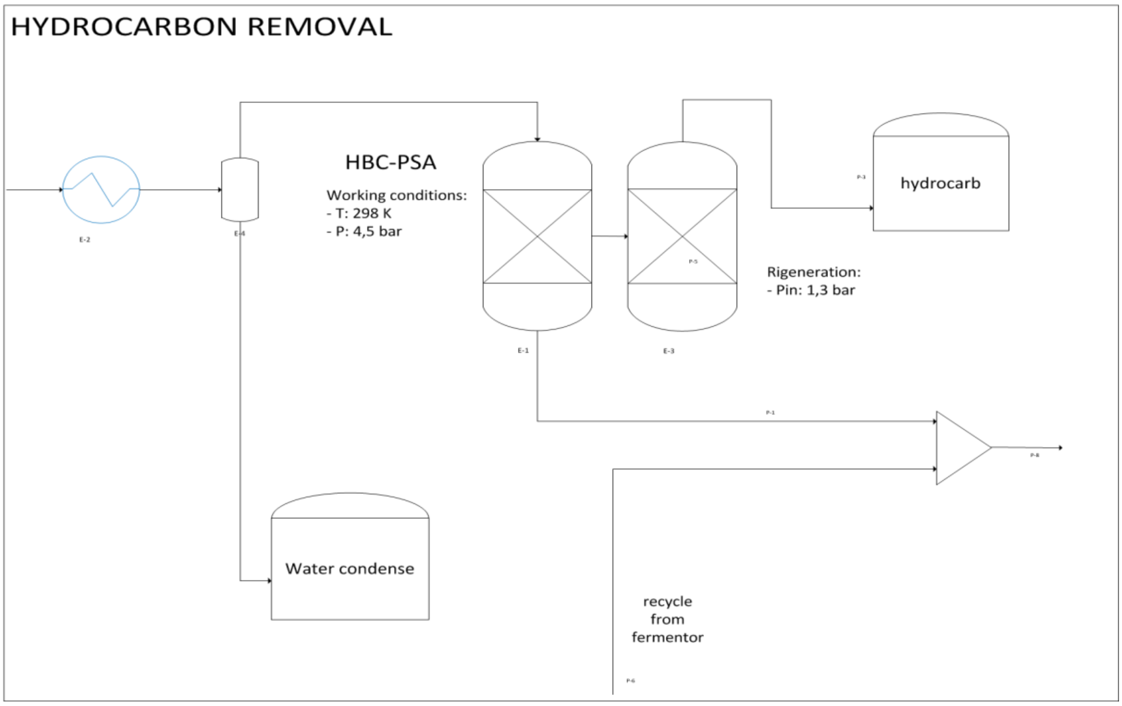


Figure 60: Hydrocarbon removal – HBC PSA.

The goal is to remove the hydrocarbons:

- The traces of hydrocarbons that have not been eliminated in the reformer are withdrawn from the gas stream using a PSA system.
- The working conditions for PSA systems are 25°C and pressure 4.5 bar.
- A bed of silica gel is the most appropriate for the removal of hydrocarbons.
- We assume that the PSA will retain any hydrocarbon left in the gas stream as well as the ammonia, so that the efficiency is 1 for HYDROCARBONS, NH_3 and N_2, and 0 for the rest.

The equations used are:

$$P_{sat} = \exp\left(A + \frac{B}{T} + C\log(T) + D\,T^{E}\right)$$

$$P_{vap} = P_{sat} * U_r$$

$$U_s = \frac{MW_{H2O}}{MW_{gas}} * \frac{P_{vap}}{P - P_{vap}}$$

$$U = \frac{MW_{H2O}}{MW_{gas}} * \frac{P_{sat}}{P - P_{sat}}$$

$$fc^{L}('H2O','HX6','PSA_{HCB}') = fc('H2O','HX6','PSA_{HCB}') * \ \mathrm{U}_{s} \sum_{i=1}^{nc} \left(c, fc(c,'HX6','PSA_{HCB}')\right)$$

$$fc('H2O','PSA_{HCB}','Mix1') = \sum_{i=1}^{nc} \mathrm{U} * fc(c,'HX6','PSA_{HCB}')$$

$$fc('Solids',' \ PSA_{HCB}','Snk9') = \eta_{sep} * \ fc('Solids','HX6','PSA_{HCB}')$$

3.5.3 Composition adjustment – H2 PSA

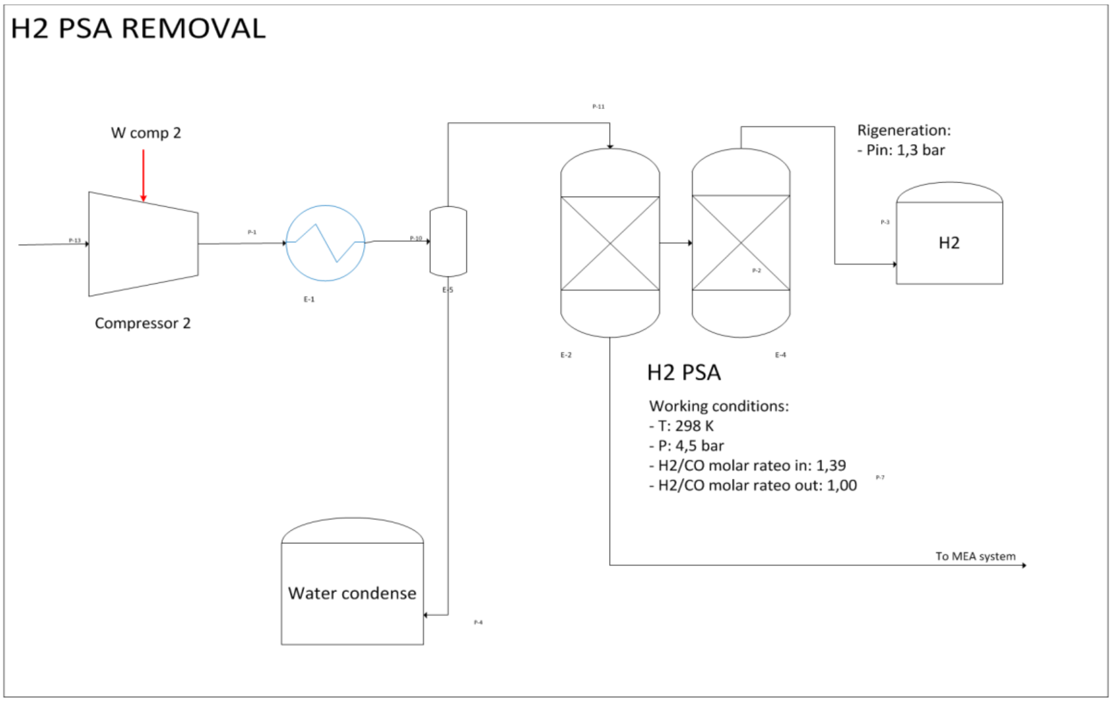


Figure 61: H_2 removal - H_2 PSA.

The stream to be treated in the hybrid membrane/PSA system for the recovery of hydrogen has to be set to a temperature of 25°C and a pressure of 4.5 bar. New hybrid PSA-membrane systems have been developed to improve the purity of the separation.[96] In this system condensed water is removed.

The final goal is to remove H_2:

- The stream is treated in the hybrid membrane/PSA system with a bed of zeolite.
- The recovery of hydrogen has to be set to a temperature of 25°C and a pressure of 4.5 bar, assuming that the inlet pressure is $0.9*P_{PSA}$ (P_{in} = 4 bar) due to the pressure drop in the previous PSA system.
- The gas is re-pressurized to 4.5 bar and cooled down to 25°C.

The equations used are:

$$\frac{fc_{mol}(H2,'\,PSA'_{H2},'\,Compressor3')}{PM(H2)} = \frac{fc_{mol}(CO,'\,PSA'_{H2},'\,Compressor3')}{PM(CO)}$$

$${Ratio_{H2,CO}}^{IN} = \frac{fc_{mol}(CO,' HX7', 'PSA_{H2}')}{fc_{mol}(H2,' HX7', 'PSA_{H2}')}$$

$${Ratio_{H2,CO}}^{OUT} = \frac{fc_{mol}(CO,' PSA'_{H2},' Compressor3')}{fc_{mol}(H2,' PSA'_{H2},' Compressor3')}$$

3.5.4 CO2 and H2S removal

3.5.4.1 CO2 - PSA

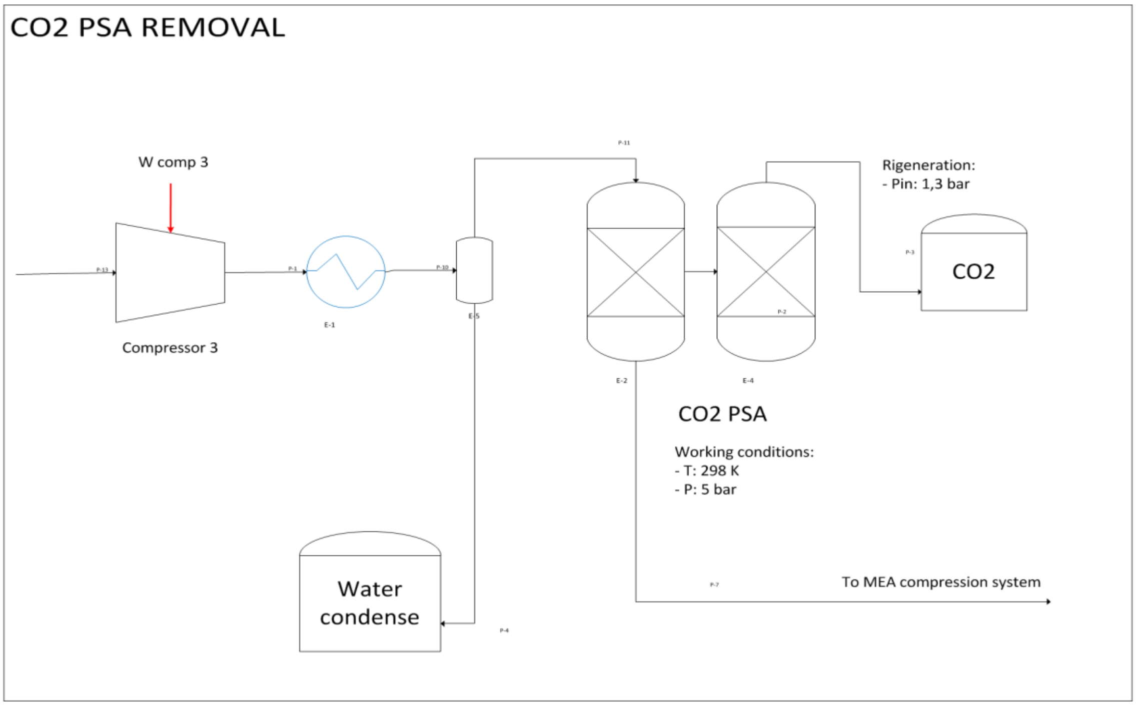


Figure 62: CO_2 removal - CO_2 PSA.

The removal of CO_2 and H_2S is the last cleaning stage for the preparation of syngas before the bioreactor. PSA system uses a bed of zeolite to remove CO_2 from the stream. However, the H_2S is not adsorbed as it should, and another unit is therefore needed.

Heat exchanger is used to cool down the gas where the water may condense. The condensed water is separated from the gas exiting the heat exchanger, which is saturated, before entering the PSA bed.

The goal is to remove CO_2:

- The stream is treated in the membrane/PSA system with a bed of zeolite.
- The gas is re-pressurized to 4.5 bar and cooled down to 25°C.
- The system is modeled as two beds in parallel, one operating and the second one in regeneration to allow continuous operation of the plant.
- The recovery of the PSA system is assumed to be 95% for CO_2 and 0% for any other gas of the mixture.

The equations used are:

$$fc(c,'\,PSA_{CO2}','Snk_{CO2}') = \eta_{PSA} * \ fc(c,'\,HX8','PSA_{CO2}')$$

$$\mathrm{P_{sat}} = exp\left(A + \frac{B}{T} + C\ log(T) + \ D\ T^{E}\right)$$

$$\mathrm{P_{vap}} = \mathrm{P_{sat}} * \mathrm{U_r}$$

$$\mathrm{U}_s = \frac{MW_{H2O}}{MW_{gas}} * \frac{\mathrm{P_{vap}}}{P - \ \mathrm{P_{vap}}}$$

$$fc('H2O','PSA_{CO2}','Snk_{CO2}') = fc('H2O','PSA_{CO2}','Snk_{CO2}') * \ \mathrm{U}_s\ ('\,PSA_{CO2}','Snk_{CO2}')$$

3.5.4.2 MEA System

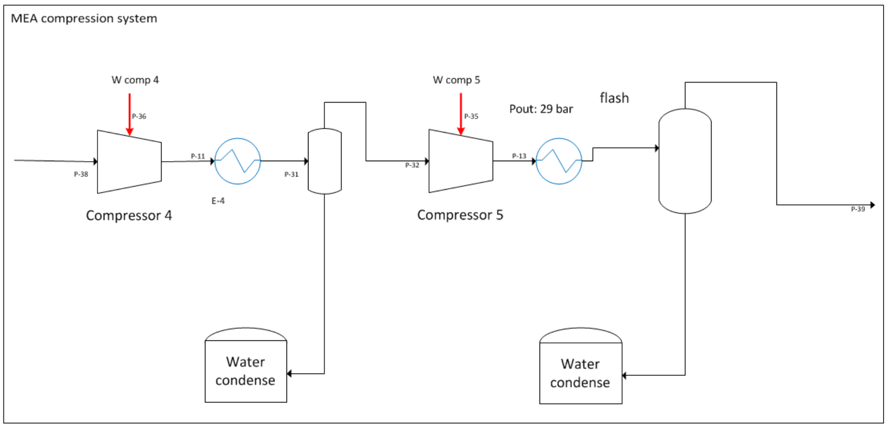


Figure 63: MEA compression system.

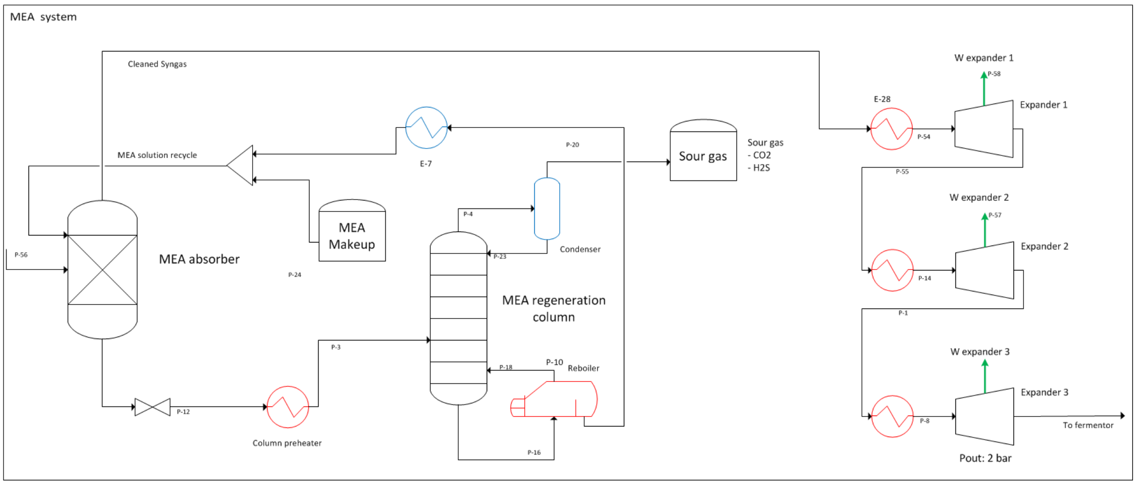


Figure 64: MEA system.

The removal of CO_2 and H_2S is the last cleaning stage for the preparation of syngas before the bioreactor.

- MEA (absorption of CO_2 and H_2S in monoethanolamine)
  - There is a chemical reaction between the sour gas and the amine.
  - If it operates at high pressure, it requires high energy to regenerate the MEA.
  - The pressure increase, from $0.9*P_{PSA}$ (P_{MEA} = 4 bar) to 29 bar, is reached with a two stage intercooling system (temperature after each compressor is calculated assuming polytropic behavior taking into account that the pressure ratio is the same at each compression stage).

- The total amount of solution of MEA needed to absorb the H_2S and the CO_2 from the gas stream is calculated as a function of the amount of sour gases eliminated with a molar ratio of 1:1 between the sour gas and the amine.

$$MEA_{Absorber} = \frac{MW_{MEA}}{C_{MEA} * \alpha} * \left(\frac{Recovery_{CO2} * CO2_{Absorber}}{MW_{CO2}} + \frac{Recovery_{H2S} * H2S_{Absorber}}{MW_{H2S}}\right)$$

- The concentration of solution will be 25% [kg_{MEA}\$kg_{H2O}$] and a loading factor of 0.40 [$kmol_{GAS}$\$kmol_{MEA}$] is used.
- In order to calculate the losses of MEA, typical humidification models are used. Some of the MEA is lost with the sour gases, which are saturated with MEA (on the top of the absorber and on the top of the column).

- MEA (absorption of CO_2 and H_2S in monoethanolamine)
  - _ABSORBER_:

    The removal of CO_2 and H_2S using MEA operates at 29°C and 29 bar.

    The efficiencies for the recovery of sour gases are assumed to be 1 for H_2S and 0.9 for CO_2.

    The outlet temperature is calculated from the energy balance.
  - _COLUMN_ (to regenerate the amine):

    The inlet temperature to the column is 93°C. The temperature at the bottom $Tout_{reb}$ =125°C while at the condenser it is $Tout_{cond}$ = 54°C.

    The efficiencies for the recovery of sour gases are assumed to be 1 for H_2S and 1 for CO_2.

The equations used are:

- _ABSORBER_:

$$fc('MEA','Absorber','HX51') = \sum_{i=1}^{nc} fc(c,'Absorber','HX51') * U_s\_MEA$$

$$fc('MEA','Src\_MEA\_H2O','Absorber') = fc('H2O','Src\_MEA\_H2O','Absorber') * C_{MEA}$$

$$fc('H2O','Absorber','HX51a') = \sum_{i=1}^{nc} fc(c,'Absorber','HX51a') * U_s\_H2O$$

$$fc('CO2','Absorber','HX51a') = (1 - Recovery_{CO2}) * fc('CO2','Flash5','Absorber')$$

$$fc('H2S','Absorber','HX51a') = (1 - Recovery_{H2S}) * fc('H2S','Flash5','Absorber')$$

$$Q = \sum_{i=1}^{nc} \left(c, \left(fc(c,'e','u') * \Delta h^{\circ L}_{f} \int_{Tr}^{T} Cp^{L}\, dT \right) \right)$$

$$Q = \sum_{i=1}^{nc} \left(c, \left(fc(c,'e','u') * \Delta h^{\circ V}_{f} \int_{Tr}^{T} Cp^{V}\, dT \right) \right)$$

- *__COLUMN__*:

$$fc('MEA','Column','Snk10') = \sum_{i=1}^{nc} fc(c,'Column','Snk10') * U_{s}\_MEA$$

$$fc('H2O','Column','Snk10') = \sum_{i=1}^{nc} fc(c,'Column','Snk10') * U_{s}\_H2O$$

$$Q^{S}_{Reboiler} = fc('HX12','Column') \int_{Tin}^{Tout} Cp^{mix}('HX12','Column')\, dT$$

$$Q^{V}_{Reboiler} = \left(fc^{V}('H2O','Reboiler','HX11') * \left(\Delta h^{\circ vap}_{H2O} \right) \right) + \left(fc^{V}('MEA','Reboiler','HX11') * \left(\Delta h^{\circ vap}_{MEA} \right) \right)$$

$$Q^{D}_{Reboiler} = \left(fc('MEA','Column','HX11') * (\Delta h^{\circ abs}_{CO2}) \right)$$

Now the syngas is purified by sour gases and is ready to be sent to the bioreactor. Before entering the bioreactor, the stream should be expanded from the initial pressure, 29 bar, to the final pressure, 2 bar.

3.6 *Fermentation*

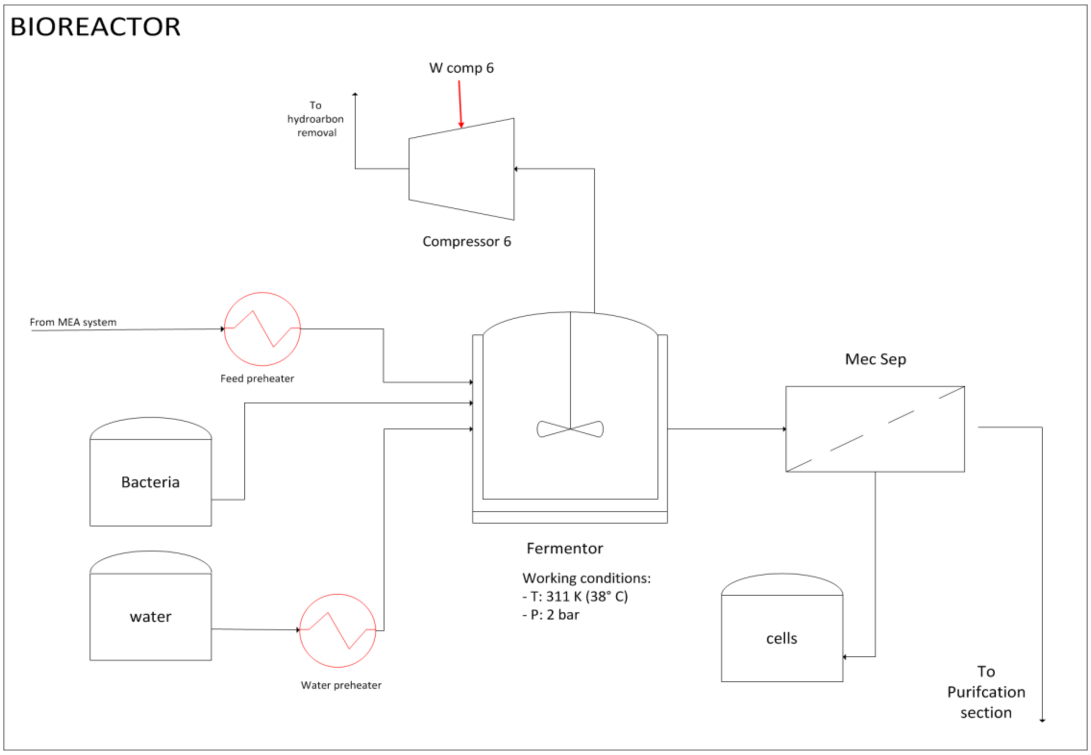


Figure 65: Biorector.

Purified syngas, with a molar ratio of 1:1, is sent from the cleaning section to the bioreactor. New microorganisms are fed to the biorector (as a make up).

The best current practice claims a maximum concentration of ethanol in the reactor of 5%. New systems are in development to adsorb ethanol from the water during the synthesis, in order to reduce the concentration so that bacteria can produce more ethanol. Water must be fed to the reactor to maintain ethanol concentration below the limit. BRI and Coskata industries have recently reported that their bacteria are capable of producing only ethanol. The conversion of the H_2 (or CO since H_2:CO = 1) is about 70%.

The energy involved in the fermentation process cannot be calculated as for typical reactions due to the consumption of energy for cells growth. We assume that the enthalpy of reaction is approximately equal to the free energy.

It is not used any energy balance of the reactor. This is possible because the heat of reaction is negligible compared to other energies taken into consideration in the process and this would result in a minimum error estimated in energy costs. Mass balances with reactions are solved automatically, introducing CO and H_2 conversions and stoichiometric reactions (look at paragraph 3.3.2). Conversions are assumed 0.7 for both reactants.

The simplified overall reaction used for the balance is:

$$3CO + 3H_2 \rightarrow C_2H_5OH + CO_2$$

Organic matter is not considered in the mass balances and it is assumed that it can be separated with a mechanical separation located after the fermenter. The liquid stream from the mechanical separation is fed to the beer column in the purification section. The water leaving the reactor with the liquid ethanol is calculated as the difference between the one that enters and the one that is dragged by the gas.

Unreacted gas is sent to an energy recovery unit, producing steam (steam boiler).

Heat necessary to preheat water is calculated by solving a simple energy balance on the heat exchanger. Liquid heat capacities for each component of the stream are here used (the same stands for all heat exchangers with liquid phases without phase transition).

The equations used are:

$$\mathrm{fc}('EtOH','BioReactor','MecSep2') = \mathrm{fc}('H20','Src10','HX22') * \mathrm{C}_{EtOH\_Max}$$

3.7 *Purification*

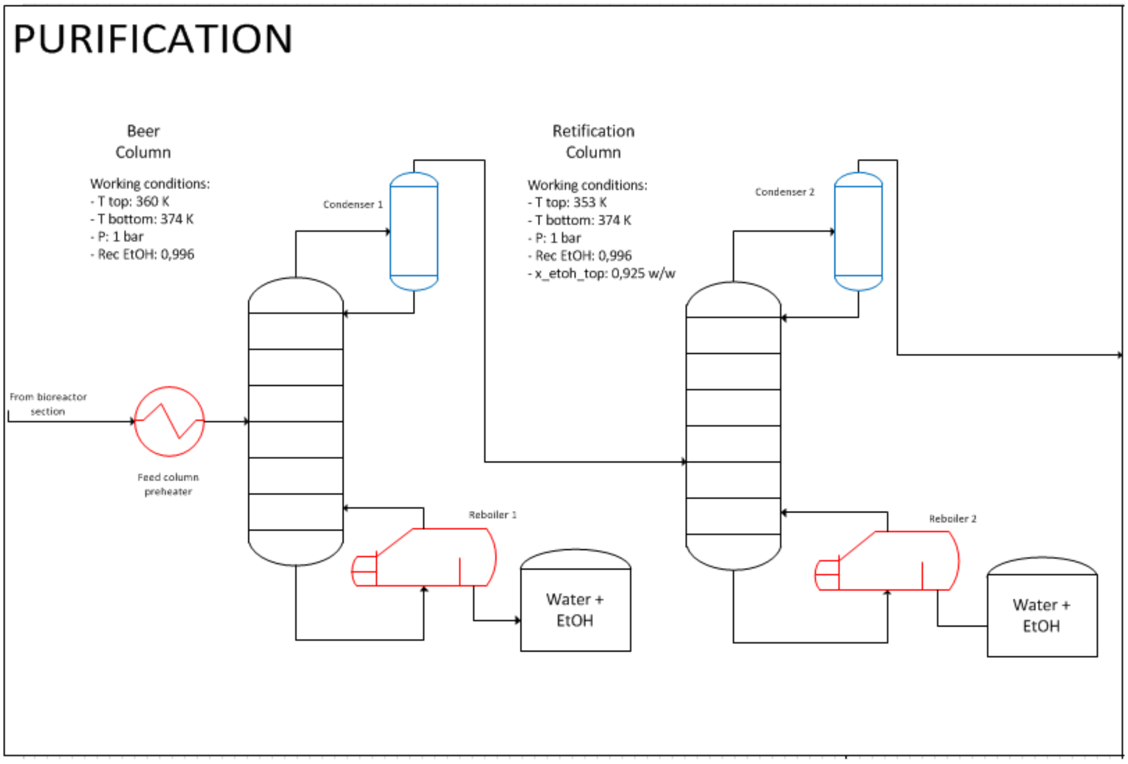


Figure 66: Purification.

3.7.1 Beer column and Rectification column (GAMS)

Beer Column design: The heat exchanger, before the column, preheats the feed stream until the bubble point. Only ethanol and water are considered to be present in the ethanol purification section. We model this column using a simple correlations assuming ideal behaviour (binary column) because it works far from azeotropic conditions. The ethanol relative volatility, respect to water (α), is taken as 2.2389 and is assumed to be constant over the temperature range of the column.[69] Water is chosen to be the heavy key and ethanol the light key for the calculations, both the beer column as well as the rectification column.

A partial condenser is used for beer column to obtain a vapor distillate. In the reboiler the effect of ethanol on the bubble point is negligible since its mole fractions are very small. The vapor pressures of water and ethanol are predicted by the Antoine equation. The beer column operates at atmospheric pressure (P = 1 atm), and a pressure drop of 0.1 atm across the column is assumed. Therefore, the temperature of the inlet stream is calculated at 1 atm, the temperature of the reboiler is computed at 1.05 atm and the temperature in the condenser is calculated at 0.95 atm.[69] The recovery of ethanol is fixed at 0.996. The theoretical number of trays of the column is calculated using Fenske's equation.[138] The actual number of trays is calculated assuming an efficiency of 50%. The temperatures of the inlet and outlet streams are calculated based on the bubble and dew points.[138] A partial condenser is used in the beer column to save energy. Thus, the composition of the condensed liquid in the distillate (reflux) is not the same as the top product which is removed as saturated vapour. It is assumed that the extracted vapor is in equilibrium with the liquid phase. The composition of the reflux stream can be calculated using the vapor-liquid equilibrium relationship for water and ethanol at the temperature of the condenser. The heat balances in the reboiler and the condenser depend on the reflux ratio. A reflux ratio ($R_{\_col3}$) of 1.5 is selected for the beer column.[139] Since the recovery of ethanol at the top is fixed at 99.6%, the bottom stream contains almost no ethanol. The ethanol contribution to the heat of vaporization in the reboiler may be neglected.

Rectification Column design: Since the azeotropic composition of an ethanol-water mixture at atmospheric pressure is about 95 wt% of ethanol, this is the maximum achievable purity of ethanol in an atmospheric rectification column.[69] The required purity for fuel grade ethanol is much higher, so the mixture must be further dehydrated. The rectification column is modeled in a similar way as the beer column in terms of pressure drop and vapour-liquid equilibrium. A partial condenser is used in this column so that this stream can be fed to the dehydration technologies. The ethanol recovery is fixed at 99.6%. The purity of ethanol in the top of the column is selected 92,5 wt%. Furthermore, it is assumed that only water is vaporized in the reboiler. A reflux ratio of 5 is selected so that the column design is feasible due to the fact that the operation is close to the azeotrope. The outlet of the column does not meet fuel quality specifications. Thus, the stream has to be further treated in order to dehydrate it.

Main equations (the same for beer column and rectification column):

Fenske equations:

$$\mathrm{N_{min}} = \frac{\ln\left(\frac{x_D}{1-x_D}\frac{1-x_B}{x_B}\right)}{\ln\left(\overline{\alpha}\right)}$$

Actual trays number equations:

$$\mathrm{N} = \frac{\mathrm{N_{min}} - 1}{\acute{\eta}_{\mathrm{trays}}}$$

Mass Balances:

$$\mathrm{F} = \mathrm{D} + \mathrm{B}$$

$$\mathrm{Fz_{etoh}} = \mathrm{Dx_{D,etoh}} + \mathrm{Bx_{B,etoh}}$$

$$\mathrm{Fz_{etoh}} * \mathrm{Rec_{etoh}} = \mathrm{Dx_{D,etoh}}$$

$$\mathrm{x_{D,etoh}} + \mathrm{x_{D,water}} = 1$$

$$\mathrm{x_{B,etoh}} + \mathrm{x_{B,water}} = 1$$

Raoult equation:

$$\mathrm{y_{etoh}} * \mathrm{P} = \mathrm{x_{,etoh}} * \mathrm{P^{0}_{sat,etoh}}$$

Relative volatility:

$$\alpha = \frac{P^{0}_{sat,etoh}}{P^{0}_{sat,water}}$$

Enriching section equations:

$$R = \frac{L}{D}$$

$$V = D + L$$

Feed section equations:

$$L1 - L = q * F$$

$$F + L + V1 = V * L1$$

Reboiler and condenser duty:

$$Q_{reb} = \Delta H_{ev,water}(T_B) * V1$$

$$Q_{cond} = L * \left(\left(x_{eq,etoh} * \Delta H_{ev,etoh}(T_D)\right) + \left(x_{eq,water} * \Delta H_{ev,water}(T_D)\right)\right)$$

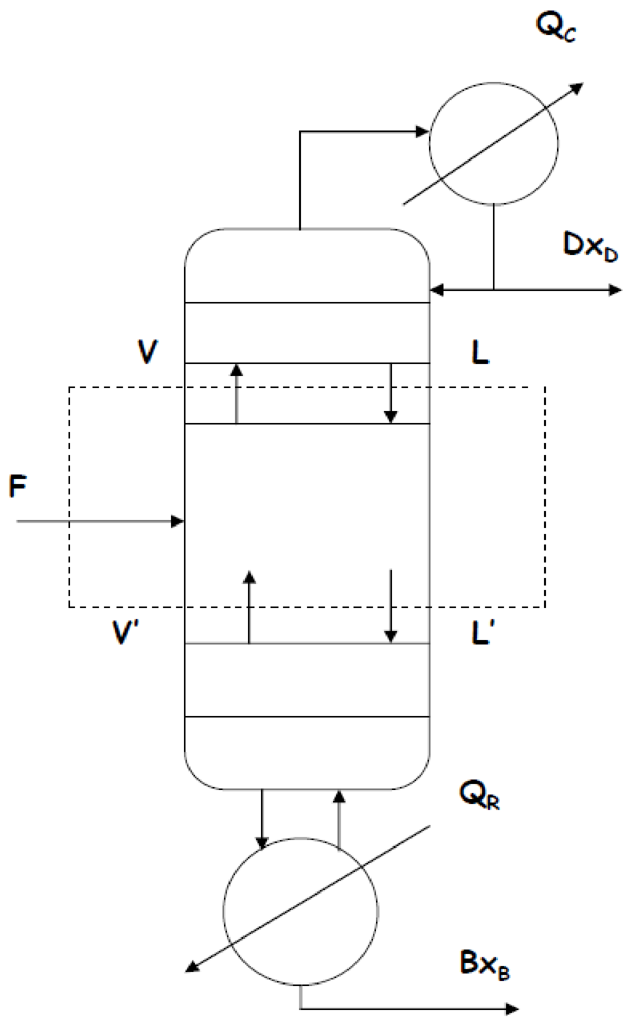


Figure 67: Distillation Column.

3.7.2 Beer column and rectification column (ASPEN HYSYS)

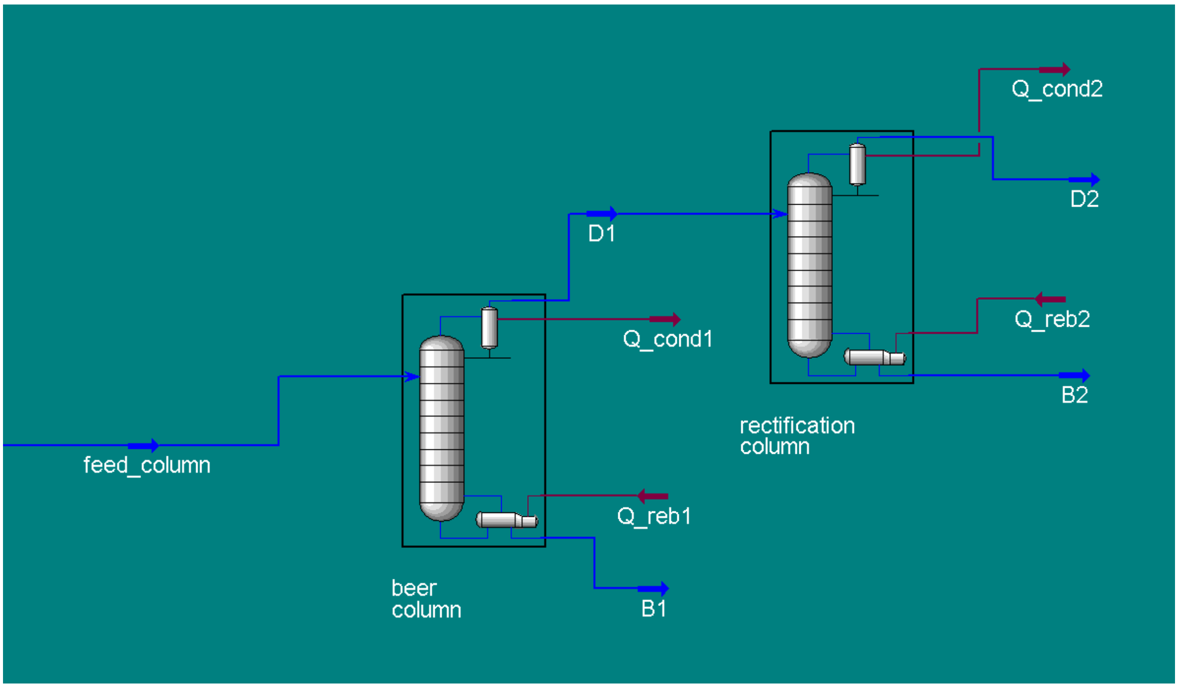
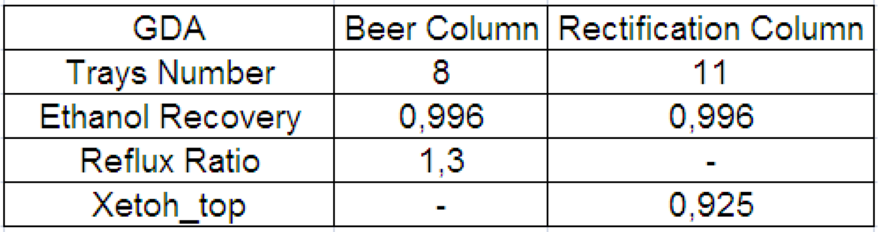


Figure 68: Aspen HYSYS configuration.

The distillation section is carried out with ASPEN HYSYS in order to obtain rigorous results. The simulation thermodynamic fluid package is NRTL (Non-Random Two-Liquid model)[145], which is capable of representing VLE phase behaviour of binary mixtures of ethanol and water.

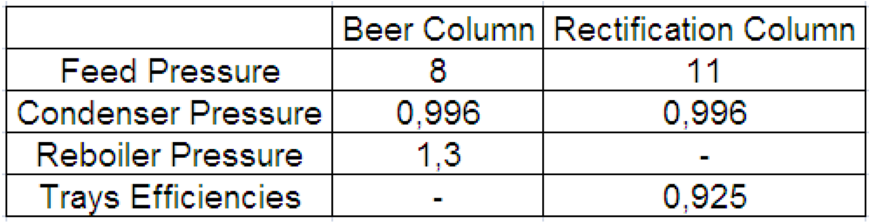
The distillation columns work at atmospheric condition with pressure drop of 0.1 atm across the column and full reflux condenser is connected to them. The columns degrees of freedom are saturated with:



GDA	Beer Column	Rectification Column
Trays Number	8	11
Ethanol Recovery	0,996	0,996
Reflux Ratio	1,3	-
Xetoh_top	-	0,925

Figure 69: Column Carateristics.

And the main specifications are:



	Beer Column	Rectification Column
Feed Pressure	8	11
Condenser Pressure	0,996	0,996
Reboiler Pressure	1,3	-
Trays Efficiencies	-	0,925

Figure 70: Column Specifications.

The solving method is "Modified HYSYS Inside-Out".

3.7.3 Molecular sieves

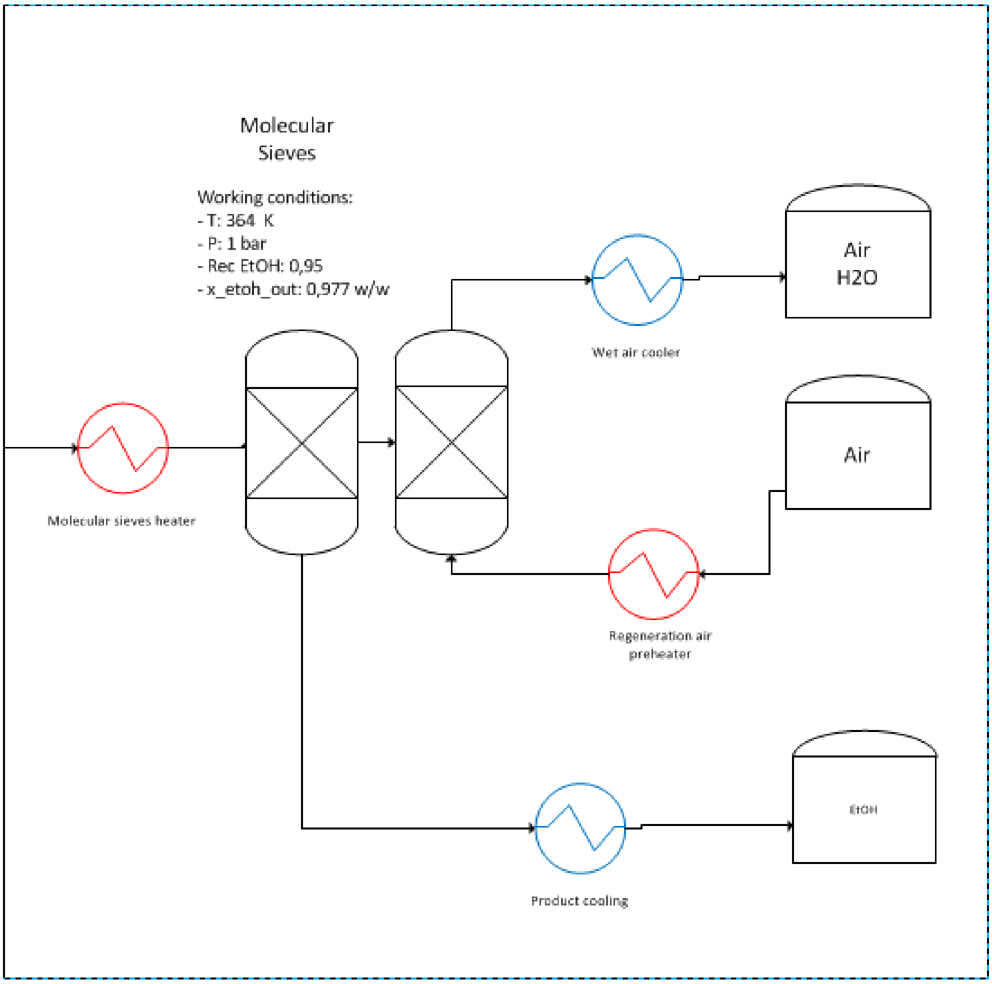


Figure 71: Molecular Sieves.

Molecular sieves is a convenient alternative in terms of energy consumption, but it can only be used if the inlet flow has a water concentration lower or equal to 80% w/w.

The equations used are:

$$fc('H2O','MolecularSieves','EtOH') = \left(1 - X_{H2O}^{in}\right) * fc('H2O','HX19','MolecularSieves')$$

Here X^{in}_{H2O} is the fraction of incoming water removed in the hydrating molecular sieve. As already said, there is a lower bound on the fraction of ethanol entering the molecular sieve, which is $X^{in}_{EtOH} = 0.8$.

The molecular sieve is then regenerated under vacuum, applying an air stream. This stream, which has a relative humidity of 70%, is heated in the heat exchanger HX21 from the temperature of 20°C to 95 °C.

4. RESULTS

Simulation results, using GAMS, are presented in the flowsheet resume table. The results do not take into account energy integration but this topic will be discussed later. The purification section results, obtained using Aspen Hysys, are also reported.

Streams names are introduced in the same way as in the mathematical modelling chapter, naming each process stream after the two units it connects.

4.1 Pretreatment

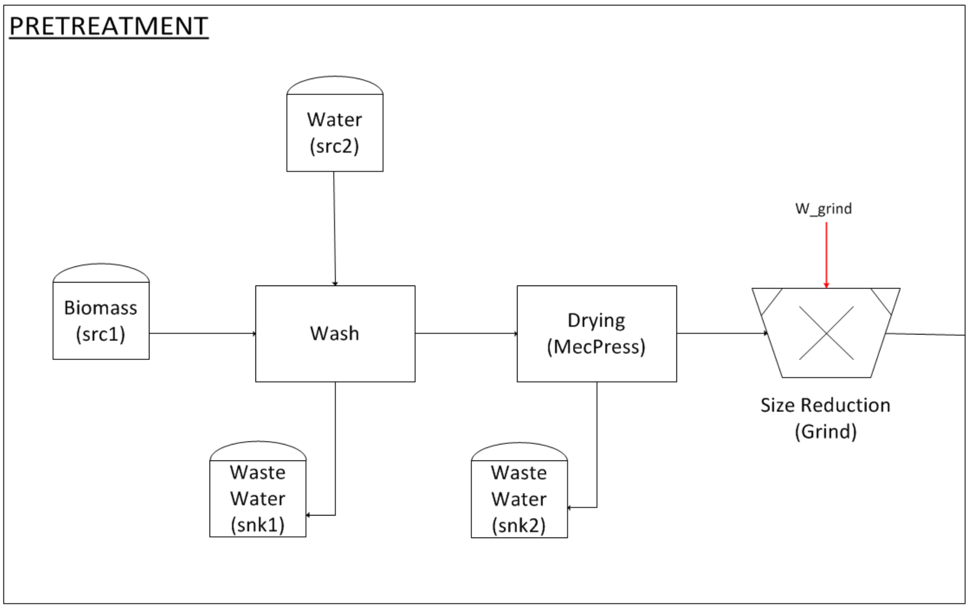
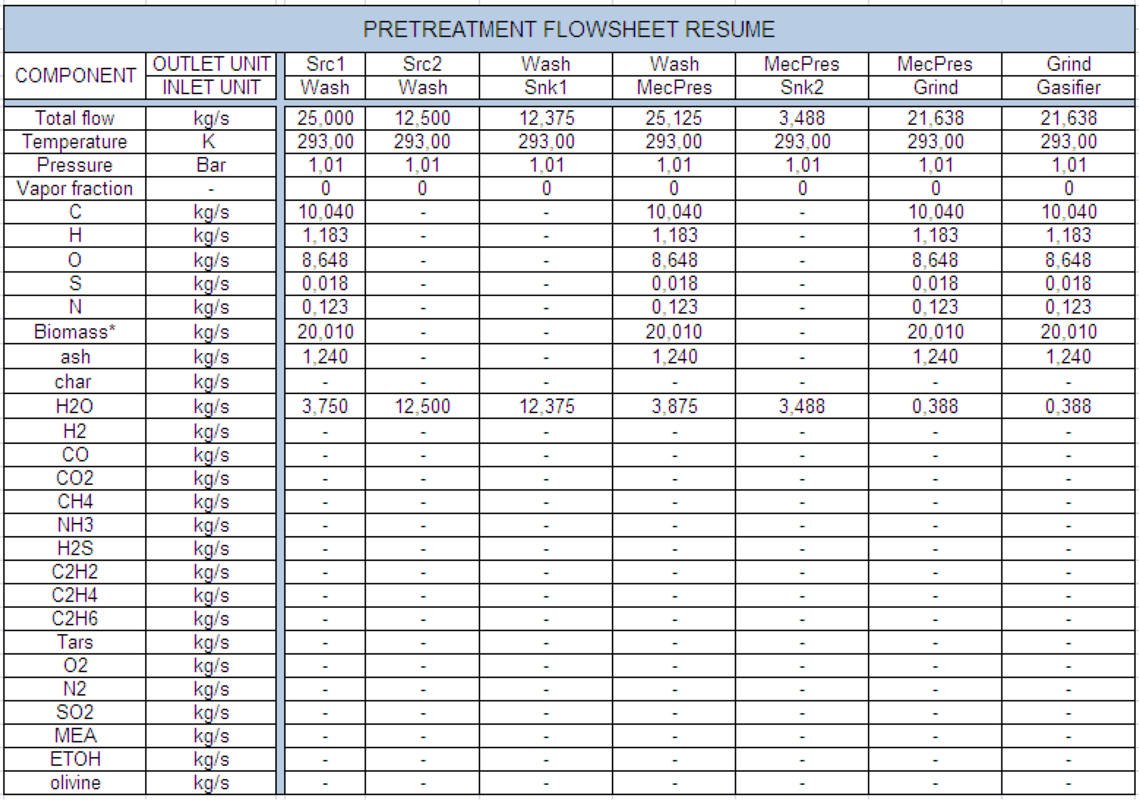
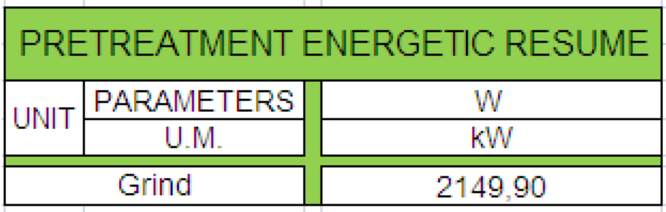


Figure 72: Pretreatment.



PRETREATMENT FLOWSHEET RESUME								
COMPONENT	OUTLET UNIT	Src1	Src2	Wash	Wash	MecPres	MecPres	Grind
	INLET UNIT	Wash	Wash	Snk1	MecPres	Snk2	Grind	Gasifier
Total flow	kg/s	25,000	12,500	12,375	25,125	3,488	21,638	21,638
Temperature	K	293,00	293,00	293,00	293,00	293,00	293,00	293,00
Pressure	Bar	1,01	1,01	1,01	1,01	1,01	1,01	1,01
Vapor fraction	-	0	0	0	0	0	0	0
C	kg/s	10,040	-	-	10,040	-	10,040	10,040
H	kg/s	1,183	-	-	1,183	-	1,183	1,183
O	kg/s	8,648	-	-	8,648	-	8,648	8,648
S	kg/s	0,018	-	-	0,018	-	0,018	0,018
N	kg/s	0,123	-	-	0,123	-	0,123	0,123
Biomass*	kg/s	20,010	-	-	20,010	-	20,010	20,010
ash	kg/s	1,240	-	-	1,240	-	1,240	1,240
char	kg/s	-	-	-	-	-	-	-
H2O	kg/s	3,750	12,500	12,375	3,875	3,488	0,388	0,388
H2	kg/s	-	-	-	-	-	-	-
CO	kg/s	-	-	-	-	-	-	-
CO2	kg/s	-	-	-	-	-	-	-
CH4	kg/s	-	-	-	-	-	-	-
NH3	kg/s	-	-	-	-	-	-	-
H2S	kg/s	-	-	-	-	-	-	-
C2H2	kg/s	-	-	-	-	-	-	-
C2H4	kg/s	-	-	-	-	-	-	-
C2H6	kg/s	-	-	-	-	-	-	-
Tars	kg/s	-	-	-	-	-	-	-
O2	kg/s	-	-	-	-	-	-	-
N2	kg/s	-	-	-	-	-	-	-
SO2	kg/s	-	-	-	-	-	-	-
MEA	kg/s	-	-	-	-	-	-	-
ETOH	kg/s	-	-	-	-	-	-	-
olivine	kg/s	-	-	-	-	-	-	-

Figure 73: Pretreatment Flowsheet Resume.



PRETREATMENT ENERGETIC RESUME		
UNIT	PARAMETERS	W
	U.M.	kW
Grind		2149,90

Figure 74: Pretreatment Energetic Resume.

Remarks:

- The amount of raw biomass (relative humidity 15%) fed to the washing unit is 25 kg/s (about 161500 tons/yr).
- The amount of moisture present in the biomass is reduced from 15 wt% to 1.18 wt%, equivalent to a reduction percentage of 89.7%.
- The amount of water required for the washing of biomass is 0.5 kg of H_2O per kg of biomass.
- The amount of waste water generated by adding the washing unit and the drying unit is equal to 15.863 kg/s, which consists of the washing water flow and the moisture removed from the biomass.
- The power required for grinding biomass (W_{grind}) to bring it to a final size of 10 mm diameter is 2149.9 kW.
- All treatments take place at atmospheric pressure and room temperature.

4.2 Gasification

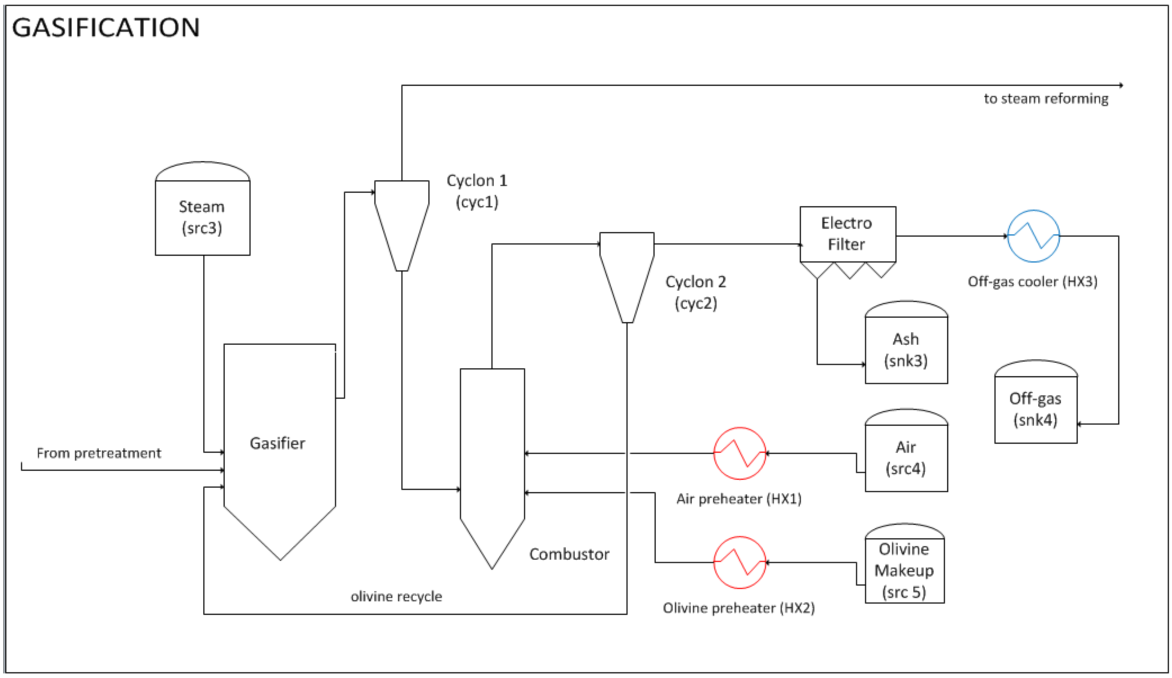


Figure 75: Gasification.

GASIFICATION FLOWSHEET RESUME															
COMPONENT	OUTLET UNIT	src3	gasifier	cyc1	cyc1	combustor	src4	HX1	src5	HX2	cyc2	cyc2	elettrof	elettrof	HX3
	INLET UNIT	gasifier	cyc1	combustor	reformer	cyc2	HX1	combustor	HX2	combustor	eletrofilter	gasifier	snk5	HX3	snk6
Total flow	kg/s	8,50	603,89	577,50	26,38	607,41	29,85	29,85	0,06	0,06	33,66	573,75	1,31	32,35	32,35
Temperature	K	433,00	1163,00	1163,00	1163,00	1268,00	293,00	573,00	298,00	1163,00	1268,00	1268,00	1268,00	1268,00	573,00
Pressure	Bar	6,00	1,60	1,60	1,60	1,60	1,01	1,01	1,01	1,01	1,60	1,60	1,60	1,60	1,60
Vapor fraction	-	1	1	sol	1	1	1	1	sol	sol	1	sol	sol	1	1
C	kg/s	0,000	2,196	2,174	0,022	0,022	0,000	0,000	0,000	0,000	0,022	0,000	0,022	0,000	0,000
H	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-
O	kg/s	0,000	0,346	0,342	0,003	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
S	kg/s	0,000	0,001	0,001	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
N	kg/s	0,000	0,008	0,008	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
ash	kg/s	0,000	1,240	1,228	0,012	1,228	0,000	0,000	0,000	0,000	1,228	0,000	1,228	0,000	0,000
char*	kg/s	0,000	2,552	2,526	0,026	0,022	0,000	0,000	0,000	0,000	0,022	0,000	0,022	0,000	0,000
H2O	kg/s	8,500	8,651	0,000	8,651	0,299	0,299	0,299	0,000	0,000	0,299	0,000	0,000	0,299	0,299
H2	kg/s	0,000	0,535	0,000	0,535	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
CO	kg/s	0,000	9,368	0,000	9,368	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
CO2	kg/s	0,000	4,373	0,000	4,373	7,892	0,000	0,000	0,000	0,000	7,892	0,000	0,000	7,892	7,892
CH4	kg/s	0,000	1,934	0,000	1,934	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
NH2	kg/s	0,000	0,114	0,000	0,114	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
H2S	kg/s	0,000	0,016	0,000	0,016	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
C2H2	kg/s	0,000	0,088	0,000	0,088	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
C2H4	kg/s	0,000	0,930	0,000	0,930	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
C2H6	kg/s	0,000	0,055	0,000	0,055	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Tars	kg/s	0,000	0,281	0,000	0,281	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
O2	kg/s	0,000	0,000	0,000	0,000	1,489	6,888	6,888	0,000	0,000	1,489	0,000	0,000	1,489	1,489
N2	kg/s	0,000	0,000	0,000	0,000	22,669	22,661	22,661	0,000	0,000	22,669	0,000	0,000	22,669	22,669
SO2	kg/s	0,000	0,000	0,000	0,000	0,003	0,000	0,000	0,000	0,000	0,003	0,000	0,000	0,003	0,003
MEA	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ETOH	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-
olivine**	kg/s	0,000	573,750	573,750	0,000	573,807	0,000	0,000	0,057	0,057	0,057	573,750	0,057	0,000	0,000

Figure 76: Gasification Flosheet Resume.

Remarks:

- The dry molar composition of the outlet gas from the gasifier is (excluding the char):

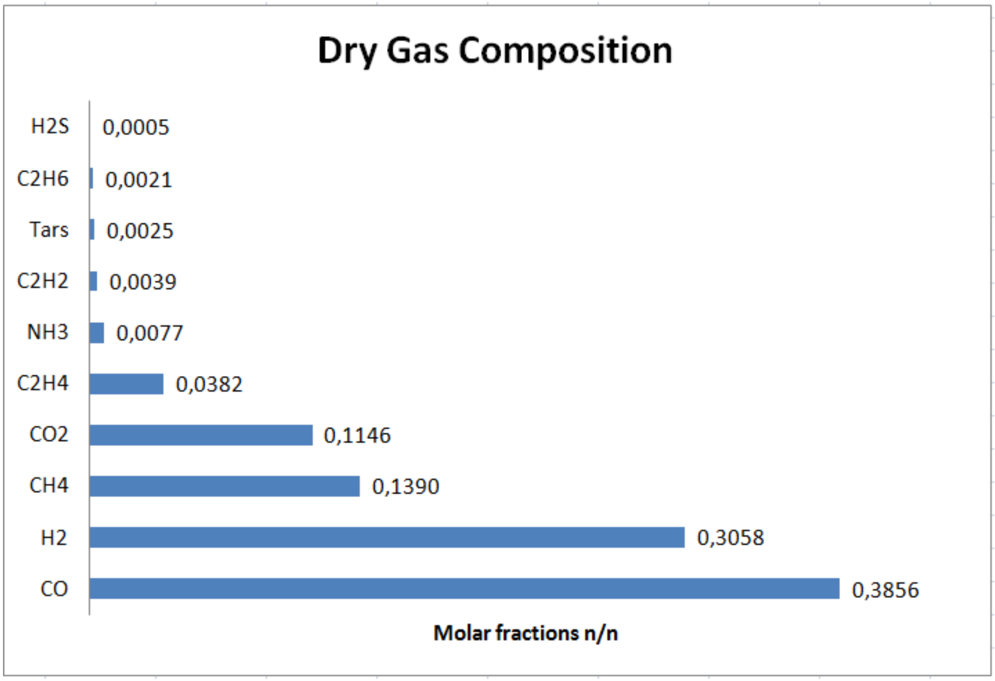


Figure 77: Dry Gas Composition.

- The composition of the char formed in the gasifier and sent to the combustor is:

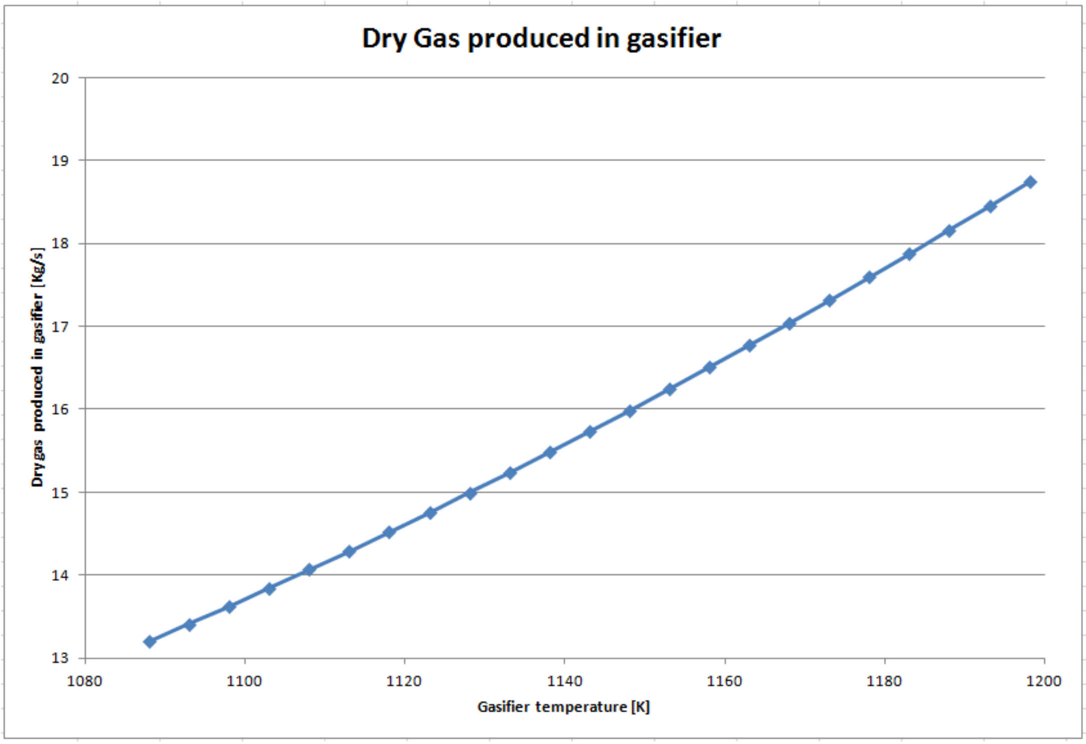


Figure 78: Dry Gas Pruduced In The Gasifier.

- Increasing the operating temperature of the gasifier increases the amount of syngas produced; in particular, increasing the mole fractions of CO and H_2, it is possible to mildly increase the mole fractions of CO_2 and CH_4 but the amount of char decreases because of the increase in carbon conversion. Also, a greater quantity of steam reacts and there is a slight decrease in the tars molar fraction.

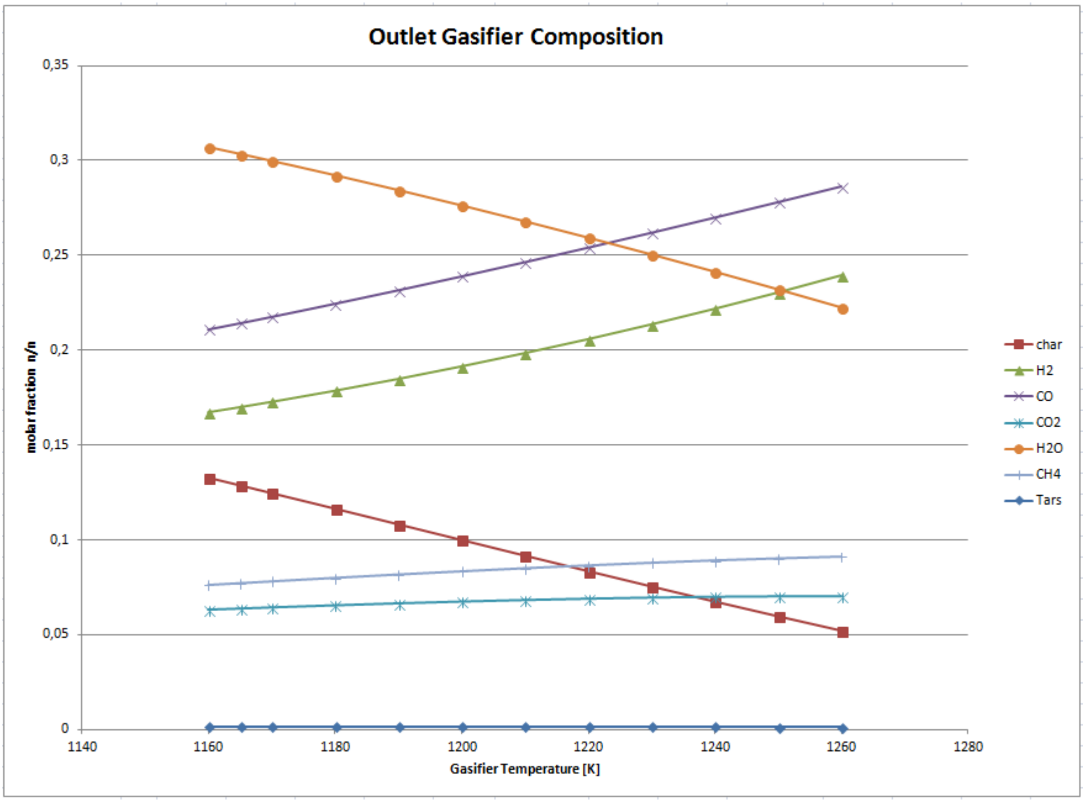


Figure 79: Outlet Gasifier Composition.

- For the combustion of char is necessary to supply air, which has to be preheated from room temperature to 300°C, applying 8663.33 kW.
- The combustor is also fed with the makeup of olivine that is lost in the gas-solid separation. The heating of olivine up to the temperature of the combustor requires a small amount of heat because the flow rate of the make-up is very small as well. The amount of steam entering the combustor was not taken as a variable, and the model does not take it into account.
- Heat exchanger (HX3) must reduce the temperature of the process stream from the temperature of the combustor to 313°C. In order to achieve the specific request, a considerable amount of energy has to be released. It can

be advantageous to use this sensible heat as a heat source both for preheating the olivine (HX1 and HX2) and to generate steam.

- Carbon fraction present in the gases (CO, CO_2, CH_4, hydrocarbons and tars) is 78.43% of the carbon fed. The 21.22% is retained in the char and the remaining 0.44% is lost in the cyclones. This loss will be recovered in a electrostatic precipitator after the combustion section and then in a scrubber located before the steam reforming section.

4.2.1 Hydrocarbon removal

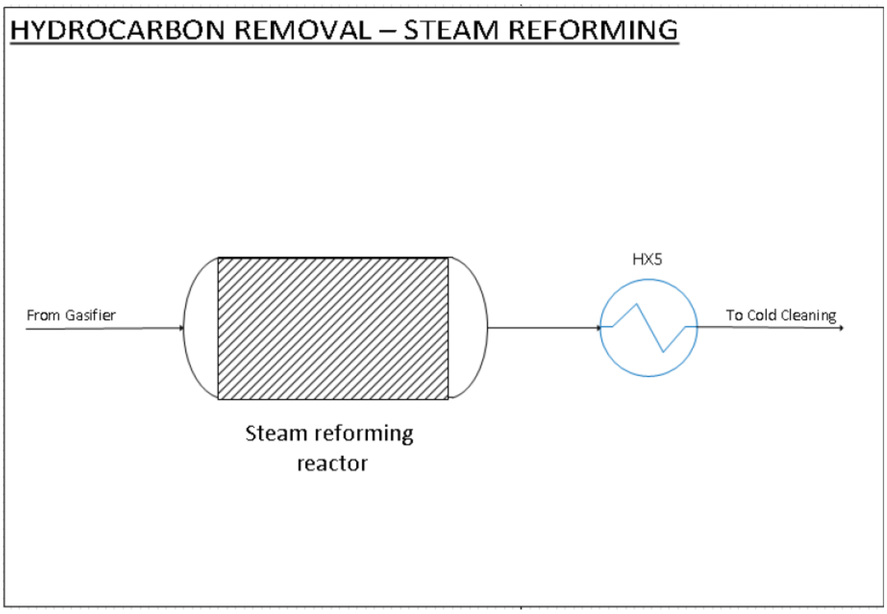
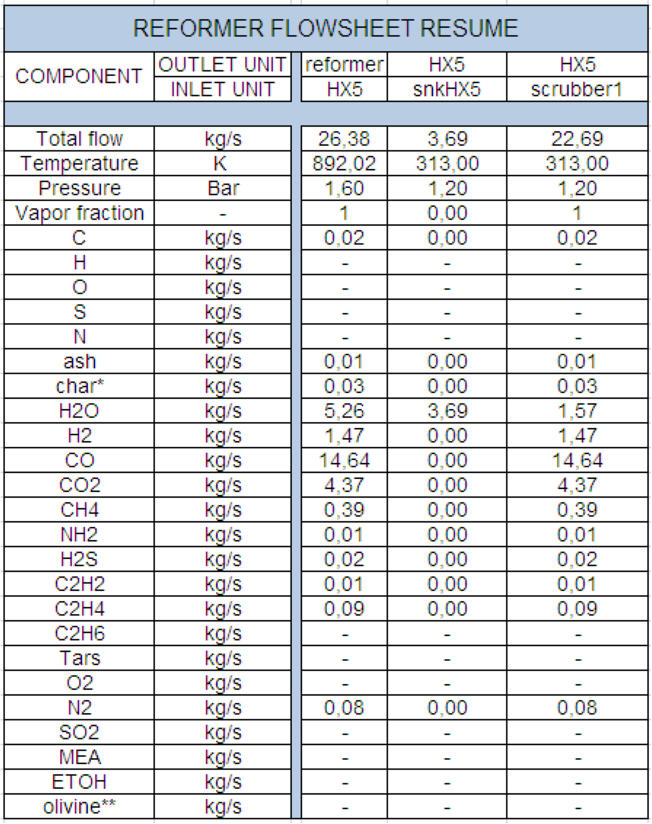


Figure 80: Hydrocarbon Removal – Steam Reforming.

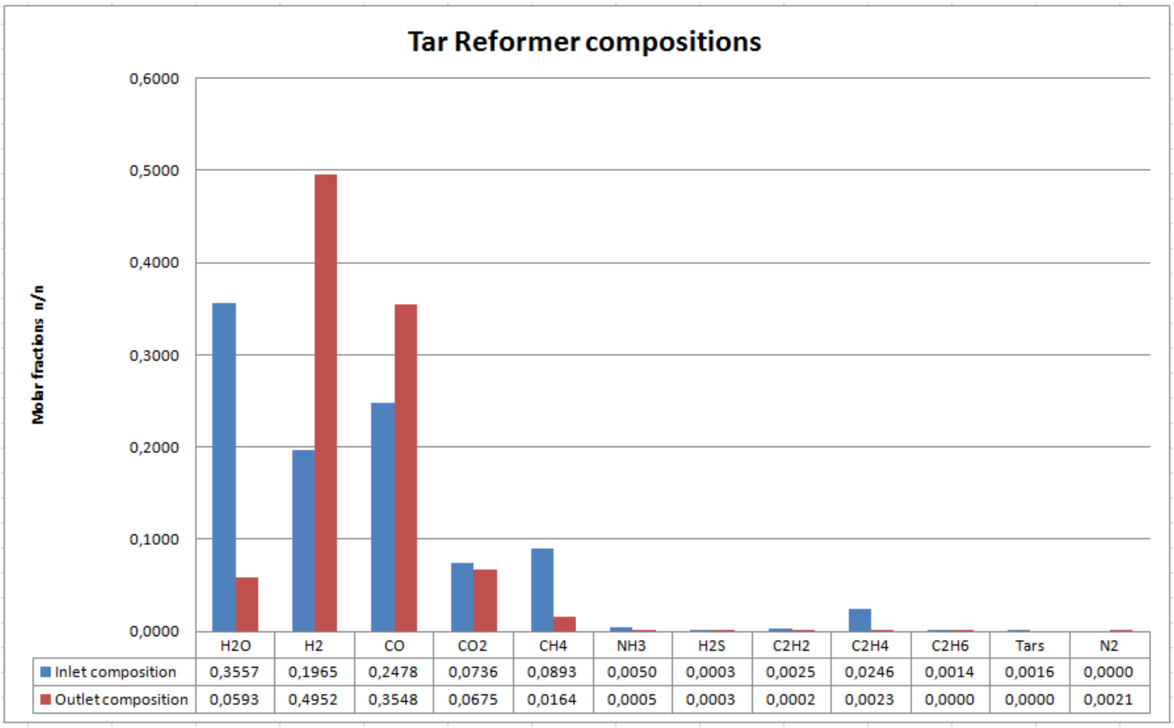


REFORMER FLOWSHEET RESUME				
COMPONENT	OUTLET UNIT	reformer	HX5	HX5
	INLET UNIT	HX5	snkHX5	scrubber1
Total flow	kg/s	26,38	3,69	22,69
Temperature	K	892,02	313,00	313,00
Pressure	Bar	1,60	1,20	1,20
Vapor fraction	-	1	0,00	1
C	kg/s	0,02	0,00	0,02
H	kg/s	-	-	-
O	kg/s	-	-	-
S	kg/s	-	-	-
N	kg/s	-	-	-
ash	kg/s	0,01	0,00	0,01
char*	kg/s	0,03	0,00	0,03
H2O	kg/s	5,26	3,69	1,57
H2	kg/s	1,47	0,00	1,47
CO	kg/s	14,64	0,00	14,64
CO2	kg/s	4,37	0,00	4,37
CH4	kg/s	0,39	0,00	0,39
NH2	kg/s	0,01	0,00	0,01
H2S	kg/s	0,02	0,00	0,02
C2H2	kg/s	0,01	0,00	0,01
C2H4	kg/s	0,09	0,00	0,09
C2H6	kg/s	-	-	-
Tars	kg/s	-	-	-
O2	kg/s	-	-	-
N2	kg/s	0,08	0,00	0,08
SO2	kg/s	-	-	-
MEA	kg/s	-	-	-
ETOH	kg/s	-	-	-
olivine**	kg/s	-	-	-

Figure 81: Reformer Flowsheet Resume.

Remarks:

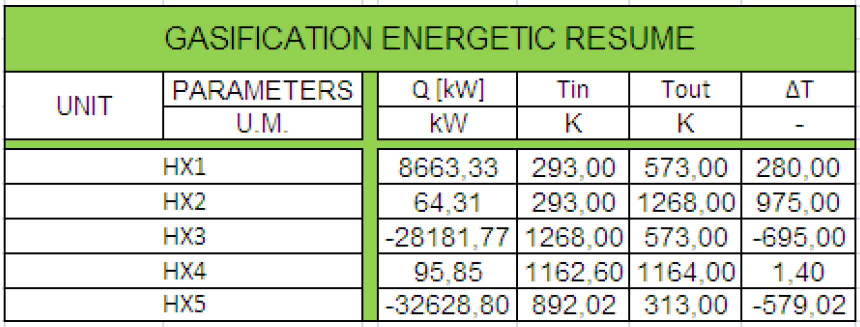
- The temperature calculated from the energy balance of the steam reforming reactor is 892 K.
- The hydrocarbon fraction decreased and ater is consumed because it reacts during steam reforming. Molar percent increase of CO is 43.2% and H_2 is 152%, so that, altogether, H_2/CO ratio increased from 0.793 to 1.396.



	H2O	H2	CO	CO2	CH4	NH3	H2S	C2H2	C2H4	C2H6	Tars	N2
🟦 Inlet composition	0,3557	0,1965	0,2478	0,0736	0,0893	0,0050	0,0003	0,0025	0,0246	0,0014	0,0016	0,0000
🟥 Outlet composition	0,0593	0,4952	0,3548	0,0675	0,0164	0,0005	0,0003	0,0002	0,0023	0,0000	0,0000	0,0021

Figure 82: Tar Reformer Composition.

- Heat exchanger HX5 must reduce the temperature of the stream exiting the tar reforming until a temperature of 40°C. There are no issues of hydrocarbons condensation (tars is liquid at 40°C) because these compounds were just reformed. This current, when is cooled down, faces a temperature drop that is greater than 500°C and the heat released in this way can be recovered by generating low pressure steam.

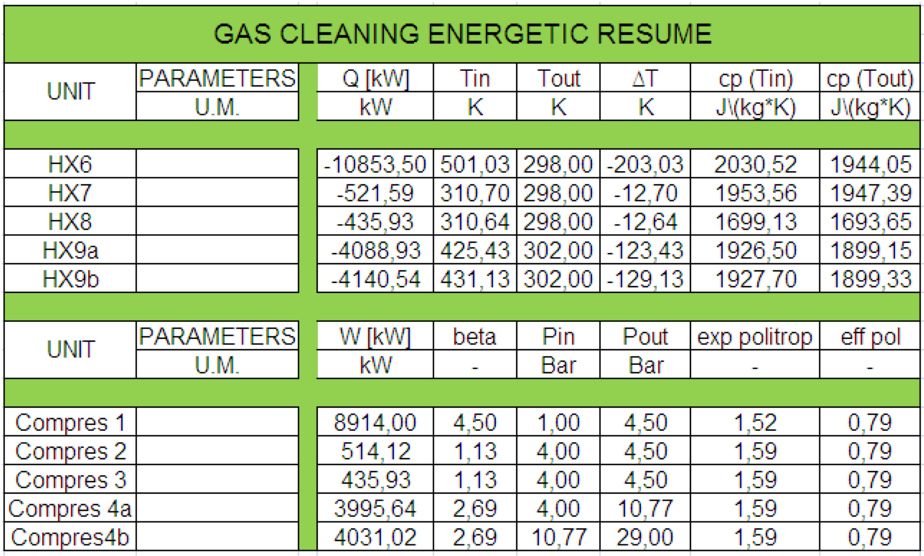


GASIFICATION ENERGETIC RESUME

UNIT	PARAMETERS	Q [kW]	Tin	Tout	ΔT
	U.M.	kW	K	K	-
HX1		8663,33	293,00	573,00	280,00
HX2		64,31	293,00	1268,00	975,00
HX3		-28181,77	1268,00	573,00	-695,00
HX4		95,85	1162,60	1164,00	1,40
HX5		-32628,80	892,02	313,00	-579,02

Figure 83: Gasification Energetic Resume.

4.3 Gascleaning



GAS CLEANING ENERGETIC RESUME							
UNIT	PARAMETERS	Q [kW]	Tin	Tout	ΔT	cp (Tin)	cp (Tout)
	U.M.	kW	K	K	K	J\\(kg*K)	J\\(kg*K)
HX6		-10853,50	501,03	298,00	-203,03	2030,52	1944,05
HX7		-521,59	310,70	298,00	-12,70	1953,56	1947,39
HX8		-435,93	310,64	298,00	-12,64	1699,13	1693,65
HX9a		-4088,93	425,43	302,00	-123,43	1926,50	1899,15
HX9b		-4140,54	431,13	302,00	-129,13	1927,70	1899,33
UNIT	PARAMETERS	W [kW]	beta	Pin	Pout	exp politrop	eff pol
	U.M.	kW	-	Bar	Bar	-	-
Compres 1		8914,00	4,50	1,00	4,50	1,52	0,79
Compres 2		514,12	1,13	4,00	4,50	1,59	0,79
Compres 3		435,93	1,13	4,00	4,50	1,59	0,79
Compres 4a		3995,64	2,69	4,00	10,77	1,59	0,79
Compres4b		4031,02	2,69	10,77	29,00	1,59	0,79

Figure 84: Gas Cleaning Energetic Resume.

4.3.1 Solids removal – Cold cleaning

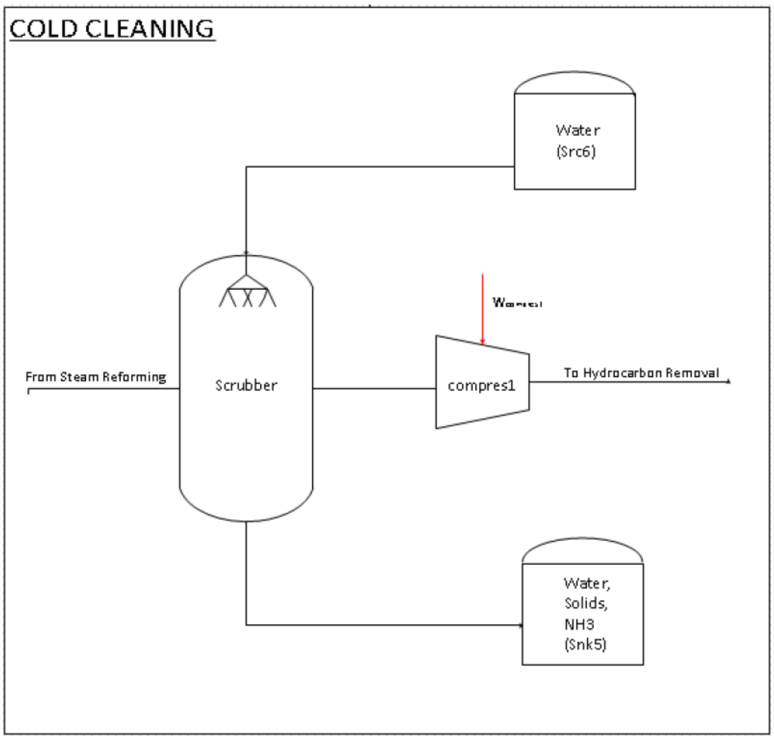
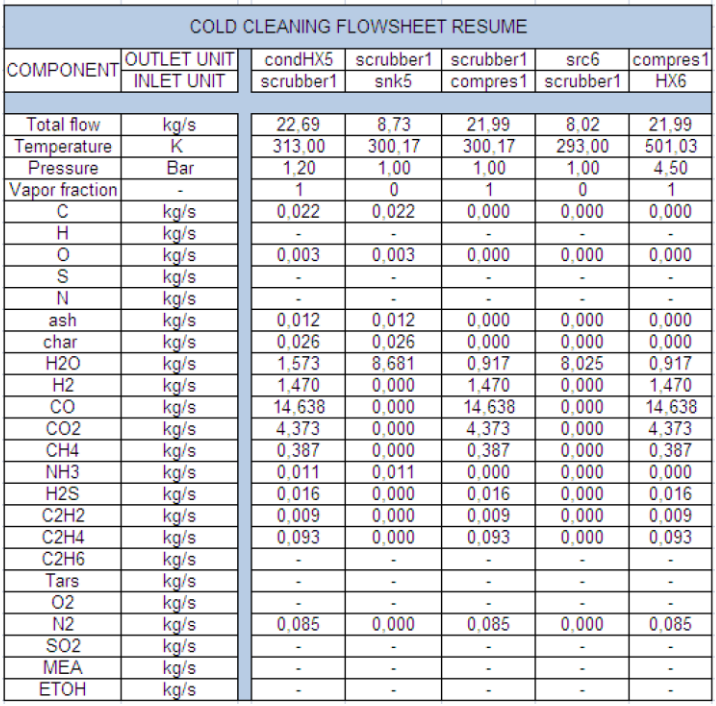


Figure 85: Cold Cleaning.



COLD CLEANING FLOWSHEET RESUME

COMPONENT	OUTLET UNIT	condHX5	scrubber1	scrubber1	src6	compres1
	INLET UNIT	scrubber1	snk5	compres1	scrubber1	HX6
Total flow	kg/s	22,69	8,73	21,99	8,02	21,99
Temperature	K	313,00	300,17	300,17	293,00	501,03
Pressure	Bar	1,20	1,00	1,00	1,00	4,50
Vapor fraction	-	1	0	1	0	1
C	kg/s	0,022	0,022	0,000	0,000	0,000
H	kg/s	-	-	-	-	-
O	kg/s	0,003	0,003	0,000	0,000	0,000
S	kg/s	-	-	-	-	-
N	kg/s	-	-	-	-	-
ash	kg/s	0,012	0,012	0,000	0,000	0,000
char	kg/s	0,026	0,026	0,000	0,000	0,000
H2O	kg/s	1,573	8,681	0,917	8,025	0,917
H2	kg/s	1,470	0,000	1,470	0,000	1,470
CO	kg/s	14,638	0,000	14,638	0,000	14,638
CO2	kg/s	4,373	0,000	4,373	0,000	4,373
CH4	kg/s	0,387	0,000	0,387	0,000	0,387
NH3	kg/s	0,011	0,011	0,000	0,000	0,000
H2S	kg/s	0,016	0,000	0,016	0,000	0,016
C2H2	kg/s	0,009	0,000	0,009	0,000	0,009
C2H4	kg/s	0,093	0,000	0,093	0,000	0,093
C2H6	kg/s	-	-	-	-	-
Tars	kg/s	-	-	-	-	-
O2	kg/s	-	-	-	-	-
N2	kg/s	0,085	0,000	0,085	0,000	0,085
SO2	kg/s	-	-	-	-	-
MEA	kg/s	-	-	-	-	-
ETOH	kg/s	-	-	-	-	-

Figure 86: Cold Cleaning Flowsheet Resume.

Remarks:

- The amount of syngas to be purified in the scrubber is 22.69 kg/s.
- The amount of water needed to wash the syngas is 8.025 kg/s, using L/G = 0.25 kg_{H2O}/m^3_{gas}.
- Solids (Ash, Char, Olivine) and NH_3 are completely eliminated, while the gas exits the scrubber with a humidity calculated based on saturated conditions (H_2O^{out} = 0.917 kg/s).
- Compressor consumes (W_{comp1}) 8914 kW.
- The temperatures of the streams exiting the scrubber are determined by an energy balance considering that the equipment operates adiabatically, T^{out} = 300.17 K.

4.3.2 Hydrocarbon removal – HBC PSA

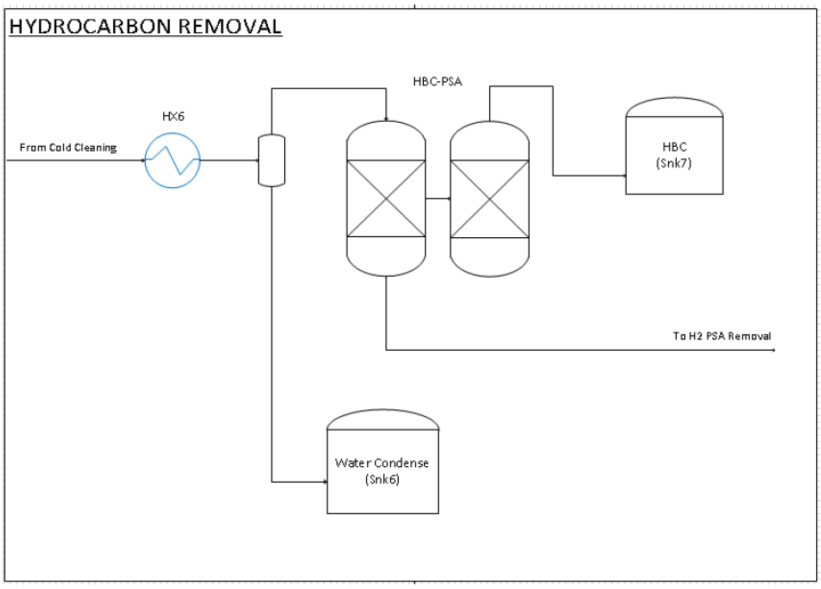
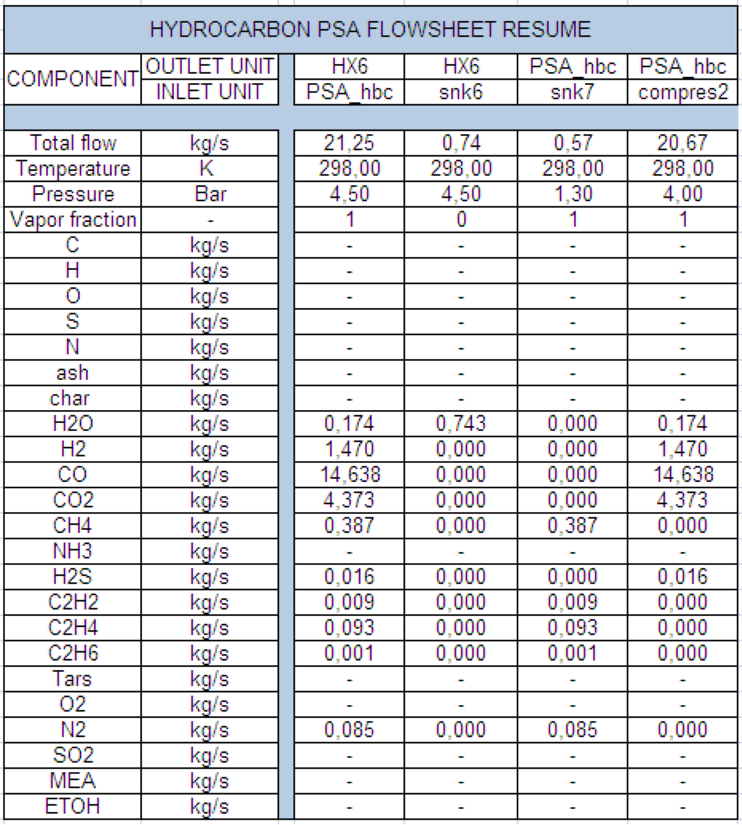


Figure 87: Hydrocarbon Removal – HBC PSA.



HYDROCARBON PSA FLOWSHEET RESUME

COMPONENT	OUTLET UNIT	HX6	HX6	PSA_hbc	PSA_hbc
	INLET UNIT	PSA_hbc	snk6	snk7	compres2
Total flow	kg/s	21,25	0,74	0,57	20,67
Temperature	K	298,00	298,00	298,00	298,00
Pressure	Bar	4,50	4,50	1,30	4,00
Vapor fraction	-	1	0	1	1
C	kg/s	-	-	-	-
H	kg/s	-	-	-	-
O	kg/s	-	-	-	-
S	kg/s	-	-	-	-
N	kg/s	-	-	-	-
ash	kg/s	-	-	-	-
char	kg/s	-	-	-	-
H2O	kg/s	0,174	0,743	0,000	0,174
H2	kg/s	1,470	0,000	0,000	1,470
CO	kg/s	14,638	0,000	0,000	14,638
CO2	kg/s	4,373	0,000	0,000	4,373
CH4	kg/s	0,387	0,000	0,387	0,000
NH3	kg/s	-	-	-	-
H2S	kg/s	0,016	0,000	0,000	0,016
C2H2	kg/s	0,009	0,000	0,009	0,000
C2H4	kg/s	0,093	0,000	0,093	0,000
C2H6	kg/s	0,001	0,000	0,001	0,000
Tars	kg/s	-	-	-	-
O2	kg/s	-	-	-	-
N2	kg/s	0,085	0,000	0,085	0,000
SO2	kg/s	-	-	-	-
MEA	kg/s	-	-	-	-
ETOH	kg/s	-	-	-	-

Figure 88: Hydrocarbon PSA Flowsheet Resume.

Remarks:

- The amount of syngas to be purified entering the HBC-PSA is 21.25 kg/s.
- The amount of water discharged from the heat exchanger is 0.743 kg/s (≈80%).
- Hydrocarbons (CH_4, C_2H_2, C_2H_4, C_2H_6) are completely eliminated with efficiency equal to 1. HBC^{out} = 1.39 kg/s.

4.3.3 *Composition adjustment – H2 PSA*

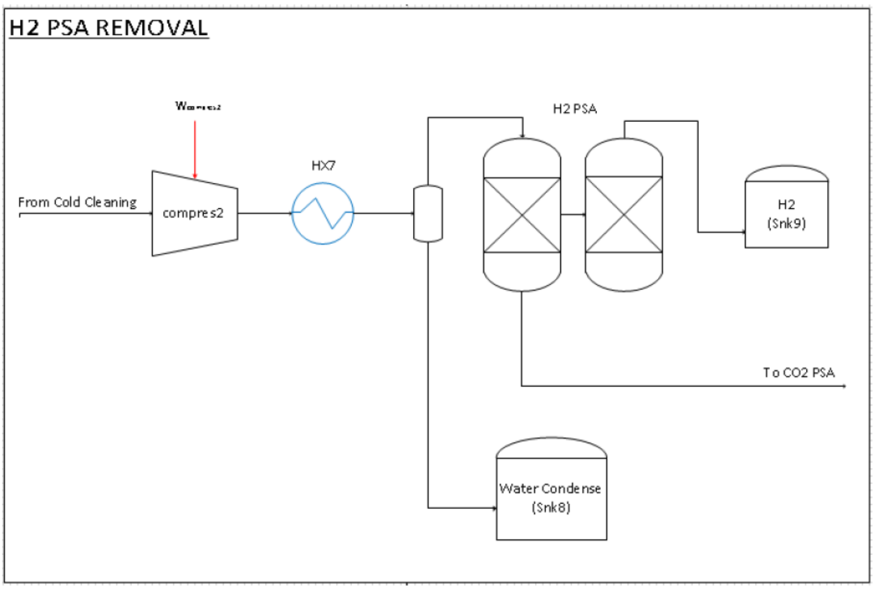
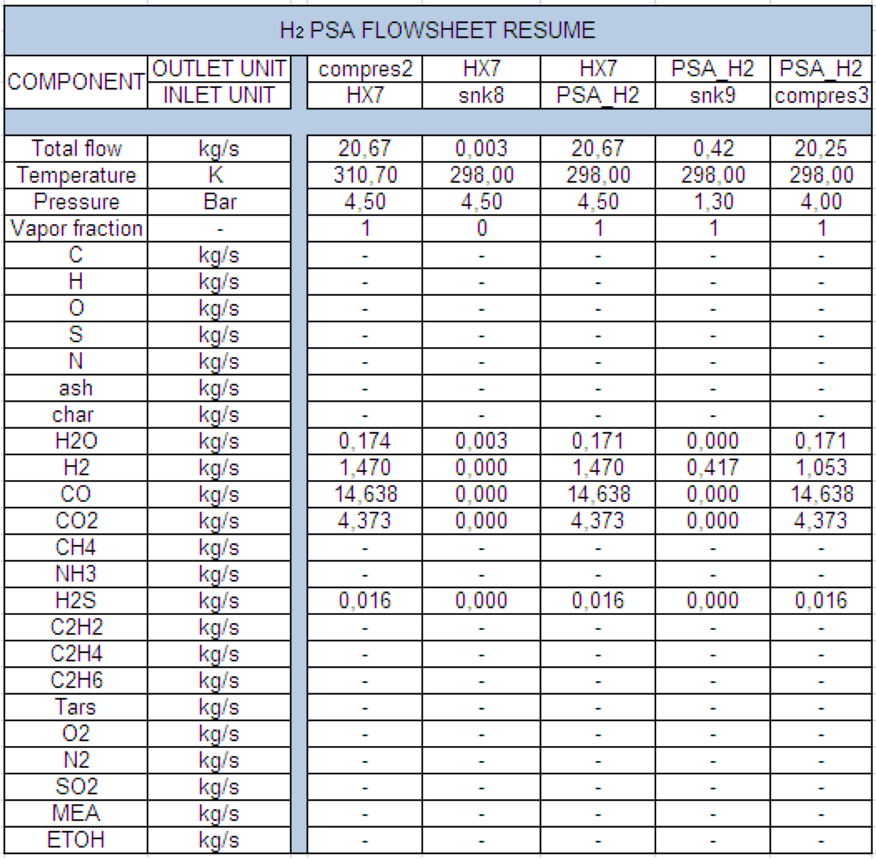


Figure 89: H2 PSA Removal.



H_2 PSA FLOWSHEET RESUME						
COMPONENT	OUTLET UNIT	compres2	HX7	HX7	PSA_H2	PSA_H2
	INLET UNIT	HX7	snk8	PSA_H2	snk9	compres3
Total flow	kg/s	20,67	0,003	20,67	0,42	20,25
Temperature	K	310,70	298,00	298,00	298,00	298,00
Pressure	Bar	4,50	4,50	4,50	1,30	4,00
Vapor fraction	-	1	0	1	1	1
C	kg/s	-	-	-	-	-
H	kg/s	-	-	-	-	-
O	kg/s	-	-	-	-	-
S	kg/s	-	-	-	-	-
N	kg/s	-	-	-	-	-
ash	kg/s	-	-	-	-	-
char	kg/s	-	-	-	-	-
H2O	kg/s	0,174	0,003	0,171	0,000	0,171
H2	kg/s	1,470	0,000	1,470	0,417	1,053
CO	kg/s	14,638	0,000	14,638	0,000	14,638
CO2	kg/s	4,373	0,000	4,373	0,000	4,373
CH4	kg/s	-	-	-	-	-
NH3	kg/s	-	-	-	-	-
H2S	kg/s	0,016	0,000	0,016	0,000	0,016
C2H2	kg/s	-	-	-	-	-
C2H4	kg/s	-	-	-	-	-
C2H6	kg/s	-	-	-	-	-
Tars	kg/s	-	-	-	-	-
O2	kg/s	-	-	-	-	-
N2	kg/s	-	-	-	-	-
SO2	kg/s	-	-	-	-	-
MEA	kg/s	-	-	-	-	-
ETOH	kg/s	-	-	-	-	-

Figure 90: H2 PSA Flowsheet Resume.

Remarks:

- The amount of syngas to be purified entering into the H_2-PSA is 20,67 kg/s.
- The amount of water discharged from the heat exchanger is 0.003 kg/s (≈ 18 %).
- The hydrogen separated is H_2^{out} = 0.417 kg/s (≈ 28 %).
- The ratio between treated biomass and hydrogen surplus is:
  $X_{H2/Biomass}$= 0,2 $m^3_{H2}/kg_{Biomass}$
  (ρ_{H2} = 0,082 kg/m^3 at T = 15 °C, P = 1 atm).
- H_2 is sold at 1,58 $/kg.[163]
- Compressor consumes (W_{comp2}) 514,12 kW.

4.3.4 CO₂ and H₂S removal

4.3.4.1 CO₂ PSA

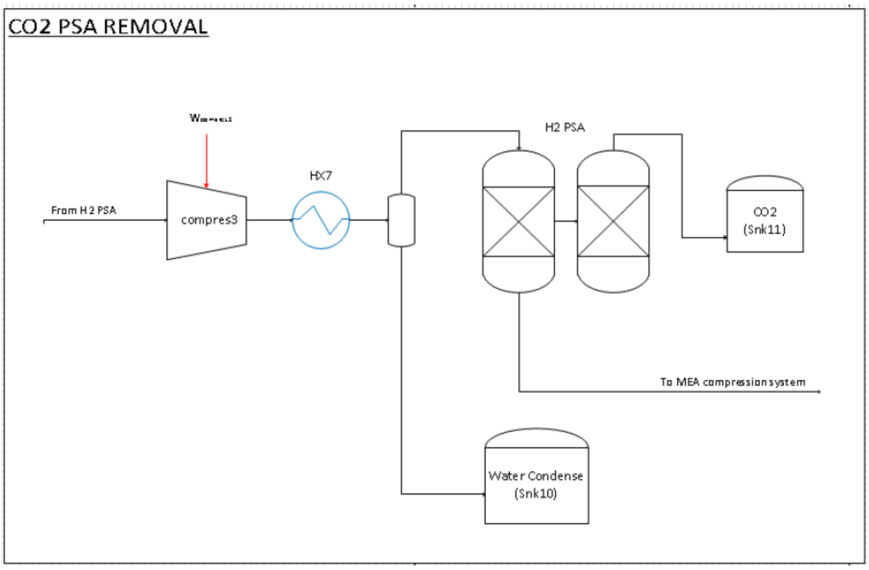
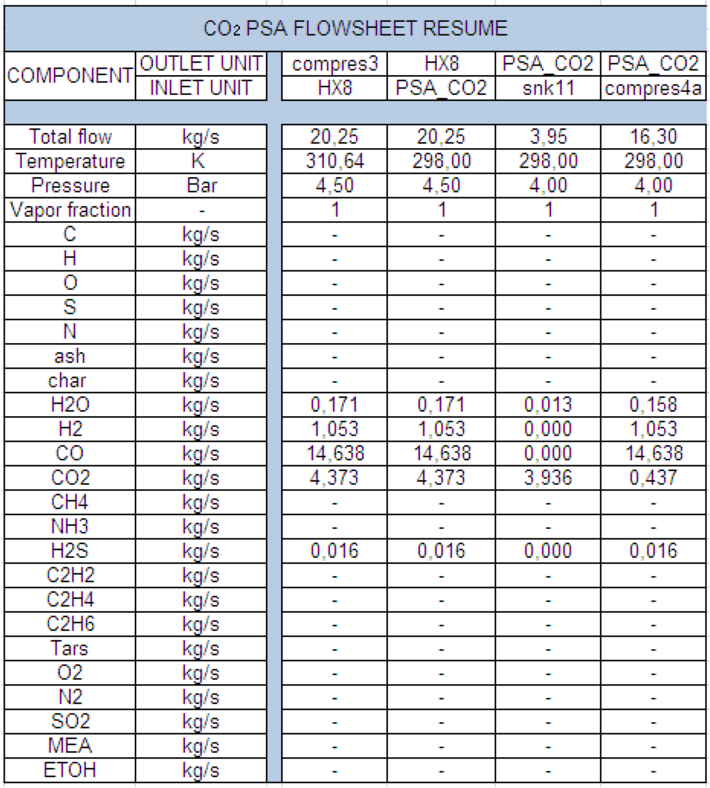


Figure 91: CO_2 PSA Removal.



CO₂ PSA FLOWSHEET RESUME					
COMPONENT	OUTLET UNIT	compres3	HX8	PSA_CO2	PSA_CO2
	INLET UNIT	HX8	PSA_CO2	snk11	compres4a
Total flow	kg/s	20,25	20,25	3,95	16,30
Temperature	K	310,64	298,00	298,00	298,00
Pressure	Bar	4,50	4,50	4,00	4,00
Vapor fraction	-	1	1	1	1
C	kg/s	-	-	-	-
H	kg/s	-	-	-	-
O	kg/s	-	-	-	-
S	kg/s	-	-	-	-
N	kg/s	-	-	-	-
ash	kg/s	-	-	-	-
char	kg/s	-	-	-	-
H2O	kg/s	0,171	0,171	0,013	0,158
H2	kg/s	1,053	1,053	0,000	1,053
CO	kg/s	14,638	14,638	0,000	14,638
CO2	kg/s	4,373	4,373	3,936	0,437
CH4	kg/s	-	-	-	-
NH3	kg/s	-	-	-	-
H2S	kg/s	0,016	0,016	0,000	0,016
C2H2	kg/s	-	-	-	-
C2H4	kg/s	-	-	-	-
C2H6	kg/s	-	-	-	-
Tars	kg/s	-	-	-	-
O2	kg/s	-	-	-	-
N2	kg/s	-	-	-	-
SO2	kg/s	-	-	-	-
MEA	kg/s	-	-	-	-
ETOH	kg/s	-	-	-	-

Figure 92: CO_2 PSA Flowsheet Reoval.

Remarks:

- The amount of syngas to be purified entering the CO_2-PSA is 20.25 kg/s.
- Carbon dioxide molar fraction entering the CO_2-PSA is: X_{CO2} = 0.0861 (≈9%).
- Hydrogen sulfide molar fraction entering the CO_2-PSA is: X_{H2S} = 0.000408 (≈0.04%).
- Carbon dioxide separated is CO_2^{out} = 3.936 kg/s (≈90%).
- Hydrogen sulfide is not separated.
- Compressor consumes (W_{comp3}) 435.93 kW.

4.3.4.2 MEA system

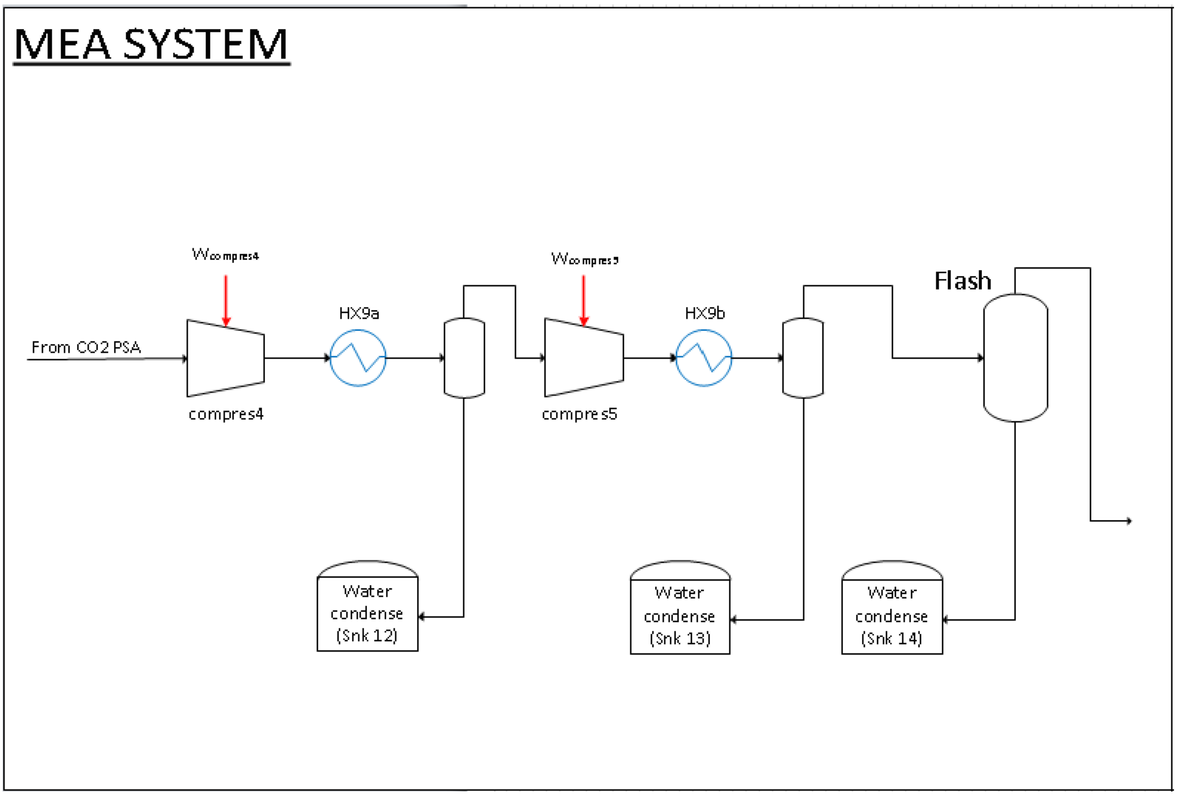


Figure 93: MEA Compression.

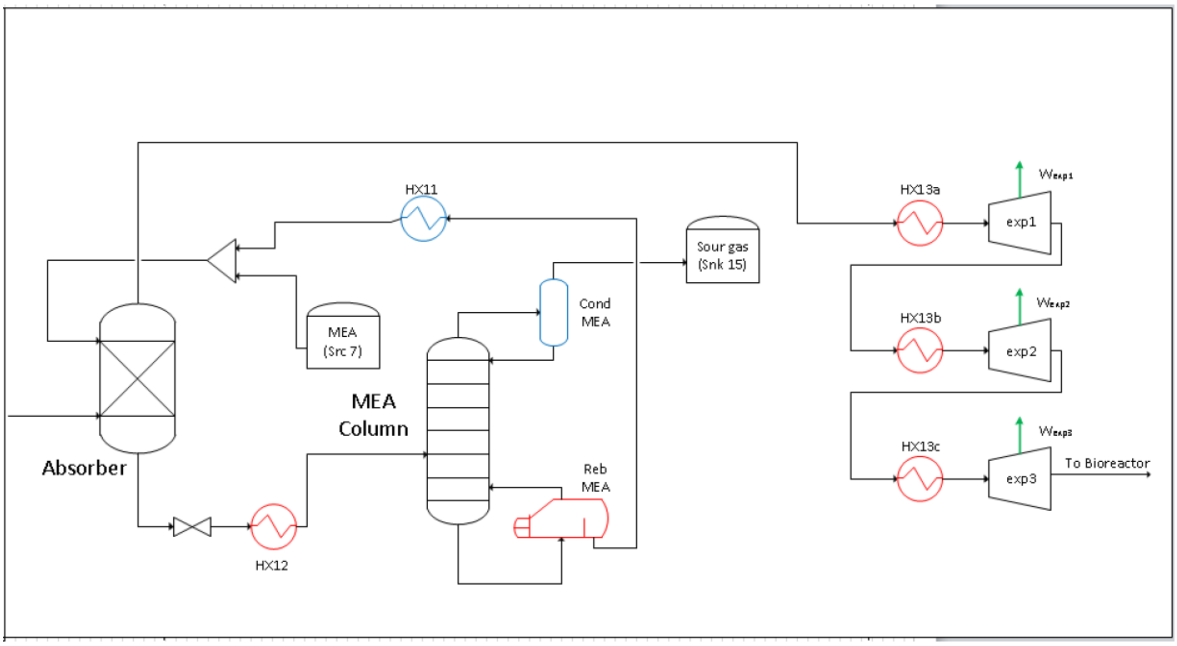
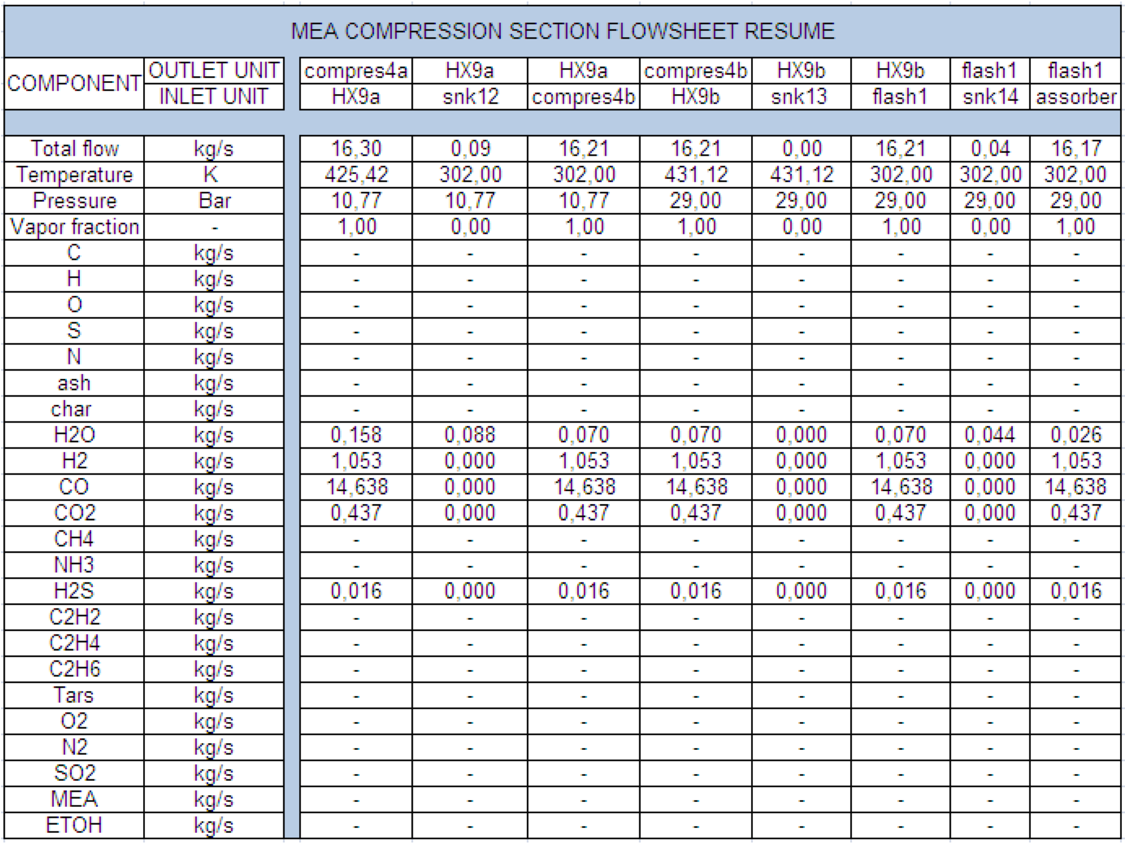
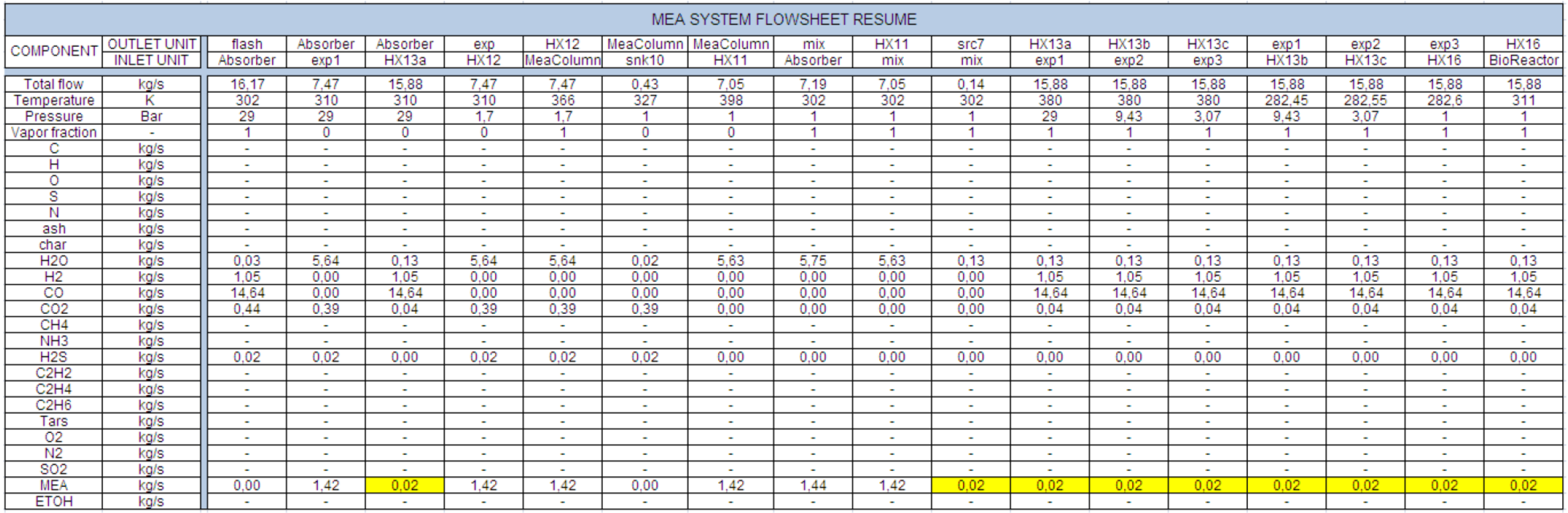


Figure 94: MEA System.



MEA COMPRESSION SECTION FLOWSHEET RESUME									
COMPONENT	OUTLET UNIT	compres4a	HX9a	HX9a	compres4b	HX9b	HX9b	flash1	flash1
	INLET UNIT	HX9a	snk12	compres4b	HX9b	snk13	flash1	snk14	assorber
Total flow	kg/s	16,30	0,09	16,21	16,21	0,00	16,21	0,04	16,17
Temperature	K	425,42	302,00	302,00	431,12	431,12	302,00	302,00	302,00
Pressure	Bar	10,77	10,77	10,77	29,00	29,00	29,00	29,00	29,00
Vapor fraction	-	1,00	0,00	1,00	1,00	0,00	1,00	0,00	1,00
C	kg/s	-	-	-	-	-	-	-	-
H	kg/s	-	-	-	-	-	-	-	-
O	kg/s	-	-	-	-	-	-	-	-
S	kg/s	-	-	-	-	-	-	-	-
N	kg/s	-	-	-	-	-	-	-	-
ash	kg/s	-	-	-	-	-	-	-	-
char	kg/s	-	-	-	-	-	-	-	-
H2O	kg/s	0,158	0,088	0,070	0,070	0,000	0,070	0,044	0,026
H2	kg/s	1,053	0,000	1,053	1,053	0,000	1,053	0,000	1,053
CO	kg/s	14,638	0,000	14,638	14,638	0,000	14,638	0,000	14,638
CO2	kg/s	0,437	0,000	0,437	0,437	0,000	0,437	0,000	0,437
CH4	kg/s	-	-	-	-	-	-	-	-
NH3	kg/s	-	-	-	-	-	-	-	-
H2S	kg/s	0,016	0,000	0,016	0,016	0,000	0,016	0,000	0,016
C2H2	kg/s	-	-	-	-	-	-	-	-
C2H4	kg/s	-	-	-	-	-	-	-	-
C2H6	kg/s	-	-	-	-	-	-	-	-
Tars	kg/s	-	-	-	-	-	-	-	-
O2	kg/s	-	-	-	-	-	-	-	-
N2	kg/s	-	-	-	-	-	-	-	-
SO2	kg/s	-	-	-	-	-	-	-	-
MEA	kg/s	-	-	-	-	-	-	-	-
ETOH	kg/s	-	-	-	-	-	-	-	-

Figure 95: MEA Compression Section Flowsheet Resume.



MEA SYSTEM FLOWSHEET RESUME

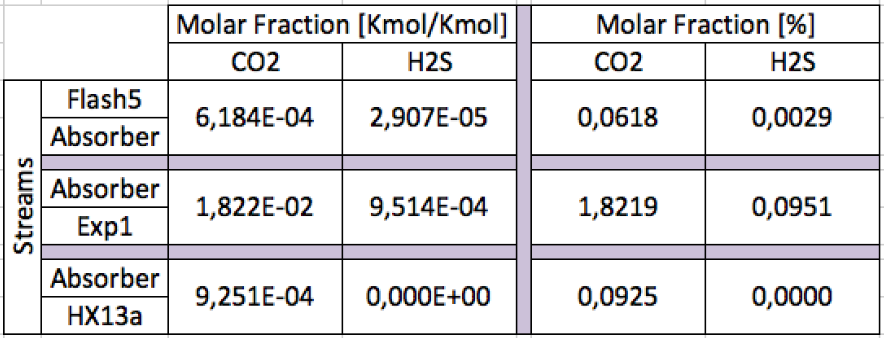
COMPONENT	OUTLET UNIT	flash	Absorber	Absorber	exp	HX12	MeaColumn	MeaColumn	mix	HX11	src7	HX13a	HX13b	HX13c	exp1	exp2	exp3	HX16
	INLET UNIT	Absorber	exp1	HX13a	HX12	MeaColumn	snk10	HX11	Absorber	mix	mix	exp1	exp2	exp3	HX13b	HX13c	HX16	BioReactor
Total flow	kg/s	16,17	7,47	15,88	7,47	7,47	0,43	7,05	7,19	7,05	0,14	15,88	15,88	15,88	15,88	15,88	15,88	15,88
Temperature	K	302	310	310	310	366	327	398	302	302	302	380	380	380	282,45	282,55	282,6	311
Pressure	Bar	29	29	29	1,7	1,7	1	1	1	1	1	29	9,43	3,07	9,43	3,07	1	1
Vapor fraction	-	1	0	0	0	1	0	0	1	1	1	1	1	1	1	1	1	1
C	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
O	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
S	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
N	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ash	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
char	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H2O	kg/s	0,03	5,64	0,13	5,64	5,64	0,02	5,63	5,75	5,63	0,13	0,13	0,13	0,13	0,13	0,13	0,13	0,13
H2	kg/s	1,05	0,00	1,05	0,00	0,00	0,00	0,00	0,00	0,00	0,00	1,05	1,05	1,05	1,05	1,05	1,05	1,05
CO	kg/s	14,64	0,00	14,64	0,00	0,00	0,00	0,00	0,00	0,00	0,00	14,64	14,64	14,64	14,64	14,64	14,64	14,64
CO2	kg/s	0,44	0,39	0,04	0,39	0,39	0,39	0,00	0,00	0,00	0,00	0,04	0,04	0,04	0,04	0,04	0,04	0,04
CH4	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NH3	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H2S	kg/s	0,02	0,02	0,00	0,02	0,02	0,02	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
C2H2	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C2H4	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C2H6	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Tars	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
O2	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
N2	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SO2	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MEA	kg/s	0,00	1,42	0,02	1,42	1,42	0,00	1,42	1,44	1,42	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02
ETOH	kg/s	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Figure 96: MEA System Flowsheet Resum

Remarks:

- The amount of water discharged from the heat exchanger is
  0.088 kg/s (≈ 18 %) into Snk12
  0.044 kg/s (≈ 18 %) into Snk14
- Compressors consume:
  (W_{comp4}) 3946 kW
  (W_{comp5}) 4031 kW.
- The amount of syngas to be purified entering the MEA System is 16.15 kg/s.

- *ABSORBER*:
  - The efficiencies for the recovery of sour gases are assumed to be 1 for H_2S and 0.9 for CO_2.
  - CO_2 and H_2S molar fractions are:



Streams		Molar Fraction [Kmol/Kmol]		Molar Fraction [%]	
		CO2	H2S	CO2	H2S
Streams	Flash5 Absorber	6,184E-04	2,907E-05	0,0618	0,0029
	Absorber Exp1	1,822E-02	9,514E-04	1,8219	0,0951
	Absorber HX13a	9,251E-04	0,000E+00	0,0925	0,0000

Figure 97: CO_2 and H_2S Molar Fraction.

  - The amount of carbon dioxide fed to the bioreactor (≈900 ppm) is acceptable because microorganisms are highly tolerant.
  - The outlet temperature is calculated from the energy balance and is: T^{out} = 310 K.

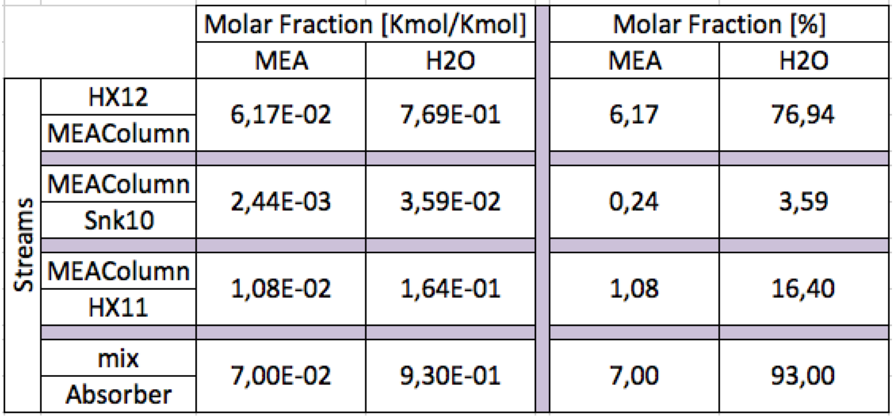
- *COLUMN:*
  - The total amount of solution of MEA needed to absorb the H_2S and the CO_2 from the gas stream is calculated as a function of the amount of sour gases eliminated with a molar ratio of 1:1 between the sour gas (CO_2 and H_2S) and the amine.

$$MEA_{Absorber} = \frac{MW_{MEA}}{C_{MEA} * \alpha} * \left(\frac{Recovery_{CO2} * CO2_{Absorber}}{MW_{CO2}} + \frac{Recovery_{H2S} * H2S_{Absorber}}{MW_{H2S}} \right)$$

The amount of mea is $MEA_{Absorber}$ = 1.438 kg/s.

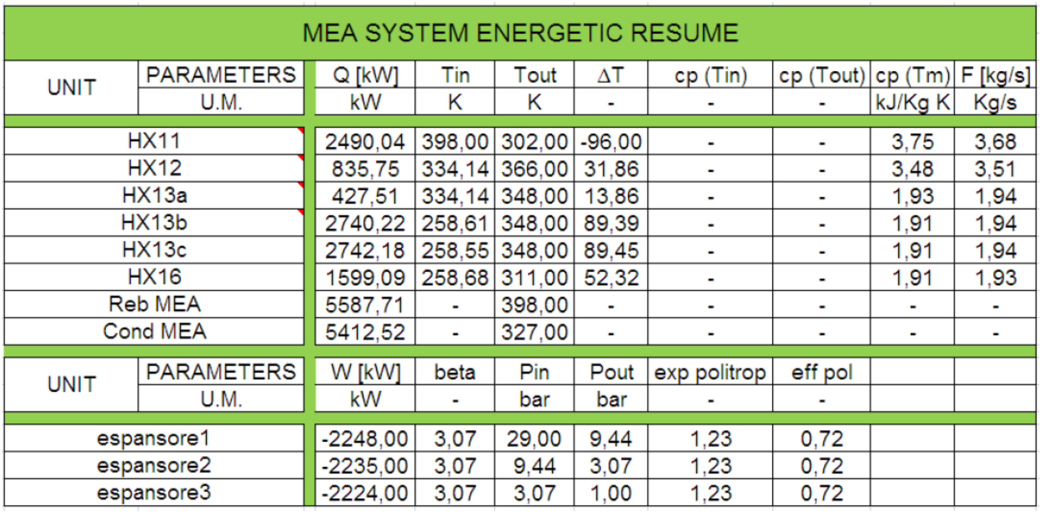
The ratio between the sour gas incoming and the MEA solution is $X_{SourGas/MEA}$ = 0.3 $kg_{SourGas}/kg_{MEA}$ (≈30%)

- The concentration of solution between MEA and water is 25% $kg_{MEA} \backslash kg_{H2O}$.
- In order to calculate the MEA loss, typical humidification models are used. Some of the MEA is lost with the sour gases, which are saturated with MEA (on the top of the absorber and on the top of the column).
- The efficiencies for the recovery of sour gases are assumed to be 1 for H_2S and 1 for CO_2.



		Molar Fraction [Kmol/Kmol]		Molar Fraction [%]	
		MEA	H2O	MEA	H2O
Streams	HX12 MEAColumn	6,17E-02	7,69E-01	6,17	76,94
	MEAColumn Snk10	2,44E-03	3,59E-02	0,24	3,59
	MEAColumn HX11	1,08E-02	1,64E-01	1,08	16,40
	mix Absorber	7,00E-02	9,30E-01	7,00	93,00

Figure 98: MEA and H_2O Molar Fraction.



MEA SYSTEM ENERGETIC RESUME									
UNIT	PARAMETERS	Q [kW]	Tin	Tout	ΔT	cp (Tin)	cp (Tout)	cp (Tm)	F [kg/s]
	U.M.	kW	K	K	-	-	-	kJ/Kg K	Kg/s
HX11		2490,04	398,00	302,00	-96,00	-	-	3,75	3,68
HX12		835,75	334,14	366,00	31,86	-	-	3,48	3,51
HX13a		427,51	334,14	348,00	13,86	-	-	1,93	1,94
HX13b		2740,22	258,61	348,00	89,39	-	-	1,91	1,94
HX13c		2742,18	258,55	348,00	89,45	-	-	1,91	1,94
HX16		1599,09	258,68	311,00	52,32	-	-	1,91	1,93
Reb MEA		5587,71	-	398,00	-	-	-	-	-
Cond MEA		5412,52	-	327,00	-	-	-	-	-
UNIT	PARAMETERS	W [kW]	beta	Pin	Pout	exp politrop	eff pol		
	U.M.	kW	-	bar	bar	-	-		
espansore1		-2248,00	3,07	29,00	9,44	1,23	0,72		
espansore2		-2235,00	3,07	9,44	3,07	1,23	0,72		
espansore3		-2224,00	3,07	3,07	1,00	1,23	0,72		

Figure 99: MEA System Energetic Resume.

4.4 *Fermentation*

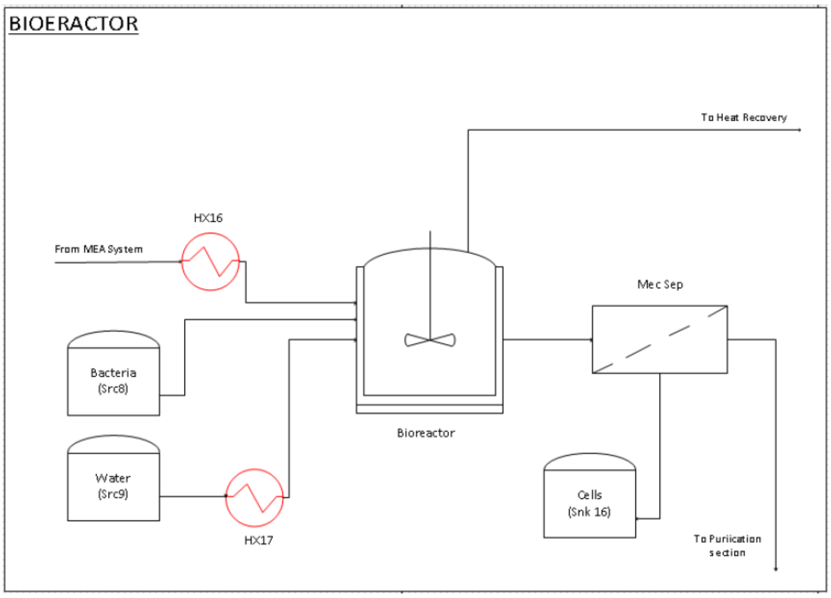
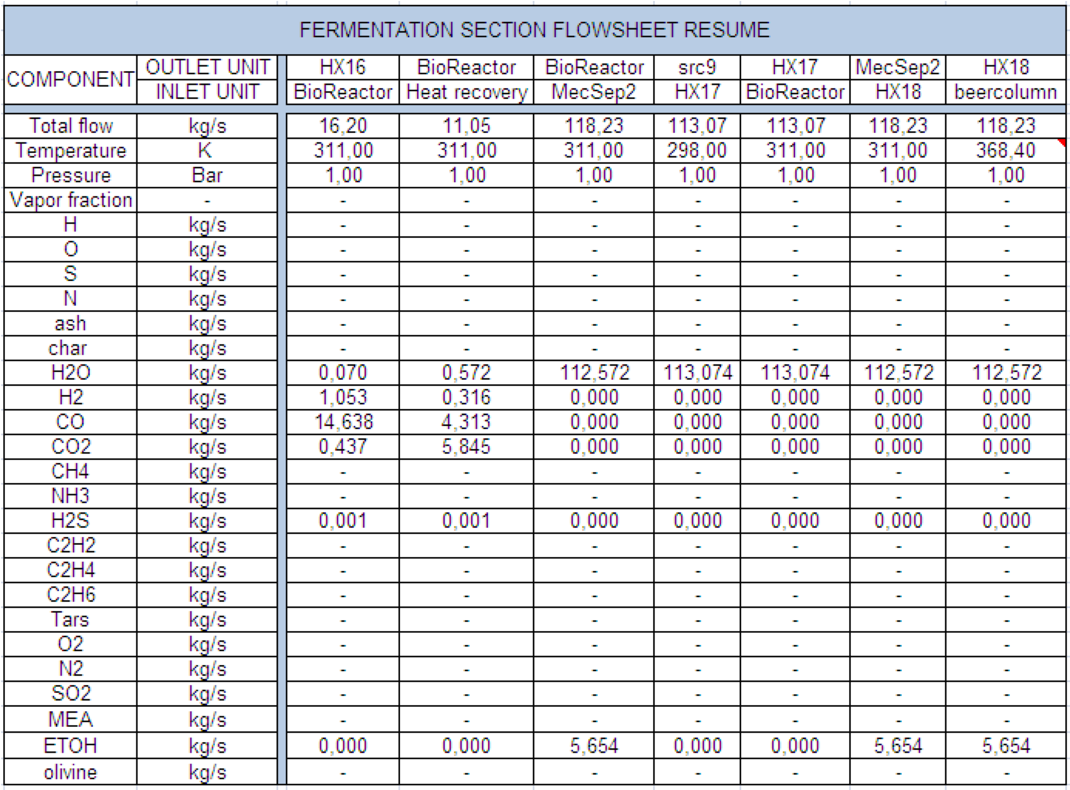


Figure 100: Bioreactor.

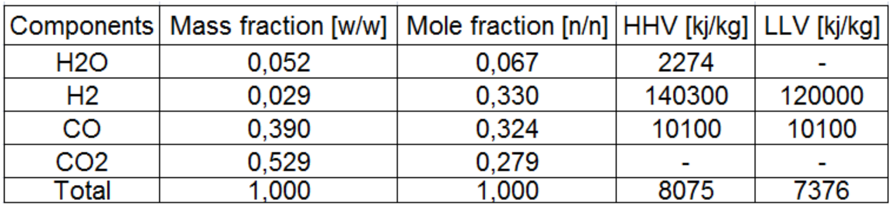


FERMENTATION SECTION FLOWSHEET RESUME								
COMPONENT	OUTLET UNIT	HX16	BioReactor	BioReactor	src9	HX17	MecSep2	HX18
	INLET UNIT	BioReactor	Heat recovery	MecSep2	HX17	BioReactor	HX18	beercolumn
Total flow	kg/s	16,20	11,05	118,23	113,07	113,07	118,23	118,23
Temperature	K	311,00	311,00	311,00	298,00	311,00	311,00	368,40
Pressure	Bar	1,00	1,00	1,00	1,00	1,00	1,00	1,00
Vapor fraction	-	-	-	-	-	-	-	-
H	kg/s	-	-	-	-	-	-	-
O	kg/s	-	-	-	-	-	-	-
S	kg/s	-	-	-	-	-	-	-
N	kg/s	-	-	-	-	-	-	-
ash	kg/s	-	-	-	-	-	-	-
char	kg/s	-	-	-	-	-	-	-
H2O	kg/s	0,070	0,572	112,572	113,074	113,074	112,572	112,572
H2	kg/s	1,053	0,316	0,000	0,000	0,000	0,000	0,000
CO	kg/s	14,638	4,313	0,000	0,000	0,000	0,000	0,000
CO2	kg/s	0,437	5,845	0,000	0,000	0,000	0,000	0,000
CH4	kg/s	-	-	-	-	-	-	-
NH3	kg/s	-	-	-	-	-	-	-
H2S	kg/s	0,001	0,001	0,000	0,000	0,000	0,000	0,000
C2H2	kg/s	-	-	-	-	-	-	-
C2H4	kg/s	-	-	-	-	-	-	-
C2H6	kg/s	-	-	-	-	-	-	-
Tars	kg/s	-	-	-	-	-	-	-
O2	kg/s	-	-	-	-	-	-	-
N2	kg/s	-	-	-	-	-	-	-
SO2	kg/s	-	-	-	-	-	-	-
MEA	kg/s	-	-	-	-	-	-	-
ETOH	kg/s	0,000	0,000	5,654	0,000	0,000	5,654	5,654
olivine	kg/s	-	-	-	-	-	-	-

Figure 101: Fermentation Section Flosheet Resume.

Remarks:

- Microorganisms are able to produce ethanol up to a maximum concentration of 5% w/w. It causes a high consumption of water because every 5 L of Ethanol, 95 L of water must be fed at 38°C. Water must be preheated at reactor operating temperature, applying 6145.7 kW.
- Unreacted gases are extracted from the upper side of the reactor and sent to an energy recovery unit. It is possible to use this unreacted stream, consisting of H_2 and CO, as a fuel in a steam boiler to generate low pressure steam reusable in the process. The stream composition is:



Components	Mass fraction [w/w]	Mole fraction [n/n]	HHV [kj/kg]	LLV [kj/kg]
H2O	0,052	0,067	2274	-
H2	0,029	0,330	140300	120000
CO	0,390	0,324	10100	10100
CO2	0,529	0,279	-	-
Total	1,000	1,000	8075	7376

Figure 102: Stream Composition.

It is assumed a release of heat, obtainable from the combustion of H_2 and CO, equal to the 75% of the calorific value of the current.[159] Simulating with Aspen HYSYS an heat exchanger, it is imposed an inlet of water at room temperature and a pressure of 6 bar, and a quantity of energy equal to that hypothesized is applied to the water stream.

The result is the generation of a flow rate of 22.74 kg/s of LP steam with a combustion efficiency of 75% (referred to LLV) and 15.6 kg/s with a combustion efficiency of 50% (reported the LLV)

4.5 Purification

4.5.1 Beer column and Rectification Column

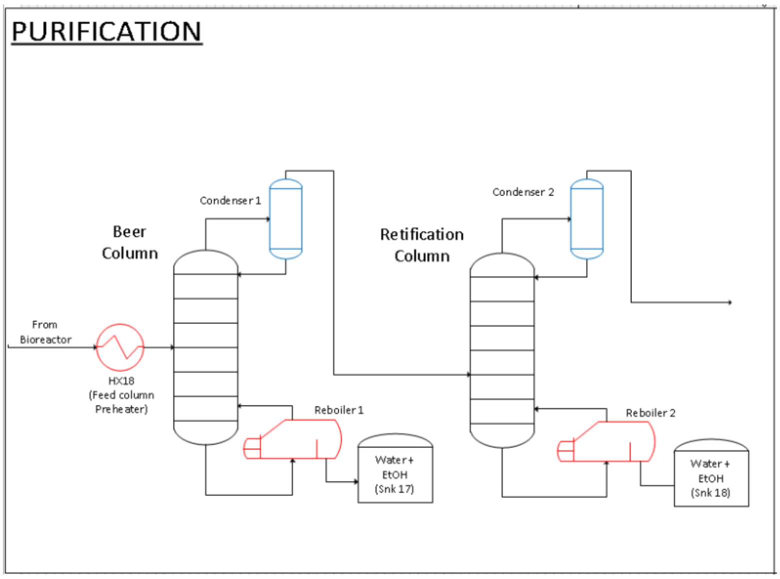
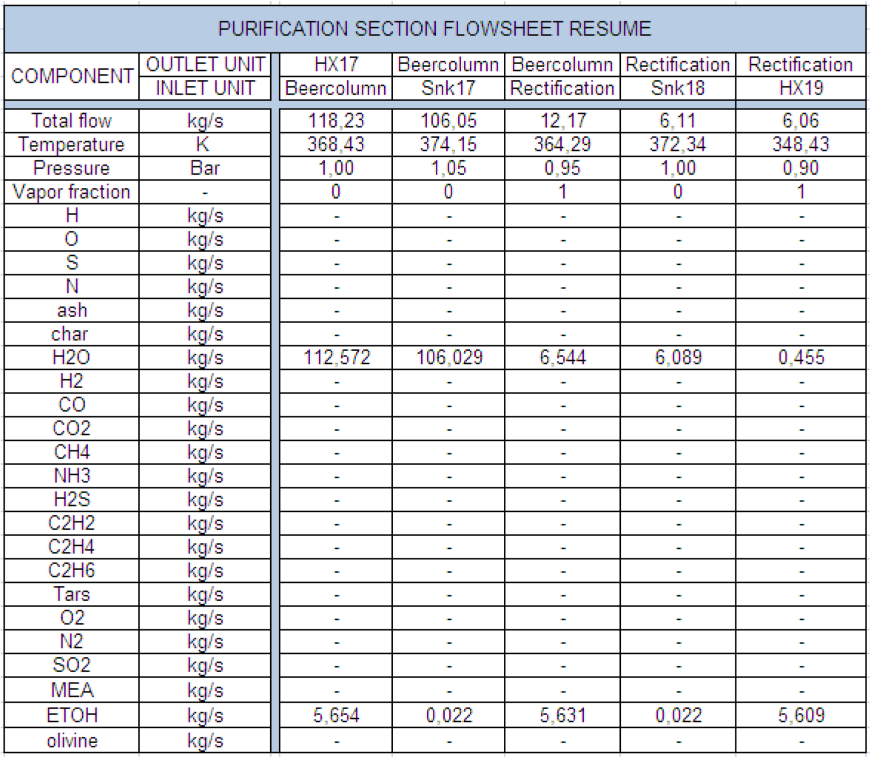


Figure 103: Purification.



PURIFICATION SECTION FLOWSHEET RESUME						
COMPONENT	OUTLET UNIT	HX17	Beercolumn	Beercolumn	Rectification	Rectification
	INLET UNIT	Beercolumn	Snk17	Rectification	Snk18	HX19
Total flow	kg/s	118,23	106,05	12,17	6,11	6,06
Temperature	K	368,43	374,15	364,29	372,34	348,43
Pressure	Bar	1,00	1,05	0,95	1,00	0,90
Vapor fraction	-	0	0	1	0	1
H	kg/s	-	-	-	-	-
O	kg/s	-	-	-	-	-
S	kg/s	-	-	-	-	-
N	kg/s	-	-	-	-	-
ash	kg/s	-	-	-	-	-
char	kg/s	-	-	-	-	-
H2O	kg/s	112,572	106,029	6,544	6,089	0,455
H2	kg/s	-	-	-	-	-
CO	kg/s	-	-	-	-	-
CO2	kg/s	-	-	-	-	-
CH4	kg/s	-	-	-	-	-
NH3	kg/s	-	-	-	-	-
H2S	kg/s	-	-	-	-	-
C2H2	kg/s	-	-	-	-	-
C2H4	kg/s	-	-	-	-	-
C2H6	kg/s	-	-	-	-	-
Tars	kg/s	-	-	-	-	-
O2	kg/s	-	-	-	-	-
N2	kg/s	-	-	-	-	-
SO2	kg/s	-	-	-	-	-
MEA	kg/s	-	-	-	-	-
ETOH	kg/s	5,654	0,022	5,631	0,022	5,609
olivine	kg/s	-	-	-	-	-

Figure 104: Purification Section Flowsheet Resume.

4.5.2 *Molecular sieves*

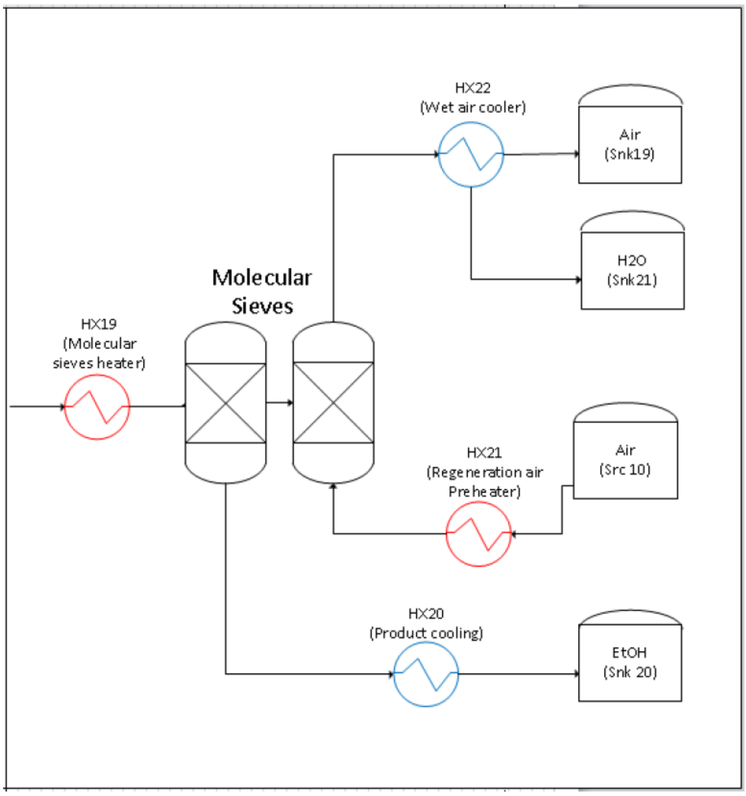
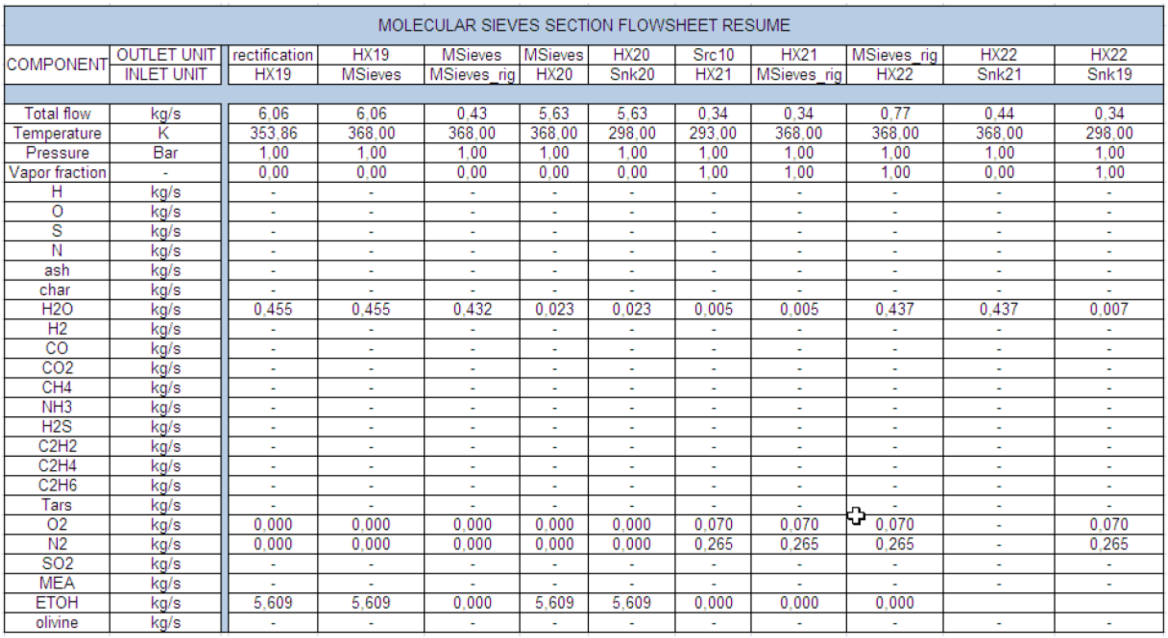


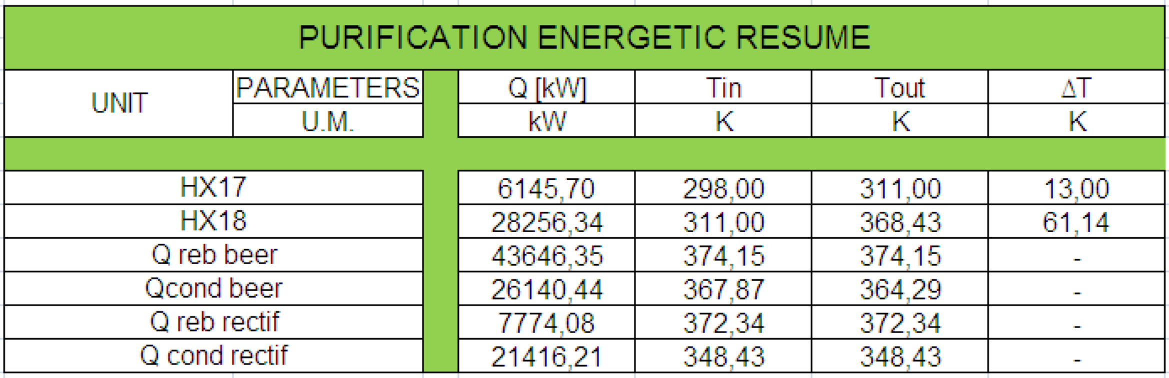
Figure 105: Molecular Sieves.



MOLECULAR SIEVES SECTION FLOWSHEET RESUME

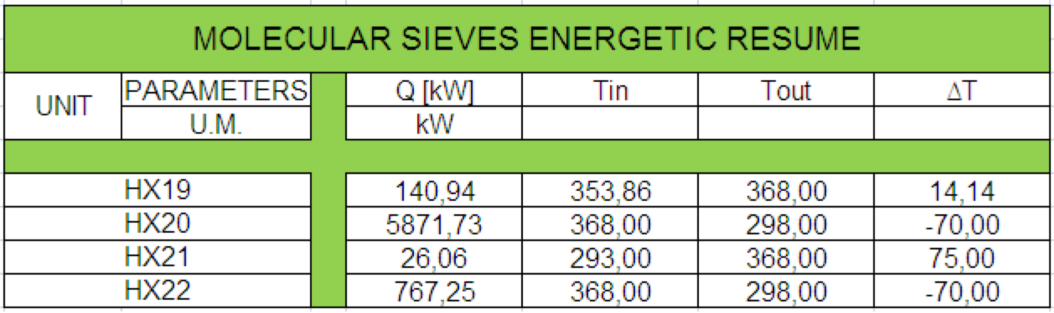
COMPONENT	OUTLET UNIT	rectification	HX19	MSieves	MSieves	HX20	Src10	HX21	MSieves_rig	HX22	HX22
	INLET UNIT	HX19	MSieves	MSieves_rig	HX20	Snk20	HX21	MSieves_rig	HX22	Snk21	Snk19
Total flow	kg/s	6,06	6,06	0,43	5,63	5,63	0,34	0,34	0,77	0,44	0,34
Temperature	K	353,86	368,00	368,00	368,00	298,00	293,00	368,00	368,00	368,00	298,00
Pressure	Bar	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00
Vapor fraction	-	0,00	0,00	0,00	0,00	0,00	1,00	1,00	1,00	0,00	1,00
H	kg/s	-	-	-	-	-	-	-	-	-	-
O	kg/s	-	-	-	-	-	-	-	-	-	-
S	kg/s	-	-	-	-	-	-	-	-	-	-
N	kg/s	-	-	-	-	-	-	-	-	-	-
ash	kg/s	-	-	-	-	-	-	-	-	-	-
char	kg/s	-	-	-	-	-	-	-	-	-	-
H2O	kg/s	0,455	0,455	0,432	0,023	0,023	0,005	0,005	0,437	0,437	0,007
H2	kg/s	-	-	-	-	-	-	-	-	-	-
CO	kg/s	-	-	-	-	-	-	-	-	-	-
CO2	kg/s	-	-	-	-	-	-	-	-	-	-
CH4	kg/s	-	-	-	-	-	-	-	-	-	-
NH3	kg/s	-	-	-	-	-	-	-	-	-	-
H2S	kg/s	-	-	-	-	-	-	-	-	-	-
C2H2	kg/s	-	-	-	-	-	-	-	-	-	-
C2H4	kg/s	-	-	-	-	-	-	-	-	-	-
C2H6	kg/s	-	-	-	-	-	-	-	-	-	-
Tars	kg/s	-	-	-	-	-	-	-	-	-	-
O2	kg/s	0,000	0,000	0,000	0,000	0,000	0,070	0,070	0,070	-	0,070
N2	kg/s	0,000	0,000	0,000	0,000	0,000	0,265	0,265	0,265	-	0,265
SO2	kg/s	-	-	-	-	-	-	-	-	-	-
MEA	kg/s	-	-	-	-	-	-	-	-	-	-
ETOH	kg/s	5,609	5,609	0,000	5,609	5,609	0,000	0,000	0,000		
olivine	kg/s	-	-	-	-	-	-	-	-	-	-

Figure 106: Molecular Sieves Section Flowsheet Resume.



PURIFICATION ENERGETIC RESUME					
UNIT	PARAMETERS	Q [kW]	Tin	Tout	ΔT
	U.M.	kW	K	K	K
HX17		6145,70	298,00	311,00	13,00
HX18		28256,34	311,00	368,43	61,14
Q reb beer		43646,35	374,15	374,15	-
Qcond beer		26140,44	367,87	364,29	-
Q reb rectif		7774,08	372,34	372,34	-
Q cond rectif		21416,21	348,43	348,43	-

Figure 107: Purification Energetic Resume.



MOLECULAR SIEVES ENERGETIC RESUME					
UNIT	PARAMETERS	Q [kW]	Tin	Tout	ΔT
	U.M.	kW			
HX19		140,94	353,86	368,00	14,14
HX20		5871,73	368,00	298,00	-70,00
HX21		26,06	293,00	368,00	75,00
HX22		767,25	368,00	298,00	-70,00

Figure 108: Molecular Sieves Energetic Resume.

Remarks:

- The results of the purification section were chosen from those obtained with ASPEN HYSYS because they are more rigorous than the ones simulated with GAMS.
- The separation of the outlet stream from the bioreactor is energetically expensive because the composition of ethanol is only 5% wt. Indeed, the heat exchanger that preheats the inlet stream until bubble conditions, must provide a power of 28256.34 kW.
- Columns work to ensure a final purity of 92.5 wt% ethanol, deliberately close to the azeotropic composition. From the graphic we see that as we move closer to the azeotropic composition, the cost of separation increases because columns have to be designed with more trays and a higher reflux ratio.

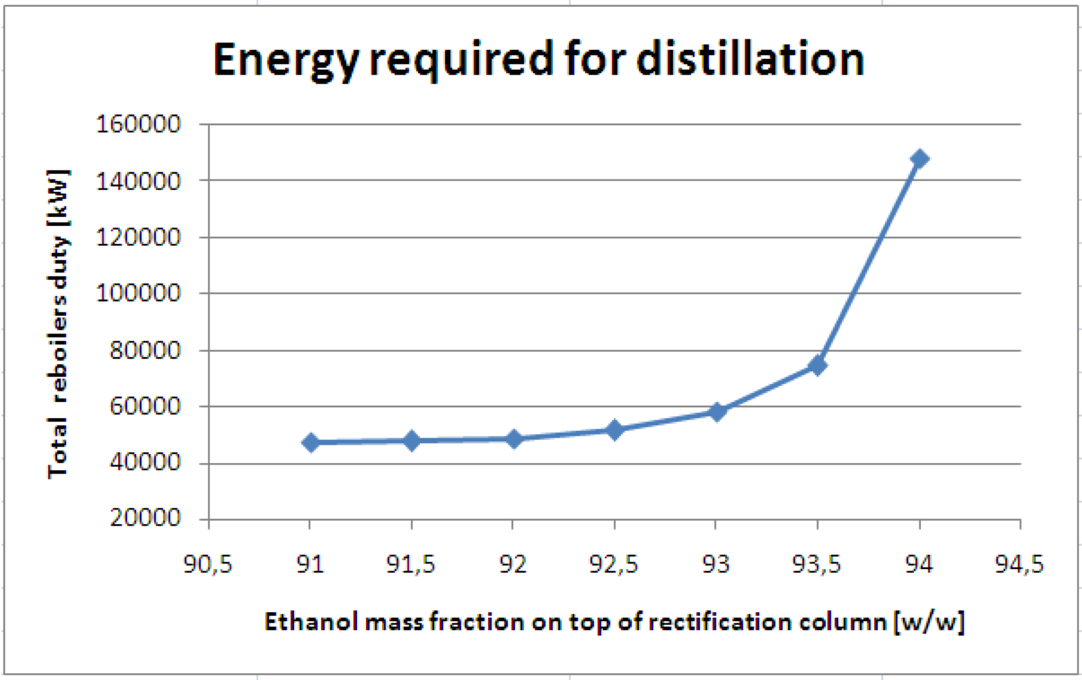


Figure 109: Energy Requiered for Distillation.

The power required can be seen in figure 107.

The mixture separation with ethanol concentrations lower than 80wt% is rather easy from the physical point of view. Moreover, the minimum number of theoretical trays in the beer column, required to obtain a purity of 40 wt% of ethanol, is 3.74. In the rectification column, instead, 5.39 theoretical trays are needed to obtain a purity of 92.5 wt% of ethanol.
These values were obtained from short-cut models that follow Fenske equation for the calculation of the minimum number of trays (infinite reflux ratio).

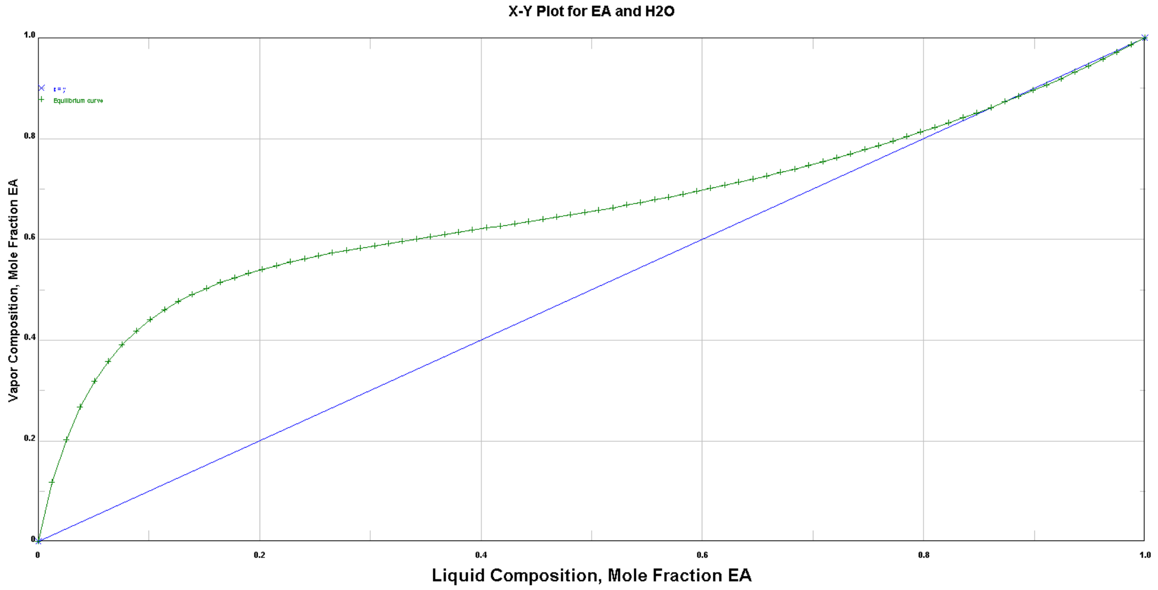


Figure 110: Molar Vapor-Liquid H_2O-EtOH Composition.

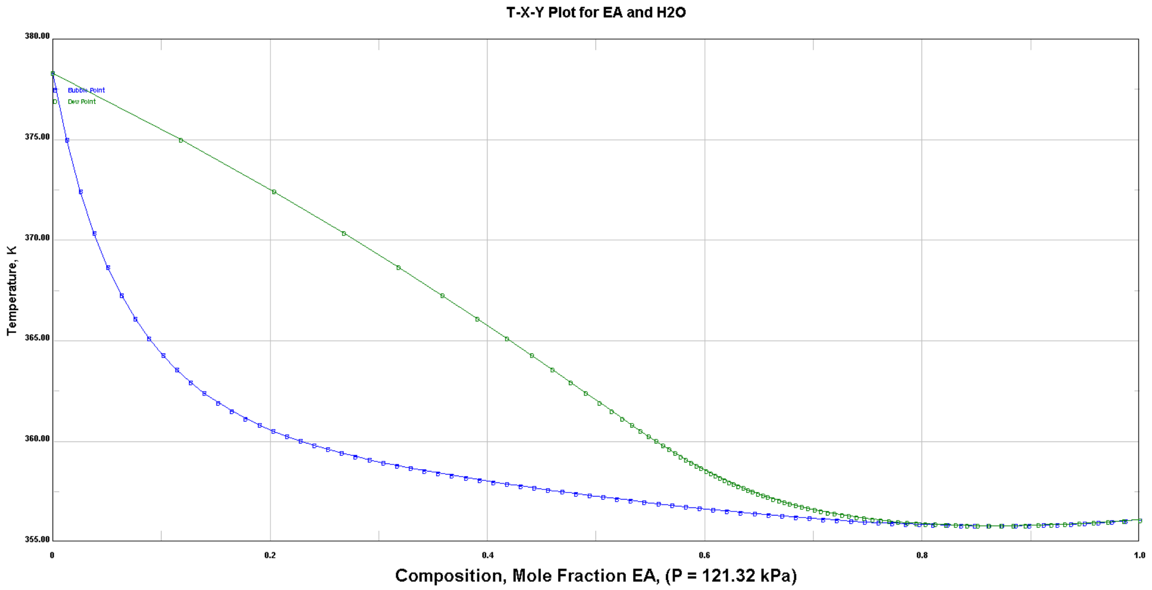


Figure 111: Variation of the Molar Vapor-Liquid H_2O-EtOH Composition.

Actually, separation is more complex with the presence of many reaction byproducts (higher alcohols) because the columns need a higher number of trays and side cuts.

Using process simulation carried out with the short-cut columns of ASPEN HYSYS, numerous problems were reported:

- The condenser and reboiler duties of the beer column have opposite signs; physically, it means that heat is provided to the condenser and that it is removed from the reboiler.
- Duties absolute values (assuming a sign error in the duty estimation) increase when operating specific requests are less restrictive.
- The minimum reflux ratio of beer column is 1.294. Anyways, this value and even lower ones, when they are used in the simulation of a rigorous distillation column, make it possible to simulate the process and to achieve the desired purity, creating doubts about results interpretation.
- Short-cut columns were replaced with rigorous ones because of the problems encountered. The rigorous columns are more reliable because they do not show physical mistakes, respecting variables and process specifications from literature.

Columns degrees of freedom (3 FD) have been saturated imposing:

- Ethanol recovery at the head of two columns is 0.996.
- The number of trays in the two columns, calculated via the short-cut method (with the Fenske equation), have been increased to take account of an overall efficiency of 50% (Murphree efficiency).
- Ethanol purity on the top of rectification column is 92.5 wt%.
- Reflux ratio in the beer column is set to 1.3 based on considerations of reduction reboiler duty.

4.6 Energy Integration

Analyzing flowsheets, it is possible to reduce the energy consumption of the process by acting on process streams integration.

Solutions are proposed to reduce energy consumption, re-estimating the energy system consumption, which will bring a considerable saving on the final product.

Possible solutions are:

- use the process stream, which leaves the tar reformer, to feed heat exchangers HX1 and HX2, and use the available thermal energy to generate low pressure steam. The results are shown in Figure 112 and the integration streams is shown in Figure 111.

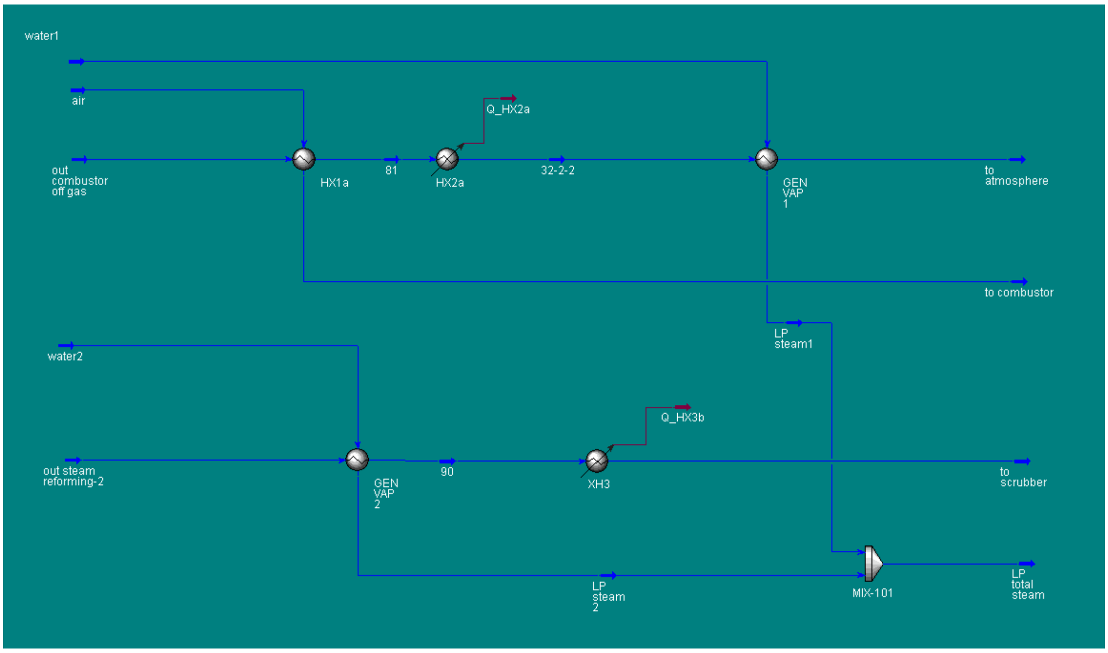
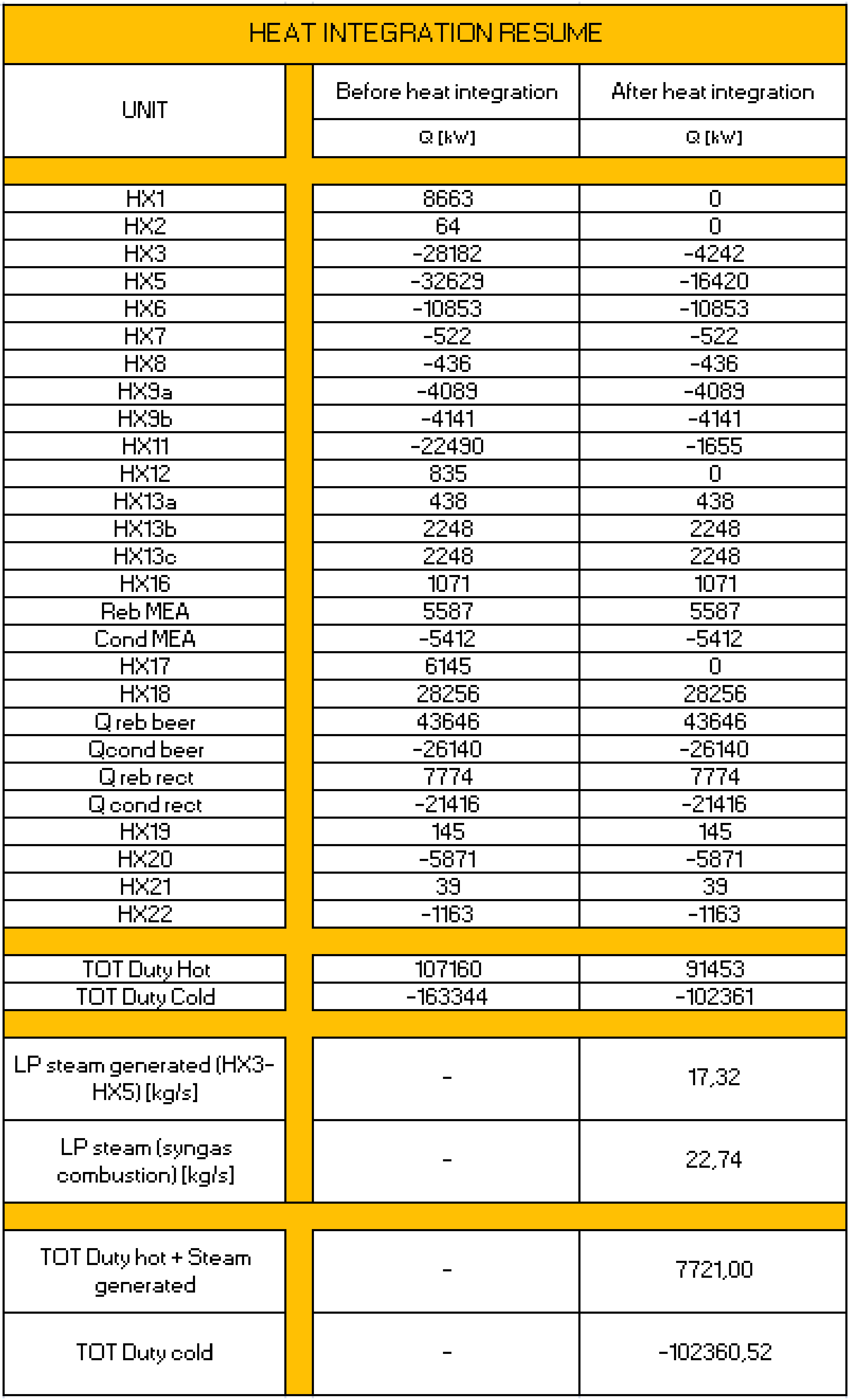


Figure 112: HX1 and HX2 Energy Integration.

- Use MEA stream, regenerated into the regeneration column (Column MEA), to provide heat to HX12. This solution has two advantages: it saves 835.75 kW of heat that should have been supplied to HX12 heat exchanger, and it permits to save the heat that should have been removed from the MEA stream in HX11 heat exchanger, which is now 1655 kW.
- Unreacted gas combustion coming out from bioreactor (see fermentation results table).

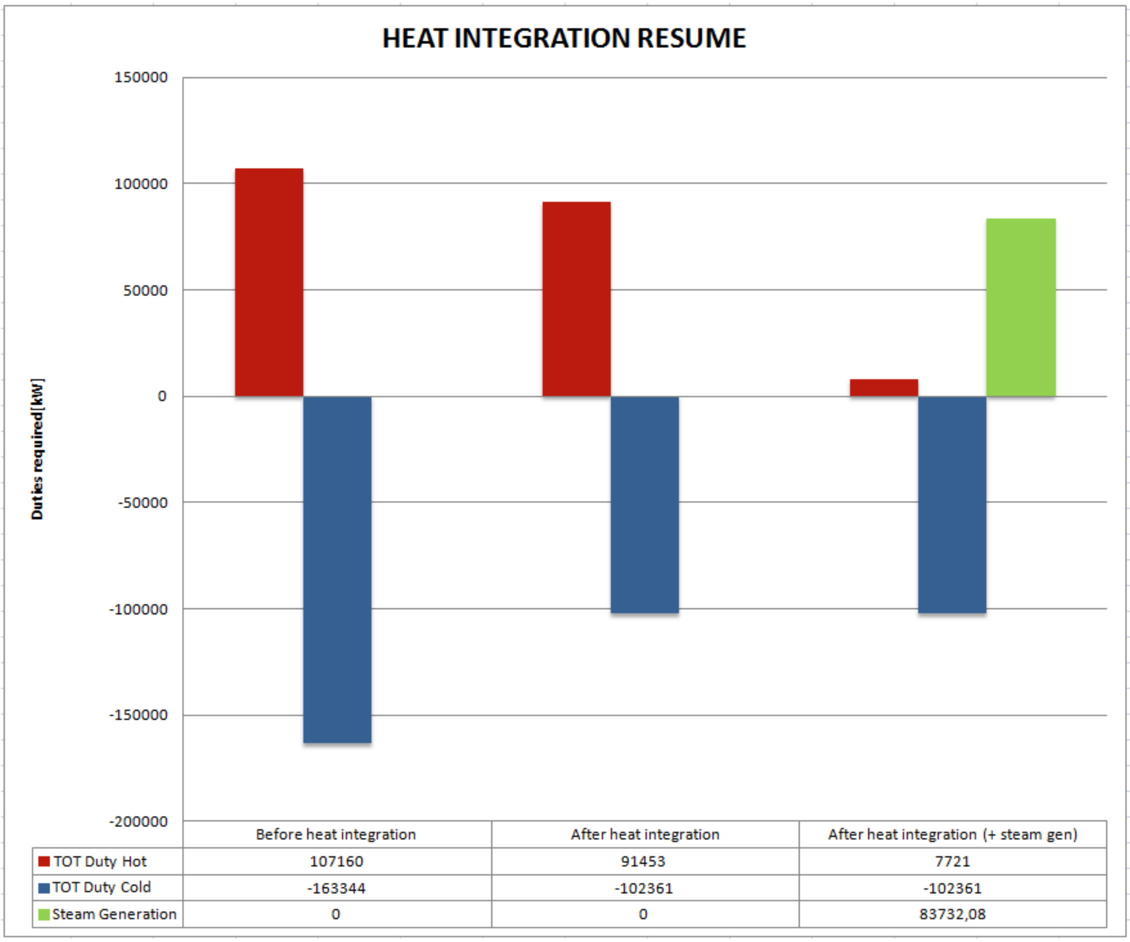
- Use outgoing streams (composed mainly of water) from the bottom of distillation columns (mass fraction of water <0.5 wt%) as a water supply to the bioreactor. In this way it is possible to save more than 90% of fresh water that should have been fed to the fermenter and save all the heat required to preheat this water.

Figure 112b summarizes energy consumption in terms of hot and cold duties, required by the plant for the production of 125 Ml / year of ethanol to 99.6% wt. TOT Duty Hot + steam reforming is the heat to be supplied to the process taking into account the surplus steam generated due to energy recovery. Heat reduction is 91.6%, which allows economical savings, since providing calories is much more expensive than taking them away



HEAT INTEGRATION RESUME		
UNIT	Before heat integration	After heat integration
	Q [kW]	Q [kW]
HX1	8663	0
HX2	64	0
HX3	-28182	-4242
HX5	-32629	-16420
HX6	-10853	-10853
HX7	-522	-522
HX8	-436	-436
HX9a	-4089	-4089
HX9b	-4141	-4141
HX11	-22490	-1655
HX12	835	0
HX13a	438	438
HX13b	2248	2248
HX13c	2248	2248
HX16	1071	1071
Reb MEA	5587	5587
Cond MEA	-5412	-5412
HX17	6145	0
HX18	28256	28256
Q reb beer	43646	43646
Qcond beer	-26140	-26140
Q reb rect	7774	7774
Q cond rect	-21416	-21416
HX19	145	145
HX20	-5871	-5871
HX21	39	39
HX22	-1163	-1163
TOT Duty Hot	107160	91453
TOT Duty Cold	-163344	-102361
LP steam generated (HX3-HX5) [kg/s]	-	17,32
LP steam (syngas combustion) [kg/s]	-	22,74
TOT Duty hot + Steam generated	-	7721,00
TOT Duty cold	-	-102360,52

Figure 113a: Heat Integration Resume.



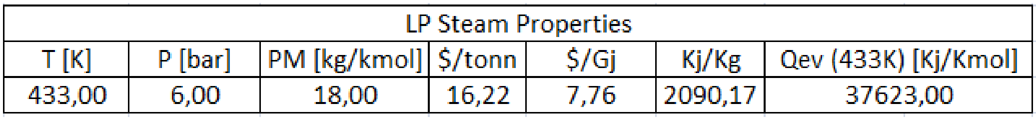
	Before heat integration	After heat integration	After heat integration (+ steam gen)
🟥 TOT Duty Hot	107160	91453	7721
🟦 TOT Duty Cold	-163344	-102361	-102361
🟩 Steam Generation	0	0	83732,08

Figure 113b: Heat Integration Resume.

4.7 *Process Analysis*

Possible solution:

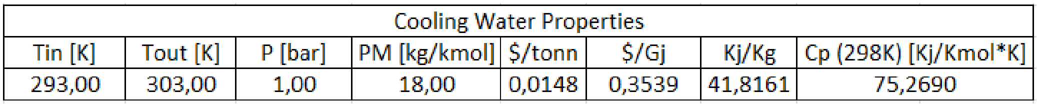
- Heat exchangers that provide heat, using, as a service fluid, LP saturated steam at 5 barg and a temperature of 158.9°C. After making energy integrations, the highest temperature to be reached is 125°C, which is the temperature at the reboiler of MEA regeneration column.



LP Steam Properties						
T [K]	P [bar]	PM [kg/kmol]	$/tonn	$/Gj	Kj/Kg	Qev (433K) [Kj/Kmol]
433,00	6,00	18,00	16,22	7,76	2090,17	37623,00

Figure 114: LP Steam Properties.

- To cool process streams, cooling water at 20 ° C is used.



Cooling Water Properties							
Tin [K]	Tout [K]	P [bar]	PM [kg/kmol]	$/tonn	$/Gj	Kj/Kg	Cp (298K) [Kj/Kmol*K]
293,00	303,00	1,00	18,00	0,0148	0,3539	41,8161	75,2690

Figure 115: Cooling Water Properties.

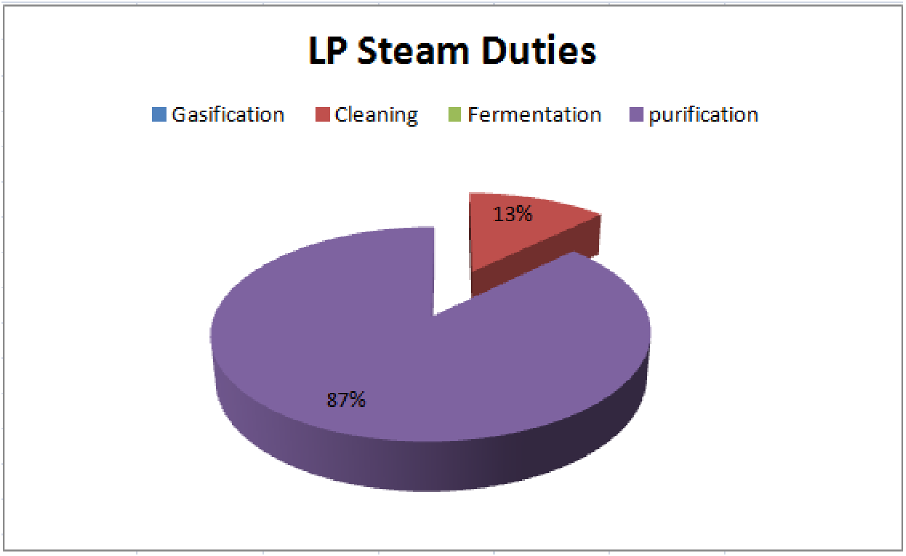


Figure 116: LP Steam Duties.

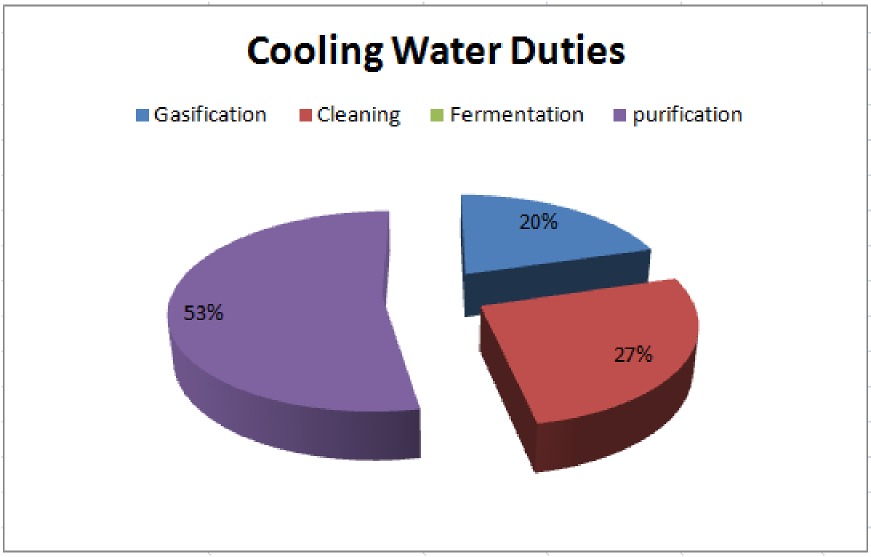


Figure 117: Cooling Water Duties.

5. ECONOMICAL EVALUATION

5.1 Costs correlations

The accuracy of an economical evaluation depends on the amount of design detail available: the accuracy of the cost data available and the time spent on preparing the evaluation. In this project an approximate evaluation was carried out. Preliminary (approximate) evaluations have a typical 30% of uncertainty, and they are used for the estimation of the product final cost.

An approximate capital cost evaluation can be obtained from a knowledge of the cost of previous projects using the same manufacturing process.

The method usually used to update historical cost data makes use of published cost indices. Project capital cost is related to capacity and year, of an evaluation by the equation:

$$C_2 = C_1 \left(\frac{P_2}{P_1}\right)^n \left(\frac{I_2}{I_1}\right)$$

where:

C_2 = capital cost of the project with capacity P_2

C_1 = capital cost of the project with capacity P_1

I_2 = Cost index in evaluation year of project 2

I_1 = Cost index in evaluation year of project 1

n = index traditionally taken as 0.6 (six-tenths rule)

The equipment cost correlations are obtained directly from the source[http://www.matche.com/equipcost/Default.html]. Later, the final cost of the equipment is updated to 2009 prices (CEPCI May 09 = 509,1).[160]

5.1.1 *Evaluation of purchased equipment cost (direct cost)*

The addition of a fluidized bed gasifier (low pressure indirect gasification) is cheaper than the fixed-bed gasifier (high pressure direct gasification with air or oxygen) according to the evaluation of costs.

The costs of the two types of gasifiers are estimated using the following equations:

$$C_{indirect,gasifier} = 1049500 * (Flow[kg/s])^{0.698}$$

$$C_{direct,gasifier} = 1530000 * (Flow[kg/s])^{0.752}$$

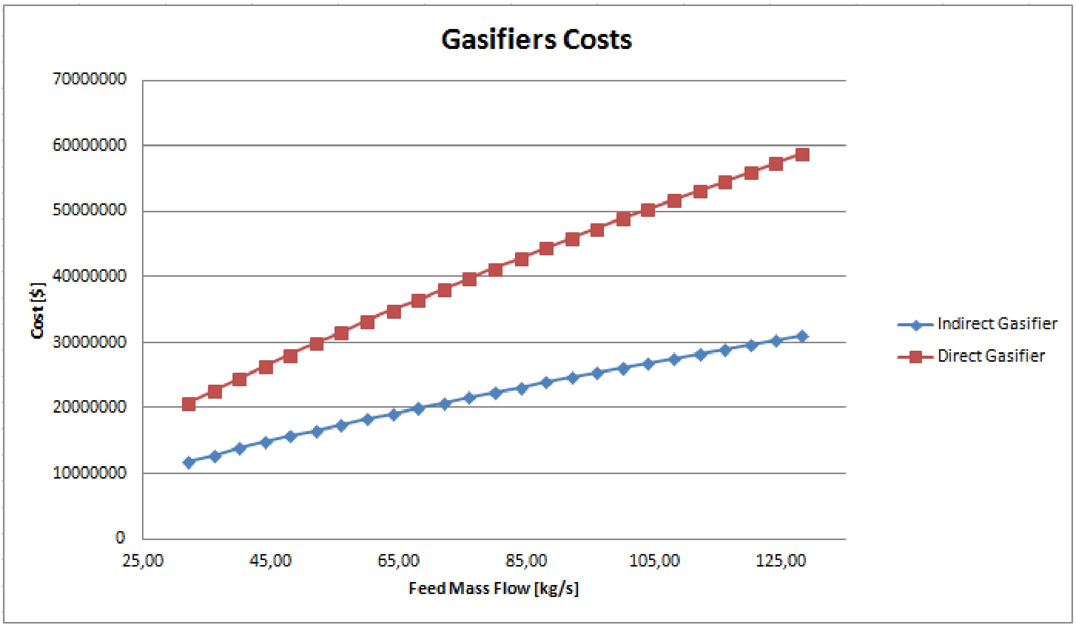


Figure 118: Gasifier Costs.

According to the cost evaluations and using literature information regarding different types of gasifiers[73] the cost of gasification section is appropriately scaled and updated.

The equations for the others units are:

- Washing unit:

$$C_{Wash} = 28{,}899 \cdot \left(\frac{Load_{(Solids+water)}(lb/h)}{277 \cdot d_{screw}(in) - 494} \right)$$

- Mechanical Separation:

$$C_{MechSep} = 892 \cdot d \cdot \left(\frac{Load(gal/\min)}{200(gal/\min)} \right)$$

- Vessels:

$$Volume = \left(\frac{\dot{m}}{\rho} \right) \tau$$

L = 4Dc

$$D_C = \sqrt[3]{\frac{6 \cdot Volume}{7 \cdot \pi}}$$

$$W = \rho_{steel} \left(\pi \left[\left(\frac{D_c}{2} + e \right)^2 - \left(\frac{D_c}{2} \right)^2 \right] L + \frac{4}{3} \pi \left[\left(\frac{D_c}{2} + e \right)^3 - \left(\frac{D_c}{2} \right)^3 \right] \right)$$

e = 0.0023 + 0.003Dc (Sinot, 1999)

- MEA Column:

$$C_{column}(\$) = 56.181 \, .W^{0.878}$$

- Storage Tankes:

$$C_{Str} = 5723.3 \cdot \mathrm{Volume}^{0.65}$$

- Fermentation tanks:

$$C_{Fermentors} = 66532 \cdot \mathrm{Volume}^{0.5}$$

$$Volume = \left(\frac{\dot{m}}{\rho} \right) \tau$$

- Compressor costs:

For Low pressures till 125 psi $C_{Compressor} = 302 \cdot P(kW) + 32650$

For pressure till 1000psi $C_{Compressor} = 2283.6 \cdot P(kW)^{0,8302}$

- Gasifiers:

  $C_{Gasifier} = 1049500 Flow(kg/s)^{0,698}$

- Cyclons:

  $C_{Cyclon} = 4027.9 \cdot Flow(m^3/s)^{0,894}$

- Electrostatic precipitator and filter:

  $C_{PE} = 4572.2 \cdot Flow(m^3/s) + 154397$

  $C_{Filter} = 4943 \cdot Flow(m^3/s) + 17244$

- Wet Scrubber:

  $C_{Scrubber} = 4796.1 \cdot Flow(m^3/s) + 10173$

- Molecular sieves and PSA systems:

  Molecular sieves with a bulk density of 45 lb/ft$^{3.}$

$$\text{Volume of bed} = \frac{\text{Bed size}}{\text{Bulk density}} = \frac{1.1 \cdot \text{Mass(Kg)}}{41.5\frac{\text{lb}}{\text{ft}^3} \cdot 0.454\ \frac{\text{Kg}}{\text{lb}} \cdot (\frac{1\ \text{ft}}{0.3048\ \text{m}})^3}$$

  The price is around 1000$ per ton either for zeolite 13x 5A or silica gel (Shandong Sinchem Silica gel Co)

  $C_{MS} = 2.(\cos t\ of\ bed + 56.181\ W^{0.878})$

- Heat exchangers:

  $C_{\text{Reboiler}} = 734.58\text{A} - 5961.5$

$C = 293.59\text{A}^{1.4915}$ A < 25m^2

$C = 1436.4\text{A} + 2275.3$ 25 < A < 140m^2

$C = 20044\mathrm{A}^{0.4669}$ A > 140m^2

C in \$, *A* is the area in m^2.

- Columns:

$$D_C = 2\cdot\sqrt{\frac{1}{\pi}\cdot\frac{\text{Vapor rate(kg/s)}}{\rho_v\cdot\text{(vapor velocity(m/s))}}}$$

$$\text{Vapor rate(kg/s)} = (1+R)\cdot D$$

R is the reflux ratio and D is distillate withdrawn from top.

In case the diameter of the column is bigger than 3 meters the feed should be split into as many columns as those which allow a D_c of around 3 meters.

$$vapor\ velocity(m.s) = 0.8\cdot\max\ vapor\ velocity = 0.8\cdot 0.3048\cdot 0.3\cdot\sqrt{\frac{\rho_L-\rho_v}{\rho_v}}$$

(0.8 is the fraction of the flooding velocity)

($0.3\cdot\sqrt{\frac{\rho_L-\rho_v}{\rho_v}}$ ft /s is the maximum vapor velocity corresponding to a plate separation of 2 ft) (rule of thumb)

(0.3048 if because 0.3 is given for a velocity in ft/s instead of m/s.

$$\mathrm{n_{Plates}}=\mathrm{Round}\left(\frac{\dfrac{\ln\left(\dfrac{\xi_{etho}(1-\xi_{wa})}{\xi_{wa}(1-\xi_{etho})}\right)}{\ln(\alpha_{etho/wa})}-1}{Efficiency}+1\right)$$

Efficiency = $0.5/(0.3\cdot\alpha_{etho/wa})^{0.25}$

The height of the column will be

$$\mathrm{H = n_{Plates}\cdot Esp + 4\cdot 1.5}$$

Esp is the separation between plates and is commonly taken as 0.6m (Douglas, 1988). The factor 4 times 1.5m is a consideration (Grossmann notes) for space above the top plate and below the bottommost plate.

Since the column thickness is small compared to its diameter, we can calculate its weight using:

$$W=\rho_{steel}\cdot\left(\pi\cdot D_C\cdot e\cdot H+\frac{4}{3}\cdot\pi\cdot\left[\left(\frac{D_C}{2}+e\right)^3-\left(\frac{D_C}{2}\right)^3\right]\right)$$

$\rho_L=950kg/m^3$ (Liquid phase density)

$\rho_v=\frac{P\cdot M_{Water-EtOH}}{R\cdot T}(kg/m^3)$ (Gas phase density)

The bottoms pressure and temperature is used for calculating the vapor density. Thickness calculation:

$$P>atm \quad t=0.0032+\frac{P.D_c}{2.S.E-0.2P}$$

$$P<atm \quad t=0.0032+4.\frac{D_c}{2}.\sqrt{\frac{P_{out}}{S}}$$

Corrosion allowance, 0.0032m (from 2 to 4 mm; typically 1/8 in = 3.2 mm is used)

t (m): thickness

E: joint efficiency, equal to 1

P (psi): Design pressure – We have selected 1.5 times the working pressure since bottom pressure is higher than atmospheric pressure

P_{out} (psi): Pressure outside the column (= atmospheric pressure). units consistent with those of S

S (psi): Design stress (S = 13300 psi for stainless steel working at 100°C.

D_c (m): column diameter.

Another correlation for thickness:

t (m) = 0.0023 + 0.003D_c

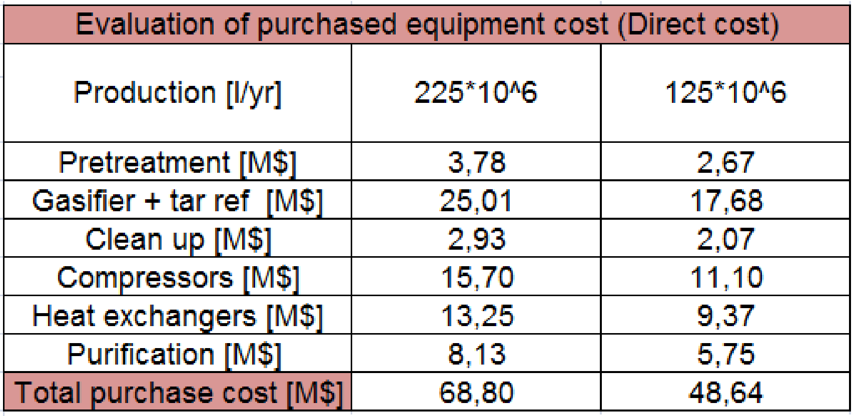
where D_c is in m

The cost of the plates:

$$Cost\ \ Plates(\$)=\mathrm{n}_{\mathrm{Plates}}\cdot 315\cdot \mathrm{e}^{0.72\cdot \mathrm{D_C}}$$

where D_c is in m

$$C_{column}(\$) = 56.181\,.W^{0.878} + \cos t\ of\ \ plates$$



Evaluation of purchased equipment cost (Direct cost)		
Production [l/yr]	225*10^6	125*10^6
Pretreatment [M$]	3,78	2,67
Gasifier + tar ref [M$]	25,01	17,68
Clean up [M$]	2,93	2,07
Compressors [M$]	15,70	11,10
Heat exchangers [M$]	13,25	9,37
Purification [M$]	8,13	5,75
Total purchase cost [M$]	68,80	48,64

Figure119: Evaluation of Purchased Equipment Cost.

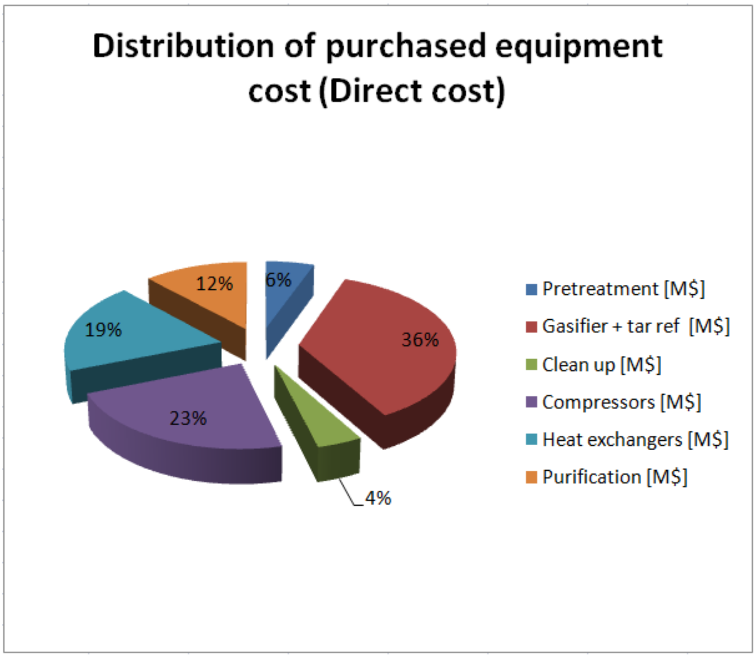
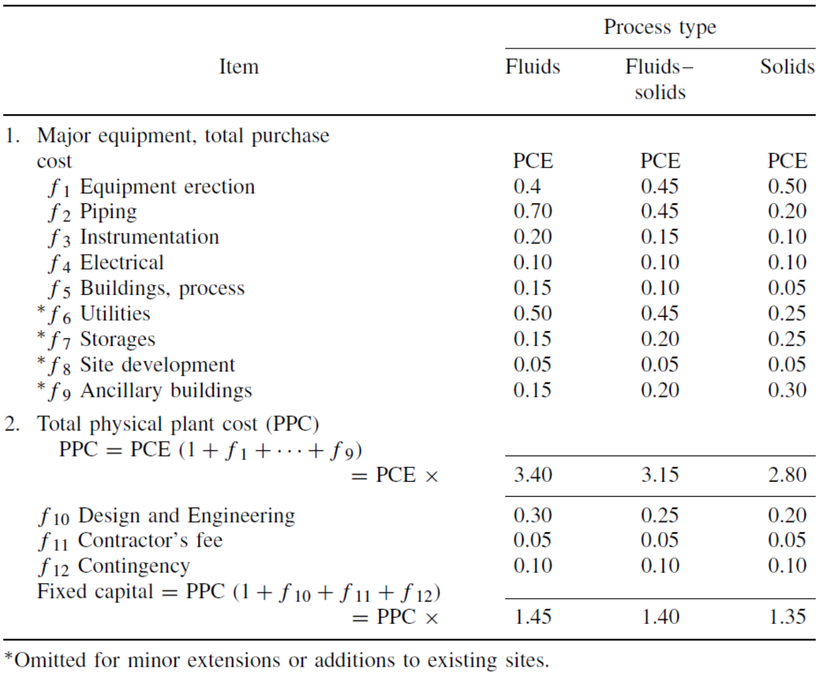


Figure 120: DIstribution of Purchased Equipment Cost.

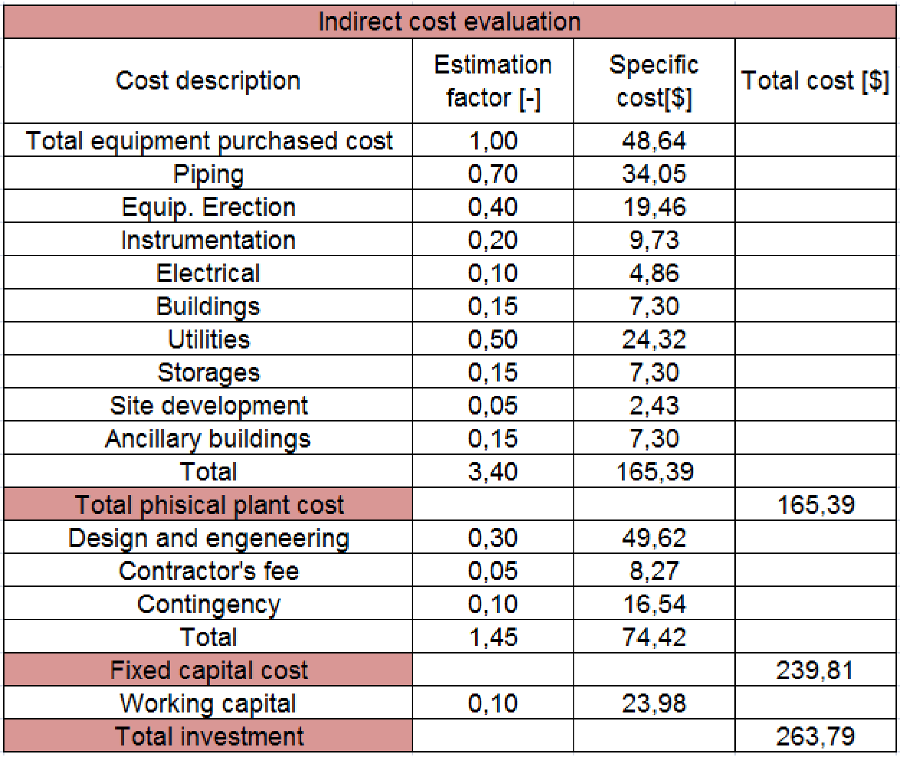
5.1.2 Indirect cost evaluation



Item	Process type Fluids	 Fluids–solids	 Solids
1. Major equipment, total purchase cost	PCE	PCE	PCE
f_1 Equipment erection	0.4	0.45	0.50
f_2 Piping	0.70	0.45	0.20
f_3 Instrumentation	0.20	0.15	0.10
f_4 Electrical	0.10	0.10	0.10
f_5 Buildings, process	0.15	0.10	0.05
$^*f_6$ Utilities	0.50	0.45	0.25
$^*f_7$ Storages	0.15	0.20	0.25
$^*f_8$ Site development	0.05	0.05	0.05
$^*f_9$ Ancillary buildings	0.15	0.20	0.30
2. Total physical plant cost (PPC) $\text{PPC} = \text{PCE}\,(1 + f_1 + \cdots + f_9)$ $= \text{PCE} \times$	3.40	3.15	2.80
f_{10} Design and Engineering	0.30	0.25	0.20
f_{11} Contractor's fee	0.05	0.05	0.05
f_{12} Contingency	0.10	0.10	0.10
Fixed capital $= \text{PPC}\,(1 + f_{10} + f_{11} + f_{12})$ $= \text{PPC} \times$	1.45	1.40	1.35

*Omitted for minor extensions or additions to existing sites.

Figure 121: Typical Factors for Estimation of a Project Fixed Capital Cost.[161]



Indirect cost evaluation			
Cost description	Estimation factor [-]	Specific cost[$]	Total cost [$]
Total equipment purchased cost	1,00	48,64	
Piping	0,70	34,05	
Equip. Erection	0,40	19,46	
Instrumentation	0,20	9,73	
Electrical	0,10	4,86	
Buildings	0,15	7,30	
Utilities	0,50	24,32	
Storages	0,15	7,30	
Site development	0,05	2,43	
Ancillary buildings	0,15	7,30	
Total	3,40	165,39	
Total phisical plant cost			165,39
Design and engeneering	0,30	49,62	
Contractor's fee	0,05	8,27	
Contingency	0,10	16,54	
Total	1,45	74,42	
Fixed capital cost			239,81
Working capital	0,10	23,98	
Total investment			263,79

Figure 122: Indirect Cost Evaluation..

5.1.3 Operating cost

An evaluation of the operating costs is needed to judge the viability of a project. These costs can be estimated from the flow-sheet, which gives the raw material and service requirements, and the capital cost evaluation.

The cost of producing a chemical product will include the items listed below.

They are divided into two groups:

1. Fixed operating costs: costs that do not vary with production rate. These are the bills that have to be paid whatever the quantity produced.

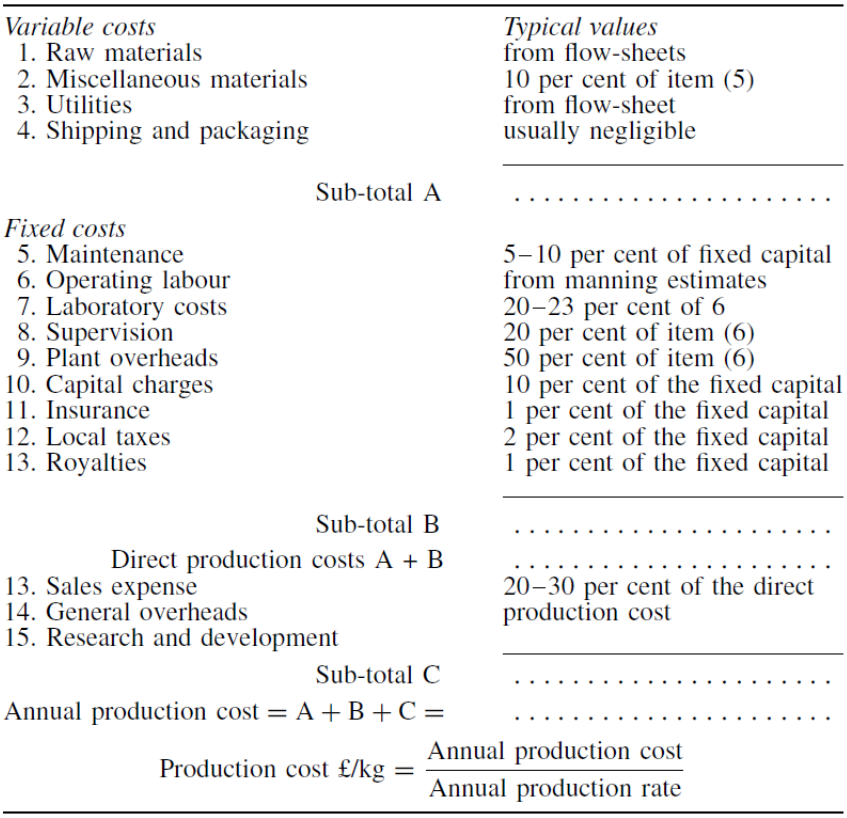
    1) Maintenance (labour and materials).
    2) Operating labour.
    3) Laboratory costs.
    4) Supervision.
    5) Plant overheads.
    6) Capital charges.
    7) Rates (and any other local taxes).
    8) Insurance.
    9) Licence fees and royalty payments.

2. Variable operating costs: costs that are dependent on the amount of product produced.

    1) Raw materials.
    2) Miscellaneous operating materials.
    3) Utilities (Services).
    4) Shipping and packaging.

Assumptions regarding economic evaluation:

- Annual working hours: 8000.
- Method of depreciation ("straight line") without residual final value.
- Ethanol density (from mass production to the volume ones): 0.789 kg/L.
- Prices utilities (Figures 113/114).



Variable costs	*Typical values*
1. Raw materials	from flow-sheets
2. Miscellaneous materials	10 per cent of item (5)
3. Utilities	from flow-sheet
4. Shipping and packaging	usually negligible
Sub-total A	. . . .
Fixed costs	
5. Maintenance	5–10 per cent of fixed capital
6. Operating labour	from manning estimates
7. Laboratory costs	20–23 per cent of 6
8. Supervision	20 per cent of item (6)
9. Plant overheads	50 per cent of item (6)
10. Capital charges	10 per cent of the fixed capital
11. Insurance	1 per cent of the fixed capital
12. Local taxes	2 per cent of the fixed capital
13. Royalties	1 per cent of the fixed capital
Sub-total B	. . . .
Direct production costs A + B	. . . .
13. Sales expense	20–30 per cent of the direct production cost
14. General overheads	
15. Research and development	
Sub-total C	. . . .
Annual production cost = A + B + C =	. . . .

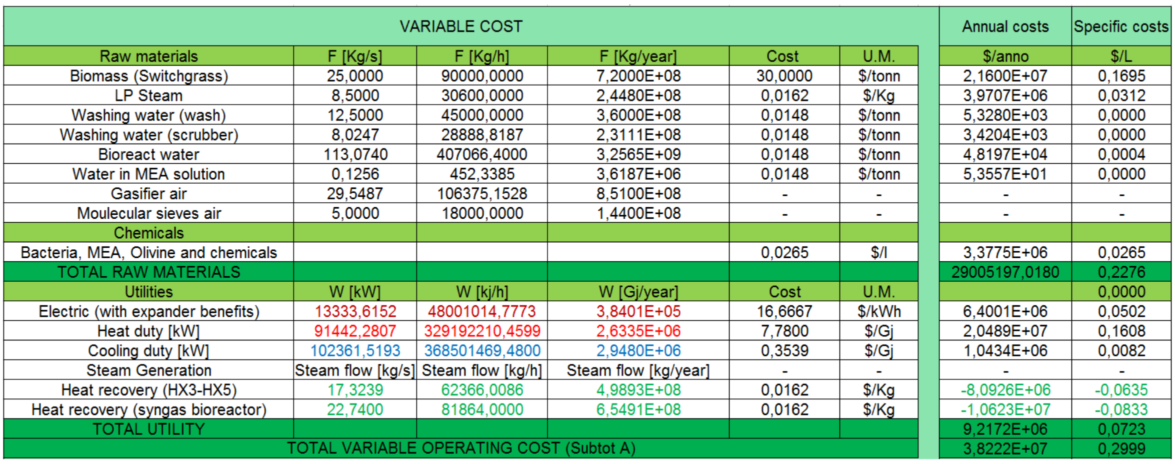
$$\text{Production cost £/kg} = \frac{\text{Annual production cost}}{\text{Annual production rate}}$$

Figure 123: Summary of Production Cost.[161]

5.1.4 *Summary of production cost*

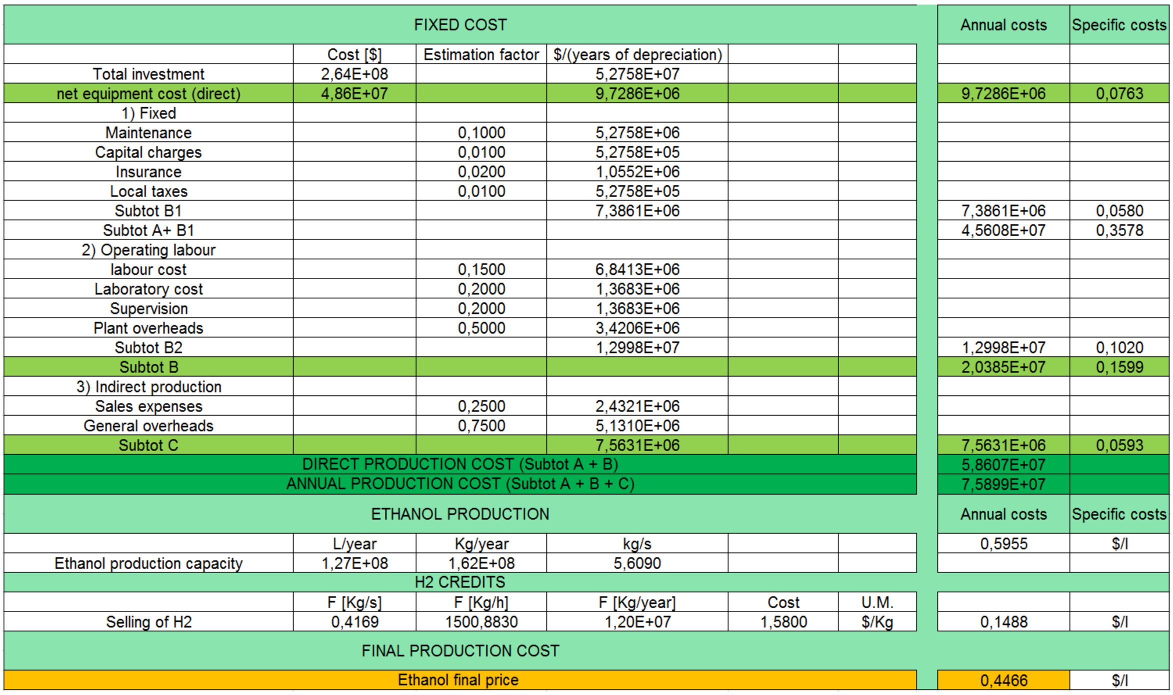
Assumptions regarding economic evaluation:

- Annual working hours: 8000.
- Method of depreciation ("straight line") without residual final value.
- Depreciation period: 5 years.
- Ethanol density (from mass production to the volume ones): 0.789 kg/L.
- Utilities price (Figures 113-114).[161]
- Switchgrass price : 30 $/tonn.[162]
- Hydrogen selling price: 1.58 $/kg.[163]



VARIABLE COST						Annual costs	Specific costs
Raw materials	F [Kg/s]	F [Kg/h]	F [Kg/year]	Cost	U.M.	$/anno	$/L
Biomass (Switchgrass)	25,0000	90000,0000	7,2000E+08	30,0000	$/tonn	2,1600E+07	0,1695
LP Steam	8,5000	30600,0000	2,4480E+08	0,0162	$/Kg	3,9707E+06	0,0312
Washing water (wash)	12,5000	45000,0000	3,6000E+08	0,0148	$/tonn	5,3280E+03	0,0000
Washing water (scrubber)	8,0247	28888,8187	2,3111E+08	0,0148	$/tonn	3,4204E+03	0,0000
Bioreact water	113,0740	407066,4000	3,2565E+09	0,0148	$/tonn	4,8197E+04	0,0004
Water in MEA solution	0,1256	452,3385	3,6187E+06	0,0148	$/tonn	5,3557E+01	0,0000
Gasifier air	29,5487	106375,1528	8,5100E+08	-	-	-	-
Moulecular sieves air	5,0000	18000,0000	1,4400E+08	-	-	-	-
Chemicals							
Bacteria, MEA, Olivine and chemicals				0,0265	$/l	3,3775E+06	0,0265
TOTAL RAW MATERIALS						29005197,0180	0,2276
Utilities	W [kW]	W [kj/h]	W [Gj/year]	Cost	U.M.		0,0000
Electric (with expander benefits)	13333,6152	48001014,7773	3,8401E+05	16,6667	$/kWh	6,4001E+06	0,0502
Heat duty [kW]	91442,2807	329192210,4599	2,6335E+06	7,7800	$/Gj	2,0489E+07	0,1608
Cooling duty [kW]	102361,5193	368501469,4800	2,9480E+06	0,3539	$/Gj	1,0434E+06	0,0082
Steam Generation	Steam flow [kg/s]	Steam flow [kg/h]	Steam flow [kg/year]	-	-	-	-
Heat recovery (HX3-HX5)	17,3239	62366,0086	4,9893E+08	0,0162	$/Kg	-8,0926E+06	-0,0635
Heat recovery (syngas bioreactor)	22,7400	81864,0000	6,5491E+08	0,0162	$/Kg	-1,0623E+07	-0,0833
TOTAL UTILITY						9,2172E+06	0,0723
TOTAL VARIABLE OPERATING COST (Subtot A)						3,8222E+07	0,2999

Figure 124: Variable Costs.



FIXED COST						Annual costs	Specific costs
	Cost [$]	Estimation factor	$/(years of depreciation)				
Total investment	2,64E+08		5,2758E+07				
net equipment cost (direct)	4,86E+07		9,7286E+06			9,7286E+06	0,0763
1) Fixed							
Maintenance		0,1000	5,2758E+06				
Capital charges		0,0100	5,2758E+05				
Insurance		0,0200	1,0552E+06				
Local taxes		0,0100	5,2758E+05				
Subtot B1			7,3861E+06			7,3861E+06	0,0580
Subtot A+ B1						4,5608E+07	0,3578
2) Operating labour							
labour cost		0,1500	6,8413E+06				
Laboratory cost		0,2000	1,3683E+06				
Supervision		0,2000	1,3683E+06				
Plant overheads		0,5000	3,4206E+06				
Subtot B2			1,2998E+07			1,2998E+07	0,1020
Subtot B						2,0385E+07	0,1599
3) Indirect production							
Sales expenses		0,2500	2,4321E+06				
General overheads		0,7500	5,1310E+06				
Subtot C			7,5631E+06			7,5631E+06	0,0593
DIRECT PRODUCTION COST (Subtot A + B)						5,8607E+07	
ANNUAL PRODUCTION COST (Subtot A + B + C)						7,5899E+07	
ETHANOL PRODUCTION						Annual costs	Specific costs
	L/year	Kg/year	kg/s			0,5955	$/l
Ethanol production capacity	1,27E+08	1,62E+08	5,6090				
H2 CREDITS							
	F [Kg/s]	F [Kg/h]	F [Kg/year]	Cost	U.M.		
Selling of H2	0,4169	1500,8830	1,20E+07	1,5800	$/Kg	0,1488	$/l
FINAL PRODUCTION COST							
Ethanol final price						0,4466	$/l

Figure 125: Fixed Costs.

The final results of the economical evaluation are:

1. The final price to produce one liter of ethanol with a purity of 99.6%wt is 0.4466 $/L
2. Selling hydrogen allows to reduce the final cost of production of 0.1488 $/L, with a percentage reduction of 25%.
3. The factor that affects the most the final cost of production is the price of the raw biomass. Indeed, it accounts for the 44% of the cost of production.
4. The depreciation period has great influence on the final cost (see figure 125)
5. Ethanol yield (kg ethanol/kg biomass): 0.2244.
6. Energetic integration allows a reduction of 0.1468 $/L on the final ethanol price, which corresponds to a percentage of 25%.

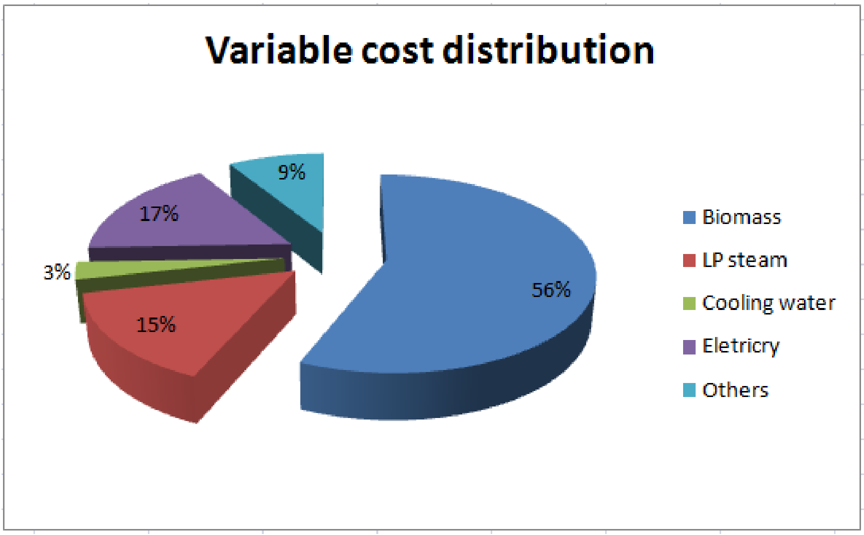


Figure 126: Variable Cost Distribution.

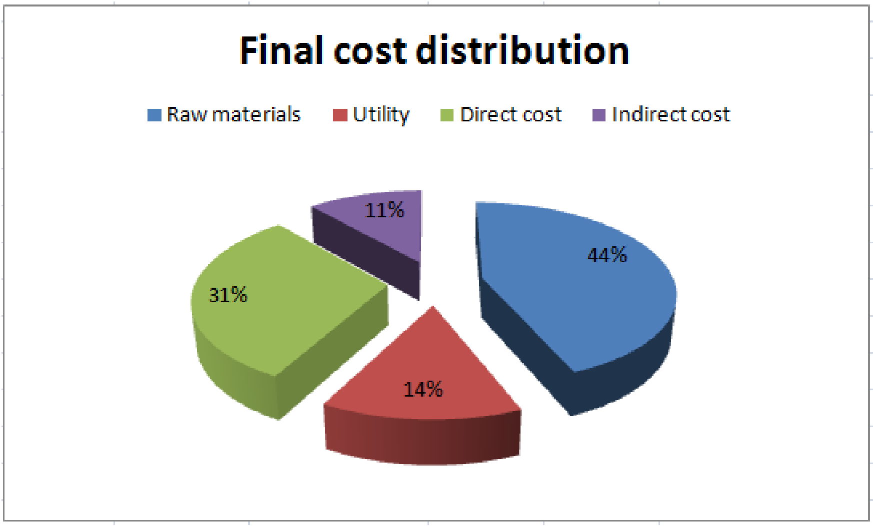


Figure 127: Final Cost Distribution .

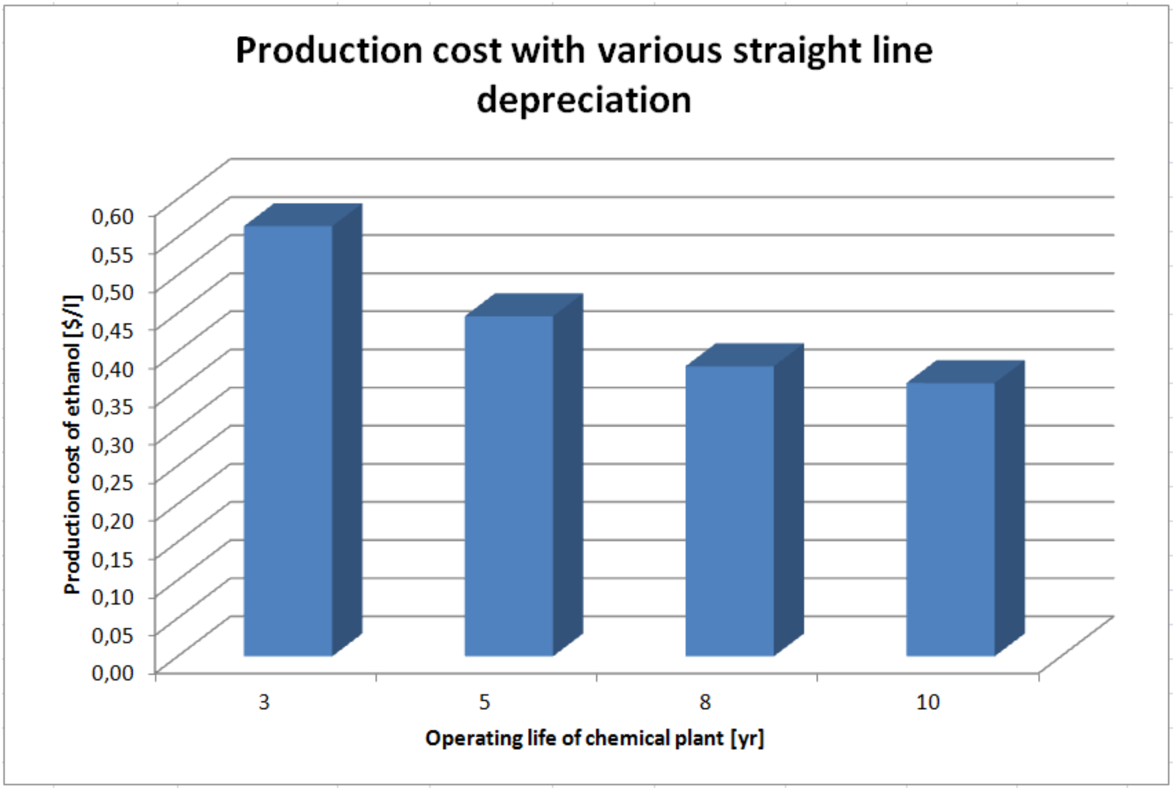


Figure 128: Depreciation periods.

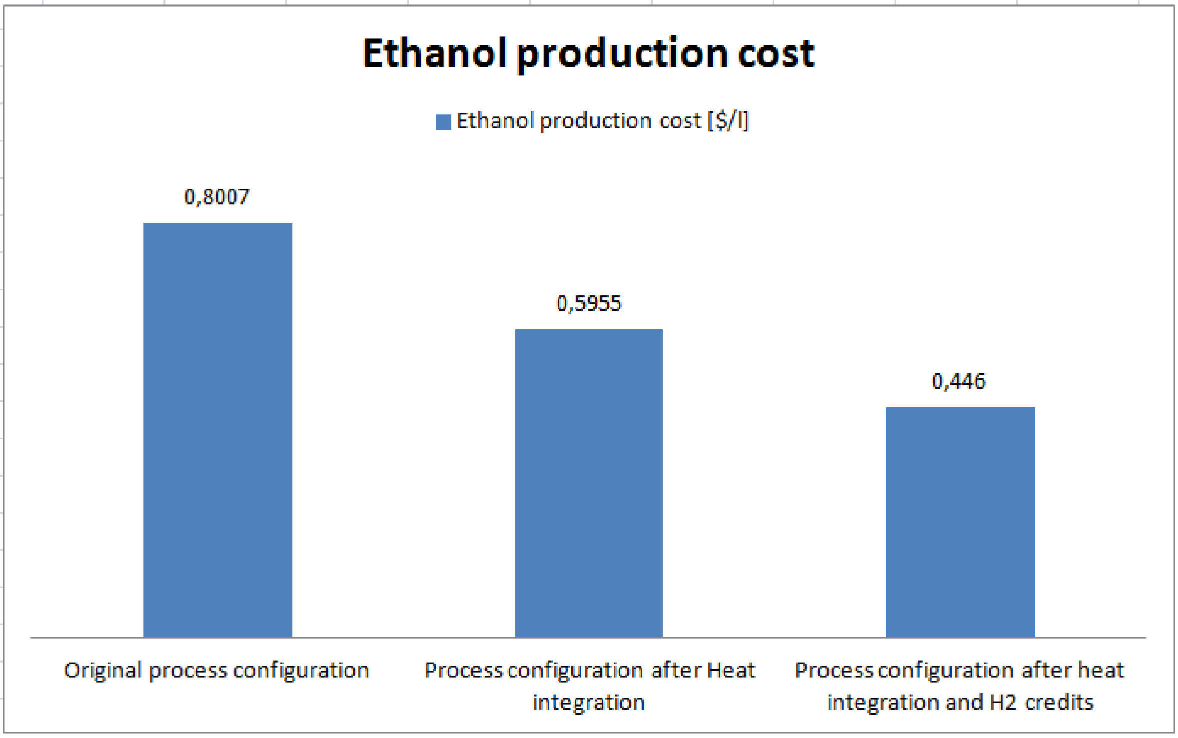


Figure 129: Ethanol Production Cost.

6. CONCLUSIONS

Biofuels should not be considered, in isolation, as alternatives to fossil fuels but as a part of a drive towards the production of sustainable products normally produced from crude oil.[16]

Production costs of fuel ethanol are higher than production costs of gasoline in some cases, although there is a strong influence of factors as the prices of oil and feedstocks for ethanol production.

Nevertheless, many groups and research centers in different countries are continuously carrying out studies aimed at reducing ethanol production costs for a profitable industrial operation. Diverse research trends and process improvements could have success in the task of lowering ethanol costs. These research tendencies are related to the different steps of processing, nature of utilized feedstocks, and tools of process engineering, mainly process synthesis, integration and optimization. Process engineering could provide the means to develop economically viable and environmentally friendly technologies for the production of fuel ethanol.[140]

An important part of the research trends on fuel ethanol production is oriented to the reduction of feedstock costs, especially through the utilization of less expensive lignocellulosic biomass. The key factor for enhancing the competitiveness of biomass-to-ethanol process is the increase in the specific activity of cellulases and the decrease in their production costs. In addition, the technology of recombinant DNA will provide important advances for the development of fuel ethanol industry. The development of genetically modified microorganisms capable of converting starch or biomass directly into ethanol and with a proven stability under industrial conditions will allow the implementation of the consolidated bioprocessing of the feedstocks.[140]

Process synthesis will play a very important role in the evaluation of different technological proposals, especially those related to the integration of reaction–separation processes, which could have the major effects on the economy of the global process. Similarly, the integration of different thermo-chemical and biological processes for the complete utilization of the feedstocks should lead to the development of big ‘‘biorefineries’’ that allow the production of large amounts of fuel ethanol and many other valuable co-products at smaller volumes, improving the overall economical effectiveness of the conversion of a given raw material. Integration opportunities may provide the ways for a qualitative and quantitative improvement of the process so that not only techno-economical, but also environmental criteria can be met.[140]

Current development of ethanol industry shows that complex technical problems affecting the indicators of global process have not been properly solved. The growing cost of energy, the design of more intensive and compact processes, and the concern of the humanity by the environment, have forced the necessity of employing totally new approaches for the design and operation of bioethanol production processes, quite different to those utilized for the operation of the old distilleries. Every time, the spectrum of objectives and constraints that should be taken into account for the development of technologies for biofuels production is wider and more diverse. The social-economical component involved during the production of biofuels in the global context should be highlighted. Practically, every country can produce its own biofuel. In this way, the feedstock supply for ethanol production is ‘‘decentralized’’ and does not coincide with the supply centers of fossil fuels. In addition, human development indexes could be improved by two ways: creation of new rural jobs and reduction of gas emissions with greenhouse effect.

However, ethanol production costs are higher than those of the fossil fuels, especially in the case of biomass ethanol (see Figure 129). Nevertheless, during the last two years, oil prices have persistently increased. There is no doubt that the price of gasoline and other oil-derived fuels has a subsidy paid by all taxpayers of the world and that is not necessarily made effective in gas stations.

Therefore, the relatively higher production cost of ethanol is the main obstacle to be overcome. To undertake this, process engineering plays a central role for the generation, design, analysis and implementation of technologies improving the indexes of global process, or for the retrofitting of employed bioprocesses. Undoubtedly, process intensification through integration of different phenomena and unit operations as well as the implementation of consolidated bioprocessing of different feedstocks into ethanol (that requires the development of tailored recombinant microorganisms), will offer the most significant outcomes during the search of the efficiency in fuel ethanol production. Additionally, the intensification of biological processes implies a better utilization of the feedstocks and the reduction of process effluents improving the environmental performance of the proposed configurations. Attaining this set of goals is a colossal challenge to be faced through the fruitful interaction between the biotechnology and the chemical engineering.[140]

6.1 ***Discussion of the main parameters in the production process***

It is important to mention that there are a uncertainties regarding the cost of the different raw materials, the hydrogen as well as the process itself. Now it is briefly discuss the effect of these parameters in the production process:

- The increase of the price of the raw material affects the processes according to their use of raw material and ethanol and hydrogen yield. In case of an increase in the price of lignocellulosic switchgrass from 30 $/MT to 75 $/MT.

- The expectations of hydrogen as a future fuel makes its production a good asset for the supply chain of biofuel production. However, the biomass cannot only be a source of hydrogen but a source of carbon too. Thus, even though the economics of the hydrogen is important for the profitability of the process, the carbon from the biomass has to be used for the production of biofuels or chemicals.

- Another topic is the concentration of ethanol in the fermentor. Further developments in the fermentation reaction (the bacteria, the fermentor itself) will make the processes based on that technology more competitive. Ideally, the concentration of ethanol in the reactor should be above 15%. New technologies are in the development stage to capture the ethanol as it is produced so that the actual concentration in the liquid remains low.[118] However, its applicability to industrial processes is still far into the future.

- Equipment cost is another source of uncertainty. It is widely acknowledged that any costing correlation in the literature has at least 10-20% error. Even though correlations from different sources have been used, the cost of the main equipment has been checked versus the data in the literature with good agreement.

- Finally, the composition of the gas generated by the gasifiers may be uncertain since no experimental values for switchgrass gasification were found. However, the data used were based on lignocellulosic material for gasification[65,158] and the gas composition was readjusted based on the feed composition.

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