# UNIVERSIDAD SAN FRANCISCO DE QUITO USFQ

## Colegio de Ciencias e Ingenierías

# Techno-economic Analysis of the Production of Acetic Acid by means of a Thermochemical Process from Woody Biomass Residues

Proyecto de Investigación

.


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### Ingeniería Mecánica


Trabajo de titulación presentado como requisito para la obtención del título de Ingeniero Mecánico

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## HOJA DE CALIFICACIÓN
## DE TRABAJO DE TITULACIÓN

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# Resumen


Existe un creciente interés en reducir el uso de petróleo para la manufactura de diferentes productos. La biomasa se presenta como una alternativa a la problemática latente de la dependencia mundial en el petróleo, no solo para la manufactura de biocombustibles pero también para la creación de productos de valor agregado como químicos de diferentes características. En el Ecuador se tiene una amplia disponibilidad de residuos de biomasa de diverso tipo, entre estas tenemos residuos de la industria ganadera, agrícola y forestal. Además, existe una industria química poco desarrollada por lo cual la mayoría de productos que se comercializan en este mercado son de origen importado aumentando sus precios. Solo en 2017, se importaron alrededor de 349 químicos mientras que solo se exportaron 44. Se presenta como alternativa, fabricar diferentes productos químicos a partir de residuos de biomasa local aprovechando este recurso que no se toma en cuenta.

Los químicos que se escogieron como candidatos a ser producidos fueron: Fenol, ácido fórmico, ácido acético, propanodiol y n-propanol. De estos candidatos se escogió el ácido acético ya que es el tercer químico más importado, alrededor de 1000 toneladas anuales, es el único que puede ser obtenido mediante dos caminos: termoquímico y bioquímico, además, existe tecnología madura la cual consigue altos rendimientos del proceso a nivel industrial. Se diseñó una planta con una capacidad del 10% del total importado, es decir, una producción de 100 toneladas anuales de ácido acético con un precio objetivo de 23.50 $/kg ya que este es el precio más bajo al cual se puede comprar un ácido acético con una pureza del 99.9% en el mercado ecuatoriano y es el que se desea producir. Como proceso a ser modelado se escoge la gasificación de la biomasa debido a sus altos niveles de conversión y facilidad para adoptar a nivel industrial. En base al proceso se determinó que se necesitan procesar 0.57 MTPD de biomasa al día para obtener la producción deseada. El proceso simulado con el software Aspen Hysys, cuenta con 5 etapas principales: Separación $N_2$-$O_2$ (El oxígeno es usado en la etapa de gasificación), gasificación de biomasa, separación de agua de la mezcla, síntesis de metanol y finalmente la síntesis de ácido acético.

Para el primer escenario planteado, donde las 100 toneladas anuales de ácido acético producido es vendido a 23.50 $/kg, no se obtienen resultados alentadores. Si se considera un tiempo de vida de planta de 10 años se obtiene una TIR negativa del -15% y una pérdida de 20.54 millones $ mientras que si se considera un periodo de vida de 20 años se obtiene una TIR negativa del -12% y una pérdida de 18.28 millones $. No obstante, en el análisis de sensibilidad se consideran 4 factores que podrían cambiar este aspecto: Tasa de interés, factor de servicio, precio del nitrógeno como coproducto y rendimientos de reacción. El único factor que presenta resultados favorables es aumentar el factor de servicio, es decir la producción de ácido donde se encuentran beneficios de las economías de escala. Si se considera un tiempo de vida de planta de 10 años al aumentar el factor de servicio al 80% se obtiene una TIR de 40% y un VPN de 39.43 millones $. Por otro lado, si se considera un periodo de 20 años, la inversión se hace aún más atractiva obteniendo una TIR de 43% y un VPN de hasta 71.45 millones $


Palabras Clave: Ácido acético, biomasa, energías renovables, gasificación, procesos termoquímicos, aspen hysys, análisis tecno-económico, análisis de sensibilidad, TIR, VPN, PMV

# Abstract

There is a growing interest in reducing the use of fossil fuels for the manufacture of different products. Biomass is presented as an alternative to the latent problem of global dependence on petroleum, not only for the manufacture of biofuels but also for the creation of value-added products such as chemicals of different characteristics. In Ecuador there is a wide availability of biomass waste of various types, among these we have waste from the livestock, agricultural and forestry industry. In addition, there is a poorly developed chemical industry so most of the products that are marketed are imported thereby increasing their prices. Only in 2017, 349 chemicals were imported while only 44 were exported. Manufacturing different chemical products from local biomass waste is presented as an alternative, taking advantage of this resource that is being unused.

The chemicals that were chosen as candidates to be produced were: Phenol, formic acid, acetic acid, propanediol and n-propanol. Acetic acid was chosen from these candidates since: It is the third most imported chemical, around 1000 tons per year. Also, it is the only one that can be obtained through two pathways: thermochemical and biochemical. In addition, there is mature technology which achieves high yields of the process at an industrial level. A plant with a capacity of 10% of the total imported is designed, in other words, a production of 100 annual tons of acetic acid with a target price of 23.50 $ / kg since this is the lowest price at which acetic acid can be purchased with a purity of 99.9% in the market which is the product´s purity obtained . The pathway chosen to be modelled is gasification of biomass due to its high levels of conversion and ease of adoption at an industrial level. Based on the process, it was determined that 0.57 MTPD of biomass per day must be processed to obtain the desired production. The simulated process with Aspen Hysys software, has 5 main stages: Separation N2-O2 (Oxygen is used in the stage of gasification), biomass gasification, separation of water from the mixture, methanol synthesis and finally the synthesis of acetic acid.

For the first scenario, in which the 100 tons of acetic acid produced per year is sold at 23.50 $ / kg, discouraging results were obtained. If a plant lifespan of 10 years is considered, a negative IRR of -15% and a loss of 20.54 million dollars is obtained, whereas if a lifespan of 20 years is considered, a negative IRR of -12% and a loss of $ 18.28 million is obtained, The sensitivity analysis performed considers 4 factors that could change the previous aspect: Interest rate, service factor, price of nitrogen as a co-product and reaction yields. The only variation that presents favorable results is an increase in the service factor, that is, the production of acid where benefits of economies of scale are presented. If a plant lifespan of 10 years is considered by increasing the service factor to 80%, an IRR of 40% and a NPV of 39.43 million $ are obtained. On the other hand, if a period of 20 years is considered, the investment becomes even more attractive, obtaining an IRR of 43% and a NPV of up to 71.45 million dollars.


Key Words: Acetic acid, renewable energies, biomass, gasification, thermochemical process, aspen hysys, techno-economic analysis, sensitivity analysis, IRR, NPV, MSP.

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# 1. Introduction

The need to eliminate the global dependence on the use of petroleum for the elaboration of different products and the search of alternatives that allow the mitigation of polluting emissions of CO, CH4 and NOx, to comply with the environmental objectives, show the use of biomass as a promising solution to a latent problem (Dang et al., 2016). In recent years, the research for the production of chemical products from biomass has taken much importance, both by thermochemical and biochemical production pathways. A vast variety of methods have been proposed, for example, gasification technologies as a thermochemical process, has increased the interest in this same platform (Wright and Brown, 2007). The literature indicates that the transformation of biomass into other intermediate chemicals, both liquid and gaseous can be enhanced to transport fuels or highly commercial chemicals. Although certain technologies are more mature than others, most certainly the majority have an encouraging future (Dang et al., 2016).

The movement of chemical production from a matrix dependent on fossil fuels to one of renewable origin justifies an investigation of the potential development of the chemicals from the abundant biomass resources scattered around all regions of Ecuador. According to the Bioenergetic Atlas of the country released in 2014, there exists a great availability of usable biomass in the country, located mainly in three provinces: Guayas, El Oro and Los Ríos (ESIN Consultora S.A). Biomass availability in Ecuador is high, including residual biomass that nowadays is not being used and has great potential. Residues of biomass include the by-products of the natural and industrial transformations of organic matter. Even though the agricultural sector in Ecuador only represents the 6.7% of the country's GDP (World Bank, 2019) the majority of biomass residues come from agricultural crops or activities related to the first sector of the economy. We can identify different types of agricultural products such as: Bananas, coffee, tea, rice, sugar, beans and corn (Teodorescu, 2014). Besides residues related to agricultural processes, forest waste also accounts for an important source of biomass. According to FAO, only 28% of a tree is used for wood production while the rest is considered as unused products: 38% used in wood and branches while other 34% is lost in sawing processes (1990). Biomass and its residues in Ecuador come from different industries: Agricultural, livestock and forestry.

On the one hand, Ecuadorian industries that use chemicals in their daily activities such as the textile, food and chemical industries import the vast majority of their requirements. The majority of chemical products used in the country are imported, as an Ecuadorian underdeveloped and traditional chemical industry of the country cannot comply with the existing demand for it. It´s also important to consider the high prices charged by suppliers to consumers of this products, as prices almost double when they enter the country, given to different factors that need to be determined such as an strong economic policy of the country or the long chain of distribution that increases the difficulty of transporting this products to their final destination. In the year 2017, 5 chemicals corresponding to two specific classifications were identified as the most imported. The first classification considered is the Specific Classification 1 of products corresponding to pyrolysis and catalytic pyrolysis of biomass: Acetic Acid, Formic Acid and Phenol. The second classification considered is the Specific Classification 2, of chemical products corresponding to aerobic and anaerobic processes of biomass transformation in which Acetic Acid is also considered, with two other products which are Propanodiol and n-Propanol. According to data retrieved from SENAE, 2019, the chemical product which was imported in a higher quantity corresponding to the classification of products from pyrolysis and catalytic pyrolysis is Phenol with 13,0 Gg, followed by Formic Acid with 2,3 Gg and in third place comes

Acetic Acid with 0,9 Gg. On the other hand, analyzing the chemicals related to the second classification considered, products corresponding to aerobic and anaerobic processes of biomass. Acetic Acid figures as the most important one with a total quantity of 0,94 Gg imported in 2017, followed closely by n-Propanol with a total of 0,91 Gg and in third place Propanediol with 0,75 Gg in the same time period. There are only two products that exceed acetic acid in imports quantity, Phenol and Formic Acid.

As established before, Phenol and Formic acid exceed the importation of acetic acid, however the last one is the only chemical which appears in both classifications considered, furthermore, increasing the number of pathways in which the product could be carried out both by the thermochemical and by the biochemical way. Thermochemical processes involve the use of heat and catalysts to convert biomass into different products such as solids, liquids, gases and thermal energy. The basic processes considered are four: Direct Combustion, Gasification, Pyrolysis, and Solvolysis. On the other hand, processes considered for the biochemical conversion of wet biomass involve Alcoholic Fermentation, transesterification and esterification, and anaerobic digestion. As an illustration, fermentation is a biological process in which enzymes produced by microorganisms catalyze reactions that release energy to break down organic substrates. Although only small fractions of the commercial production of organic components come from biochemical processes, that is, microbials, there are certain products besides the most common. These chemicals include carboxylic acids, amino acids, antibiotics and enzymes for the food industry. Most of the microorganisms used in commercial fermentation require six-carbon sugars (hexoses) or disaccharides as substrates although the microbial world has organisms that can destroy virtually any organic compound (Brown, 2013). As an important platform chemical, acetic acid is mainly produced synthetically, with only 10% produced by means of bacterial fermentation to manufacture vinegar, as it is stipulated that vinegar used in food must have a biological origin (Vidra & Németh, 2017). Despite this, both pathways are not exclusively isolated since there are hybrid processes that combine both thermochemical and biochemical processes (Brown, 2013).

To date, there have been no local studies on the production of chemicals from biomass with a techno-economic approach, which allows gathering information about the capital and operating costs of an operating plant in the country. According to Brown, a techno-economic analysis (TEA) is a useful tool employed by several universities and the national laboratories of the U.S. Department of Energy to calculate information that usually is missing in an inexpensive approach: “TEA uses process models to quantify the technical and economic performance of a biorefinery employing one or more specific process pathways and generates a financial return on capital investment” (Brown, 2015, p. 167). As underinvestment has result in a chicken-and-egg dilemma, investors don’t provide financing opportunities to biorefineries due to production cost uncertainty, however, the lack of biofuel and chemicals production prevents additional knowledge of production costs being gained. Different techno-economic analysis had been performed around the globe for gasification, Fischer-Tropsch synthesis (FTS), pyrolysis, syngas fermentation and other pathways. The total project investments (TPI) for biorefineries of 2000 MTPD capacity range from $217 million to over $800 million (Brown, 2015). As an illustration, a techno-economic comparison was performed between two gasification processes to produce ethanol identifying two possible investment scenarios with TPI of $665 million for an indirectly-heated gasification process and a total of $752 million for a directly-heated oxygen-blown gasifier approach (2015). The feedstock cost is assumed to be $69/metric ton (MT) of poplar woody chips in a 20-year biorefinery lifespan. An internal rate of return (IRR) of 10% is achieved with a minimum selling fuel price (MFSP) of $4.37/gallon of gasoline equivalent (gge). Another process considered by Brown is the Fischer-Tropsch synthesis pathway for a process plant with a capacity of 1371 MTPD in which a range of TPI was calculated from $408 million to a high $587 million. Finally, a syngas fermentation plant with a capacity of 2030 MTPD, which uses lignocellulosic feedstock with a price of $85.77/MT, was calculated with a TPI of $562 million and a MFSP of $7.29/gge (Brown, 2015).

Even though there are different suitable candidates for developing a process plant in the country, acetic acid was chosen for two main reasons:

- Despite of being in third place with a total import quantity of 940 tons in 2017, it is the only chemical product which appears in both classifications considered for the following research, specific classification 1 of products corresponding to pyrolysis and catalytic pyrolysis of biomass and specific classification 2, of chemical products corresponding to aerobic and anaerobic processes of biomass transformation therefore increasing the quantity of pathways that could be potentially analyzed and suitable.
- A second strong reason are the high yields of process that transform biomass into acetic acid, as an illustration, the Cativa process which has high selectivity and yields with a conversion up to 91.5 % (Brown, 2015). Another example of this process was presented by Choi, Johnston, Brown, Shanks & Lee in which red oak is pyrolyzed. Of the 61.90% of bio-oil obtained from the process the fraction of acetic acid obtained was of 7.75 higher than other fractions such as 1.71 for glycolic acid and 1.24 for formic acid (2015).

Furthermore, in the following research, the most encouraging path for acetic acid production will be selected, considering both biochemical and thermochemical pathways, using parameters such as in yield terms or feasibility of reaching a formal industrial process. Once the path selection is completed, biochemical or thermochemical, an initial market study will be carried out to determine the current acetic acid demand, the acetic acid price and the source of the high process usually charged in the local market and the supply and production capacity will be determined in order to determine the initial biomass feed in metric tons per day (MTPD) used in the process plant. It's important to remark that the acetic acid production feed will take advantage of biomass residues widely available in the country. Another key aspect of the process is the biomass characterization used as feed for the process based on local species in which biomass and its residues are available as this would directly affect the process outcome. The process plant design for the production of acetic acid will be carried out using Aspen technologies, a software used in the chemical industry for process simulation. Once the process is completed, a techno-economic analysis (TEA) is performed to determine the capital and operational costs for process selected. An analysis of different economical aspects will be completed with an investment analysis, taking into account indicators such as the internal rate of return and the net present value.

## 2. Methods

To date, there are no studies of TEA in the country for the development of a process plant, which produces chemicals from biomass. In the first place, the chemicals that are desired to be produced are defined based on two classifications:

1. Chemicals corresponding to products of pyrolysis and catalytic pyrolysis of biomass.

2. Products of aerobic and anaerobic processes of biomass transformation.

The three chemicals with the highest demand, both in quantity and cost, of each of the two previously mentioned classifications were initially chosen. As mentioned before, the chemicals selected for the first classification are Acetic Acid, Formic Acid and Phenol and those corresponding to the second are Acetic Acid, Propanodiol and n-Propanol. Even though Phenol and Formic Acid exceeds the importation of acetic acid, the main reasons to consider Acetic Acid as the chemical product to be produced as established in the introduction are:

1. It is the only chemical product which appears in both classifications therefore increasing the quantity of pathways that could be potentially analyzed and suitable. A higher number of pathways implies in which way the product could be carried out both by the thermochemical and by the biochemical way. There is a wide availability of processes already developed for the production of acetic acid, both biochemical and thermochemical
2. High yields of process that transform biomass into acetic acid, as an illustration, the Cativa process (Brown, 2015) or in the pyrolysis of red oak presented by Choi, Johnston, Brown, Shanks & Lee in 2015.

In a global scale, the production of acetic acid in 2015 reached a global market consisting of 13 million tons and it is predicted to expand in 2020 to 16 million tons (Vidra & Németh, 2017). It is also important to note that the production of acetic acid in 2015 reached a global market consisting of 13 million tons and it is predicted to expand in 2020 to 16 million tons. The market price in the world varies between US $1200 to US $1600 per ton in different countries around the world (Vidra & Németh, 2017). Furthermore, research will be carried out in order to determine which process will be selected between the biochemical or thermochemical pathway, mostly based on the process yields and the feasibility of adopting the process on an industrial level.

Once the process is selected, an initial market study will be carried out in order to determine the total demand of acetic acid based mostly on imports and also its price in the local market. Information of the country´s imports, in both quantity and CIF (Cost, insurance and freight) will be taken from the national government´s records, mainly information available in the database of the National Customs Service, SENAE which stands for "Servicio Nacional de Aduana del Ecuador", web page from the year 2013 to the year 2019 (SENAE, 2019). Regarding the price of acetic acid, the factors that directly effect on the high importation prices must be determined and taken into consideration. The factors that may determine the acetic acid price are such as existence of taxes imposed in the chemical product, transportation costs or country of origin. Different suppliers in the local market will be contacted and considered in order to determine the acetic acid price targeted for the plant design, taking into consideration the distributors which hold higher market shares such as SOLVESA Ecuador S.A, NOVACHEM, RESIQUIM S.A and QUIMPAC S.A. This initial market study will also consider the determination of the supply and production capacity determination. Several authors regarding the subject in the United Estates consider the initial feed of biomass in the process plants to be 2000 metric tons per day (MTPD), even though, an analysis of the local demand that is targeted and the availability of the biomass resources locally must be considered in order to determine the initial feed of biomass used for the plant design and production. Additionally, it is important to determine the residues availability in the country involving the type of residue that would be needed for the production and where will be the plant located in order to confirm the feasibility of building it in the country. Once the initial market study is carried out and the source of biomass residues is determined, another key step to perform is the determination of the biomass feed characterization as it directly impacts the process outcome.

Once the previous key steps are completed the process chosen will be designed using the software Aspen Hysys, a software used by the chemical industry for process simulation. When the simulation is completed a TEA is made for the product, considering the process results following the methodology developed by Peters and Timmerhaus in plant design and economics for chemical engineers similar to the methodology presented by Brown in "Economics of Biorenewable Resources" (2013). This methodology consists on direct, indirect and capital costs estimation, to determine the capital investment for the process plant. Financial costs such as loan interests are also included. The capital costs are calculated as the costs of the equipment used in the plant, costs indirect and indirect and finally the operational costs. Operational costs are calculated based on the total costs of energy and materials used, as well as fixed operational costs (such as salaries and maintenance). The objective, according to Brown, is to obtain estimated values with a margin of error of + -30% of the real value of the plant. To eliminate subjectivities inherent to the nature of the TEA, parameters are established, to illustrate, all the monetary figures are adjusted to the year 2018 based on the inflation of the country. As established before, the cost estimation of the equipment was carried out starting from the tool “Aspen Process Economic Analyzer”. Data of the industrial services such as energy consumption was also obtained from the process designed in Aspen Hysys. It´s important to mention that the software estimates costs as if the plant was located in the United States, therefore it is important to establish adjust the monetary figures using a Location Cost Adjustment Factor to transform the costs in the US, to local costs in the country. The location factor established is 1,7336, mainly due to concepts related to nationalization taxes and tariffs that apply to the Ecuadorian market. The taxes and tariffs imposed on the market are summarized below:

**Table 1. Tariff Rates for Imports**

| Tariff Rate | Value |
|---|---|
| **Ad-Valorem** | 19% of Equipment Value |
| **Insurance** | 0,29% of Equipment Value |
| **Fodinfa** | 0,5% of Equipment Value |
| **Salvaguarda** | 0,35% of Equipment Value |
| **IVA** | 12% of Equipment Value + Ad-Valorem+Insurance+Fodinfa+Salvaguarda |

**Table 2. Factors Totalized**

| Tariff Rate | Factor |
|---|---|
| **Ad-Valorem + Insurance** | 0,1929 |
| **Fodinfa** | 0,005 |
| **Salvaguarda** | 0,35 |
| **IVA** | 0,1854 |
| **Total** | 1,7336 |

To evaluate which is the best alternative and estimate the economic feasibility of the implementation of the process plant different indicators will be used, considering their unique advantages and disadvantages. The first indicator considered is the Minimum Selling Price (MSP) defined as the lowest product cost that yields an NPV of zero. To obtain the MSP, the Internal Rate of Return (IRR) must be predetermined. The MSP accounts also for an annual discount rate. The main advantages of the MSP are that it allows the comparison of the biorenewable product costs to the market prices from the non-biorenewable counterparts. This allows an insight of the economic competitiveness of the biorefinery. The main drawback of the MSP is the decreasing suitability of the analysis for biorefineries with a portfolio of products instead of a single one. Another important indicator considered is the IRR, the annual compounded rate of return required to make the Net Present Value (NPV) of the monetary flows from the investment equal to zero. In other words, the IRR is a rate obtained that must be compared to the rate of the local productive loans. If the IRR exceeds this rate, the investment is a suitable one (Brown, 2013). In the country, there are different types of loans with different rates, for example, there are loans given by the National Financial Corporation, CFN for its acronym in Spanish, to small and medium-sized enterprises (SMEs) from $50 000 to $50 million dollars with interest rates varying from 7,50% to 9,75% (Zapata, 2018). Although the highest interest rate reported by Ecuador´s Central Bank was of 11.83% (BCE, 2019) and this would be the rate compared to the IRR obtained. The final indicator used will be the Net Present Value (NPV), which is reported as an absolute value calculated based on a predetermined rate, being 10% the most common. When the NPV is positive it represents that the investment adds value in discounted terms while a negative NPV indicates that the investment actually reduces value (Brown, 2013). Finally a sensitivity analysis of factors such as changes in the initial cost of biomass will be performed to determine and how this directly affects the production costs and therefore the economic performance of the biorefinery. The sensitivity analysis quantifies the sensitivity of the point estimates that resulted from the TEA parameters, comparing different scenarios more “pessimistic” and “optimistic”.

Assumptions used for TEAs must be made due to lack of necessary data when analysing different pathways. Although, the number of assumptions used in TEAs for biorefineries vary widely among authors with little justification, most common used are the feedstock cost used for production, the biorefinery lifespan, capacity, Lang Factors for example, the ratio of TPI to total purchased equipment cost, and finally the stream factor which refers to the percentage of hours annually in which the plant is operational. Large biorefineries achieve a lower TPI as they benefit from economies of scale; however, there is not an established optimal capacity for the plant. According to Brown, as the majority of studies consider a plant size of 2000 MTPD, this uniformity can be misleading as the optimal capacity depends on different factors such as feedstock type and cost (2014). Also, even though analyses use 2000 MTPD as plant capacity, it is unclear whether assumed feedstocks are abundant enough to supply the assumed biorefineries capacities. Additionally, feedstock cost is one of the primary drivers of MFSP, IRR and NPV making i tan important factor to be included in the sensitivity analysis. Absence of commercial-scale biorefineries also proves it difficult to identify an appropriate lifespan, making it also an important factor to be included in sensitivity analysis. According to Brown, “the sensitivity analyses employed by the reviewed publications accomplish their task by adjusting a single factor value by a predetermined amount and quantifying the resulting impact on MFSP, IRR, or NPV” (Brown, 2014, p. 175). The factors considered in the sensitivity analysis would be considered with a variation of -20% of the base value and +20% of the base value, as recommended by Dang, Hu, Rover, Brown & Wright in their report Economics of biofuels and bioproducts from an integrated pyrolysis biorefinery (2016).

# 3. Development (Results and Discussions)

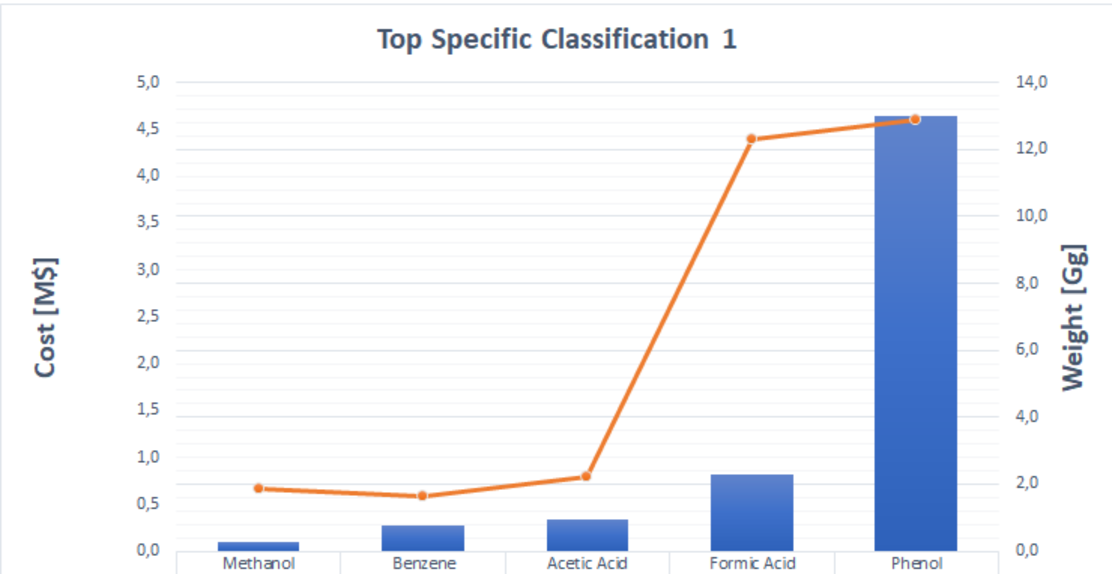
## 3.1 Preliminary Market Study

### *3.1.1 Production Capacity Determination (Plant Size)*

The top chemicals imported to Ecuador in 2017 were identified into 2 categories:

1. Specific classification 1, considering products of pyrolysis and catalytic pyrolysis of biomass (Pyro + CatPyro)
2. Specific classification 2, such as products of other aerobic and anaerobic processes of biomass transformation (BioChem)

Data from Ecuador's imports from 2017 indicate the top chemicals corresponding to the specific classification 1 entering the country are various including the following in decreasing quantity: Phenol, Formic Acid, Acetic acid, Benzene and Methanol. The figure below indicates the top products corresponding to this classification in quantity (weight) and in CIF (Cost, insurance and freight):




| | Methanol | Benzene | Acetic Acid | Formic Acid | Phenol |
|---|---|---|---|---|---|
| Weight [Gg] | 0,3 | 0,8 | 0,9 | 2,3 | 13,0 |
| Cost [M$] | 0,7 | 0,6 | 0,8 | 4,4 | 4,6 |

**Figure 1 Total Quantity in Gigagrams and Total Cost only for the top importations of 2017 for the Specific Classification 1.**

**Taken from Cabezas et al, 2018, p. 9**

On the other hand, the top chemicals that figure in the imports of the country corresponding to the specific classification 2 are: Acetic acid, Propanediol, n-Propanol, Ethanol and Citric acid. The figure below presents the total quantity in kilograms and total cost for the 2017 imports of the products corresponding to the specific classification 2. We are able to notice that acetic acid figures in the top products of both specific classifications. A total of 940 tons of acetic acid were imported into the country only in 2017, which accounted for a total cost of almost 1 million US dollars.

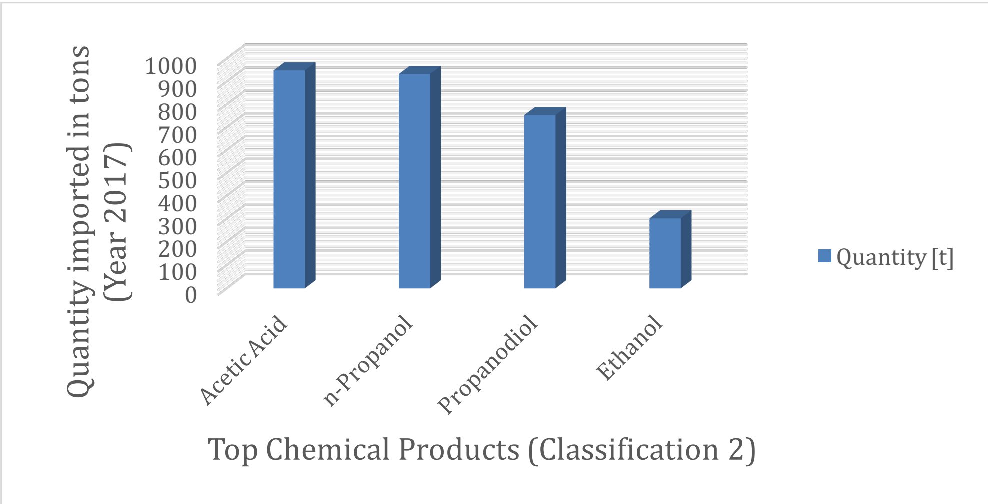



**Figure 2 Total Quantity in Kilograms only for the top importations on 2017 for the Specific Classification 2.**

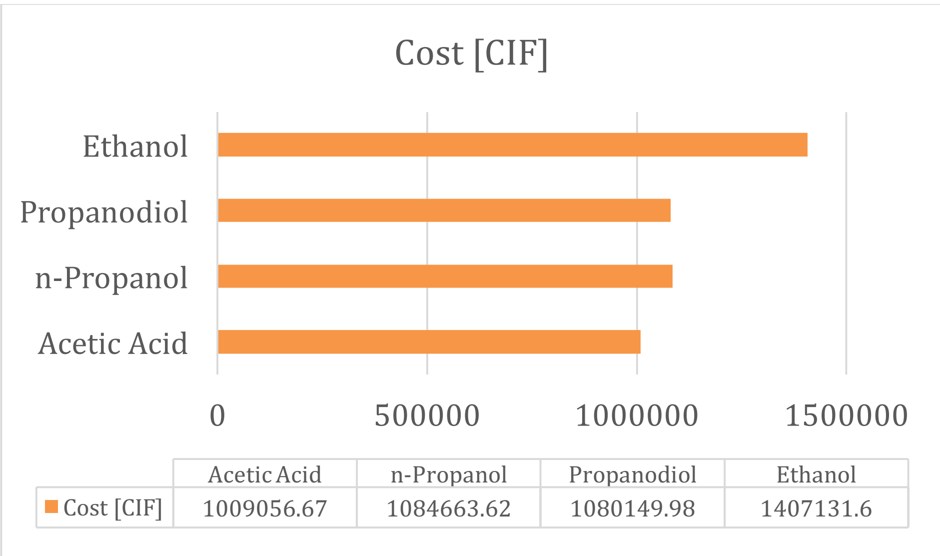



**Figure 3. Total Quantity in Total Cost (CIF) only for the top importations on 2017 for the Specific Classification 2**

In the process designed by Zhu & Jones, “Techno-economic analysis for the thermochemical conversion of Lignocellulosic Biomass to Ethanol via Acetic Acid synthesis”, we are able to identify an initial biomass feed of 2000 metric ton per day to produce a total of 145 millions of gallons/year or 548 884, 71 $m^3$/year of ethanol. Considering an ethanol density of 789 kg/$m^3$, a total of 430,33 Gg/year is produced by the model plant established by Zhu & Jones (2009). In other words, a total of 2000 MTPD of biomass is needed to produce a total of 430,33 Gg/year of ethanol. Based on the high yields reported in the process, almost all of the acetic acid produced is the converted into ethanol with yields up to 91.5%.

As mentioned before, a total of 940 tons of acetic acid were imported into the country. Based on a Baca Urbina study in 2011, the process plant capacity must be around 10% of the total demand of the product on a free market, as establishing a plant with a capacity of the total demand, in this case 0,98 Gg of acetic acid, would be too risky. In order to produce 10% of the total acetic acid imports, 94 tons of acetic acid per year a total of 0.560 MTPD biomass feed is needed. The amount required was calculated based on the production yields reported by Zhu & Jones in 2009. The amount of biomass required for the process is vastly available in any of the cantons of the province of Pichincha.

### *3.1.2 Acetic Acid Price and Imports.*

A first approach for acetic price determination was performed during investigation performed by Cabezas et al in 2018, for acetic acid imports in 2017 in which a CIF of USD $1 121,11 per ton of acetic acid. According to the National Foreign Trade Committee, COMEX by its acronym in Spanish, in resolution number 59, chapter VII, acetic acid is not charged with taxes or tariff rates (SENAE, 2012). The only two values charged to acetic acid are: FODINFA, a development fund for children, which is a percentage of 0.5% over the CIF value and an income tax of 12% which the majority of products sold in the country must be paid by the consumer.

Different suppliers of acetic acid in the market were contacted in order to determine the market value selling price. The price for glacial acetic acid 99.9% ranged from a price of USD $23,50 per litre, distributed by NOVACHEM S.A to a price of USD $134,4 per litre distributed by "Laboratorio Cevallos". Although, acetic acid is sold in other forms per kilogram with a price of USD $2,20 per kilogram, distributed by SOLVESA. This value compares to the USD $1,323 per kilogram of acetic acid in the US, meaning the price increases about 39,7% when entering the country. Although, the price used as a target to achieve is the one of USD 23,50 distributed by NOVACHEM S.A. which is the one which resembles more in characteristics, especially the high purity, of the one that is to be produced in the process plant.

As mentioned before, the imports of acetic acid in the year 2017 were approximated to 980 tons. It is important to analyse the total imports of acetic acid during the last years, as presented in the figures below:

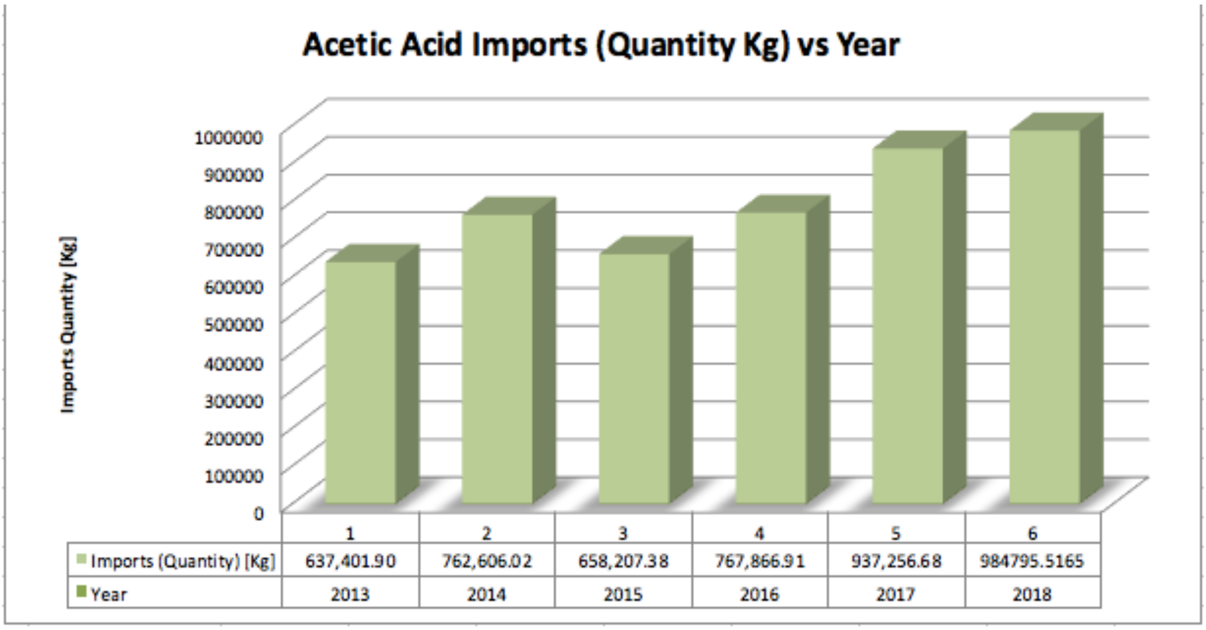



**Figure 4. Total Quantity of Acetic Acid Imports in Kilograms (2013-2018)**

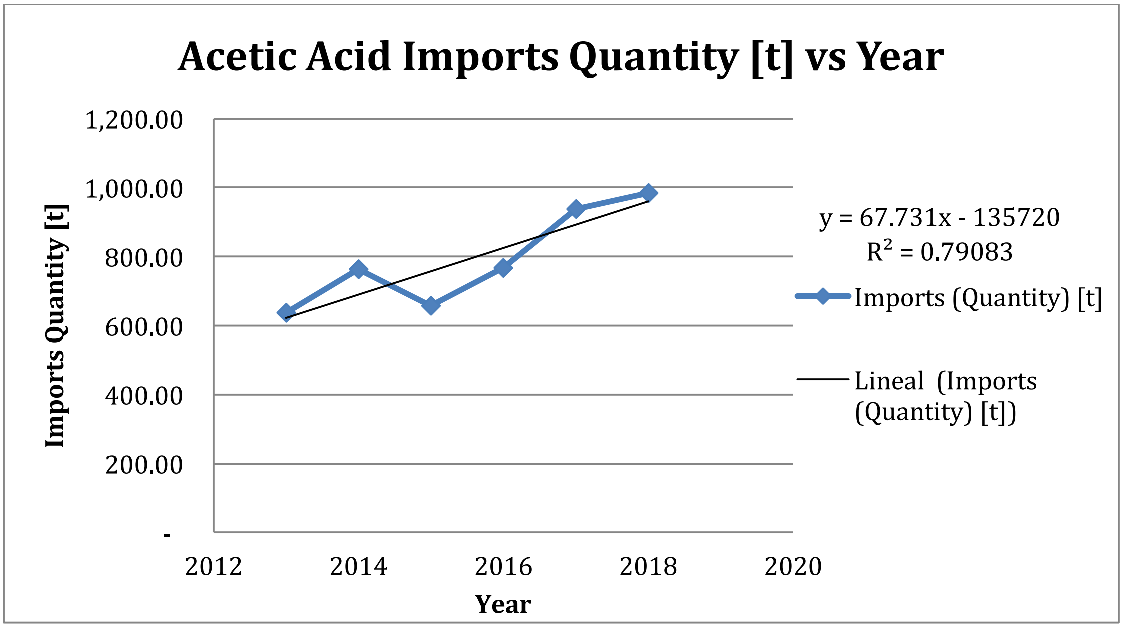



**Figure 5. Quantity in tons of Acetic Acid Imports (2013-2018) growing tendency.**

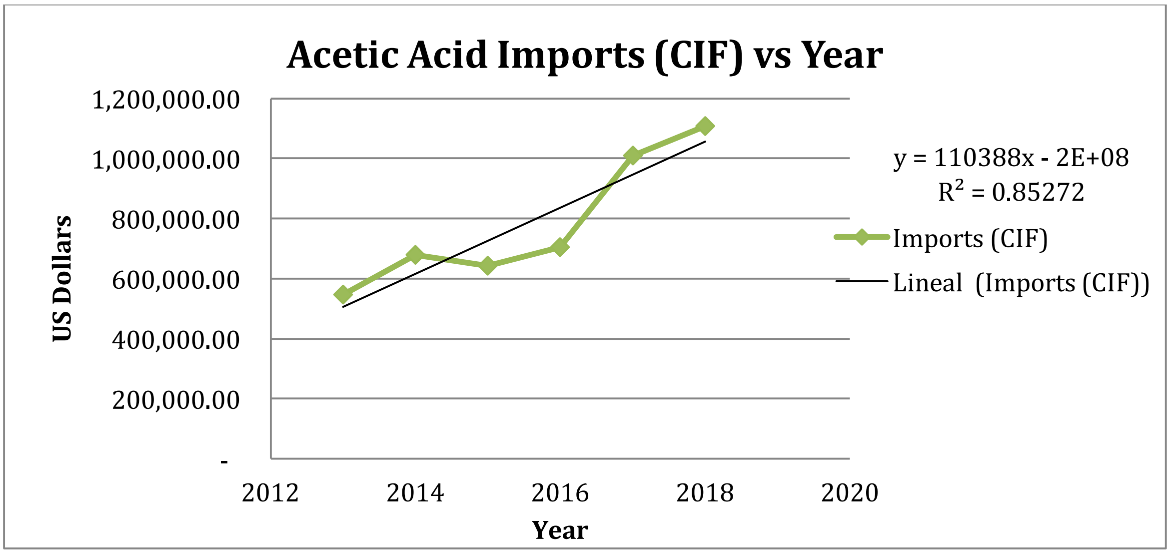



**Figure 6. Quantity in USD of Acetic Acid Imports (2013-2018) growing tendency.**

As shown in the figure above, acetic acid imports have a tendency of sustained growth both in total quantity and in CIF. This is corroborated by the high value of data adjustment $R^2$ by performing a lineal regression. This promotes the development of a biorefinery for the product as demand is continuously growing. The only year which breaks this tendency is

2015, this could be attributed to the economic recession that the country was experiencing during the same time period. In 2018, acetic acid imports incremented to 985 tons per year and until February 2019, the quantity imported grew 11% compared to the imports in the same time period of the previous year.

## 3.2 Biomass Residues

### *3.2.1 Availability*

The types of products, residues and processing residues of biomass according to the Bioenergetic Atlas of Ecuador of 2014 (ESIN Consultora S.A) are summarized in the tables and classified into two categories, thermochemical and biochemical:

**Table 3. Types of Product, Field Residue and Processing Residue for Biochemical Processes**

| Product | Field Residue | Processing Residue |
|---|---|---|
| Rice (Oryza sativa) | Panca (Straw) | Shell |
| Banana (Musa Paradisiaca) | Leaf / Pseudostem | Spine , Product Rejection |
| Cocoa (Theobroma cacao L) | Pruning, discarded cob, husk of cob | Spine, Product Rejection |
| Coffee (Coffea arabica) | Pruning, Renovation of plants | Tarilla |
| Sugar cane (Saccharum officinarum) | Stems and leaves | Bagasse |
| Hard Corn (Zea mays) | Leaves, stems, ears | Cob depending on the purpose |
| African Palm (Elaeis guineensis) | Leaves and trunks of palm tree | Rachis, mesocarp fibers, walnut husk |
| Palmito (Bactris Gasipaes) | Leaves and trunks of palm tree | Pinching, outer layers, product rejection |
| Pineapple (Ananas comosus) | Leaves and trunks of palm tree | Crown, Shell, Heart, Leaves of the plant |
| Banana (Musa spp) | Leaves, Pseudostem | Spine, Product Rejection |
| Poultry | Excreta | |
| Porcine | Excreta | |
| Bovine | Excreta | |
| Implanted Forest (Wood and paper) | Ramas, corteza, raices | Sawdust, Scraps, Chips |

**Table 4. Types of Product, Field Residue and Processing Residue for Thermochemical Processes**

| Product | Field Residue | Processing Residue |
|---|---|---|
| Rice (Oryza sativa) | Panca (Straw) | Shell |
| Banana (Musa Paradisiaca) | Leaf / Pseudostem | Spine , Product Rejection |
| Cocoa (Theobroma cacao L) | Pruning, discarded cob, husk of cob | Spine, Product Rejection |
| Coffee (Coffea arabica) | Pruning, Renovation of plants | Tarilla |
| Sugar cane (Saccharum officinarum) | Stems and leaves | Bagasse |
| Hard Corn (Zea mays) | Leaves, stems, ears | Cob depending on the purpose |
| African Palm (Elaeis guineensis) | Leaves and trunks of palm tree | Rachis, mesocarp fibers, walnut husk |
| Palmito (Bactris Gasipaes) | Leaves and trunks of palm tree | Pinching, outer layers, product rejection |
| Pineapple (Ananas comosus) | Leaves and trunks of palm tree | Crown, Shell, Heart, Leaves of the plant |
| Banana (Musa spp) | Leaves, Pseudostem | Spine, Product Rejection |
| Implanted Forest (Wood and paper) | Branches, Bark, Roots | Sawdust, Scraps, Chips |

Contour maps developed in the report “Moving Ecuador towards a Greener Chemical Industry” by Cabezas et al. in 2018 illustrate the idea of the wide biomass availability in the country. The maps represent the waste density of biomass production per year in t / km$^2$ / year. Maps are also classified with the most probable technology to transform the biomass into valuable chemicals or other products. For both pathways, biochemical and thermochemical, three provinces represent the highest biomass waste production: Guayas, El Oro and Los Rios. Although, these provinces lead the provinces there is also a high potential in other locations such as Pichincha, Esmeraldas, Manabí, Cañar and Santo Domingo. The maps are presented in the following page:

a) b)

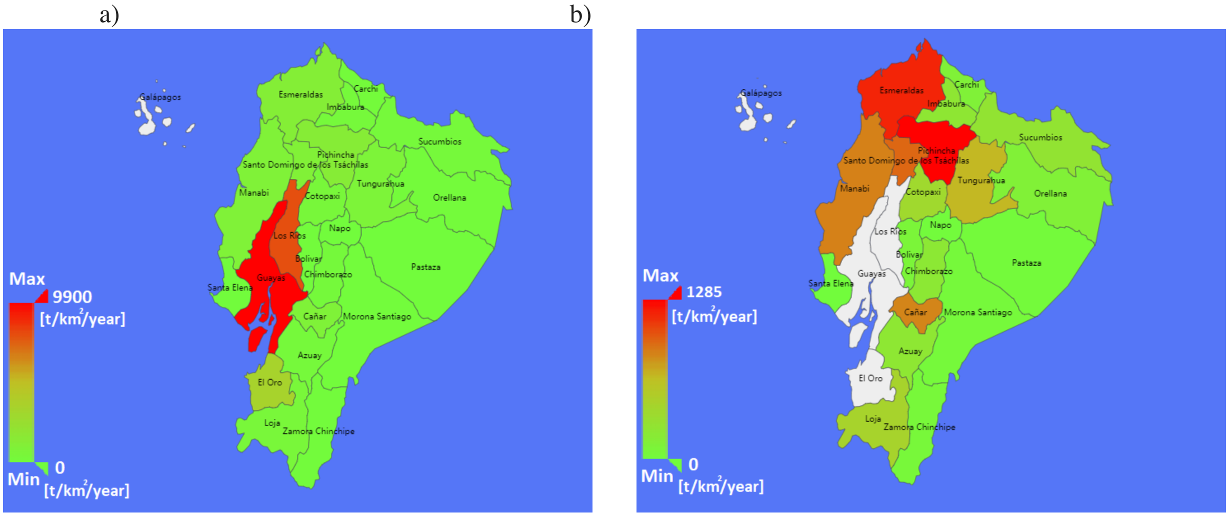



**Figure 7. Geographical distribution of waste biomass production which could be transformed by biochemical methods. in tons per square kilometer for the year 2014. a) Top three biomass waste producers. b) Other provinces (production density below 1285 ton/km2/yea**

In the figures above, Guayas produces a density of 9900 ton/km$^2$/year biomass waste followed by Los Ríos with a density of 7875 ton/km$^2$/year.

a) b)

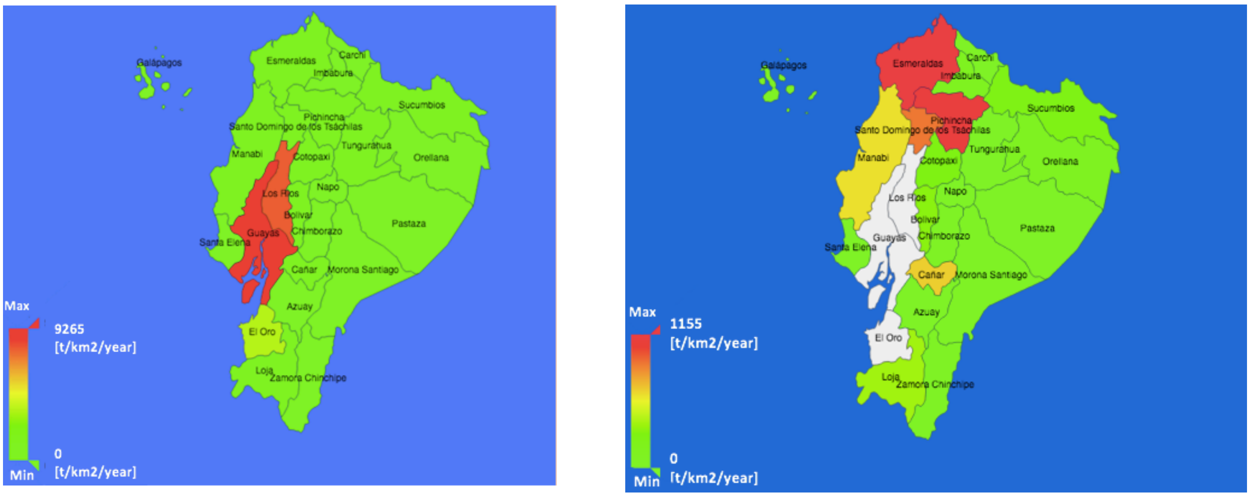



**Figure 8. Geographical distribution of waste biomass production which could be transformed by thermochemical methods. in tons per square kilometre for the year 2014. Three provinces have the highest production density of biomass waste. a) Top three biomass waste.**

The values of biomass residue density per province in detail, classified according to the technology of conversion, are summarized in the table below:

**Table 5. Available biomass resources for each province for biochemical or thermochemical applications.**

| Province | Biochemical Residue Density ($t/km_2/year$) | Termochemical Residue Density ($t/km_2/year$) |
|---|---|---|
| Azuay | 229.05 | 9.04 |
| Bolívar | 71.64 | 318.92 |
| Cañar | 843.54 | 676.25 |
| Carchi | 116.52 | 7.98 |
| Chimborazo | 213.41 | 38.48 |
| Cotopaxi | 380.25 | 274.86 |
| El Oro | 3365.84 | 3177.34 |
| Esmeraldas | 1170.05 | 1154.79 |
| Guayas | 9899.39 | 9264.59 |
| Imbabura | 235.05 | 139.30 |
| Loja | 440.50 | 379.60 |
| Los Ríos | 7875.18 | 7835.02 |
| Manabí | 857.74 | 627.22 |
| Morona Santiago | 32.91 | 18.50 |
| Napo | 10.43 | 6.97 |
| Orellana | 121.62 | 117.52 |
| Pastaza | 18.18 | 1.09 |
| Pichincha | 1285.83 | 1121.31 |
| Santa Elena | 3.96 | 1.70 |
| Santo Domingo | 943.24 | 903.18 |
| Sucumbios | 266.23 | 263.54 |
| Tungurahua | 671.06 | ND |
| Zamora Chinchipe | 45.85 | 23.65 |

As mentioned above, biomass resources in the country come from different industries, such as the agricultural, livestock and forestry. Although the agricultural sector presents the major contribution to biomass residues, the forestry sector also accounts for a considerable value of usable biomass for conversion into valuable chemicals, such as acetic acid. Quantification of residues was performed taking into account different criteria such as variables related to implantation yields: region, climate, management and uses of the resource. The residues of clearance range between 30% to 40% of the total woody volume (ESIN Consultora SA). Ecuador counts with 148 415 ha of implanted forestry, with an estimated amount of residues of 216 157 t/year, in which only 8 provinces concentrate the 69% of woody biomass residues. Although the coastal region concentrates the major density of biomass residues, it is the highlands region that achieves the major residues related to forestry being the first one Imbabura with the canton of Otavalo concentrating the 14.2% of the total residues. Imbabura leads with a total of 50 123.36 t/year (Density of 95.23 t/km$^2$/year), in second comes Los Ríos with a total amount of 45 146.84 t/year (Density of 58.39 t/km$^2$/year), Cotopaxi is in third place with a total of 36 404.25 tons of residues produced annually (Density of 29.71 t/km$^2$/year) followed by Pichincha with 28 931.24 t/year (Density of 30.36 t/km$^2$/year) (Atlas Bioenergético del Ecuador, 2014). The different locations according to The main species found in the country are *Eucalyptus, Pinus radiata* and *Tectona grandis.*

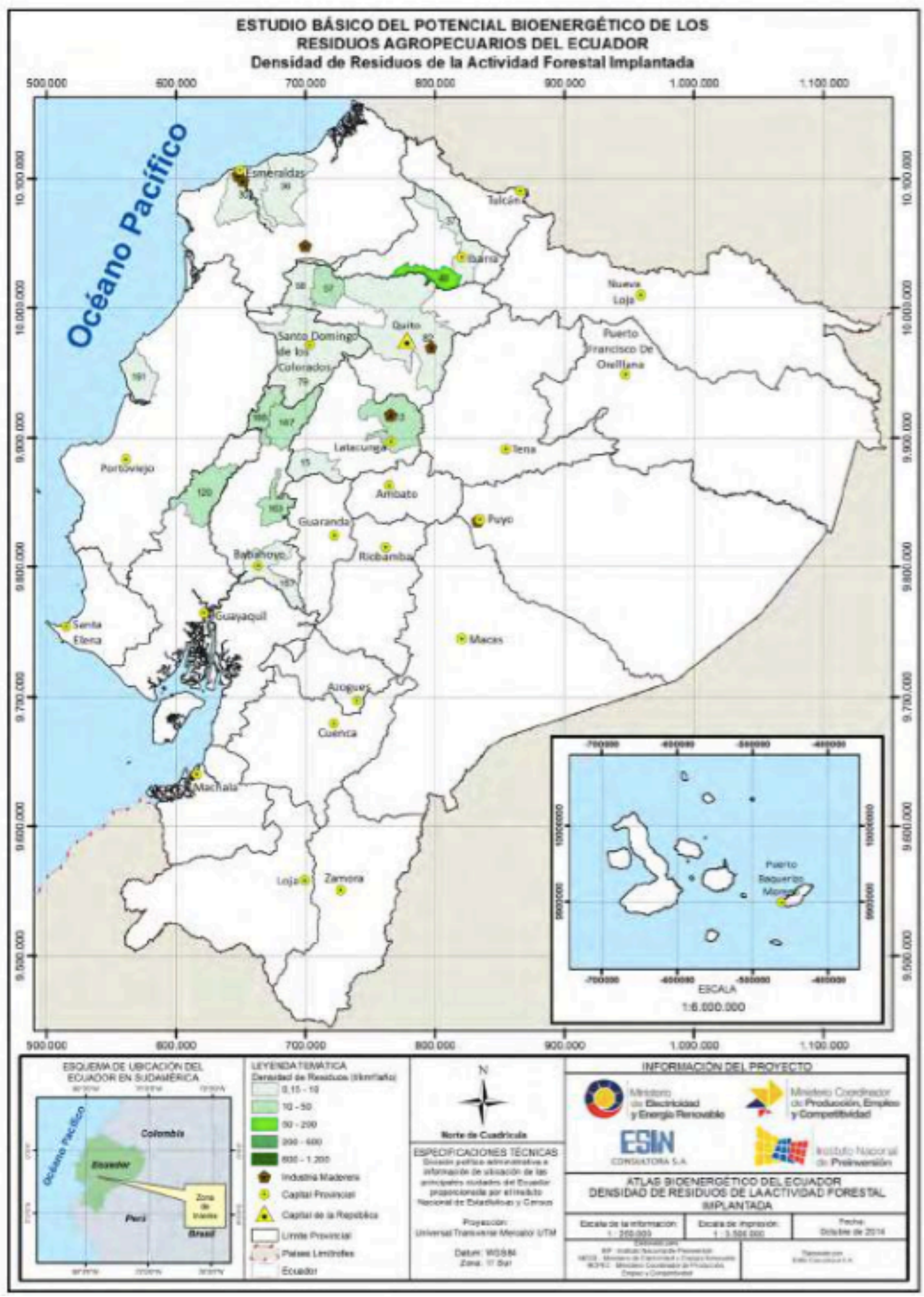



**Figure 9. Forestry Residues of Ecuador. Density of Residues of Implanted Forestry Activity.**

**Taken from: Atlas Bioenergético del Ecuador (ESIN Consultora S.A, 2014, p.146)**

The table below summarizes useful data about provinces with their respective cantons with forestry residues:

**Table 6. Summary of the Implanted Forestry Sector in Ecuador.**

**Source: Atlas Bioenergético del Ecuador (ESIN Consultora S.A, 2014)**

| Province | Forestry Area (ha) | Residues (t/year) | Density of Residues ($t/km^2/year$) |
|---|---|---|---|
| **Imbabura** | 23 313.19 | 50 123.36 | 95.23 |
| **Los Ríos** | 20 998.53 | 45 146.84 | 58,39 |
| **Cotopaxi** | 16 932.21 | 36 404.25 | 29.71 |
| **Pichincha** | 13 456.39 | 28 931.24 | 30.36 |
| **Santo Domingo de los Tsáchilas** | 9 808.70 | 21 088.71 | 6.12 |
| **Guayas** | 9 278.63 | 19 949.05 | 16.80 |
| **Esmeraldas** | 4 482.96 | 9 638.36 | 6.79 |
| **Manabí** | 2 267.70 | 4 875.56 | 6.88 |

Although the province of Pichincha is not the leading province for forestry residues, it also has great potential. The table below summarizes important information about the implanted forestry sector in the province of Pichincha for the studied cantons:

**Table 7. Summary of the Implanted Forestry Sector in Pichincha.**

| Canton | Surface ($km^2$) | Forestry Area (ha) | Forestry Density ($ha/km^2$) | Residues (t/year) | Residue Density ($t/km^2/year$) | Brute Energy (TJ/year) |
|---|---|---|---|---|---|---|
| **Pedro Vicente Maldonado** | 623.33 | 5 764.10 | 9.25 | 12 392.82 | 19.88 | 238.68 |
| **Puerto Quito** | 694.70 | 2 537.66 | 3.65 | 5 455.97 | 7.85 | 105.08 |
| **Quito** | 4 215.54 | 5 154.63 | 1.22 | 11 082.45 | 2.63 | 213.44 |

### *3.2.2 Biomass Selection and Characterization.*

In order to design a robust downstream process for transforming biomass into bio-oil and valuable chemicals, it is necessary to know its chemical properties and characteristics of the initial feedstock. In the literature only compounds of interest have been quantified. Choi, Johnston, Brown, Shanks & Lee, had characterized red oak particles between 250 – 500 um for different pyrolysis experiments (2014). According to the composition analysis, it was composed of 40.7% cellulose, 22.8% hemicellulose and 33.3% lignin, which indicates nearly two-thirds of the feedstock composition is holocellulose. This type of biomass also presented a moisture of 8.3% which is in the typical range (Choi, Johnston, Brown, Shanks & Lee, 2014). The ultimate analyses of red oak feedstock us presented in the table below:

**Table 8. Ultimate and Proximate Analyses of the red oak feedstock (wt%)**

| Ultimate analysis | | Proximate analysis | |
|---|---|---|---|
| Carbon | 45.8 | Moisture | 8.3 |
| Hydrogen | 6.7 | Volatiles | 78.6 |
| Nitrogen | 0.1 | Fixed carbon | 12.7 |
| Oxygen | 47.4 | Ash | 0.3 |
| Total | 100 | Total | 99.9 |
| HHV, MJ/kg | 17.6 | | |

**Taken from:** Choi, Johnston, Brown, Shanks & Lee, 2014, p. 148.

Between the most common species in the country, Eucalyptus is the main in the Ecuadorian region and that will be used for the process design. Although various data is available about the composition of red oak feedstock in the US, there is short information about Eucalyptus. It is important to establish the biomass chemical composition as it is a crucial aspect influencing the products yield and quality. According to Joubert, Carrier, Stahl & Knoetze, "it has been suggested that relative fractional contributions of the respective lignocellulosic compounds making up a specific biomass, outweighs the influence of the intermolecular bonds existing between these compounds" (2019) remarking on the importance of biomass characterization. The characterization analysis used by Cerone (2016), of Eucalyptus is the one that will be used for this process design and is as follows:

**Table 9. Eucalyptus Biomass Residues Characterization.**

| Item | Metric | Value |
|---|---|---|
| **Particle Density** | $kg/m^3$ | 520 |
| **Humidity** | wt% | 13.9 |
| **Particle Size** | cm | 1.8 |
| **C** | wt% | 48.1 |
| **H** | wt% | 6.3 |
| **N** | wt% | 41.7 |
| **N** | wt% | 0.3 |
| **O** | wt% | 41.7 |
| **H/C Ratio** | mol/mol | 1.57 mol/mol |
| **O/C Ratio** | mol/mol | 0.65 mol/mol |

## 3.3 Process Selection for Acetic Acid Production.

Production of acetic acid was chosen due to the high number of processes which exist already to promote its manufacturing on an industrial level. Although, different processes corresponding to both pathways, biochemical and thermochemical were considered. The biochemical processes are those that use different enzymes and microorganisms to convert the biomass in the desired chemicals while the thermochemical processes are based mainly on the use of heat and catalysts to convert the lignocellulosic biomass into products. For industrial production, acetic acid is obtained by chemical synthesis; although, acetic acid fermentation is inevitable and certain process such as the production of vinegar depend on the aerobic fermentation o acetic acid (Chen & Wang, 2016). There are different acetic acid producing biochemical pathways, to mention some of them: From ethanol by two step, the Wood-Ljungdahl pathway, the glycine synthase pathway and fermentation processes. We can identify two distinct groups of acetic acid producing microorganisms, the acetic acid bacteria aerobic pathway or the acetogens, which produce the acid anaerobically (Vidra & Németh, 2017). Acetic acid bacteria, abbreviated as AAB, are known to oxidize ethanol as substrate into acetic acid in both neutral and acidic media in aerobic conditions. These types of bacteria are polymorphoues, elipsoidal to rod shaped, 0.6 to 0.8 µm long, and occurring singly, in pairs or chains (Vidra & Németh. 2017). The taxonomy of AAB has undergone many changes and improvements in accordance to new technologies and are classified into 10 genera and 45 species summarized in the table below, being the main genera of AAB: *Acetobacter, Gluconacetobacter* and *Gluconbacter*. Species are differentiated by morphology in fluid media, iodine reaction and other characteristics such as DNA and polymerase chain reactions (PCR).

**Table 10. AAB genera and number of species (Vidra & Németh, 2017)**

| Genera | Number of Species |
|---|---|
| Acetobacter | 16 |
| Gluconobacter | 5 |
| Acidomonas | 1 |
| Gluconacetobacter and Komagatabacter | 15 |
| Asaia | 3 |
| Kozakia | 1 |
| Saccharibacter | 1 |
| Swaminathania | 1 |
| Neoasaia | 1 |
| Granulibacter | 1 |

Another path of producing acetic acid is converting hexose into three molecules of acetic acid by means of acetogenic bacteria (acetogens) in anaerobic conditions. The acetogenic bacteria are not identical to AAB, these are prokaryotes initially studied for their $CO_2$ fixing properties. There are over 23 genera of acetogens with more than 100 species, being *acetobacterium*, *clostridium* and *moorella thermoacetica* the main species (Vidra & Németh, 2017). According to Vidra & Németh, 2017, p.246, in the anaerobic production of acetic acid:

*Moorella thermoacetica* was used to elucidate the mechanism of homofermentation of acetic acid, which converts 1 mol of glucose into 3 mol of acetic acid. Among all the homoacetogens known to date, only *M. thermoacetica* has been previously considered to have industrial application and, thus, is the only one having been extensively studied for anaerobic acetic acid fermentation.

As mentioned before, one of the pathways to produce acetic acid is from ethanol in a two-step process. Acetic acid bacteria convert ethanol to acetate in two consecutive steps using membrane-bound quinoproteins (Li, Li, Feng & Luo, 2015). Ethanol oxidises to acetaldehyde by means of dehydrogenase, then, the aldehyde produced is oxidized to acetic acid. Different bacteria such as the Acetobacter genera use pyrroquinoline (PQQ) which serves as a hydrogen acceptor that transfer electrons from the reactions. According to Vidra & Németh, "Electrons are initially transferred to ubiquinone, which will be reoxidized by a membrane-associated oxidase. Finally, oxygen is the last electron acceptor, resulting in the formation of $H_2O$ and a proton motive force necessary for energy production through a membrane-bound adenosine triphosphatase" (2017, p.246). AAB would have a requirement for oxygen so the process is described as aerobe. Acetic acid is cytotoxic, and AAB kill competing organisms by secreting this acid. It acidifies the cytoplasm of microorganisms, disrupting their proto gradients poisoning them. Even though the cytoplasmic pH drops to 3.7 and the cytoplasm becomes acidic, cells continue growing and oxidizing ethanol (Nakano & Fukaya, 2008).

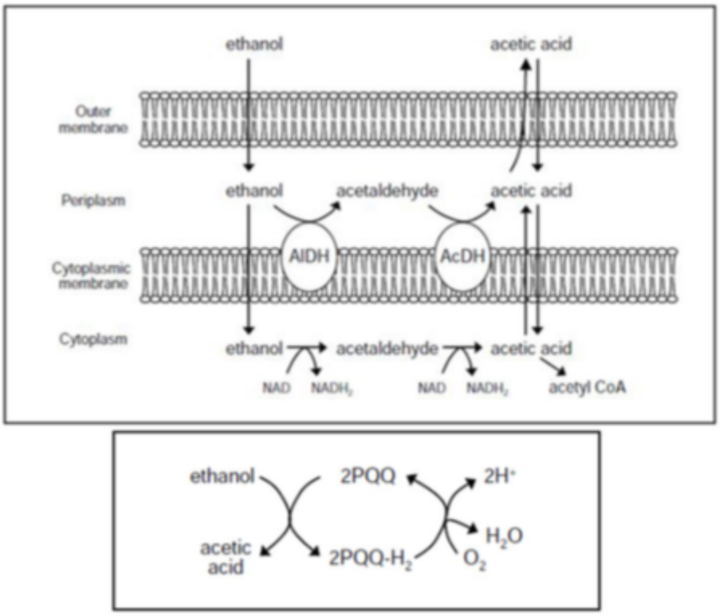



**Figure 10. Formation of acetic acid form ethanol by Acetic Acid Bacteria (AAB). Taken from Vidra & Németh, 2017, p. 247**

Another process to produce acetic acid through a biochemical pathway is the Wood-Ljungdahl way. This pathway uses acetogens to fermentate hexose, which then is passed through glycolysis to form a pyruvate and finally it's oxidized to acetyl-CoA and $CO_2$ (Vidra & Németh, 2017). By means of phosphotransacetylase, the acetyl-CoA is converted to acetyl phosphate and then to acetate by acetate kinase. The process is resumed in the following reaction:

$$C_6H_{12}O6+4ADP+ 4\ Pi \rightarrow 2\ CH_3COOH+2\ CO_2+4\ ATP +2\ H_2O+8[H]$$

The equivalents and the 2 moles of $CO_2$ which figure as products of the reaction are shuttled to the Wood Ljungdahl pathway. In this way, a third molecule of acetate is produced:

$$2CO_2+8[H]+nADP+nPi \rightarrow CH_3COOH+nATP+(2+n)H_2O$$

Then, glucose is oxidized to 3 mole of acetate:

$$C_6H_{12}O_6+(4+n)ADP+(4+n)Pi \rightarrow 3\ CH_3COOH+(4+n)ATP + (4+n)H_2O$$

The oxidation equivalents derive from the oxidation of sugars, but also can derive from the oxidation of $H_2$. Acetogens can convert $H_2$ and $CO_2$ to $CH_3COOH$:

$$2CO_2+4H_2+nADP+nPi \rightarrow CH_3COOH+nATP+(2+n)H_2O$$

The Wood-Ljungdahl pathway is summarized and illustrated in the figure below:

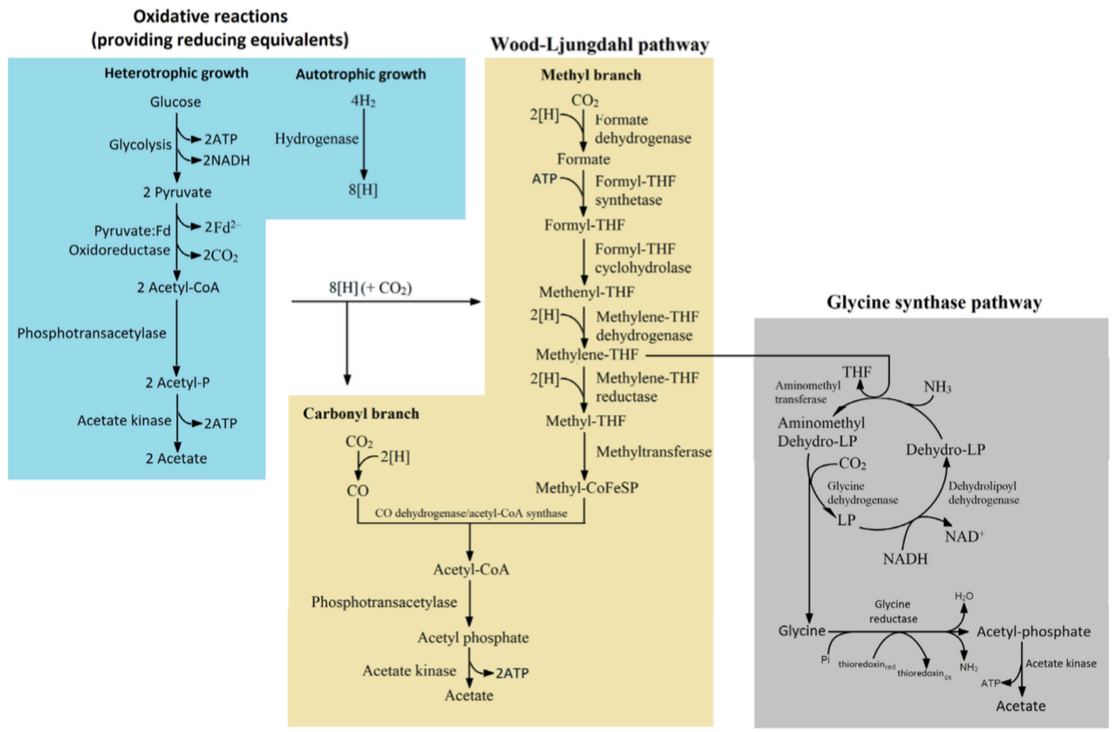



**Figure 11. The Wood–Ljungdahl pathway of acetogenesis and the glycine synthase pathway. THF: tetrahydrofolate Fd2–: reduced ferredoxin; LP: lipoyl-protein CpFeSP: corrinoid iron-sulphur protein [H]: reducing equivalent (= 1e− + 1H+).**

**Taken from (Schuchmann & Müller, 2014, p.5)**

As could be seen in the right hand side of the figure above, there is a pathway which consists in the glycine synthase pathway. Synthesis of acetate from $CO_2$ and one-carbon compounds can be achieved through bacteria such as: *Clostridium acidiurici*, *C. cylindrosporum*, *C. purinolyticum*, and *Eubacterium angustum.* $CO_2$ fixation serves as an electron sink to recycle electron carriers during fermentation of purines and amino acids, by reducing two molecules of $CO_2$ to glycine. The glycine produced is later synthetized to acetate and secreted from the cell. The core of the glycine synthase pathway is the glycine cleavage system which is a multi-protein complex. As can be seen, both the acetyl-CoA pathway and the glycine synthase pathway are quite similar in the general reaction sequence (Vidra & Németh, 2017). Although the similarities between the processes, the glycine synthase pathway serves only as an electron sink while the reductive acetyl-CoA is more versatile, and its used for energy conservation, and autotropic growth besides its function as an electron sink.

An ancient method of producing acetic acid is as vinegar from ethanol by souring of wine and beer (Hailu, Admassu & Jha, 2012). There is a two stage fermentation process, consisting of alcoholic fermentation under anaerobic conditions and acetous fermentation, under aerobic conditions. Fermentable sugars are converted to ethanol by yeasts such as *Saccharomyces cerevisiae*. In the acetous fermentation, AAB can further oxidize the ethanol produced into acetic acid. Vinegar production can be classified into two well defined methods, slow processes which involve the Orleans method and the generator method while the quick methods involve the submerged method and the immobilized cells method (Hailu, Admassu & Jha, 2012). Nowadays, the production of selected vinegars is the surface culture fermentation, in which the AAB are placed on the liquid-air interface in contact with oxygen. The bacteria are placed on the surface of the acidifying liquid and are considered to be a static method. The acetic acid concentration in vinegar depends on the period of time; hence, the production time and more importantly costs are also increased (Vidra & Németh, 2017).

As indicated before, the Orleans method is a slow process to produce acetic acid as vinegar and its one of the oldest. The process, which originated in France, uses high grade vinegar to start, to which wine is added at weekly intervals. In this process, acetous fermentation is slow, because it only takes effect in the surface of the liquid with sufficient dissolved oxygen, which converts alcohol into acetic acid. Vidra & Németh establish that "The vinegar is fermented in large (200 litre) capacity barrels. Approximately 65 to 70 litres of high grade vinegar is added to the barrel along with 15 litres of wine" (2017, p. 249). After a week, 10 to 15 litres of wine are added to the barrel and about four week 10 to 15 litres of vinegar are withdrawn from the barrel. This process repeats itself, adding the respective amount of wine to the barrel and withdrawing the amounts of vinegar.

Although, during fermentation processes it has been identified that the most energy intensive and expensive step is the one of product separation. There are several technologies for acetic acid separation from water such as fractional distillation, azeotropic dehydration distillation, adsorption and solvent extraction. The effectiveness of acetic acid recovery is established in the table below:

**Table 11. Possible operation results of acetic acid recovery**

| Method | Volume | Recovery |
|---|---|---|
| Adsorption | 50mL | 82% |
| Extraction | 40mL | 96% |
| Extraction | 750mL | 88% |
| Extractive Distillation | 372mL | 68% |
| Nano filtration | 800mL | 99% |
| Reactive Distillation | n.a. | 57.6% |
| Solvent Extraction | 200mL | 96.3% |

In the case of liquid-liquid extraction, three main aspects play an important role including: The pH, in order to have the acid in undissociated form, the extraction solvent for the process must have a high partition coefficient of the carboxylic acid and a high selectivity for extraction of carboxylic acid over water and finally, that a reversible extraction system is needed so the solvent could be recovered (Jipa et al, 2009). In these cases, there are three main groups of extraction solvents:

1. Carbon-bonded oxygen bearing extractants (i.e. alcohols and ethers).
2. Organophosphorus extractants such as triotylphophine oxide (TOPO) and tributylphosphate (TBP).
3. Aliphatic amine extractants such as tri-n-octylamine (TOA)
4. Liquid-liquid extraction is mainly used as a process for intermediate concentrations, between 10% and 50% followed by azeotropic distillation. Low molecular weight solvents have a sufficiently high distribution coefficient for these concentrations.

Other way of acetic acid recovery is by means of adsorption, for example, in activated carbon. Adsorbents need a good selectivity and high adsorption capacity, however, according to Jipa et al, this is not cost effective and highly uneconomical to implement in the industry (2009). Distillation is also considered, in which it is necessary to have equilibrium stages and a high reflux ratio to obtain glacial grade acid. According to Poste, "in extractive distillation, counter current washing of mixed vapours in a distillation column takes place via a descending stream of a high boiling point liquid, which is preferentially solvent for one of the components" (2010, p. 43). Although, the process proposed by Poste about distillation is also characterized by expensive equipment, a great amount of steam used to vaporize the volatile water used in the process, and the high latent heat of vaporization. Another type of distillation is also considered, known as Reactive Distillation (RD) which combines the chemical reaction and the distillative product separation in one equipment. RD offers a great advantage over traditional distillation, such as half energy consumption, reduction in capital and operating costs, simpler maintenance and process control, however, this way of product recovery is only in the early stages of their developing (Vidra & Németh, 2017). Membrane processes and in situ removal are also considered, as filtrations of acid is feasible by means of microfiltrations, ultrafiltration, nanofiltration and electrodyalisis, although, drawbacks such as membrane fouling, frequent cleaning and maintenance, membrane instability and high complexity must be considered.

Although the biochemical pathway is a promising method for the production of acetic acid production from renewable biomass, it is still challenging to separate organic acids from different diluted components in an efficient degree. It´s relevant to consider the different factors that limit the use of biochemical technology in the production of chemicals:

1. The production rates by micro-organisms in an aqueous medium are inherently low, since these microorganisms are sensitive to inhibitors and operating conditions such as temperature and pH.
2. Moreover, most fermentation processes require aseptic conditions which can be difficult to achieve on a large scale and in an industrial level.
3. Another challenging aspect to consider is the reduction of impurity organic acids with similar properties to a minimum value. Some of the methodologies presented above have different limitations and drawbacks such as inefficient yield productions, low purity and high energy consumption. Vidra and Németh establish that “there is a need to develop a process that should ideally be simple to carry out and allow the purification of acetic acid directly from the fermentation broths” (2018).

Although, in some of the processes, the emergence of new technologies and materials are still promising to develop mature recovery processes that allow the biochemical pathway to be more competitive against the traditional synthesis processes. Within the end of the next century, the depletion of CO, natural gas and petroleum resources will promote a green chemical industry that takes full advantage of bacteria-based processes for the industrial production of acetic acid. Until then, it is important to emphasize in the benefits of the other green and more developed pathway proposed for the production of chemicals: The Thermochemical one.

On the other hand, gasification is considered as a promising thermochemical process for the production of acetic acid. Gasification is understood to be the conversion of solid, carbon-rich materials in conditions of high temperature, typically in the wide range between 750 °C to 1500 °C and oxygen starved conditions into a mixture of different flammable gases such as: carbon monoxide (CO), carbon dioxide ($CO_2$), methane ($CH_4$) and hydrogen ($H_2$) and also other minor components such as ammonia ($NH_3$). The mixture of gases previously mentioned before is known as producer gas. Producer gas, is a raw gas that is cleaned and more processed on order to produce synthesis gas (syngas) (Brown, 2013). Gasification is a process that has been into commercial practice for several years, since 1812, used for the conversion of coal into gas. More importantly, gasification is proposed as the basis for energy refineries as its flexibility could provide a variety of chemicals, energy and transportation fuels.

Steps of gasification can be broken down into:

- Heating and Drying.
- Pyrolysis.
- Solid-Gas reactions that consume char.
- Gas-Phase reactions. They adjust the chemical composition of the raw gas initially produced.

The steps are summarized in the figure below:

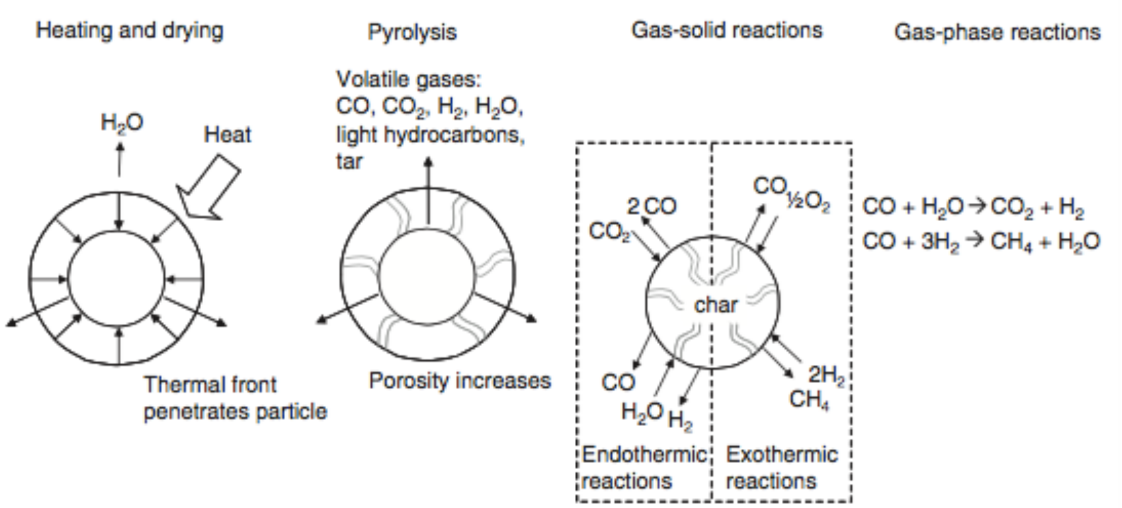



**Figure 12. Process of thermal Gasification.**

**Source: Brown, p. 202, 2013.**

In case of acetic acid produced with gasification, it is an intermediate product of pyrolysis that begins at a temperature between 300 °C and 400 °C. Acetic acid is part of the char produced, mainly the condensable vapours that includes water, methanol and acetone. The distribution of the products obtained mainly depends on the conditions of pyrolysis: temperature, heating rate and chemical composition of the fuel. As the heating and drying are endothermic processes as they require heat in order to achieve them. When this necessary heat is supplied by an external source, gasification is classified as indirectly heated gasification. As established above, the next step of gasification is gas-solid reactions. The raw gas obtained is further conditioned and cleaned as they are not directly usable as fuel gas or for the production of chemicals. The conditioning of gas includes the gas enrichment of certain chemicals such as hydrogen. Once the gas is conditioned and adjusted to a ratio of two moles of hydrogen for every mole of carbon monoxide (CO), it provides the carbon, hydrogen and energy to synthesize the hydrocarbons and also the oxygen necessary to synthesize organic compounds such as methanol and ethanol. There are two approaches that convert synthesis gas to chemicals: Catalytic Synthesis and Biocatalytic synthesis. The second one also uses microorganisms that grown one carbon compounds to convert syngas into different chemical products such as organic acids and alcohols. These microorganisms known as unicarbontrophs, grow on one carbon compounds as a source of carbon and energy. According to Brown, "syngas can be biologically converted to a variety of fuels and chemicals including ethanol, methane, acetic acid and butanol" (Brown, p. 214, 2013). A rod-shaped anaerobic bacterium called *Clostridium ljungdahlii* which is isolated from chicken waste has the ability to metabolize carbon monoxide (CO) and $H_2$ to form acetic acid ($CH_3COOH$) and ethanol ($CH_3CH_2OH$) by the following reactions:

$$4CO + 2H_2O \rightarrow CH_3COOH + 2CO_2$$
$$4H_2 + 2CO_2 \rightarrow CH_3COOH + 2H_2O$$
$$6CO + 3H_2O \rightarrow CH_3CH_2OH + 4CO_2$$
$$6H_2 + 2CO_2 \rightarrow CH_3CH_2OH + 3H_2O$$

**Figure 13. Biocatalytic Synthesis of Acetic Acid and Ethanol**

**Source: Brown, p. 214, 2013.**

However, one of the most promising processes for acetic acid production is the one proposed by Zhu and Jones in 2009 in their report Techno-economic analysis for the thermochemical conversion of Lignocellulosic Biomass to Ethanol via acetic acid synthesis in which the local plant design in Ecuador will be based. The process is based on the conversion of biomass to syngas, then to methanol and finally to acetic acid. This conversion is a well proven technology with high conversions and yields. For the Zhu and Jones study, high yields of acetic acid production were achieved up to 91,5% before it is hydrogenated to produce ethanol. The investigation by Zhu and Jones studies two types of gasification technologies: a directly-heated oxygen-blown gasifier and an indirectly-heated gasifier. For both gasification types, the feedstock is the same and consists of wood chips at 2000 metric ton/day (Dry basis).

The total production in millions of gallons respectively in each process is:

- Indirectly-Heated Gasifier: 145 mmgal/y with a thermal efficiency of 60.7%
- Directly-Heated Gasifier: 176 mmgal/y with a thermal efficiency of 61.9%

The syngas produced is rich in CO and $H_2$, that could be used to produce methanol and other chemicals such as acetic acid. The process could be described in three major steps:


**Figure 14. Biomass Gasification to Acetic Acid**

Two technologies were evaluated:

- Indirectly-heated, entrained-bed gasifier.
- Directly-heated, pressurized, fluidized bed gasifier.

Firstly, wood chips are converted to syngas is the gasifiers. Then, the syngas is sent to a tar reformer and a scrubber. Syngas, free of tars and other contaminants is sent to a sulfur removal unit to remove all the sulfur impurities. The synthesis gas is then sent to convert the $CH_4$ to $H_2$ and CO and to adjust the $H_2$:CO ratio required by methanol synthesis. Methanol is purified and then sent to generate acetic acid in the acetic acid synthesis process by the reaction of methanol with CO. The system consists in 6 main processes:

1. Feed Handling and Preparation.
2. Gasification
3. Tar Reforming and gas scrubbing.
4. Gas purification and steam reforming.
5. Methanol synthesis and purification
6. Acetic Acid Synthesis

## 3.4 Plant Design.

As described above the plant design will be based on the thermochemical pathway of gasification.

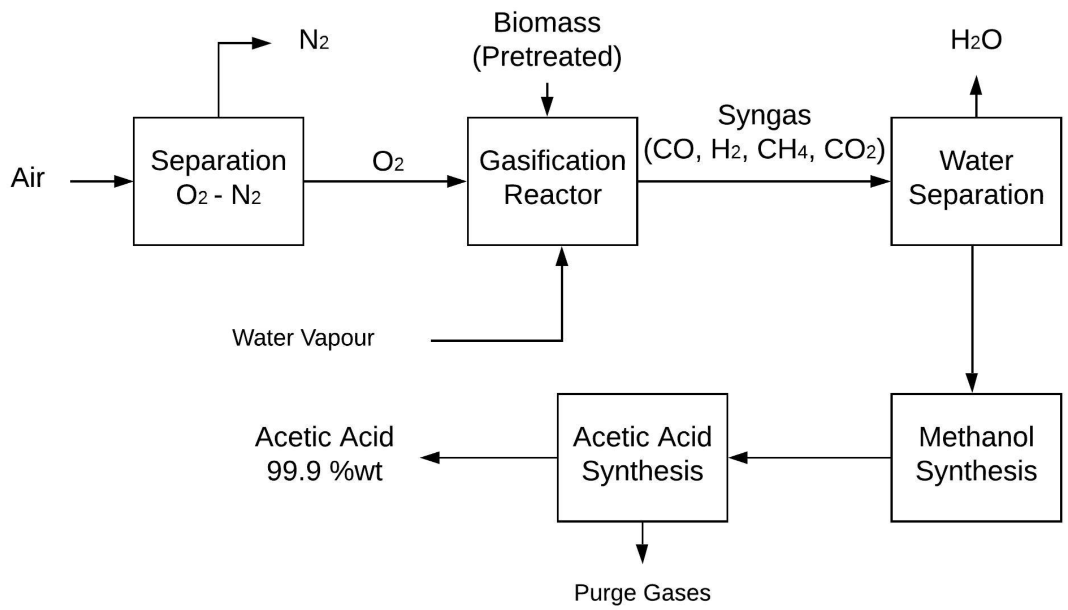



**Figure 15. Simplified Conceptual Diagram of Biomass to Acetic Acid based on Gasifier System**

### 3.4.1 Process Design Basis

The gasification of biomass from residues of eucalyptus wood is basically divided into five (5) sections: Air Purification (oxygen separation), Gasification of biomass, Synthesis gas purification, Methanol synthesis and Synthesis and purification of acetic acid.

**<u>Air Purification (oxygen separation)</u>**

The previously dried air (dehumidified) is introduced at a rate of 94.73 Kg / h to a compressor where air is brought to the conditions of the fractionation process (distillation), until it reaches 2930 kPa and then cooled until the condition is reached of saturated liquid to be fed to a distillation column of 149 stages, where nitrogen of 99.9 mol% purity is obtained on the top of the distillation column and oxygen at the bottom at 99.9% purity are obtained.

This separation is made in order to avoid the formation of ammonia that could be carried out because of the formation of hydrogen in the gasification process.

**Biomass Gasification**

Previously pretreated biomass (Dried in rotary dryers to a moisture content of 6 wt% and triturated to Wood chips around 1.6 cm diameter). The purified oxygen, water vapor and biomass, previously conditioned at 23 psia and 810ºC in the gasification reactor, are introduced to the biomass gasification reactor, where the reactions of biomass gasification and methane gasification are carried out, as follow:

$$C_6H_{10}O_{4(s)} + H_2O_{(g)} \rightarrow 2CO_{2(g)} + 3CO_{(g)} + 2CH_{4(g)} + 2H_{2(g)}$$

$$CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)}$$

$$CH_{4(g)} + 2H_2O_{(g)} \rightarrow CO_{2(g)} + 4H_{2(g)}$$

The global conversion of biomass reaches 98%, while the gasification of methane reaches 27.3% for the formation of Carbon Monoxide and 8.2% for the formation of carbon dioxide.

**Syngas Depuration**

The effluent from the gasification reactor is cooled to condense the remaining water which does not react in the process, cooling the current to -25ºC to promote the condensation process, where more than 99.9% of the water is retired by the bottom of the V-100 separator, from the inlet current to the separator

**Methanol Synthesis**

The synthesis gas is conditioned in the K-101 compressor up to 20 MPa and is subsequently cooled to 473 K (Kuipers, 2014) to reach the optimum conditions for the reactor, which allows a conversion of at least 98%. The importance of reaching a high conversion with this technology is that the process of separation and recirculation, of other similar processes for methanol synthesis, is eliminated.

$$CO_{(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(g)}$$

**Acetic Acid Synthesis and Purification**

The methanol-rich stream leaving the reactor is conditioned to 450 psia and 189 ° C and then fed to the acetic acid synthesis reactor, where a conversion to 91.1% methanol is achieved. Subsequently, the pressure of the mixture is reduced to 37.5 psia to be subjected to a separation process (distillation) in a column of 22 theoretical stages, in which the bottom product consists of acetic acid with a purity greater than 99.9% wt.

$$CH_3OH_{(g)} + CO_{(g)} \rightarrow CH_3COOH_{(g)}$$

### 3.4.2 Aspen Hysys Simulation

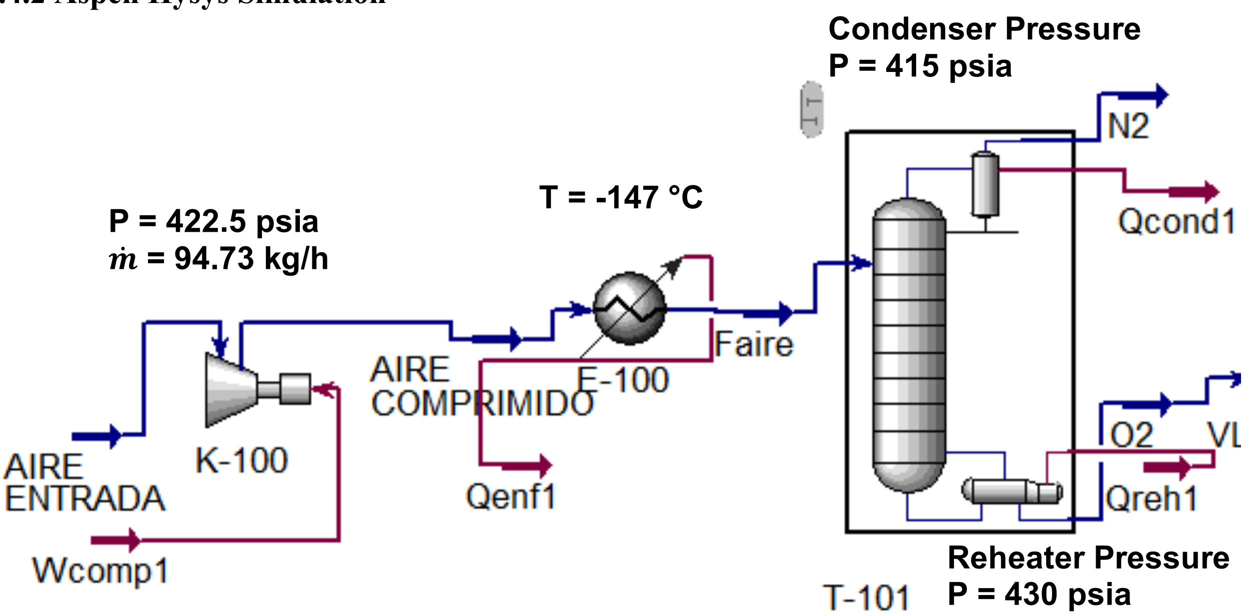



**Figure 16. Separation O2 – N2 Flow Diagram (Aspen Hysys)**

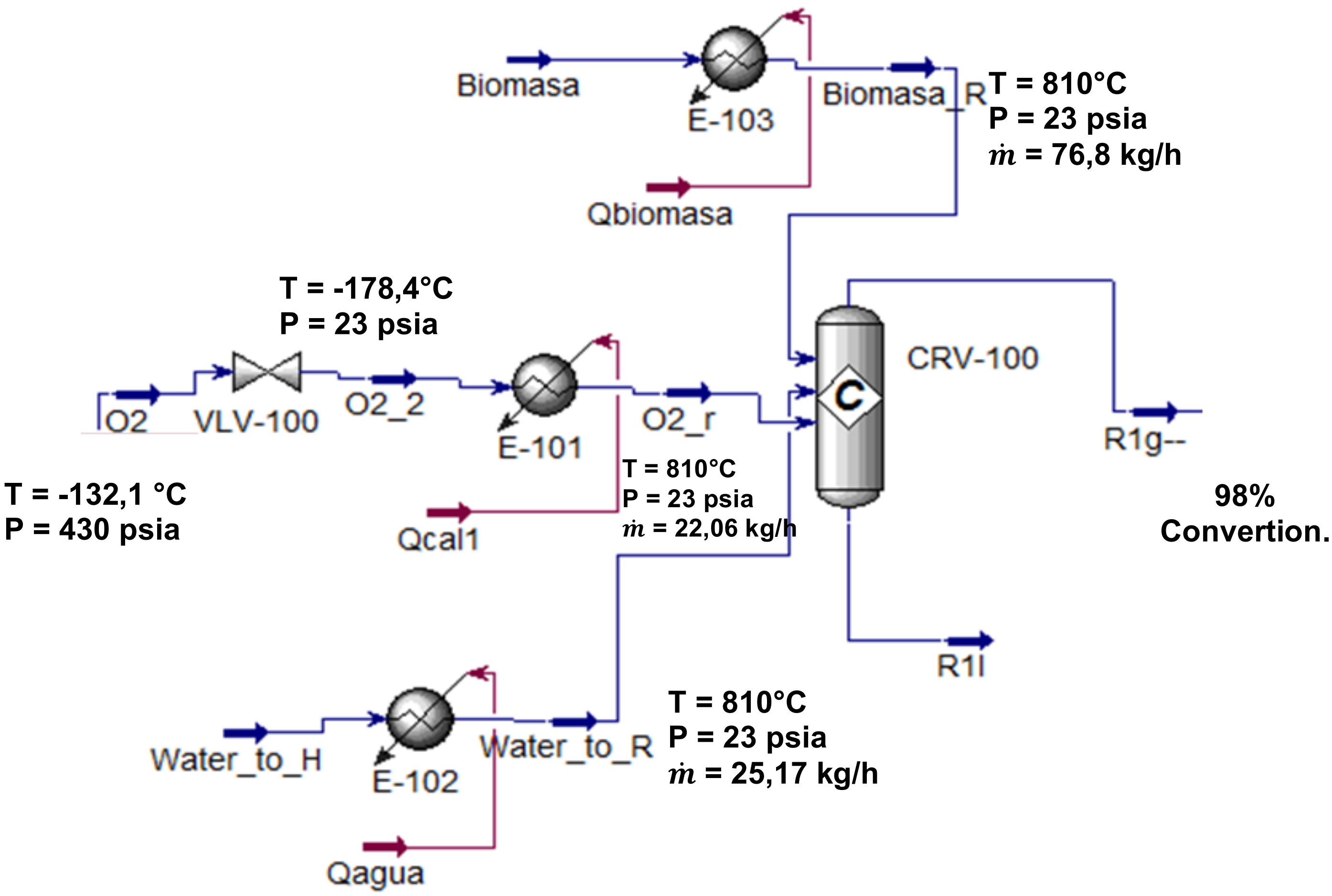



**Figure 17. Gasification Flow Diagram (Aspen Hysys)**

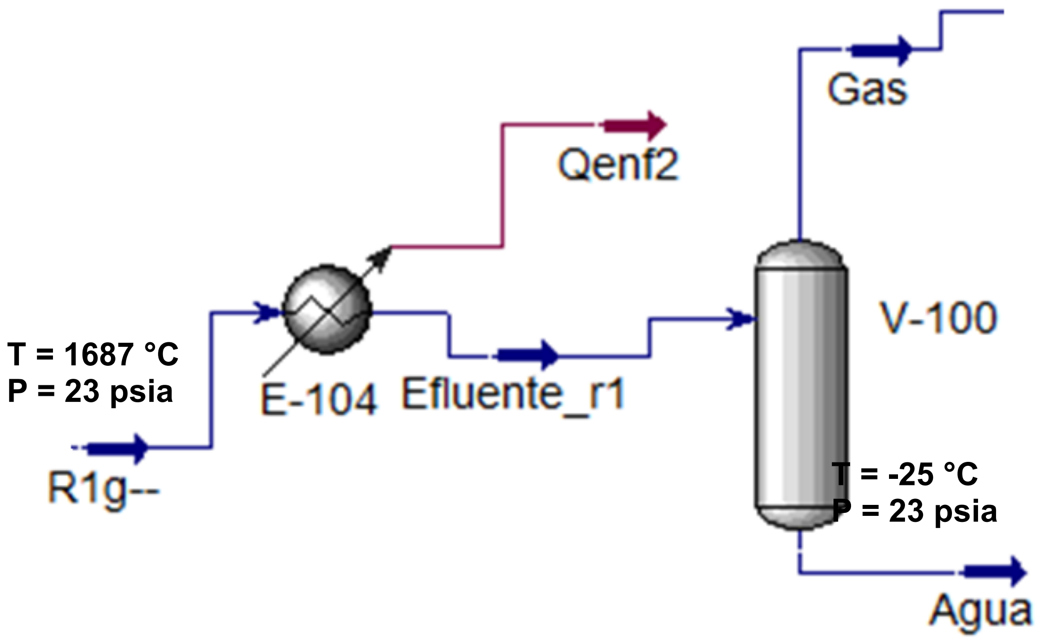



**Figure 18. Water Sepration Flow Diagram (Aspen Hysys)**

**Table 12. Current Composition before and after wáter separation step**

| Component | R1g Current Composition | Gas Current Composition |
|---|---|---|
| Oxygen | 0,1114 | 0,1195 |
| Methane | 0,1077 | 0,1156 |
| Hydrogen | 0,3173 | 0,3406 |
| $CO_2$ | 0,0976 | 0,1047 |
| CO | 0,2972 | 0,3190 |
| $H_2O$ | 0,0689 | 0,0005 |

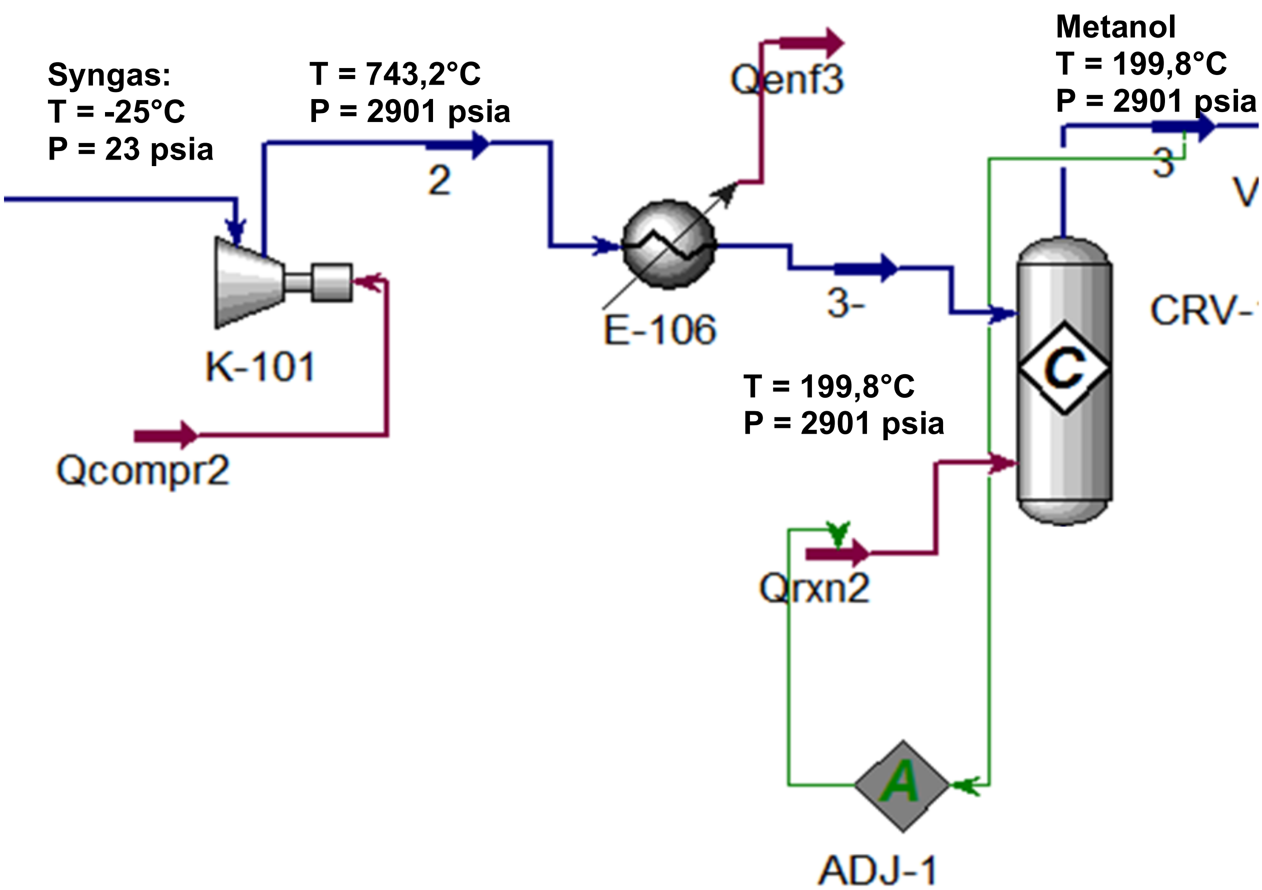



**Figure 19. Methanol Synthesis Flow Diagram (Aspen Hysys)**

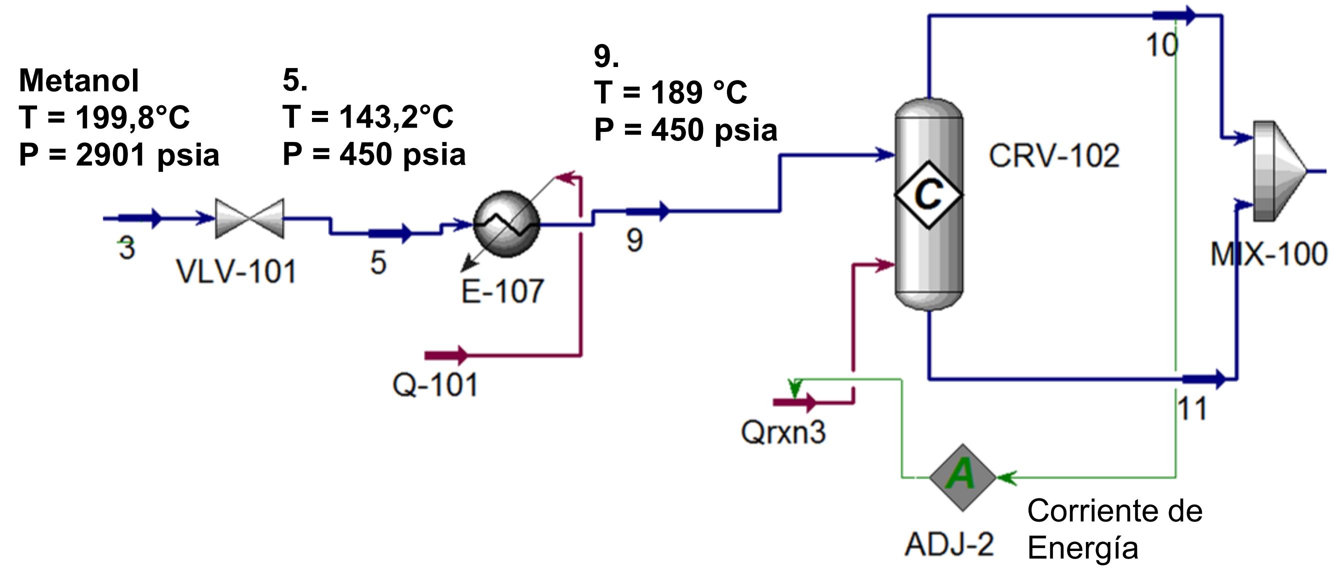



Figure 20. Acetic Acid Synthesis Flow Diagram (Aspen Hysys)

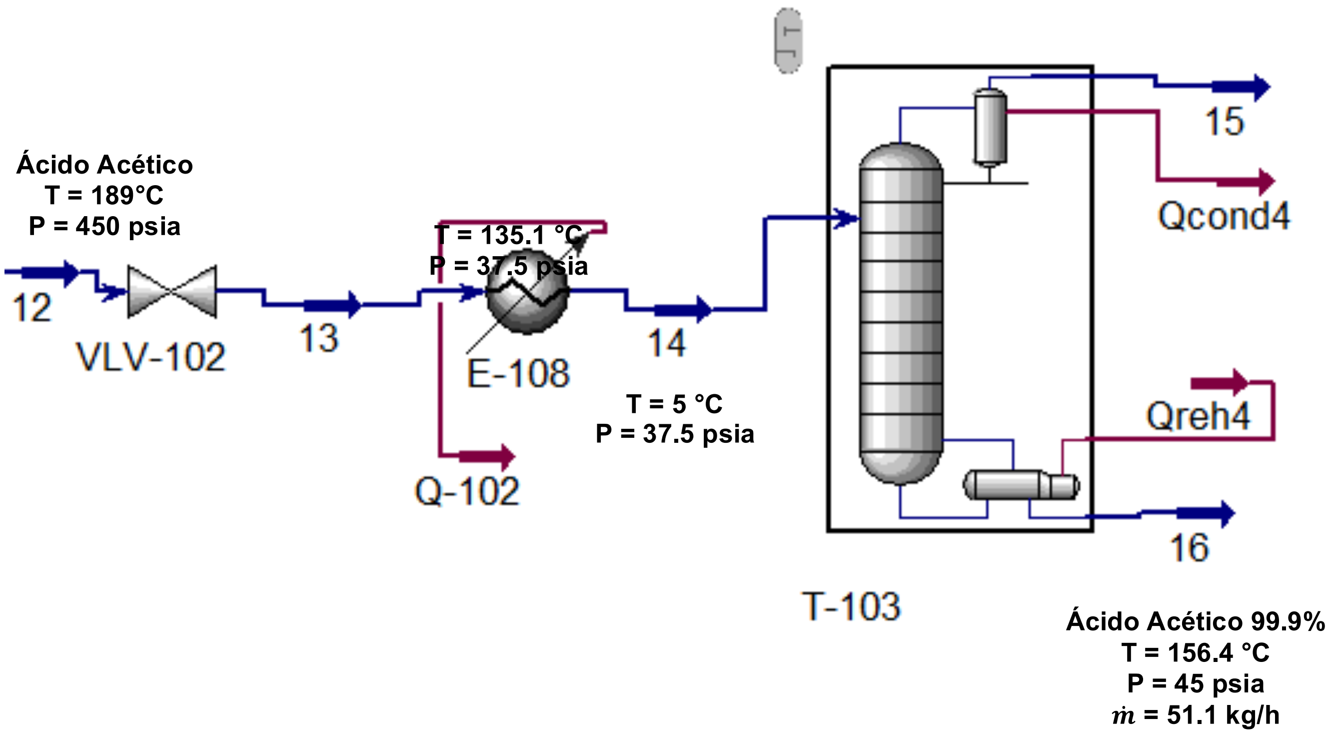



Figure 21. Acetic Acid Purification Flow Diagram (Aspen Hysys)

### 3.4.3 Techno-economic Analysis.

For the initial established parameters for the plant in terms of productivity, 100 t of acetic acid per year, the following results were obtained. With “Aspen Process Economic Analyzer” the initial cost of purchased equipment was obtained with a total of 2.753 mm USD. The value of the purchased equipment is multiplied with a location factor of 1.7336, as established in the methodology, the values given by Aspen are considered to be in the US, however, the objective of the investigation is to locate the plant locally in Quito, Ecuador. The initial capital cost of equipment was 2.753 million USD. Considering the Location Factor, this value in Ecuador is estimated to rise up to 4.773 million USD. The total capital investment rises to 27.142 million USD, as is calculated as the sum of the Fixed Capital Investment (FCI) + Working Capital (WC). The direct costs were calculated using the Peters and Timmerhaus methodology, considering the factors used for a Solid-Fluid processing plant, as shown below:

**Table 13. Direct Costs based on Delivered Equipment**

| Parameters | Solid-Fluid Processing Plant Factor | Calculated Values, million $ |
|---|---|---|
| **Purchased equipment, E'** | | **4.773** |
| **Delivery, fraction of E'** | 0.10 | 0.477 |
| **Subtotal: delivered equipment** | | 5.250 |
| **Purchased equipment installation** | 0.39 | 2.047 |
| **Instrumentation&Controls(installed)** | 0.26 | 1.365 |
| **Piping (installed)** | 0.31 | 1.627 |
| **Electrical systems (installed)** | 0.10 | 0.525 |
| **Buildings (including services)** | 0.29 | 1.522 |

| | | |
|---|---|---|
| **Yard improvements** | 0.12 | 0.630 |
| **Service facilities (installed)** | 0.55 | 2.887 |
| **Total direct costs** | 2.02 | 15.855 |

**Table 14. Indirect Costs Base on Delivered Equipment**

| **Parameters** | **Solid-Fluid Processing Plant Factors** | **Calculated Values, million $** |
|---|---|---|
| **Delivered Equipment** | | 5.250 |
| **Engineering and supervision** | 0.32 | 1.680 |
| **Construction expenses** | 0.34 | 1.785 |
| **Legal expenses** | 0.04 | 0.210 |
| **Contractor's fee** | 0.19 | 0.997 |
| **Contingency** | 0.37 | 1.942 |
| **Total indirect costs** | 1.26 | 6.615 |

The Fixed Capital Investment (FCI) obtained from the sum of the Direct Costs and the Indirect cost result in a total of **22.467 million** $. The working capital calculation is indicated below:

**Table 15. Working Capital.**

| **Parameters** | **Solid-Fluid Processing Plant Factors** | **Calculated Values, million $** |
|---|---|---|
| **Working Capital (WC)** | 0.75 | 3.927 |

The Total Capital Investment (TCI), considering the WC and the FCI is **26.407 million $.**

The annual raw material costs and initial product values considered are summarized in the following tables:

**Table 16. Annual Value of Products, Coproducts and Byproducts**

| Name of Material | Price, $/kg | Annual Amount million kg | Annual value of product, million $/y |
|---|---|---|---|
| **Acetic Acid** | 23.50 | 0.100 | 2.35 |
| **Nitrogen** | 18.00 | 0.145 | 2.61 |
| **Total Annual Value of Products =** | | | 4.96 |

For this scenario, the plant's labour needed is of 8 operators, with one shift per day. The salary of each operator is considered as 400 $:

**Table 17. Annual Operating Labour Costs.**

| Number of Operators per shift | Shifts per day | Operator rate $/h | Annual operating labor cost million $/y |
|---|---|---|---|
| 8 | 1 | 3.125 | 0.073 |

The cost of biomass residues, eucalyptus wood residues, is only considered to be the cost of transporting these residues from the farther location Puerto Quito, 150 km from the process plant facility in Quito and the feed preparation and drying costs. Biorenewable resources are classified as either processing residues, harvesting residues or dedicated energy crops. One the one hand processing residues are acquired at low or even negative costs with minimal transportation cost and on the other hand harvesting residues are underutilized and could even represent an additional income for produces if they are collected and sold as biorenewable resource. In terms of cost, harvesting residues tend to be costlier than processing residues as they need to be collected from fields (Brown, 2013). Moreover, the cost of dedicated energy crops is the highest of the three as they bear with all the expenses of cultivation and harvest. The table below summarizes the prices of agricultural and forest residues and wastes:

**Table 18. Cost of Potential Feedstock (US Data)**

**Taken from Brown, 2013, p. 289**

| Feedstock | Price (2010 $/Mg) |
|---|---|
| **Agricultural Residues and Wastes** | |
| Low Cost | <40 |
| Mid Cost | <50 |
| High Cost | <60 |
| **Forest Residues and Wood Wastes** | |
| Low Cost | <20 |
| Mid Cost | <40 |
| High Cost | <80 |

Transportation of biomass residues consider the amount of wood that needs to be transported, in this case, the most important factor is the volume of wood to be transported which is 601.25 $m^2$ per year. A truck with a capacity of 15 $m^2$ is considered to be purchased, which gives a total of 40 trips per year. The costs considered for the price of transportation, are summarized in the following table:

**Table 19. Transportation Cost of Biomass (150 km)**

| Item | $ USD/year |
|---|---|
| **Truck Cost** | 4223 |
| **Fuel Cost (Diesel)** | 1314,1 |
| **Maintenance Cost (Tires, Repairs, Taxes, Permits)** | 1500 |
| **Workforce** | 3500 |
| **Total Cost** | 10537 |
| **Biomass Cost per kg** | 0,07 $/kg |

Although a biomass pre-treatment process is not included in the simulation, it is considered for the techno-economic analysis which accounts for the 7% of the total purchased equipment (Around 0.19 m$). This gives a biomass price which does not surpass 0.08 $/kg.

**Table 20. Raw Materials Cost**

| Name of Material | Price, $/kg | Annual Amount | Annual value of product, million $/y |
|---|---|---|---|
| **Eucalyptus Wood Residues** | 0.08 | 0.152 | 0.012 |
| **Total Annual Cost of Raw Materials** | | | 0.012 |

Aspen Hysys was also used to obtain the total amount of utilities such as electricity, refrigeration and steam used in the plant.

**Table 21. Utility Costs**

| Utility | Cost Units | Annual Utility Requirement | Annual Utility Cost, million $/y |
|---|---|---|---|
| **Electricity** | | | |
| **Purchased average** | 0.082 $/kWh | 320000 kWh/y | 0.026 |
| **Refrigeration, to temperature** | | | |
| **5°** | 5.00 $/GJ | 125 GJ/y | 0.001 |
| **-20°** | 8.00 $/GJ | 881 GJ/y | 0.007 |
| **-50°** | 14.00$/GJ | 227 GJ/y | 0.003 |
| **Steam, saturated** | | | |
| **790 kPa** | 6.00 $/1000 kg | 41 (10000 kg/y) | 0.0002 |
| **Exhaust (150 kPa)** | 2.00 $/1000 kg | 149 (1000kg/y) | 0.0003 |
| **Total** | | | 0.038 |

The annual Total Product Costs (TPC), includes the variable costs, fixed charges, general plant overhead and manufacturing cost. Some aspects such as Administration, distribution and selling and R&D are also considered for the plant's costs. The following tables establish the different costs related to the production of acetic acid and nitrogen as a coproduct:

**Table 22. Variable Costs**

| Item | Factor (Default) | Basis | Cost, million $/y |
|---|---|---|---|
| **Raw materials** | | | 0.012 |
| **Operating labor** | | | 0.073 |
| **Operating supervision** | 0.15 | of operating labor | 0.011 |
| **Utilities** | | | 0.038 |

| | | | |
|---|---|---|---|
| **Maintenance and repairs** | 0.06 | of FCI | 1.385 |
| **Operating supplies** | 0.15 | of maintenance & repair | 0.208 |
| **Laboratory charges** | 0.15 | of operating labor | 0.011 |
| **Royalties** | 0.01 | of $c_o$ (Product Cost) | 0.071 |
| **Variable Cost** | | | 1.808 |

**Table 23. Fixed Charges and Plant Overhead**

| **Item** | **Factor (Default)** | **Basis** | **Cost, million $/y** |
|---|---|---|---|
| Taxes (property) | 0.02 | of FCI | 0.462 |
| Financing (interest) | 0 | of FCI | 0 |
| Insurance | 0.01 | of FCI | 0.231 |
| Rent | 0 | of FCI | 0.000 |
| **Fixed Charges** | | | 0.692 |
| Plant overhead, general | 0.6 | of labor, supervicion and maintenance | 0.881 |
| **Plant Overhead** | | | 0.881 |

**Table 24. Total Manufacturing Costixed Charges and Plant Overhead**

| | |
|---|---|
| **Manufacturing Cost = Variable Costs + Fixed Charges + Plant Overhead** | 3.351 |

**Table 25. General Expense**

| Item | Factor (Default) | Basis | Cost, million $/y |
|---|---|---|---|
| **Administration** | 0.2 | of labor, supervision and maintenance | 0.294 |
| **Distribution & selling** | 0.05 | of $c_o$ | 0.200 |
| **Research & Development** | 0.04 | of $c_o$ | 0.160 |
| **General Expense** | | | 0.654 |

**Table 26. Total Product Cost**

| | |
|---|---|
| **Total Product Cost= Manufacturing Cost + General Expense** | 4.005 |

To proceed with the economic evaluation, two scenarios are considered, one with a plant lifespan of 10 years and another one with a plant lifespan of 20 years. For the both cases, 10 and 20 years, the Internal Rate of Return (IRR) and the Net Present Value (NPV) of the investment were calculated:

**Table 27. Investment Results**

| | | |
|---|---|---|
| **Plant Lifespan: 10 years** | **TIR (%)** | -15% |
| | **NPV (million $)** | $ (20.54) |
| **Plant Lifespan: 20 years** | **TIR (%)** | -12% |
| | **NPV (million $)** | $ (18.28) |

Both scenarios are discouraging, as both present negative net present values and negative IRR. Also, it's important to notice that as shown on the table above, the worst scenario occurs for a plant lifespan of 20 years, mainly due to a longer time paying a sustained interest rate of 10% for a longer period of time and sustained loses during the whole time period. Another aspect to consider is that the income in both cases is assumed to be constant, calculated mainly on a production of 100 tons of acetic acid per year with a unit price of 23.5 \$/kg as established by the market, and a co-production of 0.145 kg/y nitrogen with a price of 18 \$/kg. The total expenses were also assumed to be constant over the plant's lifespan for both cases with a total of 6.570 million \$ as shown in table TOTAL PRODUCT COST. Even though both scenarios seem to be an important drawback for the project, a sensitivity analysis must be performed considering different variables to determine their impact on the outcome.

## 3.5 Sensitivity Analysis.

A sensitivity analysis must be performed in order to analyse the different variables that may have an important impact on the project's feasibility. As shown before, two scenarios will be considered for this, the first one considering a plant's lifespan of 10 years and another one considering a plant's lifespan of 20 years. In both cases, four variables will be considered: A variation in the TMAR, plant's service factor, the price of nitrogen as a coproduct and finally a variation on the process' yields. Variation in the price of biomass, such as transportation and pre-treatment, will not be considered for this analysis as changes on this aspect have a negligible impact on the project's economic performance, as an illustration, biomass prices doesn't exceed a total cost of 0.08 $/kg which translates in 0.015 million $/y, which is a little figure compared to the initial investment and the annual expenses of the biorefinery.

### 3.5.1 Case A: Plant's Lifespan of 10 years:

The variation of the factors presented above and its impact in the acetic acid minimum selling price is going to be evaluated. The first aspect to consider is a variation in the rate from 7% to 12%. It's important to remark that when one variable is modified, the rest remain constant. In this case, as the rates vary, other variables such as nitrogen price, plant's service factor and yields remain constant. The table below summarizes the results obtained:

**Table 28. Rate's variation impact in Acetic Acid MSP (10 years)**

| Rate | Acetic Acid Income [ million $/y] | Unit Price [$/kg] |
|---|---|---|
| 12% | 8.64 | **60.70** |
| 11% | $8.45 | 58.79 |
| 10% | $8.26 | 56.90 |

| | | |
|---|---|---|
| 9% | $8.08 | 55.10 |
| 8% | $7.90 | 53.30 |
| 7% | $7.72 | 51.55 |

The initial MSP of acetic acid is $82.58, the highest value obtained from a variation in rates with a rate of 12% is of $86.35. On the other hand, the lower value obtained with a rate of 7% is of $77.20. The second aspect to consider, is a variation in the plant's service factor, maintaining constant a rate of 10%, a nitrogen price of 18 $/kg and the initial yields. The results are summarized in the following table:

**Table 29. Service Factor variation impact in Acetic Acid MSP (10 years)**

| Service Factor | Annual Production [kg] | Acetic Acid MSP [$/kg] |
|---|---|---|
| 0.219178082 | 100000 | 56.94 |
| 0.438356164 | 200000 | 16.44 |
| 0.657534247 | 300000 | 4.22 |
| 0.789041096 | 360000 | 2.91 |
| 1 | 456250 | 1.98 |

It is important to notice that a change in the plant's service factor is really noticeable. There is a high sensitivity on acetic acid price when a variation of the service factor, in other words, the production increases. Only when the production of acetic acid doubles from 100 tons to 200 tons, the acetic acid's MSP decreases in 53.13 $/kg. The lowest value achieved when production increases in a fivefold is an acetic acid MSP of 3.39 $/kg, however, this would imply that the factory is working the whole year, in three shifts of 8 hours the 365 days of the year. A more recommended and realistic scenario occurs with a service factor of 0.789, as factory's need to work at 70% – 80% capacity to perform daily maintenance and account for unforeseen cases. In this case, the price of acetic acid achieved is encouraging as it is of $5.72 $/kg, below the acetic acid's benchmark price of 23.5 $/kg.

Another variable considered for the sensitivity analysis is the one related to the price of the co-product, liquid nitrogen. The price of liquid nitrogen is fixated to a price of 18 $/kg due to its purity. A variation in the price of $\pm$ 30% is considered, obtaining the following results:

**Table 30. Nitrogen Price variation impact in Acetic Acid MSP (10 years)**

| Case | Nitrogen Price $/kg | Annual Production [kg] | Acid MSP [$/y] |
|---|---|---|---|
| **Original Price** | 18.00 | 0.145 | 56.94 |
| **-30 %** | 12.60 | 0.145 | 49.15 |
| **+ 30%** | 23.40 | 0.145 | 64.79 |

A variation in the price of nitrogen has a greater impact on the acetic acid's minimum selling price, however, it has a lower impact when compared to the plant's service factor. When the price of nitrogen increases in 30% to a price of 23.40 $/kg, the acid's MSP could be established to 74.79 $/y. However when it decreases in a 30% it also affects the MSP, causing an increase in about 90.43 $/y which is higher than the one obtained for an increase in a rate of 12%. Finally, a variation in yields is considered to assess their impact on the minimum selling price. The following table presents the results obtained in which it's important to remember that an initial yield of 89% was obtained in the process model.

**Table 31. Yield's variation impact in Acetic Acid MSP (10 years)**

| Process Yields | Acetic Acid Income [million $/y] | Acetic Acid MSP [$/kg] |
|---|---|---|
| 100% | 8.635 | 48.21 |
| 90% | 8.26 | 56.94 |
| 80% | 8.635 | 71.29 |
| 70% | 8.635 | 84.29 |

As noticed in the table above, interesting results occur when there is a variation in the process yields. When the yield increases to 100%, there is not a significant impact on acetic acid MSP, as it is 77.10 $/y. Although, when the yields decrease in 70%, the MSP increases to 109.86 $/y which is the highest price of acetic acid achieved from the 4 factors considered in the analysis.

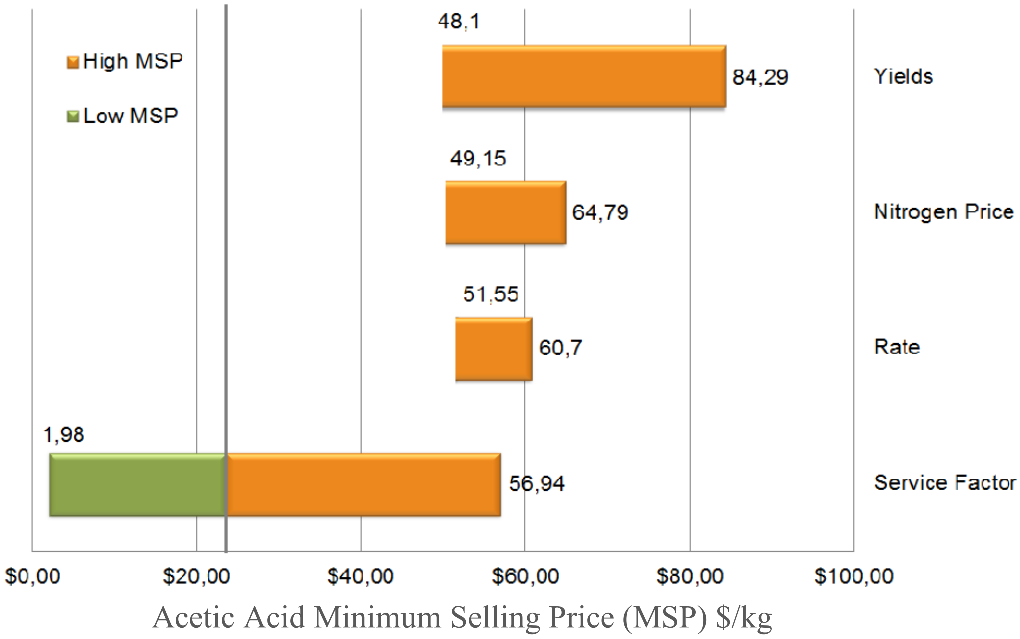



**Figure 22. Sensitivity Analysis for Acetic Acid MSP in a plant lifespan of 10 years.**

It is clear from the figure above that the highest price of acetic acid results from a decrease In the process yields, as a negative impact results in a price of 109.86 $/kg. However, the variable that has a greater positive impact in the acid's MSP is the service plant factor, in other words, an increase in the global production. This is mainly due to a benefit in economies of scale, as the increase of production results in major income for the factory and a minimum increase in the plant's variable costs. This is represented in the figure below, as an increase in the volume of production translates in a decrease of acetic acid unit cost:

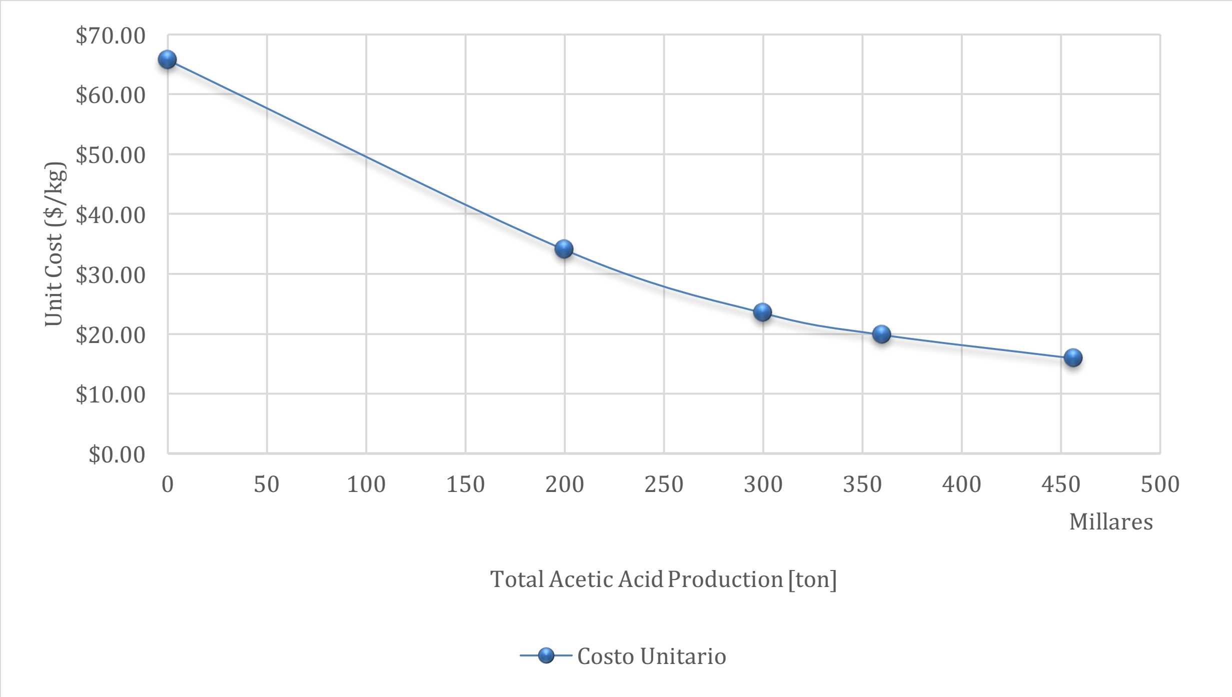



**Figure 23. Acetic Acid Unit Cost.**

As can be noticed, the best scenario to consider is when the plant operates at 75% of capacity (Plant service factor of 0.79), when the minimum selling price obtained was 5.72 $/kg. This was obtained fixing a rate of 10%, obtaining a Net Present Value of 0. The price market for acetic acid of this characteristics is of 23.50 $/kg, so this gives the possibility of establishing different prices for acetic acid and analyse its impact on the economic indicators as established in the following table:

**Table 32. Best Case Scenario. Acetic Acid Price Impact on IRR and NPV (10 years)**

| Acetic Acid MSP [$/kg] | Interanal Rate of Return [IRR %] | Net Present Value [million $] |
|---|---|---|
| 2.91 | 10% | 0 |
| 8 | 20% | 5.15 |
| 10 | 23% | 9.57 |
| 12 | 26% | 13.99 |
| 15 | 31% | 20.63 |
| 20 | 38% | 31.69 |
| 23.5 | 44% | 39.43 |

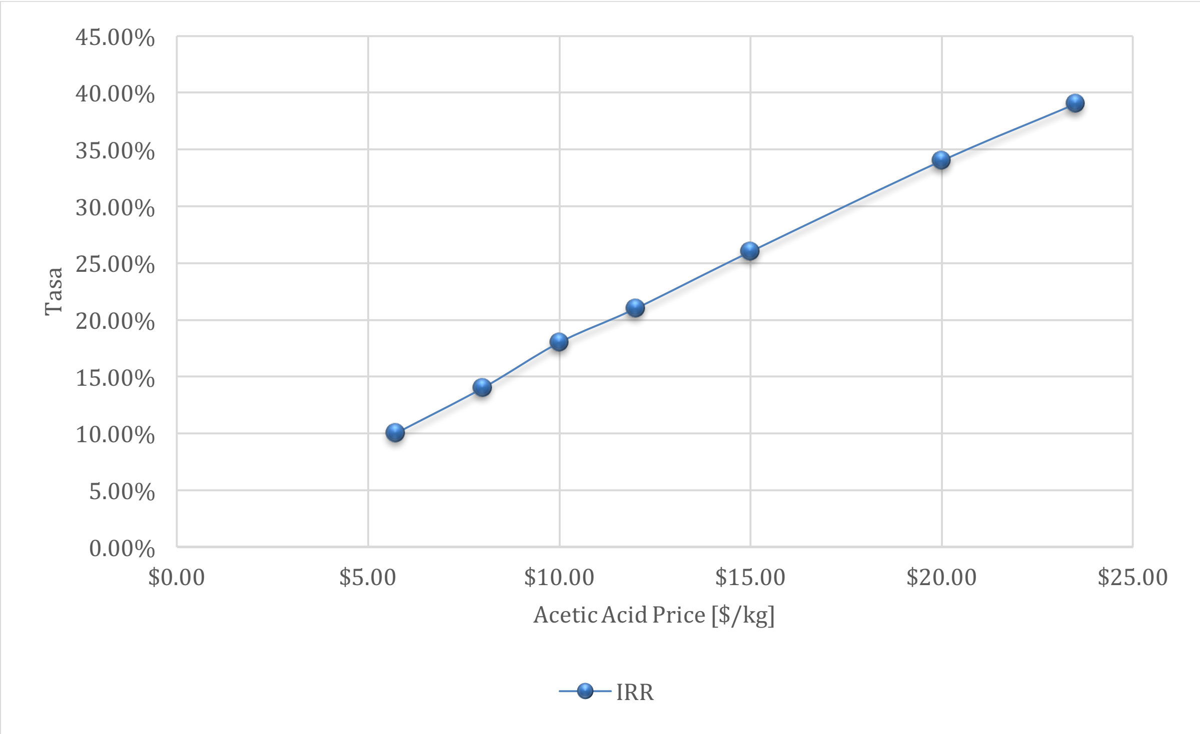



**Figure 24. IRR [%] vs Acetic Acid Price [$/kg]**

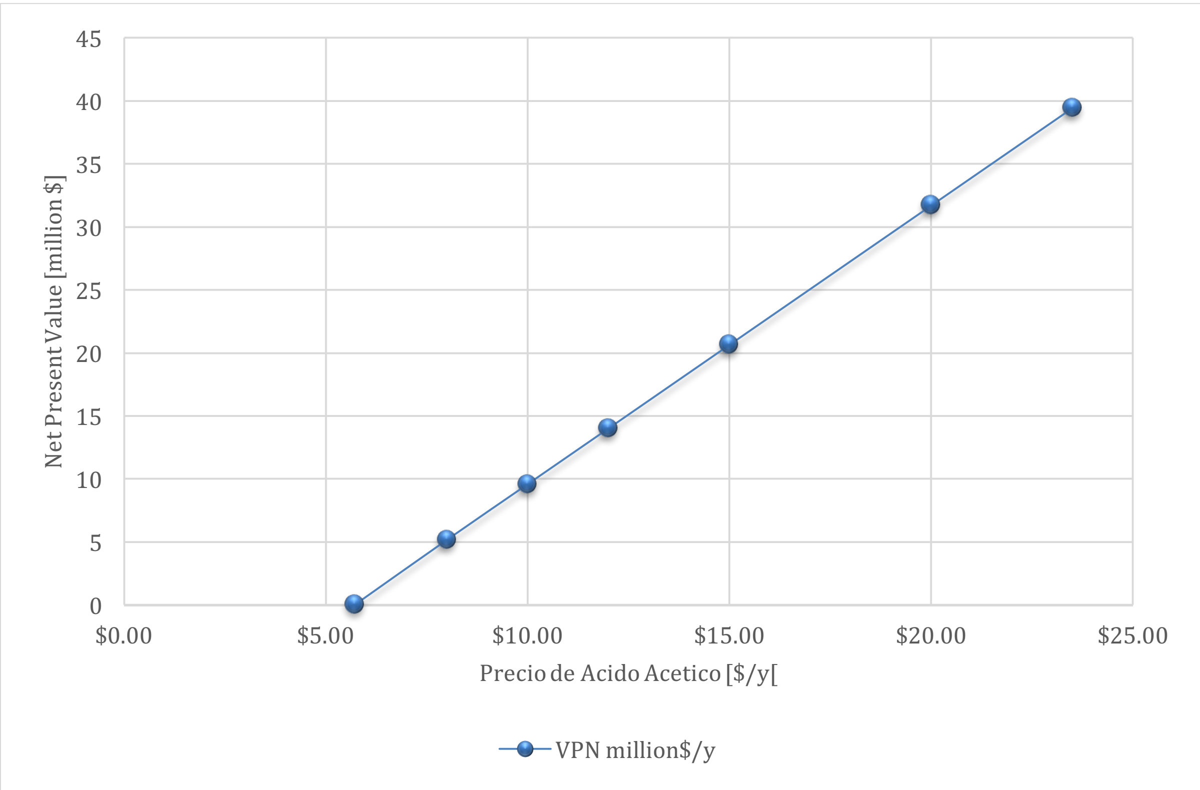



**Figure 25. Net Present Value [million $] vs Acetic Acid Price [$/kg]**

### 3.5.2 Case B: Plant's Lifespan of 20 years:

As in case A, where the plant lifespan considered was 10 years, in case B a plant lifespan of 20 years is analysed. As in the case before, the variation of the factors considered are the same and its impact in the acetic acid minimum selling price is going to be evaluated. The first aspect to consider as well is a variation in the rate from 7% to 12%. It's important to remark that when one variable is modified, the rest remain constant. In this case, as the rates vary, other variables such as nitrogen price, plant's service factor and yields remain constant. The table below summarizes the results obtained:

**Table 33. Rate's variation impact in Acetic Acid MSP (20 years)**

| Rate | Acetic Acid Income [ million $/y] | Unit Price [$/kg] |
|---|---|---|
| 12% | $7.50 | $49.40 |
| 11% | $7.28 | $47.10 |
| 10% | $7.06 | $44.98 |
| 9% | $6.85 | $42.90 |
| 8% | $6.65 | $40.80 |
| 7% | $6.45 | $38.90 |

The initial MSP of acetic acid for a plant's lifespan of 20 years is $70.60, the highest value obtained from a variation in rates with a rate of 12% is of $74.95 which is lower than the one obtained for a plant's lifespan of 10 years of $86.35 under the same conditions. On the other hand, the lower value obtained with a rate of 7% is of $64.50, again obtaining a more encouraging outcome compared to the one obtained of  $77.20 for a plant's lifespan of 10 years. The second aspect to consider, is a variation in the plant's service factor, maintaining constant a rate of 10%, a nitrogen price of 18 $/kg and the initial yields. The results are summarized in the following table:

**Table 34. Service Factor variation impact in Acetic Acid MSP (20 years)**

| Service Factor | Annual Production [kg] | Acetic Acid MSP [$/kg] |
|---|---|---|
| 0.219178082 | 100000 | $44.98 |
| 0.438356164 | 200000 | $10.46 |
| 0.657534247 | 300000 | $3.32 |
| 0.789041096 | 360000 | $0.22 |
| 1 | 456250 | - |

Again, It is important to notice that a change in the plant's service factor is really noticeable. There is a high sensitivity on acetic acid price when a variation of the service factor, in other words, the production increases. Only when the production of acetic acid doubles from 100 tons to 200 tons, the acetic acid's MSP decreases in 47.14 $/kg which is a lower proportion than the one obtained for a plant's lifespan of 10 years which was a difference of 53.13 $/kg. However, the lowest value achieved when production increases in a fivefold is an acetic acid MSP is enormous, with an acetic acid MSP of 0.60$ compared to the minimum of 3.39 $/kg for a 10 years lifesan, however, this would imply that the factory is working the whole year, in three shifts of 8 hours the 365 days of the year. A more recommended and realistic scenario occurs with a service factor of 0.789, as factory's need to work at 70% – 80% capacity to perform daily maintenance and account for unforeseen cases. In this case, the price of acetic acid achieved is even more encouraging than before as it is of $2.40 $/kg, below the acetic acid's benchmark price of 23.5 $/kg.

Another variable considered for the sensitivity analysis is the one related to the price of the co-product, liquid nitrogen. The price of liquid nitrogen is fixated to a price of 18 $/kg due to its purity. A variation in the price of $\pm$ 30% is considered, obtaining the following results:

**Table 35. Nitrogen Price variation impact in Acetic Acid MSP (20 years)**

| Case | Nitrogen Price $/kg | Annual Production [kg] | Acid MSP [$/y] |
|---|---|---|---|
| **Original Price** | 18.00 | 0.145 | 45.01 |
| **-30 %** | 12.60 | 0.145 | 59.25 |
| **+ 30%** | 23.40 | 0.145 | 37.19 |

A variation in the price of nitrogen has a greater impact on the acetic acid's minimum selling price, however, it has a lower impact when compared to the plant's service factor. When the price of nitrogen increases in 30% to a price of 23.40 $/kg, the acid's MSP could be established to 62.83 $/y. However when it decreases in a 30% it also affects the MSP, causing an increase in about 78.47 lower than the 90.43 $/y obtained for a lifespan of 10 years. The price obtained of 78.47 is higher than the one obtained for an increase in a rate of 12%. Finally, a variation in yields is considered to assess their impact on the minimum selling price. The following table presents the results obtained in which it's important to remember that an initial yield of 89% was obtained in the process model.

**Table 36. Yield's variation impact in Acetic Acid MSP (20 years)**

| Process Yields | Acetic Acid Income [million $/y] | Acetic Acid MSP [$/y] |
|---|---|---|
| 100% | 8.635 | $37.46 |
| 90% | 8.26 | $44.98 |
| 80% | 8.635 | $47.05 |
| 70% | 8.635 | $53.28 |

As noticed in the table above, interesting results occur when there is a variation in the process yields. When the yield increases to 100%, there is not a significant impact on acetic acid MSP, as it is 67.56 $/y. Although, when the yields decrease in 70%, the MSP increases to

76.15 which is noticeable lower than the obtained of 109.86 \$/y which is the highest price of acetic acid achieved from all of the 4 factors considered in the analysis for both cases. The price of 76.15 \$/y is also lower than the one obtained for 82.58 in the initial scenario. This confirms the case in which a plant's lifespan of 20 years is significantly better in every variation considered. It is recommended that the plant's lifespan is planned for 20 years. A tornado diagram is presented below, considering the different factors discussed above

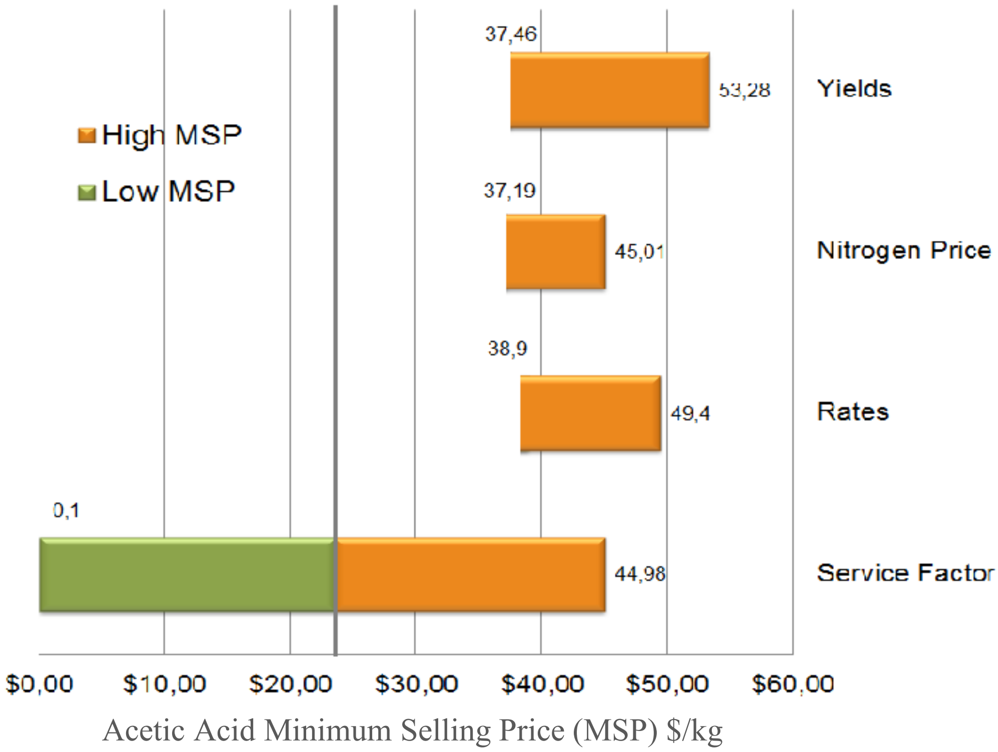



**Figure 26. Sensitivity Analysis for Acetic Acid MSP in a plant lifespan of 20 years**.

It is clear from the figure above that the highest price of acetic acid results from a decrease in the nitrogen as a process' co-product with a price of 78.47 \$/kg. This contrasts with the previous case of a plant's lifespan of 10 years in which the process yields were the factor that influenced more in the highest acetic acid price of 109.86 \$/kg. The highest price is considerable lower, considering a plant lifespan of 20 years, decreasing from 109.86 \$/kg to \$78.47 \$/kg. However, the variable that has a greater positive impact in the acid's MSP is the service plant factor again, in other words, an increase in the global production. As well as in the previous case this is mainly due to a benefit in economies of scale, as the increase of production results in major income for the factory and a minimum increase in the plant's variable costs. The lowest price achieved for acetic acid is of 0.60 $/kg, lower than the previous case in which the lowest achieved was of 3.39 $/kg. This is represented in the figure below, as an increase in the volume of production translates in a decrease of acetic acid unit cost:

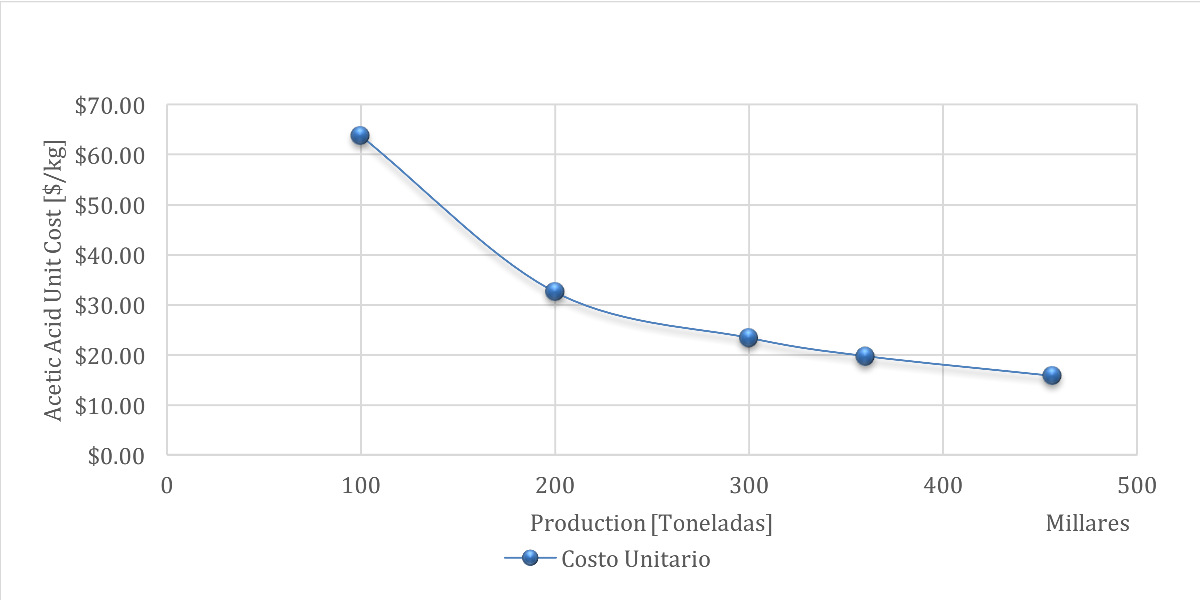



**Figure 27. Acetic Acid Unit Cost (20 years).**

As can be noticed, the best scenario to consider is when the plant operates at 75% of capacity (Plant service factor of 0.79), when the minimum selling price obtained was 2.40 $/kg. This was obtained fixing a rate of 10%, obtaining a Net Present Value of 0. The price market for acetic acid of this characteristics is of 23.50 $/kg, so this gives the possibility of establishing different prices for acetic acid and analyse its impact on the economic indicators as established in the following table:

**Table 37. Best Case Scenario. Acetic Acid Price Impact on IRR and NPV (20 years)**

| Acetic Acid MSP [$/kg] | Internal Rate of Return [IRR %] | Net Present Value [million $] |
|---|---|---|
| 0.22 | 10% | 0 |
| 5 | 18% | 14.75 |
| 10 | 25% | 30.07 |
| 12 | 28% | 36.2 |
| 15 | 32% | 45.40 |
| 20 | 39% | 60.72 |
| 23.5 | 43% | 71.45 |

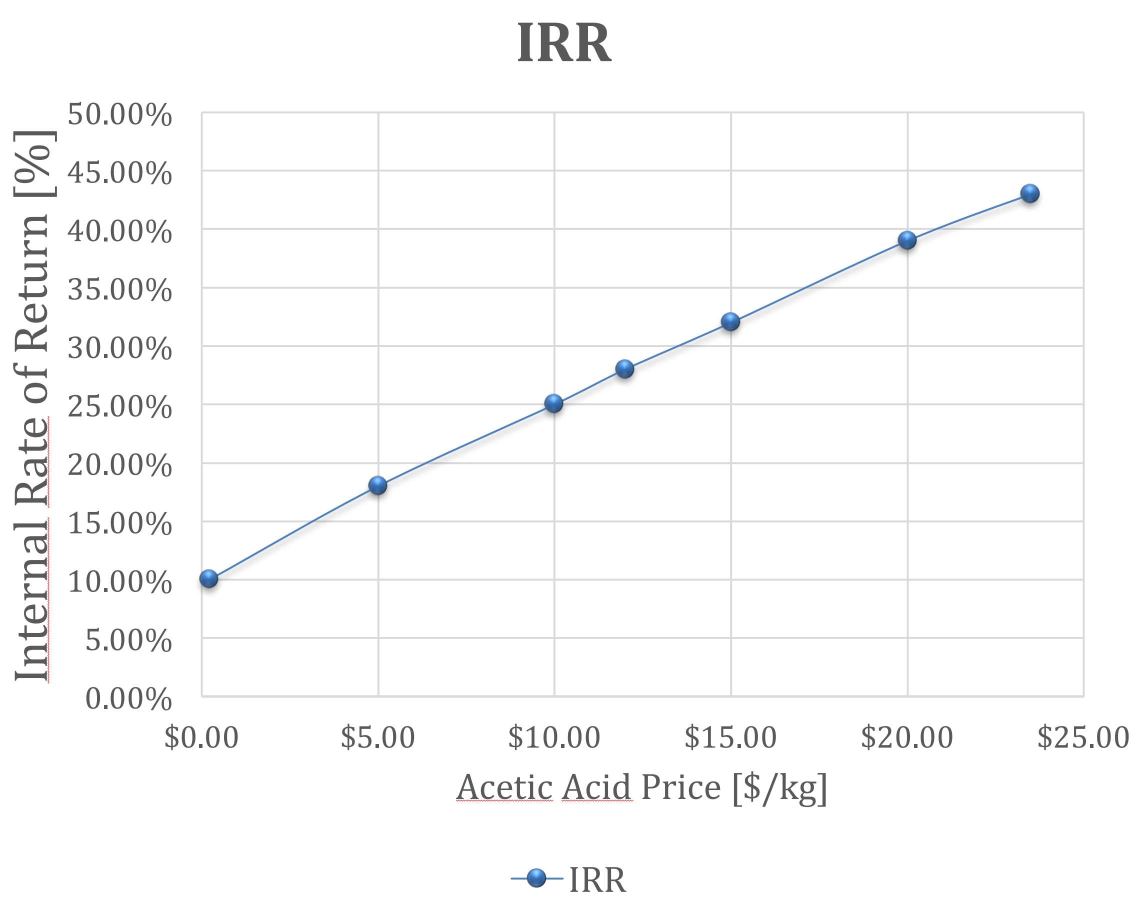



**Figure 28. IRR [%] vs Acetic Acid Price [$/kg] Lifespan 20 years**

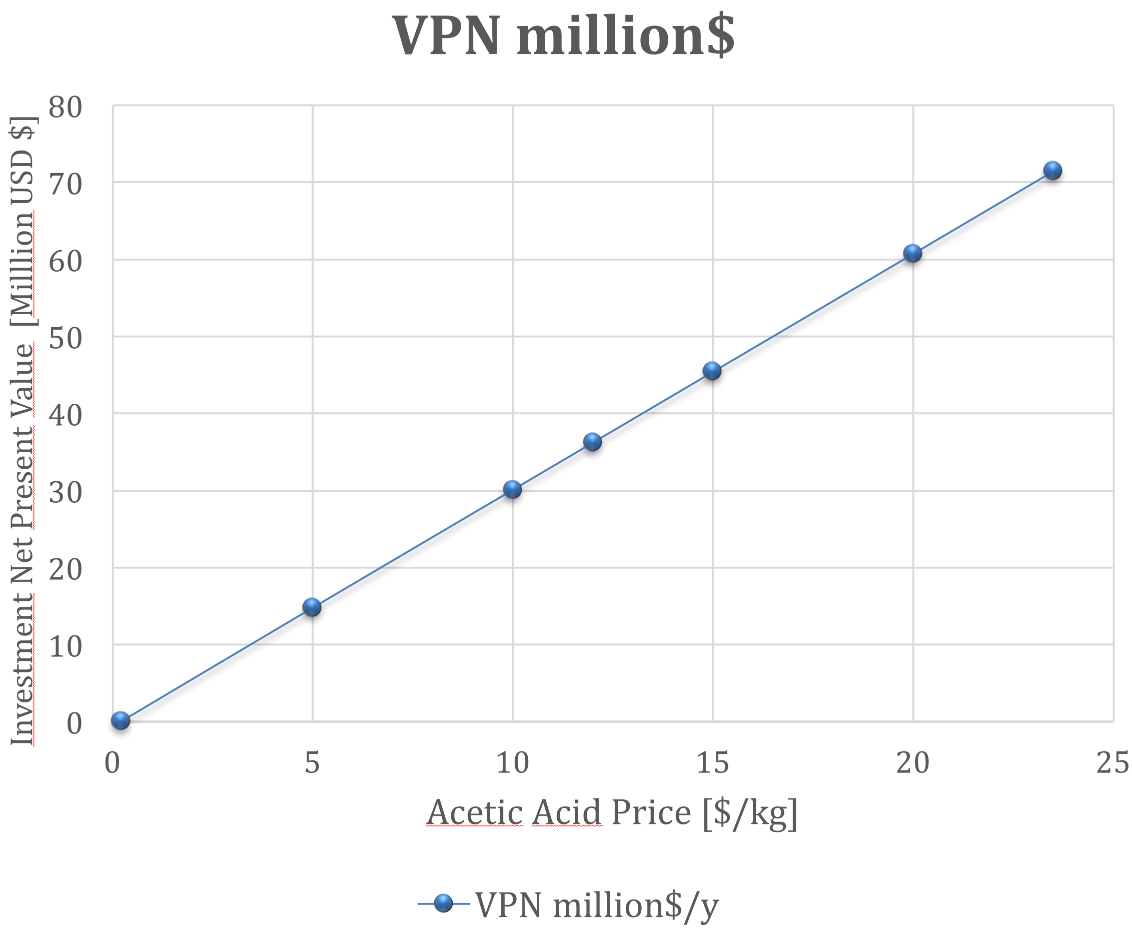



**Figure 29. Net Present Value [Million $] vs Acetic Acid Price [$/kg]. Lifespan 20 years**

Indicators such as the Internal Rate of Return (IRR) and Net Present Value (NPV) present a significant improvement. In the best possible scenario, which involves a plant lifespan of 20 years and an increase of production to a total of 360 tons of acetic acid per year, about a 35% of the possible market, a maximum IRR of almost 45%with an acetic acid price of 23.50 $/kg which translates to a Net Present Value (NPV) of 71.45 million $. In this case the investment is feasible as the IRR notably greater than the rate of 10%  in which the loans and financial costs will be obtained.

### 3.5.3 Case C: Increasing the capacity factor without an increase in Production

The only factor analysed from the previous in the sensitivity analysis in which positive results were obtained is increasing the capacity factor of the plant, in other words, increasing the total number of hours in which the factory is producing acetic acid. However, an increase in the capacity factor would also mean to increase the production up to 360 tons of acetic acid annually from the 100 tons initially stated. This means that the percentage of the market aimed would increase up to 36%, which would imply several challenges such as an increase in distribution costs and difficulty related to obtaining that high percentage of market share as a new enterprise.

Considering these aspects, a new plant with scaled equipment and modified flows was considered, with a capacity factor of 0.80 maintaining an annual production of 100 tons of acetic acid. In this case, a total capital investment of 25.584 million $ was obtained around 2 million $ less than the initial plant considered. The total annual costs obtained were 4.320 million $. In this case, the minimum selling price of acetic acid was calculated again, considering two scenarios: A plant´s lifespan of 10 years and a plant´s lifespan of 20 years. The results are summarized in the following table:

**Table 38. Acetic Acid MSP, Production of 100 tons annually and capacity factor 0.8**

| Plant´s Lifespan [years] | Acetic Acid MSP [$/kg] |
|---|---|
| 10 | 56.94 |
| 20 | 43.88 |

The prices obtained are still not good enough to compete in the market in which acetic acid of the characteristics obtained in the simulation has a price of 23.50 $/kg . Comparing the values to the previous obtained in which a capacity factor of 0.20 was used the MSPs are almost the same. On the one hand, for a plant´s lifespan of 10 years and a capacity factor of

0.80 an acetic acid MSP of 56.94 $/kg was obtained and considering a capacity factor of 0.20 an acetic acid MSP of 56.90 $/kg was calculated. These two values are virtually the same. On the other hand, for a plant´s lifespan of 20 years and a capacity factor of 0.80 an acetic acid MSP of 43.88 $/kg was obtained and considering a capacity factor of 0.20 an acetic acid MSP of 44.98 $/kg was calculated. In the case of a plant´s lifespan of 20 years, the difference is greater of approximately 1 dollar per kg of acetic acid produced, contrasting to the 0.04 dollars per kg of the 10 year lifespan. The total capital investment decreases in a minimum way mainly due to the already small scale of equipment used. Even though prices decrease a small percentage, it´s important to remark that in this scenario the positive results obtained in the best scenarios of Case A and Case B are not replicated, as an increase in production is not an option as equipment is already operating at optimum capacity.

# 4. Conclusions

The most promising pathway for acetic acid production was determined to be gasification, which is a thermochemical technology. Biochemical technologies were considered as a possible pathway to obtain acetic acid; however, this technologies present different challenges when adapting them to an industrial level such as low rates of production, low purity in compounds, high energy consumption and a strict control of different variables such as temperature and pH. Although, there exists around 45 species of acetic acid bacteria and several studies are performed to increase the feasibility of adapting this technology on an industrial level. A gasification process adapted from Zhu and Jones was chosen to be developed for its high conversion rates of 65%.

The market for acetic acid imports in the country reached the 1000 tons in 2018, and continues to increase in 2019. As its recommended, a 10% of the market is the target for the plant production, in other words, the plant production is determined to be 100 tons of acetic acid annually. Also, there exists a wide variety of prices for acetic acid in the market, from 2.20 $/kg to 135 $/kg. However, the price considered as a reference is 23.50 $/kg, as this is the minimum price for the acetic acid in the market with the characteristics that is targeted to be produced in the process plant. Considering the process' yields and the size of the market, the plant's size is determined to 0.57 MTPD of woody biomass residues. The characterization of biomass used in the simulation is from Eucalyptus residues, which is the most abundant in the province of Pichincha. Forest residues in the Pichincha province are reported to be more than 20 000 tons per year, so raw material availability is not considered as a limitation for the process.

The process consists on five main steps which involve the separation of $N_2$ and $O_2$, from dehumidified air. Nitrogen is analysed as a coproduct later in the techno-economic analysis. The second step in the process is the gasification in which pretreated biomass, oxygen and water vapour enter the gasificator at a pressure of 23 psia and 810 °C. The raw syngas obtained is sent to a water separation unit in which more than 99.9% of the water present in the mixture is removed. The fourth step is the methanol synthesis in which syngas enters the reactor at a pressure of 2900 psia, above the critical point of methanol to increase the conversion rates of reaction. Finally, methanol is sent to the acetic acid synthesis step in which in the final stream an acetic acid of 99.9% purity is obtained.

Aspen Hysys was used to design the plant and to obtain the cost of the purchased necessary equipment. The price of purchased equipment that the software delivers are prices in the United States, so a location factor of 1.7336 was used to consider the price variation of equipment when they enter the country. The total capital cost of the plant obtained was of 26 million $, the total costs of operating the plant obtained were 4.005 million $/year and an income of 4.96 million $/year, considering a production of 100 tons of acetic acid with a price of 23.50 $/kg. In this initial scenario, the investment indicators obtained are not encouraging. Considering a lifespan of 10 years with an annual production of 100 tons of acetic acid a negative IRR is obtained of -15% and a NPV of (20.54) million $. In case we consider a plants lifespan of 20 years and a production of 100 tons of acetic acid an IRR of -12% is obtained and a NPV of (18.28) million $. There exist an improvement when the plant lifespan is considered to be 20 years, however there is still a loss of money in the investment.

Even though the scenario initially stated is not encouraging a sensitivity analysis is performed evaluating two cases: the first one considered, Case A, which involves a plant lifespan of 10 years and the second one, Case B, which considers a plant’s lifespan of 20 years. Four different factors are considered for the sensitivity analysis: Loan rates, the plant´s service factor which would involve an increase in the volume of production, the price of nitrogen as a coproduct and the process’ yields. Considering a plant’s lifespan of 10 years, the worst scenario would occur if the process’ yields decrease to 70% in which a MSP of

84.29 $/kg of acetic acid is obtained. This means that if the yields decrease to 70% the price in which acetic acid must be sold is 84.29 $/kg to have a NPV of 0: however, the market price of acetic acid is 23.50 $/kg meaning that it wouldn't be possible to compete. The best scenario considering a 10 year lifespan occurs when production is increased to 360 tons of acetic acid per year in which a MSP of 1.98 $/kg is obtained, allowing the product to compete in the local market as the minimum price for a product with the same characteristics is 23.50 $/kg. In other words, this allows the establishment of an acetic acid price between the range of 1.98 $/kg and 23.50 $/kg. By establishing an acetic acid price of 23.50 $/kg an IRR of 44% and a NPV of 39.43 $ million. It's important to remark that this scenario is considered to increase the plant's service factor, thereby increasing the production of acetic acid to 360 tons which translates in a market size of 36%. Even though the market exists, the recommendation for a new enterprise entering a free market is only about 10 %. Increasing the market size could be a challenging aspect and present numerous difficulties.

On the other hand, analyzing the case in which the plant's lifespan is considered to be 20 years, the acetic acid's MSP presented better results in every factor when compared to the case in which the plant's lifespan is 10 years. The worst scenario also occurs when the process' yields decrease to 70% in which an acetic acid MSP of 53.28 $/kg. Comparing this price to the same scenario of 10 years, the MSP decreased in 31.01 $/kg, Even though the price is better, it still doesn't reaches the target established of 23.50 $/kg. The best scenario considering a lifespan of 20 years, still presents when the service factor of the plant is increased, in other words, the plant's volume of production per year increases to 360 tons of acetic acid. In this case, a minimum selling price of 0.22 $/kg is obtained. In the case that a price of 23.50 $/kg is considered with this volume of production an IRR of 45% and a NPV of more than 60 million $, proving a plant's lifespan of 20 years the better scenario possible. Considering that the capacity factor was the only factor which changed the project´s outcome, a new scenario was considered consisting in an increase of the capacity factor although maintaining the initial production of 100 tons of acetic acid annually. In this case, acetic acid´s minimum selling price was obtained, a price of 56.94 $/kg for a plant´s lifespan of 10 years was calculated and a price of 43.88 $/kg for a plant´s lifespan of 20 years was obtained. Both results are really alike to the ones obtained for a lower capacity factor. Operating in this way would still imply a negative IRR and a loss in the long term, making the previously discussed scenarios in Case A and Case B the best ones.

As a recommendation to improve the plant´s efficiency, there exists multiple areas in the process were energy co-generation must be analyzed, to sell this energy as a coproduct or to take advantage of it in other energy consuming steps in the plant. As an illustration, energy is released in the two final exothermic reactions, during methanol and acetic acid synthesis. As an illustration, this energy could be used in the methanol stage compressor K101 which is one of the elements that consumes more power in the plant.

Another aspect to consider is to perform a real analysis of the biomass to be used in the process and obtain a better characterization of it in an experimental level. Biomass composition is key in the design of the process and the technology chosen to obtain the value-added chemical. Also, it’s important to analyze the composition to obtain different values of ashes, lignin and sulfur content which are components that need to be removed from the streams in order to obtain the final product. The removal of these components is another challenge in the design of the process and would also have an impact in the costs of the plant. Finally, it’s important to consider that a techno-economic analysis is an estimate that is within +/- 30% of the actual cost if the enterprise is pursued. To increase the accuracy in the values, the real value of equipment to be imported in the country must be obtained as a next step to further analyze the feasibility of the project. In this case, acetic acid was aimed to be the product produced, however there exist several opportunities in the country to take advantage of the wide availability of biomass residues that exist in the country leading the road to a greener chemical industry.

## Bibliographic References


Baca Urbina, G. (2011). *Evaluación de proyectos*. México: McGraw-Hill.

BCE. (2019). *Tasas de Interés*. Retrieved from https://contenido.bce.fin.ec/docs.php?path=/documentos/Estadisticas/SectorMonFin/TasasInteres/Indice.htm

Brown, T. (2014). A techno-economic review of thermochemical cellulosic biofuel pathways. *Bioresource Technology*, *178*, 166-176. doi: 10.1016/j.biortech.2014.09.053

Brown, T. (2013). *Economics of Biorenewable Resources.* Printer: Yet to Come.

Cabezas, C., Fernández, E., Guevara, D., Moreno, A. y Proaño, J. (nd). *Moving Ecuador Towards a Greener Chemical Industry.* To be Published.

Cerone, N., Zimbardi, F., Villone, A., Strjiugas, N. y Kiyikci, E. (2016). Gasificación de madera y madera torrefificada con aire, oxígeno y vapor en una planta piloto de lecho fijo. *Energía y combustibles* , 30 (5), pp. 4034-4043.

Choi, F., Johnston, P., Brown, R., Shanks, B., & Lee, K. (2015). Erratum to "Detailed characterization of red oak-derived pyrolysis oil: Integrated use of GC, HPLC, IC, GPC and Karl–Fischer" [J. Anal. Appl. Pyrol. 110 (2014) 147-154]. *Journal Of Analytical And Applied Pyrolysis*, *112*, 401-402. doi: 10.1016/j.jaap.2015.02.014

Dang, Q., Hu, W., Rover, M., Brown, R. and Wright, M. (2016). Economics of biofuels and bioproducts from an integrated pyrolysis biorefinery. *Biofuels, Bioproducts and Biorefining*, 10(6), pp.790-803.

ESIN Consultora S.A., (2014). *Atlas Bioenergético del Ecuador,* Edición 1.

Hailu, S., Admassu, S., Jha, Y. K. "Vinegar Production Technology – An Overview." *Beverage & Food World*. 2012. Retrieved from https://www.researchgate.net/publication/280722745_Vinegar_Production_Technology_-_An_Overview

SENAE. (2012). Comité de Comercio Exterior, Resolución No 59. Retrieved from https://www.aduana.gob.ec/archivos/Boletines/2013/ARANCEL_FINAL_1_DE_ENERO_R93.pdf

Jipa, I., Dobre, T., Stroescu, M., Stoica, A. (2009). Acetic Acid Extraction from Fermentation Broth Experimental and modelling studies". Revista de Chimie. 60(10), pp. 2084-1090.

Li, S., Li, P., Feng, F., & Luo, L. (2015). Microbial diversity and their roles in the vinegar fermentation process. *Applied Microbiology And Biotechnology*, *99*(12), 4997-5024. doi: 10.1007/s00253-015-6659-1

Kuipers, K. (2014). Kinetics of High Pressure Methanol Synthesis. *University of Groningen*.

Nakano, S., & Fukaya, M. (2008). Analysis of proteins responsive to acetic acid in Acetobacter: Molecular mechanisms conferring acetic acid resistance in acetic acid bacteria. *International Journal Of Food Microbiology*, *125*(1), 54-59. doi: 10.1016/j.ijfoodmicro.2007.05.015

Vidra, A., & Németh, Á. (2017). Bio-produced Acetic Acid: A Review. *Periodica Polytechnica Chemical Engineering*, *62*(3), 245-256. doi: 10.3311/ppch.11004

Wright, M. and Brown, R. (2007). Comparative economics of biorefineries based on the biochemical and thermochemical platforms. *Biofuels, Bioproducts and Biorefining*, 1(1), pp.49-56.

Zapata, B. (2018). Créditos para Emprendedores y Pymes en Ecuador. Retrieved from https://www.eluniverso.com/noticias/2018/07/03/nota/6840290/creditos-emprendedores-pymes-ecuador

Zhu, Y. and Jones, S. (2009). Techno-economic Analysis for the Thermochemical Conversion of Lignocellulosic Biomass to Ethanol via Acetic Acid Synthesis. *Pacific Northwest National Laboratory*.