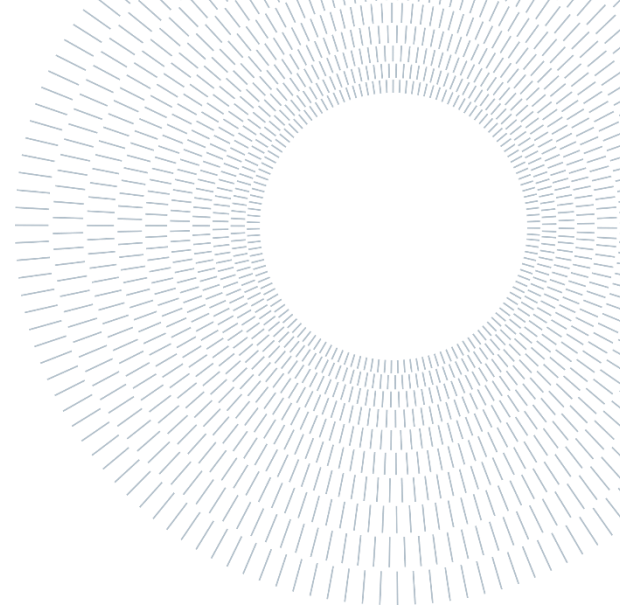




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EXECUTIVE SUMMARY OF THE THESIS

Acetic Acid Production from Biogas: An Economic and Feasibility Assessment

TESI MAGISTRALE IN CHEMICAL ENGINEERING – INGEGNERIA CHIMICA

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1. Introduction

Acetic acid (chemical formula CH_3COOH) is the most important organic acid produced worldwide. At ambient conditions acetic acid is a clear, colorless liquid with a pungent odor. It is soluble in water, alcohol, acetone, benzene, and other organic solvents. It has a pKa of 4.5 and its corrosiveness justifies caution in handling as it can irritate skin and mucous membranes when in solution and severe damage when in concentrated forms. Acetic acid has been produced as vinegar (an aqueous solution containing up 5% of acetic acid) since ancient times for culinary purposes. The process to produce biological acetic acid is referred to as fermentation and it is still relevant today for the production of goods related to food and cosmetics, accounting for almost 10% of the global production of acetic acid [1].

Industrial production of acetic acid started in the early 20th century mainly by acetaldehyde oxidation. This process has been progressively abandoned starting from the 1960s when BASF and later Monsanto developed a more advantageous catalyzed process based on methanol carbonylation, which is still the most relevant production path for acetic acid manufacture [1].

Acetic acid finds many different applications in industrial production, and its market has reached a value of 8.48 billion USD in 2022 [2]. Its main derivatives are vinyl acetate monomer (used for paint applications, paper coatings, textile treatments, and adhesive production), acetic anhydride (used in the production of plastic materials, explosives, brake and drilling fluids, detergents, dyes, pharmaceuticals, flavors and fragrances), butyl and ethyl acetate. Acetic acid is also used as a solvent in the production of esters and purified terephthalic acid (a raw material for polyethylene terephthalate production) [1].

The production of acetic acid is strongly dependent on the use of fossil fuels, as both the chemical species required for its production (methanol and carbon monoxide) are produced from synthesis gas (a mixture of hydrogen and carbon monoxide). Synthesis gas production is a heavily environmentally impacting process as it is very energy demanding (temperatures in the order of 900°C need to be reached using a furnace fueled by natural gas) and it uses nonrenewable fossil fuels (mainly natural gas and naphtha) as raw materials [1].

A greener way to produce acetic acid could be represented by using renewable feedstocks and sources of energy in the production of synthesis gas. Biogas can fulfill these tasks as it is a renewable source of methane that can be used both as a reactant and as a fuel in synthesis gas production.

Biogas is a mixture of methane and carbon dioxide generated via anaerobic digestion by microorganisms called methanogens. All organic matter can be transformed under anaerobiosis, and this process naturally occurs in a huge variety of environments. Starting from the 1970s biogas generated in landfills started to be utilized all over the world and in the 1990s dedicated plants started to be built to convert biomasses (mainly agricultural waste and manure) into biogas. Nowadays the main utilization for biogas is to generate electric power and heat in CHP (combined heat and power) applications. Alternatively, biogas can be upgraded to biomethane (methane content greater than 95%) with a purification process aimed at removing carbon dioxide and other contaminants and can then be injected into the gas grid [1], [3].

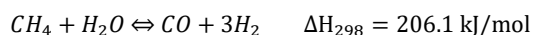
This work aims to model a chemical plant that produces acetic acid starting from biogas and to provide an economic feasibility study to evaluate the plant's potential.

2. Acetic acid production

To better understand the production of acetic acid in its entirety, a brief description of the principal industrial operations involved, starting from the raw materials, (hydrocarbons) is provided.

2.1. Syngas production

The main technology in syngas production is known as reforming. Reforming is a catalytic process that converts hydrocarbons (usually methane) into a mixture of carbon dioxide and hydrogen using a reforming agent, the most common of which is steam. Steam reforming of methane follows the reaction reported below:

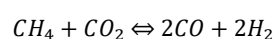


Which is always accompanied by water-gas shift equilibrium reactions:



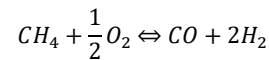
Reforming reactions are highly endothermic and therefore require high temperatures (in the order of 900°C) that are provided by fired heater tubular reactors. The reforming reaction is catalyzed by a nickel-based catalyst that needs to withstand the high temperatures reached in the reactor. This catalyst is very sensitive to poisoning (mainly by sulfur) and therefore the hydrocarbons used in reforming need to be treated to reduce the concentration of pollutants [1], [4].

An alternative reforming agent to steam is represented by carbon dioxide. The process using carbon dioxide as a reforming agent is known as dry reforming:

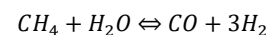
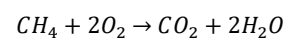


This process is an interesting alternative to steam reforming as it converts two greenhouse gases into a valuable product (syngas with a ratio of hydrogen over carbon monoxide that tends to one). Its main disadvantage is that carbon formation heavily impacts the catalyst activity [1], [4].

Other less common syngas production technologies include hydrocarbon partial oxidation



which has the advantage of being an exothermic process but has low selectivity towards syngas as other reactions are involved (like total oxidation) [1], [4], and autothermal catalytic reforming, which combines total oxidation of hydrocarbons with steam reforming

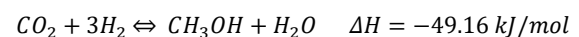


This last process has the advantage of being less energy intensive compared to steam reforming as part of the heat needed for the reforming reaction is directly provided by the combustion of hydrocarbons [1], [4].

The composition of syngas (ratio of hydrogen over carbon monoxide) can be adjusted through water gas shift equilibrium in separate reactors. The carbon dioxide produced during syngas synthesis can be removed by pressure swing adsorption, water scrubbing or chemical washing (using alkaline solutions) [1], [4].

2.2. Methanol synthesis

Methanol is produced starting from syngas through a catalytic process that involves the following reactions:



The overall process is exothermic and proceeds with a reduction in the number of moles, therefore it is favored at low temperatures and high pressure. Industrial operations are conducted between 200°C and 300°C and at 50-100 atm in the presence of a copper/zinc oxide-based catalyst. Several reactor configurations are used worldwide and are designed to maintain temperature in optimal conditions. The most common ones are ICI's adiabatic reactor (where fresh syngas is added at different points through the length of the reactor) and Lurgi's pseudo isothermal reactor (a reactor resembling a shell and tube heat exchanger, where cooling is provided by steam production in the shell side). Methanol synthesis is strongly influenced by thermodynamic equilibrium and the conversion of syngas is never complete. A recycling of the unreacted syngas to the reactor is therefore mandatory to prevent

economic losses. Methanol separation is usually carried out by flash separation followed by distillation (to separate water from methanol and other side products) [1].

2.3. Acetic acid synthesis

Two main routes exist in the industrial production of acetic acid. The first one is related to acetaldehyde oxidation



and is a process that has gradually been abandoned in favor of methanol carbonylation



which represents the most used route [1].

Methanol carbonylation is carried out at around 180°C and 50 atm in continuously stirred tank reactors (CSTR). Carbon monoxide is bubbled inside the reactor, where it enters in contact with methanol. It is a homogeneous catalytic process which relies on a carbonylated metal species as a catalyst and methyl iodide as a co-catalyst. The two main industrial methanol carbonylation technologies are Monsanto's rhodium catalyzed process and BP chemicals iridium catalyzed Cativa™ process. The processes' configuration is similar, the only difference is represented by the catalyst used (and consequently the different reaction kinetic mechanism). Acetic acid separation is carried out in distillation columns. First the catalyst is separated from the reacting mixture, and it is recirculated to the reactor. Then light species are separated from the mixture (dissolved gases and methyl iodide). Water separation is usually very demanding when standard distillation is applied, therefore more efficient methods, like azeotropic distillation and solvent extraction are applied [1], [5].

3. Simulation

A conceptual design of the biogas to acetic acid plant has been carried out through Aspen HYSYS® V11. For the sake of simplicity, the plant has been divided into five main sections: syngas production, syngas refining, methanol production, acetic acid production, and separation section.

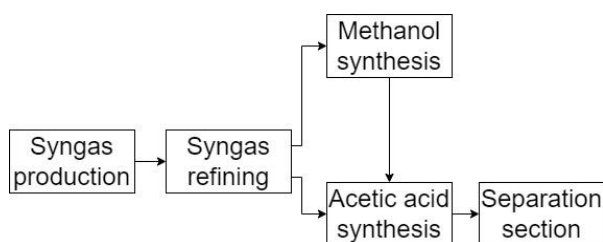


Figure 3.1 Plant simplified diagram

3.1. Syngas production section

The first section of the plant is dedicated to syngas production. Syngas is produced starting from biogas with a molar composition of 60% methane and 40% carbon dioxide. The plant has been designed to convert 1052 m³/h (44.61 kmol/h) of biogas available at 25°C and atmospheric pressure.

Biogas is compressed to 2030 kPa with two compressors with intermediate cooling. Then it is heated to 230°C in a heat exchanger before it is mixed with steam. The mixed stream is sent to a process-process heat exchanger where it is heated to 650°C using the reactor effluent. The stream is sent to the reforming reactor where steam reforming is carried out at 900°C and 2010 kPa. The reactor effluent is quenched to 533.5°C in the heat exchanger used to preheat the reactor feed and it is then sent to a series of two process-process heat exchangers where it is cooled to 126.5°C. The heat provided is used to generate the steam necessary to the reformer (49.21 kmol/h of steam at 210°C and 2020 kPa). The produced syngas stream is further cooled down to 35°C in another heat exchanger before entering a flash separator where syngas is separated from water. Water is recovered and recirculated to the steam generating heat exchangers with a pump. Makeup water is added with a second pump. The composition of syngas exiting the separator is reported in Table 3.1.

CH₄ molar flow	3.0610 kmol/h
CO₂ molar flow	11.7241 kmol/h
CO molar flow	29.8283 kmol/h
H₂O molar flow	0.3823 kmol/h
H₂ molar flow	65.0049 kmol/h
Temperature	35°C
Pressure	1770 kPa

Table 3.1 Produced syngas composition

3.2. Syngas refining section

The second section of the plant is dedicated to syngas refining. First of all, the syngas stream is divided into two separate streams. The first one is the syngas necessary for methanol synthesis (59% of total syngas), the second one is the one containing the carbon monoxide needed for methanol carbonylation. The first stream of syngas is compressed to 8000 kPa in two compressors with intermediate cooling before entering an absorber. In the absorber syngas is washed with water to reduce the content of carbon dioxide to levels compatible with methanol production. The composition of the syngas stream exiting the absorber is reported in Table 3.2.

Chemical species	Molar fraction
CH ₄	0.0302
CO ₂	0.0349
CO	0.2923
H ₂ O	0.0010
H ₂	0.6416

Table 3.2 composition of the syngas exiting the absorber

The absorber water is sent to a flash separator working at ambient pressure where water is degassed before being recirculated to the adsorber through a pump. The recycled water is cooled to 35°C in a heat exchanger before entering the absorber.

The gas stream exiting the flash separator is rich in carbon dioxide and is compressed to 1770 kPa with two compressors with intermediate cooling before it is mixed with the second stream of syngas to improve its composition. The mixed stream is sent to a process-process heat exchanger where it is heated to 690°C before entering a reverse water-gas shift reactor (the heat provided by the reactor effluent is used to preheat the feed). The reaction is carried out at 900°C and 1760 kPa to maximize the content of carbon monoxide. The reactor inlet and outlet composition are reported in Table 3.3. The outlet stream is quenched to 279.8°C in the heat exchanger used to preheat the reactor feed and it is further cooled to 130°C in a heat exchanger before being compressed to 4010 kPa by two compressors with intermediate cooling. The compressed stream is then cooled to 180°C in a heat exchanger to meet the temperature requirements for acetic acid synthesis.

Chemical species	Inlet stream	Outlet stream
CH ₄	1.2551	1.6304
CO ₂	9.6325	4.3012
CO	12.3693	17.3240
H ₂ O	0.5019	6.2085
H ₂	26.6782	20.2262

Table 3.3 Reverse water gas shift reactor inlet and outlet composition (kmol/h)

3.3 Methanol production section

The third section is dedicated to methanol synthesis. The syngas stream exiting the absorber is mixed with the recycled unreacted syngas of the methanol synthesis section and is sent to the methanol synthesis reactor. The reactor inlet stream is heated to 200°C in a process-process heat exchanger using the heat of the reactor effluent. The reaction proceeds at 250°C and 7990 kPa. The reactor inlet and outlet composition are provided in Table 3.4.

Chemical species	Inlet stream	Outlet stream
CH ₄	14.8760	14.8760
CO ₂	7.4150	6.9995
CO	23.4294	6.7175
H ₂ O	0.0639	0.4794
H ₂	69.5190	34.8486
Methanol	0.2727	17.4001

Table 3.4 Methanol synthesis reactor inlet and outlet composition (kmol/h)

The outlet stream of the reactor is quenched from 250°C to 132.4°C in the process-process heat exchanger used to preheat the reactor inlet stream. A second heat exchanger is used to reduce the stream temperature to 35°C before entering a flash separator operating at 7770 kPa and 35°C. The gaseous stream exiting the flash separator is rich in unreacted syngas and is recirculated to the reactor after part of it is purged (10%) to limit inert accumulation. The non-purged stream is compressed to 8000 kPa before it is recycled to the reactor. The liquid stream exiting from the separator is sent to a stabilizer distillation column working at ambient pressure where the remaining traces of gas are removed. The bottom product is a mixture of water and methanol with the composition reported in Table 3.5.

Chemical species	Stabilizer bottom stream composition
H ₂ O	0.4758
Methanol	16.9586

Table 3.5 stabilizer bottom stream composition (kmol/h)

The bottom stream is pumped to 4010 kPa and heated to 180°C in a heat exchanger to respect acetic acid synthesis parameters.

3.4 Acetic acid production section

The fourth section of the plant is dedicated to acetic acid synthesis. The methanol stream produced in the methanol synthesis section, the carbon monoxide rich stream produced in the syngas refining section, and the recycled stream containing the homogeneous catalyst for methanol carbonylation are sent to the acetic acid synthesis reactor. The reactor is modeled as a CSTR reactor working at 180°C and 4000 kPa. The composition of the reactor outlet streams is reported in Table 3.6.

Chemical species	Outlet gaseous stream	Outlet liquid stream
CH ₄	1.6091	0.0213
CO ₂	4.1820	0.1192
CO	0.3638	0.0017
H ₂ O	3.4744	5.5628
H ₂	20.1581	0.0681

Methanol	0	0
Acetic acid	3.7949	13.6240
CH ₃ I	0.1307	0.1450
Rhodium catalyst	0	0.0224

Table 3.6 Acetic acid reactor outlet streams composition (kmol/h)

The reactor's gaseous outlet stream is expanded at 2000 kPa and cooled to 35 °C before it is sent to a flash separator. The separated gaseous stream is rich in hydrogen and can be used as fuel in the reforming furnace. The liquid stream is recovered as it contains acetic acid and methyl iodide and is expanded from 1990 kPa to 111.3 kPa. The reactor's liquid outlet stream is expanded to 121.3 kPa and is heated to 140 °C before entering a flash separator. The separated gaseous stream is mixed with the liquid stream coming from the first flash separator. The separated liquid stream is mixed with the recycled stream coming from the separation section of the plant and it is compressed to 4000 kPa. 1% of this stream is purged and a makeup of catalyst is added before the stream is recycled to the reactor.

3.5 Separation section

The last section of the plant is dedicated to product separation, and it is designed to produce commercial-grade glacial acetic acid. The product stream exiting from the acetic acid production section is cooled to 90 °C before entering a distillation column with full reflux where the most volatile species are removed. The bottom stream is sent to a second distillation column where methyl iodide is removed. The column top stream is cooled to 35 °C and recirculated to the acetic acid reactor with a pump. The bottom stream is sent to a third distillation column where water is removed from the top using propyl-acetate as entrainer. The top stream exiting from the column is sent to a phase separator tank. The aqueous phase is discharged while the propyl-acetate rich phase is recirculated to the column after 1% of it is purged and make-up propyl acetate is added. The bottom stream exiting from the third distillation column is the final product stream. 1008 kg/h of glacial acetic acid are produced.

4. Economic analysis

The economic analysis has been carried out using the Turton handbook as the main reference [6]. The economics of the plant consider capital expenses to build the plant (CAPEX) and operative expenses to run the plant (OPEX). Once the plant revenue is known, the economic potential of the plant can be evaluated through different profitability criteria and a cash flow diagram

can be produced. Lastly a risk analysis using the Monte-Carlo method has been carried out.

4.1. CAPEX

The CAPEX of the plant has been computed using the equipment module costing technique introduced by Guthrie. The bare module cost of each piece of equipment is calculated with (1)

$$C_{BM} = C_P^0 F_{BM} \quad (1)$$

Where C_P^0 is the cost of equipment at the base condition and is calculated with (2) (A is the size parameter of the equipment and K_i are specific parameters for the considered equipment), while F_{BM} is a series of multiplying parameters that take into account non-base conditions (related to working pressure and materials)

$$\log_{10} C_P^0 = K_1 + K_2 \log_{10}(A) + K_3 (\log_{10}(A))^2 \quad (2)$$

The effect of inflation is considered with CEPCI indexes through (3):

$$C_{BM}^{2022} = C_{BM}^{2001} \left(\frac{CEPCI_{2022}}{CEPCI_{2001}} \right) \quad (3)$$

The total module cost of the equipment (that considers contingencies and fees) is calculated through (4) and the grassroots cost (that considers also auxiliary facilities) is calculated through (5).

$$C_{TM} = 1.18 C_{BM} \quad (4)$$

$$C_{GR} = C_{TM} + 0.5 C_{BM}^0 \quad (5)$$

4.2. OPEX

The OPEX of the plant can be divided into three groups:

- Direct expenses (factors that vary with the rate of production). They can be divided into the cost of raw materials, cost of utilities (electrical power, cooling water, steam), cost of waste treatment and cost of operating labor.
- Fixed manufacturing costs (factors that are not related to the rate of production). They include taxes, insurance, and depreciation, all of which are charged even when the plant is not operating.
- General expenses. They are costs related to business functions (like management, distribution, and financing research)

Fixed manufacturing costs and general expenses can be estimated, once the direct expenses (raw materials, utilities, waste treatment, operating labor) and the fixed capital investment are known, through empirical formulas (the formulas taken for this analysis are from the book "Chemical engineering cost estimation" [7]). Once all these costs are known the total cost of manufacturing can be determined.

4.3. Economic assessment

The results for the CAPEX AND OPEX of the plant are reported in Table 4.1.

Costs	€/year
FCI	19277413,89
Operating labor	720000
Utilities	1471509,69
Waste treatment	2198,35
Raw materials	4484868,99
Cost of manufacture	10018995,26

Table 4.1 Plant estimated costs

The revenues of the plant are calculated by multiplying the amount of acetic acid produced each year by the price of acetic acid (1800€/ton in 2022). Three cases of depreciation have been considered (straight line, double declining line, sum of the years digit) and for each one of them, the profitability indicators have been calculated and confronted (payback period, cumulative cash position, discounted payback period, net present value). The lifetime of the plant has been assumed to be 10 years, with a taxation of 50% of the profits and a discount rate of 5%. Results are reported in Table 4.2.

case	PBP (years)	CCP (€)	DPBP (years)	NPV (€)
SL	6,00	12842317	8,24	3.048.825
SOYD	5,33	13155555	7,51	3.715.338
DDL	5,54	12120607	7,94	3.005.486

Table 4.2 Profitability indicators for the three cases of depreciation

All the cases considered present positive profitability indicators with the best performance provided by the sum of the years digit case, suggesting that the plant project is profitable. The conducted Monte-Carlo risk analysis, however, suggests that the risk related to the plant investment is high. 1000 scenarios have been randomly generated taking into considerations possible variations in the price of the produced good and in the cost of manufacture during the years of the plant operations. In 17% of the generated scenarios, the plant does not reach the break-even point. Only 31.3% of the scenarios present CCP higher than 5 million €. 90.1% of the scenarios generated have negative net present values at the end of the plant operations.

5. Conclusions

The main advantage related to the realization of the proposed plant is the possibility to convert a renewable and easily available raw material like biogas into a valuable chemical product, integrating the production of acetic acid in the circular economy. The economic

evaluation that has been carried out suggests that the project is economically viable according to the evaluated profitability indicators. A deeper analysis using the Monte Carlo method, however, shows that the risks correlated to the project are high as the probability of a negative net present value is much greater than that of a positive one. Two main possibilities exist to reduce the plant's economic risks. The first one is to implement new and cheaper production processes. The use of cheaper catalysts, for example, could reduce manufacturing costs with a direct positive impact on the project profitability, reducing the overall risks related to the plant investment. A second possibility is represented by government incentives that could in principle make the production of acetic acid from biogas more profitable, reducing the plant payback period and increasing its net present value. In conclusion, the production of acetic acid from biogas is a promising technology for the future, especially within perspective of a green circular economy, but its implementation seems economically non-convenient when compared with traditional hydrocarbon-based production.

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