Master's Thesis Chemical Engineering

Technoeconomic assessment of thermochemical biorefinery based on DME as a platform chemical

Author: Esther Navarro Cintas Tutor: Pedro García Haro

Chemical and Environmental Engineering Department Technical College of Engineering in Seville University of Seville

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The tribunal appointed to judge the project indicated above, composed of the following members:

President:

Vocals:

Secretary:

Agree to grant the rate of:

Seville, Spain 2016

Secretary of Tribunal

To my parents A mis padres

The aim of this Master's thesis is to revaluate a techno-economic analysis of thermochemical biorefinery concept based on DME as platform chemical in order to see the implications of new results made in the laboratory. A secondary aim of the thesis proves the advantage of multi-production in thermochemical biorefineries.

To this end, several simulations of the process have been made with slightly differences respect on the initial configuration and developing a new train separation due to the presence of new products, such as ethyl acetate, derived from recent analysis and results obtained in the laboratory until the 8 of July 2016.

The methodology followed has been conducting experiments in the laboratory to model a section of the entire plant and then, based on those results again simulate the plant. This process was done iteratively until a consensus of acceptance of results between laboratory and simulation for each section. This paper has managed to simulate well the Carbonylation but has not come to refine the simulation hydrogenation would still polishing.

The economic outlook obtained after the assessments of the various cases have been better than the initial case but there is still quite develop the process before it can lead to a larger scale profitably.

Este proyecto persigue reevaluar los análisis económicos que se hicieron del concepto de biorrefinería termoquímica basada en DME como producto intermedio en la tesis doctoral en la que se basa este proyecto con el fin de analizar las implicaciones de los nuevos descubrimientos realizados en el laboratorio y demostrar la importancia de la multi-producción.

Para ello, se han realizado varias simulaciones del proceso, cambiando ligeramente su configuración inicial y desarrollando un nuevo tren de separación debido a la presencia de nuevos productos como el etil acetato y de los recientes análisis y resultados obtenidos en el laboratorio hasta el día 8 de Julio de 2016.

La metodología seguida ha sido la realización de experimentos en el laboratorio para modelar alguna sección de la planta completa y, después, en base a esos resultados simular de nuevo la planta. Este proceso se ha realizado de forma iterativa hasta llegar a un consenso de aceptación de resultados entre laboratorio y simulación para cada sección. En este trabajo se ha logrado simular bien la etapa de carbonilación pero no se ha llegado a afinar la simulación de la hidrogenación que quedaría aún por pulir.

Las perspectivas económicas obtenidas tras las evaluaciones de los distintos casos han sido mejores que la del caso inicial pero aún queda desarrollar bastante el proceso para que se pueda llevar a una mayor escala de forma rentable.

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1 INTRODUCTION

Increasingly, it is evident the need for more respectful processes with the environment due to population growth, industry and living standards experienced by society. Thereby, it is clear the increase in demand for fuel and everyday products by the billions of people on the planet. Therefore, industrial philosophy should be changed in order to find environmental friendlier processes, which have lower emissions and waste, higher efficiency and they are compact; through which is known as process intensification. Based on this concept and following the European target 2020 premises, the ethanol synthesis from biomass using dimethyl ether (DME) as a platform chemical is studied in this paper because through this process it can be possible to get several products from a renewable source, such as biomass, in a single process.

This master's thesis is supported by the BIOTER(Thermochemical Biorefineries base on DME) project and its aim is to propose process improvements based on recent laboratory data. The BIOTER project, funded by the Spanish Ministry of Economy and Competitiveness, seeks to produce second generation biofuels (bioethanol), electricity power and other chemicals (methyl acetate, H_2 , DME and so on), which are produced by biofuel synthesis process. For that, the thermochemical gasification biorefinery concept based on an indirect synthesis route with DME as a platform chemical, which leads to bioethanol and chemical production, is conceived. As a result of product (energy and chemicals) polygeneration, the biorefinery may become profitable in the future due to the fact that it allows business sector diversification, which reduces its dependence on market developments and economy of scale.

The proposed process has a number of advantages and disadvantages that make it an attractive process which must be improved to be achievable with a certain level of profitability and efficiency. The main advantages can discern in the preceding paragraphs, such as:

- (a) Market price uncertainty reduction because of income diversification through coproduction.
- (b) Better energy and materials integration through the use of a platform chemical.
- (c) Catalyst cost reduction because high selectivity is not required in the indirect route.
- (d) Mild operating conditions (170-250 °C and 10-30 bars) so that operating and investment costs are reduced.

However, there are also some drawbacks which hinder the progress and development of this biorefinery concept:

- (a) The thermochemical route, both using gasification or pyrolysis as conversion pathways, involves severe operating conditions, causing a large dependence on the economy of scale.
- (b) The need for cleaning and conditioning of the syngas increases considerably the processing costs compared to current fossil fuel refineries.
- (c) As a polygeneration plant is more complex, several alternatives for calculating energy efficiency can be applied [2].

As a result of these characteristics, some studies and analysis are done such as the following analysis exposed in this paper in order to solve or reduce the drawbacks and upgrade the advantages. Hence, this analysis starts with a process configuration shown in the paper 5 ([3]) of the doctoral thesis "Thermochemical biorefineries base on DME as a platform chemical" ([1]) and recent laboratory data, from which arise new studies and improvements to the base case.

2 OBJETIVES AND SCOPE

The aim of this master's thesis is the BIOTER project process analysis since its latest version, which is exposed in "Thermochemical Biorefineries based on DME as platform chemical" doctoral thesis ([1]), in order to modify and improve the process based on new experimental data obtained after writing it. Other objective is proposing new experiments which allow check simulated data and, therefore, a study as representative as possible of reality.

Based on all these facts, this master's thesis seeks to perform a techno-economic study of the thermochemical biorefinery by two different operation modes and thus detecting the best of both or even an arisen intermediate operation mode.

3 BASE CASE DESCRIPTION

This chapter describes in detail the process in which this thesis is based to understand the studies and simulations which are explained in later sections. This process is the option SR-01 developed and analyzed in reference [3]. Producing ethanol as the main product and electricity supply (500 MWth in HHV) from 2,140 dry tons of poplar chips per day is the main objective of this alternative.

3.1. Process description

The aim of this process is the ethanol synthesis from biomass using DME as a platform chemical. For this purpose, some treatments and reactions are required. Firstly, solid biomass must be dried, milled and gasified in order to get a syngas, which is mainly composed of CO and H_2 . This gas must follow purification and conditioning steps in order to synthesize several products and avoid unwanted compounds. After that, syngas is prepared for reactions, shown in Figure 1: methanol (MeOH) synthesis from CO and H_2 , DME synthesis from MeOH, methyl acetate (MA) synthesis from DME and ethanol (EtOH) synthesis from MA, the latter two can be grouped in a single step, called hydrocarbonylation. To this reaction sequence they will be added other reactions which has been detected by experimental experiences in the laboratory. These new reactions synthesize ethyl acetate, whose economic value is high. Therefore, a new case study is appeared which will be analyze in this thesis.



Figure 1. Reactive process sequence [1].

It is possible to appreciate that there is not an only one product, ethanol, but also there are others such as methyl acetate, H_2 , DME and electricity power, which is generated from waste streams process.

As it is described below, the process consists of a set of very different stages which can be named and sequenced as follows:

- 1. Feedstock pretreatment and gasification
- 2. Syngas clean up and conditioning
- 3. Methanol (MeOH) and Dimethyl ether (DME) synthesis
- 4. Carbonylation and Hydrogenation (or hydrocarbonylation)
- 5. Products separation

Then, each of the stages is going to be described, indicating its main objectives and characteristics.

3.1.1 Feedstock pretreatment and gasification

Lignocellulosic biomass, which is shaped by hemicelluloses, lignin and uncommon materials, is used in this process as feedstock. The reason of this fact is that this kind of biomass is cheap, it does not compete with other sectors and it allows produce chemical products with low impact on the health and environment of the human being.

In addition, as added, it requires moderate operating conditions thus it is possible a cost of equipment and working reduction. Therefore, it has been selected poplar chips as raw material, whose properties are shown in Table 1.

Component	%wt, dry basis
Carbon	50.90
Hydrogen	6.05
Oxygen	41.92
Nitrogen	0.17
Sulphur	0.04
Ash	0.92
Moisture	30% p/p
High Heat Value (HHV)	20.18 MJ/kg

Table 1. Properties of biomass feedstock (poplar chips) [1].

Considering this composition, the need to remove moisture to increase its heat value is evident, in addition to reduce the size of particles in order to increase its surface area and achieve optimum gasification and combustion conditions of biomass. It can be achieved with a rotary dryer, where moisture is reduced from 30wt% to 12wt% with combustion gases from the gasifier (iCFBG) [1].

Remark that, it can be possible to take advantage in heat of combustion gas to produce high pressure (HP) steam, before the dried stage, in a heat recovery steam generator (HRSG). In this equipment the gas is cooled from 800°C down to 450°C in order to get flue gas at 150°C on leaving the rotary dryer, ensuring good dispersion of the plume. Subsequently, the particle size is reduced below 4cm by a hammer mill.

The aim to gasification stage is simply to get a synthesis gas, which is composed mainly by CO and H_2 , from solid biomass. To do this, there are several technologies available that can be adapted to this process. These technologies are:

- (a) EFG: it is required an air separation unit (ASU) plant and it is more expensive than the others.
- (b) CFBG with O_2 and steam: it is required an air separation unit (ASU) plant, as above.
- (c) iCFBG using air and steam: it is a circulating fluid bed gasifier with indirect heating (heat comes from the combustor) which works at atmospheric pressure. This option does not need an ASU plant thus; it has lower power consumption, being cheaper than previous technologies. Because of these reasons, this technology which has been modelled based on experimental data [4] is selected. The results of this simulation are shown in Table 2.

Gasifier performance		
Pressure	1.5 bar	
Temperature	900°C	
Steam (2 bar, 140 °C)/ dry biomass	0.4 kg/kg	
Heat loss in gasifier	1.53 % HHV	
Cold gas efficiency (% HHV)	77.07	
Component	Mole (%)	
H_2	14.55	
СО	23.64	
CO ₂	6.92	
H ₂ O	43.43	
CH ₄	8.43	
NH ₃	0.18	
Tras	0.15	
C2+	2.70	
H ₂ S	184 ppm	

Table 2. iCFBG operating parameters, exit gas composition and efficiency [1].

3.1.2 Syngas clean-up and conditioning

In order to process and convert syngas, it should be pretreated to prevent unwanted compounds such as tars, sulphur and alkalis, among others; which may damage the equipment operation, cause unwanted reactions, catalyst poisoning and so on. Therefore, a series of steps is required to eliminate substances which may lead these phenomena.

First, particles present in syngas are removed by high temperature cyclone, because of the high temperature gas at the gasifier outlet.

After this, tars and other particles are removed. With the purpose of making it, there are two technologies available. The first one is OLGA, which is oil and water scrubbing developed by ECN, and the second one is a

water scrubbing. After these options analysis, the first one was chosen because it is better suited to process needs and it can burn tars and solvent in the gasifier.

Subsequently, nitrogen compounds, alkalis and HCl are removed by water scrubbing. After this, the sulphur compounds (H_2S y COS) are removed by an oxidation process in liquid phase (LO-CAT) at 17 bars, pressure at which H_2S is oxidized to S [5, 6], and a double filter bed (CO-MoZnO), where H_2S concentration is removed even more. The reason of using LO-CAT is justified because it allows treat gas with low H_2S content without removing CO₂, which will be feed to steam reformer inlet to achieve a H_2 /CO molar ratio 1 at the hydrocarbonylation reactor inlet.

After this cleaning, gas has to be suitable to reach the desired conditions for its conversion,

Table 3.



Table 3. Requirement for syngas conversion to products [1].

Thereby, there are three available technologies, previously studied in previous publications BTL/G, which led the tars and light hydrocarbons reforming. These technologies are Steam Reforming (SR), Autothermal Reforming (ATR) and Thermal Reforming (TR), which may be used alone or in conjunction with H_2 y CO₂ removal systems [7, 8, 9-18]. In this case, the Steam Reforming (SR) is used because ATR needs O₂ removal and TR requires particles removal and CO₂ separation, which has poor efficiency. In this way, desulphurized gas is fed to the SR unit where methanol and light paraffins are converted into syngas, what led to adjust H_2 /CO ratio through the steam used in this equipment, ensuring no carbon deposition over catalyst.

Finally, large amount of CO_2 gas is removed by an amine scrubbing, due to the low CO_2 partial pressure, and it is dehydrated by a molecular sieve to avoid the presence of water in the hydrocarbonylation stages because water causes the H-Mordenite catalyst deactivation, which damages the reaction. Another aspect to consider is the amount of H₂ present in gas because if it is in excess, it should use a PSA (Pressure Swing Adsorption) in order to reduce this amount of H₂ which could be used elsewhere in the process, sold or burnt in a gas turbine,

3.1.3 Methanol (MeOH) and Dimethyl ether (DME) synthesis

DME is synthesized by direct route from syngas because of the higher CO conversion per pass in direct than indirect route (methanol synthesis from syngas and methanol dehydration in order to get DME) and the fact that there is more information and technical data about direct route. With the purpose of making it, the reactor operating conditions are 50 bars and 250°C and γ -alumina catalyst is used to intensify the following reactions:

Reaction 1 $CO + 2H_2 \leftrightarrow CH_3OH$

Reaction 2 $CH_3COOCH_3 + 2H_2 \rightarrow CH_3OH + C_2H_5OH$

Reaction 3 $3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2$

Reaction 4 $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$

 H_2O separation from DME at the outlet reactor is necessary with the purpose to recirculate DME without water to hydrocarbonylation because, as it has said, water is a H-Mordenite catalyst poison. While methyl acetate is recirculated to hydrocarbonylation in order to increase the ethanol and methanol production.

3.1.4 Carbonylation and Hydrogenation or hydrocarbonylation

The ethanol and methanol synthesis from DME mainly occurs in 5 reactors in series whose operating conditions are 30 bars and 220°C. Between each reactor, there is some coolers and flashes in order to upgrade DME conversion. In addition, syngas recirculation is not necessary to reach CO/DME molar ratio 10 because DME is fractionally fed to each reactor while syngas is totally introduced in the first reactor. In these reactors occur the following reactions:

• DME Carbonylation (Reaction 5) is a heterogenic catalytic reaction which is catalyzed by H-Mordenite zeolites. Other possibility may be the methanol Carbonylation but, in this case, water appears which is a drawback because water deactives H-Mordenite catalyst.

Reaction 5 CO + 1.464H₂ + 0.4096CH₃OCH₃ \rightarrow 0.07831CH₃COOCH₃ + 0.4578C₂H₅OH + 0.1265CO₂ + 0.542CH₃OH

• Acetates hydrogenation (Reaction 2) is a well-known reaction. Therefore, Cu-ZnO catalyst is selected for this reaction based on the knowledge.

Reaction 2 $CH_3COOCH_3 + 2H_2 \rightarrow CH_3OH + C_2H_5OH$

Based on these characteristics, hydrocarbonylation takes places in a double fixed bed reactor fixed with H-Mordenite and Cu-ZnO and syngas and DME as inlet. This configuration has been successfully demonstrated on a laboratory scale through experiences that conclude the need for a CO/DME molar ratio 10 [19-21].

3.1.5 Product Separation

The liquid hydrocarbonylation products are methanol, ethanol and, in lower amount, methyl acetate. First, methyl acetate is separated by stabilizer column and it is recirculated to hydrocarbonylation section in order to react to extinction. Then, ethanol is separated from methanol by a distillation column, with the purpose of getting ethanol in the sale conditions and recirculating methanol to DME synthesis section, where it is dehydrated.

3.2. Simulation

The process described in the previous section, shown in Figure 2, was simulated in Aspen Plus software. For gasification, gas clean-up and conditioning, the DME conversion and DME synthesis sections, the equation of state Redlich-Kwong-Soave with Boston-Mathias alpha function (RKS-BM) was used. In addition, the Non-Random Two Liquids (NRTL) method with the Redlich-Kwong equation of state was used to simulate the product separation.

Focusing on economic study, discounted cash flow analysis cash (DCFA) was used. The assumptions made for it are shown in

Table 4, where working capital and cost of land are recovered at the end of plant life. In addition, the internal rate of return (IRR) was calculated by setting the market price of products in the DCFA. Table 5 shows the market prices in the economic scenario assumed.

Parameter	Value
Debt/Equity	0/100 %
Plant life	20 years
Depreciation (linear)	10 years
Salvage value	0 M USD
Construction period	1 year
Income tax	30 %
Working capital	1-month operating cost
Land	6 % TIC

Working capital and cost of land are recovered at the end of plant life.

Product	Price
Ethanol	0.61 USD ₂₀₁₀ /l
Methyl Acetate	1.71 USD ₂₀₁₀ /l
Hydrogen	1 USD ₂₀₁₀ /kg
DME	692 USD ₂₀₁₀ /m ³
Electric power	5 cUSD ₂₀₁₀ /kWh



Figure 2. Base case process flow diagram.

3.3. Results and conclusions

As it can be observed in Figure 3, the total operating costs of this case were 78.56 M USD₂₀₁₀/year, while the total plan investment (TPI) was 421.51 M USD₂₀₁₀/year (see Figure 4).



Figure 3. Total operating costs of case base.



Figure 4. Total plant investment of base case.

In this way, the internal rate of return (IRR) for this case was 10.44%. According to Figure 5, an IRR decrease causes an important increase in total operating costs and total plant investment. In addition, this decrease causes a decrease in ethanol and power electricity income.



Figure 5. Sensitivity analysis [1].

Due to the high biomass price and moderate commercial price of ethanol in DME hydrocarbonylation, the total plant investment is critical, so the feasibility of the process is questionable. Furthermore, the TPI is very sensitive to variations of the ethanol price. For this reason, it is necessary to seek new alternatives with diversified income, which provokes a decrease in this sensitivity.

3.4. Aspects to improve

Based on the results of this case, it is clear that it is needed a new concept which reduced commercial prices dependency. It could be achieved by different products generation and the process optimization in order to maximize the valuable products generation.

4 LABORATORY **S**TUDIES

Following studies were crucial to simulate the process in a quite real way. Due to these experiments, this thesis was needed in order to represent the new products, behaviours and modifications which were obtained as a result of the experiences.

The first experiment after the PhD thesis in which is based on this master's thesis was a Hydrocarbonylation analysis which revealed the ethyl acetate synthesis as subproduct, when MA conversion to ethanol is low, which was not taken into account in the PhD thesis. After that, a Carbonylation analysis and a hydrogenation analysis were done. Based on the result of these two analysis has made all the master's thesis simulations.

4.1. DME (Hydro)Carbonylation

As it said previously, in this analysis was detected EA synthesis in hydrocarbonylation section which has been included in this master's thesis because:

- 1) Due to the EA production, the products mixture with new azeotropes which makes more difficult the products separation than the base case.
- 2) This new product is more valuable than the others, which gives more incomes. However, EA production implies ethanol consumption which is the main product in base case. Because of that, it will be studied which is more interesting product to maximize in order to get more revenue. This can lead to some options: a) maximising ethanol, b) maximising ethyl acetate or c) producing both of them at the same time.

4.1.1 Experiment design

In this study, DME and CO (synthesis gas) were fed to reactor in molar amount of 10. The reaction carried out at 170°C and 7.2 bar CO partial pressure. The SV was imposed in 3600 hr⁻¹, 0.5 g of H-Mordenite catalyst and 10% molar of each inert compound (N_2 and CH_4).

4.1.2 Effects analyzed and results

The effects which were evaluated in this study were:

- 1) Catalyst regeneration: there was main loss of activity and it does not have any effect on selectivity to EA. Based on this, the use of this catalyst was analysed and it could estimate the conversion in the reactor.
- 2) H_2 presence: it was studied introducing a H_2 /CO molar number of which provoked a slight DME conversion increase and it caused a decrease in selectivity to MA. This effect can condition in the recirculation to reactor.
- 3) Temperature: the higher temperature the higher conversion, being stable below 200°C. However, catalyst deactivation occurred at temperature up to 200°C. In this way, it is necessary to change the operating conditions of hydrocarbonylation used in the base case.
- 4) Feedstock system: unfriendly compounds in the DME inlet stream such as butane can reduce conversion. Because of that, it is clear that DME inlet stream must be as pure as possible.
- 5) Space Velocity: the lower velocity the higher selectivity to MA and conversion. This increase is quite interesting because the opposite occurs as usual.

4.1.3 Conclusions

In this analysis the main problems were the catalyst deactivation and the effect of temperature because if temperature decreases, the DME conversion will decrease too.

Other conclusions were:

- Methyl acetate (MA) production \geq 0.24 mol/h per each mol of Al (this element is present in catalyst).
- MA selectivity ≥ 90% leads to get only methanol and light hydrocarbons as by-products.
- High conversion because of no catalyst compacting.
- Water is not synthesized in the process, which is good because it is an H-Mordenite catalyst poison.

4.2. Carbonylation analysis

This experience and the next one were carried out in the following pilot plant Figure 6. As it can be seen, it has a pre-heater in the inlet which is followed by two reactors (a Carbonylation and a Hydrogenation reactor). These reactors can operate separately or in series and they have three beds inside, two of silica in order to advantage heat transference and one of H-Mordenite catalyst in the middle (Figure 7). Then, there is a flash before the emission in order to condensate the possible products.

Under it, there is a mass spectrometer in order to get the different products flows. Due to this fact, CH_4 and N_2 are used as inert which let to detect the different products.



Figure 6. Pilot plant.



Figure 7. Catalyst distribution scheme.

In this study a stream composed by CO, DME and two inert (N_2 and CH_4), as it is shown in Table 6, was introduce in Carbonylation reactor at 170°C and 11,1 bar (7,2 bar CO pressure). As it can be seen, there is a CO/DME ratio of 10 which is imposed in simulations cases.

Component	Nml/min
СО	40
DME	4
N_2	12
CH ₄	6

	Table 6.	Carbonylation	inlet stream	composition.
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In addition, the reactor was filled with 2gr of H-Mordenite catalyst and was operating for 28 hr at 170°C and 11bar.

4.2.1 Result and discussion

In these conditions, it was obtained the results showed in the next table (Table 7) and the uptime catalyst which is the time period for getting $\pm 10\%$ of 6.30% DME conversion (Figure 8).

Parameter	Value
DME Conversion	6.30%
MA productivity	0.336 mmol/g·hr
MeOH productivity	0.024 mmol/g·hr
MA selectivity	97.67%
MeOH productivity	2.12%

|--|



Figure 8. DME conversion in Carbonylation analysis.

Based on these results, a correlation was made in order to calculate the DME conversion in others inlet stream composition (maintaining the CO/DME of 10) with the aim to simulate this event at industrial level. In addition, it is confirmed 12 hours uptime catalyst because of that it is necessary three sets in parallel of five Carbonylation reactors in series to ensure a continuous production, as it can be verified in Figure 9. This estimation is taken into account in feasibility analysis.



Figure 9. Carbonylation reactors set schedule operation.

4.3. Hydrogenation analysis

This analysis was made in order to evaluate the MeOH and EtOH effect on hydrogenation reactions. Besides, the aim of this experiment is getting suitable results to simulate it and reproduce the reality. For those targets, it was necessary doing several experiments which are explained below.

In the first one, it was changing the inlet stream composition in order to analyse the MeOH and EtOH effect on the reaction. The experience which was used to simulate these facts has an inlet stream composition as Table 8 shows and it was introduced to Hydrogenation reactor at 220°C and 20bar which was filled with 1.5gr of H-Mordenite catalyst and was operating in the same temperature and pressure.

Component	Nml/min	Component	Nml/min
СО	98.6	MA	9.74
H_2	109.04	MeOH	0.09
N_2	27.84	EA	1.08
CH ₄	14.62		

Table 8. Hydrogenation inlet stream composition, first experiment.

In the second one, three experiences were carried out, changing the H_2/MA ratio at the inlet of the hydrogenation reactor, see Table 9. With these experiments, a new important effect was found out and the recirculation effects, which were modelled by Aspen, were taken into account. As well as, their results were used to test the simulation results.

Table 9. Hydrogenation experiences, second experiment.

H ₂ /MA molar ratio	MA conversion (%)
10	37,7
20	61,9
30	69,7

4.3.1 Results and discussion

In the first experiment, for the inlet stream composition showed in Table 8 the MA conversion was 16.40%. In addition, it was analysis the MeOH and EA percentage at the inlet stream effect on MA conversion, getting the following results.



Figure 10. MeOH effect on MA conversion in hydrogenation reactor.

As it can be seen in Figure 10, there is an optimum value of MeOH percentage at the inlet to rich the maximum possible MA conversion. This value is quiet low which means that if it desired a great MA conversion, it should not recirculate MeOH to hydrogenation reactor.



Figure 11. EA effect on MA conversion in hydrogenation reactor.

Analysing Figure 11, it can be said that there is an optimum value of EA percentage at the inlet to achieve a good MA conversion. This effect is quiet low so it would be preferable to avoid EA recirculation, although if it could not be possible, its effect would not be important.

In the second study, it was observed the inlet H_2/CO ratio influence on MA conversion, which is shown in Figure 12.



Figure 12. MA conversion dependence on H_2/MA ratio.

As it can be noticed, there is an optimum H_2/MA ratio value (31) to rich the maximum possible MA conversion (71.77 %) and it makes no sense searching H_2/MA ratio upper than 55 because the conversion tends to negative values.

Based on all these results, it was made a correlation in order to calculate the MA conversion in every kind of inlet stream composition with the aim to simulate this section at industrial level with high approximation to the reality. Thus, the simulation takes the following specifications in order to reproduce the laboratory results.

Parameter	Value
H ₂ /MA ratio	31
MA conversion	71.77 %
MeOH at inlet stream	< 0.60%
EA at inlet stream	< 1.00%

Table 10. Hydrogenation specifications for simulation.

4.4. H-Mordenite catalyst surface area analysis

The catalyst H-Mordenite activity was studied in two cases, hydrocarbonylation reaction and after regeneration of it, by gas adsorption porosimetry analysis in order to identify the loss and recovery of activity, respectively.

This method consist of a degasification stage of solid sample (the catalyst), using He as inert gas, and a N_2 adsorption step where gas is adsorbed from small to large pores. In this way, an adsorption isotherm is obtained at the end of the analysis. With this isotherm the specific surface can be evaluated.

The experiences were carried out with compact H-Mordenite catalyst simple because of their dustiness which hinders the experiment. With the goal of obtaining representative and conclusive results, each experience was made twice. In this way, it was analyzed fresh catalyst (without undergoing reactions), wasted catalyst (after the reaction) and regenerated catalyst.

4.4.1 Results and discussion

Mainly, the catalyst specific surface variation due to different situations was analyzed. The results obtained in each experience are shown below, Table 11.

Sample	Sample weight (g)	Surface area (m²/g)	Hole volume (cm³/g)	Hole diameter (\hat{A})
Fresh H- Mordonito	0.2106	450.02	0.26	22.75
Wordenne	0.1055	429.36	0.23	21.75
Wasted H- Mordonite	0.0875	337.53	0.19	23.16
Wordenne	0.1163	322.17	0.19	23.37
Regenerate H- Mordenite	0.1455	65.89	0.04	21.16

Table 11	H-Mordenite	surface area	analysis	results
	. II-MOIGEIIIC	surface area	i anai ysis	resuits.

4.4.2 Conclusions

Based on these results, it is clear to see that there is around a 25% catalyst specific surface loss during hydrocarbonylation reaction. This estimation is made with the 0.1663 g and 0.1055 g samples data, which is reasonable and acceptable.

Regarding regeneration, it is obvious that the obtained data are not representative since the new specific surface is much smaller than fresh and wasted cases. This is because of the silicon carbide presence in catalyst structure, which distorts the test results making impossible to get reliable results. Therefore, it should find an alternative method for analyzing the surface area recovery degree which is achieved by the regeneration method used, since silicon carbides are part of the catalyst structure, which cannot be removed without alter the catalyst.

5 SIMULATION

5.1. General description

Following studies simulations are quite similar to the base case but they have some modifications because of the laboratory experiments conclusions. The great difference is the fact that in these studies, the simulations are started with syngas, avoiding feedstock pretreatment and gasification stages.

Firstly, the same thermodynamic method is used in all simulations steps which are simulated by Aspen Plus V8.4. Therefore, the Non-Random Two Liquids (NRTL) method with the Redlich-Kwong equation of state is used to simulate all these cases because of it models all properties components well.

Secondly, the mainly modifications respect on the base case are hydrocarbonylation, methanol and DME synthesis and separation sections due to the laboratory results. Each modification is explained below.

5.1.1 Carbonylation and Hydrogenation or Hydrocarbonylation

As far as it was checked in laboratory experiences, Carbonylation and hydrogenation stages are modified respect on the case base because of there is an ethyl acetate production apart from methyl acetate in these reactions. It is due to H-Mordenite catalyst operating at 170°C and 7.2 bar CO partial pressure. In simulations are used 5 Carbonylation reactors in series whose Co partial pressure average is 7.2 bar, taking into account exchangers and reactor pressure drops (3psi). In this way, temperature, pressure and reactions are modified in Carbonylation stage. The reactions which take part in Carbonylation section are Reaction 6 and Reaction 7 which represent the MA synthesis and coke formation on catalyst, respectively:

Reaction 6 $CO + CH_3OH \rightarrow CH_3COOCH_3$

Reaction 7 $2CH_3OH \rightarrow C_2H_4 + CH_3OH$

To conclude with Carbonylation step, it is modelled by RStoic block where reaction conversions are changed according to laboratory results. In addition, MA condensation between each reactor is used in order to increase global conversion due to the fact that MA decreases the catalyst activity. Finally, it has to say that the catalyst deactivation is taking into account evaluating the number of reactors in parallel that are necessaries in order to ensure a continuous production, see Figure 9.

As far as hydrogenation is concerned, it is modelled by a calculator block because of each reaction conversion is not clear. Therefore, a global conversion correlation is calculated in order to recreate laboratory experiences where the following reactions take part in at 220°C and 20 bar.

Reaction 2 $CH_3COOCH_3 + 2H_2 \rightarrow CH_3OH + C_2H_5OH$

Reaction 8 $CH_3COOCH_3 + C_2H_5OH \rightarrow CH_3OH + CH_3COOC_2H_5$

Reaction 9 $CH_3COOC_2H_5 + 2H_2 \rightarrow C_2H_5OH$

Reaction 10 $CH_3COOC_2H_5 \rightarrow 2CH_3CHO$

An interesting issue is the fact that, DME is not separated before hydrogenation inlet. It is done in this way because of DME is not an inhibitor of these reactions, which was verified in laboratory experiments, and the difficulty of this separation (cryogenic conditions).

5.1.2 Methanol and DME synthesis

This stage is modelled by a REquil block where reactions 1 to 4 are carried out at 50 bar and 250°C.

5.1.3 Product separation

Separation sequence depends on the production target (what product is maximized for being sold). It is because of every product has different sold specifications. Therefore, there are cases in which it is necessary a

great separation in order to get the product specifications and others that it is not because it is recirculate. For that reason, product purity specifications were searched for taking it into account in the different study cases, see Table 12.

Product	Purity demanded by market
Ethanol	Automotive: 96,7 % (m/m) [UNE EN 15376]
Methanol	99,85 % (P/P) by IMPCA 001-02 method
Ethyl Acetate	99,7 % (v/v)
Methyl Acetate	80 % (v/v)
DME	90 % (v/v)

Table 12. Floudet pullty specifications.	Table 12.	Product	purity	specifications.
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Moreover purity specifications, the component mixture to separate is must be analyse in order to design an adequate separation sequence because if there is azeotropes the separation will be really difficult or if the mixture are in liquid face it will be easier one separation method than the other. For this reason, azeotropes, which affect separation system, have been detected, as it is shown below.

Table 13. Azeotropes which affect separation system.

Azeotrope	Affected separation	
Methanol-Water	Water separation	
Ethanol-Water	Water separation	
Methanol-MA	Methanol separation to recirculation and/or to sell	
Methanol-EA	Methanol separation to recirculation and/or to sell	
Ethanol-MA	Ethanol with product quality	
Ethanol-EA	Ethanol with product quality	
Methanol-Ethanol	Ethanol with product quality	
MA-EA	MA separation to recirculation and EA with product quality production	

Based on these considerations, a distillation column series and flashes are used to achieve the targets in each case study. These distillation columns are simulated by Radfrac column and the flashes by flash block.

5.2. Maximum EA case analysis

This case has been impossible to simulate because of the poor EA production. In this EA percentage in the outlet stream, its separation is too much difficult because of the MA-EA and MeOH-EA azeotropes. Therefore, this case could not be simulated and the only conclusion is that it is necessary improving conversion to EA or finding out a sharp separation system which made possible getting EA in suitable conditions.

5.3. Maximum EtOH case analysis

In this case, it is searched the maximum EtOH production. However, DME is sold as well sinceit is generated in a large quantity and cannot be completely converted at a reasonable recirculation rate.

For this propose, it is necessary two distillation columns at separation stage. In the first one, DME is obtained as product and the endings are bringing to the second column where ETOH is getting as product and the lights are recirculated to Hydrogenation.

As it can be seen in Figure 13, there is a main difference in the process scheme respect on the base case. It is the fact that, Hydrogenation outlet stream is divided in order to achieve the CO/DME=10 at Carbonylation and $H_2/MA=31$ at Hydrogenation.

5.4. Maximum EtOH and MeOH production case analysis

This case was done in order to study the influence of the multi-production because it implies more investment and operating costs than only one product.

The fact that choosing MeOH as product is that MA is crucial to produce a high quantity of EtOH and EA is difficult to separate and, therefore, getting it in selling specifications.

If Figure 14 is watched, it is clear to see that the process is quite similar to the previous case. The only difference is the separation stage. In this case, there is one more distillation column where MEOH is obtained as product and MA and EA are recirculated to Hydrogenation.



Figure 13. Maximum EtOH case process flow diagram.



Figure 14. Maximum EtOH and MEOH production case process flow diagram.

6 ECONOMIC FEASIBILITY

This chapter analyses the economic viability of each cases studies in order to evaluate if it is possible to execute them and what would be the most feasible of them. If neither is possible due to poor profitability, it will assess which parameters are the most influential for further research to minimize the influence of the same.

With the purpose of making this study, the conventional analysis of flows discounted annual cash is followed. To do this, the assumptions in Table 14 and Table 15 data have been taken as analysis inputs. As can be noticed, the commercial prices data have been taken for the same year as the doctoral thesis, on which this master's thesis is based, and it has made the same assumptions in order to obtain comparable results with those obtained in the doctoral thesis.

Parameter	Value
Debt/Equity	0/100 %
Plant life	20 years
Depreciation (linear)	10 years
Salvage value	0 M USD
Construction period	1 year
Income tax	30 %
Working capital	1-month operating cost
Land	6 % TIC

Table 14. Economic assumptions for discounted cash flow analysis [1].

Working capital and cost of land are recovered at the end of plant life.

Table 15. Commercial prices of products in 2010 for the economic assessment.

Product	Value
Ethanol	523 (USD ₂₀₁₀ /m ³), [22]
Methyl Acetate	$1710 (\text{USD}_{2010}/\text{m}^3), [23]$
\mathbf{H}_2	1 (USD ₂₀₁₀ /kg), [24]
DME	692 (USD ₂₀₁₀ /m ³), [1]
Ethyl Acetate	1918 (USD ₂₀₁₀ /kg), [25]
Electricity power	16 (cUSD ₂₀₁₀ /kWh), [1]
Methanol	$241(\text{USD}_{2010}/\text{m}^3), [1]$

7.1. Maximum EtOH case analysis

7.1.1 Material results

With the aim to analyse the global material balance, Table 16 shows the inlet and outlet mass flow streams and the product purity.

Inp	outs	Outputs				
Biomass	127404 kg/hr	EtOH	1462,266 kg/hr			
Water	903600 kg/hr		97.8 %(v/v)			
Amines	17259,38 kg/hr	DME	49698,222 kg/hr			
Air	219600 kg/hr		91.7% (v/v)			
NH ₃	108000 kg/hr					

Table 16. Maximum EtOH case material results.

In this case, there are only two material outputs. However, there are other outputs like electricity power which is the main revenue. As it can be seen, the products are obtained with good purity level which lets to get more revenues.

7.1.2 Energy results

Firstly, it is important to know if this plant need buy electricity power because it would be the main operating costs. As it can be observed in Figure 15, there is a generation of electricity power. Thus, it is an output and it gives revenue.



Figure 15. Maximum EtOH case power consumption and generation.

As far as Power distribution is concerned, it is clear to see in Figure 16 that Gas clean-up & conditioning, Carbonylation and cryogenic plant are the most power consumers, whereas the Gasification, DME section and Steam plant are the less power consumers.



Figure 16. Maximum EtOH case power consumption and generation distribution.

For all reasons, it is recommended to improve the most power consumer sections in order to reduce the power consumption and getting more revenues to electricity power selling.

7.1.3 Economic feasibility results

With the target to evaluate the economic feasibility, total plant investment (TPI), total operating costs (TOC) and revenues are studied. The first one, Figure 17, it is determined by heat exchangers and power plant island investment. Therefore, if it is possible reduce the number of exchangers or its scales the TPI could be lower.



Figure 17. Maximum EtOH case total plant investment.

In the second one, Figure 18, the main costs are fixed costs whose cost distribution is as Figure 19 shows. According to these figures, a reduction in general expenses, labour and maintenance implies a great reduction total operating costs.



Figure 18. Maximum EtOH case total operating costs.



Figure 19. Maximum EtOH case fixed operating costs distribution.

If the variable costs are analysed the main costs is biomass because of that, it would be interesting searching another cheaper biomass than the actual feedstock.



Figure 20. Maximum EtOH case variable operating costs.

In the third one, the revenues are distributed as follow, Figure 21. The main revenue is given by electricity power and then by DME. Sadly, the main product (EtOH) is the lower revenue producer because of its low production.



Figure 21. Maximum EtOH case revenues.

Finally, according to the conventional analysis of flows discounted annual cash, the inversion would be recovered in more than 20 years (22 years). It is due to the main dependency to electricity power production and the low EtOH production. If it was desired recover the inversion in 20 years, it would be necessary a 9.66% IRR.

7.2. Maximum EtOH and MeOH production case analysis

7.2.1 Material results

As 7.1.1, the global material balance is analysed by Table 17, which shows the inlet and outlet mass flow streams and the product purity.

Inputs		Outputs				
Biomass	127404 kg/hr	EtOH	1385,25 kg/hr			
Water	903600 kg/hr		98.8 % (v/v)			
Amines	17259,38 kg/hr	МеОН	1607,405 kg/hr			
Air	219600 kg/hr		80.5 % (v/v)			
NH ₃	108000 kg/hr	DME	49749,199 kg/hr			
			92.4\$ %v/v)			

Table 17. Maximum EtOH and MeOH production case material results.

In this case, there is one more material product. However, although there are more products than the previous case, the main revenues are given by electricity power.

7.2.2 Energy results

Firstly, there is a global energy balance in order to know if it is necessary buy electricity power or not. As it can be observed in Figure 22, there is a generation of electricity power. Thus, it is an output and it gives revenue.



Figure 22. Maximum EtOH & MeOH production case Power consumption and generation.

As far as Power distribution is concerned, it is clear to see in Figure 23 that Gas clean-up & conditioning, Carbonylation and cryogenic plant are the most power consumers, whereas the Gasification, DME section and Steam plant are the less power consumers.



Figure 23. Maximum EtOH & MeOH production case Power distribution.

After all these analysis, it is easy to say that this case and the previous case are quiet similar in energy balance. Due to this fact, it can be conclude that the sale of an extra product has an important effect on energy plant.

7.2.3 Economic feasibility results

With the aim to evaluate the economic feasibility, total plant investment (TPI), total operating costs (TOC) and revenues are studied. The first one, Figure 24Figure 17, it is determined by heat exchangers and power plant island investment, as in the previous case.



Figure 24. Maximum EtOH & MeOH production case total plant investment.

In the second one, Figure 25, the main costs are fixed costs whose cost distribution is as Figure 26 shows. According to these figures, a reduction in general expenses, labour and maintenance implies a great reduction total operating costs.



Figure 25. Maximum EtOH & MeOH production case total operating costs.



Figure 26. Maximum EtOH & MeOH production case fixed operating costs distribution.

Biomass costs are the main variable costs so that, it would be interesting searching another cheaper biomass than the actual feedstock. It is the same conclusion as in Maximum EtOH case.



Figure 27. Maximum EtOH & MeOH production case variable operating costs distribution.

In the third one, the revenues are distributed as Figure 28 shows. The main revenue is given by electricity power and then by DME. Sadly, the main product (EtOH) is the lower revenue producer because of its low production.



Figure 28. Maximum EtOH & MeOH production case revenues.

Finally, according to the conventional analysis of flows discounted annual cash, the inversion would be recovered in more than 20 years (21 years). It is due to the main dependency to electricity power production and the low EtOH production. However, due to the fact that there is an extra product and it supposes more percentage of revenue than the EtOH, the inversion recovery will be earlier than the previous case. In fact, the required IRR to recover the inversion in 20 years is 9.84% which is higher than the previous case and nearer to the case base's IRR (10 %).

Because of this reflection, it is clear to conclude that a multi-production is quite beneficial and it does not require huge efforts.

7.3. Cost comparison

After analysing each case, it has been done some figures that show a cost comparison to see the influence of everyone in each case.

As it can be seen in Figure 29, the new cases have higher total plant investment than the base case but they have the same investment distribution than the base case, being the heat exchangers and power plant the main investment.



Figure 29. Total Plant investment comparison.

The total operating costs are quite difference as the Figure 30 shows. The new cases are quite similar but they do not have the same cost distribution than the base case because in base case the main operating cost is the biomass whereas in the others are the fixed costs. In addition, the total operating costs are higher in the new cases than in the base case, except biomass and catalyst costs.



Figure 30. Total operating costs comparison.

Although the inversion is higher in the new cases the revenues are higher too. Hence, these options are better than de base case and as it was said previously the Maximum EtOH and MeOH production is better than the others because of the revenue distribution.

8 CONCLUSIONS

After comparing the two analysed cases, the conclusion is that in these configurations the multi-production (polygeneration) is quite beneficial to the feasibility of the process with any important effect on the TPI or TOC. Because of that, it is recommended searching multi-production in order to diversify the revenues.

As far as base case is concerned, the main total operating cost is not the fixed costs as the other cases but it is the biomass costs. It is due to the great difference that has been done in the process. However, the main contributor to the total plant investment is the heat and power investment as usually in these kind of studies.

Paying attention to the laboratory analysis and results, it is clear that it is necessary to continue with the experiments in order to get more information that lets to simulate perfectly the reality.

The ethyl acetate (EA) issue is very important because it is a huge commercial opportunity but nowadays it is quite difficult to get this product in commercial conditions in these quantities. Therefore, it is recommended to search the way to hence the EA generation in order to be able to separate it with good composition.

To conclude, this project is improving but it has to be more developed in order to demonstrate all its possibilities and commercial opportunities. With this master's thesis this project has been a positive evolution but it needs more than that to be possible in real way.

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ANNEXES

- A. Hydrogenation analysis
- B. Hydrogenation's simulation results analysis at laboratory
- C. Cash flows analysis cases

A. Hydrogenation analysis

This study was done because it was believed that hydrogenation was an equilibrium reaction in this process. However, it was checked at laboratory that it was not true. Even though, it is explained as an annexe in order to show all the steps which were followed to achieved a good reality simulation. Knowing that, it is explained it below.

This analysis evaluates the hydrogenation reaction sensibility of methanol or ethanol in the inlet stream due to MA recirculation.

In addition, the kinetic reactions are studied in order to get the kinetic constants and equations and to analyse the temperature effect.

A.I. Simulation description

In this analysis, it was not necessary doing the simulation completely. Therefore, it was simulated the process without products separation steps. So that, the sensibility to methanol and ethanol was evaluated assuming a 10 kmol/hr MA recirculation stream flow, in which the composition stream was modifying introducing higher or lower methanol or ethanol molar percentage, according to which was evaluated. The process scheme which was followed in this analysis can be seen in Figure 31

In order to calculate the equilibrium constants, the process was simulated with only unreacted DME recirculation and the reaction temperature and feed stream was changing with the aim to get the equilibrium kinetic equation by linear regression.



Figure 31. Hydrogenation process flow diagram.

A.II. Results and discussion

As a result of the sensibility to methanol or ethanol in the MA recirculation stream, Figure 32 and Figure 33 were got. Each product productivity evolution according to the methanol and ethanol molar percentage in MA recirculation stream is shown in these figures.

Productivity was defined $\gamma_i = \frac{c_{ij}}{c_{i0}}$, being the product and j the methanol or ethanol molar percentage in MA recirculation stream.



Figure 32. Productivity-% MeOH in MA recirculation to hydrogenation.



Figure 33. Productivity-% EtOH in MA recirculation to hydrogenation.

According to these figures it is clear to get the following conclusions:

• The methanol presence in the hydrogenation reactor can be beneficial while it was less than 20% molar in MA recirculation stream, because of the MA and EA productivities increase in this range.

Focus on productivities, methanol productivity is mainly constant which means that it is not affected by fed methanol while the others productivities decrease in linear way with higher scope EA and MA productivities. The last important fact is the productivity variation range which is narrow so the methanol has a moderate-low influence due to the fact that productivity changes between 1.22 and 0.96.

• The ethanol presence in this system causes a linear decrease of each productivity except on ethanol productivity which is benefited very little as compared to the decline of the others. The highest decrease is the MA which makes sense because Ma is consumed to produce ethanol in this reactor. However, the scopes are quite different which means that it is necessary a huge amount of reagents in order to produce low amount of ethanol. Still, as in the case of methanol the range of productivity variation is so small so it can say that ethanol has a very low influence on the reaction.

In the study of reactions, it was obtained Figure 34 in which the behaviour of each of the reactions and reaction equations shown, obtained by linear regression with acceptable R^2 .



Figure 34. K(T)-T Hydrogenation reaction system.

According to this figure, the kinetic equations of Reaction 2 and Reaction 8 were the Equation 1 and Equation 2, respectively.

Equation 1 $K_2(T) = -0,0059 \cdot T + 1,3762$

Equation 2 $K_8(T) = 0,0008 \cdot T + 0,4957$

Base on the equations and Figure 31, it can be said that Reaction 2 is more sensitive to temperature than Reaction 8. Therefore, if it is desired to maximise ethanol production it will be needed a good temperature control in order to benefit this reaction. The desired temperature will have to be low in order to avoid the Reaction 8. However, if the goal is to maximise the Ethyl acetate it should search a high temperature because of Reaction 2 is slower than Reaction 8 at high temperature which allows ethanol to react with methyl acetate.

B. Hydrogenation's simulation results analysis at laboratory

B.I. Experiment description

The aim to this experiment is testing simulation results at the laboratory (see Table 18) in order to verify if simulation represents the reality. Therefore, an inlet stream with a volume composition quite similar to the simulation inlet stream was introduced to Hydrogenation reactor at the same simulation conditions.

At the end of this experiment was gotten the outlet stream composition which is compared to simulation results.

	Hydrogenation	Hydrogenation Outlet (%molar)			
	Laboratory	Simulation	Laboratory	Simulation	
H ₂	38.35	38.40	37.62	40.20	
СО	39.09	39.10	39.26	37.90	
CO ₂	1.49	1.50 1.50		0.03	
CH ₄	5.58	5.40	5.40	5.30	
MeOH 0.60		0.60	0.60 1.10		
EtOH	0.01	0.01	0.12	0.80	
DME	12.17	12.20	12.20	11.90	
МА	2.69	2.70	2.25	1.30	
EA	0.008	0.01	0.11	0.40	
	H ₂ conversion (%)	2.1	6.3		
	MA conversion (%)	17.4	50.3		

Table 18. Hydrogenation experiment at laboratory Vs. Simulation

B.II. Conclusions

As I can be seen in Table 18, there are main differences between simulation and laboratory results. Due to this fact, it is recommended more experiments and simulation analysis in order to get a great Hydrogenation model.

C. Cash flow analysis cases

C.I. Maximum EtOH case

Year ending	Investment (I)	Production costs (PC) (2010)	Selling (S)	Devaluation (D)	Profit before tax (PBT)	Taxes (T)	Profit after tax (PAT)	Net cash flow (NCF)	updated NCF	Accumulate updated NCF
0	0							0	0,00	0,00
1	-1086,77272							-1.087	-987,98	-987,98
2		124,86	272,34	107,7	39,83	11,95	27,88	135,53	112,01	-875,97
3		124,86	272,34	107,7	39,83	11,95	27,88	135,53	101,83	-774,14
4		124,86	272,34	107,7	39,83	11,95	27,88	135,53	92,57	-681,57
5		124,86	272,34	107,7	39,83	11,95	27,88	135,53	84,15	-597,41
6		124,86	272,34	107,7	39,83	11,95	27,88	135,53	76,50	-520,91
7		124,86	272,34	107,7	39,83	11,95	27,88	135,53	69,55	-451,36
8		124,86	272,34	107,7	39,83	11,95	27,88	135,53	63,23	-388,14
9		124,86	272,34	107,7	39,83	11,95	27,88	135,53	57,48	-330,66
10		124,86	272,34	107,7	39,83	11,95	27,88	135,53	52,25	-278,40
11		124,86	272,34	107,7	39,83	11,95	27,88	135,53	47,50	-230,90
12		124,86	272,34	0,0	147,48	44,24	103,24	103,24	32,89	-198,01
13		124,86	272,34	0,0	147,48	44,24	103,24	103,24	29,90	-168,10
14		124,86	272,34	0,0	147,48	44,24	103,24	103,24	27,19	-140,92
15		124,86	272,34	0,0	147,48	44,24	103,24	103,24	24,71	-116,20
16		124,86	272,34	0,0	147,48	44,24	103,24	103,24	22,47	-93,74
17		124,86	272,34	0,0	147,48	44,24	103,24	103,24	20,42	-73,31
18		124,86	272,34	0,0	147,48	44,24	103,24	103,24	18,57	-54,74
19		124,86	272,34	0,0	147,48	44,24	103,24	103,24	16,88	-37,86
20	10,3	124,86	272,34	0,0	147,48	44,24	103,24	113,50	16,87	-20,99

Table 19. Maximum EtOH case cash flow analysis.

C.II. Maximum EtOH & MeOH production case

Year ending	Investment (I)	Production costs (PC) (2010)	Selling (S)	Devaluation (D)	Profit before tax (PBT)	Taxes (T)	Profit after tax (PAT)	Net cash flow (NCF)	updated NCF	Accumulate updated NCF
0	0							0	0,00	0,00
1	-1088,34667							-1.088	-989,41	-989,41
2		124,96	274,75	107,8	41,98	12,59	29,39	137,20	113,38	-876,02
3		124,96	274,75	107,8	41,98	12,59	29,39	137,20	103,08	-772,94
4		124,96	274,75	107,8	41,98	12,59	29,39	137,20	93,71	-679,24
5		124,96	274,75	107,8	41,98	12,59	29,39	137,20	85,19	-594,05
6		124,96	274,75	107,8	41,98	12,59	29,39	137,20	77,44	-516,61
7		124,96	274,75	107,8	41,98	12,59	29,39	137,20	70,40	-446,21
8		124,96	274,75	107,8	41,98	12,59	29,39	137,20	64,00	-382,20
9		124,96	274,75	107,8	41,98	12,59	29,39	137,20	58,18	-324,02
10		124,96	274,75	107,8	41,98	12,59	29,39	137,20	52,89	-271,12
11		124,96	274,75	107,8	41,98	12,59	29,39	137,20	48,09	-223,04
12		124,96	274,75	0,0	149,79	44,94	104,85	104,85	33,41	-189,63
13		124,96	274,75	0,0	149,79	44,94	104,85	104,85	30,37	-159,26
14		124,96	274,75	0,0	149,79	44,94	104,85	104,85	27,61	-131,64
15		124,96	274,75	0,0	149,79	44,94	104,85	104,85	25,10	-106,54
16		124,96	274,75	0,0	149,79	44,94	104,85	104,85	22,82	-83,72
17		124,96	274,75	0,0	149,79	44,94	104,85	104,85	20,74	-62,98
18		124,96	274,75	0,0	149,79	44,94	104,85	104,85	18,86	-44,12
19		124,96	274,75	0,0	149,79	44,94	104,85	104,85	17,14	-26,98
20	10,3	124,96	274,75	0,0	149,79	44,94	104,85	115,12	17,11	-9,86

Table 20. Maximum EtOH & MeOH production cash flow analysis.