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RENEW

Renewable fuels for advanced powertrains

Integrated Project

Sustainable energy systems

Subproject 4

"Optimization of second generation bioethanol production"

Final Scientific Report

Abengoa Bioenergía

Asociación de Investigación y Cooperación Industrial de Andalucía (AICIA)

1   Introduction

1.1 General approach

RENEW project aimed to develop, compare, (partially) demonstrate and train on a range of fuel production chains for motor vehicles. Ligno-cellulosic biomass sources have been used as feedstock to produce synthesis gas from which various vehicle fuels can be derived: Methanol/DME, ethanol (thermo chemical and enzymatic pathway) and a novel biomass-to-liquid (BTL) fuel

One of the six RENEW subprojects, "SP4: Optimisation of Bioethanol Production", is led by Abengoa Bioenergía and counts like main partner with the Asociación de Investigación y Cooperación Indiustrial de Andalucía (AICIA). This subproject has explored the ethanol production by two pathways: the enzymatic pathway (enzymatic hydrolysis of ligno-cellulosic biomass) and the thermo-chemical pathway (biomass gasification and catalytic conversion of the generated synthesis gas to ethanol) the project work plan included six work packages having individual research and technical objectives and deliverables.

In work package 4.1, an assessment of the biological pathway has been undertaken to integrate the information generated by current R&D projects being developed by Abengoa Bioenergía.

Work packages 4.2 to 4.5 were related to the thermo chemical pathway for biomass transformation into ethanol, analysing every stage of the complete process.

Work package 4.2 dealt with the catalytic conversion of syngas to ethanol, at lab scale, using different catalysts that were developed by Abengoa Bioenergía, externally to RENEW Project, with the collaboration of AICIA. With the most promising catalysts, conversion and selectivity have been related to feed composition and operating conditions, more over, the long term life of the catalyst was assessed. A model of the reaction process was carried out in order to include it in an overall process model, and being able to assess the complete transformation technology.

Work package 4.3 was devoted to biomass gasification focused on ethanol production. A bubbling fluidised bed and several gasification conditions were considered. AICIA's existing test rig was modified. A gasification empirical model was developed in order to be included in the models of the process.

Work package 4.4 was aimed to model the gas cleaning and gas conditioning stages, which are necessary to match the requirements of the catalytic synthesis process. It was also devoted to the design of the separation processes and distillation train to separate ethanol from the reactor products streams, composed by remaining reactants, light hydrocarbons and other alcohols oxygenated hydrocarbons.

Work package 4.5 aimed to identify the best process alternative to produce bioethanol using the term chemical pathway. It included the simulation and optimisation of the most promising alternatives for the entire process (i.e., it includes the integration of different subsystems through components recycle and some energy integration). Special attention was paid to by-product utilisation or recycle.

Work package 4.6 collected all the data required to perform detailed economic, environmental, reliability, safety and life-cycle assessments. These data were delivered to SP5, and then used to assess and compare the different biofuel production technologies covered in the integrated RENEW project as a total.

Workpackage 4.7 consisted on the scientific and technical organisation of the subproject, in order to ensure the correct flow of information between the WP within the subproject and the relationship between the coordination of the IP.

1.2 Main overall objectives

The main objectives of the "SP4: Optimisation of Bioethanol Production" were:

- To assess the enzyme pathway for producing ethanol from lignocelluloses bioresidue and energy crops.

- To assess a promising catalyst for the conversion of biomass-derived syngas to ethanol, and to model the catalyst reactor.

- To assess biomass steam gasification concept for ethanol synthesis, and to develop gasification models based on bibliography and on real experimental data.

- To develop models for the gas cleaning and gas conditioning stages, as well as for the separation train, and generate several promising process alternatives related to different ways of by-product utilisations.

- To identify the most promising process alternative to produce ethanol by means of the term chemical pathway, and to simulate the complete processes.

- To carry out an overall and objective assessment of both bioethanol production processes (biological and term chemical) taking into account socio-economic, environmental and technical aspects.

1.3 Description of team and responsibilities

Abengoa Bioenergía has co-ordinated the subproject between two partners, Abengoa Bioenergía and AICIA.

The subproject group has extensive experience and know-how related to R&D and large-scale projects in biomass gasification, bioethanol production, catalytic processes, gas cleaning and in bioethanol production and commercialisation. This subproject seeks the most promising ways to produce bioethanol from lignocellulose biomass and bioresidue to achieve significant improvements in the overall feasibility of large-scale production. Close communication among the partners during the project has ensured efficient use of all skills in the network and good progress in all work packages.

The progress of the work has been followed and monitored through progress meetings. Progress meetings has been arranged and led by the co-ordinator.

Responsible representatives of each partner have attended the meeting and presented their progress reports to other partners.

The co-ordinator has been also responsible for communication with the RENEW coordinator, and for facilitation of the contact with participants in other subprojects.

2 WP4.1. Enzymatic hydrolysis – Biological pathway

2.1 Scope and objectives

The enzymatic hydrolysis process is the only pathway among all the alternatives considered within RENEW project that is based in biological transformation steps, such as the enzymatic hydrolysis itself, and other like fermentation of sugars. The process is devoted to the production of bioethanol.

Main objectives set for the workpackage were:

- Analysis of the biological technologies for bioethanol production.

- Conceptual definition of the overall process of biomass to ethanol production.

- Generation of general information of the process, in order to be able to perform techno-economical assessments, in further work-packages, to have comparable data of both thermo chemical and biological pathways.

2.2 Methodology

Abengoa Bioenergía is global leader in technology development of biomass conversion into ethanol by means biological pathway. The information used in the workpackage comes from its previous experience, mainly from the projects:

- Pilot plant of bioethanol from lignocellulosic biomass, including enzymatic hydrolysis, biomass fractionation and fermentation of xylose (C5) and glucose (C6) sugars. The project is being carried out in York (NE – USA). The developed plant has a capacity of 0,076 millions litres of ethanol per year. Granted by DOE. The project is aimed to the development of the technologies in a preindustrial scale and their integration.

- Demonstration plant of bioethanol from lignocellulosic biomass, including enzymatic hydrolysis and glucose fermentation in Salamanca (Spain) The plant has a capacity of 5 millions litres of ethanol per year. The project is granted by the V Framework Program of the European Commission. The project is aimed to demonstrate the technologies of pre-treatment, enzymatic hydrolysis and fermentation, and the integration of such technologies.

Based on these two concepts, it has been proposed a process configuration, considering the boundary conditions and scenarios defined in subproject 5, and to have information comparable to other processes (BTL in general). The technology status assumed has been the expected for 2020, since was stated, therefore conversions of individual processes, efficiencies etc have been stated considering certain technology development from the current status. The size of the plant is equivalent to 500 MW_{th}, using wheat straw, since it is the biomass used in the BCyL project. The composition of the biomass was taken from analysis performed to straw in the area of the plant.

Several cases have been distinguished, in order to cover a wider range of possibilities.

- On the one hand, two scenarios were considered with regards to technology development, since some uncertainty exist when talking about technology development achieved in 2020, scenario 1 considers conservative situation, scenario 2 optimist situation, in which big technology improvement would be achieved.

- On the other hand, 4 possibilities have been distinguished with regards to energy integration. Case 1 considers that all thermal energy and power comes from outside the process, thermal energy from natural gas, power from the grid, this case means the maximum fuel production. Case 2 considers that all the thermal energy comes from fresh biomass, reducing the amount of biomass to be converted into ethanol. Power would still come from the grid. Case 3 considers that thermal energy comes from residues and lignin residues and by-product of the process, power from the grid. Case 4 considers that all energy comes from biomass + lignin + residues, either thermal or power; in this case, none energy is consumed from fossil resources.

These two criteria generate a matrix of eight cases, combining potential technology development and energy integration configurations; all of them have been calculated, and analysed in further work packages.

Using the information about the process, and technical details used in the development of the two mentioned projects (BCyL and York facilities), all the mass and energy balances were calculated, to track all the individual components from the biomass to the output stream, and also to be able to calculate utilities and energy consumption, production of fuel and by-products.

2.3 Description of the process

The process comprises five main blocks or sections, and an energy plant:

- Biomass pre-treatment: straw is cleaned and grinded before being introduced to the process. After that, thermo chemical pre-treatment take place, it consists in an initial impregnation with diluted sulphuric acid in water, and the injection of high pressure steam, in order to break the internal matrix of lignin and cellulose, and make it accessible to the enzymes in following stages. Due to the effect of the acid and high pressure steam hemicellulose is hydrolyzed, and xylose is formed, which is diluted in the water. The three fractions (xylose, cellulose and lignin) are separated in the biomass fractionation step). The xylose molecules, which are sugars, will be transformed into ethanol in the fermentation block.

- Biomass fractionation: the stream holds a liquid fraction (water + dissolved xylose) and a solid fraction (cellulose and lignin). By means washing the solids, the water and xylose are easily separated. In order to remove the lignin, ph, which is acid, is increased, adding a base, and lignin is dissolved. Then the cellulose is washed again, and the water carries the lignin fraction, which is separated by means precipitation.

- Enzymatic hydrolysis: the cellulose molecules are hydrolyzed by means the action of enzymes, which break the chains introducing water molecules and simple sugars, glucose, are formed. These sugars molecules will be transformed in ethanol in the fermentation block.

- Fermentation: either C5 (xylose) and C6 (glucose) sugars are transformed into ethanol by the action of micro-organisms, in a fermentation process. The case of glucose, commercial Yeats is used, in a very well known process. In the case of xylose, new micro-organisms, not industrially used are used. Both reactions are carried out in separate fermentation reactions. Ethanol and CO2 are produced in these processes.

- Product separation: since the fermentation reactions happen in aqueous media, the produced ethanol must be separated from the water, in order to use it in commercial combustion engines. The process used is distillation up to the azeotrope concentration, and molecular sieves afterwards, to achieve purities above 99,5 %.

- Energy plant: depending on the configuration, the energy plant can be more or less complex. In the case 1, the energy plant is just a natural gas boiler to generate steam. In case 2, the energy plant is a solid biomass boiler. In case 3 it is necessary a drier, to remove water from the liquid lignin and waste streams, and a boiler. In case 4, the energy plant consist in a biomass boiler, and a backpressure steam turbine, where power is produced. The low pressure steam is used in the process as well as distillation.

2.4 Main results obtained

After performing all the calculations to the different cases defined (4 energy integration concepts per 2 potential technology improvement scenarios), the matrix of results obtained is:

- For the case considering low potential improvement of technology:

	Scenario 1			
	Case 1	Case 2	Case 3	Case 4
Biomass input, t/d	2980			
Ethanol produced, t/d	515,74	659,19	407,05	519,63
Product efficiency, % (MW EtOH HHV/MW Biomass HHV)	38,87	30,69	38,87	32,73
Energy efficiency, % (MW Energy output/MW energy input)	46,74	45,77	39,85	19,48

- For the case considering high potential improvement of technology:

	Scenario 2			
	Case 1	Case 2	Case 3	Case 4
Biomass input, t/d	2980			
Ethanol produced, t/d	504,02	628,56	429,81	510,82
Product efficiency, % (MW EtOH HHV/MW Biomass HHV)	49,10	38,87	47,05	38,87
Energy efficiency, % (MW Energy output/MW energy input)	55,52	54,87	43,11	35,03

2.5 Conclusions

Analysing the figures, it can be understood that highest productivity would be achieved using extra energy, this is, case 1, product efficiency is linked to productivity, so case one is also the highest. Since energy yield considers lignin as a product, the case in which lignin is considered a product, yield higher energy efficiency. However, case 1 will have double penalization, lignin is a very low profit product, and using fossil energy and power has high negative impact from the environmental point of view.

The generated data is used in work packages 6 to make technical, economical and environmental analysis, using inputs and outputs, and therefore deeper conclusions can be raised. Since the hypotheses are the same than for the thermo chemical route, results are comparable as well.

3 WP4.2 Catalytic synthesis optimization

3.1 Scope and objectives

The main objective of this task was to assess a promising catalyst for the conversion of biomass-derived syngas to ethanol. In this task, AICIA designed and performed a complete set of catalyst lab tests to collaborate with Abengoa in the catalysts development. Furthermore, a second optimisation stage was started, in order to find the most appropriate set of conditions to carry out the synthesis reactions, and to have a clearer vision of the overall process and its real potential.

3.2 Description of facility

The lab-scale equipment consists of a high pressure and temperature tubular fixed-bed reactor system, and a gas chromatograph for on line analysis. Both are connected each other, so that the outlet flow from de reactor is the inlet flow of the chromatograph. Feed gases are composed of CO, H2, CO2, CH4 and N2, and passed through mass flow controllers (MFC).

3.3 Resume of the methodology

Catalysts are prepared by co-impregnating supports with an aqueous solution of nitrates or chlorides of the active metal. The final catalyst is characterized by chemical analysis, X-ray diffraction, thermogravimetric analysis and quimisorption with H2 and CO. The catalysts are homogenized with particle sizes between 425 and 500 μm.

The reduction is carried out with hydrogen and at atmospheric pressure. After bypass analyses have been done, the reaction starts. Minimum of 5 analyses were done for each process conditions during Catalyst Development stage. For the latest Catalyst Optimization stage, long-term experiments with more than 100 analyses were done.

3.4 Main results obtained

All the catalysts are formed by a metallic active phase, which is composed of one or several metals, and other metals, performing as promoters and alkalis. This active phase is over a support, which have strong influence on the active phase. Therefore, a range of supports have been combined with active phases and promoters, and afterwards tested, in order to find the effects on the catalysts. Besides, other metals were used like promoters, enhancing the activity of the catalysts systems.

All the work performed in this research task was divided in four different stages. Initially, every different single metallic phase was tested, in order to study and understand its particular catalytic properties. All these phases were combined with the different supports selected, so its effects can also be tested. The second stage was focused on the combination of two previously tested metals, in order to increase efficiency of the reaction. For the third stage, a number of promoters were introduced in the previously tested catalyst to redirect the reactions and optimise the ethanol production. Finally, for the fourth stage different experiments conditions were tested in order to optimize the operations conditions of the catalyst developed. Long-term experiments were done during this last stage.

In the first experimental stage, fifteen catalysts were manufacture and tested. As was expectable, monometallic catalysts do not show brilliant overall performances. The catalysts had high CO conversion (up to 27%), but poor selectivity to ethanol, or vice versa, they has high selectivity (up to 25%), but reduced conversion.

In the second experimental stage, nineteen catalysts were synthesized. B1 catalyst showed the highest CO conversion, reaching values over 60%, but its selectivity to ethanol were less than 2%. Catalyst B13 showed selectivity over 70%. The catalyst with the highest productivity to ethanol was B19, whose CO conversion to ethanol is over 15% and its selectivity to ethanol over 10%.

Several active phases' metals were chosen, in the third experimental stage, to generate different multi-metallic catalysts with an appropriate mix of metals and a good selection of support and promoter. After several modifications were obtained CO conversions higher than 28%, selectivity to ethanol higher than 21% and ethanol productivity higher than 185 g/kgh using C3 catalyst

In the last stage, the most promising catalyst (C3) was tested on different operation setting to determinate the best work's condition to optimise the synthesis reaction. These tests including the optimization of the catalyst preparation and its composition, the optimization of the operation conditions, the study of the catalyst deactivation processes, the accomplishment of long-term tests, and finally, the study of the influence of other compounds, in addition to CO and H2, in the reactor feeding.

The CO conversion increases progressively with the temperature until reaching levels around 20% at 340ºC. The selectivity to alcohols increases until reaching maximum values next to 20% at 320ºC. The productivity to ethanol increases gradually, reaching values higher than 130 g/Kgh. The pressure modification from 30 to 50 bar produces a small increase of conversion and selectivity towards interest products.

It was observed a remarkable diminution of the catalytic activity when is omitted the previous calcination stage (C3-sc). The catalyst promoted and calcined (C3-c) showed a higher selectivity to ethanol, especially at temperatures around 320ºC. This catalyst presented a sufficient conversion in addition to a high selectivity to ethanol. Thus, productivities of 135 g/Kgh of ethanol were obtained in tests at 30 bar.

The catalysts prepared with two co-impregnations (C3-n1) or by an only co-impregnation of the support with the precursory salts (C3-n2) had similar CO conversion working at 30 bar. C3-n2 catalyst showed more activity when increasing the pressure. Operating at 50 bar and 340ºC, with C3-n2 catalyst was reached a productivity of 213 g/kgh, while with the reference catalyst (C3) was reached 185 g/kgh of ethanol. Increase the temperature up to 360ºC showed an improvement of its productivity to ethanol (C3-n2) up to 262 g/kgh

It was observed as the catalyst reduced at 300ºC (C3-n2-300) had more conversion that the catalyst reduced at 400ºC (C3-n2-400) in all rank of temperatures and pressures tested. The C3-n2-300 catalyst presented selectivity to ethanol of 22.7%, whereas the C3-n2-400 catalyst showed selectivity to ethanol clearly lesser (14,4%). It was possible to obtain a high productivity to ethanol (superior to 250 g/kgh), working at 50 bar and 340ºC when the catalyst was reduced at 300ºC.

Increasing the amount of alkaline promoter affects the activity of the catalyst negatively, with a considerable reduction of the conversion in all studied tests conditions. The productivity diminished linearly when increasing the content in alkaline promoter (from 0.075% up to 0,30%), falling down from 251 up to 28 g/kgh.

The most active catalyst was the three-phase with minor content in the third active phase (γ). Selectivity followed a tendency different, with a significant rise (values next to 30%) when increasing the content in γ. With low promoter content (0,075%), the three-phase catalyst was more active whichever minor was the content in γ. When increasing the proportion of alkaline promoter (0,15%), the activity was higher, at 360ºC, when the catalyst with higher content in γ was used. Productivity to ethanol, up to 250 g/kgh, was obtained using the catalysts with minor third active phase.

Different systems for filtering the gas streams coming from high-pressure stainless steel cylinders were use in order to minimize the formation of iron carbonyl by contact of CO with iron-containing surfaces. Several types of activated carbon, a commercial filter and a molecular sieve trap were employed as filtering element. The pre-treated activated charcoal clearly presents the best behaviour about catalyst stability. It was possible to operate 150 hours with an average conversion of 4.7% and selectivity to ethanol of 17,8%.

The last tests made within RENEW project were included to study the effect of introduce another gas (in addition to H2 and CO) in the inlet stream to the reactor. To introduce CH4 in the inlet stream to the reactor improved, in all studied cases (2.5; 7.5 and 12,5%), the CO conversion and the selectivity to ethanol. The CH4 formation is more difficult, and

thus, the formation of other final products is favoured. The conversion diminished clearly with the content in CH4. The CO2 presence in the inlet stream (2.5; 7.5 and 12,5%), reduced the CO conversion drastically. The CO2 reacts preferably to CO, reaching 15% of CO2 conversion. The selectivity to ethanol showed similar values, below 15%, whereas the productivity to ethanol presented a bell form, with a maximum value when it was introduced 7,5% of CO2 in the inlet stream. Nevertheless, the best result, as regards productivity to ethanol, was obtained introducing both gases, at 2,5%, in the inlet stream to the reactor.

3.5 Conclusions

After studying all the results of the work carried out during the RENEW project, several conclusions come out:

- Parameters for assessing the performance of catalysts, especially ethanol productivity, have increased sharply after introducing a third catalytic phase in the systems, rising above 185 g/Kgh.

- The preparation of the catalyst has a very big effect on the performance in reaction conditions. The method of preparation of the catalyst has been optimised, in order to increase selectivity, especially reducing the selectivity to hydrocarbons

- The catalyst promoted and calcined shows a higher selectivity to ethanol, especially at temperatures around 320º. Also, it is observed a remarkable diminution of the catalytic activity when is omitted the previous calcination stage.

- The catalyst prepared with the same precursory salts but different synthesis method, shows that a change in the preparation methodology can affect the catalytic properties. Then, it is possible to conclude that the best preparation method is the one used in the synthesis of C3-n2 catalyst (an only co-impregnation of the support with the precursory salts).

- It was verified that an identical chemical composition of catalyst cannot solely guarantee its catalytic properties. The precursory salt that is used (carbonate or nitrate) can lead to a different superficial structure, that influences in the catalyst activity and selectivity.

- Using the synthesis method employed in the preparation of the C3-n2 catalyst, and changing carbonate by nitrate like precursory salt for the addition of the alkaline promoter, it is possible to reach a productivity of ethanol of 262 g/Kgh, operating at 50 bar and 360ºC.

- The more suitable reduction temperature is 300ºC. In this case, it was possible to obtain a high productivity to ethanol (superior to 250 g/kgh), working at 50 bar and 340ºC.

- To increase the content in alkaline promoter (from 0.075% to 0.15% and 0.30%) has a negative influence, producing a global reduction of the productivity to ethanol.

- To increase the content in the third active phase (γ) increases the selectivity to ethanol, but do not show better results in productivity, independently of the content in alkaline promoter. Together with the increase in alkaline promoter gives as result an increase of the catalytic activity operating at 50 bar and 360ºC.

- The pre-treated activated charcoal clearly presents the best behaviour about catalyst stability. It was possible to operate 150 hours with an average conversion of 4.7% and selectivity to ethanol of 17,8%.

- To introduce CH4 in the inlet stream to the reactor improved, in all studied cases (2.5; 7.5 and 12,5%), the CO conversion and the selectivity to ethanol, but the CO conversion diminished clearly with the content in CH4 in the range tested.

- The CO2 presence in the inlet stream (2.5; 7.5 and 12,5%), reduced the CO conversion drastically, because CO2 reacts preferably, reaching 15% of CO2 conversion. While the selectivity to ethanol showed similar values.

- The best result, as regards productivity to ethanol, was obtained introducing both gases, at 2,5%, in the inlet stream to the reactor.

- A promising pathway has been identified, in order to continue the research, until reaching an industrial catalyst that enable the production pathway from biomass to ethanol. This will not be done under RENEW program.

4   WP4.3 Gasification pilot tests

4.1 Scope and Objectives

Auto-thermal biomass gasification with steam/oxygen mixture is one of the available options for   thermo-chemical BTL process. To gain knowledge about this gasification mode (operating conditions, gas composition, efficiency, tar content, etc.) several tests have been performed in a pilot plant owned by AICIA at the Seville Engineering School.

This report describes briefly performed modifications of the original gasifier designed for air gasification tests and shows main results of the set of gasification tests.

4.2 Facility description and modifications

The gasification pilot plant at the Chemical and Environmental Engineering Department of AICIA was built in 2000. Since then, several studies about the gasification performance of different biomasses and blends have been carried out.

The BFB gasifier consists of a refractory stainless steel reactor AISI 310 (150 mm ID), fitted with a distributor plate drilled with 32 holes (2.5 mm diameter) in a square arrangement with 19 mm triangular pitch. In the centre of this distributor exists a bigger hole (38 mm diameter) fitted with a tube designed for the bed-ash removal. The gasifier has a total height of 4.2 m and two sections, the bed zone of 150 mm ID and the freeboard of 250 mm ID. The system is provided with a 27 kW electrical furnace which covers completely both the reactor and freeboard. The furnace enables to operate free of heat losses thus achieving strictly auto-thermal operation.

Main retrofitting of the original air-gasification plant consists of:

- Installation of a 44 kg/h electrical steam generator.

- Installation of a 27 kW electrical furnace.

- Cyclones thermal insulation.

- Tar and particle measurement. system according to European standards

- Installation of a new ash removal system.

- Post-combustion chamber.

4.3 Experimental programme and results

32 successfully-operated long tests were made with wood pellets and "ofita" as fuel and inert material, respectively. The biomass flow rate fed to the gasifier ranged between 10 and 19 kg/h and the flow rate of gasification agent between 17 and 28 kg/h. The tests were carefully designed to assess the behaviour of the system under different gasification agent composition, including mixtures of air (with/without oxygen enrichment) and steam at different proportions. The

operation was strictly auto-thermal, which was achieved by setting the gasifier wall temperature set point slightly lower than the bed temperature.

Considerable retrofitting works were necessary for conduction of the steam and enriched oxygen tests. It was necessary the erection of an oxygen supply plant and a small boiler, as well as their corresponding control systems to fed the new gasification mixtures to the original air-blown gasification plant. Enlargement of the data acquisition system was also necessary and other minor modifications for appropriate system control under the new conditions. Details on the plant, test procedure, sampling methods and other technical details have already been described elsewhere (D4.3.1).

The gasification tests with air were performed with ER ranging from 0.23 to 0.43. As expected increasing the ER decreases the concentration of the CO, H2 and increase CO2 concentration. As a result LHV decreases with ER. The gas yield also increased with ER indicating enhancement of secondary reactions such as cracking and reforming of tar. Gasification efficiency was found to be optimal in the middle of the ER range analysed. Table 5.1 provides the main results under the range operated.

The use of steam showed, in the range of steam to biomass (SB) ratios tested, that hydrogen increases whereas carbon monoxide slightly decreases. We observed that steam improves the H2/CO ratio and the yield (H2+CO) for all tests. Despite not observed in our trials, a threshold of SB is probably reached at higher SB, since the drop in temperature cannot be longer compensated by the enhancement of steam gasification reactions due to higher presence of the oxidant. This was clearly indicated by a reduction of steam conversion observed at high SB (0.6), especially within the lower ranged of ER (0.15-0.22) , where temperature ranged between 750 and 790 ºC. In general by comparing the results with the tests carried out using air the H2 and CO2 content in the off-gas increases significantly and the CO content decreases as the steam to biomass ratio (SB) increases. This was reasonable explained by the gas–shift reaction for the high temperature tests (>800ºC). In the same way, the H2 and CO content decreases with ER, mainly due to the well-known dilution effect of nitrogen. The simultaneous analysis of both parameters was already reported in previous report (D.4.3.2). Table 5.1 summarises the principal ratios and results of interest in this project.

Air-enriched tests were made by adjusting the oxygen content of the stream to 30, 35 and 40% v. After heating and mixing with the adjusted steam flow rate, the overall stream was further heated to the desired process temperature (around 400ºC) before feeding the gasifier. For these tests two values of SB were set: 0.3 and 0.6, for the assessment of two levels of steam flow-rate. The range of ER analysed was 0.15-0.40. To achieve proper analysis and explore the simultaneous effect of ER, SB and oxygen enrichment, an experimental matrix of 16 tests was designed. Long-test trials were successfully conducted, some of them twice to check the reproducibility. A summary of the results is presented in Table 5.1.

Increasing the oxygen enrichment in the blown lead to reduce the dilution effect of the nitrogen and thus, to increase the bed temperature for the same ER and SB. This results in the enhancement of char reduction reactions as well as secondary tar reaction (cracking and steam reforming) and higher steam conversion. As a consequence tar and char yield decreased substantially and accordingly significant improvement of carbon conversion and gasification efficiency was observed. Gasification hot efficiencies up to 95% were computed, reaching this maximum the trials operated with 35% of oxygen enrichment, at the higher ER tested. In this optimum zone, SB (within the ranged 0.3-0.6) has no major effect on the process efficiency. The nitrogen-free gas composition showed CO and H2 values up to 38%, methane content around 9% and LHV close to 14 MJ/Nm3.

Table 5.1 Summary of main parameters from gasification tests at pilot scale conducted by AICIA

Parameter	Air	Air + Steam	Enriched air+Steam
LHV (MJ/Nm^3 gas)	3.5 – 6.0	4.3 – 5.5	9-14(nf)
Gasifier Cold Efficiency (%)			60-80
mol (CO+H2)/kg biomass (daf) ratio	19.6 – 22.3	15.0 – 26.0	23-30
H2/CO ratio (v/v)	0.58 – 0.95	0.97 – 1.56	0.7-1.5
%H$_2$ (v/v)	6.5 – 14.0	10.9 – 16.2	21-37 (nf)
%CO (v/v)	10.5 – 16.0	9.2 – 14.5	21-37 (nf)

nf: nitrogen free

Further analysis of the enriched oxygen-steam tests was accomplished for the assessment of hypothetical operation without nitrogen dilution, i.e. nearly pure-oxygen tests. In our test we used proportion of nitrogen in the gasification agent ranging from 76 %w. (air) to 32 (test with 40%v enriched O2 and steam) so that for tentative extrapolation of the nitrogen-free case, proper data processing and calculation was required besides some reasonable assumptions. Estimation of a hypothetical bed temperature that would be reached if no nitrogen was fed to the gasifier (pure oxygen-steam mixtures) was estimated by heat balances. The expected shifting of gas composition in this case was estimated with the help of additional experimental studies carried out in parallel in our laboratory: additional devolatilisation (nitrogen-blown and nitrogen with oxygen-carbon dioxide) tests were carried out in a 5 kWth bubbling FB with 26 mm ID. Gas composition, char and tar yield were correlated under different operating conditions. Additionally, a simplified pellet and reactor model were developed based on the experiments to estimate the behaviour of the system under conditions were some experimental data were needed. This was helpful to close heat and mass balance over the system and allowed reconciliation of data properly. A tar content in the off gases lower than 3 g/Nm3 was estimated. The temperature reached in this tested ranged 850-900 ºC under optimum operating conditions. LHV up to 15 MJ/Nm3 dry gas was computed reaching the H2/CO under this optimum values near unity. These results allowed concluding positively on oxygen-steam FB gasification of biomass as a competitive option against more complex indirect-dual gasification schemes based on dual or twin FBs.

4.4 Conclusions

The results provided by our gasification trials may be quite useful to help in the optimum adjustment of the gasification process in an integrated biomass-to-liquid process. Composition of the gas from the gasifiers should be established in conjunction with the gas treatment unit situated downstream the gasification processes. To set the proper operational ratios in the gasifier, the link between operational variables and gas composition needs to be precisely known as well as the physical-chemistry behind in the gasification reactor. This has been successfully done in these test trials, which have provided additional technical information useful for up-scaling and final design of the process. This information has been the basis of an empirical model, also developed within the framework of this project.

5   WP4.4 Design of syngas cleaning and conditioning and product separation

5.1 Scope and objectives

The thermo chemical pathway for production of ethanol basically consists on the synthesis gas generation by biomass gasification and subsequent catalytic conversion into an alcohol mixture. The syngas produced by the biomass

gasification process contains different kinds of contaminants. These contaminants must be removed from the syngas to prevent erosion, corrosion, catalyst poisoning and environmental problems in the ethanol synthesis plant. Besides, the syngas composition must be adjusted to satisfy requirements of the catalyst such as H2/CO mole ratio and maximum allowable CO2 composition. In the reactor, syngas is converted to alcohols, water, CO2 and light hydrocarbons. Separation of alcohols from syngas is carried out downstream of the reactor and recirculation of unconverted syngas is usually considered. In the recirculation it's advantageous to reform light hydrocarbons to CO and H2 in order to increase the overall biomass-to-fuel conversion in the plant and also to avoid its build-up in the synthesis loop. Design of syngas cleaning and conditioning and product separation has been carried out.

5.2 Summary of deliverable, description of the different alternatives

Gas cleaning, gas conditioning, gas-product separation and subsequent product purification stages were studied.

With regard to gas cleaning, the wet and hot gas cleaning routes were analyzed in detailed. Conventional 'wet' low-temperature syngas cleaning is the preferred technology in the short term. This technology requires additional wastewater treatment but there is little uncertainty at present about the cleaning effectiveness of such systems. Firstly, tars are destroyed in a tar cracking downstream of the gasifier. Particulates are sequentially removed in cyclones, bag filers and wet scrubbers. Alkalis and the bulk of chlorine, sulphuric and nitrogenous compounds are also removed in the wet scrubbers.

Hot gas cleaning route is not particularly advantageous for ethanol synthesis since syngas must be cooled anyway because of the relatively low temperature of the catalytic reactor (~300 ºC). Besides, some hot gas cleaning processes are not commercially proven, e.g., high temperature removal of nitrogen compounds, halides, alkali metals and heavy metals although intensive research is carried out.

Concerning syngas conditioning different processes were studied:

- Steam reforming to convert light hydrocarbons to CO and H2

- Shift conversion to adjust the H2/CO ratio

- CO2 removal. Physical (Rectisol) and chemical absorption (DEA)

5.3 Modelling of the specific processes carried out

Rigorous and simple modelling of each process was carried out and simulation models in Aspen Plus were developed. The simple models were used in the simulation of the whole ethanol synthesis plant, estimating stream flow rates and compositions, but published data was also required to estimate capital and operating costs, utilities, etc. The purpose of the rigorous models was to perform a preliminary design of each process to obtain, if possible, better estimates of capital and operating costs and utility consumption than those found in the literature.

Lastly, the separation stages were considered. The outlet stream from the synthesis reactor is comprised of unconverted syngas (mainly CO, H2) and reaction products, namely, methanol, ethanol, higher alcohols, water and CO2, CH4. Because there is a high difference in relative volatilities between light gases and alcohols, a flash drum is considered as the first step in the separation process, obtaining light gases as gas and alcohols and water as liquid. Gas is recycled to the reactor and alcohols are sent to a distillation train to be separated and purified. However, phase equilibrium modelling in the flash drum is not an easy task because the multicomponent mixture is comprised of polar, non-polar

and supercritical components. A thermodynamic method was validated in Aspen Plus for representing the phase equilibrium in the flash drum. Good agreement between experimental data and the thermodynamic method was found. This thermodynamic method is also valid for modelling the separation of alcohols and water in the distillation train.

6 WP5. Process modelling

6.1 Scope and objectives

The objective of this workpackage is the identification of the most promising thermo chemical pathway to produce ethanol. To cover this issue, different conceptual designs are presented and compared in terms of energy efficiency indicators by means of simulations. Modelling of each conceptual design is also briefly presented. Nevertheless, a technical, economic and environmental assessment is needed to identify the real best alternative for BTL plants, which cannot be selected only based on energy efficiency indicators. This overall assessment is presented in summary of Workpackage 4.6. Besides, the results of the simulations revealed that the conceptual designs could be improved and new conceptual designs are presented in the last section of this summary.

6.2 Description of concepts and technologies selected

Different conceptual designs for the synthesis of bioethanol from biomass gasification were presented.

The thermo chemical pathway basically consists on the production of synthesis gas by means of biomass gasification and the subsequent catalytic conversion into an alcohol mixture.

Firstly, biomass is pre-treated. Biomass pre-treatment is totally subject to the gasification technology adopted. After pre-treatment, biomass enters the gasifier. Two different gasifier technologies have been considered. One of them is the indirect heated circulating fluidized bed (CFB). The CFB gasifier pressure is 2 bar. Therefore, produced syngas must be compressed to the synthesis reactor pressure. In this case Tar Reforming must occur prior to cooling the syngas to prevent tar condensation and deposition on downstream equipment.

The second gasification technology is entrained flow gasifier which is characterized by fuel particles dragged along with the gas stream. This means short residence time, higher temperature (which avoids tar formation and thus the need for tar reforming downstream) and small fuel particles. Furthermore, entrained flow gasifier is operated under pressure and with pure oxygen.

The cleanup and conditioning section are dictated by the requirements of the synthesis catalyst. Requirements include tars and light hydrocarbons reforming to additional CO and H2 (in case of CFB gasification technology), gas cooling, impurities removal by water scrubbing, SH2 removal, H2/CO mole ratio tuning by WGSR, CO2 removal and syngas compression. In case of CFB gasification technology and prior to the synthesis reactor, the syngas must be compressed to the operating pressure. A multi-staged compressor with intercoolers is used.

Next, the syngas is converted to alcohols in a catalytic reactor, with alkali doped sulphur molybdenum catalyst, operating at 300 ºC. After the reactor, the effluent is cooled to 43°C by means heat exchangers, while maintaining high pressure. A knock-out drum is then used to separate the liquids (primarily alcohols) from the off gas, which is composed of unconverted syngas, CO2, and methane. From here, the liquid crude alcohols are sent to product purification. The residual gas stream is recycled back to the WGSR. In Self Sufficient cases, combined ethanol and electricity production take place. Part of the off-syngas is purged to a combined cycle for electricity production and the

remaining is recycled. In Maximum Production cases, maximum ethanol production takes place, instead of combined ethanol and electricity production. In this case, methane is sent to a SMR and the reformed syngas is recycled to the WGSR.

Besides, in Self Sufficient cases, part of the residual syngas from the synthesis reactor is purged to a combined cycle for electricity production in a power plant.

Four cases were considered, which were combinations of the aforementioned processes, i.e.:

- Circulating Fluidized Bed Self Sufficient (CFB_SS).

- Circulating Fluidized Bed Maximum Production (CFB_MP).

- Entrained Flow Self Sufficient (EF_SS).

- Entrained Flow Maximum Production (EF_MP).

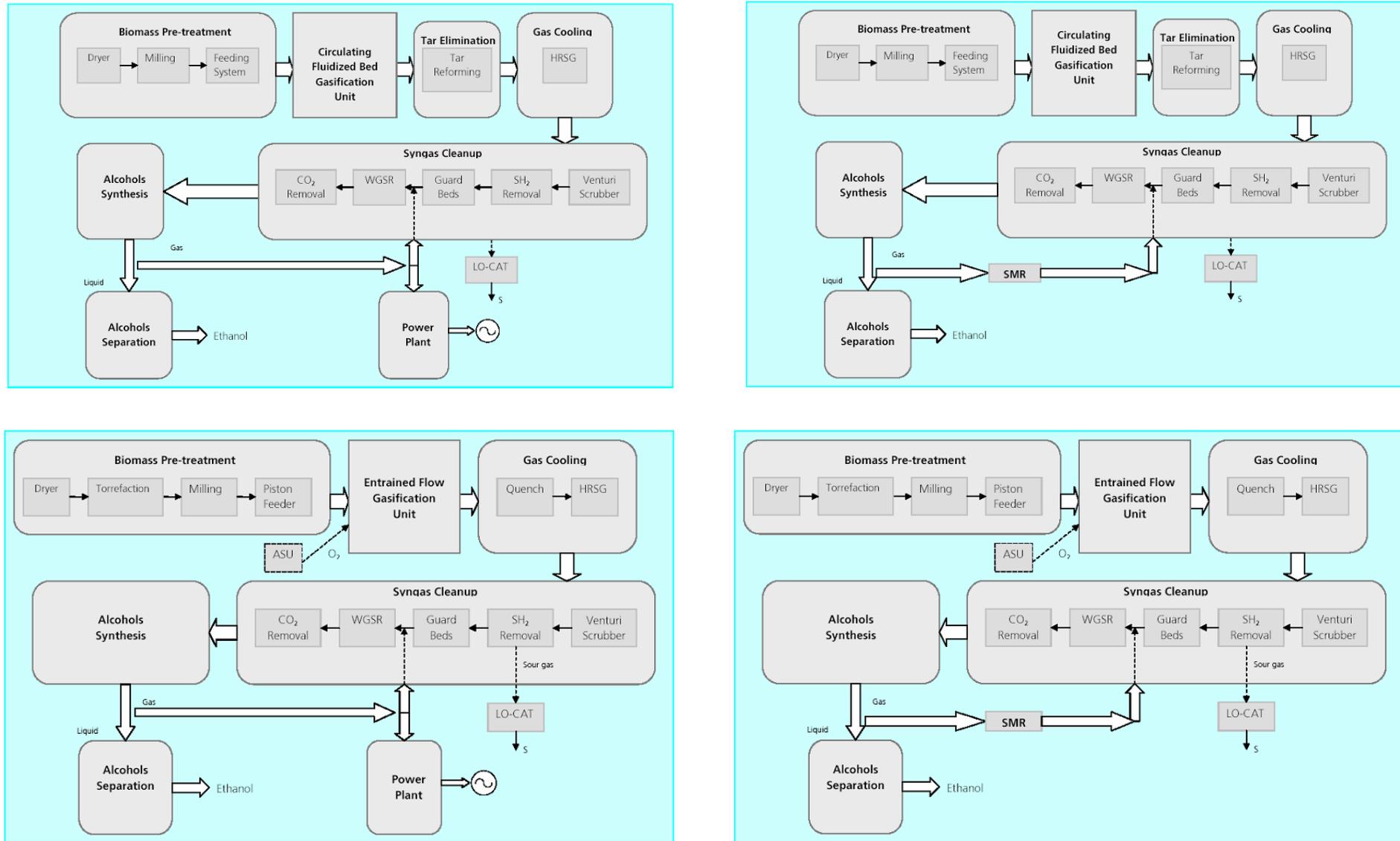A diagram of each process is presented in Figure 7.1.

Figure 7.1 Up-left: CFB self-sufficient concept; Up-right: CFB maximum production concept; Down-left: EF self-sufficient concept; Down-right: EF maximum production concept.

6.3 Description of synthesis plants models

A summary of the main unit modelling assumptions for each gasification based concept is presented.

Table 7.1 Main unit modelling assumptions for entrained flow gasification based concepts.

General	
Compressors	Polytrophic efficiency= ASME Method, Driver efficiency=1. Intercooler (if necessary): Pressure drop= 0.5 bar, Outlet gas temperature= 50 ºC
Pumps	.Pump efficiency = 0,9; Driver efficiency =0,99
Gasification	
Entrained flow Gasifier	RGibbs Block (Chemical Equilibrium). P=75 bar, T=1300 ºC, Steam/oxygen mass ratio=0.1.
Gas cooling	
Water Quench	Flash block.T=900 ºC, Pressure drop= 0, Adiabatic. Mass flow rate of liquid water is calculated for cooling the syngas from 1300 ºC to 900 ºC. HeatX block.Inlet syngas temperature= 900 ºC.
HRSG	Outlet syngas temperature= 60 ºC. Minimum temperature approach= 25 ºC. Boiler feed water conditions= 25 ºC, 59 bar. Mass flow rate of boiler feed water is calculated for obtaining superheated steam at 59 bar, 482 ºC.
Gas cleaning	
Quench Scrubber	Flash block. 1 m^3 water per 1000 m^3 gas. T=60 bar, Pressure drop=0.78 bar.
Selexol System	Separation block. Temperature= 27 ºC. Pressure drop= 0.5 bar. H_2S removal efficiency=0.9999, CO_2 removal efficiency= 0.98. Power consumption taken from literature.
ZnO Guard bed	Separation block. Temperature=375 ºC. Pressure drop=0.5 bar. H_2S removal=0.91.
Gas conditioning	
Steam Methane Reformer	RGibbs Block (Chemical Equilibrium). P=17 bar, T=850 ºC. Temperature approach= -10 ºC.
High Temperature Water Gas Shift Reactor	RGibbs Block (Chemical Equilibrium). T=364 ºC. Pressure drop=0.5 bar. Only water gas shift reaction is considered.
Reactor	Ryield block. T= 300 ºC. Pressure drop= 8bar. Mass yields are calculated from conversions taken from patents. Heat of reaction is used to generate superheated steam.
Products Separation	
Gas-liquid separator	Two outlet flash drum. T=43 ºC. Pressure drop=0.5 bar.
Distillation columns	Rigorous distillations models. Number of trays and reflux are estimated from shortcut calculations.
Molecular sieves	Separation block. H_2O removal efficiency=0.9999. Temperature= 150 ºC. Pressure= 5 bar.
Power Generation	
Gas Turbine	Compressor 3-stages compressor with intercooling. Stage polytrophic efficiency= ASME Method; Driver efficiency=1. Pressure ratio for each stage=3.1. Intercooler: temperature=50 ºC, pressure drop=0 bar. Combustor RGibss reactor (Chemical equilibrium). Pressure drop= 0 bar. Air flow

	rate fed to combustion chamber is manipulated in order to get a flue gas temperature of 550 ºC after turbine expander.
	Expander
	Turbine model; Discharge pressure= 1,2 bar; Isentropic efficiency = 0,9; Mechanical efficiency =0,98.
Steam cycle	HRSG
	HeatX block. Outlet flue gas temperature= 100 ºC. Pressure drop= 1.1 bar. Minimum temperature approach= 25 ºC. Boiler feed water: P=59 bar, 25 ºC is turned to superheated steam 59 bar 482 ºC.
	Steam turbines
	Discharge pressures: 0.04 bar, Isentropic efficiency = 0,9; Mechanical efficiency =0,98.

Table 7.2 Main unit modelling assumptions for BCL gasification based concepts.

General	
Compressors	Polytrophic efficiency= ASME Method, Driver efficiency=1. Intercooler (if necessary): Pressure drop= 0.5 bar, Outlet gas temperature= 50 ºC.
Pumps	Pump efficiency = 0,9; Driver efficiency =0,99
Gasification	
BCL gasifier	Gasification bed Ryield block. A calculator determines mass yields from experimental correlations and corrects them by atom balances. Pressure=1.5 bar. Temperature: Determined by energy balance between char combustor and gasification bed. Char combustor RGibbs block. Char is burnt with air to get a temperature of 1000 ºC. Pressure= 1.5 bar.
Gas cooling	
HRSG	Outlet syngas temperature= 60 ºC. Minimum temperature approach= 25 ºC. Boiler feed water conditions= 25 ºC, 59 bar. Mass flow rate of boiler feed water is calculated for obtaining superheated steam at 59 bar, 482 ºC.
Gas cleaning	
Tar reformer	Rstoic block. Temperature=870 ºC. Pressure drop=0.27 bar. The following reactions are taken into account: $CH_4+H_2O \rightarrow CO+3H_2$ CH4 conversion=0.8 $C_2H_6+2H_2O \rightarrow 2CO+5H_2$ C2H6 conversion=0.99 $C_2H_4+2H_2O \rightarrow 2CO+4H_2$ C2H4 conversion=0.9 $C_6H_6+6H_2O \rightarrow 6CO+9H_2$ C6H6 conversion=0.99 $2NH_3 \rightarrow N_2+3H_2$ NH3 conversion=0.9 $C_{10}H_8+10H_2O \rightarrow 10CO+14H_2$ C10H8 conv=0.999
Quench Scrubber	Flash block. 1 m^3 water per 1000 m^3 gas. T=60 bar, Pressure drop=0.78 bar.
Selexol System	Separation block. Temperature= 27 ºC. Pressure drop= 0.5 bar. H_2S removal efficiency=0.9999, CO_2 removal efficiency= 0.98. Power consumption taken from literature.
ZnO Guard bed	Separation block. Temperature=375 ºC. Pressure drop=0.5 bar. H_2S removal=0.91.
Gas conditioning	
Steam Methane Reformer	RGibbs Block (Chemical Equilibrium). P=17 bar, T=850 ºC. Temperature approach= -10 ºC.
High Temperature Water Gas Shift Reactor	RGibbs Block (Chemical Equilibrium). T=364 ºC. Pressure drop=0.5 bar. Only water gas shift reaction is considered.
Reactor	Ryield block. T= 300 ºC. Pressure drop= 8bar. Mass yields are calculated from conversions taken from patents. Heat of reaction is used to generate superheated steam.
Products Separation	
Gas-liquid separator	Two outlet flash drum. T=43 ºC. Pressure drop=0.5 bar.
Distillation columns	Rigurous distillations models. Number os trays and reflux are estimated from shortcut calculations.
Molecular sieves	Separation block. H_2O removal efficiency=0.9999. Temperature= 150

	ºC. Pressure= 5 bar.
Power Generation	
Gas Turbine	Compressor
	3-stages compressor with intercooling. Stage polytropic efficiency= ASME Method; Driver efficiency=1. Pressure ratio for each stage=3.1. Intercooler: temperature=50 ºC, pressure drop=0 bar.
	Combustor
	RGibss reactor (Chemical equilibrium). Pressure drop= 0 bar. Air flow rate fed to combustion chamber is manipulated in order to get a flue gas temperature of 550 ºC after turbine expander.
	Expander
	Turbine model; Discharge pressure= 1,2 bar; Isentropic efficiency = 0,9; Mechanical efficiency =0,98.
Steam cycle	HRSG
	HeatX block. Outlet flue gas temperature= 100 ºC. Pressure drop= 1.1 bar. Minimum temperature approach= 25 ºC. Boiler feed water: P=59 bar, 25 ºC is turned to superheated steam 59 bar 482 ºC.
	Steam turbines
	Discharge pressures: 0.04 bar, Isentropic efficiency = 0,9; Mechanical efficiency =0,98.

6.4 Main results and conclusions

In this section they are briefly shown. The reader is reminded that these results are based on the simulation of the first conceptual designs, and it is expected that the new conceptual designs described above will yield better results.

In this case, only energy efficiency indicators were taken into account when comparing different conceptual designs of the synthesis plant. Regarding liquid fuel production, the entrained flow gasification concept yields the highest biomass to liquid conversion rate for both scenarios (self sufficient and maximum fuel production), and several points higher with respect to the circulating fluidized bed concept.

The entrained flow gasification concept also shows a good trade-off between conversion rate and energy efficiency for both scenarios, so it can be considered as the first candidate for the best alternative. Nevertheless, a technical, economic and environmental assessment is needed to identify the real best alternative for BTL plants. This will be presented in Workpackage 4.6.

6.5 New conceptual designs

The results of the simulations revealed us that the conceptual designs could be improved and new conceptual designs have been developed. The new conceptual designs are presented in this section.

The self-sufficient scenario is the only one considered in the new conceptual designs in order to design a "total renewable plant". Within this scenario, two conceptual designs based on the corresponding two gasification concepts (Entrained flow gasifier and Twin bed gasifier) were developed. The catalyst considered in each case was an alkali doped cobalt based molybdenum sulphide catalyst.

In the plant concept based in the entrained flow gasifier, biomass is firstly converted to bio-slurry in multiple flash pyrolysis plants distributed around the large synthesis plant. Then, bio-slurry is transported to the synthesis plant and stored. In the synthesis plant, the bio-slurry is pressurized via pumps and fed to the gasifier which operates at slightly

higher pressure than the synthesis reactor one. The advantages of this option are that slurry feeding is a state-of-the-art and slurry transport and transhipment is relatively cheap compared to solid biomass.

At the outlet of the gasifier, the syngas is cooled by water quenching and sent to a Heat Recovery Steam Generator (HRSG). After that, remaining particles are removed in a candle filter. Next, the H2/CO mole ratio is adjusted in a raw water gas shift so the H2/CO mole ratio at the inlet of the synthesis reactor is equal to 1. After the raw water gas shift, the syngas is cooled in order to preheat boiler feed water and then sent to a venturi scrubber, where remaining traces of alkalis, NH3 and particles are removed. Next, the synthesis gas enters a synthesis loop. Firstly, the syngas is mixed with a recycle stream and sent to a Selexol unit, where H2S and CO2 are removed. The acid gas stream from the Selexol system is sent to a LO-CAT unit, where H2S is converted to elemental sulphur. The clean syngas is mixed with recycled methanol and preheated before entering the synthesis reactor. The outlet stream from the synthesis reactor is sent to a flash drum, obtaining H2, CO, CO2 and CH4 as gas and alcohols as liquid. Gas is recycled and alcohols are sent to a separation train. The gas stream from the flash drum is sent to an autothermal reformer where light hydrocarbons are reformed. The reformed stream is compressed and recycled. The liquid stream is sent to a stabilizer, where methanol is recovered and recycled to the synthesis reactor. The bottom of the stabilizer column is sent to molecular sieves where water is totally removed. The mixture of C2+ alcohols, free of water, is sent to distillation columns, where alcohols are sequentially recovered.

Regarding the plant concept based in the BCL gasifier, biomass is firstly screened and particles larger than 2 inches are sent to a hammer mill for further reduction. Then, biomass is dried using flue gas from the char combustor of the BCL gasifier. The syngas from the gasification bed is sent to cyclones to remove particles. Then, tars and light hydrocarbons present in the syngas gas are converted to CO and H2 in a catalytic tar reformer. In the tar reformer steam is added so as the H2/CO mole ratio at the inlet of the synthesis reactor is one. After the tar reformer, the syngas is cooled in a HRSG and then remaining particles and alkalis are removed in a candle filter. Then, the syngas is cooled again before entering a venturi scrubber where remaining traces of alkalis, NH3 and particles are removed. Because the BCL operates at atmospheric pressure, the cooled syngas is compressed to the synthesis pressure (70 bar) in several compression stages with intermediate cooling. The compressed syngas is mixed with a recycle stream and sent to a Selexol unit where H2S and CO2 are removed. The acid gas stream from the Selexol system is sent to a LO-CAT unit, where H2S is converted to elemental sulphur. The clean syngas is mixed with recycled methanol and preheated before entering the synthesis reactor. The outlet stream from the synthesis reactor is sent to a flash drum. The gas stream from the flash drum is not reformed and recycled upstream of the Selexol unit. To prevent build-up of some chemical species in the synthesis loop, part of the off-gas is sent to a combined cycle for power production. The liquid stream is treated in the same way as explained above.

7   WP6. Technical-economical-environmental assessments

7.1 Scope and objectives

A global assessment of both bioethanol production processes has to be done taking into account economic, environmental and technical aspects.

The objectives of WP4.6 are briefly described in the following.

First, the economics of each pathway taking into account the results of the previous work packages are to be assessed. Market and commercial issues are to be introduced into this analysis.

After that, the environmental impacts of each pathway according to the data collected from previous work packages are to be analysed. In any event, the emissions have to be taken into account in the optimisation of the process. The inventory of all process inputs and outputs for both alternatives (enzyme and thermochemical) will be prepared. This set of data will be used in SP5 to perform the life-cycle assessment.

7.2 Brief description of the biological and thermochemical pathways processes

7.2.1 Biological pathway

The biomass plant is designed to convert lignocellulosic biomass into ethanol. The production capacity of the plant will be approximately 216 million litres of ethanol per year, based on 350 days of operation. This production capacity is given by the thermal input of 500 MWth, as it has already been said.

The process consists of the transformation of biomass; by means dilute acid prehydrolysis of the hemicellulose and enzymatic hydrolysis of the cellulose with fermentation of the glucose and xylose, arabinose and galactose to ethanol in different reactors. After that, the ethanol is extracted from the beer in a distillation stage until reaching the chemical composition of the azeotrope (95% w/w, this is the composition above which standard distillation becomes ineffective). Finally ethanol is obtained in the 99, 5 % w/w using dehydration molecular sieves.

In addition to these units operations, the process involves feedstock storage, wastewater treatment, yeast and enzyme production, product storage, power isle boiler and other utilities, but they will not be described here in detail since they are standard operations.

The key processes of this technology are:

- Prehydrolysis of hemicellulose by means thermochemical pre-treatment

- Separation of xylose, cellulose and lignin fractions.

- Fermentation of xylose and arabinose. Conversion of C5 sugars into ethanol.

- Enzymatic hydrolysis (cellulose hydrolysis)

- Fermentation of glucose. Biological conversion of glucose into ethanol.

- Lignin recovery.

- Ethanol recovery and purification.

Four areas can be distinguished, involving seven sub-processes:

- Pre-treatment: mechanical pre-treatment and dilute acid steam explosion.

- Fractionation: C5 sugars and lignin fractionation.

- Conversion: enzymatic hydrolysis and sugars fermentation.

- Purification: lignin and ethanol recovery.

Four cases have been considered. These cases depend on the used fuel:

- Case 1: Production maximisation concept where the employed fuel for heating purposes, natural gas, is bought. In this case electricity energy is also bought and all the biomass input is treated to obtain the maximum ethanol quantity as possible.

- Case 2: Electricity energy is also bought and part of the biomass input is burnt for generating the necessary heat.

- Case 3: In this case, the used fuel is a mix of biomass, lignin by-product and waste solids. First, waste solids are taken into account. If the total necessary heat is not supplied by means waste solids combustion, lignin is burnt. It could be possible that not all the lignin by-product had to be burnt and consequently could be sold for additional revenue. Finally, if all the lignin and waste solids do not supply the necessary heat, part of the biomass feedstock is used. Electricity energy is bought.

- Case 4: Self sufficient plant concept; what means no external contribution neither of energy nor power. In this case, power and energy consumes are satisfied by means biomass, lignin and waste solids in a biomass fed boiler, and a steam turbine running on the steam produced in the boiler.

There are two scenarios for each case. The first situation is a conservative situation where the percentages in conversion are very low. In the second situation, the percentages in conversion and in recoveries are relaxed to be less strict. The assumptions in each situation are issued as follows:

- Conservative situation

    The assumptions made for the calculation of scenario in the future situation are:

    ➢ C5 sugar fraction recovered during pre-treatment: 70%

    ➢ C5 sugar percentage of C5 inlet in washing outlet stream: 5%

    ➢ C5 sugar conversion to ethanol: 70%

    ➢ Solubilized lignin after caustic soda addition: 96%

    ➢ Lignin recovery percentage from lignin input in the process: 65%

    ➢ Lignin percentage in washing outlet stream: 5% lignin inlet in lignin fractionation

    ➢ C6 sugar fraction recovered during hydrolysis: 80%

    ➢ C6 sugar conversion to ethanol: 95%

    ➢ Minimum ethanol concentration in beerwell previous distillation: 5%

    ➢ Solids percentage in:

        o Xylose fractionation: 40%

        o Lignin fractionation: 40%

        o Lignin recovery: 40%

- Optimistic situation

    If we consider for the calculation of 2020 a more optimistic situation, the assumptions made are:

    ➢ C5 sugar fraction recovered during pre-treatment: 80%

    ➢ C5 sugar percentage in washing outlet stream: 5%

    ➢ C5 sugar conversion to ethanol: 90%

    ➢ Solubilized lignin after caustic soda addition: 100%

    ➢ Lignin recovery percentage from lignin input: 75%

> ➢ Lignin percentage in washing outlet stream: 5% lignin inlet

> ➢ C6 sugar fraction recovered during hydrolysis: 90%

> ➢ C6 sugar conversion to ethanol: 95%

> ➢ Minimum ethanol concentration in beerwell previous distillation: 5%

> ➢ Solids percentage in:

>> o Xylose fractionation: 45%

>> o Lignin fractionation: 40%

>> o Lignin recovery: 45%

7.2.2 Thermochemical pathway

The thermochemical pathway basically consists on the production of synthesis gas by means gasification and the subsequent catalytic conversion into an alcohol mixture.

Firstly, biomass is pre-treated. Biomass pre-treatment is totally subject to the gasification technology adopted. After pre-treatment, biomass enters the gasifier. Two different gasifier technologies have been considered. One of them is the indirect heated circulating fluidized bed (CFB). The CFB gasifier pressure is 2 bar. Therefore, produced syngas must be compressed to the synthesis reactor pressure. In this case Tars Reforming must occur prior to cooling the syngas to prevent tar condensation and deposition on downstream equipment.

The second gasification technology is entrained flow gasifier which is characterized by fuel particles dragged along with the gas stream. This means short residence time, higher temperature (which avoids tar formation and thus the need for tar reforming downstream) and small fuel particles. Furthermore, entrained flow gasifier is operated under pressure and with pure oxygen.

The cleanup and conditioning section are dictated by the requirements of the synthesis catalyst. Requirements include tars and light hydrocarbons reforming to additional CO and H2 (in case of CFB gasification technology), gas cooling, impurities removal by water scrubbing, SH2 removal, H2/CO mole ratio tuning by WGSR, CO2 removal and syngas compression. In case of CFB gasification technology and prior to the synthesis reactor, the syngas must be compressed to the operating pressure. A multi-staged compressor with intercoolers is used.

Next, the syngas is converted to alcohol in a catalytic reactor, which operates at 300 ºC. After the reactor, the effluent is cooled to 43°C by means heat exchangers, while maintaining high pressure. A knock-out drum is then used to separate the liquids (primarily alcohols) from the off gas, which is composed of unconverted syngas, CO2, and methane. From here, the liquid crude alcohols are sent to product purification. The residual gas stream is recycled back to the WGSR. In Self Sufficient cases, combined ethanol and electricity production take place. Part of the residual syngas is purged to a combined cycle for electricity production and the remaining is recycled. In Maximum Production cases, maximum ethanol production takes place, instead of combined ethanol and electricity production. In this case, methane is sent to a SMR and the reformed syngas is recycled to the WGSR.

In Self Sufficient cases, part of the residual syngas from the synthesis reactor is purged to a combined cycle for electricity production in a power plant. In the combined cycle power plant, a gas turbine generator generates electricity and the waste

heat (550ºC gas stream) from the gas turbine is used to make steam to generate additional electricity via a steam turbine, this last step enhances the efficiency of electricity generation.

The outlet stream from the synthesis reactor is composed of unconverted syngas (mainly CO, H2) and reaction products, namely water, methanol, ethanol, higher alcohols (n-propanol, n-butanol, n-pentanol) and CO2, CH4. As mentioned before, the first step in the separation process is carried out in a flash drum, obtaining H2, CO, CO2 and CH4 as gas and alcohols as liquid. Gas is recycled and alcohols are sent to a separation train.

Four cases have been considered, which are combinations of the aforementioned processes, i.e.:

- Circulating Fluidized Bed Self Sufficient (CFB_SS).

- Circulating Fluidized Bed Maximum Production (CFB_MP).

- Entrained Flow Self Sufficient (EF_SS).

- Entrained Flow Maximum Production (EF_MP).

7.3 Main conclusion of the techno-economic assessment

A techno-economical assessment of different conceptual designs for the synthesis of bioethanol from biomass has been carried out, simulating the different conceptual designs in Aspen Plus®.

The following aspects had to be considered prior to the analysis of the results:

- Showed results are attached to the several technical hypotheses assumed for this study, most of them taken from literature and thus not based in realistic plant information.

- Most hypotheses assumed are also very conservative, leading to unrealistic worst case results.

- Economical results are attached to the several hypotheses assumed for this study, most of them taken from literature and thus not based in realistic situations.

- Significant better results can be expected from other studies based on more optimistic assumptions and thermal integrated process models.

On the one hand, a technical assessment has been carried out based on different indicators.

On the subject of the biological pathway the following statements have been concluded:

- Based on the Maturity-related indicators, no difference between the different cases can be stated but for the indicator - Investment cost of the concept-.

- According to the indicator -Investment cost of the concept-, the higher investment cost correspond to case 4 - conservative situation concept being case 2 - conservative situation concept the most favourable.

- Concerning efficiency-related indicators case 1 in the optimistic situation is considered the best choice, which means that in terms of efficiency, maximizing ethanol production leads to better results than carrying out energetic integration.

- According to the feedstock and product quality -related indicators, no difference between considered concepts can be stated.

Regarding the thermochemical pathway the following conclusions have been extracted:

- Based on the indicator -T€/MW biomass input for Gas Cleaning and Gas Conditioning sections-, the circulating fluidised bed concepts show higher costs. The higher Gas Cleaning and Gas Conditioning sections specific costs correspond to the maximum fuel production circulating fluidised bed concept. This is mainly due to the greater number of units required.

- According to the indicator - Experiences/Ratio of Commercial Systems -, the EF concepts show higher maturity.

- Concerning syngas efficiency indicator, the entrained flow concepts show higher values.

- According to the -Synthesis gas quality - indicator, the self-sufficient entrained flow gasification concept is the most favourable, being the maximum production circulating fluidised bed concept the worst case.

On the second hand, an economical assessment has been carried for both the biological and the thermochemical pathways.

On the subject of the biological pathway the following statements have been concluded:

- The optimistic situations are more profitable according to their economic indicators values. The reason is the higher xylose and glucose conversion to ethanol and the bigger lignin recovery related to the non optimistic situations. Furthermore selling lignin instead of burning it is a little less profitable.

- The minimum biofuel production cost belongs to the cases where lignin and waste solids are employed as fuel, in the optimistic situation.

- From the economic point of view, the best alternative is case 3 in the optimistic situation.

- Regarding the thermochemical pathway the following conclusions have been extracted:

- Only the maximum production circulating fluidised bed concept is profitable because it yields positive net present values while the rest of the concepts do not.

- The circulating fluidised bed concepts profitabilities are higher than those corresponding to the entrained flow ones. The main reason is the much higher total cost investment of the entrained flow gasification concept with regard to the circulating fluidised bed concept. This is largely due to the high investment cost related to the pre-treatment and entrained flow gasifier.

- Thus, although the entrained flow gasification concepts could be selected concerning energy efficiency indicators, the highest profitability correspond to the maximum fuel production circulating fluidised gasifier concept.

Comparing the biological and the thermochemical pathways, the following statements can be made:

- Regarding the indicator – Development stage "single components"- both the biological and the thermochemical pathways show very similar results.

- Concerning the indicator – Development stage "R&D facilities" biological pathway shows remarkable higher results.

- The indicator – Technical design- results more favourable for the biological pathway.

- In all cases, the thermochemical shows significant higher TCI than the biological pathway.

- According to the indicator – Effort on feedstock preparation- the CFB-gasifier related concepts of the thermochemical pathway result to be the most favourable.

- Taking into account the statements above, the biological pathway shows, in general, better technical indicators results.

- Furthermore, from the economical point of view, the biological pathway most profitable case (case 3 optimistic situation) shows significant higher profitability than the thermochemical pathway best case (maximum production CFB gasifier- related concept).

The maximum production entrained flow gasification concept is favoured concerning energy efficiency indicators. Nevertheless, that concept is not profitable and concerning economic indicators the maximum production circulating fluidised gasifier concept is considered the best choice for a biomass to ethanol plant.

7.4 Main conclusions of the environmental assessment

- The results largely depend on the case considered for both pathways. Particularly, if the biological pathway is taken into account, cases 1 in which natural gas is consumed and the electricity is imported show very higher net GHG emission values than the rest of the cases.

- On the one hand, if only the -Ethanol from wheat straw, biological pathways- cases are considered, it can be stated that, in general, better energy integration leads to more favourable GHG emission values and that for each energy integration concept, optimistic cases also show better results, since performances for optimistic cases are higher which leads to lower energetic consumption for a given bioethanol production. -Ethanol from wheat straw, biological pathway- optimistic case 4 shows a very promising GHG emission value.

- On the other hand, if only the –Ethanol from farmed wood, thermochemical pathways- cases are considered, it can be stated that self sufficient concepts (SS) show more favourable GHG emission values than maximum production concepts. Furthermore, concepts based on Entrained Flow gasifier (EF) are more favourable than CFB-concepts due to higher performances which leads to lower energetic consumption for a given bioethanol production. -Ethanol from farmed wood, thermochemical pathway- EF-SS concept also shows a very promising GHG emission value.

8 General conclusions of overall work

Analysing the enzymatic hydrolysis process, it can be stated that highest productivity would be achieved using extra energy i.e., all thermal energy and power comes from outside the process, thermal energy from natural gas, power from the grid (maximum fuel production case or Case 1). Product efficiency is linked to productivity, so Case 1 is also the most efficient. Since energy yield parameter considers lignin as a product, the case in which lignin is considered a product, yields higher energy efficiency. However, Case 1 has double penalization, lignin is a very low profit product, and using fossil energy and power has high negative impact from the environmental point of view.

The main objective of WP 4.2 was to assess a promising catalyst for the conversion of biomass-derived syngas to ethanol. In this task, a complete set of catalyst lab tests was designed and performed. Furthermore, a second optimisation stage was started, in order to find the most appropriate set of conditions to carry out the synthesis reactions, and to have a clearer vision of the overall process and its real potential.

A promising pathway has been identified, in order to continue the research to assess a catalyst for the conversion of biomass-derived syngas to ethanol, until reaching an industrial catalyst that enable the thermochemical pathway. Parameters for assessing the performance of catalysts, especially ethanol productivity, have increased sharply after introducing a third catalytic phase in the systems, rising above 262 g/Kgh. The preparation of the catalyst has a very big effect on the performance in reaction conditions. The pre-treated activated charcoal clearly presents the best behaviour

about catalyst stability. Regarding CO2 and CH4, the best result, as regards productivity to ethanol, was obtained introducing both gases, at 2,5%, in the inlet stream to the reactor.

The results provided by the gasification trials may be quite useful to help in the optimum adjustment of the gasification process in an integrated biomass-to-liquid process. Composition of the gas from the gasifiers should be established in conjunction with the gas treatment unit situated downstream the gasification processes. To set the proper operational ratios in the gasifier, the link between operational variables and gas composition needs to be precisely known as well as the physical-chemistry behind in the gasification reactor. This has been successfully done in these test trials, which have provided additional technical information useful for up-scaling and final design of the process. This information has been the basis of an empirical model, also developed within the framework of this project.

Design of syngas cleaning and conditioning and product separation has been carried out. The syngas produced by the biomass gasification process contains different kinds of contaminants. These contaminants must be removed from the syngas to prevent erosion, corrosion, catalyst poisoning and environmental problems in the ethanol synthesis plant. Besides, the syngas composition must be adjusted to satisfy requirements of the catalyst such as H2/CO mole ratio and maximum allowable CO2 composition.

Different conceptual designs were presented and compared in terms of energy efficiency indicators by means of simulations. Modelling of each conceptual design was also briefly presented. The results of the simulations revealed that the conceptual designs could be improved and new conceptual designs were presented in the last section of WP4.5 summary.

A techno-economical assessment of different conceptual designs, i.e. thermochemical and biological pathways for the synthesis of bioethanol from biomass has been carried out, simulating the different conceptual designs in Aspen Plus®. Showed results are attached to the several technical and economical hypotheses assumed for this study, most of them taken from literature and thus not based in realistic plant information. Significant better results can be expected from other studies based on more optimistic assumptions and thermal integrated process models.

The biological pathway shows, in general, better technical indicators results. Furthermore, from the economical point of view, the biological pathway most profitable case (case 3 optimistic situation) shows significant higher profitability than the thermochemical pathway best case (maximum production CFB gasifier- related concept).

The environmental impacts of each pathway according to the data collected from previous work packages have been analysed. The inventory of all process inputs and outputs for both alternatives (enzyme and thermochemical) has been prepared. The results largely depend on the case considered for both pathways. Particularly, if the biological pathway is taken into account, cases 1 in which natural gas is consumed and the electricity is imported show very higher net GHG emission values than the rest of the cases.

On the one hand, if only the -Ethanol from wheat straw, biological pathways- cases are considered, it can be stated that, in general, better energy integration leads to more favourable GHG emission values and that for each energy integration concept, optimistic cases also show better results, since performances for optimistic cases are higher which leads to lower energetic consumption for a given bioethanol production. -Ethanol from wheat straw, biological pathway- optimistic case 4 shows a very promising GHG emission value.

On the other hand, if only the –Ethanol from farmed wood, thermochemical pathways- cases are considered, it can be stated that self sufficient concepts (SS) show more favourable GHG emission values than maximum production concepts.

Furthermore, concepts based on Entrained Flow gasifier (EF) are more favourable than CFB-concepts due to higher performances which leads to lower energetic consumption for a given bioethanol production. -Ethanol from farmed wood, thermochemical pathway- EF-SS concept also shows a very promising GHG emission value.