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Biofuel for biotravels

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Abbreviations

BtL	Biomass-to-Liquid
TAGs	Triglycerides
DFBG	Dual Fluidized Bed Gasification
CAPEX	Capital Expenditures
RED	Renewable Energy Directive
HRSG	Heat Recovery Steam Generator
WP	Work Package
CHP	Combined Heat & Power
RES	Renewable Energy Sources
PSA	Pressure Swing Adsorption
ST	Steam Turbine
ATR	Autothermal Reforming
SMR	Steam Methane Reformer
CGE	Cold Gas Efficiency
WGS	Water-Gas Shift
CCU	Carbon Capture & Utilization
CCS	Carbon Capture & Storage
CU	Carbon Utilization
EFE	Energetic Fuel Efficiency

Contents

1 Executive Summary

This deliverable aims to define the overall process of the BioSFerA concept and set an initial design and operational framework for each component of the proposed value chain. The full process definition was carried out targeting to large-scale applications of the concept.

Initially, a thorough description of each identified section of the Biomass-to-Liquid (BtL) plant was performed including the feedstock selection & handling, the gasification & gas conditioning, the double-stage syngas fermentation to triglycerides (TAGs) as well as the obtained TAGs purification and their subsequent hydrotreatment till drop-in liquid biofuels. The overall process can be separated in three distinct parts: the thermochemical part, the biotechnological part and the thermocatalytic part.

An overall process model was developed and process simulations were performed at full-scale for the BtL plant investigating different configurations and operational parameters. Apart from the main parts of the concept (i.e. thermochemical, biotechnological, thermocatalytic), additional units (i.e. water electrolysis, heat recovery steam generation, steam turbine) were involved in the simulations and their key specifications were assessed. The Heat & Balances for the examined case studies were solved and evaluated via overall performance indicators.

The boundary conditions between the different parts of the BioSFerA concept are provided and will act as a benchmark for the forthcoming experimental and pilot activities.

It should be mentioned that the present concept description as well as the process simulations represent an initial estimation of the BioSFerA operating scheme based on preliminary data. The complete development of the experimental activities will throw light on several design and operational parameters of the process and navigate its optimization that will take place in later stages of the project (WP6).

2 Introduction

The present document aims to provide the guidelines for the development of the different parts of the BioSFerA Biomass-to-Liquid (BtL) concept. A first overall display of the process is performed and a preliminary operational spectrum for each component is defined that will act as a benchmark for the following lab and pilot activities.

The suggested process chain can be divided into three distinct parts: the thermochemical, the biological/biotechnological and the thermocatalytic. The holistic consideration of an integrated plant is mainly based on existing technologies and procedures, taking also into account the characteristics, requirements and restrictions of each individual sub-process. Concerning the thermochemical part, a Dual Fluidized Bed Gasification (DFBG) unit is considered for the biomass-to-syngas conversion followed by a catalytic tar reformer, while for the biotechnological part a double-stage syngas-to-triglycerides (TAGs) fermentation unit is involved accompanied by a lipids purification system. The thermocatalytic part refers to the hydrotreatment unit that will convert the obtained TAGs into drop-in liquid fuels.

Section 3 contains a description of the BioSFerA concept including all the main sub-units. The suggested process scheme can be considered as an initial outline, which will be extended, adjusted and optimized during the project, using data generated during the upcoming experimental and modelling activities. In Section 4, the development of the integrated process model is explained and the heat & mass balances for the overall process are solved via three different operational scenarios of the concept. Finally, in Section 5, the main key design and operational parameters for the core components of the concept are collected.

Disclaimer: *The process description and the presented configuration within this document are based on preliminary data and input from the BioSFerA technology providers. Several components of the process value chain may be replaced or modified as the experimental activities grow up. The final and optimized description of the BioSFerA concept will be presented in Deliverable D6.2.*

3 BioSFerA concept description

The BioSFerA concept aims to develop a combined thermochemical – biochemical pathway for the treatment of biogenic residues, that minimizes the shortcomings of the existing technologies and takes advantage of their strong aspects in order to produce elevated yields of the desired fuels with limited energy consumption.

In particular, the presence of a semi-commercially proven technology like Dual Fluidized Bed Gasification (DFBG) ensures extended fuel flexibility, syngas of high quality, complete fuel conversion and optimal heat integration while avoiding CAPEX intensive equipment like Air Separation Unit. Then, a two-stage biochemical route is proposed: initially syngas fermentation (anaerobic) into acetate and subsequently acetate fermentation (aerobic) into targeted triglycerides (TAGs) that will be finally purified and hydrotreated to form the desired drop-in biofuels.

The tolerance of the bacteria to syngas contaminants minimizes the gas cleaning requirements. The biological process of syngas fermentation inherently has limited side products, a fact that reduces the risk of deactivation of hydrotreatment catalysts. Moreover, the low-pressure requirements (1-10 bar) along with the mild operating temperatures (30-60 ^{o}C) reduce drastically the capital and operational cost of the process.

The BioSFerA concept is illustrated in Figure 1 in a block formation:

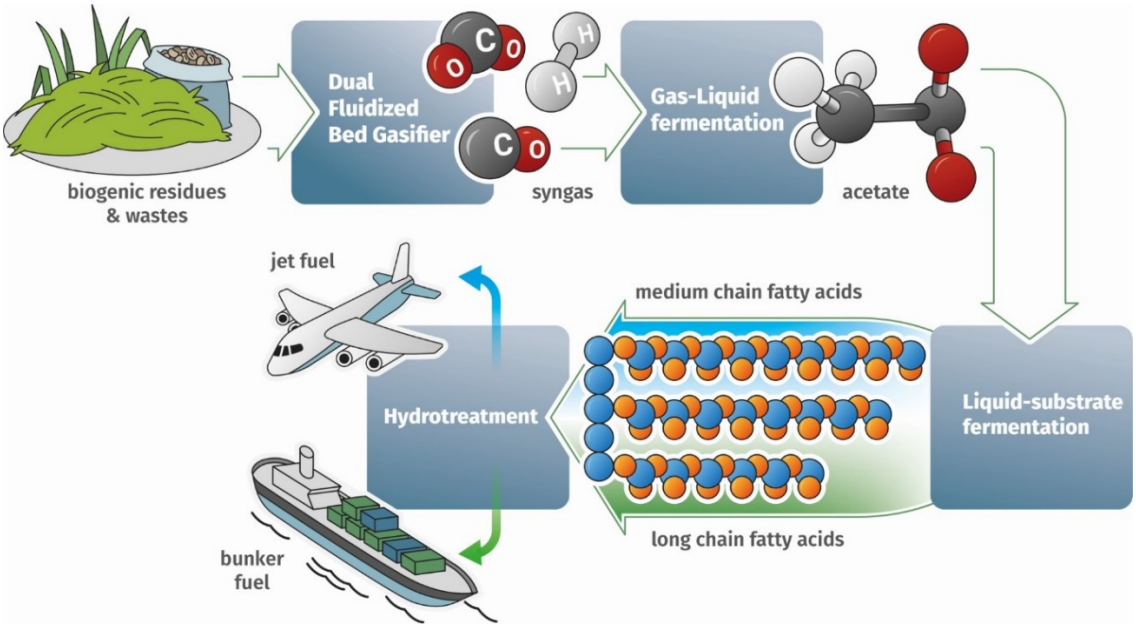

Figure 1. The BioSFerA concept from start-to-end

3.1 Feedstock selection & handling

Thanks to the DFBG technology, the process can be driven feedstock-flexible using a broad and variable portfolio of biogenic residues which may be lower quality carbon sources compared to the sugar-, starch- and oil plants used for conventional liquid biofuels, but do not come in conflict with food production and tend to avoid land use restrictions. Using biogenic residues also has the advantage of being in line with the EU's biofuels policy documented in the RED II directive, mentioning the promotion of residue based biofuels (or so-called advanced biofuels).

Within Task 2.3, an extended feedstock screening around Europe was performed, followed by the BioSFerA feedstock selection and characterization that can be found in detail in Deliverable D2.3 (https://biosfera-project.eu/project/pubblications/) [1]. In general, the BioSFerA feedstock inventory includes the most promising types of feedstock from each residual biomass category involving agricultural residues (prunings, straw), forestry residues (logging, bark), wood industry residues (sawdust) as well as biogenic wastes from airports/ports or other 'waste-productive' fields (Figure 2).

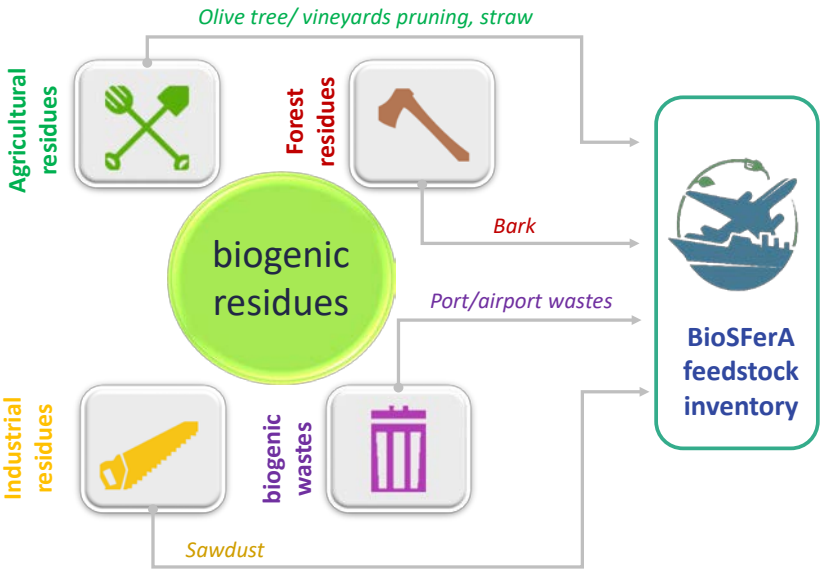

Figure 2. The wide spectrum of BioSFerA feedstock

It has to be mentioned that within BioSFerA project the feedstock preparation in pellets form will be attempted in order to avoid feeding problems in the bench- and pilot-scale tests. However, the general description of the concept, that is aimed within this document and refers to potential large-scale applications of the scheme, should make clear that the feedstock pre-processing requirements and the respective costs would be significantly lower at commercial scale.

In general, pre-treatment methods of the feedstock are used in order to optimize the process performance. These pre-treatment requirements are more intense in feedstock exhibiting high contaminant concentrations, low energy densities or low ash melting temperatures. The BioSFerA feedstock selection aimed to elect feedstock with mild pre-treatment requirements for commercial applications. However, each feedstock involvement should be assessed in terms of gasification requirements fulfillment as well as supply chain economics optimization, and subsequently the

appropriate pre-treatment pathway should be applied including from the mildest (e.g. drying, chipping) to more energy & cost intensive measures (e.g. torrefaction, pelletizing).

3.2 Dual Fluidized Bed Gasification (DFBG) & Gas Cleaning

The conversion of the biomass feedstock into syngas is carried out with the DFBG technology. The DFBG system consists of two interconnected reactors, the gasifier where gasification takes place, and the oxidizer where partial combustion of the char or supplementary fuel combustion takes place in order to secure the heat requirements of the gasifier.

In particular, the produced char, other residues (i.e. ash) and part of the bed material are transported to the combustor where they react with the oxidizing medium (air) to produce heat. The (hotter) bed material returns to the gasifier, serving as an external heat source for the endothermic pyrolysis and steam gasification reactions, leading to higher carbon conversion rate and thermal efficiency. Raw syngas of moderate heating value and relatively low tar levels is achieved and filtered at gasifier exit temperature. Then, the already secured low content of heavy tars along with hydrocarbon gases are catalytically reformed with the presence of oxygen or steam. The reformer is heated by partial combustion with oxygen or air, and in addition, the reforming reactions consume steam and/or CO_2.

A typical layout of a DFBG configuration that contains the filter and the catalytic reformer at the exit of the gasifier as well as an indicative gas cleaning section is presented in Figure 3. It was assumed the hot syngas thermal utilization for the accomplishment of gasification steam requirements, while the flue gases from the oxidizer are used for the pre-heating of the air that will enter the reactor. Both hot streams (i.e. syngas & flue gas) may be available for further thermal utilization in a Heat Recovery Steam Generator (HRSG).

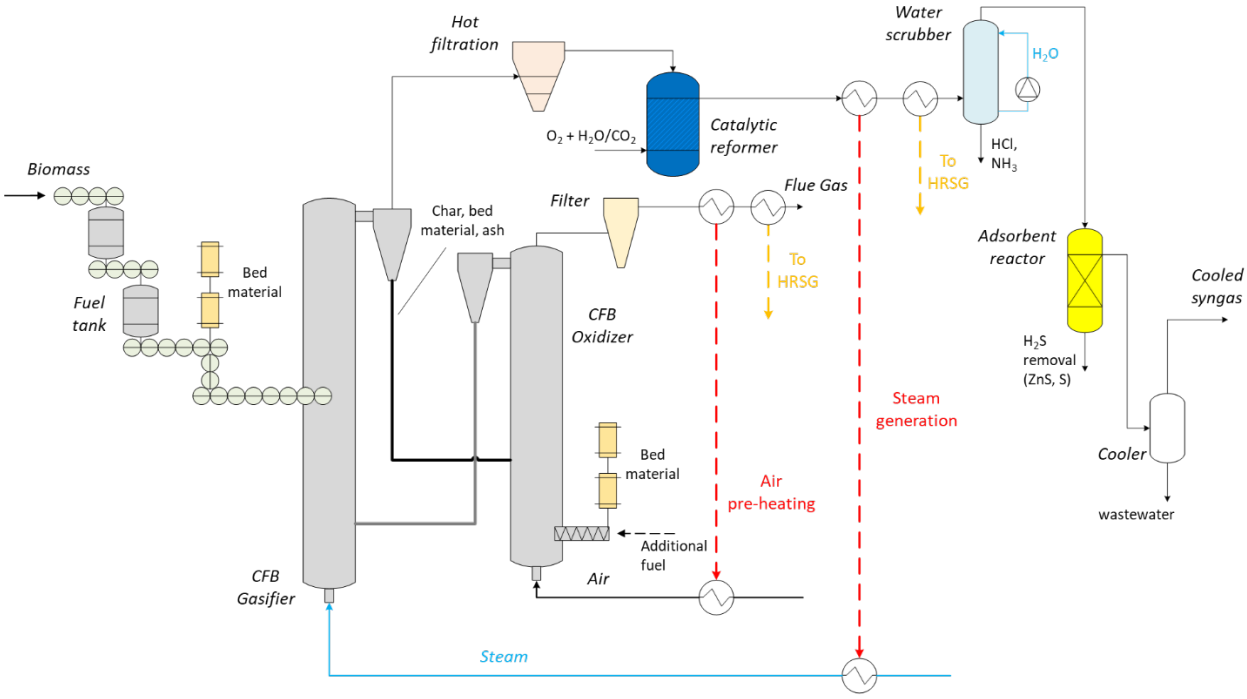

Figure 3. Dual Fluidized Bed Gasification (DFBG) typical scheme accompanied with a mild gas cleaning section

Concerning the appropriate syngas preparation in terms of cleaning requirements before the gas enters the syngas fermentation unit, the catalytic reformer is a key component of the process. The primary function of the reformer may be to convert tars and hydrocarbon gases to H_2 and CO, but nevertheless it can be modified to attain several targets as needed in achieving optimal fermentation results. Depending on the gas cleaning requirements, different catalyst loadings and reactor design can be applied. For example, the reformer can be designed to largely decompose ammonia (NH_3) or hydrogen cyanide (HCN) and especially the latter which has turned out to be a major contaminant causing deactivation of the fermentation bacteria. HCN contents can be reduced to 1-10 ppm by using calcium-based bed materials in the gasifier followed by a reformer that is also active for NH_3 decomposition. Beyond that, depending on the target purity level, additional scrubbers and adsorbents can be implemented for the efficient removal of other syngas contaminants (e.g. H_2S, HCl, COS) before the fermentation unit. Figure 3 indicates a simplified gas treatment unit consisting of a water scrubber and an adsorbent reactor that utilizes metal oxides (e.g. Zn) and activated carbons (AC) for partial removal of sulfur compounds.

Within BioSFerA project, the optimum gas cleaning chain will be selected in terms of performance and cost reduction. The exact gas cleaning scheme will be defined after the finalization of the lab scale activities related to bacteria tolerance, but it is expected to be simplified and milder than the exhaustive gas cleaning that is required in chemical synthesis applications (e.g. Fischer – Tropsch).

No biomass pre-treatment unit is considered as the specific gasifier type can handle a wide range of raw feedstock quite effectively and no complex biomass upgrading unit (e.g. torrefaction) is required, contributing to the reduction of the investment cost while establishing fuel flexibility with various biomass and waste feedstock. Of course, there is the possibility/requirement to dry (up to <10-20%) feedstock with high moisture content by utilizing low-temperature waste heat streams derived from heat recovery systems.

3.3 Syngas fermentation

In the first step of the biotechnological part of the process, syngas is converted into acetate under anaerobic conditions. Several anaerobic bacteria (*Clostridium, Acetobacterium, Eubacterium*) have shown their ability to ferment single carbon gases such as CO and CO_2 plus H_2 into chemicals, usually acetate, through the acetyl-CoA pathway. These bacteria are named acetogens. The acetyl-CoA pathway (Wood-Ljungdahl pathway) can utilize both CO and H_2 as a source of electrons and CO and CO_2 as a source of carbon (Figure 4). Depending on the composition of the single carbon gases and particularly depending on the CO content of syngas, which may act as an inhibitor for specific types of bacteria (e.g. Acetobacterium woodii), some bacteria can be more efficient than others to produce acetate.

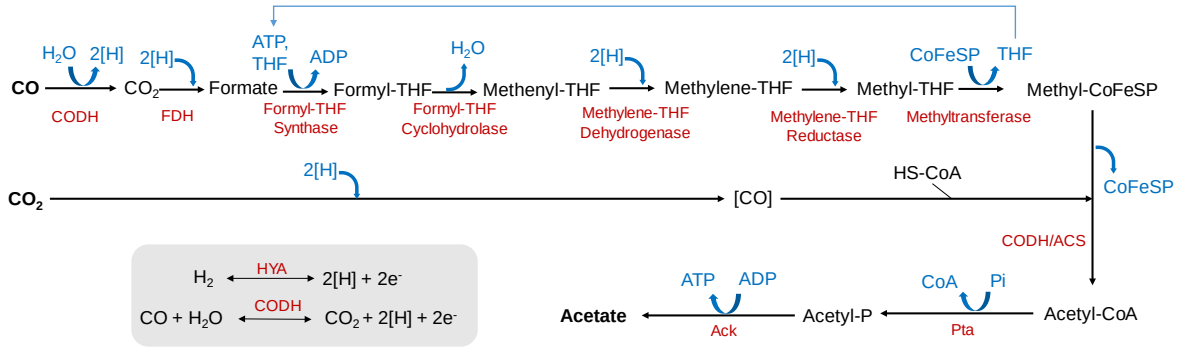

Figure 4. Wood – Ljungdahl pathway for acetate synthesis from syngas

Since acetogenic bacteria can secrete a mixture of compounds (acetate, ethanol, lactate, etc.) during syngas fermentation, metabolic engineering and synthetic biology are powerful tools to increase the acetate production and reduce the spectrum of unwanted by-products. Within BioSFerA project, and more specifically within WP3 lab scale activities, the best acetate producer strain based on the syngas composition will be selected. Subsequently, synthetic biology approaches and genetic engineering will be applied in order to modify the strains (*Clostridium autoethanogenum, C. ljungdahlii, Moorella thermoacetica*) targeting to further improvement of acetate production along with the elimination of by-products formation.

The procedure of acetate production in a continuous mode is illustrated in Figure 5. The interaction of syngas with the acetogenic bacteria under anaerobic conditions leads to acetate production. Two critical factors, that highly influence the fermentation kinetics and consequently the acetate productivity, are the gas solubility and the ratios of CO_2/CO/H_2. Syngas and specifically CO and H_2 are known to present low solubility in water. By recirculating the off-gas stream back to the fermenter, the unconverted syngas components can be recovered and recycled. At the same time, the broth containing the produced acetate in low concentration is extracted in continuous way, and the liquid volume is kept constant by adding fresh culture medium. Increasing the pressure improves the gas solubility as expressed by Henry's law, and consequently the acetate production yield. A cell recycling system (hollow fiber membrane) is required to keep the cells in the fermenter while extracting the liquid effluent. The fermenter is also preceded by a buffer tank with NaOH solvent which is used periodically in order to avoid toxic gases accumulation (e.g. H_2S) (H_2S + 2 NaOH → Na_2S + 2 H_2O).

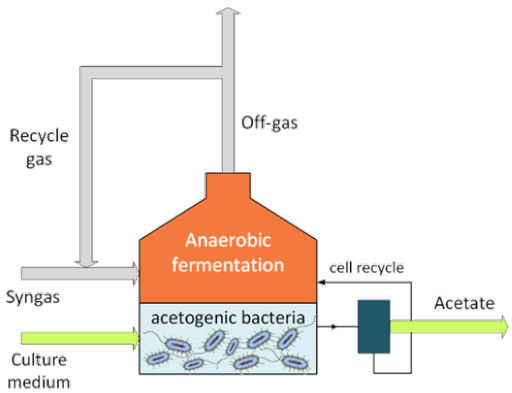

Figure 5. Syngas fermentation – Acetate production in a continuous mode

3.4 Acetate fermentation

The second fermentation step refers to the production of TAGs via aerobic fermentative process of the diluted acetate stream. The production of lipids from acetate has been described in different microbial species. So far, the most efficient microorganisms in carrying out this conversion are the so-called oleaginous yeasts, as *Yarrowia lipolytica* and *Cutaneotrichosporon oleaginosus*. *Y. lipolytica* wild type strains that have a well-primed metabolism for the biosynthesis of TAGs when grown in nutrient-limited conditions. In order to obtain strains that exhibit high lipid concentration, yield and acetate conversion, a metabolic engineering strategy of *Y. lipolytica* is adopted. Genetic engineering tools and metabolic models have been rapidly developed for non-conventional yeasts. The produced intracellular microbial oil mainly consists of fatty acids like oleate, stearate and palmitate.

Within BioSFerA project, a metabolic engineering strategy will be followed as well. Via genome scale metabolic models, the prediction of substrate and product fluxes into the cell will be attempted, as well as the required genetic modifications for the improvement of yeast strains. In addition, attention will be given to the yeast membrane transporters to improve fatty acids accumulation, but also to the tolerance of the yeast to high acetate concentrations in the medium. Finally, another willing direction of the biosynthesis will be the production of unsaturated medium and long chain fatty acids in high concentrations that should reduce the hydrogen and energy demands of the afterwards hydroprocessing.

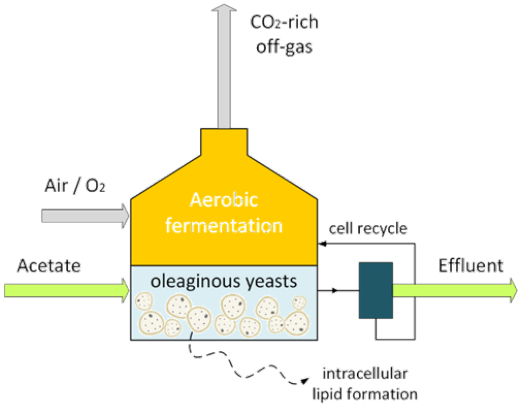

Figure 6. Acetate fermentation – TAGs production in a continuous mode

The continuous acetate fermentation process is schematically shown in Figure 6. The diluted acetate effluent stream from the syngas fermentation enters the aerobic fermenter, where the targeted TAGs are produced in the presence of oxygen, additional nutrients, salts and the oleaginous yeast (*Y. lipolytica*). A cell recycle system (hollow fiber membrane) can be installed to recirculate the cellular biomass in the bioreactor while extracting the effluent. During the continuous feed of the diluted acetate into the reactor, metabolic reactions take place and lipids are formed as intracellular products. At the same time, a gaseous CO_2-rich stream is formed and leaves the reactor from the top. Depending on the oxygen content of this stream, the resulting CO_2 can be partially recycled back to the inlet of the syngas fermenter or cover other CO_2 needs of the plant (e.g. gasifier, reformer).

The complete double-stage fermentation scheme, containing both the anaerobic syngas fermentation and the aerobic acetate fermentation, is presented in Figure 7:

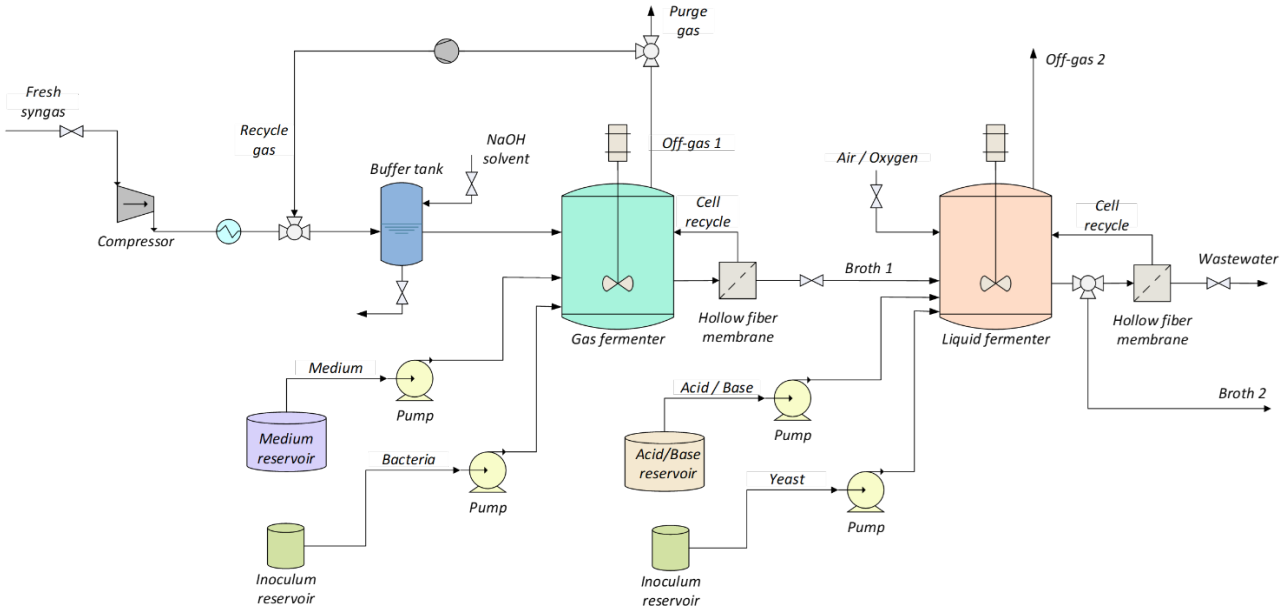

Figure 7. The double-stage fermentation scheme and the Syngas-to-Acetate-to-TAGs pathway

3.5 Triglycerides (TAGs) purification

Lipids extraction from the oleaginous yeasts is an important step before hydrotreatment and the final liquid biofuel formation. As oleaginous yeasts store lipids in intracellular forms, extraction is required to obtain TAGs. Cell disruptions alongside lipid extraction steps are critical for large-scale biofuel production in terms of cost adequacy. Mechanical disruption requires energy inputs such as shear forces, electrical pulses, waves or heat. Mechanical processes generally provide high products recovery yields with good management and scalability, but they are energy intensive. Among the options actually available, there are novel technologies with considerably lower power consumptions such as steam explosion, centrifugation and membrane separation considering different process parameters and extraction procedures. Within BioSFerA project, it will be aimed the pre-treatment process optimization and improvement of selected lipids production from the fermentation steps.

Steam explosion is an innovative method with reduced environmental impact, lower costs and energy demand, compared to other techniques that are widely used. In steam explosion, raw material exposed to steam at 180-240°C for several minutes and then subjected to depressurization to ambient conditions. This generates an explosion that causes cell-wall disruption [2]. In context in which heat flows are available as downstream of other processes, and so steam could be generated at low cost, steam explosion should be considered as potential technology for cellular biomass fractionation with high yields of recovery. The process converts the thermal energy into mechanical energy and the shear forcing caused by the expansion of water vapor leads to the disruption of cell wall.

Centrifugation could be evaluated for the ability to separate oil from the broth deriving from steam explosion. Using centrifugation, an efficient lipids fraction separation, at least from water, can be achieved. Lipids are partially phase-separated as a top layer and partially form an oil-in-water emulsion. After this, if a purification of singular lipids category is needed, the oil fraction could be further processed in a membrane plant. Membrane separation is well suited for such purposes and is therefore a promising option for the downstream processing.

The microbial oil purification and recovery process to be developed within BioSFerA is presented in Figure 8.

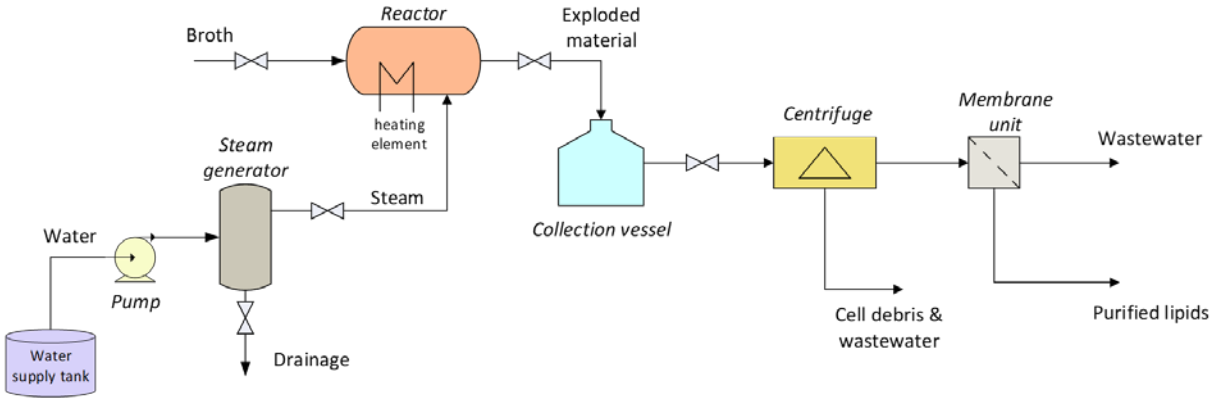

Figure 8. TAGs purification and recovery process via steam explosion, centrifugation and membrane separation

3.6 Triglycerides (TAGs) hydrotreatment

The final section of the BioSFerA value chain includes the upgrading of microbial oil into drop-in aviation and marine biofuel. The catalytic hydrotreatment process is generally divided into three main steps:

The first two steps refer to hydrogenation and subsequent hydrodeoxygenation plus decarboxylation. In particular, unsaturated fatty acids and triglycerides are converted into saturated fatty acids by catalytic hydrogenation. Then, the saturated fatty acids are converted to straight chain alkanes by hydrodeoxygenation and decarboxylation, co-producing propane, water, CO and CO_2. The desired products from these two steps are mainly straight chain paraffins containing no oxygen.

In the last step, the deoxygenated straight chain paraffins are selectively hydrocracked or isomerized yielding highly branched alkanes. This step is essential to improve the cold properties of the product. The common catalysts for this step are Pt, Ni or other metals based on Al_2O_3 or zeolite molecular sieves. The resulted organic product is a mixture of straight and branched C_vH_{2v+2} that can be suitably used as drop-in liquid fuel.

The hydrotreatment unit is presented in Figure 9:

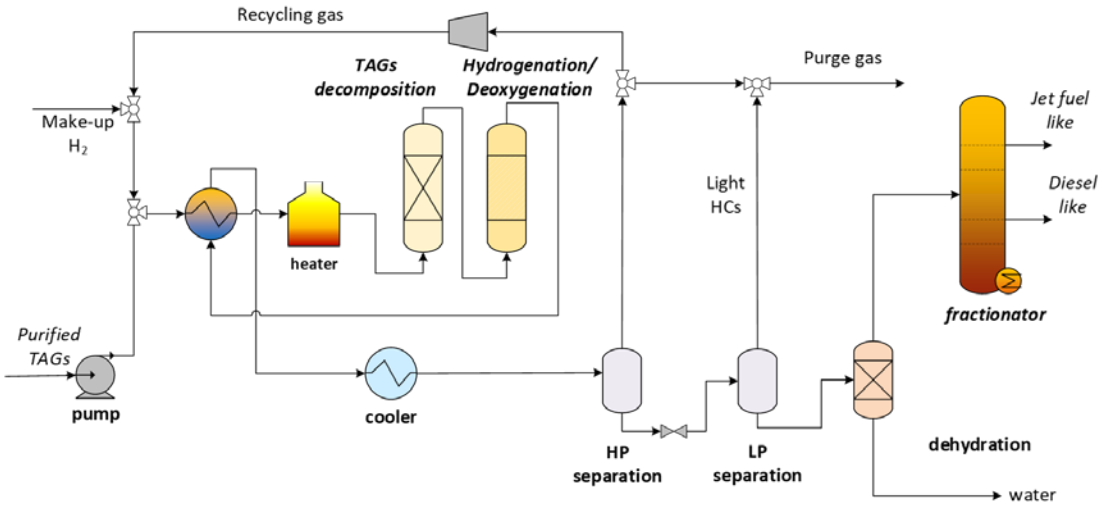

Figure 9. TAGs to drop-in liquid fuels via hydrotreatment

The hydrogen requirements of the hydrotreatment unit will be secured through water electrolysis using electricity either from a potential accompanying CHP of the BioSFerA concept or from a RES plant. Another option is to extract the required amount of hydrogen from syngas using a common industrially applied technology like Pressure Swing Adsorption (PSA). This is due to be determined with the assistance of the heat and mass balances of the concept as well as the complete techno-economic analysis that will take place in later stages of the project.

3.7 Integrated Biomass to Liquid (BtL) plant

The integrated Biomass to Liquid (BtL) plant refers to the most efficient coupling of the individual BioSFerA sub-units in terms of equipment and operational costs as well as carbon and energy utilization. In this direction, a series of issues (e.g. recycle ratios, CO_2 utilization, electrolyzer involvement, oxy/air reforming, etc.) concerning the final value chain definition are due to be optimized during the project implementation. This will be achieved by extracting information from the lab & pilot scale activities, the full process simulations as well as the techno-economic analysis of the concept.

At this stage of the project, the main objective is the determination of the main design and operation parameters for each component and the formation of a consistent and technically feasible value chain that will act as the reference point for any further enhancement during the project. A general concept description, that could adequately serve this target, is presented in Figure 10, which was also firstly presented in the project application phase. The thermochemical part, the biological/biotechnological part as well as the thermocatalytic part of the process are integrated in an indicative functional way where the oxygen and hydrogen requirements are covered from an electrolyzer.

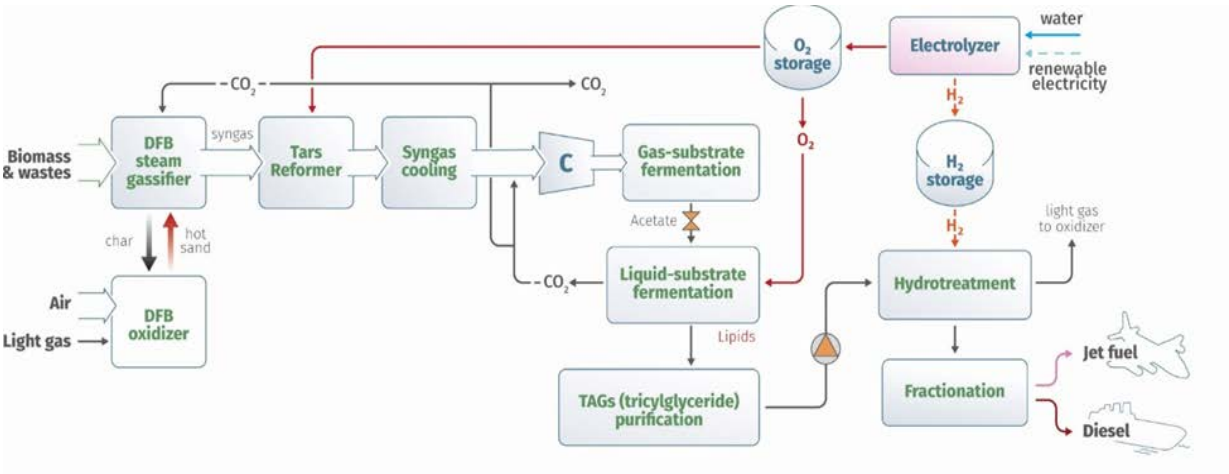

Figure 10. The integrated BioSFerA process chain (a reference case)

Of course, as already mentioned, the illustrated configuration represents only a possible integrated scenario and in no case can be considered as the final and optimized BioSFerA plant case. Process simulations within this document as well as the forthcoming lab-scale activities will shed more light concerning the specifications and requirements that should be met for the integrated plant and probably transform the suggested concept. However, the presented scheme utilizes all the primary data available at this stage of the project and can act as a reliable benchmark for the further development of the concept and future more detailed process simulations.

4 Process chain Heat and Mass balances

This section presents the heat and mass balance calculations for the integrated process scheme via full-scale process simulations. The first part (4.1) refers to the model development and its basic input parameters, the second part (4.2) contains the description of the integration strategy and the elected examined scenarios, while the process simulation results are presented and discussed in subsection 4.3.

4.1 Model description

The BioSFerA BtL value chain could be separated in three main parts. The thermochemical part, the biotechnological part and the thermocatalytic part. The thermochemical part refers to the DFB gasification unit as well as the following syngas cleaning and conditioning that will secure the smooth transition to the biotechnological part, which contains the double-stage syngas fermentation scheme. The thermocatalytic part refers to the TAGs hydrotreatment unit and the fractionation in order the final liquid fuels to emerge.

Two additional units, that could potentially interact with the BtL value chain and determine the plant operation mode, are investigated. The first one is a RES-based water electrolysis unit that will be able to secure the hydrogen and pure oxygen requirements of the plant, while the second one is a Heat Recovery Steam Generator (HRSG) unit for efficient heat recovery and steam generation from the thermochemical part and furthermore self-power plant production with the involvement of a Steam Turbine (ST).

The described concept is illustrated in a block form in Figure 11:

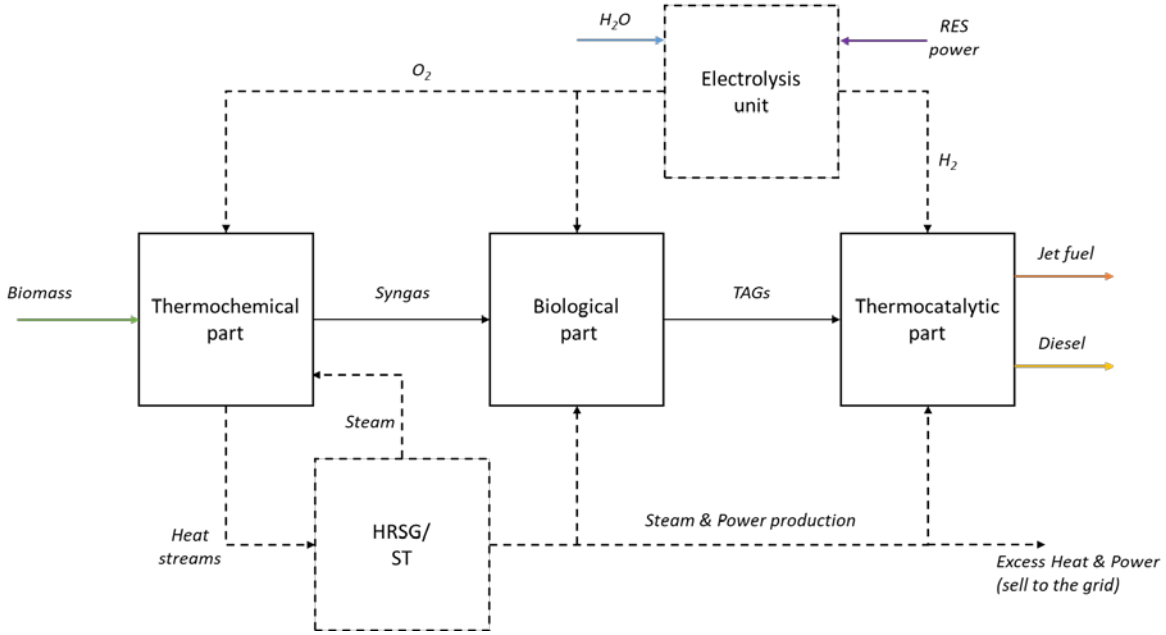

Figure 11. Process scheme of the integrated BioSFerA BtL plant in a block form (in dash lines the blocks and streams that interact with the main BtL chain)

The process model was developed in the commercial software ASPEN PLUS™. The simulations were performed at full-scale (200 MWth) and the selected feedstock was crushed bark, the main specifications of which were extracted from Deliverable D2.3 [1] and presented in Table 1:

Table 1. Fuel properties and analysis for crushed bark involved in the process simulations

Crushed Bark						
Mass flow a.r. (kg/s)				11.24		
Net Calorific Value LHV a.r. (MJ/kg)				17.79		
Proximate Analysis (%)						
Moisture		FC		VM		Ash
8.4		18.5		77.8		3.7
Ultimate analysis (%)						
Ash	Carbon	Hydrogen	Nitrogen	Chlorine	Sulfur	Oxygen
3.7	51.5	5.8	0.3	-	0.06	38.64

An important aspect for the correct operation and integration of the individual units in the simulation environment is the definition of the appropriate property methods for the efficient estimation of the thermo-physical properties present in the components and streams of the process. The initially selected property methods for each main sub-unit are presented in Table 2. As the process simulations grow-up and more validation material will be available, revision of the selected property methods for some components may be required.

Table 2. Property methods for the Aspen Plus™ process simulation

Thermochemical part	Biotechnological part	Thermocatalytic part
IDEAL	Predictive Soave-Redlich-Kwong (PSRK)	Predictive Soave-Redlich-Kwong (PSRK)

The water electrolysis unit was modeled in a simplified way that includes the mass balance of the water electrolysis reaction ($2\ H_2O \rightarrow 2H_2 + O_2$) as well as an average required electricity demand equal to 180 MJ/kg of produced hydrogen that reflects to an electrolyzer efficiency of 70-80% [3]. For the development of the HRSG model, it was used the IAPWS-95 property method in the water side and the IDEAL property method for the flue gases side.

4.1.1 Model development of the Thermochemical part

The thermochemical part of the process consists of the DFBG unit, the catalytic reformer as well as the gas cleaning steps required for a subsequent efficient syngas fermentation. Equilibrium models have been used for the implementation of the gasification and the reforming reactions, while for kinetically and hydrodynamically controlled phenomena that cannot be predicted with the rules of chemical equilibrium (e.g. unconverted solid carbon, formation of gaseous hydrocarbons), fitting of selected parameters with experimental data was followed. The selected parameters and the fitting of the model are based on previous steam DFBG pilot tests of crushed bark [4],[5].

For the DFBG unit, a gasifier operated with 100% steam at 780 °C and an oxidizer operated with air at 880 °C are considered. An additional gas (e.g. CO_2) may be needed to secure the fluidization conditions inside the gasifier, but this will be investigated in later stages of the project with the development of a more detailed DFBG model (WP6). Char is the main fuel source of the oxidizer, but also off-gases from other sub-units of the integrated BtL scheme can be used as supplementary fuel. Filtration of syngas takes place at gasifier outlet temperature, while the filter ashes are also directed to the oxidizer. A mixture of sand and calcium carbonate was used to represent the bed material. The governing reactions in the gasifier are the steam gasification reaction (1), the WGS reaction (2), the Boudouard reaction (3), the homogeneous gas reactions that form hydrocarbons (4) – (7) and the partial combustion reactions (8) – (9):

$$C + H_2O \rightarrow CO + H_2 \quad (1)$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (2)$$

$$C + CO_2 \leftrightarrow 2\,CO \quad (3)$$

$$CO + 3\,H_2 \leftrightarrow CH_4 + H_2O \quad (4)$$

$$2\,CO + 4\,H_2 \leftrightarrow C_2H_4 + 2\,H_2O \quad (5)$$

$$6\,CO + 9\,H_2 \leftrightarrow C_6H_6 + 6\,H_2O \quad (6)$$

$$10\,CO + 14\,H_2 \leftrightarrow C_{10}H_8 + 10\,H_2O \quad (7)$$

$$H_2 + 0.5\,O_2 \rightarrow H_2O \quad (8)$$

$$CO + 0.5\,O_2 \rightarrow CO_2 \quad (9)$$

For the non-equilibrium conversions in the gasifier, the following fitting scheme was followed after consulting VTT:

- Carbon: 78% to gases and tars, 22% to unreacted carbon (90% of unreacted carbon to char and 10% to gasifier filter ash)
- Nitrogen: 10% to char, 80% to NH_3, 0.5% to HCN
- Sulfur: 10% to char, 85% to H_2S, 5% to COS
- Sand (bed material): 10% to gasifier bottom ash, 85% to oxidizer bottom ash, 5% to oxidizer filter ash

- Calcium (bed material): 5% to gasifier bottom ash, 15% to gasifier filter ash, 20% to oxidizer bottom ash, 60% to oxidizer filter ash

For the prediction of gaseous hydrocarbons formation:

- CH_4: 6.05 mol/kg biomass volatile matter
- C_2H_4: 2.0 mol/kg biomass volatile matter
- C_6H_6: 0.43 mol/kg biomass volatile matter
- $C_{10}H_8$: 0.2 mol/kg biomass volatile matter

The main input and process parameters for the DFBG unit are gathered in Table 3:

Table 3. DFBG unit process parameters

Parameter	Input
Pressure (bar)	1.5
Gasifier temperature (°C)	780
Carbon conversion in the gasifier (%)	78
Pressure drop in the gasifier (bar)	0.2
Steam-to-biomass ratio (kg/kg dry,ash free)	0.7
Steam pre-heating temperature (°C)	350
Oxidizer temperature (°C)	880
Air pre-heating temperature (°C)	400
Oxygen in flue gas (% vol.)	4
Heat losses (gasifier + oxidizer) (%)	1
Sand input (% of biomass input)	1
Calcium carbonate input (% of biomass input)	1

For the catalytic reformer, there are two design options. On the one hand, there is the autothermal reforming (ATR) where the reformer operates under autothermal conditions with the addition of oxygen as oxidation media, and steam or carbon dioxide as reforming agent. The presence of oxygen leads to partial oxidation of syngas and subsequently heat production that covers internally the reforming heat requirements. On the other hand, the steam methane reformer (SMR) is heated externally with the assistance of an air-heated combustor where purge gases are burnt in order to cover the energy requirements of the strongly endothermic steam reforming reactions (Figure 12).

Both design options have been taken into consideration. The ATR can operate also with air instead of pure oxygen, but in this case large volumes of N_2 would enter the gas stream increasing in this way the difficulty and cost of the subsequent syngas processing. Therefore, in terms of the overall plant efficiency, autothermal reforming with pure oxygen, if available, would be preferable. For the externally heated SMR design, pure oxygen is not required since the exothermic reactions take place out of the reformer, but part of the valuable syngas (purge gas) is utilized in a combustor instead of the liquid fuels production chain. All these design parameters are analyzed in more detail in section 4.2.

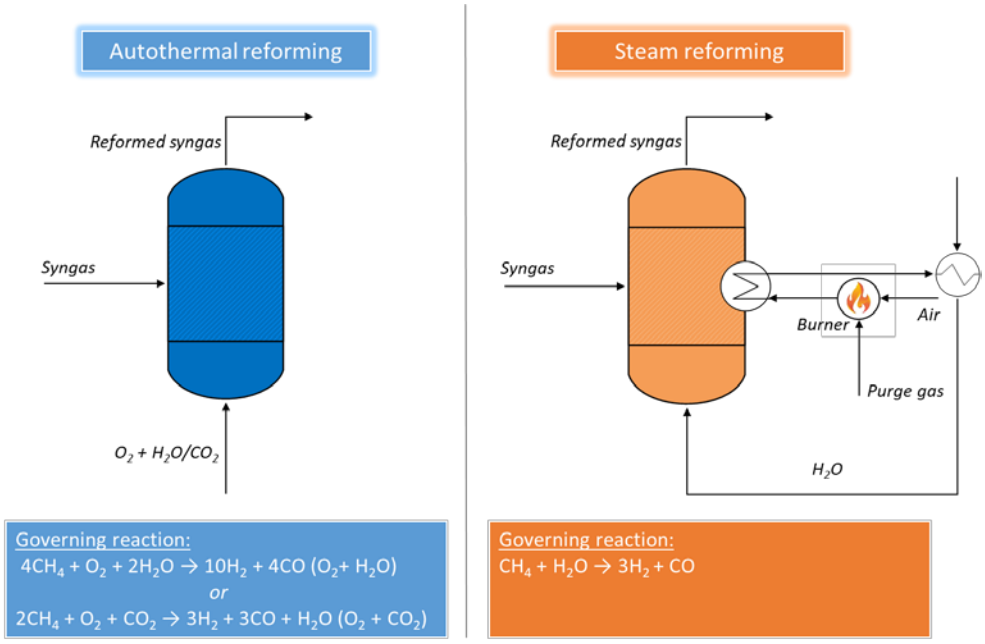

Figure 12. Autothermal and Allothermal operation of catalytic reformer

The non-equilibrium conversions that were used for the appropriate description of the reforming section are:

- CH_4: 80% conversion in the reformer
- C_6H_6: 99% conversion in the reformer
- $C_{10}H_8$: 99.9% conversion in the reformer
- NH_3: 80% conversion in the reformer
- HCN: 80% conversion in the reformer

The main input and process parameters for the reforming unit are gathered in Table 4. The model parameters that are applicable for autothermal reformer are labeled with the indication ATR, while those for allothermal with the indication SMR.

Table 4. Reforming unit process parameters

Parameter	Input
Outlet temperature (°C)	900
Steam-to-oxygen ratio (ATR) (kg/kg)	1
Steam-to-carbon ratio (SMR) (mol/mol)	1.5
Oxygen temperature (ATR) (°C)	400
Steam temperature (°C)	350
Combustor temperature (SMR) (°C)	950
Oxygen in flue gas (SMR) (% vol.)	6
Pressure drop (bar)	0.2

The gas cleaning requirements have not been determined decisively yet, since the experiments related to the bacteria resistance to syngas contaminants are still ongoing. However, these gas cleaning requirements are expected to be remarkably lower than those required for chemical synthesis applications. For the needs of the preliminary value chain definition, that is the objective of the present document, a water scrubber was used for the removal of NH_3 and HCl, and an adsorbent reactor was applied for the partial removal of H_2S. The removal of H_2S is achieved with the assistance of metal oxides (e.g. ZnO) and their ability of adsorbing inorganic compounds:

$$ZnO + H_2S \rightarrow ZnS + H_2O \quad (10)$$

The conversion rates that were assumed for the gas cleaning unit are:

- H_2S: 70% removal in the adsorbent reactor
- NH_3: 40% removal in the scrubber
- HCl: 100% removal in the scrubber

4.1.2 Model development of the Biological/Biotechnological part

The core of the biotechnological part of the BioSFerA process model is the two fermenters where syngas and acetate fermentation take place respectively. For the needs of Task 2.5, both fermenters were modelled as stoichiometric reactors (RStoic), with specific reaction stoichiometry and fixed conversions.

For the syngas fermentation stage, *Moorella thermoacetica* was used as the reference acetogenic bacterium and thus an anaerobic reactor operating at 55 °C was considered, since the optimal temperature range for these strains is 55 – 60 °C [6]. The operating pressure of the reactor was considered to be 5 bar in order to achieve higher solubility of the reacting gases in the liquid phase. Syngas derived from the reforming and purification units (plus the recycle gas) enters the fermenter where syngas is mainly converted to acetate. The only by-product considered is ethanol, yet with very low production. The 97.5% of the bioreactor's off-gas, which mainly consists of the unreacted syngas and the produced CO_2, is recycled back to the fermenter. Not all gas is recycled in order to avoid accumulation, but the experimental activities will shed more light in the recycling parameters of the gas fermentation process.

Reactions (11) – (14) were selected as the key reactions occurring during syngas fermentation:

$$4\,CO + 2\,H_2O \rightarrow CH_3COOH + 2\,CO_2 \quad (11)$$

$$2\,CO_2 + 4\,H_2 \rightarrow CH_3COOH + 2\,H_2O \quad (12)$$

$$6\,CO + 3\,H_2O \rightarrow C_2H_5OH + 4\,CO_2 \quad (13)$$

$$2\,CO_2 + 6\,H_2 \rightarrow C_2H_5OH + 3\,H_2O \quad (14)$$

For convenience, it was assumed that acetic acid is the product of gas fermentation. In fact, due to the base added to adjust the culture's pH, an acetate salt is formed instead. Depending on the base, a certain salt is formed. For example, when NH_4OH is used as the base, NH_4-acetate will be the product.

($CH_3COOH + NH_4OH \rightarrow NH_4COOH + H_2O$). Another assumption taken was that the culture medium stream is pure water and no nutrients were included. Additionally, it was considered that the H_2 and CO utilization of the syngas inlet stream (fresh plus recycled gas) by the bacteria in each pass is 43% and 61%, respectively. The selected values were based on literature data [7],[8]. Furthermore, neither cellular biomass components nor biomass formation reactions were included in the simulations. Nevertheless, it was assumed that a fixed fraction of 4.9% of the utilized substrate is consumed for biomass growth and is separated from the system.

The main input and process parameters for the syngas fermentation unit are presented in Table 5:

Table 5. Gas fermentation process parameters

Parameter	Input
Pressure (bar)	5
Temperature (°C)	55
CO utilization per pass (%)	61
H_2 utilization per pass (%)	43
Conversion of CO in reaction (11)	0.95
Conversion of H_2 in reaction (12)	0.95
Conversion of CO in reaction (13)	0.001
Conversion of H_2 in reaction (14)	0.001
Substrate utilization for microbial growth (%)	0.049
Off-gas recycle (%)	97.5

The aerobic fermenter, where the acetate fermentation takes place, operates at 30 °C and atmospheric pressure. The acetate extracted by the first fermenter reacts with oxygen for the production of TAGs and non-lipid biomass. For convenience, $C_{55}H_{98}O_6$ and $C_{51}H_{98}O_6$ were considered as the only TAGs produced. Reactions (15) – (16) represent the intracellular lipid formation by the yeasts:

$$58.2\ CH_3COOH\ +\ 39.83\ O_2 \rightarrow C_{55}H_{98}O_6\ +\ 61.35\ CO_2 +\ 67.4\ H_2O \quad (15)$$

$$51\ CH_3COOH\ +\ 29.5\ O_2 \rightarrow C_{51}H_{98}O_6\ +\ 51\ CO_2 +\ 53\ H_2O \quad (16)$$

As concerns the bioreactor's oxygen supply, two different options are present; pure oxygen and air supply. Pure oxygen supply results in off-gases rich in CO_2 with traces of O_2, whereas air to off-gases consisting of N_2, CO_2 as well as traces of O_2. The two different cases are depicted in Figure 13:

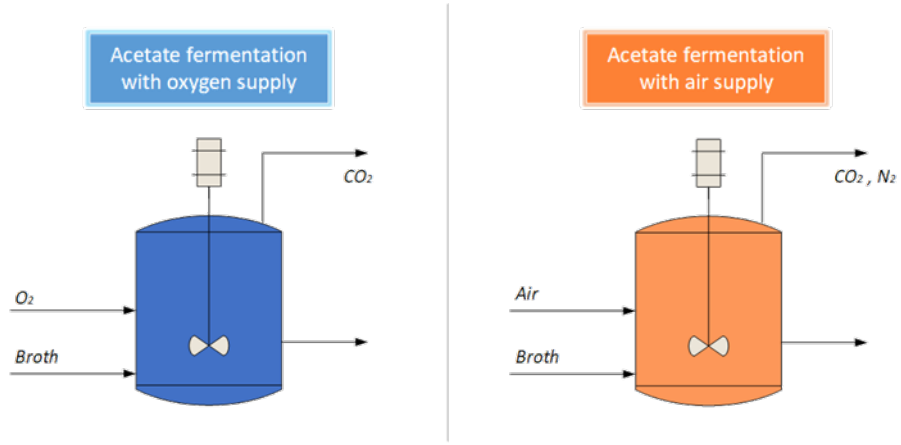

Figure 13. Oxy- and Air-fermentation of the aerobic fermenter

It was assumed that the TAG production phase is the governing phase during acetate fermentation. The non-lipid cellular biomass and its formation reactions were not included in the simulations. Nevertheless, it was assumed that a fixed fraction of 5% of the substrate is consumed for non-lipid biomass formation and is separated from the system. In fact, the TAG production phase is preceded by a biomass formation phase during which almost all acetate is used for biomass. The cell recycle system is also not included. As a result, the TAGs do not accumulate, but continuously leave the reactor in the outlet stream.

The main input and process parameters for the acetate fermentation unit are presented in Table 6:

Table 6. Liquid fermentation process parameters

Parameter	Input
Pressure (bar)	1
Temperature (°C)	30
Conversion of CH_3COOH in reaction (15)	0.80
Conversion of CH_3COOH in reaction (16)	0.15
Substrate utilization for non-lipid cellular biomass formation (%)	5
Oxygen-to-acetic acid ratio (mol/mol)	0.63

In order to extract the lipids from the yeast cells, the fermentation broth containing the cells undergoes some lipid purification steps. The estimated energy demand for conventional lipids purification techniques (i.e. bead milling, ultrasound, microwave) for *Y. lipolytica* is in the range of 115-194 MJ/kg of extracted oil [9]. However, with the novel steam explosion-based technologies that will be applied within BioSFerA project for the lipids purification procedure, the corresponding energy demands are expected to be remarkably lower.

4.1.3 Model development of the Thermocatalytic part

The thermocatalytic part of the process refers to the hydrotreatment of the produced TAGs to obtain the willing drop-in liquid fuels [10]. Initially, the decomposition of the two representative triglycerides ($C_{51}H_{98}O_6$ & $C_{55}H_{98}O_6$) is taken into account to simulate the fatty acid distribution that contains palmitic

acid ($C_{16}H_{32}O_2$), oleic acid ($C_{18}H_{34}O_2$), stearic acid ($C_{18}H_{36}O_2$) and linoleic acid ($C_{18}H_{32}O_2$). Total conversion of the triglycerides into acids and propane (C_3H_8) is assumed. Then an equilibrium reactor is employed for the simulation of the hydrotreating reactor involving hydrogenation, deoxygenation and reduction reactions. The product yield is determined by the equilibrium state of the occurred reactions in it [11],[12]. The formed light gases, mainly containing propane, are sent back to the the DFBG unit to be used as supplementary fuel for the oxidizer.

- Initial reactions for triglycerides decomposition:

$$C_{51}H_{98}O_6 + 3H_2 \rightarrow 3C_{16}H_{32}O_2 + C_3H_8 \quad (17)$$

$$C_{55}H_{98}O_6 + 4H_2 \rightarrow C_{16}H_{32}O_2 + C_{18}H_{34}O_2 + C_{18}H_{32}O_2 + C_3H_8 \quad (18)$$

- Hydrogenation:

$$C_{18}H_{32}O_2 + H_2 \rightarrow C_{18}H_{34}O_2 \quad (19)$$

$$C_{18}H_{34}O_2 + H_2 \rightarrow C_{18}H_{36}O_2 \quad (20)$$

$$C_{18}H_{32}O_2 + 2H_2 \rightarrow C_{18}H_{36}O_2 \quad (21)$$

- Decarboxylation:

$$C_{18}H_{36}O_2 \rightarrow C_{17}H_{36} + CO_2 \quad (22)$$

$$C_{16}H_{32}O_2 \rightarrow C_{15}H_{32} + CO_2 \quad (23)$$

$$C_{18}H_{34}O_2 \rightarrow C_{17}H_{34} + CO_2 \quad (24)$$

- Decarbonylation:

$$C_{18}H_{36}O_2 + H_2 \rightarrow C_{17}H_{36} + CO + H_2O \quad (25)$$

$$C_{16}H_{32}O_2 + H_2 \rightarrow C_{15}H_{32} + CO + H_2O \quad (26)$$

$$C_{18}H_{34}O_2 + H_2 \rightarrow C_{17}H_{34} + CO + H_2O \quad (27)$$

- Reduction:

$$C_{18}H_{36}O_2 + 3H_2 \rightarrow C_{18}H_{38} + 2H_2O \quad (28)$$

$$C_{16}H_{32}O_2 + 3H_2 \rightarrow C_{16}H_{34} + 2H_2O \quad (29)$$

The main process parameters for the hydrotreatment reactor are presented in Table 7:

Table 7. Hydrotreatment process parameters

Parameter	Input
Reactor pressure (bar)	40
Reactor temperature (°C)	350
Hydrogen-to-TAGs ratio (kg/kg)	0.03

Apart from the reactor, the feed stream pre-heating with the outlet stream cooling is taken into account. The hydrotreated microbial oil is separated from the gas phase (unreacted hydrogen, light hydrocarbons, produced CO/CO_2) and sent to a distillation column in order to retrieve the targeted drop-in biofuels. The last part of the process (i.e. isomerization, fractionation) has not been modeled in detail at this stage of the project and the produced alkanes are considered as the final product in this analysis.

4.2 Description of the examined scenarios

The BioSFerA concept is a BtL process that, apart from the nutrients and microorganisms for the biological step, has heat, electricity, steam, air/oxygen and hydrogen requirements. The overall plant efficiency, its operation mode and its full spectrum of capabilities are highly dependent on the effective securement and integration of all these parameters in the BtL scheme. The oxygen-based components (i.e. autothermal reformer, aerobic fermenter) have been identified as key aspects concerning the overall process character and functionality.

An oxy-blown autothermal reformer covers its heat requirements for the reforming reactions with partial oxidation of syngas. The high quality syngas along with the relatively low content of light hydrocarbons derived from the DFBG unit make the energy degradation of the gas that takes place with its partial oxidation affordable, since the gas that leaves the reformer is a nitrogen-free gas which still maintains a high energetic content (i.e. CGE > 80%) that can be used entirely for the liquid fuels production. An ATR can be operated also with air instead of oxygen, but the extended presence of nitrogen in the reformed gas may cause problems in the biotechnological part and its handling in general. On the other hand, an allothermal steam reformer can be operated with external heating from a combustor that utilizes air and not necessarily oxygen. The impact of WGS reaction in this case, due to the excess steam in the reformer and absence of oxidation, may be stronger creating a local energetic upgrade of the reformed syngas, but the external heat requirements are larger and remarkable part of the syngas should be used for combustion instead of fermentation. The latter is rather inefficient from the overall BtL point of view.

The other procedure that has oxygen requirements is the aerobic fermentation of acetate. The process can be driven as oxy-fermentation or air-fermentation. The difference is that fermentation with pure oxygen will lead to the formation of a quite pure CO_2 stream in the fermenter outlet and consequently strengthen the CCS & CCU ability of the plant. Therefore, in the reforming as well as in the aerobic fermentation case, it can be observed the beneficial impact of pure oxygen involvement. However, the cost of its production or purchase must be taken into consideration. The accurate estimation of the off-gas composition at the second fermenter and the ability to eliminate any remaining oxygen traces will be further investigated in the experimental and piloting activities of the project in WP3 and WP4.

There are also hydrogen requirements in the process chain and in particular in the hydrotreatment unit, but they are expected to be low. The disproportionately lower hydrogen requirements in comparison with the oxygen requirements of the plant, means that potential oxygen securement via water electrolysis would be accompanied with excess of pure hydrogen. The establishment of an electrolysis unit to cover primarily oxygen demands instead of hydrogen seems rather unreasonable and inefficient for the plant. However, in this way two valuable off-gases (i.e. pure CO_2 from oxy-fermentation of acetate & pure H_2 from the water electrolysis) are produced that are capable of completely upgrading the plant

either via their re-utilization in the biotechnological part (i.e. CO_2 + H_2 fermentation) or via other catalytic routes of fuel synthesis. If there is not electrolysis implementation, then the required hydrogen for the hydrotreatment can be obtained from syngas via PSA.

Finally, the steam requirements of the plant can be covered with a HRSG section that utilizes the waste heat from the DFBG unit and produces steam. A Steam Turbine (ST) system for power production could be applied also in the end of the HRSG unit in case of excess heat in high temperatures.

After taking all the above mentioned points into consideration, the following preliminary scenarios have been developed and simulated for the BioSFerA concept:

- **1st scenario:** In this case study, the establishment of an electrolysis unit is assumed for hydrogen production. This means, that pure oxygen can be available also for the autothermal reformer as well as for the aerobic fermentation of acetate. The produced syngas is utilized entirely for the final fuels production, meaning that the efficiency of the BtL plant is high and it can be further enhanced from the emerging pure streams of H_2 and CO_2. Of course, since water electrolysis is a rather expensive choice, it can be considered only in case of low-cost RES electricity. Otherwise, this scenario refers to a scheme with high electricity demands.

- **2nd scenario:** In this case study, electrolysis unit is not involved. Pure industrial oxygen can be purchased externally for oxy-autothermal reforming or oxy-fermentation of acetate. Otherwise, autothermal reforming with limited air can be applied and respectively air fermentation that will lead in a N_2/CO_2 mixture in the fermentor gas outlet. The chemical energy of the produced syngas is utilized once again almost entirely for the biofuels production, apart from a small portion of hydrogen that is extracted via PSA from the recirculating off-gases of the anaerobic fermentor in order to secure the hydrotreatment hydrogen requirements.

- **3rd scenario:** In this case study, no use of pure oxygen is considered neither in the reformer nor in the aerobic fermentor. The technology of allothermal steam reforming is applied, which imposes an assisting combustor that utilizes air and part of the syngas to provide the appropriate heat to the reformer. This is achieved by extracting a portion of the recirculating off-gases of the anaerobic fermentor and sending them in the SMR combustor. The hydrogen requirements are covered again from the same stream via PSA and therefore the syngas 'losses' in terms of fuels production are expected remarkable and the BtL plant efficiency low. However, the flue gases stemming from the SMR combustor in this case is an additional hot source that can be thermally exploited. The primary objective is the steam generation for the reforming, but its further thermal utilization could boost a potential power generation of the plant with the addition of a ST.

The preliminary examined scenarios in a more concise form (Table 8):

Table 8. Preliminary integration scenarios for the BioSFerA concept

	1st scenario	2nd scenario	3rd scenario
Water electrolysis unit	✓		
Oxy-autothermal reformer	✓	✓	
Allothermal reformer			✓
Acetate oxy-fermentation	✓		
Acetate air-fermentation		✓	✓
PSA		✓	✓
HRSG	✓	✓	✓
Steam Turbine			✓

4.3 Process simulations results

In this section, the basic stream results from each sub-unit are presented as well as some key performance indicators for the overall process efficiency are calculated. The heat and mass balances are performed for each case study and indications for the overall plant performance are assessed. Two critical factors are introduced:

- Total carbon utilization factor is the fraction of carbon in initial feedstock that is converted to the final fuels. Hereinafter referred to as **Carbon Utilization (CU).**
- Drop-in fuel to feed energy ratio is the fraction of the chemical energy in the initial feedstock that is transferred to the final fuels. Hereinafter referred to as **Energetic Fuel Efficiency (EFE)**.

4.3.1 1st scenario

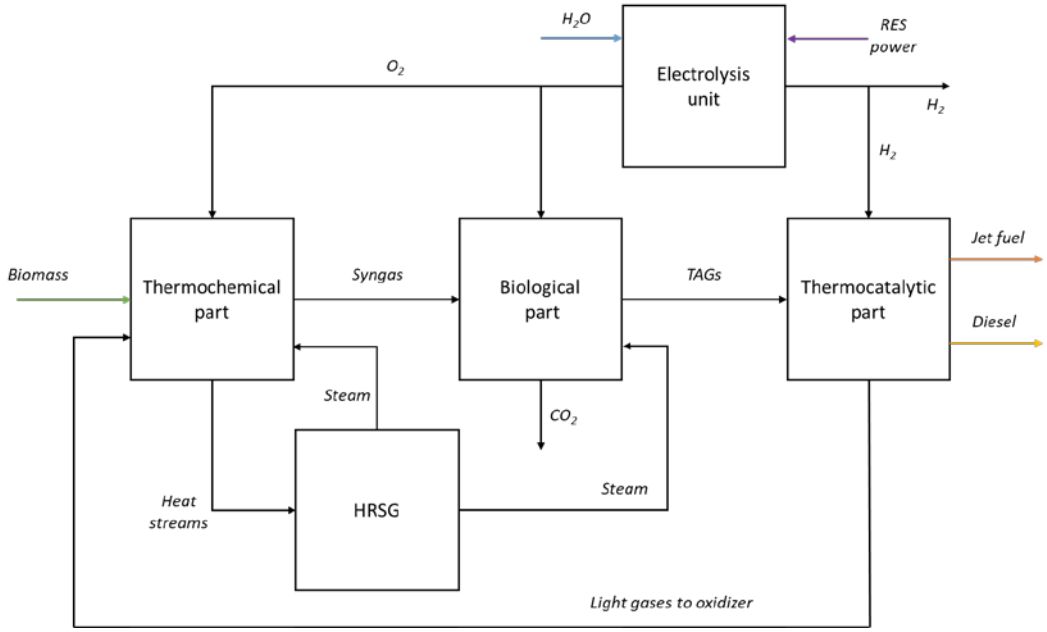

Figure 14. The block flow of the 1st scenario integrated concept

The integrated concept of the 1st case study is illustrated in Figure 14. A water electrolysis unit feeds the BtL plant with oxygen and hydrogen, while the HRSG unit exploits the thermal load of the hot gases to cover the process steam requirements (i.e. gasification, reforming, lipids purification). In case all the oxygen requirements are covered from the electrolyzer, excess of hydrogen and a quite pure stream of CO_2 are obtained along with the final liquid products.

Thermochemical part:

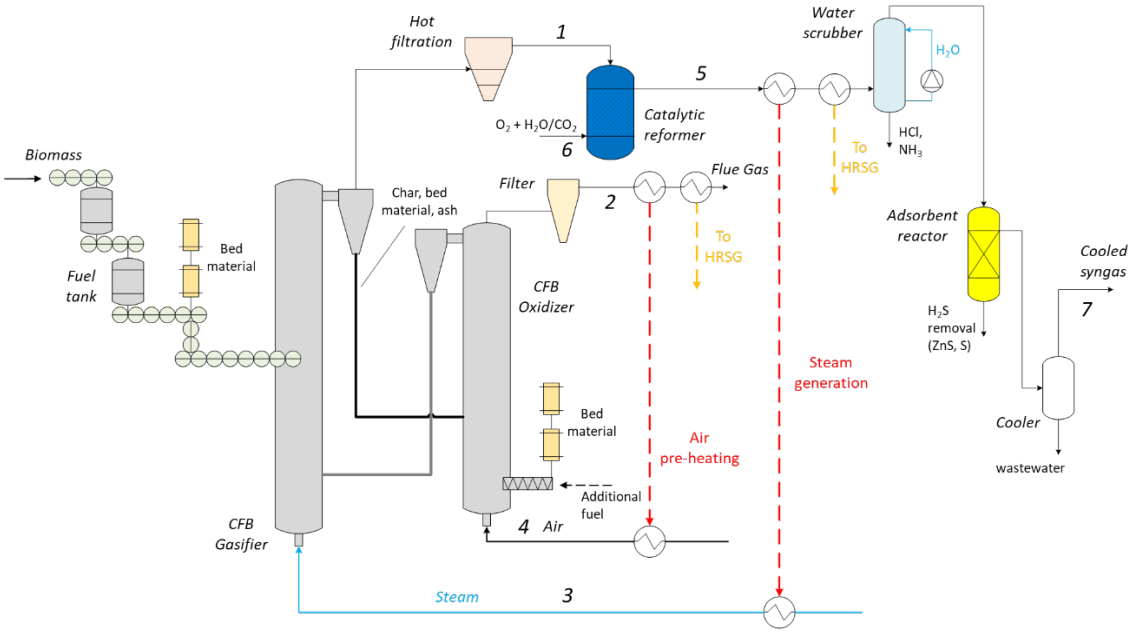

Table 9. Main stream results for the DFBG unit (Scenario 1)

Stream No	1 Syngas after filtration	2 Flue gases after filtration	3 Pre-heated steam	4 Pre-heated air	5 Reformed syngas (ATR)	6 Reforming agent (ATR)	7 Cooled syngas
Mass flow (kg/s)	16.60	20.24	6.92	18.83	19.70	3.10	12.89
Temp (°C)	780	880	350	400	900	350	15
Press (bar)	1.3	1.1	1.5	1.5	1.1	1.5	1.1
Composition (vol. %)							
H_2	29.07	-	-	-	35.75	-	53.38
CO	10.95	-	-	-	16.64	-	24.85
CO_2	14.78	16.16	-	-	12.59	-	18.79
H_2O	37.09	1.91	1	-	34.05	63.98	1.57
N_2	119 ppm	77.90	-	0.79	712 ppm	-	0.1
H_2S	186 ppm	-	-	-	143 ppm	-	64 ppm
CH_4	5.49	-	-	-	0.85	-	1.27
NH_3	0.2	-	-	-	308 ppm	-	112 ppm
HCN	12 ppm	-	-	-	2 ppm	-	2.5 ppm
COS	11 ppm	-	-	-	-	-	-
C_2H_4	1.81	-	-	-	-	-	-
C_6H_6	0.4	-	-	-	30 ppm	-	36 ppm
$C_{10}H_8$	0.2	-	-	-	1 ppm	-	-
O_2	-	4.02	-	0.21	-	36.02	-

For the evaluation of the DFBG unit performance, a critical parameter is the Cold Gas Efficiency (CGE). CGE is the fraction of the chemical energy in the initial feedstock that is transferred to syngas in the gasifier. This is measured to be 85% after the hot filtration of syngas, while it drops to 80% after the ATR since partial oxidation of syngas takes place at the auto-reforming procedure.

Biotechnological part:

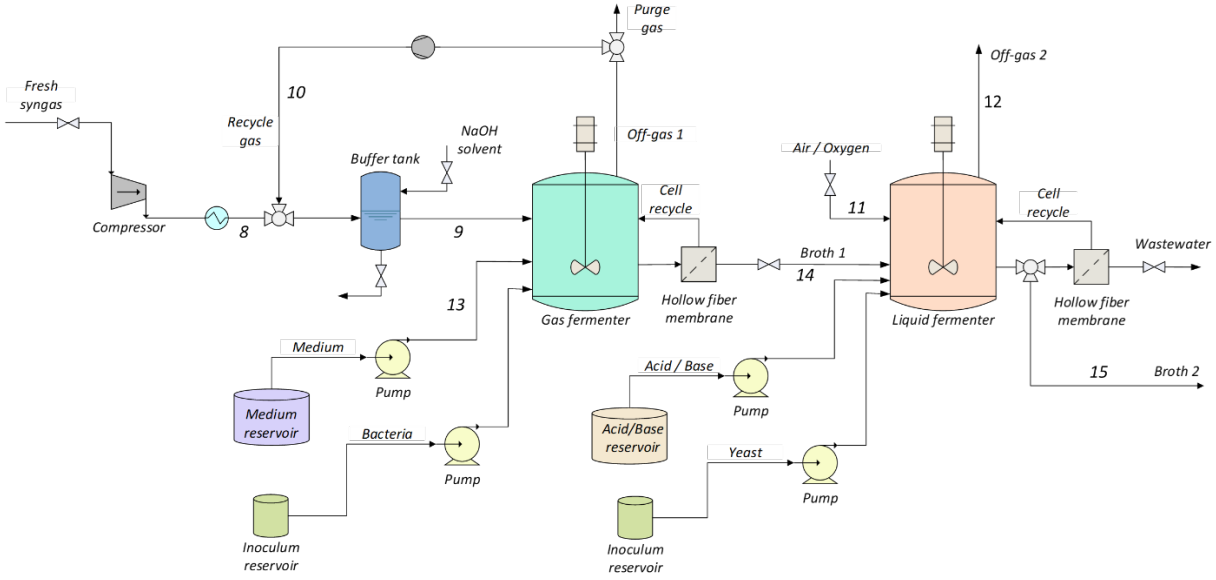

Table 10. Main stream results for the double-stage fermentation (Scenario 1)

Stream No	8 Compressed fresh syngas	9 Gas prior fermenter	10 Recycle gas	11 Oxygen	12 Off-gas	13 Medium	14 Broth -1	15 Broth -2
Mass flow (kg/s)	12.89	84.97	72.08	2.81	6.37	193.06	203.81	21.75
Temp (°C)	55	55	55	30	30	55	30	30
Press (bar)	5	5	5	1	1	5	1	1
	Composition (vol. %)					**Composition (wt. %)**		
H_2	53.38	28.81	21.06	-	-	-	-	-
CO	24.85	9.61	4.81	-	-	-	-	-
CO_2	18.80	47.48	56.52	-	95.5	-	0.2	0.1
H_2O	1.57	1.38	1.32	-	4.3	1	95.7	90.9
N_2	0.1	0.98	1.26	-	0.2	-	-	-
H_2S	64 ppm	120 ppm	150 ppm	-	-	-	-	-
CH_4	1.27	11.69	14.97	-	-	-	-	-
NH_3	112 ppm	28 ppm	-	-	-	-	-	-
C_6H_6	36 ppm	70 ppm	82 ppm	-	-	-	-	-
O_2	-	-	-	1	-	-	-	-
Acetate	-	-	-	-	-	-	4.1	-
Ethanol	-	-	-	-	-	-	22 ppm	-
$C_{51}H_{98}O_6$	-	-	-	-	-	-	-	1.5
$C_{55}H_{98}O_6$	-	-	-	-	-	-	-	7.5

The acetate concentration in the effluent stream (Broth-1) from the syngas fermentation is around 30 g/L, while the TAGs are collected in the effluent stream (Broth-2) from the aerobic fermentation in a concentration of 100 g/L as a result of the cell recycle system applied in the fermenter.

Thermocatalytic part:

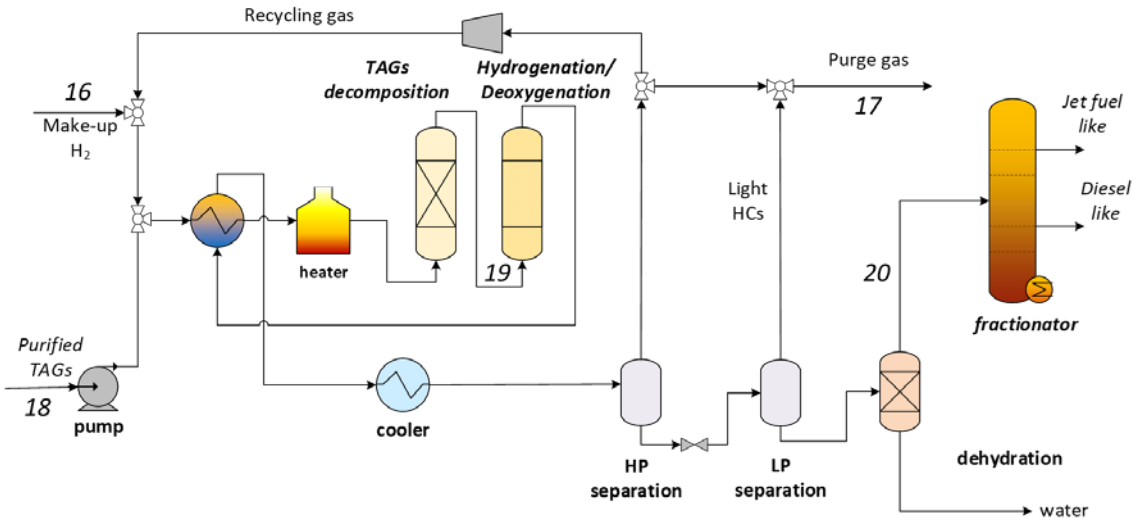

Table 11. Main stream results for the hydrotreatment unit (Scenario 1)

Stream No	16 Hydrogen	17 Light gases	18 Purified TAGs	19 Fatty acids /propane	20 Jet/Diesel paraffins
Mass flow (kg/s)	0.06	0.24	1.96	2.02	1.64
Temp (°C)	350	30	30	350	30
Press (bar)	40	40	1	40	40
	Composition (vol. %)		**Composition (wt. %)**		
$C_{51}H_{98}O_6$	-	-	16.8	-	-
$C_{55}H_{98}O_6$	-	-	83.2	-	-
$C_{16}H_{32}O_2$	-	-	-	40.55	-
$C_{18}H_{32}O_2$	-	-	-	20.26	-
$C_{18}H_{34}O_2$	-	-	-	28.90	-
$C_{18}H_{36}O_2$	-	-	-	5.14	-
H_2	1	33.25	-	-	-
CO	-	0.6	-	-	-
CO_2	-	39.38	-	-	-
C_3H_8	-	26.78	-	5.15	-
$C_{15}H_{32}$	-	-	-	-	16.69
$C_{16}H_{34}$	-	-	-	-	25.49
$C_{17}H_{36}$	-	-	-	-	23.61
$C_{18}H_{38}$	-	-	-	-	34.21

According to the model, the decomposition of triglycerides leads to the formation of palmitic acid, oleic acid, linoleic acid and stearic acid as well as propane. The dominant species in the final liquid products are C_{16} & C_{18} alkanes. The light gases leaving the hydrotreatment reactor, consisting of propane, carbon dioxide and any remaining hydrogen are directed to the oxidizer of the DFBG unit in order to boost the gas production efficiency.

It should be mentioned that there is an amount of unconverted H_2 in the purge gas. At this stage of the project, the light gas stream is sent entirely to the oxidizer of the DFBG unit having an impact on the hydrogen make-up demands of the hydroprocessing unit. This issue will be further investigated in later stage when more realistic data from the hydrotreatment step will be available and therefore for any unconverted hydrogen handling.

Carbon & Energy Balance:

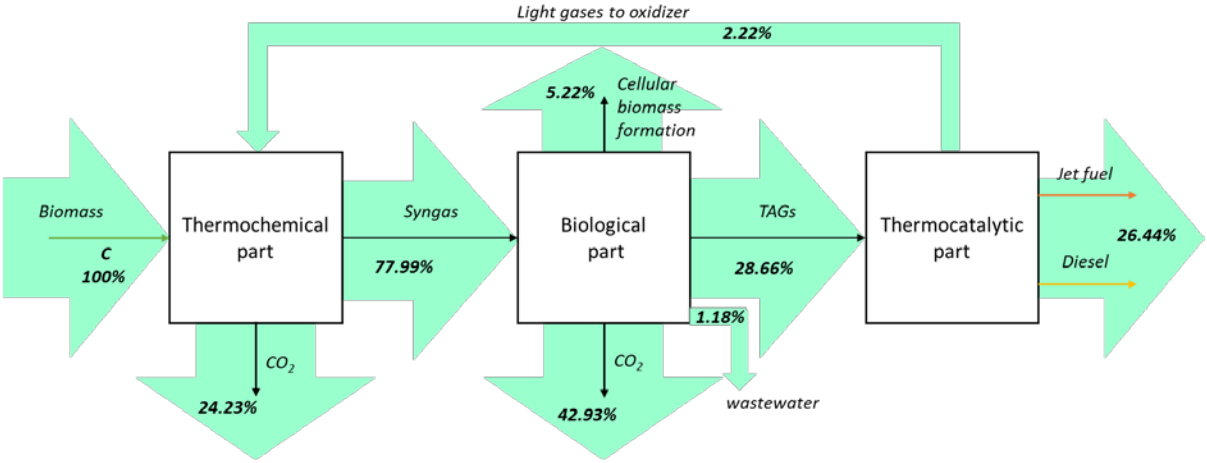

Figure 15. Carbon balance (Scenario 1)

The Carbon Utilization (CU) of the BtL plant, meaning the carbon content of the final liquid fuels, has been calculated equal to **26.44%**. A high carbon content (42.93%), as expected, is found in the rich CO_2 stream that leaves the aerobic fermenter. Further utilization of this CO_2 along with the hydrogen excess sourcing from the electrolyzer can remarkably increase the CU of the BtL plant and reach values greater than 37%. The rest carbon 'expenses' of the process are the flue gases leaving the oxidizer (24.23%), the carbon utilized for the cellular biomass formation in both fermenters (5.22%) as well as the low organic content of wastewaters (1.18%).

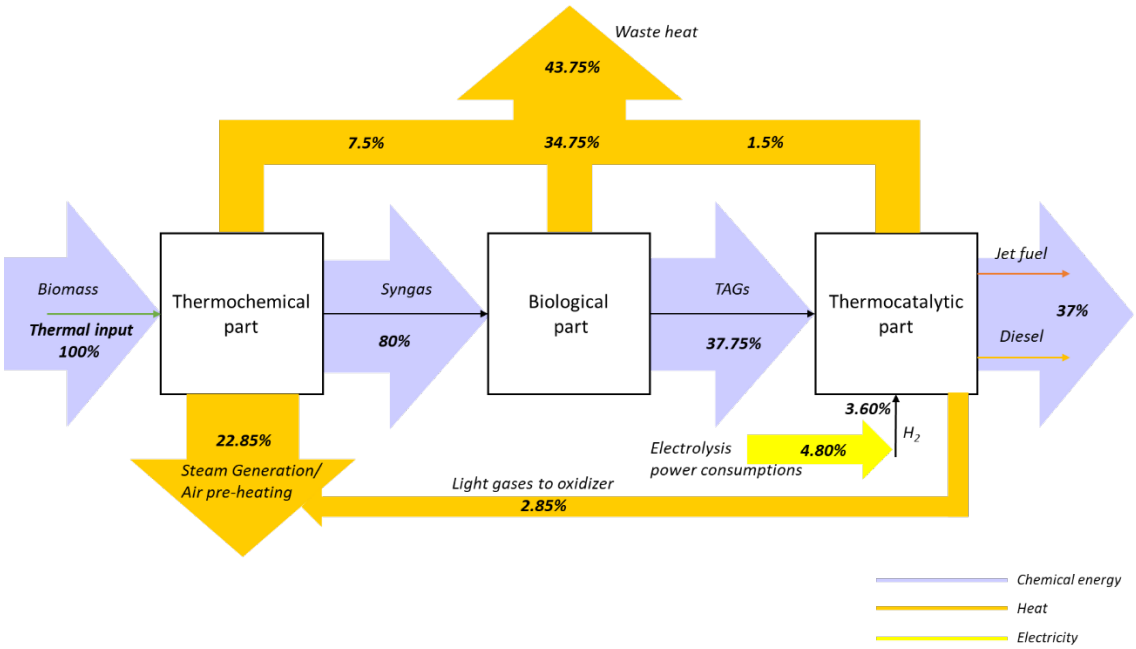

Figure 16. Energy Balance (Scenario 1)

The Energetic Fuel Efficiency (EFE) is measured at **37%**. Heat recovery for steam generation and the oxidizer's air pre-heating is performed from the hot streams of the DFBG unit (i.e. syngas & flue gases) (22.85%). The main energy losses are observed in the double-stage fermentation (34.75%), while the losses from the syngas cooling to the operating temperatures of the biotechnological part (7.5%) and the hydrotreatment unit (1.5%) are lower. Once again, the regulator concerning the EFE of the BtL plant is the further utilization of the rich CO_2 stream deriving from the aerobic fermenter. With re-involvement of this stream in the syngas fermentation process, EFE values greater than 45% can be achieved.

In general, it can be observed that the quite pure CO_2 stream sourcing from the oxy-fermentation of acetate is a key stream for the overall plant performance**. Its redirection and the re-utilization of its carbon content will enhance the CU as well as the EFE of the plant in a remarkable way (i.e. CU>37% & EFE>45%)**. A prerequisite of this strategy is the relative purity of CO_2, something that is achieved with controllable oxy-fermentation of acetate.

4.3.2 2nd Scenario

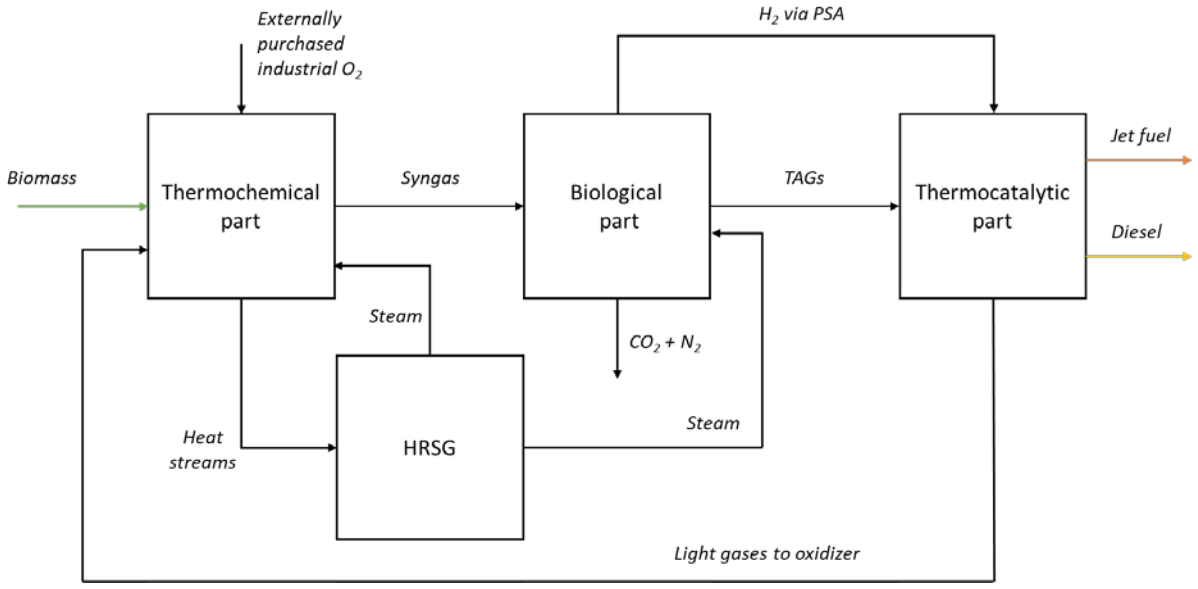

Figure 17. The block flow of the 2nd scenario integrated concept

The integrated concept of the 2nd case study is illustrated in Figure 17. In the absence of an electrolysis unit, autothermal reforming is performed with the assistance of externally purchased industrial oxygen, while the hydrogen requirements of the hydrotreatment unit are covered via PSA with extraction from the off-gases of the anaerobic fermenter. Industrial oxygen could be purchased also for the aerobic fermentation in order to achieve high CO_2 purity in the off-gases, but this would lead to remarkably higher operational costs.

Thermochemical part:

There is no substantial difference in the stream results of the thermochemical part that were presented in section 4.3.1, since the slight differentiation in the configuration of the 2nd scenario lies on the biotechnological part and specifically in the H_2 extraction. The same oxygen quantities that were secured from the electrolyzer of the 1st case are also purchased in this case externally, so the autothermal reforming is not influenced. The only deviation that might be observed is in the oxidizer's flue gases composition due to the slightly different light gases composition that occurs from the hydrotreatment unit, but it is negligible.

Biotechnological part:

As mentioned, the PSA technology is involved in the recirculating gases of the gas fermentation unit in order to extract the required hydrogen for the subsequent triglyceride's hydrotreatment. This extraction, that can be assumed as a light syngas 'loss' for the BtL plant, affects the efficiency of the syngas fermentation and is translated to slightly lower syngas conversion to acetate and consequently lower liquid fuels production and carbon conversion to biofuels. On the other hand, since the plant's hydrogen requirements are not extended, PSA technology, that permits internal hydrogen exploitation from

syngas, might be preferable in terms of pure hydrogen generation in comparison with the establishment of a whole electrolysis unit. Nevertheless, the latter offers the pure oxygen capability that, as explained in section 4.3.1, is of high importance for the plant's full spectrum of abilities and overall efficiency.

If air-fermentation will be applied in the aerobic fermenter, the emerging gas presents a high nitrogen percentage (N_2~65% vol.) and the re-utilization of its carbon content (CO_2~31%) becomes a very challenging and surely energy and cost intensive task.

The configuration of the biotechnological part for the 2nd scenario is illustrated in Figure 18. Highlighted is the PSA addition.

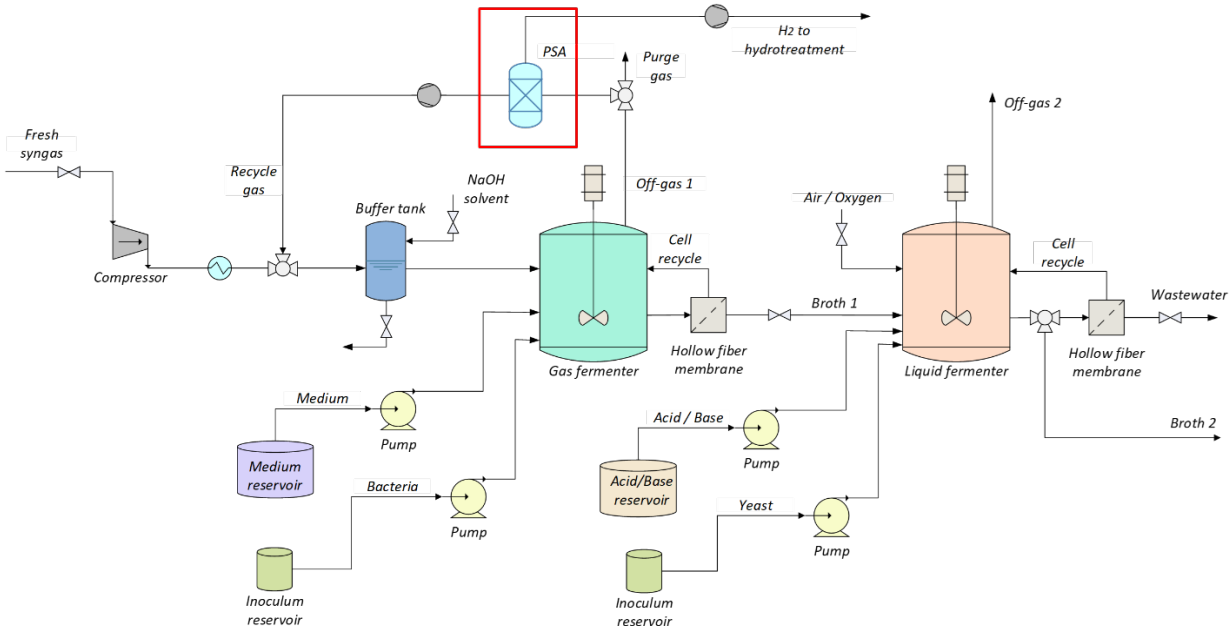

Figure 18. PSA & Air-fermentation in the biotechnological part (Scenario 2)

Thermocatalytic part:

The configuration and the operational parameters of the hydrotreatment unit do not change. The two differences are located in the hydrogen source and the liquid fuels yield. Concerning the hydrogen, the hydrotreatment of the triglycerides is carried out by utilizing hydrogen extracted from syngas instead of hydrogen produced from electrolyzer, while the lower syngas conversion to acetate will be reflected to lower yields of final products (i.e. liquid fuels).

Carbon & Energy Balance:

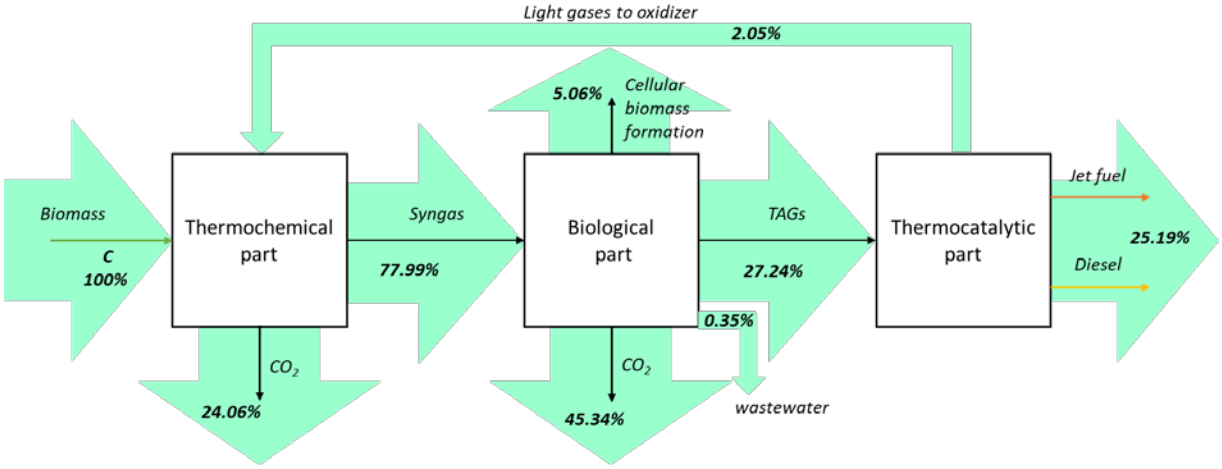

Figure 19. Carbon Balance (Scenario 2)

The obtained CU for the 2nd scenario is measured at **25.19%**. The slightly lower fuel yield is reflected also in terms of carbon exploitation. The extracted syngas may consist only of hydrogen, but this syngas 'loss' influences the composition of the recirculating off-gases and subsequently reduces the carbon conversion to acetate in the anaerobic fermenter.

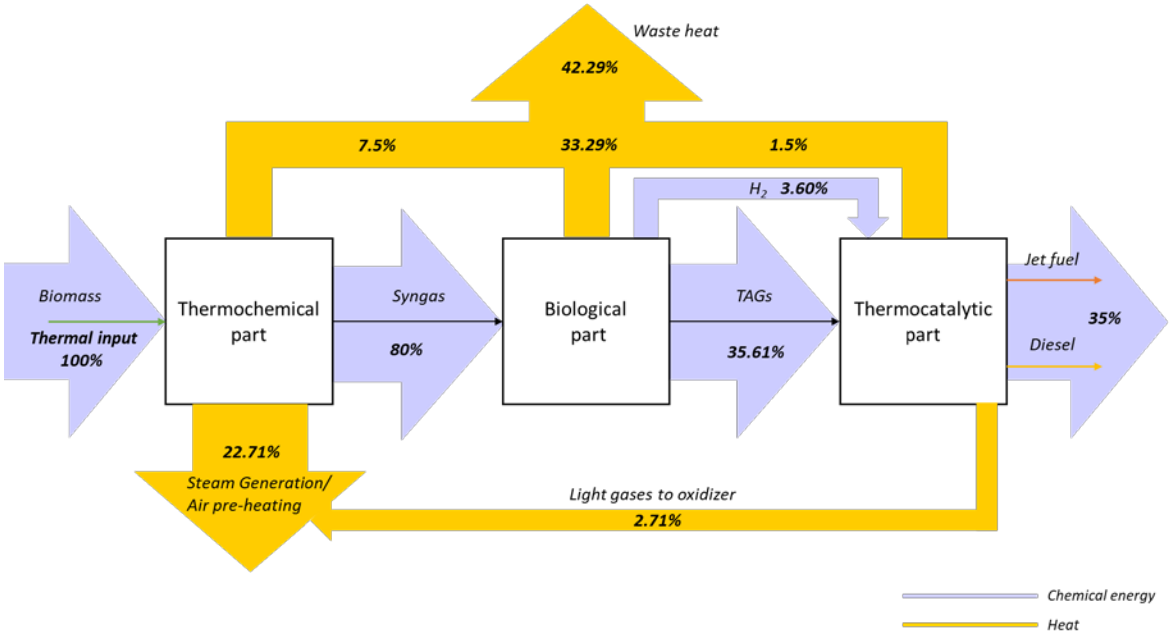

Figure 20. Energy Balance (Scenario 2)

The impact of the internal hydrogen extraction in the energy balance of the process can be observed in Figure 20. An EFE equal to **35%** is obtained. The lower acetate production leads to lower energy content of the produced TAGs.

In general, the observed decrease in CU & EFE of the BtL plant can be characterized as affordable. The involvement of the PSA technology and the internal securement of the limited hydrogen needs of the process seem to have a controllable effect on the process performance. The avoidance of an electrolysis unit would drastically reduce the capital and operational costs of the plant. However, the main shortcoming of a scheme without the capability of pure oxygen is that the off-gases of the aerobic fermenter will be a mixture of CO_2 and N_2 and therefore their carbon re-utilization will be difficult. The pros & cons of each approach should be thoroughly considered in the techno-economic analysis that will take place in later stages of the project.

4.3.3 3rd Scenario

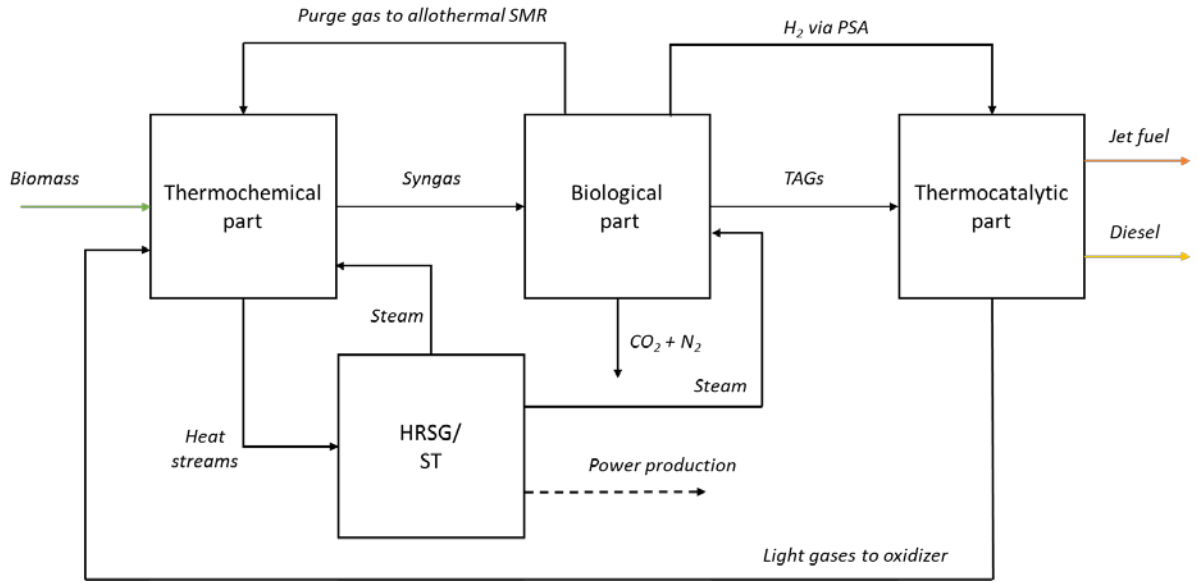

Figure 21. The block flow of the 3rd Scenario integrated concept

The integrated concept of the 3rd case study is presented in Figure 21. In this scenario, there is not any pure oxygen involvement since the reforming (i.e. allothermal) as well as the aerobic fermentation procedures are performed with air utilization. The required heat input for the allothermal reformer is secured with partial gas extraction from the recirculating gases of the anaerobic fermenter. The same goes for hydrogen, which is extracted via PSA from the same stream. The possibility of a Steam Turbine (ST) addition for power production is left open in this case, since, due to the flue gases of the allothermal SMR, waste heat streams in higher temperatures are expected and subsequently higher steam production capacity.

Thermochemical part:

The major difference that this configuration presents in comparison with the previous case studies is the allothermal reforming, where air is used instead of oxygen. No partial oxidation of syngas takes place and therefore only with the impact of the reforming reactions, a syngas quality upgrade is observed. However, the energy demand of the reforming reactions and the steam production is quite high and subsequently remarkable amounts of syngas are required as supporting heat source for the reformer. The reformer operates at 900 °C and the assisting combustor at 950 °C.

The flowsheet of the thermochemical part for the 3rd scenario is illustrated in Figure 22. Highlighted is the operating scheme of allothermal reforming.

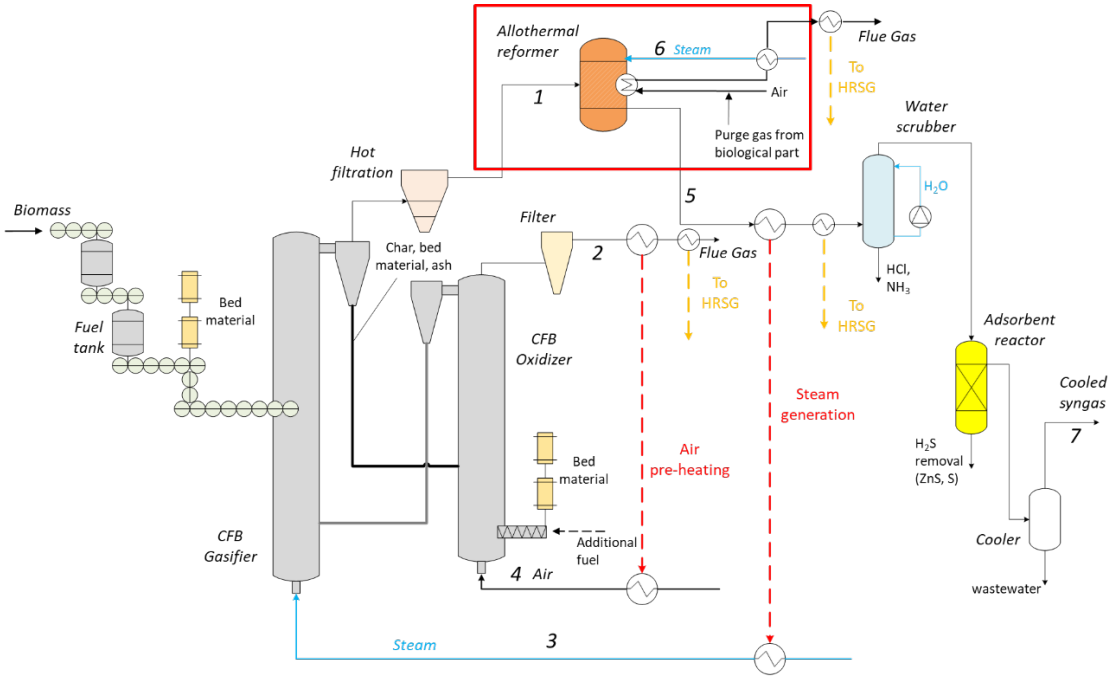

Figure 22. Allothermal reformer integration in the thermochemical part (Scenario 3)

Biotechnological part:

A remarkable portion of the recirculating off-gases from the anaerobic fermenter is directed to the allothermal reforming unit. In particular, 35% of this stream is used as energy source for the appropriate reforming procedure. Therefore, the mentioned syngas losses are reflected to the observed lower acetate yields of the anaerobic fermentation process. Concerning the aerobic acetate fermentation, air is used as in the previous case study.

The biotechnological configuration of the 3rd scenario is presented in Figure 23. Highlighted are the extractions from the recirculating off-gases.

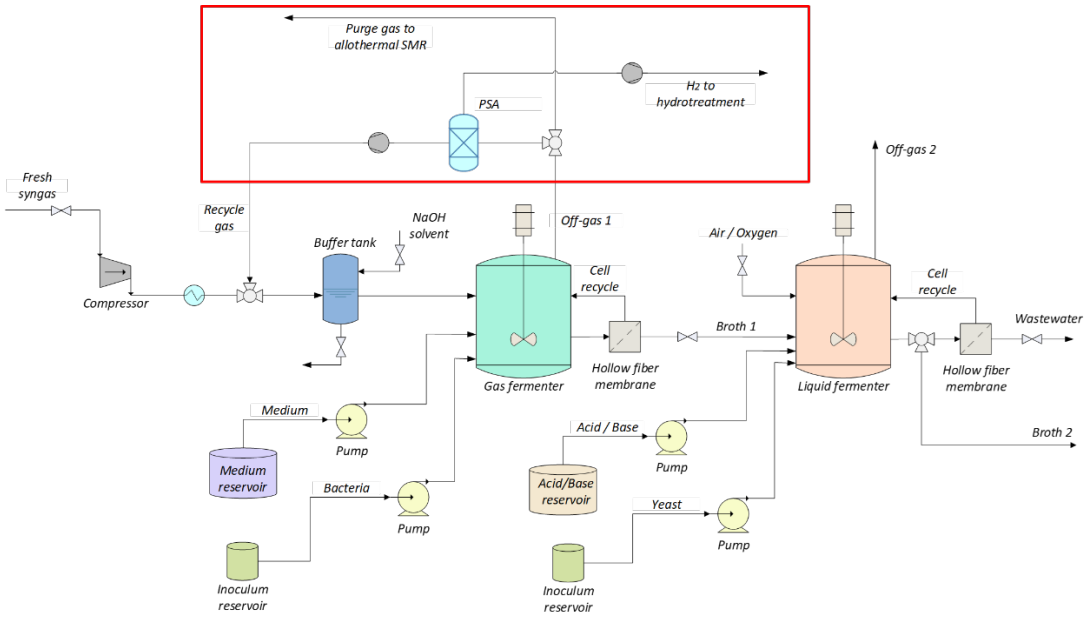

Figure 23. Extracted purge gas and hydrogen from the biotechnological part (Scenario 3)

Thermocatalytic part:

Since the TAGs production will be lower, due to the syngas losses in the biotechnological part, slightly lower hydrogen will be required for the hydrotreatment unit. As mentioned, lower yield of the final liquid products are present. The configuration of the hydrotreatment unit as well as the operational parameters are the same.

Carbon & Energy Balance:

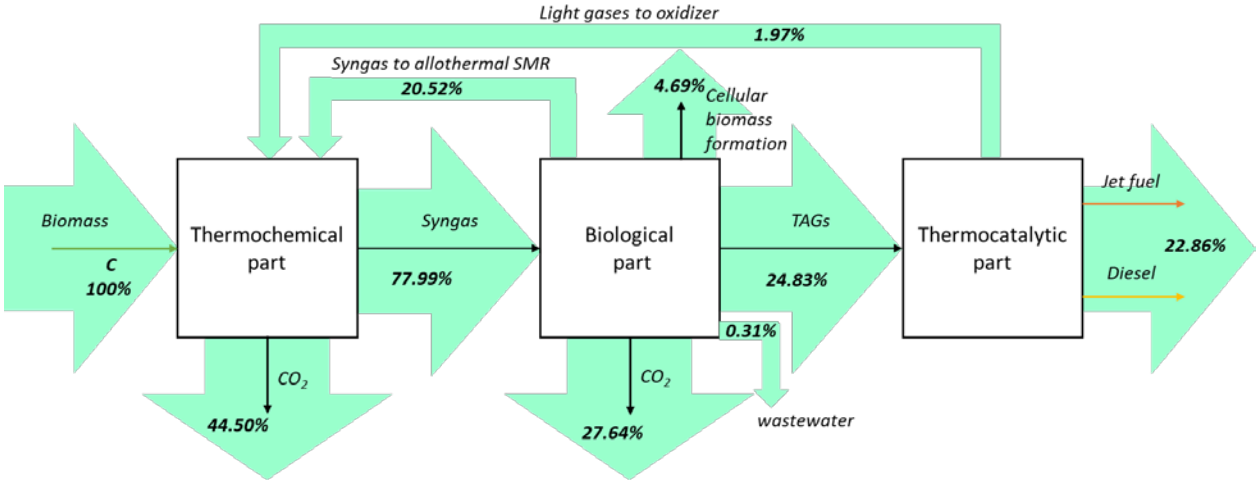

Figure 24. Carbon Balance (Scenario 3)

The obtained CU for this case study is equal to **22.86%**. A remarkable carbon content (20.52%) is transferred to the supporting combustor of SMR and ends up as an additional CO_2 emission from the

thermochemical part. Therefore, in terms of carbon, an increase in the carbon content that is released from the thermochemical unit is observed due to the presence of two flue gas sources now (i.e. DFBG oxidizer & SMR combustor). The allothermal operation of the reformer seems to have a notable negative impact on the overall performance of the BtL plant, since a non-negligible amount of syngas ends up as flue gas in the SMR combustor instead of acetate and subsequently liquid fuel.

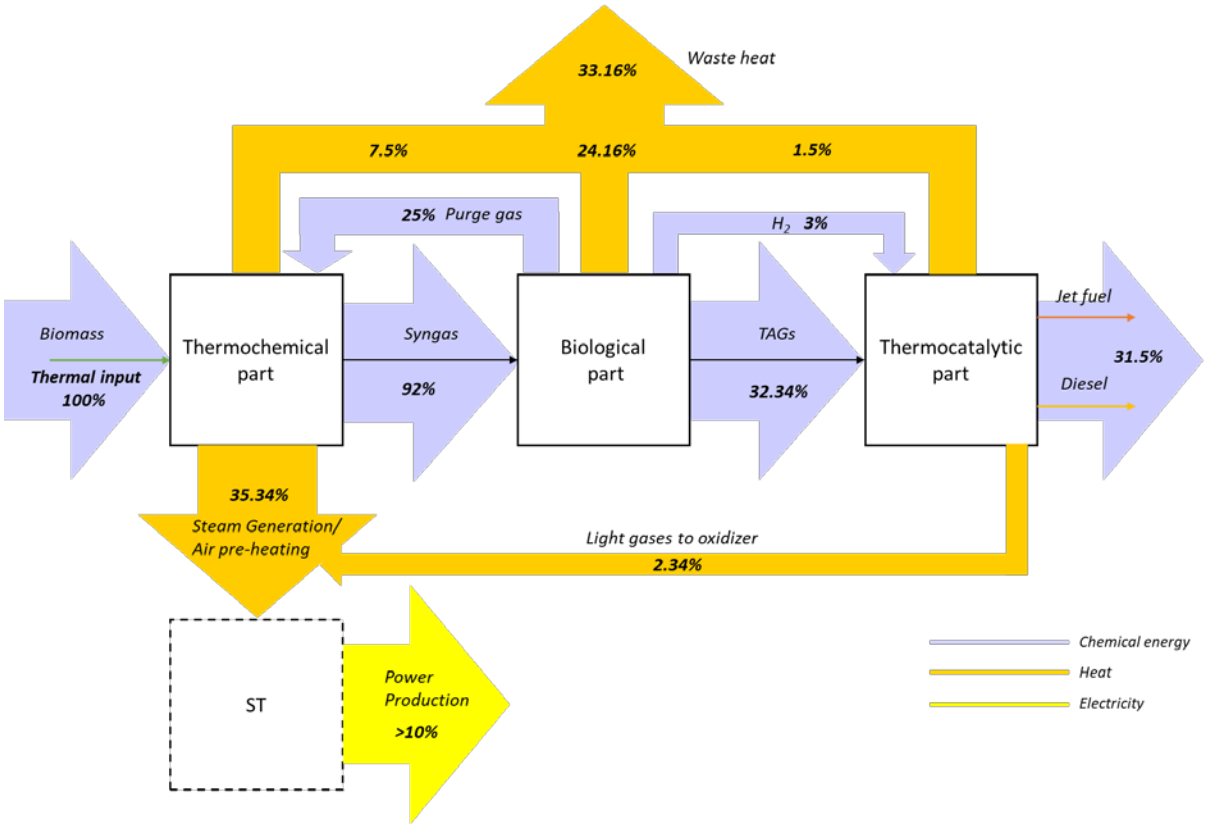

Figure 25. Energy Balance (Scenario 3)

The decreased performance of the BtL plant is also reflected in the EFE that is calculated at **31.5%**. The purge gas that is transferred to the reforming combustor contains a remarkable energy content (25%) that does not participate in the CU or EFE enhancement. However, the flue gases of the SMR combustor is a hot stream that updates the heat recovery and steam generation capability of the plant. For this reason, this is the only case study that the addition of a Steam Turbine could make sense in terms of power production (>10% of thermal input). The exact steam requirements of the plant and especially for the lipids purification, where quite novel techniques will be applied, have not been decisively defined yet. Therefore, only a generic estimation for the power production ability could be extracted for the time being. Nevertheless, it has to be mentioned that this is the only case that seems to have the potential to offer partial power-independence of the plant via a polygeneration scheme of power, heat and fuel production, although this is beyond the scope of the concept.

4.3.4 Scenarios assessment

The two overall performance indicators, **CU & EFE**, are gathered and presented for all case studies in Table 12:

Table 12. Overall performance indicators for all three scenarios

Scenario No	1st Scenario	2nd Scenario	3rd Scenario
Carbon Utilization (CU)	26.44% (37*)	25.19%	22.86%
Energetic Fuel Efficiency (EFE)	37% (45*)	35%	31.5%

* These numbers refer to further exploitation of the pure CO_2 & H_2 streams that are obtained in the 1st scenario

A general finding from the simulation results is that an efficient combination of hydrogen and oxygen securement is a crucial factor for the overall plant performance. The approach that seems to come closest in this direction is the 2nd case study. The minor hydrogen requirements of the plant turn the PSA technology into a smart option for internal hydrogen extraction without extended losses for the liquid fuels production. An economic purchase of external industrial oxygen could secure the autothermal reforming procedure (ATR) and perhaps partially an oxy-fermentation of acetate. The establishment of an electrolysis unit for the acquirement of pure oxygen primarily, since hydrogen needs are limited, can stand only in case of further re-utilization of the obtained pure H_2 and CO_2 streams in the BtL plant, but even in this case the financial penalty that occurs due to the electrolysis involvement seems unable to be covered. The establishment of an electrolysis unit would drastically increase the operational costs of the plant and only a thorough techno-economic analysis would be able to assess the eligibility and sustainability of such a configuration.

Concerning the alternative scheme that was investigated within scenario 3, the involvement of allothermal reforming seems inappropriate for this concept. Remarkable percentage of valuable syngas ends up as flue gas for the thermal assisting of the reformer operation and the reflected impact on the final products yield was evident.

Of course, as it has already been mentioned, this is a first assessment of the conceptual design of the process based on preliminary data. The complete development of the experimental activities will shed light on various parameters of the process and permit a more mature and targeted re-evaluation of the concept and its subsequent optimization that will take place in later stages of the project (WP6).

5 Main key design & operational parameters

In this section, the boundary conditions between the different parts of the BioSFerA concept are provided. The presented operational conditions will act as a benchmark for the forthcoming experimental and pilot activities as well as for the general development of the technology.

5.1 Thermochemical part

The main components of the thermochemical part are the gasifier, the oxidizer, the catalytic reformer and any gas cleaning step that will be required prior the connection with the biological part. The spectrum of the most important process parameters is presented in Table 13:

Table 13. Operating conditions for the DFBG unit and the catalytic reformer

Process parameter	Range
Gasifier temperature (°C)	760 - 830
Gasifier pressure (bar)	1 - 1.5
Steam-to-Biomass ratio in the gasifier (kg/kg)	0.7 - 1.2
Oxidizer temperature (°C)	850 - 920
Oxidizer pressure (bar)	1 - 1.1
O_2 content in the oxidizer flue gases (% vol.)	4 - 6
Catalytic reformer temperature (°C)	800 - 980
Catalytic reformer pressure (bar)	1 - 1.1
Steam/oxygen ratio in the reformer (ATR) (kg/kg)	1 - 1.2
Steam & Air pre-heating temperature (°C)	300 - 400

The exact gas cleaning chain is still to be defined, since the experiments related to the bacteria resistance to syngas contaminants are still ongoing. However, a mild gas cleaning, involving scrubbers and adsorbers for partial removal of contaminants in order to avoid inert accumulation in the gas fermentation process, is expected to be applied. Indicatively, the removal of H_2S with the assistance of metal oxides (e.g. ZnO) as adsorbent materials is performed effectively at temperatures >200 °C.

5.2 Biotechnological part

The biotechnological procedure of the BioSFerA concept includes the anaerobic syngas fermentation, the aerobic acetate fermentation and the subsequent lipids purification via steam explosion. *Moorella thermoacetica* is the preferable reference acetogenic bacterium for syngas fermentation, while *Yarrowia lipolytica* is the yeast strain that will be involved in the liquid substrate fermentation of acetate. The main operating parameters for the biotechnological part are presented in Table 14:

Table 14. Operating conditions for the biotechnological part of the process

Process parameter	Range
Syngas fermentation temperature (°C)	55 - 60
Syngas fermentation pressure (bar)	5 - 8
Syngas fermentation recycle rate (%)	95 - 100
Acetate fermentation temperature (°C)	25 - 30
Acetate fermentation pressure (bar)	1 – 1.1
Steam temperature for steam explosion (°C)	180 - 240

The higher the anaerobic fermenter's off-gases recycle rates, the higher the syngas conversion into acetate that will be achieved. A potential inhibitor for high recycle rates is the inerts and unconverted gases accumulation in the recirculating stream, something that depends on the H_2/CO/CO_2 ratio of fresh syngas, operating pressure, etc. The experimental activities for the optimization of the biotechnological process are ongoing and are expected to upgrade the efficiency of the plant.

5.3 Thermocatalytic part

The core of the thermocatalytic part of the concept is the hydrotreatment unit where the consecutive hydrogenation, deoxygenation, isomerization and fractionation procedures of the purified triglycerides take place. The main process parameters for the hydrotreatment unit are presented in Table 15:

Table 15. Operating conditions for the hydrotreatment unit

Process parameter	Range
Hydrotreatment temperature (°C)	350 - 400
Hydrotreatment pressure (bar)	40 - 50
H_2/ TAGs ratio (kg/kg)	0.03 - 0.05

6 Conclusions & Outlook

In this deliverable, the preliminary definition of the overall BioSFerA concept and its individual components has been performed. The heat and mass balances for alternative configurations have been calculated and the operational framework of the process sub-units has been set.

The feedstock selection, the DFBG unit and gas conditioning, the syngas fermentation, the acetate fermentation as well as the TAGs purification and subsequent hydrotreatment have been identified as the appropriate sections to describe the concept at full-scale from start to end. A more general definition of the BioSFerA BtL plant would separate the process into a thermochemical part, a biotechnological part and a thermocatalytic part. The DFBG unit accompanied with the catalytic reformer and the gas conditioning section form **the thermochemical part** of the process. Then, **the biotechnological part** follows and consists of the double stage syngas fermentation and the obtained TAGs purification via steam explosion. Finally, **the thermocatalytic part** refers to the hydrotreatment procedure as well as the final isomerization and fractionation actions in order the liquid drop-in fuels to emerge.

The cases of autothermal and allothermal reforming were investigated as well as the cases of oxy- and air-fermentation of acetate. Moreover, the securement of hydrogen needs externally via water electrolysis, but also internally via PSA have been taken into account. The heat recovery and steam generation capability of the plant is assessed and potentially the self-power production via a ST addition. Three case studies, involving all these factors, were developed and simulated aiming to carry out a wide evaluation of the different concept pathways and integration schemes.

The 1st case study involves a water electrolysis unit that offers the ability of pure hydrogen and oxygen production of the plant. The 2nd case study investigates the hydrogen extraction internally via PSA and the external purchase of industrial oxygen for autothermal reforming, while within the 3rd case the pure oxygen requirements of the plant vanish via allothermal reforming and air-fermentation of acetate.

A short description of the three scenarios along with the identified pros & cons are presented in Table 16.

Table 16. Examined case studies advantages & disadvantages

Case study No	1	2	3
Short description – key aspects	water electrolysis, oxy-autothermal reformer, oxy-fermentation of acetate, HRSG	oxy-autothermal reformer, air-fermentation of acetate, PSA, HRSG	allothermal reformer, air-fermentation of acetate, PSA, HRSG, ST
Advantages	- High BtL efficiency - Pure oxygen production - Potential reutilization of pure H_2 & CO_2 streams	- High BtL efficiency - Low power consumptions - Water electrolysis avoidance	- No pure oxygen requirements - High potential of power independence
Disadvantages	- Extended power consumptions - External purchase of industrial oxygen*	- External purchase of industrial oxygen	- Low BtL efficiency

* In case the electrolyzer operates only to secure the limited hydrogen requirements of the hydrotreatment unit, then the corresponding oxygen production is not enough to cover autothermal reforming or/and oxy-fermentation of acetate. The additional required oxygen should be purchased externally.

Carbon Utilization (CU) and **Energetic Fuel Efficiency (EFE)** were the main performance indicators that were used for the assessment of each scenario's heat and mass balances. Values between 22 and 27 % were obtained for the CU of the BtL plant and values between 31 and 37 % for the EFE. The major carbon and energy losses are observed in the biotechnological part. **The ongoing experimental activities concerning the optimization of the double-stage syngas fermentation (recirculation rates, gas solubility, optimum parameters, etc.) are expected to reduce these losses and enhance the overall performance of the BtL plant.** If re-utilization of CO_2 is considered, these values reach 37 % for the CU and 45% for the EFE.

The limited hydrogen requirements of the plant cannot probably justify the presence of such an energy-consuming unit like electrolyzer for its production. The securement of the oxygen requirements of the plant (ATR & oxy-fermentation of acetate) entirely via electrolyzer would create remarkable excess of H_2 production that could potentially be re-utilized in the biotechnological part, but an electrolyzer establishment primarily for oxygen production is unreasonable and inefficient. The only way in which the electrolyzer could maybe justify its presence, is the limited hydrogen production for the hydrotreating unit and the corresponding produced oxygen utilization of the plant. Additional oxygen needs should be secured externally. **Therefore, the scheme of internal hydrogen extraction via PSA and the external purchase of industrial oxygen seems at first glance the most effective combination in terms of cost and performance.**

The scheme with the allothermal SMR seems inappropriate for this concept, since notable decrease in the performance indicators of the BtL plant was observed. The low temperatures that the biotechnological part operates turn the partial syngas return to the high-temperature thermochemical part inefficient from the energy as well as the exergy point of view. Remarkable portions of valuable syngas end up as flue gases for the thermal assisting of the reformer instead of participating in the fuel synthesis. This scheme rather refers to a polygeneration plant with parallel power, heat and fuel production while **the main objective of the BioSFerA concept is the high BtL efficiency.**

The present process description and the attached process configuration serve the initial illustration of the overall BioSFerA concept. The performed full-process simulations were based on primary data and input from the BioSFerA technology providers. As the experimental activities grow-up, a continuous re-evaluation and optimization of the proposed concept and its individual components will be performed. A more solid and mature operational framework of the BioSFerA BtL process chain will be presented in Deliverable D6.2. In particular:

- The potential of air-ATR and how the presence of nitrogen affects the efficiency of the biotechnological process has to be investigated. Moreover, the utilization of CO_2 stream, derived from oxy-fermentation of acetate, has to be assessed.
- A more detailed gasification model will be developed, validated against the corresponding pilot runs and capable of predicting the performance of the process (i.e. char conversion, CGE, syngas composition) for different parameters such as gasification temperature and steam-to-biomass ratio.
- The layout of the gas cleaning train will be determined as soon as the most appropriate strain will be selected and the corresponding requirements for impurities removal will be set.

- The gas/liquid fermentation product streams as well as the recirculation rates will be updated based on the forthcoming experimental findings.
- The type and the specifications of the microbial oil purification technology will be updated according to the findings from the respective experimental campaign.
- The accurate product yields from the hydroprocessing of the TAGs will be re-evaluated after the corresponding lab/pilot trials.
- Alternative low-cost oxygen production technologies will be investigated, if required, and will be compared with the scenario of external purchase. The latter will be further investigated in the techno-economic analysis of WP7.

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