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Aviation and maritime biofuels production via a combined thermochemical/biochemical pathway: A conceptual design and process simulation study

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Abstract:
A combined thermochemical-biochemical Biomass-to-Liquid (BtL) pathway for the production of aviation and maritime liquid fuels is presented. 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. Moreover, the low-pressure requirements (1-10 bar) along with the mild operating temperatures (30-60°C) reduce drastically the capital and operational cost of the process. In terms of efficiency, the biological process of syngas fermentation inherently has limited side products, a fact that reduces the risk of deactivation of hydrotreatment catalysts. The aim of this study is to develop the process model of this novel biorefinery in Aspen Plus™ and to perform the energy and mass balance calculations of the whole value chain, to determine the appropriate key process specifications and to estimate the production cost of the targeted drop-in biofuels.

Keywords:
Biofuels; Gasification; Fermentation; Biomass to Liquid (BtL); Process Simulations; Aspen Plus.

1. Introduction

The Paris Agreement's objectives related to climate change put aviation and shipping sectors, along with other industries, under great pressure and environmental inspection. Biofuels have recently started to attract great interest and have been identified by IATA[1] and IMO[2] as a promising strategy to reduce CO_2 emissions in the aviation and shipping sector respectively. IEA[3] claims that biofuels by 2050 could provide 27% of total transport fuel, mainly replacing diesel, kerosene and jet fuel. Lignocellulosic biomass conversion into liquid biofuels through thermochemical routes has been considered as a favorable option that offers several advantages. The

[1] https://www.iata.org/en/programs/environment/sustainable-aviation-fuels/

[2] https://www.imo.org/en/About/Events/Pages/Symposium-on-IMO-2020-and-Alternative-Fuels--.aspx

[3] https://www.iea.org/news/biofuels-can-provide-up-to-27-of-world-transportation-fuel-by-2050-iea-report-says-iea-roadmap-shows-how-biofuel-production-can-be-expanded-in-a-sustainable-way-and-identifies-needed-technologies-and-policy-actions

main challenge for these pathways is to develop advanced technologies with reduced energy consumption in a cost-effective way.

Today, the main types of synthesized paraffinic kerosene, approved by ASTM (ASTM D7566 -20) as blending components for conventional jet fuel (Jet A1) to make up bio-jet fuels, are the Fischer-Tropsch synthetic paraffinic kerosene (FT-SPK), Fischer-Tropsch synthetic kerosene with aromatics (FT-SKA), Hydroprocessed Ester and Fatty Acids (HEFA), synthesized iso-paraffins (SIP) and Alcohol to Jet (ATJ). Aviation biofuels must comply almost entirely with conventional jet fuel specifications, since blending regulations for aviation sector are stricter than other transportation. In the marine sector, there are two types of fuels, distillate (e.g. Marine Gas Oil) and residual fuels (e.g. Heavy Fuel Oil). The most common bio variants of MGO are Fatty Acid Methyl Ester (FAME/Biodiesel) and Hydrotreated Vegetable Oil (HVO).

In general, sustainability issues (e.g. food vs fuel, costly feedstock) and uncertainty over cost reduction related to the most of the mentioned current biofuels, impose the incorporation of alternate approaches in the current biofuels production pathways that target to more competitive drop-in biofuels prices.

2. Concept description

The developed concept within this study aims to establish 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. 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 (Fig. 1).

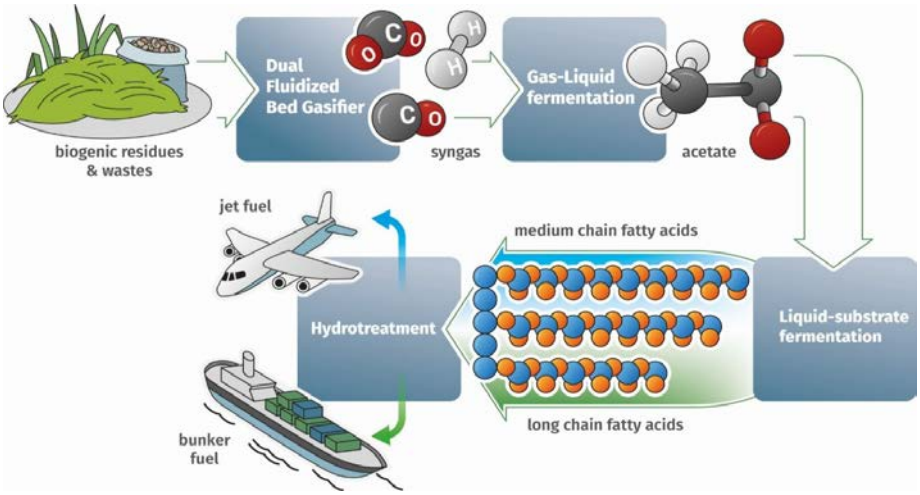

Fig. 1. The BtL concept from start-to-end. [1]

2.1. 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 this study, an extended feedstock screening around Europe was performed and 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 were selected. The selection was also based on the pre-treatment requirements of each feedstock 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.

In general, 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).

2.2. Dual Fluidized Bed Gasification (DFBG) & Gas Cleaning

The conversion of the biomass feedstock into syngas is carried out with the DFBG technology [2]. 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 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. The primary function of the catalytic reformer may be to convert tars and hydrocarbon gases to H_2 and CO, but it can also be modified to attain several targets relating to the syngas purification requirements for the subsequent fermentation process. Depending on the gas cleaning needs, different catalyst loadings and reactor design can be applied. For example, 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 purity level target, 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. 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 Fig. 2.

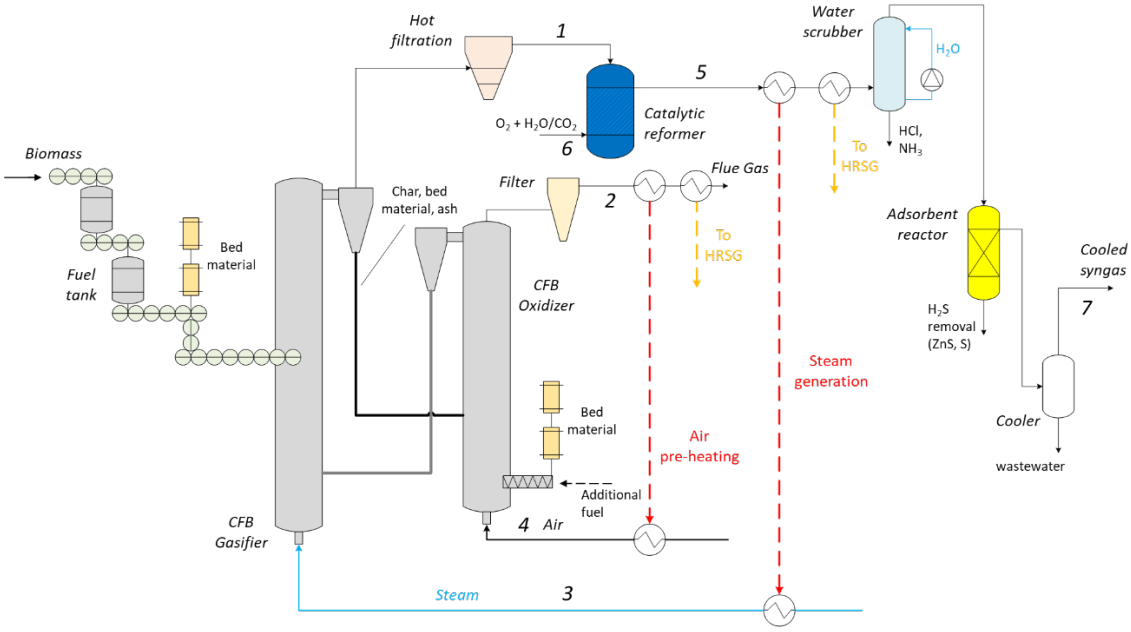

Fig. 2. Dual Fluidized Bed Gasification (DFBG) typical scheme accompanied with a mild gas cleaning section.

2.3. Syngas Fermentation

In the first step of the biological part of the process, syngas is converted into acetate under anaerobic conditions [3]. 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.

Syngas fermentation procedure is based on the interaction of syngas with the acetogenic bacteria under anaerobic conditions that 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, and consequently the acetate production yield. A cell recycling system (hollow fiber membrane) is also required to keep the cells in the fermenter while extracting the liquid effluent.

2.4. Acetate Fermentation

The second fermentation step refers to the production of TAGs via aerobic fermentative process of the 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*. In order to obtain strains that exhibit high lipid concentration, yield and acetate conversion, a metabolic engineering strategy of *Y. lipolytica* can be adopted [4]. The produced intracellular microbial oil mainly consists of fatty acids like oleate, stearate and palmitate.

During the continuous acetate fermentation process, 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 Fig. 3.

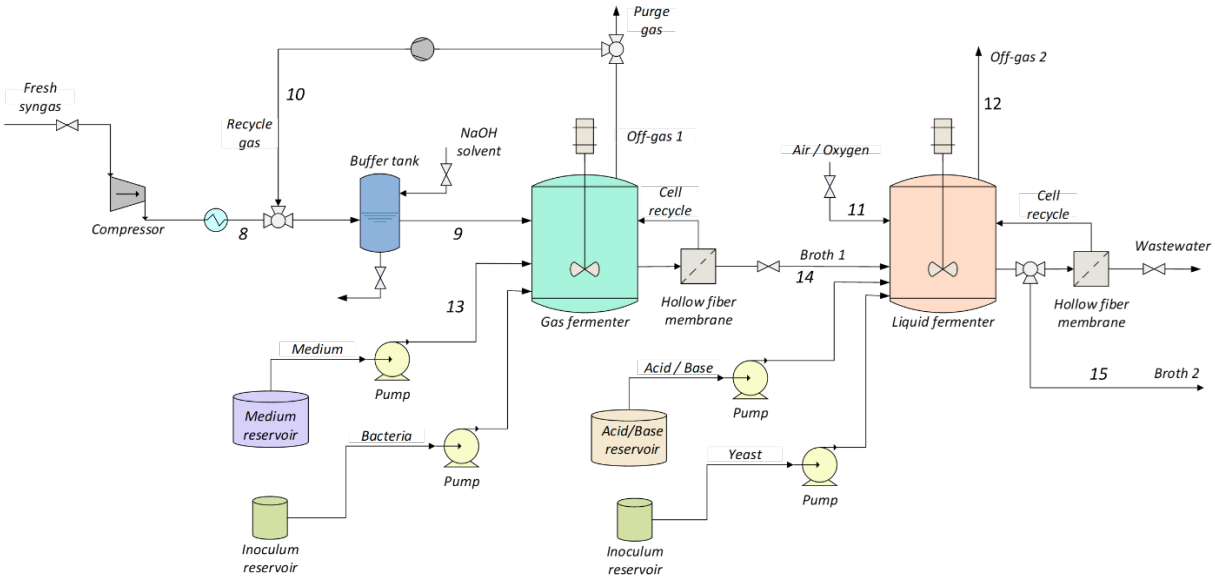

Fig. 3. The double-stage fermentation scheme and the Syngas-to-Acetate-to-TAGs pathway.

2.5. Triacylglycerides (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 processes generally provide high products recovery yields with good management and scalability, but they are energy intensive. 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 is exposed to steam at 180-240 °C for several minutes and then it is subjected to depressurization under ambient conditions. This generates an explosion that causes cell-wall disruption [5]. 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 thermal energy into mechanical energy and the shear forcing caused by the expansion of water vapor leads to the disruption of cell wall. As for the lipids extraction, 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 purification of a singular lipid 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 proposed microbial oil purification and recovery process is presented in Fig. 4.

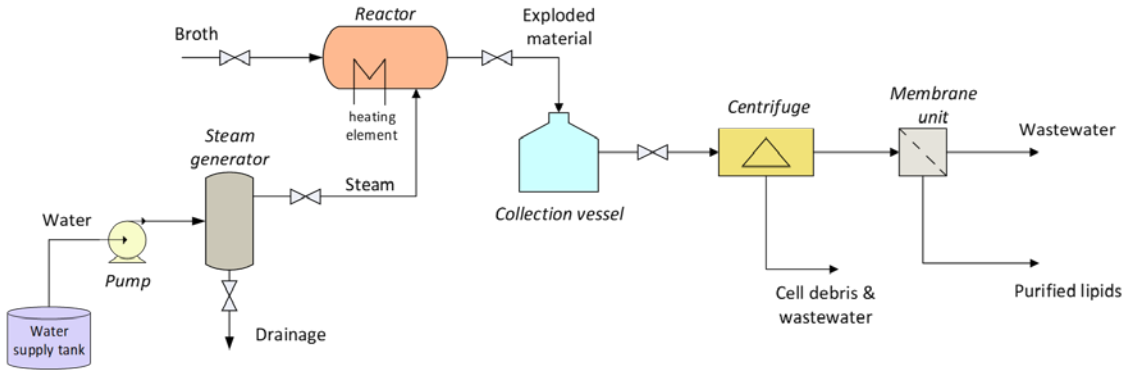

Fig. 4. TAGs purification and recovery process via steam explosion, centrifugation and membrane separation.

2.6. Triacylglycerides (TAGs) hydrotreatment

The final stage of the value chain includes the upgrading of microbial oil into drop-in aviation and marine biofuel through TAGs hydrotreatment. 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 Fig. 5. The hydrogen requirements of the hydrotreatment unit could be secured through water electrolysis using electricity from a potential CHP or a RES plant.

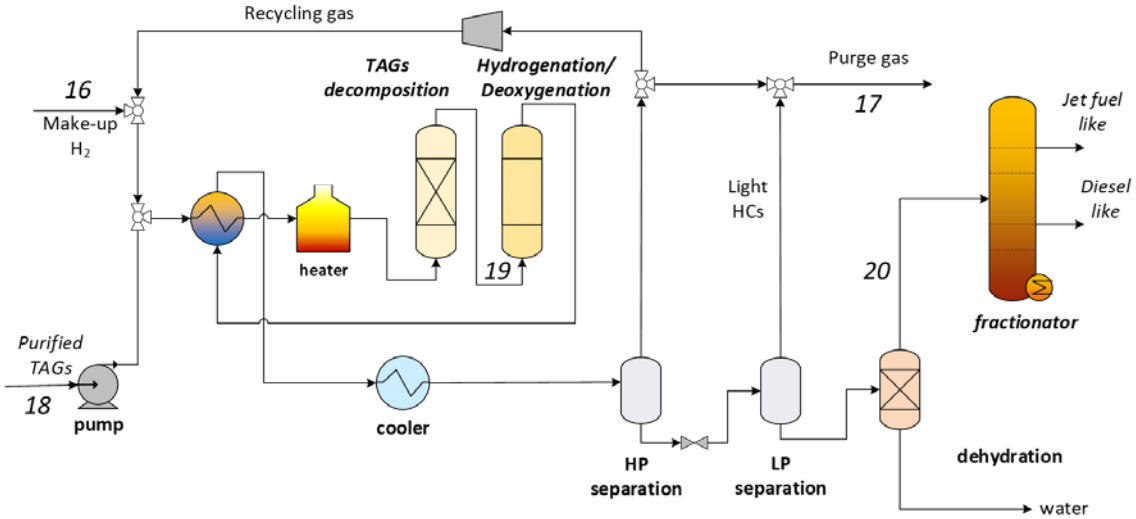

Fig. 5. TAGs to drop-in liquid fuels via hydrotreatment.

3. Model description

The proposed 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, were 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. The described concept is illustrated in a block form in Fig. 6.

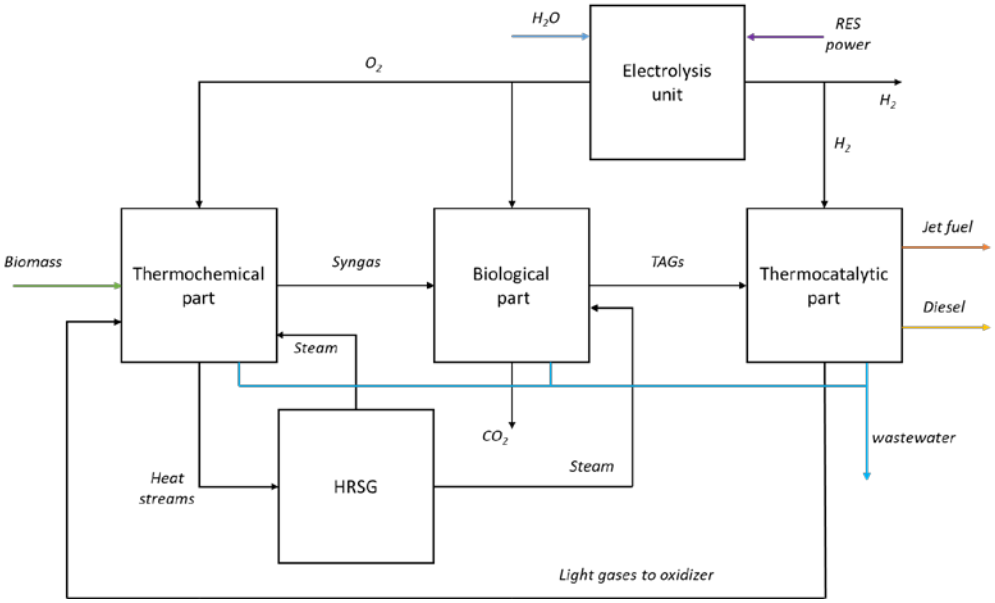

Fig. 6. Block Flow Diagram of the integrated BtL plant

The process model was developed in the commercial software ASPEN PLUS™. The simulations were performed at full-scale (200 MW_{th}) and the selected feedstock was crushed bark. The main specifications of the feedstock used in the process simulations are 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		Fixed Carbon		Volatile Matter		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

The water electrolysis unit was modelled in a simplified way that includes the mass balance of the water electrolysis reaction ($2\ H_2O \rightarrow 2\ H_2 + O_2$) 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% [6]. For the development of the HRSG model, IAPWS-95 property method was used for the water side and IDEAL property method for the flue gases side.

3.1. 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 [2, 7].

For the DFBG unit, a gasifier operating with 100% steam at 780 °C and an oxidizer operating with air at 880 °C were considered. 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, the Water-gas shift (WGS) reaction, the Boudouard reaction, the homogeneous gas reactions that form hydrocarbons and the partial combustion reactions. The main input and process parameters for the DFBG unit are gathered in Table 2.

Table 2. Thermochemical part process parameters.

DFBG unit		Reforming unit	
Parameter	**Input**	**Parameter**	**Input**
Pressure (bar)	1.5	Outlet temperature (°C)	900
Gasifier temperature (°C)	780	Steam-to-oxygen ratio (kg/kg)	1
Carbon conversion in the gasifier (%)	78	Oxygen temperature (°C)	400
Pressure drop in the gasifier (bar)	0.2	Steam temperature (°C)	350
Steam-to-biomass ratio (kg/kg dry,ash free)	0.7	Pressure drop (bar)	0.2
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		

The catalytic 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. The main input and process parameters for the reforming unit are shown in the right side of Table 2.

3.2. Model development of the Biotechnological part

The core of the biotechnological part of the process model is the two fermenters where syngas and acetate fermentation take place respectively. 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 [8]. 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. Equations (R1) – (R4) were selected as the key reactions occurring during syngas fermentation.

$$4\,CO + 2\,H_2O \rightarrow CH_3COOH + 2\,CO_2 \quad \text{(R1)}$$

$$2\,CO_2 + 4\,H_2 \rightarrow CH_3COOH + 2\,H_2O \quad \text{(R2)}$$

$$6\,CO + 3\,H_2O \rightarrow C_2H_5OH + 4\,CO_2 \quad \text{(R3)}$$

$$2\,CO_2 + 6\,H_2 \rightarrow C_2H_5OH + 3\,H_2O \quad \text{(R4)}$$

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. 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 [3, 9]. The main input and process parameters for the syngas fermentation unit are presented in Table 3.

Table 3. Biological part process parameters.

Gas fermentation		Liquid fermentation	
Parameter	**Input**	**Parameter**	**Input**
Pressure (bar)	5	Pressure (bar)	1
Temperature (°C)	55	Temperature (°C)	30
CO utilization per pass (%)	61	Conversion of CH_3COOH in Eq. (R5)	0.80
H_2 utilization per pass (%)	43	Conversion of CH_3COOH in Eq. (R6)	0.15
Conversion of CO in Eq. (R1)	0.95	Substrate utilization for non-lipid cellular biomass formation (%)	5
Conversion of H_2 in Eq. (R2)	0.95	Oxygen-to-acetic acid ratio (mol/mol)	0.63
Conversion of CO in Eq. (R3)	0.001		
Conversion of H_2 in Eq. (R4)	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. Equations (R5) – (R6) represent the intracellular lipid formation by the yeasts. The main input and process parameters for the acetate fermentation unit are presented in the right side of Table 3.

$$58.2\ CH_3COOH\ +\ 39.83\ O_2 \rightarrow C_{55}H_{98}O_6\ +\ 61.35\ CO_2 +\ 67.4\ H_2O \quad \text{(R5)}$$

$$51\ CH_3COOH\ +\ 29.5\ O_2 \rightarrow C_{51}H_{98}O_6\ +\ 51\ CO_2 +\ 53\ H_2O \quad \text{(R6)}$$

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 [10]. However, with the novel steam explosion-based technologies that are proposed for the described value chain, the corresponding energy demands are expected to be remarkably lower.

3.3. 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 [11]. 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 [12, 13]. The formed light gases, mainly containing propane, are sent back to the DFBG unit to be used as supplementary fuel for the oxidizer. The main process parameters for the hydrotreatment reactor are presented in Table 4.

Table 4. Hydrotreatment process parameters.

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

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) was not modeled in detail and the produced alkanes were considered as the final product in this analysis.

4. Results and Discussion

4.1 Main stream results

Table 5. Main stream results for the thermochemical part.

Stream No	1	2	3	4	5	6	7
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	-	122 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	-

Table 6. Main stream results for the double-stage fermentation.

Stream No	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
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	-	-	-	-	-	-
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

Table 7. Main streams results for the hydrotreatment unit.

Stream No	**16**	**17**	**18**	**19**	**20**
Mass flow (kg/s)	0.06	0.24	1.96	18.83	1.64
Temp (°C)	350	30	30	400	30
Press (bar)	40	40	1	1.5	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

4.2 Material and Energy balance

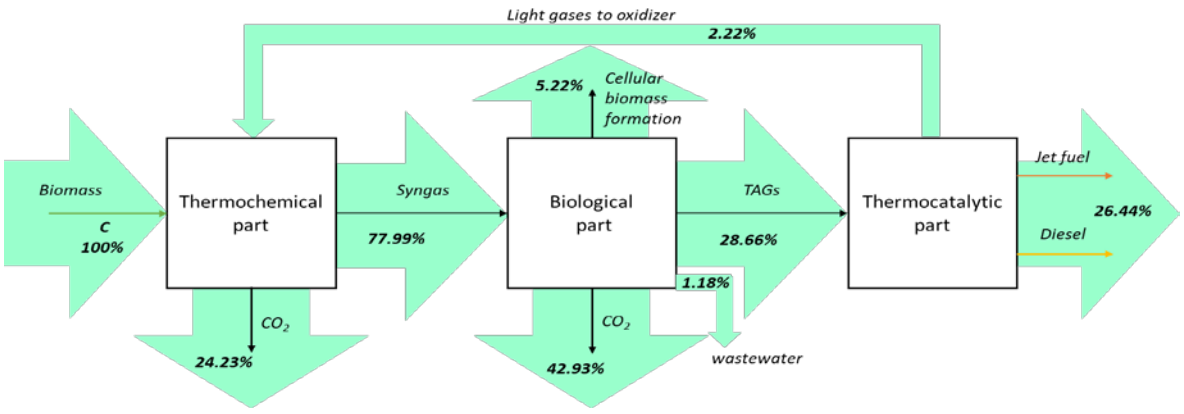

Fig. 7. Carbon balance.

The overall process heat and mass balance calculations were performed and indicators for the overall plant performance were assessed. The main performance indicators that were calculated are the Carbon Utilization (CU) and the Energetic Fuel Efficiency (EFE).

The CU of the BtL plant, which is the fraction of carbon in initial feedstock that is converted to the final liquid fuels, was calculated equal to 26.44%. A high carbon content (42.93%) is found in the rich CO_2 stream that leaves the aerobic fermenter. Further utilization of this CO_2 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 wastewater (1.18%). The results of the carbon balance calculations are depicted in Fig. 7.

The EFE, which is defined as the fraction of chemical energy in the initial feedstock that is transferred to the final fuels, was measured at 37%. The heat recovery for steam generation and the air pre-heating was performed by utilizing 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 the re-involvement of this stream in the syngas fermentation process, EFE values greater than 45% can be achieved. Fig. 8 shows the energy balance calculations for the BtL plant.

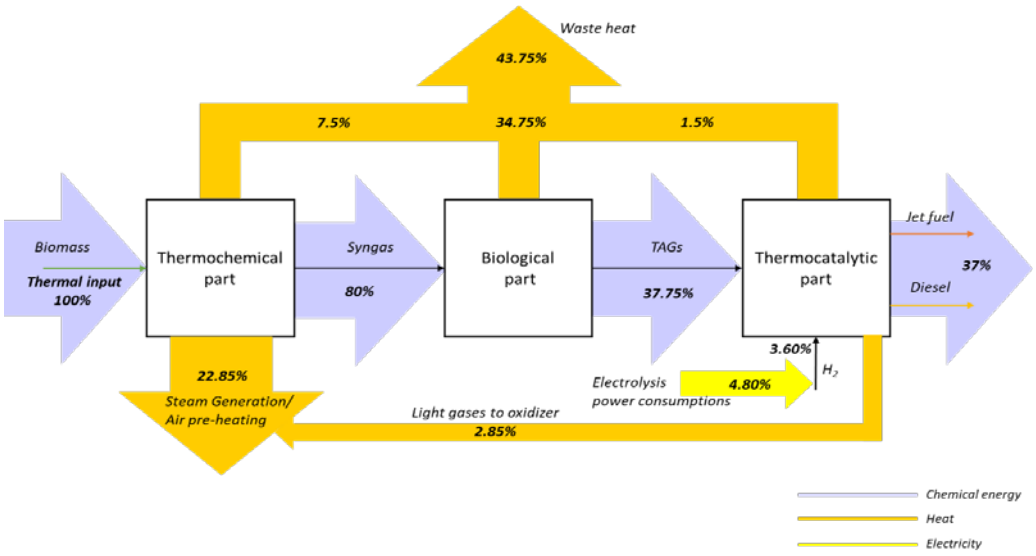

Fig. 8. Energy Balance.

4.3 Techno-economic assessment

In addition to the process simulation analysis, a preliminary techno-economic assessment is carried out to estimate the production cost of the targeted biofuels. The CAPEX and OPEX estimation is based on the Peters & Timmerhaus methodologies [14]. The cost estimation of the main units operation of the process was based on the methodology adopted by Diederichs et al. [15] as well on previous similar analyses performed by the authors [16]. The total capital cost for a DFBG plant is roughly estimated at 100M€. The selection of microorganisms for the syngas fermentation route that are durable to the syngas contaminants eliminates the need for extensive syngas cleaning (e.g. acid gas removal unit), that would be needed in the case of FT synthesis and would require an additional capital investment of 100M€. The capital cost of the fermenters is estimated at 62M€ based on the costs of the fermenters used for syngas fermentation for the production of ethanol [15]. Also, the cost of the unit for the microorganism production is considered to be 5M€ [17]. The desired biofuels are produced through the hydroprocessing of the purified microbial oil consisting of catalytic hydrotreating and catalytic isomerisation. In principle, since less harsh hydrotreating conditions are required for the TAGs upgrading to marine biofuel, the capital cost for the isomerization reactor and the H_2 plant are considered slightly lower than those of the SAF value chain. The capital costs of the fractionation unit and the hydrogen plant are also considered in this analysis. Moreover, all the peripheral units (wastewater treatment unit and CHP plant) are taken into account in the investment cost estimation.

The DFBG technology allows the utilization of a wide range of biogenic residues as feedstock for biofuel production, which diversifies the feedstock basis. Low-cost feedstock residues lower the costs for the production of fuels. However, these types of residues normally have a rather low energy density, which is associated with significant costs for transportation of the feedstock from rural areas to central biofuel production plants. The fuel flexibility of the DFB gasification system, allows the utilization of different feedstock

from different sources in a small radius around a strategically located plant, thus reducing the transportation costs and eliminating the need for extensive biomass pre-treatment to increase the energy density. For this analysis, the cost of dry biomass is set at 80 €/t. Among the other operational costs in this preliminary cost estimation analysis, we consider an O&M cost equal to 3% of the fixed capital investment, an electricity cost for the power demand that cannot be covered by the CHP unit and the labour cost. The sum of this cost is estimated at 19.9M€/year or 423€/t of produced biofuel. Also, the cost of nutrients was considered to be 10% of the biomass cost.

Table 8. Cost breakdown.

targeted drop-in biofuel	**biojet fuel**	**bunker biofuel**
Feedstock handling (M€)	4.41	4.41
Gasification plant (M€)	100.01	100.01
Fermentation (M€)	61.83	61.83
Lipids recovery (M€)	17.23	17.23
Cogeneration (M€)	38.86	38.86
Waste Water Treatment (M€)	11.53	11.53
Hydrotreating (M€)	7.35	7.35
Hydroisomerization (M€)	39.33	11.8
Hydrogen plant (M€)	11.54	10.39
Product separation (M€)	3.0	3.0
Micro-organism production (M€)	4.93	4.93
Labour cost (M€/year)	5.13	4.62
Maintenance (M€/year)	7.83	7.08
Electricity cost (M€/year)	5.36	5.09
Enzymes & nutrients (M€/year)	1.53	1.53
Total CAPEX (M€)	300.03	271.34
Total OPEX (M€/year)	19.85	18.32
Biomass feedstock (M€/year)	15.26	15.26
Production cost (€/t)	**1004**	**947**

From this preliminary analysis, the cost of the biofuel is calculated to be 1000€/t (or 82.2 €/MWh) and 947€/t or (81.2 €/MWh) for the case of aviation and marine biofuels, respectively. It is clear that the proposed concept is competitive compared to costs reported in literature [14, 16, 17, 18], for other current technologies for bio-jet fuel production (Fig. 9) contributing to a cost reduction of 26-60%. The cost of the proposed process is even lower than the cost of HEFA, the advantage is the use of much cheaper feedstock compared to vegetable oils. Compared to other lignocellulosic biomass to jet-fuel technologies FT (gasification and Fischer-Tropsch synthesis), SYN-FER-J (gasification, syngas fermentation to ethanol and ethanol to jet) and ATJ (alcohol to jet) the presented concept avoids significant capital costs, like extensive syngas cleaning and ethanol upgrading/polymerisation. As seen in Fig. 10, biomass price and CAPEX variation has the greatest influence in the final product cost

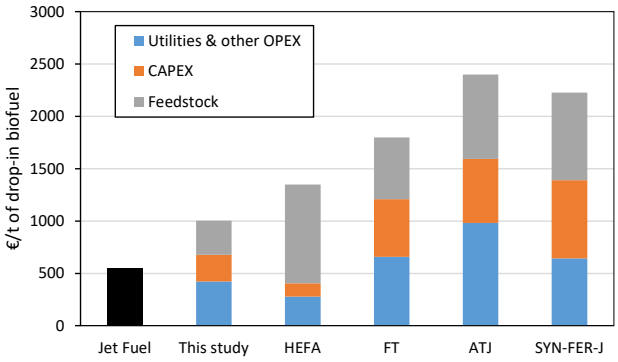

Fig. 9. Production costs for bio-jet fuel pathways.

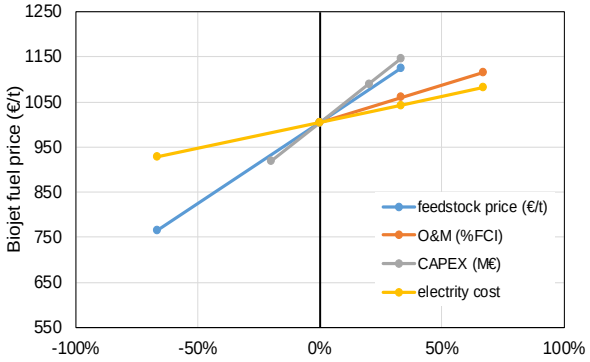

Fig. 10. Sensitivity analysis

6. Conclusions

Within this study, a basic definition of a combined thermochemical-biochemical BtL process and its individual components has been performed. An overall process model was developed and process simulations were performed at full-scale for the Biomass-to-Liquid (BtL) plant. The Heat & Mass balances for the examined configuration were solved and evaluated via overall performance indicators (i.e. CU & EFE). Moreover, a preliminary techno-economic assessment was carried out in order to estimate the production cost of the

targeted biofuels and roughly place in terms of cost the proposed pathway among other technologies. CU equal to 26.44% and EFE equal to 37% were obtained for the BtL plant. The major carbon and energy losses are observed in the biotechnological part. The optimization of the double-stage syngas fermentation (recirculation rates, gas solubility, optimum operational parameters, etc.) are expected to reduce these losses and enhance the overall performance of the BtL plant. Moreover, if utilization of CO_2 is considered, the CU and EFE of the plant can reach values of 37 and 45% respectively. The extended feedstock flexibility, the limited gas cleaning requirements as well as the low-pressure and mild operating temperatures of the biological part, turn the proposed pathway into a promising and competitive BtL technology. The standalone sub-technologies may have already been tested and involved in medium/large scale applications, but the major technology challenges of the proposed concept is the efficient coupling of the thermochemical part with the biological part as well as the avoidance of expensive purification techniques for microbial oil recovery. Of course, the presented configuration of the integrated concept is only a baseline scenario that can act as a benchmark for the further development and optimization of the technology. Aspects like PSA involvement for hydrogen extraction instead of water electrolysis, air-blown tars reforming, air/oxy fermentation of acetate and subsequent CO_2 exploitation should be considered and their techno-economic impact on the process should be assessed.

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