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

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Introduction

- The Paris Agreement's objectives related to climate change put aviation and shipping sectors under great pressure and environmental inspection
- Biofuels have been identified by IATA¹ and IMO² as a promising strategy to reduce CO₂ emissions in the aviation and shipping sector respectively
- IEA³ claims that biofuels by 2050 could provide 27% of total transport fuel, mainly replacing diesel, kerosene and jet fuel
- 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

Lignocellulosic biomass conversion into liquid biofuels through thermochemical routes has been considered as a favorable option that offers several advantages. The main challenge for these pathways is to develop advanced technologies with reduced energy consumption in a cost-effective way...

¹<u>https://www.iata.org/en/programs/environment/sustainable-aviation-fuels/</u>

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

³<u>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-ina-sustainable-way-and-identifies-needed-technologies-and-policy-actions</u>



Concept description

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 fuel flexibility, syngas of high quality, complete fuel conversion and optimal heat integration while avoiding CAPEX intensive equipment like Air Separation Unit (ASU)
- ✓ The tolerance of the bacteria to syngas contaminants **minimizes the gas cleaning requirements**
- ✓ 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
- ✓ The biological process of syngas fermentation inherently has limited side products, a fact that reduces the risk of deactivation of hydrotreatment catalysts



Feedstock selection & handling



- Thanks to the DFBG technology, the process can be driven feedstock-flexible using a broad and variable portfolio of biogenic residues. Using biogenic residues is in line with the EU's biofuels policy documented in the RED II directive, mentioning the promotion of residue based biofuels (advanced biofuels)
- 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 'waste productive' fields were selected as candidate feedstock
- 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



Dual Fluidized Bed Gasification (DFBG) & Gas Cleaning



- 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
- Raw syngas of moderate heating value and relatively low tar levels is achieved and filtered at gasifier exit temperature.
 Heavy tars along with hydrocarbon gases are catalytically reformed with the presence of oxygen or steam
- The DFBG heat integration assumes steam generation from the **thermal utilization of hot syngas**, while the flue gases from the oxidizer are used for the **pre-heating of the air** that will enter the reactor
- The **gas cleaning requirements are expected to be milder** than the exhaustive gas cleaning that is required in chemical synthesis applications (e.g. Fischer-Tropsch). Depending on the purity level target, scrubbers and adsorbents can be implemented for the efficient removal of syngas contaminants (e.g. H₂S, HCL, COS) before the fermentation unit



Syngas fermentation





- The interaction of syngas with the acetogenic bacteria (e.g. *Moorella Thermoacetica*) 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 CO₂/CO/H₂
- By recirculating the off-gas stream back to the fermenter, **the unconverted syngas components can be recovered and recycled**. A cell recycling system (hollow fiber membrane) is required to keep the cells in the fermenter while extracting the liquid effluent





Acetate fermentation





- 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 (e.g. *Yarrowia lipolytica*)
- Lipids are formed as intracellular products. The produced intracellular microbial oil mainly consists of fatty acids like oleate, stearate and palmitate. At the same time, a gaseous CO₂-rich stream is formed and leaves the reactor from the top
- A cell recycle system (hollow fiber membrane) can be installed to recirculate the cellular biomass in the bioreactor while extracting the effluent





Triglycerides (TAGs) purification





- As oleaginous yeasts store lipids in intracellular form, extraction is required to obtain TAGs. 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
- Among the options actually available, there are novel technologies with considerably **lower power consumptions** such as steam explosion, centrifugation and membrane separation
- Steam explosion is an innovative method with reduced environmental impact, lower costs and energy demand. In steam explosion, raw material is 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
- Centrifugation could be evaluated for the ability to separate oil from the broth deriving from steam explosion. If a purification of singular lipids category is needed, the oil fraction could be further processed in a membrane unit
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- The final stage of the value chain includes the upgrading of microbial oil into drop-in aviation and marine biofuel through TAGs hydrotreatment
- 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, coproducing propane, water, CO and CO₂
- In the last step, the deoxygenated straight chain paraffins are selectively hydrocracked or isomerized yielding highly branched alkanes. 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 hydrogen requirements of the hydrotreatment unit can be secured through a **RES-driven water electrolysis**



Integrated Biomass-to-Liquid (BtL) plant



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Model description



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 are shown in the Table:







Equilibrium models have been used for the implementation of the gasification and the reforming reactions, while for kinetically and hydrodynamically controlled phenomena, 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.

- 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)
- The reformer operates under autothermal conditions with the addition of oxygen as oxidation media, and steam or carbon dioxide as reforming agent (10)
- An adsorbent reactor was applied for the partial removal of H₂S. The removal of H₂S is achieved with the assistance of metal oxides (e.g. ZnO) and their ability of adsorbing inorganic compounds (11)

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				

or	$C + H_2 O \rightarrow CO + H_2$	(1)
nce	$CO + H_2O \iff H_2 + CO_2$	(2)
	$C + CO_2 \leftrightarrow 2 CO$	(3)
	$CO + 3 H_2 \leftrightarrow CH_4 + H_2O$	(4)
	$2 CO + 4 H_2 \leftrightarrow C_2 H_4 + 2 H_2 O$	(5)
	$6 CO + 9 H_2 \leftrightarrow C_6 H_6 + 6 H_2 O$	(6)
1	$10 \ CO + 14 \ H_2 \leftrightarrow C_{10} H_8 + 10 \ H_2 O$	(7)
	$H_2 + 0.5 \ O_2 \ \rightarrow \ H_2 O$	(8)
	$CO + 0.5 O_2 \rightarrow CO_2$	(9)
4 <i>CE</i>	$H_4 + O_2 + 2H_2O \rightarrow 10H_2 + 4CO$	(10)
	$ZnO + H_2S \rightarrow ZnS + H_2O$	(11)



Both fermenters were modelled as stoichiometric reactors with specific reaction stoichiometry and fixed conversions. Syngas derived from the reforming and purification units (plus the recycle gas) enters the fermenter where syngas is mainly converted to acetate (CH_3COOH). The only by-product considered is ethanol (C_2H_5OH), yet with very low production. The acetate extracted by the first fermenter reacts with oxygen for the production of TAGs and non-lipid biomass. The culture medium stream is considered as pure water and no nutrients were included.

- M. Thermoacetica was used as the reference acetogenic bacterium for gas fermentation and Y. lipolytica as the oleaginous yeast of the liquid fermentation
- Reactions (12) (15) were selected as the key reactions occurring during syngas fermentation
- For convenience C₅₅H₉₈O₆ and C₅₁H₉₈O₆ were considered as the only TAGs produced. Reactions (16) (17) represent the intracellular lipid formation by the yeasts

Gas fermentation		Liquid fermentation		·	
Parameter	Input	Parameter	Input		
Pressure (bar)	5	Pressure (bar)	1		
Temperature (°C)	55	Temperature (°C)	30	$4 CO + 2 H_2O \rightarrow CH_3COOH + 2 CO_2$	(12)
CO utilization per pass (%)	61	Conversion of CH ₃ COOH in Eq. (16)	0.80		
H ₂ utilization per pass (%)	43	Conversion of CH ₃ COOH in Eq. (17)	0.15	$2 CO_2 + 4 H_2 \rightarrow CH_3COOH + 2 H_2O$	(13)
Conversion of CO in Eq. (12)	0.95	Substrate utilization for non-lipid cellular biomass formation (%)	5	$6 CO + 3 H_2O \rightarrow C_2H_5OH + 4 CO_2$	(14)
Conversion of H ₂ in Eq. (13)	0.95	Oxygen-to-acetic acid ratio (mol/mol)	0.63		、
Conversion of CO in Eq. (14)	0.001			$2 CO_2 + 6 H_2 \rightarrow C_2 H_{\Xi}OH + 3 H_2O$	(15)
Conversion of H_2 in Eq. (15)	0.001				、 /
Substrate utilization for microbial growth (%)	0.049				
Off-gas recycle (%)	97.5			_	
					1

 $58.2 CH_3 COOH + 39.83 O_2 \rightarrow C_{55}H_{98}O_6 + 61.35 CO_2 + 67.4 H_2O$ (16)

 $51 CH_3 COOH + 29.5 O_2 \rightarrow C_{51}H_{98}O_6 + 51 CO_2 + 53 H_2O$ (17)



Model description (Thermocatalytic part)

Initially, the **decomposition** of the two representative TAGs 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.

- Triglycerides decomposition (18) (19)
- Hydrogenation (20) (22)
- Decarboxylation (23) (25)
- Decarbonylation (26) (28)
- Reduction (29) (30)

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

 $C_{18}H_{32}O_2 + H_2 \rightarrow C_{18}H_{34}O_2$ (20)

$$C_{18}H_{34}O_2 + H_2 \to C_{18}H_{36}O_2 \tag{21}$$

$$C_{18}H_{32}O_2 + 2H_2 \rightarrow C_{18}H_{36}O_2 \tag{22}$$

- $C_{18}H_{36}O_2 \to C_{17}H_{36} + CO_2 \tag{23}$
- $C_{16}H_{32}O_2 \to C_{15}H_{32} + CO_2 \tag{24}$
- $C_{18}H_{34}O_2 \to C_{17}H_{34} + CO_2 \tag{25}$
- $C_{18}H_{36}O_2 + H_2 \rightarrow C_{17}H_{36} + CO + H_2O$ (26)
- $C_{16}H_{32}O_2 + H_2 \rightarrow C_{15}H_{32} + CO + H_2O$ (27)
- $C_{18}H_{34}O_2 + H_2 \rightarrow C_{17}H_{34} + CO + H_2O$ (28)
- $C_{18}H_{36}O_2 + 3H_2 \rightarrow C_{18}H_{38} + 2H_2O$ (29)
- $C_{16}H_{32}O_2 + 3H_2 \rightarrow C_{16}H_{34} + 2H_2O \tag{30}$

 $C_{51}H_{98}O_6 + 3H_2 \to 3C_{16}H_{32}O_2 + C_3H_8 \tag{18}$

 $C_{55}H_{98}O_6 + 4H_2 \rightarrow C_{16}H_{32}O_2 + C_{18}H_{34}O_2 + C_{18}H_{32}O_2 + C_3H_8$ (19)





Stream No

Temp (°C)

Press (bar)

 H_2

CO

 CO_2

 H_2O

N₂

 H_2S

 CH_4

NH₃

HCN

COS

 C_2H_4

 C_6H_6

C10H8

O₂

Mass flow (kg/s)

Main stream results (1/3)

- **1.** Syngas after filtration
- 2. Flue gases after filtration
- 3. Pre-heated steam
- 4. Pre-heated air
- 5. Syngas after reforming
- 6. Reforming agent
- 7. Cooled syngas

1

16.60

780

1.3

29.07

10.95

14.78

37.09

119 ppm

186 ppm

5.49

0.2

12 ppm

11 ppm

1.81

0.4

0.2

2

20.24

880

1.1

16.16

1.91

77.90

4.02

3

6.92

350

1.5

Composition (vol. %)

4

18.83

400

1.5

-

0.79

0.21

1 ppm

36.02



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Main stream results (2/3)







Main stream results (3/3)

1000						D II			
Angele						Recycling gas			4 [1]
16. Hydro	gen					TAGs H	vdrogenation/	Purge gas	
17. Light	gases				16 🛓	decomposition D	Deoxygenation		lat fuel
18 . Purifie	ed TAGs				Make-up			1/	like
10. Fatty	acida (propan								
19. Fully	ucius/propun	le							
20. Jet/Di	esel paraffins	5				heater	19	Light HCs 20	Diesel
									fractionator
					Purified				,
				-	TAGS		()		
					18 🖂				
<u> </u>		·			pump	cooler			
Stream No	16	17	18	19	20		HP	LP	dehydration
Mass flow (kg/s)	0.06	0.24	1.96	18.83	1.64		separation	separation	
Temp (°C)	350	30	30	400	30				→ water
Press (bar)	40	40	1	1.5	40				
	Compositi	on (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	-				
C18H34O2	-	-	-	28.90	-				
C18H36O2	-	-	-	5.14	-				
H ₂	1	33.25	-	-	-				
CO	-	0.6	-	-	-				
CO ₂	-	39.38	-	-	-				
C ₃ H 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				

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Carbon balance



- □ The Carbon Utilization (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 CO₂ stream that leaves the aerobic fermenter. Further utilization of this CO₂ 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%)



Energy balance



□ The Energetic Fuel Efficiency (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 %

Heat recovery for steam generation and the oxidizer's air pre-heating is performed from the hot streams of the DFBG unit (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 biological part (7.5%) and the hydrotreatment unit (1.5%) are lower



Preliminary Techno-economic assessment

A **preliminary techno-economic assessment** is carried out to estimate the production cost of the targeted biofuels. The CAPEX & OPEX estimation is based on the Peters & Timmerhaus⁴ methodologies





- The proposed concept, at a first glance, seems to be competitive compared to other current technologies for bio-jet fuel production
- Compared to HEFA, that is the most common aviation biofuel, the advantage lies on the utilization of cheaper feedstock (i.e. residues) than vegetable oils
- Compared to other lignocellulosic biomass pathways (e.g. FT, ATJ) the presented concept avoids significant capital costs like extensive gas cleaning or ethanol upgrading/polymerization
- The feedstock price & the CAPEX variation are the cost variables with the larger impact in the final product cost and the price formation

⁴Peters MS, Timmerhaus K, D., West RE. Plant design and economics for chemical engineers Plant design and economics for chemical engineers. McGraw-Hill Chemical Engineering Series, 2003

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Conclusions

- The Heat & Mass balances for the examined configuration were solved and evaluated via overall performance indicators (i.e. CU & EFE). CU equal to 26.44% and EFE equal to 37% were obtained for the BtL plant. If further utilization of CO₂ is considered, the overall performance of the plant will be further enhanced
- 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 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. The standalone sub-technologies have already been tested and involved in medium/large scale applications

Future work

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- The major carbon and energy losses are observed in the biological 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 BtL plant
- Aspects like Pressure Swing Adsorption (PSA) involvement for internal hydrogen extraction instead of water electrolysis, air-blown tars reforming, air/oxy fermentation of acetate should be considered and their technoeconomic impact on the process should be assessed

Thank you for your attention!

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