Supplementary Material

S.1 Simulation in ASPEN PLUS

In this appendix Aspen Plus® simulation of supercritical fluid extraction (SFE) details are described. For more information on the simulation of the first and second generation ethanol production please go to [1,2] and on the simulation of the open pond system and microalgae growth [3].

The thermodynamic model used to represent the process was RK-ASPEN model when supercritical fluid extraction was considered and UNIQUAC model for low pressure processes. The RK-ASPEN model can be applied to the SFE process as it is particularly suitable for modeling a mixture of light gases (such as CO_2,) at medium to high pressures, with polar components. The RK-ASPEN property method distinguishes between the subcritical and supercritical components and applies either the Mathias alpha function or the Boston–Mathias extrapolation of the alpha function. The RK-ASPEN model is indicated by ASPEN PLUS user guide to this application due to the before mention characteristic, as well as the formulation of the mixing rules. This model was validated by [Lim et al, 2003]. For the simulation, CO_2 was considered a Henry component. Although the methods mentioned were the best available, it is recognized that for complex streams as present in our process the model will never be 100% accurate. Table 1 summarizes all the simulated equipment and the specification set in the Aspen Plus® simulator. Note that Aspen Plus® does not have a specific model for representing supercritical extraction with stationary bed, but this does not limit the use of the software to evaluate mass and energy balance of this unit operation. The extraction process was simulated in ASPEN Plus using the ASPEN models mixer, heat exchanger and separator. In the first model CO_2 and the emulsion was mixed at the desired pressure, than it was heated to extraction temperature and in the separator model

the experimental SFE results were inferred by a design specification calculation tool (flowsheeting options, Design Specs). Thermodynamic equilibrium was calculated in the flash tank in which CO2 is separated. In this way, simulation could represent the process successfully.

Table 1 – Equipment specification simulated in ASPEN PLUS

Equipment	Description	ASPEN model	Parameters
SFE			
H-101	Solvent CO2 cooling	Exchangers - Heater	T (293 K)
H-1101	Solvent CO2 cooling	Exchangers - Heater	T (263 K)
P-101	Solvent CO2 pumping	Pressure Changers – Pump	P (desired SFE process pressure*)
H-102	Solvent CO2 heating	Exchangers - Heater	T (desired SFE process temperature*)
M-101 H-104 EX-101	SFE extractor	Mixers - Mixer Exchangers - Heater Separators - Sep	P (desired SFE process pressure*) T (desired SFE process temperature*) Set using the design specification to achieve lipid and carotene extraction yield according to the experimental data*
S-101	CO2 separation tank	Separators - flash2	P (pressure set depending the process) T (temperature set depending the process)
S-102	CO2 separation tank	Separators - flash2	P (5 MPa) T (298 K)
Microalgae dewatering and drying			
S-001	Centrifuge	Separators - Sep	Dewatering (Set with design specification to solid content of 3%)
S-002	Centrifuge	Separators - Sep	Dewatering (Set with design specification to solid content of 33%)
S-003	Centrifuge	Separators - Sep	Dewatering (Set with design specification to solid content of 56%)
S-004 H-A101	Biomass drier Air heating	Flash2 Exchangers - Heater	Set pressure at 1 bar. The amount of air used to dry biomass was calculated using a design specification to achieve final moisture of 8% by changing the air flow inlet that was heated to 373 K
			T (100)
Milling			
MILL	Mill	Mixers - Mixer	P(set pressure constant)

S-301	Sieve	Separators - Sep	Set using the design specification to separate fine fraction with the chemical composition described in Alay (2015)
Ethanol recovery system			
S-201	Centrifuge	Separators - Sep	Dewartering
P-202	Ethanol evaporator	Pressure Changers - Valve	P (0.016 MPa)
H-203		Exchangers – Heater	T (348 K)
HEVA2		Separators - flash2	P (0.1 MPa)
H-204	Solvent ethanol cooling	Exchangers - Heater	T (30ºC)
H-205	Product cooling	Exchangers - Heater	T (30ºC)

* set according with the SFE process investigated based on the literature experimental data

S.2 OSMOSE simulation tool

OSMOSE simulation tool was used in its basic level to perform energy integration and economic analysis. OSMOSE (OptimiSation Multi-Objectifs de Systemes Energetiques integres, which means "Multi-Objective OptimiZation of integrated Energy Systems") is a computation platform that was built in Matlab, developed and continuously improved at École Polytechnique Fédérale de Lausanne in Switzerland for the design and analysis of integrated energy systems. The platform allows one to link several software such as Belsim Vali and Aspen Plus for a complete suite of computation and result analysis tools (optimization, sensitivity analysis, Pareto curve analysis, etc.) More information [R. Bolliger, OSMOSE Platform].

S.3 Energy integration and modeling

Based on the pinch analysis methodology [Linnhoff], the optimal thermal process integration is computed in the OSMOSE platform after the maximum heat recovery potential between hot and cold streams is defined and a minimum approach temperature ΔT_{min}, which represents the energy capital trade-off between the energy savings obtained by heat exchange and the required heat exchangers investment, is considered. The optimal utility integration is obtained when the combined production of fuel, power and heat are maximized, which minimizes the operating cost by solving a

linear programming problem (i.e. mathematical method used in computer modeling to find the best possible solution representing the problem using linear relationships).In the thermal integration, the primary energy requirement must be satisfied in terms of hot and cold utilities. The minimum energy requirement is computed from the hot and cold process streams using the heat cascade method, which accounts for the potential heat recovery. The potential fuels are assembled in a superstructure, which integrates different possibilities and computes the optimal solution by minimizing the operating cost using a linear programming model [M. Gassner, F. Maréchal].

The thermal integration is declared in Matlab-OSMOSE as follow. First the variables are extracted from ASPEN PLUS simulation (as in the tag assignment example), then the heat integration is performed (heat integration modeling).

Tag assignment example in Matlab-OSMOSE

```
% SFE extraction
% H-102
nt=nt+1;
technology.Tags(nt).TagName = {'t_c2_in'};
technology.Tags(nt).Unit = {'C'};
technology.Tags(nt).Aspen.Line_1 = {'Stream-Var Stream=SFE.C2 Substream=MIXED'};
technology.Tags(nt).Aspen.Line_2 = {'Variable=TEMP'};
technology.Tags(nt).Status = {'off'};
```

Heat integration modeling

```
% description of the flow
% type, unit, tag_name , T_in [K], h_in [kW], T_out [K], h_out[kW], deltaTmin

ns = 0;

% Cold streams () ---------------------------------------------------------- all in kW

ns = ns+1;
 technology.EI.Streams(ns).Short =
{'qt','sfe','h102','@t_c2_in+273','0','@t_c2_out+273','@heat_h102*1163',5};

ns = ns+1;
 technology.EI.Streams(ns).Short =
{'qt','lpse','h202','@t_e2_in+273','0','@t_e2_out+273','@heat_h202*1163',5};



% Hot streams  () ----------------------------------------------------------------

ns = ns+1;
 technology.EI.Streams(ns).Short = {'qt','sfe','h101','@t_co2+273.15','-
1*@heat_h101*1163','@t_c1+273.15','0',5};
```

S.3 Total investment and economic evaluation

Using the data from the ASPEN PLUS and thermal process integration models, the costs are estimated in Matlab-OSMOSE based on the equipment sizing and cost correlations from the literature [G.D.Ulrich, 2004; R. Turton, 1998]. Table 2 gives the cost function and the necessary parameter for its calculation for the evaluated equipment.

Table 2 – Equipment specification defined in the economic modeling

Equipment	Cost function	Reference	Parameters
SFE			
SFE extractor	Jacketed reactor	G.D.Ulrich, 2004	c, volume flow inlet, pressure, material
CO2 separation tank	Flash drum 2min	G.D.Ulrich, 2004; R. Turton, 1998	c, volume low flash, pressure, material
Milling			
Mill	Vibrating Ball Mill	G.D.Ulrich, 2004	c, mass flow, size
Sieve	Vertical Vessels and	G.D.Ulrich, 2004; R. Turton, 1998	c, diameter, height, pressure, material
	Sieve Trays		c, N, diameter, material
Centrifuges and Drier			
Centrifuges	Sedimentation Centrifuge	G.D.Ulrich, 2004	c, volume flow inlet, material
Dryer	Direct Rotary Dryers	G.D.Ulrich, 2004	c, volume
HEN	Heat exchange network	Calculated by OSMOSE after energy integration	Considered all heat exchangers including the ethanol evaporator

The c structure is the vector that carries the values of Year Index; Total Module; Grass Root; Interest Rate; tax rate and Life Time.

S.4 Electricity consumption

The electricity consumption modeling is presented in the following.

```
%% Electricity consumption(kW)
%-------------------------------------------------------------------------

% Algae growth
```

```
% Electric power for the paddle wheel

power_paddle = 2300;

% Electric power for CO2 injection

power_injection = 9400;

% Electric power for water pumping

power_waterpumping = 425;

power_growth = power_paddle + power_injection + power_waterpumping;


% SFE process

% First centrifuge 4000 kW/(m3/s)

power_cent_w1 = vol_centriw1 * 4000 * units_cw1;

% Second centrifuge 4000 kW/(m3/s)

power_cent_w2 = vol_centriw2 * 4000 * units_cw2;


power_sfe = power_pco2 + power_cent_w1 + power_cent_w2 +
power_mill_alg;
```

Reference

[1] Albarelli, J. Q.; Ensinas, A. V. and Silva, M. A., A New Proposal of Cellulosic Ethanol to Boost Sugarcane Biorefineries: Techno-Economic Evaluation. International Journal of Chemical Engineering. Article ID 537408, 11 pages. http://dx.doi.org/10.1155/2014/537408. 2014

[2] A.V. Ensinas,V. Codina, F. Maréchal, J.Q. Albarelli, M.A. Silva, Thermo-economic optimization of integrated first and second generation sugarcane ethanol plant, Chemical Engineering Transactions 35 (2013) 523-528.

[3] Mian, A., Ensinas, A.V., Marechal, F., Multi-objective optimization of SNG production from microalgae through hydrothermal gasification. Computers and Chemical Engineering, Volume 76, May 08, 2015, Pages 170-183

[4] Lim, C.S.; Manan, Z.A.; Sarmidi, M.R. Simulation modeling of the phase behavior of palm oil-supercritical carbon dioxide. J. Am. Oil Chem. Soc. 2003, 80, 1147-1156, DOI: 10.1007/s11746-003-0834-6.

R. Turton, Analysis, synthesis, and design of chemical processes (3rd ed.) Prentice Hall, Upper Saddle River, 2009.

G. Ulrich, P. Vasudevan, A guide to chemical engineering process design and economics a practical guide (2nd ed.), CRC, Boca Raton, 2003.

R. Bolliger, Méthodologie de la synthèse des systems énergétiques industriels, École Polytechnique Fédérale de Lausanne (EPFL), PhD Thesis, Lausanne, Switzerland, 2010.

M. Gassner, F. Maréchal, Methodology for the optimal thermo-economic, multi-objective design of thermochemical fuel production from biomass. Computers & Chemical Engineering 33 (2009) 769–781.

OSMOSE Platform: A tool for the design and analysis of integrated energy systems. 01 June 2013. Available from: http://leni.epfl.ch/osmose

B. Linnhoff, User Guide on Process Integration for the Efficient Use of Energy, 1st ed. Rugby: IChemE, 1982.