

# Optimal integration of a self sustained algae based facility with solar and/or wind energy

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## Abstract.

In this work we develop a conceptual design for an integrated facility that produces biodiesel (FAME) using solar and/or wind energy and CO<sub>2</sub>. Microalgae are grown to accumulate lipids that are extracted. The methanol needed for the transesterification is synthesized from CO<sub>2</sub> and electrolytic hydrogen. The electricity for the complex is produced using solar panels or wind turbines. The flowsheet is formulated as a multiperiod MINLP problem whose solution provides the optimal source of energy and the operating conditions over a year for an average production of 60 Mgal/yr of FAME. The facility requires an investment of 112 M€ for a production cost of 0.79€/gal (0.25 €/kg). The energy consumption is 3.2 MJ/gal of FAME capturing 4.05 kg CO<sub>2</sub> per kg of FAME and consuming 1L/L of water including the operation of the cooling tower and the boiler.

Keywords: Solar Energy; Biomass; Wind power; Synthetic methanol; Hydrogen; CO<sub>2</sub>

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## 1.-Introduction

Biodiesel is widely considered a biofuel, using methanol in the transesterification of the oil. While the use of methanol has been justified from technical and economic points of view, faster reaction times and cheaper than any other alcohol, not many studies have pointed out that methanol is typically produced from coal or natural gas. Therefore, the second most important raw material in the current biodiesel industry is actually a fossil based chemical. Ethanol can also be used as transesterification agent. Martín & Grossmann (2013a) designed a facility that used ethanol produced out of the same algae for the production of biodiesel, Fatty acid ethyl ester (FAEE). The biodiesel production cost was competitive with that produced from fossil methanol and algae oil, and no fossil fuel based raw material was needed. However, methanol can also be produced from either residues of the biodiesel industry or wastes. Martín & Grossmann (2013b) evaluated the production of methanol from glycerol reforming to be used in the production of FAME. However, only two thirds of the needs for methanol could be covered in this way and the production cost was higher compared with buying the methanol. CO<sub>2</sub> concentration in atmosphere has surpassed 400ppm recently (Montaigne, 2013) and, in an attempt to find further uses, it is being evaluated as a carbon source for chemicals. It has been shown that CO<sub>2</sub> can be hydrogenated to produce methane, although the production costs are high, Davis and Martín (2014). However, CO<sub>2</sub> can also be used to produce methanol via hydrogentation (Van-Dal and Bouallow,2013) and different life cycle evaluations from LCA (Trudewind, et al 2014a) to Well to Wheel analysls Trudewind, et al 2014b) have been presented. Therefore, the production of biodiesel from renewable raw materials requires the integration of renewable resources (Alwi et al 2012) using the philosophy of total site integration (Varbanov and Klemes, 2013).

While the use of CO<sub>2</sub> as raw material is interesting from the environmental and technical points of view, we are reusing a waste, the sustainability of the hydrogenation of CO<sub>2</sub> relies on the use of renewables to produce hydrogen. Actually the idea is old, but is its not until recently that it is being used (Levene et al 2005). Wind and solar energy can be used to produce the electricity that breaks down water into hydrogen and oxygen for further use. The advantage of producing chemicals out of these intermittent sources of energy is the fact that we can store the energy in a more useful state. Biomass can also be used to produce hydrogen, but in that case we are not fully using the biomass since we lose the carbon.

Therefore, in this paper we integrate the production of algae from CO<sub>2</sub> and solar energy and methanol using solar or wind energy, water and CO<sub>2</sub>, designing an integrated facility for the mitigation of CO<sub>2</sub> while producing liquid fuels. The disadvantage of using sustainable sources of energy such as biomass, wind and solar is the variability during a year in a region. Therefore, the design of such a plant must be evaluated as a function of the availability of the energy sources, wind (Archer and Jacobson, 2004) or solar (Sancho-Ávila et al 2013). The paper is organized as follows. In section 2 we describe the process. Next, in section 3 we discuss the main modeling assumptions and solution procedures for the formulated multiperiod MINLP problem. Subsequently, in section 4 we present results of the facility operation over a year long and an economic evaluation. Finally, in Section 5 we draw some conclusions.

## 2.-Process description.

The process consists of four sections. Algae oil production, water electrolysis, methanol synthesis and biodiesel production. Figure 1 shows the scheme for the integrated facility.

Figure 1.- Renewable resources integration for the production of biodiesel

### 2.1.Algae oil production.

The production of oil and starch from algae is performed by injecting CO<sub>2</sub> into the water, which can be saline water so that the consumption of freshwater is reduced, together with air and fertilizers, see Figure 2. The amount of make-up water needed, 0.006 kg per kg of biomass, and the concentration of fertilizers, 0.14 kg per kg of dry biomass, is taken from the report by Pate (2008) while the consumption of CO<sub>2</sub> depends on the growth rate (Sazdanoff, 2006)

We assume that the dry algae biomass is composed of lipids, starch and protein with 50% being lipids. Together with the algae, oxygen is produced and water is evaporated (Pate, 2008).The energy consumed by the pond system is calculated based on the results by Sazdanoff (2006). Next, the algae are harvested from the pond. This stage has typically been the most energy intensive. However, Univenture Inc. has presented an innovative technology capable of integrating harvesting and drying the algae with low energy consumption. It is based on the use of capillarity, membrane systems and paint drying to get 5% wet algae with a consumption of 40W for 500L/h of flow. The biomass is mixed with cyclo-hexane and pressed so that oil is extracted and the biomass is recovered from oil. The biomass can be used to obtain energy for

the system, or it can also be further treated to obtain glucose and protein. The oil is used for transesterification and biodiesel production.

Figure 2.- Algae oil production

### 2.2.-Methanol Synthesis:

As it can be seen in Figure 3, we consider an electrolyzer that breaks the water into hydrogen and oxygen operating at 80°C and 101 kPa a solution of 25% of KOH as electrolyte.



The energy for such an operation may come from wind turbines, solar panels, and/or the biogas generated from the biomass after oil extraction. On the one hand, the line of oxygen carries water vapor and traces of hydrogen. The water is condensed and the resulting stream dehydrated using a zeolite adsorber. Finally, the oxygen is compressed and stored. On the other hand, we have the stream of hydrogen containing traces of oxygen and water vapor. Most of the water is separated by condensation. The oxygen represents a challenge for further synthetic stages, and thus, it is eliminated using a deoxygenation reactor where water is produced. Next, a zeolite is used to dehydrate the stream. At this point, the hydrogen is mixed with the CO<sub>2</sub>. The gas phase is adjusted for the optimal operating conditions using a compressor and a heat exchanger. Methanol is produced based on a series of equilibria carried out over a catalyst, typically Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>. The optimal working conditions (ratio of H<sub>2</sub> and CO and working temperature and pressure at the reactor) are optimized. Unreacted gases are separated from the methanol and recycled back to the reactor, while the methanol is purified used at the transesterification reactor. For details of the process and the model we refer to the literature (Davis and Martín, 2014b).

Figure 3.- Methanol production

### 2.3.- Biodiesel synthesis

The use of heterogeneous catalysts for the production of biodiesel simplifies the purification stages since the catalyst can easily be removed from the products, or they can be packed in the reactor (Martín and Grossmann, 2012). Therefore, the process is simpler, see Figure 4. The reactants are prepared and fed to the reactor. The transesterification can be represented by eq. (2).



After the reactor, a distillation column is used to recover the excess of methanol. The bottoms of the distillation column contain mainly glycerol and biodiesel with small amounts of methanol, water, FFA and oil. A gravity separation allows the recovery of glycerol with a purity higher than 92%, while the biodiesel is purified in a distillation column.

Figure 4.-Oil transesterification.

The aim is to optimize the topology and the operating conditions minimizing the production cost to design a hybrid facility for the sustainable production of biodiesel using renewable resources taking into account the variation of wind and solar energy. We propose a conceptual design based on the optimization of a superstructure embedding the various process units involving solar or wind energy, algae growth, water electrolysis, CO<sub>2</sub> usage to produce methanol, and oil transesterification to biodiesel. The optimization of the superstructure is formulated as a multiperiod MINLP problem, where the model involves a set of constraints representing mass and energy balances for all the units in the system with monthly variations. While the operation of such facilities requires more details hourly analysis, the conceptual design is assumed to be carried out on a monthly grid. An economic evaluation is performed to determine the effect of the chemicals and raw materials costs on the design selection, and on the production cost of the optimal conceptual design.

### 3.-Modelling.

In this section we describe the main assumptions used in modeling the process for the production of synthetic methanol using wind / solar power and CO<sub>2</sub> to be used for the production of biodiesel. We use mass and energy balances, design equations, thermodynamic equilibrium and experimental data in order to develop models for all the units involved in the process. For the sake of the length of the paper, we refer to previous papers for more detailed modeling features of certain units related to hydrogen production (Marín and Davis, 2014) and algae growing and biodiesel synthesis (Martín and Grossmann, 2012).

#### 3.1.-Oil production and transesterification

##### 3.1.1.-Oil production

The detailed modeling for the production of oil can be seen in the supplementary material of (Martín and Grossmann, 2012). However, for this formulation we apply that model on a monthly basis where the

growth rate of the algae is a function of the solar energy as given by Park et al. (2011), eq (3), where  $I_0$  (kWh/m<sup>2</sup>/d) is the solar intensity,  $\eta_{\max}$ , the utilization of the light by the algae, 0.045 (Walker, 2009), and the algae heating value is 21 kJ/g (Park et al 2011) :

$$Growth = \frac{I_0 \cdot \eta_{\max}}{\text{algae heating value}} \quad (3)$$

The CO<sub>2</sub> consumption rate is given by eq. (4), Sazdanoff (2006):

$$\text{CO}_2 \left( \frac{\text{m}^3}{\text{d}} \right) = 0.6565 \cdot \text{Growth} \left( \frac{\text{g}}{\text{m}^2 \cdot \text{d}} \right) + 5.0784 \quad (4)$$

The accumulation of oil in the algae ranges from 40 to 65% of the dry weight (Sazdanoff, 2006). A value that can be conservative is to assume that the oil represents 50% of the dry biomass. A solvent and mechanical press are used to extract the soil. Next, the mixture solvent and oil are separated in vacuum distillation column. The oil is sent to transesterification and the solvent is recycled. We use a short cut model for the column (Biegler et al 1997), validated with CHEMCAD.

### 3.1.2.- Oil transesterification

Martín & Grossmann (2012) proved that the use of heterogeneous catalysis was promising due to the easy separation of the products. There is no need for biodiesel washing, reducing also the water consumption of the facility, and it is more robust to process different oil sources. Therefore, the reactor is modeled using a surface response model developed in the above mentioned paper given by eq. (5). Table 1 shows the lower and upper bounds of the operating conditions.

$$\text{yield} = -73.6 + 2.5 \cdot T_{\text{Trans}} + 24.9 \cdot \text{Cat} + 8.8 \cdot \text{ratio\_met} - 0.01 \cdot T_{\text{Trans}}^2 - 1.29 \cdot \text{Cat}^2 - 0.39 \cdot \text{ratio\_met}^2 - 0.26 \cdot T_{\text{Trans}} \cdot \text{Cat} \quad (5)$$

Table 1.-Range of operation of the variables. Heterogeneous catalyzed

We recover the methanol using a distillation column. Next, polar and non polar phases are separated at 40°C. The glycerol phase and the biodiesel phase have to be further purified. Vacuum distillation columns are used for methanol recovery and biodiesel purification to avoid glycerol and FAME decomposition, and modeled using a short cut method (Biegler et al 1997), validated with CHEMCAD. Thus, the bottoms of the methanol recovery column and the distillate of the biodiesel purification tower should be below 150°C and 250°C, respectively.

### 3.2.-Solar and wind sources

For a detailed description of the model related to the production of hydrogen and oxygen we refer the reader to [15].

#### 3.1.1-Wind Turbine power

We use the same turbine as in a previous paper(Davis and Martín, 2014), GE 1.5sle type (SAM, 2013). The power produced in this turbine is modeled by eq. (6) where  $P_{rated} = 1500\text{ kW}$ ,  $v$  is the average wind velocity,  $a=8.322 \text{ (m/s)}$  and  $m=0.806 \text{ (s/m)}$  .

$$P = \frac{P_{rated}}{1 + e^{(-(v-a)m)}} \quad (6)$$

#### 3.1.2-Solar panel installation

The PV panel of  $8\text{ m}^2$  that capable of using 75% of the solar energy that Earth receives is selected. The installation cost ranges from 1700 to 4000 \$/kWp (Maaben et al 2011) installed with a target of 1000\$/kWp (Goodrich et al 2012). 1kWp requires typically those  $8 \text{ m}^2$  of panel. Thus, we assume 2300€ per panel.

#### 3.1.3.-Hydrogen production and purification.

The power required to produce one kg of hydrogen is 175,000 kJ (NEL, 2012). In the electrolyzer, the water that is lost per unit of time, is not only given by water breakage, eq. (2), but also due to the evaporation, since the gas phases exit the electrolyzer saturated with water. For costing purposes, each electrolyzer generates 0.0124 kg H<sub>2</sub> per second (NEL, 2012). Both streams, either the one rich in O<sub>2</sub>, or the one rich in H<sub>2</sub>, are compressed. We considered the use of polytropic compressors with an efficiency of 0.85 and  $k = 1.4$  based on rules of thumb (Wallas, 1990). The stream consisting of mainly oxygen is first compressed in a three stage compressor system with intercooling using a pressure ratio of 5. After the first stage, we dehydrate the stream using zeolites. Similarly, the hydrogen stream is compressed to 500kPa so as to dehydrate it. Thus, zeolite adsorbants are used with a removal ratio of 99.97%. The dehydration of the oxygen takes place at 25°C, after the first compression and subsequent cooling. The hydrogen stream is dehydrated after the deoxygenation at 90°C. The Desoxo reaction is used to remove the traces of oxygen from the hydrogen stream following eq. (8). We assume a conversion of 99.97%.



### 3.3..-Synthesis Loop

The synthesis of the methanol is based on the hydrogenation of CO<sub>2</sub> (Chinchen et al 1988). Two reactions take place, apart from the methanol synthesis from CO<sub>2</sub> hydrogenation, the reverse water-gas-shift (RWGS) reaction also occurs , eq. (9)



Thermodynamically, the synthesis of methanol from CO<sub>2</sub> hydrogenation is less favored compared to that from CO, and it has a smaller heat of reaction. The reactor is modeled assuming equilibrium, where the elementary balances to the carbon, hydrogen and oxygen atoms must hold as well as the species equilibria. The values of the equilibrium constants for reactions given by eq. (9), are computed using eqs. (10-11) (Chinchen et al 1988).

$$\begin{aligned} \text{H: } 2 \cdot n_{\text{H}_2} + 2 \cdot n_{\text{H}_2\text{O}} \Big|_{\text{in}} - \left( 2 \cdot n_{\text{H}_2} + 2 \cdot n_{\text{H}_2\text{O}} + 4 \cdot n_{\text{CH}_3\text{OH}} \right) \Big|_{\text{out}} &= 0; \\ \text{C: } n_{\text{CO}} + n_{\text{CO}_2} \Big|_{\text{in}} - \left( n_{\text{CO}} + n_{\text{CO}_2} + n_{\text{CH}_3\text{OH}} \right) \Big|_{\text{out}} &= 0; \\ \text{O: } n_{\text{CO}} + 2 \cdot n_{\text{CO}_2} + n_{\text{H}_2\text{O}} \Big|_{\text{in}} - \left( n_{\text{CO}} + 2 \cdot n_{\text{CO}_2} + n_{\text{H}_2\text{O}} + n_{\text{CH}_3\text{OH}} \right) \Big|_{\text{out}} &= 0; \end{aligned} \quad (10)$$

$$\begin{aligned} \frac{\left[ P_{\text{CH}_3\text{OH}} \right] \left[ P_{\text{H}_2\text{O}} \right]}{\left[ P_{\text{CO}_2} \right] \left[ P_{\text{H}_2} \right]^3} &= K_{a2} e^{\left[ 22.225 + \frac{9143.6}{T} - 7.492 \ln(T) + 4.076 \cdot 10^{-3} \cdot T - 7.161 \cdot 10^{-8} \cdot T^2 \right]} \\ \frac{\left[ P_{\text{CO}} \right] \left[ P_{\text{H}_2\text{O}} \right]}{\left[ P_{\text{CO}_2} \right] \left[ P_{\text{H}_2} \right]} &= K_{a2} = \exp \left[ 13.148 - \frac{5639.5}{T} - 1.077 \ln T - 5.44 \cdot 10^{-4} T + 1.125 \cdot 10^{-7} T^2 + \frac{49170}{T^2} \right] \end{aligned} \quad (11)$$

### 3.4.-Raw materials

#### 3.4.1.- CO<sub>2</sub>

We selected a region given by the availability of CO<sub>2</sub> from power plants and high wind velocity, over class 3 (Archer, 2004). For our case study we locate the plant in the Gulf of Cadiz. But the formulation can be applied to any other region.

#### 3.4.2.-Wind/Solar/Biomass availability

Table 2 shows the data on the availability of solar energy and wind velocity over a year in the selected allocation. Furthermore, using eq. (1) we have computed the monthly algae growth rate.

Figure 5.- Resource availability in Spain (Sancho-Ávila, 2012; ARCHER 2004, CESR 2006]

Table 2 Monthly solar and wind availability [Windtrends, 2014; Junta de Andalucía, 2014]

### 3.5.-Solution procedure

This problem is formulated as a multiperiod MINLP of the following general formulation

$$\begin{aligned} \min Z &= C(d) + \sum_{t=1}^{\Gamma} f_t(d, x_t) \\ \text{st. } g_t(d, x_t) &\leq 0 \quad t=1, \dots, \Gamma \end{aligned} \tag{P0}$$

Where d are the design variables, some of them integer, and  $x_t$  are variables corresponding to the operation at each time period f.

We can address the solution of such a problem in several ways. The most computationally expensive requires the definition of all the mass and energy flows as a function of the period, a set of equations determining the mass and energy balances per month as indicated in P0. That multiplies the problem size by approximately the number of periods. The methods presented by Varvarezos et al either using an outer approximation (Varvarezos et al 1992) or an SQP decomposition (Varvarezos et al 1994) can be used to address the problem. Alternatively, we can take advantage of the knowledge of the operation of chemical plants, that is to say, the mass and energy balances are proportional to the operation of any month that can be taken as a reference. We assume that the optimal operating pressures, temperatures, chemical equilibria for the reactors and vapor – liquid equilibria are the same in each month. Thus, only the flows will change. Thus, we fix the annual production capacity to match the typical one for bioethanol / biodiesel plants, around 60MGal/yr (Martín and Grossmann, 2013c). The process may not operate at their full monthly capacity all year long, and therefore an efficiency is defined, effy(month). The oil produced on a monthly basis determines the needs for methanol for its transesterification. The methanol is produced via electrolytic hydrogen and CO<sub>2</sub>.

To formulate the problem in a general form, we consider two groups of equations. Those whose operation is not directly affected by the atmospheric conditions,  $g^u$ , i.e. processing steps, and those that depend on the input from the atmosphere,  $g^l$ , either in the form of raw materials (water, air) or renewable energy (wind velocity, solar o cooling systems):

$$\begin{aligned}
\min Z = & C(d) + \sum_{t=1}^{\Gamma} f_t(d, x_t) \\
\text{st.} \\
g_t^I(d, w_t^{\text{intensive}, I}, w_t^{\text{extensive}, I}) &\leq 0 \quad t=1, \dots, \Gamma \\
g_t^{II}(d, w_t^{\text{intensive}, II}, w_t^{\text{extensive}, II}) &\leq 0 \quad t=1, \dots, \Gamma
\end{aligned} \tag{P1}$$

The first group must remain untouched since its evaluation is directly dependent on time dependent variables. However, for the second group we can decompose it as follows. We consider a reference time interval for which the model of the process is written. The operating variables are computed as a function of that reference:

$$\begin{aligned}
\min Z = & C(d) + \sum_{t=1}^{\Gamma} f_t(d, x_t) \\
\text{st.} \\
g_t^I(d, w_t^{\text{intensive}, I}, w_t^{\text{extensive}, I}) &\leq 0 \\
g_{\text{ref}}^{II}(d, w_{\text{ref}}^{\text{intensive}, II}, w_{\text{ref}}^{\text{extensive}, II}, \theta_{\text{ref}}) &\leq 0 \\
w_t^{\text{intensive}, II} = w_{\text{ref}}^{\text{intensive}, II} & \quad \text{intensive} \in \{P, T\} \\
\eta_t \alpha_t w_{\text{ref}}^{\text{intensive}, II} = w_t^{\text{extensive}, II} & \quad \text{extensive} \in \{fc, F, Q, W\} \\
\alpha_t = f(t, d, w_{\text{ref}}^{\text{intensive}}, w_{\text{ref}}^{\text{extensive}}, \theta_t) & \\
\eta_t \in \{0, 1\} & \\
\theta_t = f(\text{atmospheric conditions}) = f(w_t^{\text{intensive}, I}, w_t^{\text{extensive}, I}), t = 1, \dots, \Gamma &
\end{aligned} \tag{P1}$$

Where,  $\alpha$  is a scale-up factor since the productivity of the system depends on the energy provided by the Sun or wind for instance.  $\eta$  is the factor that determines whether the system operates at the fully capacity of based on the availability of resources at a given time or not. If other raw materials are involved, such as freshwater or air at atmospheric conditions, we still need to maintain those as variable with time and evaluate the influence in the process.

Thus, the mass and energy balances presented in sections 3.1 and 3.2 are defined for a reference month,  $g^{II}$ . The operating pressures and temperatures of each unit are determined for this month and assumed constant over time. Equation (12) represents the operation of the plant in a certain reference month identifying the set of equations corresponding with  $g^{II}$ :

Mass and energy balances  $(T, P)_{\text{reference}}$  (12)

In order to compute the monthly production capacity, we can use the reference month and define a scale-up coefficient as follows:

$$\alpha \equiv \text{Scale}_{(\text{month})} = \frac{\text{Algae-Prod}_{(\text{month})}}{\text{Algae-Prod}_{(\text{reference})}} \quad (13)$$

To reach the annual production capacity, 6.07 kg/s of FAME must be produced, the following ratio must hold:

$$\begin{aligned} \text{fc(FAME)} &= \frac{1}{12} \sum_{\text{month}} \text{fc(FAME)}_{\text{reference}} \cdot \text{effy}_{(\text{month})} \cdot \text{scale}_{(\text{month})} \\ \text{fc(FAME)} &= 6.07 \text{kg / s} \end{aligned} \quad (14)$$

Thus, the power required to electrolyze water and produce the methanol required to transesterify the oil to reach de desired level of biodiesel, can be computed using eq. (15) as a function of the reference month:

$$\text{Power}_{(\text{month})} = \text{effy}_{(\text{month})} \cdot \text{Scale}_{(\text{month})} \cdot \left[ W(\text{Electrolizer}) + \sum_{i=\text{compressors}} W(\text{Compres}_i) + W(\text{Belt}) - W(\text{Press}) - W(\text{Pond}) \right]_{\text{reference}} \quad (15)$$

The power required on a monthly basis can be obtained either from wind energy using a number of wind turbines, solar energy by means of PV solar panels, and by transforming the biomass that is left after oil extraction into methane via anaerobic digestion, Ener\_biom<sub>reference</sub>. Thus, the power produced by any or a combination of them must be at least that given by eq (15) and it is computed using eqs. (17):

$$\text{Power}_{\text{month}} \leq \text{Power generated}_{\text{month}} \quad (16)$$

$$\begin{aligned} \text{Power generated}_{\text{month}} &= n_{\text{turbines}} \frac{P_{\text{nominal}}}{\left(1 + e^{(-v_{(\text{month})} - v_{\text{cut}})m}\right)} \\ &+ n_{\text{panel}} \cdot \text{Solar\_inc}_{(\text{month})} \cdot A_{\text{panel}} \cdot 3600 / (\text{days}_{(\text{month})} \cdot 243600) \\ &+ \text{Ener\_biom}_{\text{reference}} \cdot \text{Scale}_{(\text{month})} \cdot \text{effy}_{(\text{month})} \end{aligned} \quad (17)$$

Bear in mind that the number of turbines, ponds and solar panels are design variables. Apart from them, the number of electrolyzers in operation changes with the monthly production capacity. The equations involving them belong to the set g<sup>l</sup>. However, we need to pay for a number of them that will allow the operation over a year long:

$$n_{\text{electrolyzers}} \geq n_{\text{electr(month)}} \cdot \text{scale}_{(\text{month})} \quad (18)$$

Similarly, the ponds may not operate the entire year but we need to purchase the amount that will allow meeting the demand for biodiesel. Thus, the ponds to be purchased are given by eq. (19):

$$n_{ponds,total} \geq \frac{n_{pond,reference}}{effy_{(month)}} \quad (19)$$

To decide on the energy source for the operation of such a plant, the objective function, eq. (24), represent profit, income from sales of diesel and annualized costs of panels, wind turbines, electrolyzers and energy consumed in the form of steam. Specifically, the annualized cost of the panels is given by eq. (21), that of the wind turbines required is given by eq. (20), the annualized cost of electrolyzers is given by eq. (22), that of the ponds is given by eq. (23), and finally the term for the simultaneous optimization and heat integration which is responsible for the operating pressures and temperatures across the flowsheet. Since we use Duran & Grossmann's (1986) model the thermal energy is included in the objective function as  $QS_{max}$ . We assume a selling price of 1€/kg for the biodiesel.

$$Cost_{wind} = \frac{1}{3} \cdot \frac{\text{Wind}_{Invest} \cdot P_{nominal} \cdot n_{turbines}}{time} + Op\_cost_{wind} \cdot P_{nominal} \cdot n_{turbines}; \quad (20)$$

$$Cost_{solar} = \frac{1}{3 \cdot time} \cdot n_{panel} \cdot (P_{panel} \cdot c_{panel} + A_{panel} \cdot c_{area}); \quad (21)$$

$$Cost_{electro} = \frac{1}{3 \cdot time} \cdot Cost_{unit} \cdot n_{electrolyzers} \quad (22)$$

$$Cost_{ponds} = \frac{1}{3 \cdot time} \cdot Cost_p \cdot n_{Ponds,total} \quad (23)$$

$$Z = fc(FAME) - wind - solar - C_{steam} \cdot \lambda \cdot QS_{max} - Cost_{electro} - Cost_{ponds} \quad (24)$$

Therefore, the multiperiod problem is formulated as follows, P2.

$\begin{aligned} Max \quad Z = & \frac{1}{12} \sum_{month} fc(FAME)_{reference} \cdot effy_{(month)} \cdot scale_{(month)} - Cost_{wind} \\ & - Cost_{solar} - C_{steam} \cdot QS_{max} - Cost_{electro} - Cost_{ponds} \end{aligned}$	(P2)
St.	
<ul style="list-style-type: none"> <li>-Mass and energy balances for a reference month described in sections (3.1-3.3), represented by eq. (12)</li> </ul>	
<ul style="list-style-type: none"> <li>- eqs (13-23)</li> </ul>	
<ul style="list-style-type: none"> <li>-Duran &amp; Grossmann's model (Duran and Grossmann, 1986) for the</li> </ul>	

simultaneous optimization and heat integration of the flowsheet

-Where the variables that are monthly dependent are:

Effy, Algae-Pond, Power, Scale, Power generated, wind velocity, solar incidence, the electrolyzers in operation each month,  $n_{electr(month)}$ .

-The variables that are assumed to be constant on a monthly basis

Temperatures, pressures.

-The scalable variables

Energy and mass flows.

-The design variables (integer)

Number of ponds ( $n_{ponds,total}$ ), number of electrolyzers ( $n_{electrolyzers}$ ), the number of wind turbines ( $n_{turbines}$ ), the number of solar panels,  $n_{panel}$ .

Formulation P2 corresponds with a multiperiod MINLP. The number of ponds and solar panels and electrolyzers are considered to be continuous variables, since the number required is large, above 10000. However, the number of wind turbines and electrolyzers is in the order of 100-200 and 10-20 respectively. Therefore, we simplify the original MINLP given by P2 by a formulation P2' where only the number of wind turbines and electrolyzers are integer.

To solve P2', we apply a branch and bound method for the two integer variables. Thus, we first solve a relaxed NLP, considering that the number of electrolyzers and that of the turbines are also continuous variables, using a multistart solution approach with various solver and with CONOPT as the preferred one. The problem has 1700 equations and 2200 variables. It turns out that no turbines are needed and we require 15.3 electrolyzers. The value of the objective function is 5.266 \$/s. Therefore, we branch on the node for the number of electrolyzers equal to 15 and equal to 16. The first relaxed NLP is infeasible, since it is not possible to reach the desired production capacity. By fixing the number of electrolyzers to 16, the value for objective function becomes 5.265 \$/s. Thus the solution is obtained after exploring two nodes, since the number of turbines used is 0, in about 5 min CPU time.

Next, we design the heat exchanger network (Yee and Grossmann, 1990) and a water network (Ahmetovic and Grossmann, 2011) for the optimal operating conditions of the month with the highest

production capacity, which is June, in order to compute the energy and water consumption per gallon of biodiesel produced. Again, the flows will be proportional on a monthly basis, and therefore the consumptions of energy and water per unit of biofuel produced should be constant. Finally, for our selected location we perform an economic analysis to compare the operation of such an integrated facility with the ones presented in previous papers where wind or solar energy alone was used.

Bear in mind that the allocations where algae production is favorable correspond to those with high solar incidence, and therefore it is expected that solar energy is the energy source of choice. We use the Gulf of Cadiz to be consistent in the comparison with previous work (Davis and Martín, 2014a&b). Thus, next we consider the effect of the price of biomass, biomass process section cost, solar and wind availability to evaluate the optimal configuration for average conditions, establishing ranges where one or the other technologies are preferred.

#### 4.-Results and discussion

The key question regarding the selection between the use of solar or wind energy onshore depends on the costs, and the wind and solar energy availability. Over the last years, a number of studies have gathered this information. From 2010 the costs of turbines and installation have stabilized, Tegen et al. (2013). Based on the results by Tegen et al. (2013) and IRENA (2012), the range of investment cost in Europe is 1300-1900 €/kW. The cost of the turbine alone is around 1100€/kW, where the typical size for onshore wind turbines is 1500 kW. The operating costs, including the lease of land, are also variable with the country, and are within the range of 0.0077 - 0.033 €/kWh (IRENA, 2012). For offshore turbines, the investment cost ranges from 3100-3300 €/kW in Europe and 2500-3900 €/kW in the US. The operating costs including land lease 0.021-0.032€/kWh in Europe and 0.012-0.042 €/kWh in the US. The typical wind turbine size is 3.6 MW, IRENA (2012). In our case we consider the lease alone in order to compare with the solar based facility.

In the case of the photovoltaics panels, the cost ranges from 1700-4000 \$/kWp. We assume 2300€ per panel of 8m<sup>2</sup>. We also have to account for the land and its preparation, typically 5.5 €/m<sup>2</sup> (Serrano, 2013). In the United States land preparation was approximately \$5,025 per acre (Maaben, 2011). Average site preparation costs have been observed to be approximately \$25,000, although this can vary from \$5,000-\$25,000 per acre, but it is site specifics (Goodrich et al 2012).

#### 4.1.-Monthly Plant operation

The initial result to be highlighted is that solar energy is more interesting from the economic point of view, and thus solar panels are selected for the production of the electricity needed at the electrolyzers. This result was to be expected since algae growing depends on solar availability, and therefore the plant allocation is expected to be in a region with high solar incidence. The number of ponds required throughout the year is 28600, of 1000 m<sup>2</sup> each, operating at full capacity along the entire year, efficiency equal to 1 month after month. We require 20524 solar PV panels (40 MW can be produced in the best month) and no turbines. This is interesting from the investment point of view since throughout the year the most expensive equipment is fully used. Furthermore the need for ponds and panels results in a large area covered, in total around 30 km<sup>2</sup>. That does not mean that we need ground, algae can grow in sea water and panels only represent 0.16km<sup>2</sup>. However, we realize that this kind of facility is far from being operational. If we combine solar with wind, since the profile of the wind availability is different than that of the solar incidence, the effect on the plant would be that in order to provide the energy to produce the required methanol during the hottest months, more turbines would be needed. However, this electricity may be in excess for the rest of the year, depending on the availability pattern. Furthermore, a total of 16 electrolyzers are needed.

Apart from 60 Mgal/yr of FAME, 19.6 kt/yr of glycerol and 31.1 kt/yr of Oxygen are produced. In Figure (6) we present the monthly profile of the production of each chemical over the year. The advantage of producing fuels and chemicals out of solar energy is that we can store them. The disadvantage is that the process is not operating at a constant capacity over the year. In Figure (7) we show the monthly use of electrolyzers. We see that during summer time, we use more than twice the number of electrolyzers than during winter keeping the others idle. However, this is a small cost compared with the cost of ponds and solar panels that are operating at full capacity over the year.

The optimal operating conditions of the transesterification reactor turned out to be 60 °C, and a methanol to oil molar ratio of 10.1 with a catalyst added of 0.06kg/kg. These are close to the ones for the stand alone process [16], but slightly different in the amount of catalyst added. The methanol synthesis reactor operates at 200°C and 52 bar. The conditions are similar to the production of methanol from syngas [2]. Table 3 collects operating conditions of different selected units. The production of FAME captures and sequesters 4.05 kg CO<sub>2</sub> per kg of FAME, where 96% is due to algae production, and 1.4 kg of CO<sub>2</sub> /kg of

methanol produced to transesterify the oil. In terms of water consumption, because of the recycle, we feed to the process one third of the water fed to the electrolyzer, representing 0.13 kg of water per kg of FAME produced or 1.2 kg of water per kg of methanol produced.

Figure (6).- Month production of FAME and chemicals

Figure (7).- Number of electrolyzers in operation

Table 3. Main operating variables of selected units (T: TOP; B: Bottom)

Unit/Op. Condition	Transesterification Reactor	Oil Column	MeOH Column	Biodiesel Column	MeOH Purification	MetOH Synthesis
T (°C)	60	T: 31 B:350	T: 41 B:150	T: 250 B:290	T: 63 B: 101	200
P (bar)	4	0.18	0.39	0.08	1	52
H <sub>2</sub> /CO <sub>2</sub>						5.6
MeOH/Oil	10.1					

After the optimization, we design a heat exchanger network using SYNHEAT for the month with the highest production capacity. We assume that the network will not be operating at its full capacity during most of the months, but the excess of area will be able to cope with the difference in flow rates that may reduce the global heat transfer coefficients. The average energy consumption turns out to be 3.2 MJ/gal of FAME produced and the cooling, 6.9 MJ/gal. The values are higher than those when we buy methanol from the market (Martín and Grossmann, 2012) but lower than those needed for the integrated facility that produced ethanol and FAEE simultaneously, 4 MJ/gal (Martín and Grossmann, 2013a).

In terms of water consumption, we develop a water network based on the model by Ahmetovic and Grossmann (2011) for the month of the highest production capacity. We compute an average of 1 L/L including the freshwater to be consumed, 0.13 kg of water per kg of FAME produced, together with that needed for the boiler to produce the energy and the cooling tower for refrigeration. The water consumption of the process presented in this work is larger than the one reported for the integrated facility that produces ethanol and FAEE (0.59 gal/gal), (Martín and Grossmann, 2013a). The reason is the need for water as raw material for the production of the electrolytic hydrogen.

However, the design of this integrated process has several disadvantages. On the one hand, the profile of the operation of the plant indicates that the units will be operating at a low load for most of the time.

This can be addressed by integration of facilities into a complex. The second one is the large area needed. For the operation of such a plant we require around 30 km<sup>2</sup>, although 0.5% corresponds to land while the rest could be wastewater or saline water the area is large. Deserts can be an option from the solar availability point of view, but the water requirement can be a problem.

We realize that when solar and wind energy are considered, their variability and uncertainty are to be taken into account. However, as we have seen in Martín (2016), optimal operation is needed for the development of surrogate models that will allow us to go into the operational level. From the conceptual design point of view, monthly operation gives the big numbers in terms of units and operating conditions that serves as first stage for a more detailed analysis.

#### 4.2.-Economic evaluation

For the evaluation of the investment cost we use the factorial method (Sinnott, 1999). The Matche web page (MATCHE, 2014) is used to estimate the cost of the chemical processing equipment, while Goodrich et al (2012) is the reference for the solar panel cost and Saur (2008) for the electrolyzers. We size the units for the month with the largest production capacity. The details for the units sizing as a function of the flow rate or power can be found in the supplementary material of Almena and Martín, 2016]. Figure (8) shows the share for the solar field and the rest of the equipment in the plant. 70% of the investment cost of the equipment corresponds to the solar field, 25 % is due to the oil production, while the remaining 5% is due to the chemical synthesis and product purification, including compressors, reactors, heat exchangers and zeolite dehydration systems. The unit costs add up to 84 MM€.

Furthermore, the installed equipment represents 1.5 times the equipment cost except for the solar field, which has its own installation cost (Goodrich et al 2012):

$$\text{Investment} = 1,300 \text{ €/kWp} \quad (18)$$

Piping, insulation, instrumentation and utilities represent 20%, 15%, 20% and 10% of the equipment cost, except the wind turbines, respectively. The cost for the land and buildings is estimated to be 8.5 M€ for the chemical plant plus 5.5 €/m<sup>2</sup> for the solar field (Maaben et al 2011). These items add up to the fixed cost (111 M€). The fees represent 0.75% of the fixed cost. The direct costs is 112 M€. Including the working capital, the investment adds up to 120M€.

### Figure 8.- Investment cost

Furthermore, we estimate the production cost of the FAME. We consider the labour, taxes, administration, utilities, equipment maintenance (Sinnot, 1999); see Figure 9 for the breakup of the cost. We require an average of 6 MW of thermal energy (3.2 MJ/gal) and 13.7 MW of cooling. The cost adds up to 47 M€/yr for the production of 60 Mgal/yr, 0.79 €/gal, considering the credit from oxygen and glycerol at 0.02 €/kg and 0.3 €/kg, respectively, but having to pay for the fertilizers at 0.37€/kg.

### Figure 9.- Production cost break down

Comparing this process with the one that simultaneously produces ethanol and biodiesel (FAEE), the investment cost is similar 120 M€(160 M\$) for solar methanol vs 180 M\$ for the integrated multibiofuel plant. However the production of bioethanol and biodiesel has a lower production cost, \$0.35/gal with higher energy consumption (4MJ/gal) but lower water consumption (0.59 gal/gal) (Martín and Grossmann, 2013a)

## 5.-Conclusions

In this paper we have optimized an integrated facility to use renewable sources, solar and wind energy, for the production of biodiesel, FAME. We obtain the oil from algae and the methanol from the electrolysis of water and CO<sub>2</sub>.

We formulate the problem as a multiperiod MINLP, where we simplify the optimization of the operating conditions by considering a fix value for every month. Furthermore, we relax the integer variables such as the number of ponds, panels, electrolyzers or wind turbines. We simultaneously optimize and heat integrate the flowsheet to determine the optimal operating conditions of the units and over a year long operation.

It turns out that the most efficient combination with no area limitations, is the use of solar panels to provide the electricity needed for running the plant including the ponds. The advantage is that since we use solar energy, the profile of the production of oil matches that of the methanol needs for the plant, and thus the most expensive equipment, panels and ponds, are fully used the entire year. For a plant of 60 Mgal/yr of biodiesel, the investment cost is 120 M€ and the production cost of biodiesel is 0.80€/gal.

## 6.-Nomenclature

a: Adjustable parameter for the power curve (m/s)  
 $A_{\text{panel}}$  (m<sup>2</sup> /kWp) /8/  
 Algae -Prod: Flow of alga produced per s (kg/s)  
 $C_{\text{panel}}$  Investment per unit installed (€ / kWp )  
 $C_{\text{area}}$  Investment per unit installed (€ / m<sup>2</sup> )  
 $C_{\text{steam}}$  Steam cost (0.019 €/kg)  
 Cat: Catalysis added to the transesterification reactor w/w  
 $C_p$ : Constant heat capacity (kJ/kg °C)  
 $\text{Cost}_p$ : Cost of a pond 620 € per pond of 1000m<sup>2</sup>  
 $\text{Days}_{(\text{month})}$ : Days in a month  
 $\text{effy}_{(\text{month})}$ : Relative Monthly production capacity versus the maximum one  
 $Ener_{\text{biom}}$ : Energy produced form the waste biomass (kW)  
 $f_{\text{c}}(\text{FAME})_{\text{reference}}$ : Flow rate of FAME at the reference month (kg/s)  
 $F_i$ : Mass flow rate (kg/s)  
 Growth: Growth velocity of algae (g/m<sup>2</sup> day)  
 $I_0$ : Solar Intensity (kWh/m<sup>2</sup>/d)  
 k: Politropic coefficient.  
 $k_p$ : Equilibrium constants  
 m: Adjustable parameter for the power curve (m/s)  
 MW Molecular weight (kg/kmol)  
 $N_{\text{electrolyzers}}$ : Number of electrolyzers  
 $n_{\text{panel}}$ : Number of solar panels  
 $n_{\text{pond,reference}}$ : Number of ponds operating during the reference month.  
 $n_{\text{pond,total}}$ : Number of ponds bought  
 $n_{\text{turbines}}$ : Number of wind turbines  
 $P$ : Power produced by a single turbine (kW)  
 $P_i$ : Partial pressure of component i (kPa)  
 $P_{\text{panel}}$  Nominal power per panel /1kWp/  
 $P_{\text{nominal}}$  Nominal Power of a turbine 1500 kW  
 $Op_{\text{cost\_wind}}$  Rent of the ground for the turbines ( € /kWh)  
 $QS_{\text{max}}$ : Heat required in the integration ( kW)  
 $\text{ratio\_met}$ : Molar ratio between methanol and oil  
 $\text{Scale}_{(\text{month})}$  Proportional coefficient of the maximum production capacity  
 $Solar_{\text{inc}}_{(\text{month})}$  :Monthly solar incidence (kWh per m<sup>2</sup>)  
 T: Temperature (K)  
 $T_{\text{Trans}}$ : Temperature at the transesterification reactor (°C)  
 time: seconds in a year (s)  
 v: Wind velocity (m/s)  
 $V_{\text{cut}}$ : Adjustable parameter for the power curve (m/s)  
 W(unit): Electric power (kW)  
 $Wind_{\text{invest}}$  Investment required per kW of wind power installed (€ / kW)  
 yield: Conversion of the transesterification reactor  
 Z: Objective function (€/s)  
 $\eta$ : Efficiency  
 $\lambda$ : Latent heat (kJ/kg)

#### Units ( Legend for Figures9

Belt: Capillarity Belt

Col: Column

Compres: Compressor

Deoxo: Deoxo Reactor

HX: Heat Exchanger

Electr: Electrolyzer

Mix: Mixer

Reactor: Reactor

Sep: Separator  
Scr: Source  
Snk: Sink  
Tank: Tank  
Zeo: Zeolites

Sub

Reference: Under the references conditions of flow capacity

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### 7.-References

- Ahmetović, E., Grossmann, I.E., 2011. Global superstructure optimization for the design of integrated process water networks. *AIChE J.* 57 (2), 434-457
- Almena, A., Martín, M., 2016. Techno-economic analysis of the production of epichlorohidrin from glycerol. *Ind. Eng. Chem. Res.* 55 (12), 3226-3238
- Alwi, S.R.W., Rozali, N.E.M., Abdul-Manan, Z., Klemes, J.J., 2012. A process integration targeting method for hybrid power systems. *Energy* 2012; 44, 6-10
- Archer, C.L., Jacobson, M.Z., 2004. Corrections to "Spatial and temporal distribution of U.S. winds and wind power at 80 m derived from measurements", *Journal of Geophysics. Research* 2004; 109(D20116), doi:10.1029/2004JD005099, 2004.
- Archer, C.L., 2004 The Santa Cruz Eddy and U.S. wind power, Ph.D. Thesis, 190 pp., Stanford University, Stanford, 1 April 2004.
- Biegler, L.T., Grossmann, I.E., 1997. Westerberg AW. *Systematic Methods of Chemical Process Design*, New Jersey: Prentice Hall, 1997.
- Chinchen, G.C., Denny, R.J., Jennings, J.R., Spencer, M.S., Waugh, K.C., 1988. *Synthesis of Methanol: part 1. Catalysts and Kinetics Applied. Catalysis*; 36, 1-65
- CESR, 2006. Joint Emission trading as a socio-ecological transformation.  
[http://www.usf.uni-kassel.de/cesr/index.php?option=com\\_project&task=view\\_detail&agid=25&lang=en](http://www.usf.uni-kassel.de/cesr/index.php?option=com_project&task=view_detail&agid=25&lang=en)
- Davis, W., Martín, M., 2014a. Optimal year-round operation for methane production from CO<sub>2</sub> and Water using wind energy. *Energy*, 69, 497-505
- Davis, W., Martín, M., 2014b Optimal year-round operation for methane production from CO<sub>2</sub> and Water using wind and/or Solar energy. *J. Cleaner Production* 2014, 80, 252-261.
- Duran, M.A., Grossmann, I.E., 1986. Simultaneous optimization and heat integration of chemical processes. *AIChE J.*, 32, 123-138
- Goodrich, A., James, T., Woodhouse, M., 2012. Residential, Commercial, and Utility-Scale Photovoltaic (PV) System Prices in the United States: Current Drivers and Cost-Reduction Opportunities NREL/TP-6A20-53347, February 2012. <http://www.nrel.gov/docs/fy12osti/53347.pdf>

IRENA.2012. Renewable Energy technologies: Cost Analysis Series. Vol. 1. Power Sector. Wind Power. 2012

Junta de Andalucía, 2014. Radiación Solar  
<http://www.agenciaandaluzadelaenergia.es/Radiacion/radiacion2.php>

Levene, J.I., Mann, M.K., Margolis, R., Milbrandt, A., 2005. An Analysis of Hydrogen Production from Renewable Electricity Sources Conference Paper . NREL/CP-560-37612 September 2005

Maaßen, M., Rübsamen, M., Perez, A. 2011. Photovoltaic Solar Energy in Spain SEMINAR PAPERS IN INTERNATIONAL FINANCE AND ECONOMICS Seminar Paper 4/2011.

Martín, M., 2016. Methodology for solar and wind based process design under uncertainty: Methanol production from CO<sub>2</sub> and hydrogen Comp Chem Eng. 92, 43-54

Martín, M., Grossmann, I.E., 2012. Simultaneous optimization and heat integration for biodiesel production from cooking oil and algae. Ind. Eng. Chem. Res. 51 (23), 7998–8014

Martín, M., Grossmann, I.E., 2013a. Optimal engineered algae composition for the integrated simultaneous production of bioethanol and biodiesel AIChE J, 59 (8), 2872–2883

Martín, M., Grossmann, I.E., 2013b. ASI: Towards the optimal integrated production of biodiesel with internal recycling of methanol produced from glycerol. Environ. Prog. & Sust. Energ. 32(4), 791-801

Martín, M., Grossmann, I.E., 2013. On the systematic synthesis of sustainable biorefineries. Ind. Eng. Chem. Res., 52 (9), 3044-3064

Matche, 2014. <http://www.matche.com/prod03.htm>, 2014 (last accessed Feb. 2014).

Montaigne, F., 2013. Record 400ppm CO<sub>2</sub> milestone 'feels like we're moving into another era The Guardian Tuesday 14 May 2013 17.02 BS

<http://www.theguardian.com/environment/2013/may/14/record-400ppm-co2-carbon-emissions>

NEL (2012) <http://www.nel-hydrogen.com/home/?pid=75> Last accessed November 2013

Pate, R. (2008) Biofuels and the Energy-Water Nexus AAAS/SWARM April 11, 2008 Albuquerque, NM.

Park, J.B.K., Craggs, R.J., Shilton, A.N., 2011. Wastewater treatment high rate algal ponds for biofuel production. Biores. Technol. 2011; 102(1): .35-42.

Sancho Ávila, J.M., Riesco Martín, J., Jiménez Alonso, C., Sánchez de Cos Escuin, M.C., Montero Cadalso, J., López Bartolomé, M. 2013. Atlas de radiación solar AEMET (Spain) Madrid. Spain 2013 [www.aemet.es/documentos/es/serviciosclimaticos/datosclimatologicos/atlas\\_radiacion\\_solar/atlas\\_de\\_radiacion\\_24042012.pdf](http://www.aemet.es/documentos/es/serviciosclimaticos/datosclimatologicos/atlas_radiacion_solar/atlas_de_radiacion_24042012.pdf) (last accessed January 2013)

SAM, 2013. <https://sam.nrel.gov/> Last Accessed February 2014

Saur, G. 2008. Wind-To-Hydrogen Project: Electrolyzer Capital Cost Study Technical Report NREL/TP-550-44103 , December 2008

Sazdanoff, N. 2006. Modeling and Simulation of the Algae to Biodiesel Fuel Cycle. Undegraduate Thesis. The Ohio State University, Columbus, OH, 2006.

Serrano, A., 2013. ¿Cuánto vale el Suelo?.  
[http://www.fundacionsistema.com/\(X\(1\)A\(K8BoSNbrzqEkAAAAOTIzYWY5NTctNTIwYy00OTdiLTg3ZTqtM2Q2ZmZIM2VmMDBmwOXIjp7fDsycz55OgITzcDhisU8qaQUWfOgX.mSKm41\)\)/News/ItemDetail.aspx?id=4027&AspxAutoDetectCookieSupport=1](http://www.fundacionsistema.com/(X(1)A(K8BoSNbrzqEkAAAAOTIzYWY5NTctNTIwYy00OTdiLTg3ZTqtM2Q2ZmZIM2VmMDBmwOXIjp7fDsycz55OgITzcDhisU8qaQUWfOgX.mSKm41))/News/ItemDetail.aspx?id=4027&AspxAutoDetectCookieSupport=1) Last Accessed February 2014

Sinnott, R.K. 1999. Coulson and Richardson, Chemical Engineering. 3<sup>a</sup>Ed. Butterworth Heinemann, Singapore.

Tegen, S., Lantz, E., Hand, M., Maples, B., Smith, A., Schwabe, P., 2011. Cost of Wind Energy Review NREL/TP-5000-56266 March 2013

Trudewind, C.A., Schreiber, A., Haumann, D. 2014. Photocatalytic methanol and methane production using captured CO<sub>2</sub> from coal power plants. Part I a Life Cycle Assessment. J. Clean. Prod. 70, 27-37

Trudewind, C.A., Schreiber, A., Haumann, D. 2014. Photocatalytic methanol and methane production using captured CO<sub>2</sub> from coal power plants. Part II – Well-to-Wheel analysis on fuels for passenger transportation services . J. Clean. Prod. 2014, 70, 38-49

Van-Dal, E.S., Bouallou, C., 2013. Design and simulation of a methanol production plant from Co<sub>3</sub> hydrogenation. J. Clean. Prod., 57, 38-45.

Varbanov P, Klemes J., 2010. Total sites integrating renewables with extended heat transfer and recovery. Heat Transfer Engineering. 31(9), 733-41.

Varvarezos, D.K., Grossmann, I.E., Biegler, L.T., 1992. An Outer Approximation Method for Multiperiod Design Optimization, *Ind. Eng. Chem. Res.*, 31, 1466-1477.

Varvarezos, D.K., Biegler, L.T., Grossmann, I.E., 1994. Multiperiod design optimization with SQP decomposition. *Comp Chem. Eng.*, 18(7), 579-595.

Walker, D.A., 2009. Biofuels, facts, fantasy, and feasibility. *J. Appl. Phy.*, 21(5), 509-517.

Wallas, S.M. Chemical Process Equipment: Selection and Design,3rd ed.; Butterworth-Heinemann: Oxford, UK, 1990.

[http://windtrends.meteosimtruewind.com/wind\\_anomaly\\_maps.php?zone=EU](http://windtrends.meteosimtruewind.com/wind_anomaly_maps.php?zone=EU) Last accessed Dec 2014

Yee, T.F., Grossmann, I.E., 1990. Simultaneous optimization models for heat integration – II. Heat exchanger networks synthesis. *Comp. Chem. Eng.* 1990; 28: 1165-1184.