MICROALGAE BIOREFINERY ALTERNATIVES AND HAZARD EVALUATION

J. Pinedo [1], C.V. García Prieto [2], A.A. D´alessandro [2], R. Ibáñez [1], S. Tonelli [2], M.S. Díaz [2], Á. Irabien [1]

[1] Department of Chemical and Biomolecular Engineering, University of Cantabria, Avda. los Castros s/n, Santander, Spain

[2] Planta Piloto de Ingeniería Química-PLAPIQUI (UNS-CONICET), Camino la Carrindanga km 7, Bahía Blanca 8000, Argentina

E-mail: pinedoj@unican.es

Keywords: microalgae, biorefinery, optimization, hazard evaluation

ABSTRACT

Biodiesel production based on microalgae and using carbon dioxide as feedstock constitutes an attractive biofuel alternative. Technology development and process optimization are necessary to minimize the overall production cost. Moreover, in the framework of process sustainability, social and environmental impacts should include process safety aspects. In this context, the objective of this work is to develop a biodiesel production process based on microalgae and the subsequent estimation of the associated risks, thus contributing to more sustainable and safe processes.

The biodiesel biorefinery is optimized, taking into account alternative configurations for algae cultivation and lipid extraction. Algae cultivation options are open ponds and tubular photobioreactors. Regarding lipid extraction, dewatering and subsequent n-hexane extraction, and combined ethanol/n-hexane extraction are the studied alternatives. Numerical results show that open ponds and n-hexane extraction provide maximum net present value. However, n-hexane consumption dramatically rises, and industrial hazards have not been considered in the optimization process. To overcome this issue, a preliminary hazard analysis is carried out to identify hazardous materials and operations. Event trees are formulated to derive the frequencies of different accident scenarios, further determining the consequences. The major consequence accidents involve toxic releases of high quantities of n-hexane. By comparing the proposed alternatives, this work aims to highlight the need to consider not only economic but also safety and environmental objectives in the development of a biodiesel production project.

1. INTRODUCTION

Fossil fuel energy resources have shown many drawbacks, thus enhancing the development of alternative energies such as renewable solid, liquid and gaseous biofuels (Giotitsas et al., 2015). In this context, significant growth has taken place in different countries for biodiesel production, to meet both internal and external demand for home consumption. First and second generation biofuels were previous attempts to obtain renewable energy resources from food crops and forest residues respectively. However, they have raised concern over the use of arable land and food competition (Mata et al., 2010).

Third generation biofuels derived from microalgae turns up as promising, carbon neutral and technically viable alternative energy resource, overcoming the major drawbacks presented by first and second generation biofuels (Chisti et al., 2007; Gong and Yang, 2011; Rulong et al., 2012). Microalgae represent several benefits as sustainable biofuel feedstock, posing high growth rates and cultivation of large biomass amounts, as well as presenting the ability to thrive in harsh environments (Zhao et al., 2012). First, second and third generation biofuels have been evaluated to be applied in the EU (Čuček et al., 2014). Microalgae, and their entrained lipids, can provide different types of biofuels and bioenergy production options, such as biodiesel from transesterification, fermented bioethanol, photo-biological hydrogen, or methane produced by anaerobic digestion of the algal biomass (Chisti, 2007; Scott et al., 2010; Ullah et al., 2015).

Chisti (2008) stated that only biodiesel from microalgae has the potential to completely displace petroleum-derived fuels, having the ability to be directly consumed by conventional diesel engines. Algal biodiesel presents several advantages over petroleum diesel in the pursuit of sustainability: it is a renewable energy source, biodegradable, non-toxic, quasi-carbon neutral under sustainable production and contains reduced levels of non-desired contaminants (particulate matter, carbon monoxide or SO_X). Another major advantage of algal biodiesel over petroleum diesel is the need to consume CO_2 for algae cultivation, drastically reducing CO_2 emissions an even requiring CO_2 supply for an external source. This issue may produce a synergistic effect if a microalgae biorefinery is located close to CO_2-disposal industry, such as thermoelectric (Brennan and Owende, 2009; Gong and Yang, 2011; Singh and Singh, 2014)

Nonetheless, biofuels extracted from microalgae present higher costs of process technology than petroleum diesel, hindering their commercial exploitation. To overcome this problem, highly integrated production processes can be implemented, not only to reduce wastes, but also to create efficient processing of biomass into energy, fuels, chemicals, polymers or food additives, among others (Sadhukhan et al., 2014). Additionally, if an anaerobic digester is considered to produce energy from process waste streams, it can also be fed by waste paper and sludge from water treatment plants, reducing other environmental problems and promoting the sustainability within a life cycle assessment (LCA) perspective.

However, within a sustainable framework, not only economic issues should be evaluated, but also potential impacts on the environment and population must be taken into account.

Several studies highlighted the need to couple economic and environmental aspects of sustainability for the biodiesel production, usually applying LCA approaches to assess the environmental impact (You et al., 2014). Gutiérrez-Arriaga et al. (2014) complemented biorefineries with CO_2 biofixation, following LCA principles. Martinez-Hernandez et al. (2013) combined economic value and environmental impact (EVEI) analysis to define sustainability indicators based on LCA. Menetrez (2012) reviewed the potential environmental and human health impacts of different microalgae for biofuel production, including genetically modified organisms. Andiappan et al. (2015) proposed a multiobjective optimization approach to trade off different criteria simultaneously, for the incremental environmental burden within a reaction pathway. A systematic method combining process simulation, economic, environmental and energetic assessment and heat integration was proposed by Brunet et al. (2015). The multiobjective program formulated by Santibañez-Aguilar et al. (2014) included process profitability, environmental impacts through LCA and social issues by means of job generation.

However, process safety tends to be overlooked as a factor in biorefinery process studies. In this sense, the evaluation of industrial hazards would suppose an approach to the process sustainability, since no methodology has been developed for the minimisation of work-related casualties due to the unpredictable nature of workplace accidents (Ramadhan, et al., 2014). Nevertheless, only a few recent papers deal with the integration of economic and risk topics (Medina-Herrera et al., 2014; Shahriar et al., 2012).

The risk of an undesired event is a function of a set of scenarios, likelihood of occurrences and the consequences of events (AIChE, 2000). Risk analysis is a systematic method to prevent the occurrence of undesirable events by integrating information of potential causes, consequences, and likelihood. In particular, likelihood of an event refers to a quantitative measurement of occurrence, which is expressed either as frequency (i.e., events per unit time) or probability (i.e., the chance of event to occur in defined conditions) of occurrence. Then, the risk assessment (RA) of industrial processes is an interesting tool for identifying hazards and evaluating the risks of use, handling, transport and storage of dangerous substances. In the event of a spill or leak, this methodology helps to establish whether there will be a threat to people, property or the environment (Mannan, 2012).

The purpose of this work is the development of sustainable and safe biodiesel production processes based on microalgae by process economic optimization and subsequent risk evaluation. The study evaluates two alternatives for the algae cultivation system and two alternatives for lipid extraction from algae, presenting different energy and chemical requirements. We formulate a mixed integer nonlinear programming model to determine the optimal alternative for biodiesel production in terms of an economic objective function, the net present value. Furthermore, alternative schemes are assessed in terms of industrial hazards after economical optimization, since the potential solvents for lipid extraction and set out several issues not only in terms of economic assessment, but also regarding safety requirements. In this sense, within the sustainability concept, we evaluate the hazards arising from the storage and handling of dangerous chemicals. Numerical results give a quantitative support for the future decision-making regarding acceptable risks and pave the way to further proposing multi-objective optimization studies.

2. METHODOLOGY

The present work aims at determining the need to complement process optimization with industrial risk estimation, as illustrated in Fig. 1. Unit operations and process alternatives considered are firstly identified to subsequently define an optimization model based on energy and material consumption. Optimization results are compared to the potential risk assessment evaluated for different scenarios according to alternative process schemes. To better understand the influence of the economic and the safety aspects, hazard evaluation has been decoupled from the optimization problem. Risk is defined by the consequences and the frequency of a non-desirable event to occur. Whether the industrial hazards are identified as significant in the process definition, multi-objective formulation will be explored in future work.

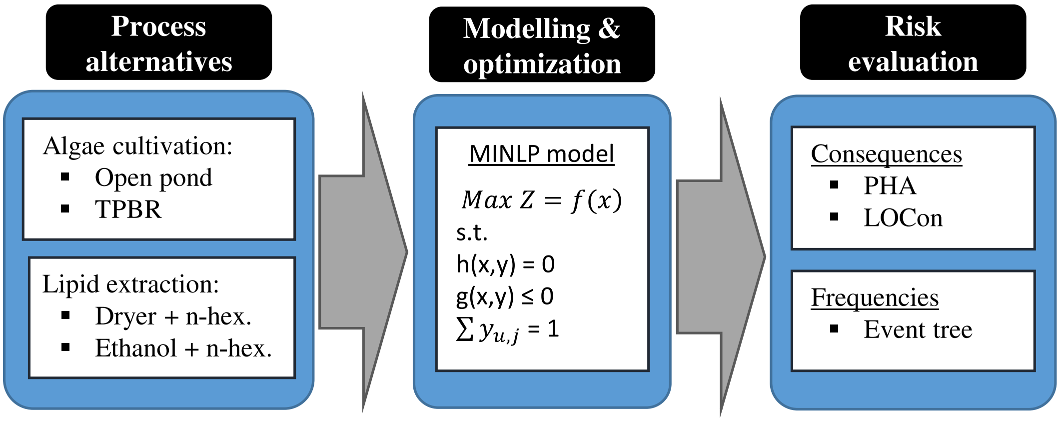

Figure 1. Process methodology for the optimization and subsequent hazard estimation.

2.1 Process description

An integrated, microalgae-based biorefinery diagram for biodiesel and energy production is shown in Fig. 2. The main operations included in the proposed biodiesel production process are algae cultivation (A), harvesting (Lee et al., 2010) and dewatering (B), lipid extraction (C), algal oil processing for obtaining biodiesel (D) and anaerobic digestion, followed by energy generation (E) (García Prieto et al., 2014; Gebreslassie et al., 2013). The oilcake, which is a waste stream obtained after lipid extraction from algae biomass, and glycerol are introduced to the anaerobic digester to produce biogas (mainly methane and carbon dioxide). Glycerol, a by-product from biodiesel production, can be also sold as a final product from the integrated biorefinery. From the anaerobic digestion process, there is a liquor stream, rich in nutrients such as nitrogen and phosphorus, which is re-circulated to the biodiesel process. Solid wastes are generated in this step, as well. These residues can be used as fertilizers to give an added value to the process. Finally, biogas is enhanced in a biogas upgrading unit where water, rich in carbon dioxide, is eliminated from the process stream and sent to the algae cultivation step. Purified methane is sent to a combined heat and power cycle to generate electric and thermal power to partly supply the plant energy requirements.

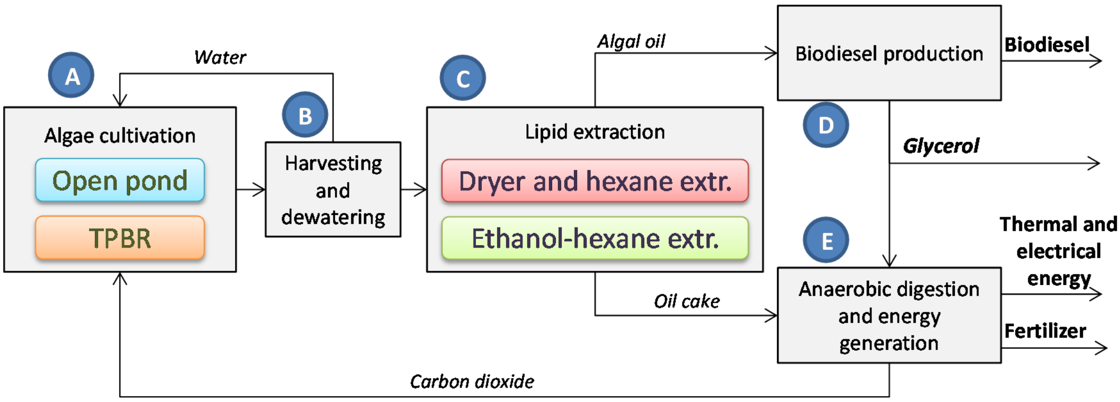

Figure 2. Simplified process flow diagram for the proposed integrated biorefinery.

Lipid content of microalgae biomass and growth rate are key factors to evaluate the potential of microalgae for biodiesel production. High lipid production has been searched for many years by testing many microalgal species, being isolated and characterized numerous oleaginous species. Li et al. (2010) have evaluated the behaviour of *Enteromorpha prolifera* at different heating rates distinguishing dehydration, primary devolatilization and residual decomposition. Algae species should provide high biomass productivity and the ability to accumulate large amounts of lipids, subsequently transformed into biodiesel (Sforza et al., 2012).

Microalgae based biodiesel production process

Microalgae require carbon dioxide, nutrients and light for growth. We consider *Haematococcus pluvialis,* which is a unicellular biflagellate freshwater chlorophyte, due to its high lipid production capacity (lipid 18.3%, carbohydrate 50.4% and protein 31.3%).This work aims at comparing two cultivation systems, presenting different energy requirements and biomass productivity. Carbon dioxide is supplied by the flue stream from a thermoelectric plant, which is previously treated to reduce its sulphur concentration.

Algae concentrations in the cultivation systems are not high enough to directly extract lipids. Therefore, a primary harvesting step concentrates algae biomass and a dewatering step is further required to reduce water content in the algae sludge before lipid extraction. Two alternative extraction methods are evaluated, in which the required algae biomass concentration depends on the type of solvent.

Transesterification is the final step to obtain biodiesel from microalgae. Several techniques are being evaluated to optimize the process, including microwave or sonication (Guldhe et al. 2014). For this study, we have considered the reaction of triglycerides from the oil with methanol in presence of sodium methoxide, to finally produce mono-esters that are termed as biodiesel. Other alkali and enzymes have been studied to catalyse the transesterification reaction (Martín and Grossmann, 2014).

Cultivation system

As mentioned before, production systems need carbon dioxide, nutrients and light for the algae cultivation, and they can be mainly classified into open and close systems. The open pond or raceway pond systems only use sunlight, resulting in an important advantage for algae production due to the usage of a free natural resource (Brennan and Owende, 2009); Gebreslassie et al., 2013). Nonetheless, sunlight availability depends on the number of sunshine hours of the area; thus seriously limiting the efficiency in areas with low solar radiation. In these cases, artificial light is supported to ensure a stable growth rate in a close system, known as photobioreactor (PBR). These systems also enable to control the process variables, allowing the growth of single-species of microalgae for long periods, with lower risk of contamination. Therefore, biomass production rates in PBRs are higher than in open pond systems. Artificial lighting enables continuous productivity, but presents significant energy requirements, as compared to open ponds systems.

Dewatering and lipid extraction

Several solvents have been commonly applied to remove lipids from the oil cake, developing novel approaches for an effective eco-friendly process (Burja et al., 2007; Li et al., 2014). The most commonly applied solvent at industrial level is n-hexane (Gebreslassie et al., 2013). An oil cake enriched in proteins and carbohydrates is obtained and can be used as feed for the anaerobic digester system. In a second step n-hexane is removed from the lipids and recirculated to the recycling system.

However, in such processes, a previous drying operation is mandatory and may consume about 80 % of total energy in the process (Gebreslassie et al., 2013; Lardon et al., 2009; Yang et al., 2014). For this reason Chen et al. (2012), have proposed a methodology to recover lipids without the need to completely dry biomass, applying a 3:1 hexane-ethanol mixture as extractant at 90°C and 1.4 MPa. Nevertheless, the ideal method for industrial-scale extraction is still under development. For this study n-hexane in dry biomass and ethanol/n-hexane in wet biomass will be evaluated to determine the pros and cons of each technology.

Energy production by anaerobic digestion process

Energy recovery from the biodiesel production process may be implemented by the inclusion of an anaerobic digester (AD), and CHP steps. In our case, the input materials are the remaining glycerol produced in the transesterification step, the oil cake, and the external supply of sources enriched in carbon and nitrogen. In order to promote more sustainable and cost efficient processes, the waste paper and sludge from a wastewater treatment plant will be fed to provide organic carbon and nitrogen, respectively. After methanogenesis, the final product is mostly composed by methane (60%) and carbon dioxide (40%).

C/N ratio in the digester must be between 20 and 25 for optimal operation of the biodigester, with high methane productivity (Yen and Brune, 2007). Liquor enriched in nutrients is obtained and it can be re-circulated to the algae cultivation system. Solid residues are also formed, with applications as high quality fertilizers. The CO_2-enriched stream is sent to the algae cultivation system. The purified biogas is the feed for the CHP to generate electric and thermal power. Table 1 summarizes the advantages and disadvantages of each alternative for algae cultivation and the lipid extraction process.

Table 1. Alternatives considered for algae cultivation and lipid extraction.

Alternative		Advantages	Disadvantages
Algae cultivation	*Open pond*	• Low energy consumption	• Limited productivity • Low control process
	TPBR	• High productivity, usage of fluorescent lamps. • Comprehensive process control	• High energy consumption
Lipid extraction	Dryer + n-hexane	• Efficient lipid extraction • Moderate solvent consumption	• High energy consumption during drying process
	Ethanol + n-hexane	• Wet algae biomass (less energy-consumption in drying step)	• Intensive solvent consumption

Based upon the selected alternative technologies, four different alternatives are defined: case 1 (open pond and drying + n-hexane), case 2 (TPBR and drying + n-hexane), case 3 (open pond and ethanol + n-hexane) and case 4 (TPBR and ethanol + n-hexane). These alternatives entail variations in a set of variables such as energy consumption, volume of reactants, size of equipment and process efficiency, thus requiring the assessment of industrial hazards to complement and support the decision-making study.

2.2 Modelling and optimization

The integrated biorefinery for biodiesel and energy production model is formulated as a mixed integer nonlinear optimization problem (MINLP), in which discrete decisions are represented with binary variables. The model is implemented in GAMS (General Algebraic Modeling System, Brooke et al., 2014),

The objective function is net present value (NPV) for the integrated biorefinery. The model equality constraints include mass and energy balances, equipment design equations and capital cost functions Mass balances for component *i* in a reactive unit *l* are formulated as:

$$\sum_i \dot{\mathrm{m}}_{\mathrm{i,l}}{}^{in} + \xi_{\mathrm{l}^*} \,.\, \mathrm{STC_i} = \sum_i \dot{\mathrm{m}}_{\mathrm{i,l}}{}^{out} \tag{1}$$

$$\xi_{l^*} \,.\, STC_i = \chi_{i,l} \,.\, \dot{\mathrm{m}}_{\mathrm{i,l}} \tag{2}$$

ξ_{l^*} is the extent of reaction in reactive unit *l*; $\mathrm{STC_i}$ is the stoichiometric number of the component *i* for the reaction in *l*; $\chi_{i,l}$ is the conversion of the reactant *i* in the reactive unit *l*; $\dot{\mathrm{m}}_{\mathrm{i,l}}{}^{in}$ is component *i* flowrate entering unit *l*; and $\dot{\mathrm{m}}_{\mathrm{i,l}}{}^{out}$ is component *i* flowrate leaving unit *l*.

To evaluate energy consumption, we have considered linear functions, as follows:

$$EC_u = ECR_u \cdot m_u \tag{3}$$

where EC_u corresponds to energy consumption for the main section of process u, m_u is the mass flowrate the mass flowrate processed in unit u or reactor volume if u corresponds to algae cultivation units; ECR_u is energy consumption per mass flowrate unit relative to u; ECR_u values are listed in Table 2.

Table 2. Energy consumption per mass flowrate unit in biodiesel production process

Energy Consumption Ratio	Value	Unit	Ref.
$ECR_{A,1}$	0.089	kWh/m^3	Jorquera et al., 2010
$ECR_{A,2}$	48	kWh/m^3	Jorquera et al., 2010
ECR_B	0.00088	kWh/kg water	Shelef and Sukenik, 1984
$ECR_{C,1}$	0.581	kWh/kg algae oil	Elsayed et al., 2003
$ECR_{C,2}$	0.1016	kWh/kg algae oil	Calculated for a stirred tank
ECR_D	0.299	kWh/kg biodiesel	Morken et al., 2013
ECR_E	1.140	kWh/kg biogas	Morken et al., 2013

Net Present Value (NPV) is used to evaluate the economic profitability of the project, as:

$$NPV = -I_0 + \sum_{p=0}^{N} \frac{F_p}{(1+r)^p} \tag{4}$$

where the summation is over all time periods *p*; N is the total number of periods (15 years); I_0 is initial investment (\$); F_p is net cash flow calculated in period *p* (\$) and r is the discount rate (10%).

Four binary variables are considered. They represent the alternative technologies for microalgae cultivation (A) and lipid extraction (C). $y_{A,1}$ is associated to open ponds; $y_{A,2}$ to TPBRs, $y_{C,1}$ to lipid extraction with n-hexane and $y_{C,2}$ to lipid extraction with n-hexane and ethanol. Big M constraints are formulated as bounds to the corresponding continuous variables as it is shown in Eq. 7where, ${F_i}^s$ is the mass flow rate of the component j in flow s, which represents the flows involved in the general mass balance, associated to binary variable $y_{u,j}$.

$$y_{A,1} + y_{A,2} = 1 \qquad (5)$$

$$y_{C,1} + y_{C,2} = 1 \qquad (6)$$

$${F_i}^s - M \cdot y_{u,j} \leq 0 \qquad \forall i \in I, s \in S, u \in U, j \in J \qquad (7)$$

Additionally, the alternative cases are solved as NLPs to set up energy consumption and solvent requirement, thus allowing to carry out hazard evaluation.

2.3 Risk evaluation

The potential risks associated to industrial processes must be evaluated to prevent and reduce the frequency of the accidents. Different conceptual methods have been proposed during the last years depending on the maturity level of the process design and the background information available. A preliminary hazard analysis (PHA) (Nolan, 2014) is applied when there is little information on design details; in this case it was performed to identify hazardous materials and process areas of the plant. To evaluate the industrial risks associated to the biodiesel production plant defined, the potential consequences of an accident must be determined together with the frequency of such accidental event.

2.3.1 Consequences calculations

The effects of managing hazardous materials are quantified through the consequence analyses. This analysis includes the estimation of physical effects (radiation, overpressure and toxic doses) and the subsequent vulnerability evaluation.

Event tree analysis is a logical modelling technique for identifying and evaluating the sequence of events in a potential accident scenario following the occurrence of an initiating event. A set of initiating events, defined as loss of containment events (LOCs), are established from the Purple Book guidelines (PGS-3, 2005). The consequences of each scenario are evaluated by means of models (AIChE, 1995), resulting in distances at which a certain damage level is expected. Finally, the levels of concern for each accident enable discern the impact for a defined scenario. These threshold values are specific for each physical effect studied.

2.3.2 Frequencies estimation

Event trees developed in the consequences analysis can be quantifying to evaluate the frequency of the potential accident scenario identified. Each possible path has a probability of occurrence, resulting in different sequences. The probability of each sequence is defined based upon the properties of the material released and other specific factors (Vilchez et al., 2011). The event trees used in this case correspond to the release of toxic and flammable materials. They are based on an initial event and the probabilities of the intermediate factors to produce a final accident. The consequences to be evaluated in this study are flash fire (FF), pool fire (PF), vapour cloud explosion (VCE) and toxic release (TR) as illustrated in Fig. 4.

Regarding the initial event, several LOCs have been defined for the proposed biorefinery plant, including stationary atmospheric tanks and pipes. With respect to stationary tanks, the following LOCs were considered: instantaneous release of the total inventory to the atmosphere, continuous release of the total inventory to the atmosphere in 10 minutes and continuous release to the atmosphere with a 10 mm opening. For pipes with a nominal diameter below 75 mm, the leaks simulated correspond to a full bore rupture and an equivalent hole of a 10% of the pipe diameter. The frequencies of the LOCs were obtained from the Purple Book (PGS-3, 2005).

3. RESULTS AND DISCUSSION

3.1 Process optimization

The resulting MINLP model for the production of 120 t/d of biodiesel has 2264 continuous variables, 4 discrete variables and 1946 constraints. It has been implemented in GAMS, selecting DICOPT as MINLP solver (CONOPT3 for NLP and CPLEX for MILP). Upper bounds on substrate availability are given by the amount of CO_2 produced in a medium-size thermoelectric power plant and equal to $1.46 \cdot 10^6$. The limits defined for the sludge and waste paper are $1.27 \cdot 10^4$ and $1.87 \cdot 10^4$ t/y respectively, which are the volumes produced in a medium city size (300,000 population). The C/N ratio in the algae cultivation system must be between 20 and 25 for an optimal operation. Besides, a lower bound constraint is required to ensure biodiesel production of $4.38 \cdot 10^4$ t/y.

Numerical results show that the optimal configuration consider OP for microalgae cultivation and hexane extraction as the lipid extraction method. . Main streams of the process are shown in Fig. 3.

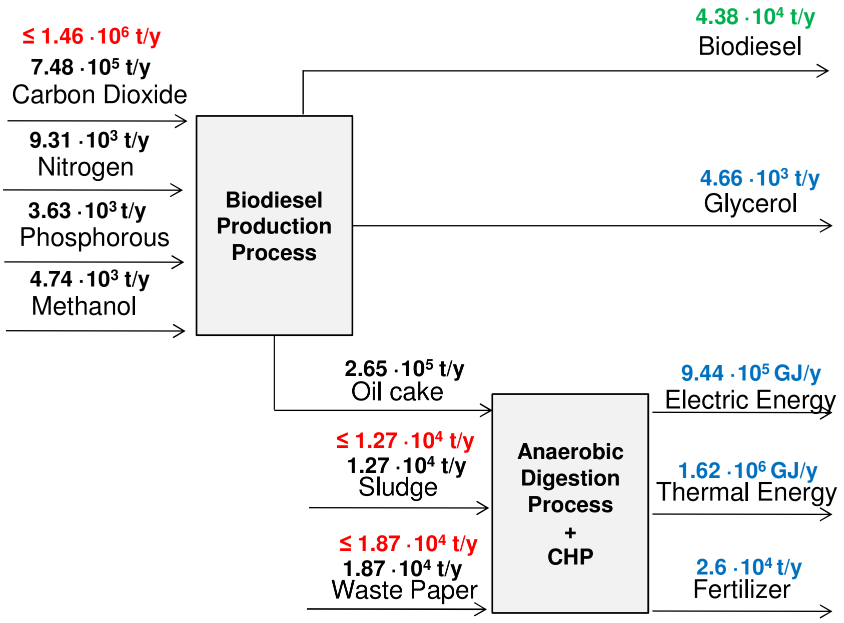

Figure 3. *Main optimization results for biodiesel biorefinery.*

Based on the considered market values for raw materials and products, the optimal net present value is negative (-3.36·10^8 US$). Biodiesel production cost for this alternative is 2.49 $/kg biodiesel. Fig. 4 shows operating cost distribution.

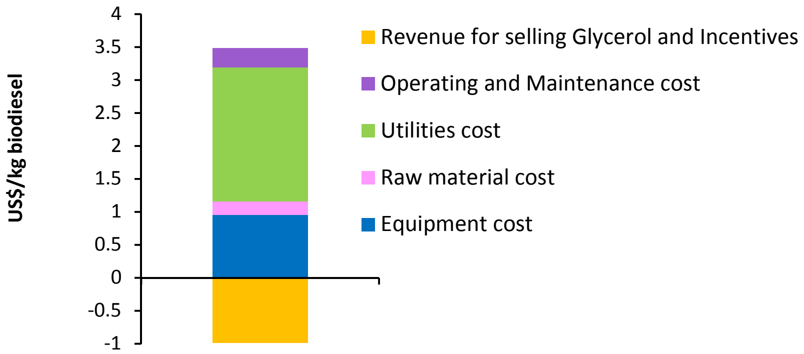

Figure 4. *Biodiesel operating cost distribution.*

Costs include operating and maintenance (0.25 $/kg), utilities (0.58 $/kg), raw material (0.09 $/kg) and equipment (0.68 $/kg), while the revenue includes glycerol and fertilizer sales, as well as incentives to promote renewable fuels (0.99 $/kg). These results clearly show the well-known fact that the production of high added products is required to make a microalgae based biodiesel biorefinery economically attractive. However, in this work, we focus on the biodiesel production plant to also take into account risk considerations and compare the different alternatives.

The assessment of energy consumption in the integrated process determines harvesting and dewatering operations as the most energy-consuming ones, requiring 8.09·10^6 kWh, as compared to 2.13·10^6 kWh required in microalgae cultivation, 8.61·10^4 kWh in the lipid extraction and 3.59·10^4 kWh in the transesterification step.

3.2 Risk analysis

Based on the potential technologies taken into account in the optimization model, four different alternatives are defined: Case 1 (open pond and drying + n-hexane; $y_{A,1} = 1$, $y_{C,1} = 1$), Case 2 (TPBR and drying + n-hexane; $y_{A,2} = 1$, $y_{C,1} = 1$), Case 3 (open pond and ethanol + n-hexane; $y_{A,1} = 1$, $y_{C,2} = 1$) and Case 4 (TPBR and ethanol + n-hexane; $y_{A,2} = 1$, $y_{C,2} = 1$). Figure 5 shows main solvent amounts required in the process extraction steps: n-hexane, ethanol, methanol and sodium methoxide. Methanol and sodium methoxide volumes remain constant for all the cases since the overall biodiesel production is the same. Hence, to carry out hazard evaluation, these last two are not considered. Differences are focused on solvent amounts required for the lipid extraction. In cases 1 and 2, no ethanol is required to carry out the extraction, while moderate n-hexane consumption is necessary. However, cases 3 and 4 require high volumes of ethanol and n-hexane. Although solvent recovery is above 95%, large quantities of solvent are available within the system and the facility has storage tanks in case of an eventual production shutdown to safely retain the total volume of solvents.

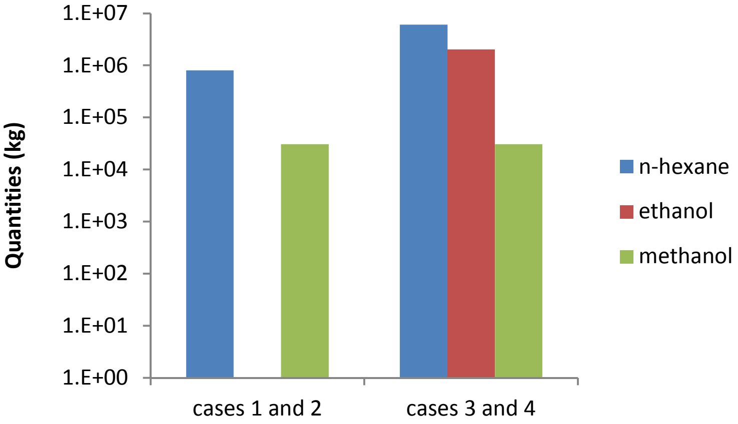

Figure 5. Solvent amount required in alternative technologies

The PHA results suggest that pumping and storage of toxic and flammable substances like n-hexane, ethanol and methanol pose the major hazard within the industrial facility, thus entailing a more detailed risk evaluation.

The event tree shows the relationship among the consequences (FF, PF, VCE and TR) and their frequencies, according to the intermediate events, as illustrated in Fig. 6. The frequencies of the LOCs were adopted from the Purple Book (PGS-3, 2005). As a general trend, risk analysis does not take into account substances with a flash point over 55°C. Since biodiesel has a flash point higher than 130°C, this compound is not considered for the comparison and assessment of alternatives. The remaining chemicals such as n-hexane, ethanol or methanol pose flash point values below 21°C, thus requiring the subsequent risk assessment. To store and handle the huge amounts of chemicals required for the lipid extraction (mainly n-hexane and ethanol, case 3 and 4) a set of six industrial tanks with 500 or 1000 m^3 are adopted depending on the required volume.

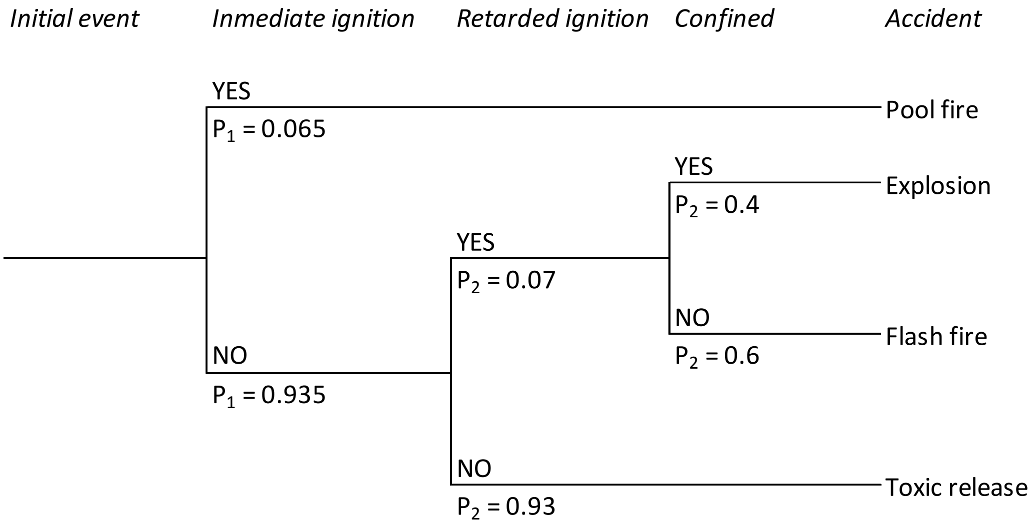

Figure 6. General event tree proposed for all initial events

To compare the potential accidents, the level of concern (LOCon) selected for the final accidents are, for the n-hexane: toxic release, AEGL-2 level of 3,300 ppm; flash fire, LEL of 12,000; VCE, pressures above 3.5 psi to pose serious damage; pool fire, radiation of 5.0 kW/m^2 produces second-degree burns in 60 seconds. The LOCon for the Ethanol: toxic release, ERPG-2 level of 3,300 ppm; flash fire, LEL of 33,000; VCE, pressures above 3.5 psi to pose serious damage; pool fire, radiation of 5.0 kW/m^2 produces second-degree burns in 60 seconds. This analysis do not include methanol because the quantity involved is the same in all alternatives. According to the proposed limit values, the maximum distance in which the LOCon can be exceeded is estimated, distinguishing four hazard levels: green, there is no effect or the LOCon is exceeded in distances lower to 10 meters; yellow, the LOCon can be exceed up to 100 meters; orange, unacceptable values can be reached up to 1000 meters; and red, distances larger than 1000 may exceed the LOCon. Table 3 shows the maximum distances obtained for n-hexane in both cases.

Table 3. Maximum distance for which the established LOCon for each scenario are exceeded

	Toxic release		Flash fire		VCE		Pool fire	
	C. 3-4	C. 1-2	C. 3-4	C. 1-2	C. 3-4	C. 1-2	C.3-4	C. 1-2
Instantaneous release of the complete inventory	2,400	2,800	1,100	1,300	1,200	1,400	653	653
Continuous release of the complete inventory in 10 min	618	3,400	310	1,600	312	1,600	653	653

Continuous release from a hole with an effective diameter of 10 mm	13	13	<10	<10	<10	<10	<10	<10
Full bore rupture of pipe	67	68	30	30	27	27	17	17
Pipe leak	<10	<10	<10	<10	<10	<10	<10	<10

Numerical results show that the major area under the LOCon was detected for TR in n-hexane storage tanks. FF and VCE present similar distances with harmful effects whether pool fire shows the minor distance values. Attending to the individual accidents, a different behavior is found between larger breaks (instantaneous release and continuous release of the complete inventory) and the minor spills. In these cases, the spilled amount of product does not entail different risks levels, but the duration of the spill may vary. On the other hand, pool fire does not suffer any distance variation for the different cases due to the identical dike size. However, the radiation time is directly proportional to the volume of spilled product, so the exposure could be longer.

Simplified risk estimation for all cases is shown in Fig. 7. Frequencies corresponding to case 1 and 2 are lower than case 3 and 4, due to the fact that the last two alternatives involve 6 tanks providing the largest amount of stored n-hexane, being then more unfavourable from the safety point of view. Consequently, the economical optimum is also the more convenient alternative regarding safety issues.

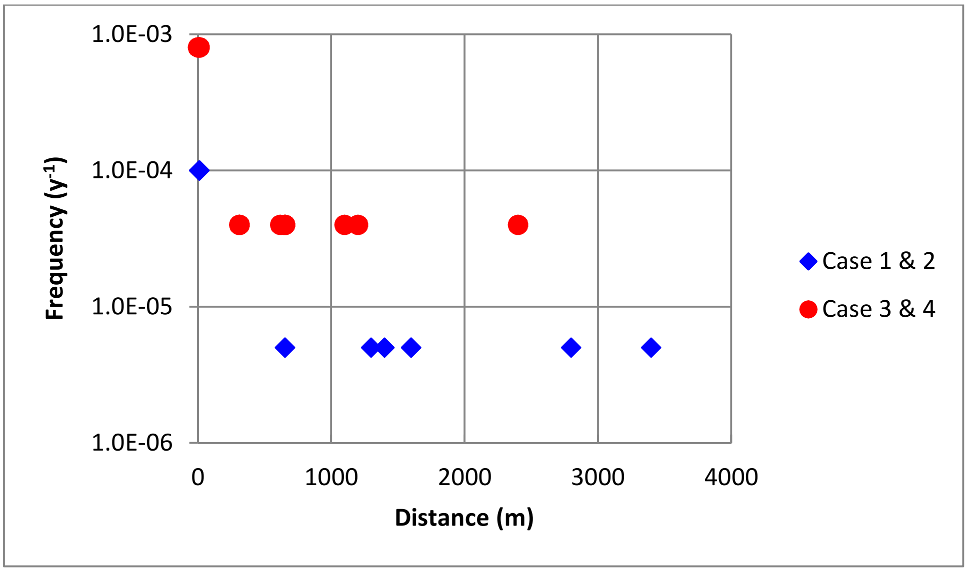

Figure 7. Relationship between the frequency of an event and the maximum affected distance

4. CONCLUSIONS

In this work we have evaluated biodiesel production based on microalgae and carbon dioxide as feedstock, in terms of economic optimization and safety assessment. The process integrates the valorisation of by-products such as glycerol and fertilizers, and the energy production. The work proposes four technological alternatives evaluated in terms of cost efficiency, complementing the study of each alternative with a safety risk assessment to determine the need to include human risks factors in the optimization model.

Two technological alternatives have been considered for algae cultivation, open pond and tubular photobioreactor, as well as for lipid extraction, drying and n-hexane and a mixture of n-hexane and ethanol. Net present value optimization determines that the implementation of open pond with extraction via drying and n-hexane is the optimal alternative, giving a biodiesel production cost of 2.49 $/kg biodiesel.

The hazard assessment supports the idea of using a minimum amount of solvent, thus the most favorable technology for the extraction of lipids is drying and n-hexane. Therefore, for the studied biorefinery, safety assessment has been successfully evaluated for each scenario and compared to economic optimization to determine the most favorable alternative, which is also the use of open ponds for algae cultivation and the use of a drier and n-hexane to recover the lipid content.

In this work, economic optimization shows the need for an integrated biorefinery that produces high added value products as biodiesel co-products, to make it economically feasible, with acceptable net present values. Furthermore, economic aspects have been complemented with safety analysis to move forward on sustainable processes, determining the same process and solvent selection that satisfies both the economical optimization and safety criteria

5. ACKNOWLEDGEMENTS

The authors are grateful for the financial support provided by CONICET and the Spanish MICINN under projects CTQ2013-48280-C3-1-R and CTM2014-57833-R. J. Pinedo would also like to thank the financial support provided by “Becas Iberoamérica JPI España 2014”.

NOMENCLATURE

AD	Anaerobic digestion
AEGL	Acute exposure guideline level
CHP	Combined heat a power
EC_u	Energy consumption for unit *u*
ECR_u	Energy consumption ratio per unit of mass flowrate relative to unit *u*
ERPG	Emergency Response Planning Guideline

FF	Flash fire
Fp	Net cash flow calculated in period *p* ($)
GAMS	General Algebraic Modeling System
I_0	Initial investment ($)
LCA	Life cycle assessment
LEL	Lower explosive limit
LOC	Loss of containment
LOCon	Level of concern
m_u	Mass flowrate
MINLP	Mixed integer nonlinear programming
N	Total number of periods (15 years)
NLP	Nonlinear programming
NPV	Net present value
PF	Pool fire
PHA	Preliminary Hazard Analysis
r	discount rate (10%)
STC_i	Stoichiometric number of the component *i* for the reaction in *l*
TPBR	Tubular photobioreactor
TR	Toxic release
VCE	Vapour cloud explosion
ξ^{1*}	Extent of reaction in reactive unit *l*
$\dot{m}_{i,l}^{in}$	Component *i* flowrate entering unit *l*
$\dot{m}_{i,l}^{out}$	Component *i* flowrate leaving unit *l*
$\chi_{i,l}$	Conversion of the reactant *i* in the reactive unit *l*

6. REFERENCES

AIChE, 2000. Guidelines for chemical process quantitative risk analysis (2nd ed.). New York: Center for Chemical Process Safety/AIChE.

AIChE, 1995. Guidelines for Consequences Analysis of Chemical Release. New York, NY: Center for Chemical Process Safety/AIChE.

Andiappan, V., Ko, A.S.Y., Ng, L.Y., Ng, R.T.L., Chemmangattuvalappil, N.G., Ng, D.K.S., 2015. Synthesis of sustainable integrated biorefinery via reaction pathway synthesis:

Economic, incremental enviromental burden and energy assessment with multiobjective optimization. AIChE Journal, 61(1), 132–146

Brennan, L., Owende, P., 2009. Biofuels from microalgae—A review of technologies for production, processing, and extractions of biofuels and co-products. Renewable and Sustainable Energy Reviews, 14, 557–577.

Brunet, R., Boer, D., Guillén-Gosálbez, G., Jiménez, L., 2015. Reducing the cost, environmental impact and energy consumption of biofuel processes through heat integration. Chemical Engineering Research and Design, 93, 203-212.

Burja, A.M., Armenta, R.E., Radianingtyas, H., Barrow, C.J., 2007. Evaluation of fatty acid extraction methods for Thraustochytrium sp. ONC-T18. Journal of Agricultural and Food Chemistry, 55, 4795–4801.

Chen, M., Liu, T., Chen, X., Chen, L., Zhang, W., Wang, J., Gao, L., Chen, Y., Peng, X., 2012. Subcritical co-solvents extraction of lipid from wet microalgae pastes of Nannochloropsis sp. European Journal of Lipid Science and Technology, 114, 205–212.

Chisti, Y., 2007. Biodiesel from microalgae. Biotechnology Advances, 25(3), 294-306.

Chisti, Y., 2008. Biodiesel from microalgae beats Bioethanol. Trends in Biotechnology, 26(3), 126-131.

Čuček, L., Martín, M., Grossmann, I.E., Kravanja, Z., 2014. Large-Scale Biorefinery Supply Network - Case Study of the European Union. Computer Aided Chemical Engineering, 33, 319-324.

D´alessandro, A.A., Tonelli, S., 2011. Risk Analysis in Biodiesel Plants. 3rd CCPS Latin American Conference, Buenos Aires, Argentine.

Elsayed, M. A.; Matthews, R.; Mortimer, N. D., 2003. Carbon and Energy Balances for a range of Biofuels Options. Report for Resources Research Unit Sheffield Hallam University: United Kingdom.

García Prieto, C., Ramos, F., Estrada, V., Díaz, M. S., 2014. Optimal Design of an Integrated Microalgae Biorefinery for the Production of Biodiesel and PHBs. Chemical Engineering Transactions, 37, 319-324.

Giotitsas C., Pazaitis, A., Kostakis V., 2015. A peer-to-peer approach to energy production. Technology in Society, 42, 28-38.

Gong, Y., Jiang, M., 2011. Biodiesel production with microalgae as feedstock: from strains to biodiesel. Biotechnol Lett, 33, 1269-1284.

Grossmann, I.E., Martín, M., Yang, L., 2014. Review of optimization models for integrated process water networks and their application to biofuel processes. Current Opinion in Chemical Engineering, 5, 101-109.

Guldhe, A., Singh, B., Rawat, I., Bux, F., 2014. Synthesis of biodiesel from *Scenedesmus sp.* by microwave and ultrasound assisted in situ transesterification using tungstated zirconia as a solid acid catalyst. Chemical engineering research and design, 92, 1503-1511.

Gutiérrez-Arriaga, C.G., Serna-González, M., Ponce-Ortega, J.M., El-Halwagi, M. M., 2014. Sustainable Integration of Algal Biodiesel Production with Steam Electric Power Plants for Greenhouse Gas Mitigation. ACS Sustainable Chemistry & Engineering, 2 (6), 1388–1403.

Jorquera, O.; Kiperstok, A.; Sales, E. A.; Embiruçu, M.; Ghirardi, M. L., 2010. Comparative Energy Life-Cycle Analyses of Microalgal Biomass Production in Open Ponds and Photobioreactors. Bioresour. Technol., 101, 1406-1413.

Lardon, L., Helias, A., Sialve, B., Steyer, J.P., Bernard, O., 2009. Life-Cycle assessment of biodiesel production from microalgae. Science and Technology, 17, 6475–6481.

Lee, A.K., Lewis, D.M., Ashman, P.J., 2010. Energy requirements and economic analysis of a full-scale microbial flocculation system for microalgal harvesting. Chemical Engineering Research and Design, 88, 988-996.

Li, D., Chen, L., Zhao, J., Zhang, X., Wang, Q., Wang, H., Ye, N., 2010. Evaluation of the pyrolytic and kinetic characteristics of Enteromorpha prolifera as a source of renewable bio-fuel from the Yellow Sea of China. Chemical Engineering Research and Design, 88, 647-652.

Li, Y., Naghdi, F.G., Garg, S., C.Adarme-Vega, T., Thurecht, K.J., Ghafor, W.A., Tannock, S., Schenk, P.M., 2014. A comparative study: the impact of different lipid extraction methods on current microalgal lipid research. Microbial Cell Factories, 13:14.

Martín, M., Grossmann, I.E., 2013. ASI: Toward the optimal integrated production of biodiesel with internal recycling of methanol produced from glycerol. Environmental Progress and Sustainable Energy, 32, (4) 891-901.

Martín, M., Grossmann, I.E., 2014. Design of an optimal process for enhanced production of bioethanol and biodiesel from algae oil via glycerol fermentation. Applied Energy, 135, 108.114.

Martinez-Hernandez, E., Campbell, G., Sadhukhan, J., 2013. Economic value and environmental impact (EVEI) analysis of biorefinery systems. Chemical Engineering Research and Design 91, 1418–1426.

Medina-Herrera, N., Jiménez-Gutiérrez, A., Grossmann, I.E., 2014. A mathematical programming model for optimal layout considering quantitative risk analysis. Computers and Chemical Engineering, 68, 165-181.

Menetrez, M.Y., 2012. An Overview of Algae Biofuel Production and Potential Environmental Impact. Environmental Science & Technology, 46, 7073−7085.

Morken, J.; Sapci, Z.; Strømme J. E. T., 2013. Modeling of Biodiesel Production in Algae Cultivation with Anaerobic Digestion (ACAD). Energy Policy, 60, 98-105.

PGS-3, 2005. ‘Purple book’, Guidelines for quantitative risk assessment. VROM, The Hague, The Netherlands.

Ramadhan, N.J., Wan, Y.K., Ng, R.T.L., Ng, D.K.S., Hassim, M.H., Aviso, K.B., Tan, R.R., 2014. Life cycle optimisation (LCO) of product systems with consideration of occupational fatalities. Process Safety and Environmental Protection, 92, 390–405.

Rulong, L., Wenxuan, C., Bingpeng, X., Xiurong, K., 2012. Optimalization of Extraction Conditions for Increasing Microalgal Lipid Yield by Using Accelerated Solvent Extraction Method (ASE) Based on the Orthogonal Array Design. Energy conservation, 9, 221-238.

Sadhukhan, J., Ng, K.S., Martinez-Hernandez E., 2014. Introduction, in Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis (1st ed.). John Wiley & Sons, Ltd. Chichester, UK. doi: 10.1002/9781118698129.ch10

Saeid, A., Chojnacka, K., 2015. Toward production of microalgae in photobioreactors under temperate climate. Chemical engineering research and design 93, 377-391.

Santibanez-Aguilar, J.E., Gonzalez-Campos, B.J., Ponce-Ortega, J.M., Serna-Gonzalez, M., El-Halwagi, M.M., 2014. Optimal planning and site selection for distributed multiproduct biorefineries involving economic, environmental and social objectives. Journal of Cleaner Production, 65, 270-294.

Scott, S.A., Davey, M.P., Dennis, J.S., Horst, I., Howe, C.J., Lea-Smith, D.J., Smith, A.G. 2010. Biodiesel from algae: challenges and prospects. Current opinion in biotechnology, 21(3), 277-86.

Sforza, E., Bertucco, A., Morosinotto, T., Giacometti, G.M., 2012. Photobioreactors for microalgal growth and oil production with Nannochloropsis salina: From lab-scale experiments to large-scale design. Chemical engineering research and design, 90, 1151-1158.

Shahriar, A, Sadiq, R, Tesfamariam, S, 2012. Risk analysis for oil & gas pipelines: A sustainability assessment approach using fuzzy based bow-tie analysis. Journal of Loss Prevention in the Process Industries, 25, 505-523.

Shelef, G. S.; Sukenik, A.; Green, M., 1984. Microalgae Harvesting and Processing: A Literature Review. Golden, CO: Solar Energy Research Institute SERI.

Singh, S.P., Singh, P., 2014. Effect of CO_2 concentration on algal growth: A review. Renewable and Sustainable Energy Reviews, 38, 172-179.

Ullah, K., Ahmad M., Sofia, Sharma, V.K., Lu, P., Harvey, A., Zafar, M., Sultana, S., 2015. Assessing the potential of algal biomass opportunities for bioenergy industry: A review. Fuel, 143, 414-423.

Vílchez, J.A., Espejo, V., Casal, J., 2011. Generic event trees and probabilities for the release of different types of hazardous materials. Journal of Loss Prevention in the Process Industries, 24, 281-287.

Yang, F., Xiang, W., Sun, X., Wu, H., Li, T., Long, L., 2014. A Novel Lipid Extraction Method from Wet Microalga *Picochlorum sp.* at Room Temperature. Marine Drugs 12, 1258-1270.

Yen, H. W., Brune, D. E., 2007. Anaerobic co-digestion of algal sludge and waste paper to produce methane. Bioresource Technology, 98, 130-134.

Yue, D., You, F., Snyder, S.W., 2014. Biomass-to-bioenergy and biofuel supply chain optimization: Overview, key issues and challenges. Computers and Chemical Engineering 66, 36-56.

Zhao, B., Ma, J., Zhao, Q., Frear, C., 2012. Anaerobic digestion of algal biomass residues with nutrient recycle. Final report. Washington State University Subcontract Work on Department of Energy Project 22902.