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Biodiesel Production from Microalgae: Ionic Liquid Process Simulation

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Biodiesel is the most used biofuel, but a large scale production requires processes which have an economic competitiveness and a low environmental impact. Microalgae easily provide oil to converted into biodiesel: they can be cultivated on non-arable land and, thus, contribute to CO_2 mitigation. The major economic concern depends on the oil extraction process: oil extraction by ionic liquids is one of the most convenient and environmental-friendly processes for biodiesel production, promising to be the benchmark for upcoming biodiesel production in large scale plants.
The novelty of this work lies in the process simulation of oil extraction using ionic liquids, implemented by Aspen HYSYS® V7.3, a professional tool which is commonly used for the industrial process design, simulation, setting and control. The application of such tools could foster the large scale application of innovative technologies, largely reducing the time required to transform a concept design into an industrial productive application.

1. Introduction

Biofuels represent a valid alternative to liquid fossil fuels; their production creates various concerns, due to the social and environmental impact of a large scale scenario enclosing intensive bioenergy crops, threatening local traditional productive activities and biodiversity, notwithstanding the food vs. fuel issue (Ajanovic, 2011). For this reason, the sustainable biofuel production should not rely on bio-energetic crops over arable lands and edible feedstocks (Balat, 2011), but rather than on bio-wastes and devoted crops from non-arable lands (the so-called second and third generation biofuels) (Jefferson, 2008). Additionally, biofuels have to reduce the overall environmental impact with respect to traditional fuels, while remaining economically competitive.
In this framework, biodiesel is the most promising biofuel. Biodiesel sustainability depends on feedstocks, the character of lands for bioenergy crops and the production process. The cultivation of oleaginous microorganisms, mostly microalgae, accomplishes all these requirements (Mata, 2012), contributing as well to CO_2 emission mitigation – around 1.7 kg of CO_2 caught by 1 kg of dry biomass (Posten, 2009).
Microalgae are cultivated into photo bioreactors by exploiting water surfaces or non-arable land, thus solving the food vs. fuel dispute (Singh, 2011). They are highly purposed for bioenergy production due to their high oil productivity: up to half of their weight is composed of triglycerides, resulting into a final productivity of more than 10,000 gal/acre – about 400 hl/ha (Pienkos, 2009).
The large scale industrial production of microalgae biodiesel requires the solution of several economical, environmental and technological issues (Oltra, 2011), such as the low oil productivity per acre of microalgae, to be solved by introducing techniques of synthetic biology, as well as improving the light supply systems (Arudchelvam, 2013). Additionally, downstream processing strongly affects the economic competitiveness of the final product, along with its environmental impact (Posten, 2009); thus, simpler and more efficient oil separation procedures should promote this technology up to its industrial application.

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Recently, oil separation by ionic liquids recently draws attention due to its efficiency and low environmental impact (Kim 2012): ionic liquids are molten organic salts, with a melting point close to or below room temperature: they are composed of an organic action and an inorganic/organic anion (Liu, 2012), thus showing amphiphilic properties: when they contact cells, they disrupt the cell wall, easing oil recovery by means of cell lysis. In addition, ionic liquids show a bio-catalytic activity in the biochemical reactions occurring in biodiesel production (Lai, 2012).

The novelty of this work is to present the process simulation of bio-oil extraction by ionic liquids in algal biodiesel production. The simulation is implemented on a professional tool, Aspen HYSYS® V7.3, aimed at testing the effect of temperature on the oil extraction. We compared the results with those for traditional processes, based on organic solvents extraction and we found this method is among the most efficient and simplest, showing the potential to become a benchmark for the industrial production of biodiesel from microalgae.

2. Process Description

The simulation covers some stages of the whole process of biodiesel production from microalgae: harvesting, dewatering, oil extraction and ionic liquid recovery (Figure 1). We mainly focused on oil extraction by ionic liquids and compared the results in terms of oil recovery.

Microalgae harvesting: we simulated the microalgae cultivation in photo bioreactors equipped with an additional CO_2 supplier (Kim, 2011). The first harvesting step aims at thickening the algae solution by bio-flocculation in a lamella settler: on the basis of literature data (Xu, 2011), we supposed to achieve 2 % dry weight (DW) after sedimentation.

Microalgae dewatering: after the bio-flocculation/settlement separation steps, we supposed microalgae sludge being treated by mechanical (centrifuge) dehydration to reach the DW required threshold (20 %) for the downstream processing. The water collected from harvesting and dewatering steps, is recycled into the microalgae cultivation system.

Oil extraction (wet route): the main equipment for the oil extraction step is the lysis reactor, working at 80 °C and atmospheric pressure. We simulated the feed stream is the microalgae slurry from the mechanical dehydration step, mixed with the ionic liquid: in the reactor, the cell disruption by the ionic liquid produces a dispersion of the intracellular content in the aqueous phase, containing ionic liquid, water, intracellular content and cell debris, further cooled to 25 °C in the lipids separation section. This section comprises a filter, which removes the cell debris (sent to an anaerobic digester or sold as animal feed or lingo-cellulosic biomass feedstock), and a two-phase decanter to separate the oil (on the top) and the aqueous solution (on the bottom).

Ionic liquid recovery: the ionic liquid recovery easily occurs if the solution is heated because of the high relative volatility of water with respect to the ionic liquid. We simulated the mixture is pre-heated to its bubble point and then fed to the L-V separator: the heavy phase (rich in ionic liquid) is cooled and recirculated to the lysis reactor, whereas the light phase (rich in water) is condensed and recirculated to the microalgae production section. Other intracellular compounds (proteins, carbohydrates, etc.) can be recovered by means of devoted downstream sections (future development).

3. Component Modelling

In the following the process components modelling will be largely detailed.

3.1 Ionic Liquid

The ionic liquid suitable for this process should have the following properties: amphiphilic nature (hydrophilic and amphiphilic); high lipid extraction yield; low toxicity and high biodegradability; catalytic activity towards the process reactions; applicability like co-solvent system mixed with polar components, to improve the lipid extraction.

According to this, we chose 1-buthyl-3-methylimidazolium chloride (hereinafter bmim Cl); although this compound has been used in several bioprocesses, many of its physical, thermodynamic and transport properties are still not available, due to its high thermolability. We estimated properties only below the decomposition point adopting estimation methods embedded in the simulator. To test the reliability of these estimation methods for the bmim Cl, we computed the following properties and compared with literature data:

Critical properties and density: we estimated critical properties by the UNIFAC method (Valderrama, 2008), testing the thermodynamic consistency by computing the liquid density according to them: the estimated density complies satisfactorily with literature experimental data (Zhang, 2006).

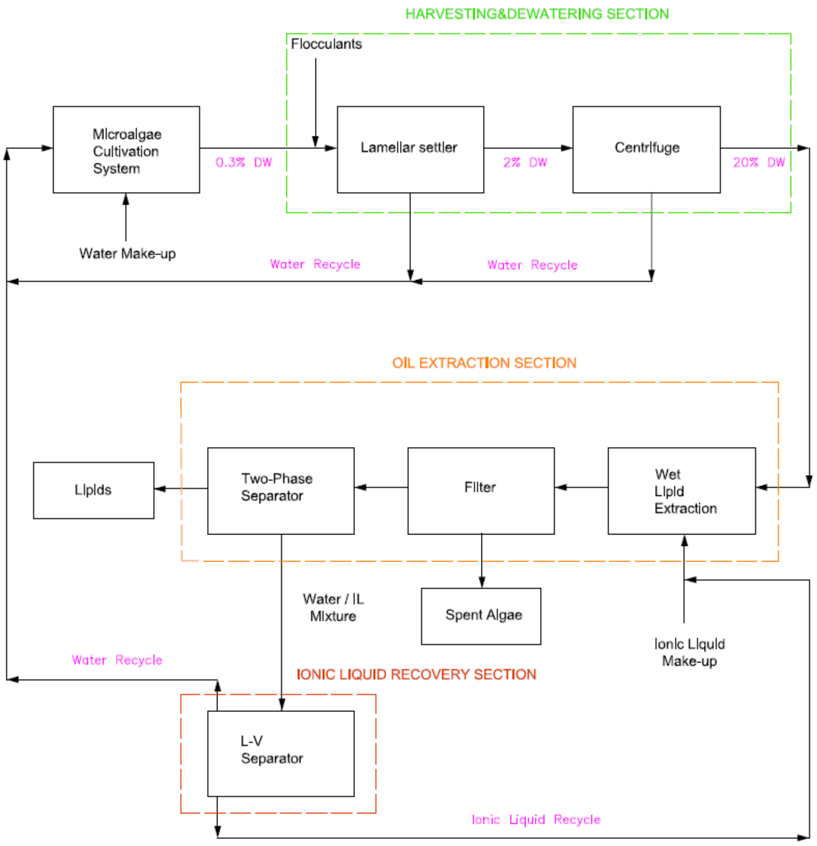


Figure 1: Block diagram of the process: the dashed lines highlight the processes stages under analysis.

Vapour pressure: we estimated this property through the Rudkin method (Rudkin, 1961), based on the application of the Antoine equation to compute the bmim Cl vapour pressure being water the reference, complying very satisfactorily with literature data. The bio-oil process extraction has been modelled by the process simulation software Aspen HYSYS® V7.3, and we added bmin Cl as a hypothetical component; the properties record has been built using the functional groups database available in the simulator's UNIFAC component builder (Table 1).

Table 1: Functional groups and their occurrence frequency in 1-buthyil-3-methylimidazolium chloride.

Groups	N°
CH_3N	1
CH_2N	1
CH	3
CH_2	2
CH_3	1
Cl	1

3.2 Microalgae

We modeled microalgae according their gross cell composition in lipids, proteins and carbohydrates. We assigned for each category a reference compound, as shown in Table 2. Thus we stoichiometrically defined the raw formula of microalgae in terms of the cell lysis reaction:

$$C_aH_bO_cN_d \rightarrow 0.0639 \cdot C_{57}H_{104}O_6 + 0.7708 \cdot C_9H_{11}NO_2 ++ 0.1653 \cdot C_{12}H_{22}O_{11}, \quad (1)$$

resulting into the empirical formula:

$$C_{12.56}H_{18.76}O_{3.743}N_{0.7708} \quad (2)$$

We neglected the solid components of microalgae, considering only the three reference components in liquid phase as representative of them.

4. Process Simulation

We performed the simulation by assuming some simplification hypotheses for the bio-oil and ionic liquid mass balance.

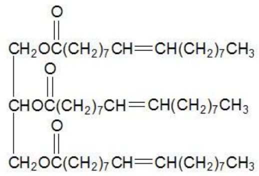
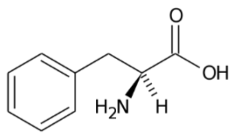
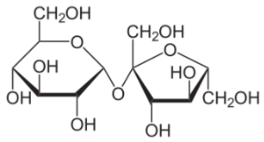
4.1 Thermodynamic Model

According to the most recent literature (Ferro, 2012), we applied the non-random two-liquid (NRTL) model to derive the chemical-physical properties of the non-ideal liquid phases involved in the bio-oil extraction process. It is noteworthy so far these properties for these systems have not been experimentally measured.

4.2 Input data and targets assigned to the process simulation

We computed the dry algae biomass inlet flow rate to bio-oil extraction section required to match a bio-oil productivity of about 1 ton/h: assuming a 100 % yield for lipid extraction, the dry algae biomass inlet flow rate is 4.25 t/h (see Table 2).
To ensure a biomass dry weight of 20 %, we set the water inlet flow rate to bio-oil extraction section to 17 ton/h. We assumed a weight ratio of bmim Cl to dry algae biomass of 7.5:1 has been assumed, so the bmim Cl inlet flow was 31.9 t/h.

Table 2: Reference compounds representing algae composition.

Representative component	Mw (g/mol)	Raw Formula	Chemical Structure	% w/w	% mol
Triolein	885.4	$C_{57}H_{104}O_6$		23.5	6.39
L-phenylalanine	165.2	$C_9H_{11}NO_2$		53.0	77.08
Sucrose	342.3	$C_{12}H_{22}O_{11}$		23.5	16.53

4.3 Process Simulation Run

The process has been simulated by Aspen HYSYS® V7.3. We modeled the Lysis Reactor by a simple vessel, fed with the algae slurry. We supposed the Lysis Products stream (comprising ionic liquid, water, intracellular content and residual algal cells) was cooled to promote the liquid demixing. We did not include the filtration step since it does not modify the overall mass balance. Bio-oil recovery is performed in a three phase separator: the Oil Phase stream coming out of the top of the separator contains 68.2 % by weight of algae lipids. The Aqueous Phase stream (comprising water, ionic liquid, lipids, proteins, carbohydrates) is heated to 145 °C (vapour fraction of 0.75) and then conveyed to the separator: the Recovered Ionic Liquid stream from the bottom contains 84 % by weight of bmim Cl. The bmim Cl recovery yield is about 91.5 %.
To test the model reliability, we performed a simulation whose results are shown in terms of oil extraction efficiency. Figure 2 depicts the recovered oil vs. ionic liquid/dry biomass weight ratio, at different

temperatures the recovered oil vs. ionic liquid/dry biomass weight ratio, at different temperatures, assuming a bio-oil extraction yield of 100. The temperature the L-L equilibrium and, as expected, the recovered oil yield increases as the temperature decreases. However, due to the underlying thermodynamic model (NTRL) hypotheses, it is not possible to get a complete (100 %) oil recovery.

5. Conclusions

In this work we have presented a process simulation of an innovative plant for bio-oil extraction from microalgae using ionic liquid. The strong point of this process, with respect to traditional oil recovery processes, is the green character of ionic liquids processes, relying on simpler equipment, carried out at milder operating.

So far, this is the first work describing a process simulation of these systems, although with some underlying simplification hypotheses. For instance, the bmin Cl characterization is still poor, such as the thermodynamic modelling (NTRL) inappropriate to describe electrolytic, notwithstanding the lack of data for the binary interaction parameters strictly required for an accurate prediction of thermodynamic properties.

In this perspective, this work represents an important and reliable starting point and provides indications for the process implementation, on the basis of results coming from a professional tool (Aspen HYSYS® V7.3) that is the benchmark for the process design, simulation, setting and control.

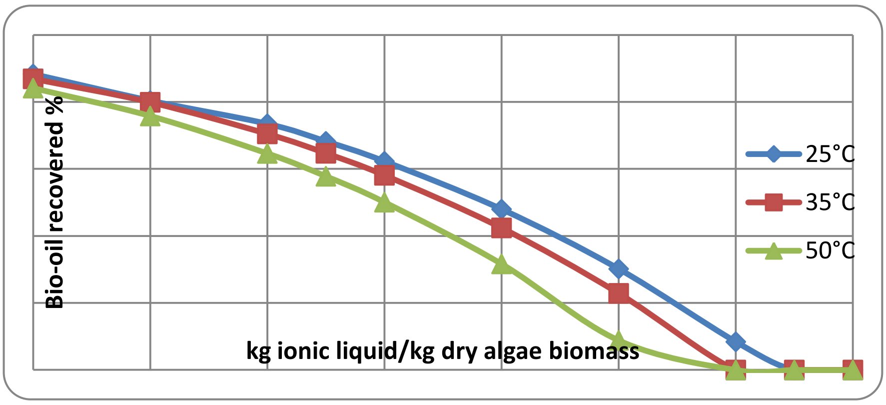


Figure 2: Recovered bio-oil versus ionic liquid dry algae biomass weight ratio with temperature as parameter

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