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Biodiesel production from microalgae: ionic liquid process simulation

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ABSTRACT

The industrial scale production of biodiesel, the most common biofuel, requires innovative solutions to become more and more competitive with a reduced environmental impact. Microalgae are the most promising feedstock for biodiesel production since they are grown on non-arable areas and reduce the greenhouse gas emissions as well. The oil extraction is the competitiveness bottleneck, largely impacting the overall process cost. Oil extraction using ionic liquids is considered a promising technique, which has the chance to become a benchmark for large scale applications. In this paper a novel process simulation of ionic liquid operation is developed, implemented by Aspen Hysys V7.3®. The chosen ionic liquid is Butyl-3-methylimidazolium chloride, a green solvent; since it is a non-conventional compound, a method to compute its properties through a thermodynamic model is provided. Moreover, a process scheme has been set up and simulated, composed of a lysis reactor, in which the ionic liquid is added for oil extraction, and a three phase separator, with recycle lines and several heat exchangers for heat recovery. Mass and energy balances have been carried out. The main results allowed to calculate the recovered oil as a function of the ionic liquid to dry biomass weight ratio (with assuming a bio-oil extraction yield of 100) and as expected, the bio-oil recovery yield increased at decreasing temperature. However, a complete recovery is not feasible, due to the physical constraints in the thermodynamic model hypotheses. Albeit some simplifying hypotheses for the thermodynamic properties, the novelty of this work is that it reports results of a process simulation, providing indication for industrial technological implementation coming from a professional tool for process simulation and control.

1. Introduction

Presently, more than 80% of the global energy demand is covered by fossil fuels. Since the future scenario on oil prices is unknown, and a peak is expected in the upcoming years (Owen et al., 2010), such a dependence should be cut by 2030 (Goldemberg, 2007). Biofuels are an interesting alternative to fossil fuels for transportation purposes (Demirbas, 2009, 2011). Their production processes poses however several concerns, such as the extensive use of farmland for bioenergy crops, often referred as the *food vs. fuel* issue (Ajanovic, 2011; Cassman and Liska, 2007, Liew et al., 2014), and the risk of endangering local biodiversity (Diaz-Chavez, 2011). In order to obtain a sustainable biofuel production, the cultivation of bioenergetics crops should not replace that of edible feedstock (Balat, 2011) nor take place on arable land (Dismukes et al., 2008). On the contrary, the use of biological waste and crops from non-arable land should be promoted (Gomez et al., 2008; Jefferson, 2008) (second and third generation biofuels), maintaining the economic competitiveness of the production processes (Hill et al., 2006).

Biodiesel is the most common and promising biofuel already introduced into the automotive fuels market (in mixture with petrodiesel) at the cost of small technological adaptations of automotive engines (Ahmed et al., 2014; Marulanda, 2012). The use of biodiesel reduces the greenhouse gases (GHG) up to 78%, as well as the unburned hydrocarbons and the residual powder emissions (Van Gerpen, 2005). As for example, the Japanese government is attempting to increase the percentage of freight vehicles using biodiesel in Japan to 80% in order to reduce GHG by 80% by 2050 (Eguchi et al., 2015; Ministry of the Environment, Japan, 2009).

Feedstocks, class of lands for bioenergy crops (whether or not arable) and the production processes affect the biodiesel production sustainability (Dovì et al., 2009). Therefore, exploring new biosources for biodiesel production such as palm oil is one of the

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priorities of industry-oriented research (Hayyan et al., 2014; Ng et al., 2012). Moreover, the use of microalgae as feedstock complies with the sustainability requirements (Mata et al., 2010; Meng et al., 2009).

Microalgae are eukaryotes, strongly adaptable to any ecosystem on earth: they convert, through photosynthesis, carbon dioxide into biofuels with the aid of light (Oncel, 2013) by means of photosynthetic metabolism. Their cultivation thus contributes to the mitigation of CO_2 emissions (around 1.7 kg of CO_2 caught by 1 kg of dry biomass) (Posten and Schaub, 2009; Sawayama et al., 1995). They are elective microorganisms for biodiesel production due to the high oil yield obtainable: microalgae produce more than 10,000 gallons of oil per acre (Pienkos and Darzins, 2009).

Microalgae photo bioreactors (Tang et al., 2012) occupy water surfaces or non-arable land, not interfering with the production of edible feedstock (Singh et al., 2011). Different economic, environmental and technological issues hinder the full development of the industrial potential of biodiesel (Oltra, 2011). From the technological point of view, it is necessary to cope with two issues: to raise the oil productivity per acre of microalgae, by means of synthetic biology and improved light supply systems (Arudchelvam and Nirmalakhandan, 2013); to improve the competitiveness and reduce the environmental impact of downstream processing. Simpler and more efficient oil extraction techniques would promote the whole technology to industrial large scale applications (Kim et al., 2011).

It is evident how the economic feasibility and the production sustainability depend on different factors (feedstocks, supply chain, distribution) and the process intensification plays a pivotal role to increase the profitability with reducing the ecological footprint of the whole production (Mizsey and Racz, 2010). Production process intensification leads to reduce the environmental impact, resulting into a reduction of GHG emissions and into a cleaner production in a general sense (AAVV, 2013).

Among the different technologies proposed for oil extraction and separation from biomass, the use of ionic liquids is highly promising thanks to the high extraction efficiency and low environmental impact of the solvents used (Fang et al., 2014). Ionic liquids accomplish many duties in the processes, including catalytic activity for the transesterification reaction (Elsheikh et al., 2011). They contribute to process intensification, by promoting the integration of stages in the biodiesel production process and reducing energy and material duties.

Ionic liquids are organic salts in a liquid phase whose melting point is not higher than room temperature. The salts are amphoters: made up of an organic cation and an inorganic/organic anion (Liu et al., 2012). Due to their chemical nature, when the ionic liquids come to contact with cells, they break their walls and membranes, resulting into oil release. Moreover, ionic liquids are biocatalysts in the biochemical reactions occurring in biodiesel production (Lai et al., 2012). For this reason, they are interesting solvents for the ligno-cellulosic treatment to produce bioethanol, mitigating the biomass recalcitrance (Liu et al., 2012). The water-ionic liquid mixtures may undergo liquid–liquid demixing under specific conditions, allowing easy, low energy co-solvent (ionic liquid) recovery. An interesting recent review by Muhammad et al. (2015) highlights the potential of applying ionic liquids as catalyst and solvent for enzymatic production of biodiesel from different oil sources. However, despite the attractiveness of the use of ionic liquids in biodiesel production (Fang et al., 2014), and as several experimental applications have proved their effectiveness in lipid extraction from several feedstocks (Young et al., 2010; Fauzi and Amin, 2012) including bioalgae (Lai et al., 2012), the lack of knowledge on their physical properties constitutes a severe drawback for their industrial application (Andreani and Rocha, 2012; Piemonte et al., 2014).

In this work a process simulation of bio-oil extraction by ionic liquids in algal biodiesel production is presented: a professional simulation tool, *Aspen Hysys V7.3*®, is used to test the effect of temperature on oil extraction by using Butyl-3-methylimidazolium chlorides (*bmimCl*) ionic liquid. A method to compute the compound properties through thermodynamic models is also provided. Process performance is described in terms of oil extraction efficiency with respect to traditional organic solvents, to verify the efficiency of the solvent selected.

2. Materials and methods

In the following a description of the methods used to carry out the process analysis and simulation is provided. In details, Section 2.1 reports the process simulation by using a commercial software and Section 2.1 shows how liquid ionic properties have been estimated.

2.1. Process simulation

The bio-oil extraction process was simulated by using the process simulation software *Aspen Hysys V7.3*®. The simulation refers to different stages of the biodiesel production from microalgae: harvesting, dewatering, oil extraction and ionic liquid recovery, as reported in Fig. 1. In this paper, particular attention is paid to oil extraction by ionic liquids and to the subsequent ionic liquid recovery.

- *Microalgae harvesting*: microalgae have been grown in a photo bioreactor with additional CO_2. In the first harvesting step, a lamella settler thickens the algae solution so to achieve 2% dry weight after bioflocculation.
- *Microalgae dewatering*: after the bioflocculation, the microalgae sludge is treated by mechanical (centrifuge) dewatering to reach the process threshold (20%) required for downstream processing. The water is further recycled into the microalgae harvesting system.
- *Oil extraction (wet route)*: the lysis reactor works at 80 °C and atmospheric pressure, treating as feed stream the microalgae slurry coming from the mechanical dehydration step, mixed with the ionic liquid. A filter removes the cell debris (recycled to an anaerobic digester or sold as animal feed or lignocellulosic biomass feedstock), while a three-phase decanter separates the oil (on the top) and the aqueous solution (on the bottom).
- *Ionic liquid recovery*: the ionic liquid recovery occurs by evaporation of water (much more volatile than the ionic liquid). The mixture is preheated to its bubble point before the flash stage: the liquid phase (rich in ionic liquid) preheats the feed and then is recirculated to the lysis reactor, whereas the vapour phase (mainly water) is condensed and recirculated to the microalgae harvesting section.

2.2. Ionic liquid and biomass properties estimation

Ionic liquids must comply with different requirements, such as high liquid extraction yield, low toxicity, high biodegradability, high catalytic activity towards transesterification, and applicability with polar co-solvents to improve lipid extraction. In the present work, the chosen ionic liquid (*bmimCl*, see Fig. 2), complies with all the requirements reported above. The *bmimCl* is poorly described in literature in terms of chemical–physical properties, although it is used in several bioprocesses: this is mainly due to its high thermolability, even at temperatures close to the normal boiling point, thus preventing a reliable measurement of its boiling point.