Toward an Efficient Biorefining of Microalgae and Biomass Alike: a Unit Operating View on How to Mimick the Optimisation History of the Crude Oil Refining Industry

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One major hindrance to biomass deployment, and one which only benefitted from an unbalanced development, is refining into the different fractions which have a market value. Indeed, most products obtained from oil refining owe to the level of sophistication and optimisation reached by energy-integrated fractioning (mostly, distillation) networks. The separation stage of microalgal and lignocellulosic biomass could be addressed by using a converging approach employing a multipurpose solvent which may be adapted by one single and simple operation to different extractions. Such a single-solvent separation approach would lend itself to scaleup to a solvent-integrated fractionation network that might help mimicking the success story of the oil refining industry.

1. Introduction

In the decade of the fastest expansion of renewable energy sources ever, microalgae and cyanobacteria, which are among the fastest-growing photosynthetic biomasses on Earth, are still confined to the specialty food market. Main energy market players actually operate thermal, destructuring processing of the biomass (Bianchi, 2014) but in perspective the extraction of high-value fractions may unleash the potential of biomasses, resulting into an independent market sector in the absence of substantial subsidising

In this scenario, beside the not yet solved issue of the primary biomass production costs (Moroni et al., 2013; Cicci et al., 2014), the evaluation and optimization of the biorefining costs is just as important and the level of optimization in this area is nothing but primitive.

The classical fossil oil refining technology relies on an advanced degree of optimization based on fractionating networks of distillation columns, coupled with highly integrated thermal networks (notwithstanding the importance of chemical reactions). The impact of oil refining products on market should be replicated by those of the biomass refining only if analogous methodologies would be developed and tuned. The hardest challenge in the full biomass exploitation is to find a separation method (most likely, solvent extraction) able to provide a selective and efficient separation of components with very different physical characteristics (González-Delgado and Kafarov, 2012), "learning the lesson" from the history of oil refining to ensure a fast track into efficient biorefining, making the most of unit operation analogy: in distillation separation is brought about by virtue of relative volatility (the driving force), and requires heat (the cost item), while in solvent extraction separation is brought about by virtue of solubility (the driving force) and requires a suitable solvent (the cost item).

The present paper discusses the possible future of biorefining in the light of breakthroughs in green solvent technology and the involved combined issues of biomass fractioning and market size and elasticity for the now-differently-valued end products.

2. Novel Solvents

Distillation recover of solvents, inasmuch as a time-honoured technique that works well for most solvent-product mixtures requires a great deal of energy and requires the solvent to be volatile (Jessop et al., 2011). Ways to avoid distillation (and the involved costs) for non-volatile solvents include resorting to membrane processes or adopting solvents that may change polarity at the user's will. Switchable-polarity solvents (SPS), meaning liquids that can be reversibly modified from a markedly nonpolar form to a markedly polar, were envisioned to be solutions to the practical dilemma called ''Murphy's Law of Solvents'', which states that "The best solvent for any process step is bad for the next step": they were designed to be modified *in situ,* and represent the extremisation of solvent tunability. The following step is usually solvent regeneration, which entails recovering the solute, but next steps in a complex extraction train may include several multiple extraction stages of different polarity solutes, with possible different degrees of association to the residual solid matrix, different molecular weight, different protic character etc. Oil extraction by using SPS has been demonstrated by Samorì et al. (2012), but a much greater treasure is still to mine.

2.1 Nature and Chemistry

Water and ethanol, the commonest polar solvents, are biocompatible solvent bases; CO_2 is amongst the most versatile solvent modifiers, and can be used as a solvent by itself through super/sub-critical operation switch (which, however, entails an energivorous operation). Emerging green and biocompatible solvents, such as ethyl lactate, may be used pure or admixed to the base solvents.

Temperature and pressure changes tune the solvent properties; the original CO_2-triggered switchable solvents were switchable-polarity solvents (SPS). They switched back and forth between a low-polarity form and a high polarity form (ionic liquid), by addition of gaseous CO_2, shifting to higher polarity forms.

The CO2-trigger is a reversible reaction so that removing CO_2 (for instance by means of heat or bubbling a non-acidic gas such as N_2) reverts back the solution polarity .

The chemical nature of "switchable-polarity solvents" has a common trait: the molecular mechanisms triggering the polarity switch due to gas (CO_2) treatment rely on a series of reversible reactions resulting into a mixture of products and reagents of very different polarity. In this sense, the switchable-polarity solvents belong to the general class of associated solutions, whose thermodynamics is determined by the properties of single components (solvent and gas) and of the chemical equilibrium (Nath & Bender 1981).

A similar class is represented by liquids strongly varying their partial molar volume upon CO_2 contact ("gas expandable liquids GXLs" , Jessop and Subramaniam 2007). CO_2 gas expanded liquids (GXLs) are one example of tunable solvent; as the organic solvent is being expanded with CO_2, many of the solvent's physicochemical characteristics are changed (such as solvation, polarity, and dielectric constant). Unfortunately, to date, from the one hand GXLs are scarcely effective from the practical point of view of extracting significant amounts of solutes (Phan, 2008) and, from the other, practically all currently known CO_2-switchable solvents are not biocompatible and therefore would not intrinsically lend themselves to an application-neutral use.
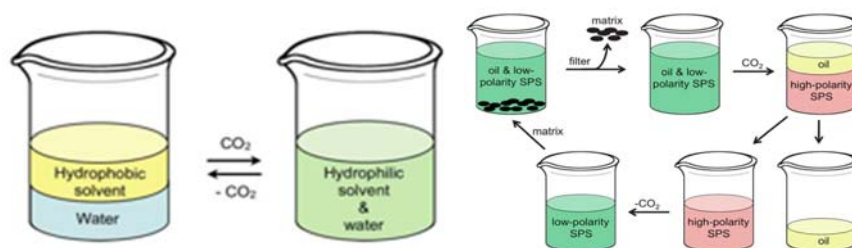

Figure 1: An SPS changes its polarity upon CO2 contact (left). Extraction of a hydrophobic organic product (such as an oil) from a solid matrix using SPS (Jessop et al., 2012b).

An alternative to CO_2-switchable ionic liquids (IL) are deep eutectic solvents (DES). Deep eutectic solvents are defined as a mixture of two or more components, which may be solid or liquid and that at a particular composition present a high melting point depression, thus becoming liquids at room temperature. In case they are natural primary metabolites (aminoacids, organic acids, sugars, or choline derivatives) their are addressed to a as natural deep eutectic solvents (NADES).

DESs share one of the most important advantages of ILs as solvents: the ability to customize physical properties and phase behavior by choosing the right constituents with regard to chemical nature, relative compositions, or water content. During DES preparation, the intermolecular interactions lead to the formation of a liquid within a range of relative molar compositions, meaning that the physical properties, the ability to dissolve certain solutes, and the phase behavior of DESs can be changed by varying the ratio of its constituents. This feature adds one more degree of freedom to the design of a task-specific solvent (Francisco et al., 2013). NADES, therefore, fully represent green chemistry principles. While natural deep eutectic solvents represent the next generation solvents, whether they can duplicate the success story of ionic liquids and the dazzling performance of switchable solvents, however, is yet to tell.

2.2 Thermodynamics and Transport issues

One of the most challenging issues in developing processes based on brand-new molecular components resides in the definition of the chemico-physical properties. The evaluation of the feasibility of the separation methodologies and the corresponding equipment design root on the knowledge of reliable properties to define the whole process.

A desirable subsitute process should minimise the multiplication of accessory processing steps, each bringing in the associated inefficiency and need of additional equipment.

A thermodynamic and kinetic analysis of the whole process is in order. From the point of view of the switch itself, the transition is easy. For instance, CO_2 recovery is facilitated not only because it is a gas, but also because the thermodynamics of the reaction is roughly balanced ($\Delta H = -136$ kJ/mol, $\Delta G = -8.6$ kJ/mol, $\Delta S = -425$ J/mol K): the forward reaction is favoured enthalpically while the reverse is favoured entropically (Jessop et al., 2012b). When the SPS in its non polar form is in contact with a non polar substance, it will dissolve it with an increase of entropy and lowering of the total energy of the system. This state of the system is obviously different from that of the solvent in the same form before the solute has been dissolved. When it comes to switch to the high polarity form of the solvent, entropy changes result from the balance of the increase entailed by the dissolution of CO_2 and the decrease entailed by the separation of the polar substance, the exact balance depending on the respective amounts. The chemical reaction is exergonic, and therefore it will be necessary to ensure that the the temperature of the SPS-nonpolar extract does not heat up too much both for thermodynamic (the associated for is unfavoured at high temperature) and mass transfer (CO_2 solubility in the liquid would be reduced, although mass diffusivity would increase) reasons.

Among the ways to investigate or predict the proton accepting ability, Kamlet-Taft parameters (α, β, and π, representing hydrogen bond acidity, hydrogen bond basicity, and polarizability, respectively) are especially convenient for a number of reasons.

Firstly, the most important property of switchable solvents is the polarizability, in the perspective of their use to selectively separate a wide range of different components of only slightly different properties (anthocyanis and polyphenols in winery wastes, citrus essential oils, hydrocarbons from microalgae), Kramer-Taft scale provides a simple scale for solvent polarity which aids in choosing the proper solvent to a given purpose. Secondly, based on the Kamlet-Taft parameters any equilibrium property K can be calculated with a linear solvation energy relationship (LSER) (Lagalante et al. 1998):

$$\log K = a + b \cdot (\pi^* + c\delta) + d\alpha + e\beta + \dots \tag{1}$$

being *a*, *b*, *c*, *d*, *e*, … empirical coefficients relative to each property and compound.

The empirical nature of this methodology is required due to the several mechanisms involved into the solute-solvent interactions, not easily interpretable in terms of thermodynamic parameters (coefficient activities (Mathias et al. 2013)). Last, but not least, Kamlet-Taft parameters are easily and directly measured by UV-visible spectrophotomery, promoting the direct monitoring of solvent polarity by means of cheap inline sensors. In the last years the great interest in switchable-polarity solvents has fostered the experimental enquiry on these compounds, in terms of solvatochromatic parameters determination (Wyatt et al. 2005; Jessop et al. 2012a): in Figure 2 a polarity comparison is reported, for traditional and SPS, addressing the amplitude of polarity differences between switch forms: it is clear SPSs span in their whole range (from green-apolar - to red –polar form) between quite different polarities. This variability could be exploited in a solvent-extraction techniques, enhancing the solvent capability to extract at high selectivity different solutes.
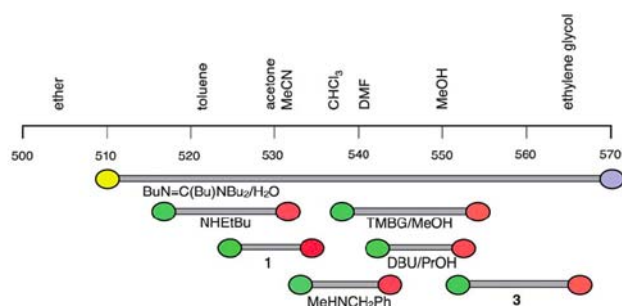
Figure 2: SPSs polarity compared with traditional solvents: the scale reports the λ_max for the Nile Red solvatochromic dye dissolved in the solvents (Jessop et al., 2012b).

Notice that the solute dissolution thermodynamics in SPS's involves mainly enthalpic contributions, due to the interactions of solute with the solvent environment, and to the enthalpic contributions of reversible reactions switching from a low-polarity (reactant) to a high-polarity form (product) upon CO_2 contact: on the other hand, the CO_2-expanded liquids, experiences a large partial molar volumes variation, upon CO_2 and solute contact, witnessing a large entropic contribution to the solvation thermodynamics.

2.3 Equipment

Optimized distillation optimized separation networks by reusing heat between different temperature levels. Thermal integration is optimized by creating composite curves of the heat demand and heat release, calculating the minimum hot and cold utility requirements and locating the thermal pinch, i.e., the thermal energy exchanged after which heat transfer becomes impossible for lack of sufficient temperature difference.

In multi-solvent extraction, distillation is required and this introduces complexity because solvents must be kept physically separated and their recovery requires multiple distillation steps which may, at best, be thermally integrated, but cannot be dispensed of.

A switchable solvent changes its polarity upon heating and/or stripping with nitrogen, leaving exhausted nitrogen:CO_2 mixture which can be readily used in the subsequent step, as confirmed by Heldebrandt et al. (2008), because in the presence of a CO_2:N_2 mixture the switchable solvent base simply picks up the former component leaving back the latter; speeding up the CO_2 release only requires a mild heating. A CO_2:N_2 mixture is not equally time-efficient for regenerating the high polarity form of the switchable solvent, though and using low concentration CO_2 requires increasing the total pressure of the mixture.

Extraction with SPSs would lend itself to both batch and continuous processing. In a sense, CO_2 duplicates in a SPS extractor the role of gradient in a chromatographic column. However, differently from chromatography, where gradient is independent of local pressure, sequential extraction by SPSs with staged contactors requires a carefully tuned balance of head loss through the beds of extracted feedstock to meet the required pressure conditions in the polarity change/solute recovery zone which shall be located in between them. A careful selection of bed unit thicknesses (and grinding size, where applicable) is required. All discontinuous extractors would do and, in principle, almost all existing extractors could be adapted to work in such conditions although some, inherently conceived for hosting multiple extracting zones featuring different pressures and temperatures, may be more ready for use (e.g. the FIC extractor by NIRO; Tzia and Liadakis, 2003).

2.4 Optimization of Fractionation Networks: a Unit Operation View

Along its history, optimized distillation separation networks by reusing heat between different temperature levels. Thermal integration is optimized by creating "composite curves" of the heat demand and release, evaluating the minimum hot and cold utility requirements and locating the thermal pinch, i.e., the thermal energy threshold corresponding to a null temperature driving force. Pinch analysis is generally applied to any complex thermal exchange problem. Distillation is still improving efficiency as an operation and again, thermal integration, this time between parts of a single piece of equipment, is the answer. Internal heat integration has made significant advances in improving energy effciency of distillation processes (Nakaiwa et al., 2003) although it has not yet made into the market.

However, optimising solvent extraction, be it on solids (leaching) or pre-extracted material that is is to be fractionated further (liquid-liquid extraction) is not just as easy, because different solubility generally imposes the requirement of a physically different solvent. In this respect, switchable solvents might become a key stone of optimization, because the same solvent can be very simply adapted to extracting molecules of different polarity. Beyond the capability of extracting small and middle sized molecules from microalgae, an "extreme" feature that would be extremely desirable would be the capability to solubilize macromolecules, a very hard

task since they're involved into a tight network of intermolecular bonds which may lead to crystallinity, such as in the case of cellulose. Recent studies have found, however, that cellulose could be dissolved, without derivatization, in some hydrophilic ionic liquids (Domínguez de María, 2014).

Inasmuch as a single solvent which can be adapted to all polarity needs of a pool of extractions, corresponding composite curves of solvent demands and releases may be drawn, whose abscissa is the solvent mass and the ordinate the solvent hydrophilicity. Just as thermal pinch analysis would target at identifying the minimum amount of heat that must be supplied from hot and cold utilities, "solvent" pinch analysis would evaluate the minimum amount of solvent that cannot be recycled within the network (e.g. because the partial pressure of the exhausted CO2 is too low, or due to some contamination effect in the liquid phase) and must be fully regenerated externally, e.g. by recompressing the gas phase to support the hydrophilicity switch or by a single evaporation/distillation purification stage applied to the liquid phase.

3. The Market Trap

Oil refining results into a fractionation of crude oil into energetic goods allocated for controlled markets or for primary commodities. The whole industrial sector developed and evolved thanks to a good balance of the commodities fluxes to market with different requirements and values, ensuring the right payback for each market. The key point to determine the breakeven point for microlgae production to be reachable and sustainable in a biorefinery logic is the influence of high-value co-products in specialized markets (nutraceuticals) without reaching the market demand saturation thus reducing the nutraceuticals value on the market. Markou and Nerantzis (2013) estimate that a 30% of biofuel marked were to be covered by microalgae a 175 Mt/y feedstock of microalgal biomass would be required. If this biomass were fractionated in all the energetic and functional products envisaged it would easily saturate the market of these latter and negate the very same sustainability from biorefining hypothesis. One can bet that high valued product may develop a bit as a consequence of the price fall, thus reducing the saturation effect. However, market elasticity is difficult to estimate and this scares any investment plan.

4. Conclusions

Solvent extraction of a complex biomass containing an array of compounds in different amounts and with different polarities should traditionally be treated with an array of solvents and this complexity undermines the economy of the full exploitation of microalgae. With the aid of novel solvents which may change polarity at the user's will only one solvent might theoretically be sufficient for the whole operation, opening a scenario of optimizations along the route of distillation trains and refinery plants evolution.

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