Mikhaylin, S.; Patouillard, L.; Margni, M.; Bazinet, L. 2018. Milk protein production by a more environmentally sustainable process : bipolar membrane electrodialysis coupled with ultrafiltration. Green Chemistry, 20 (2) : 449-456.

Milk protein production by more environmentally sustainable process: bipolar membrane electrodialysis coupled with ultrafiltration.

Sergey Mikhaylin[a], Laure Patouillard[b], Manuele Margni[b] and Laurent Bazinet[a]

[a] Institute of Nutrition and Functional Foods (INAF), Dairy Research Center (STELA) and Laboratory of Food Processing and Electromembrane Processes (LTAPEM), Department of Food Sciences, Pavillon Paul-Comtois, Université Laval, Québec (Qc), Canada

[b] Department of Mathematical and Industrial Engineering, CIRAIG, Polytechnique Montréal, Montreal (Qc), Canada

Key words: Electrodialysis, Ultrafiltration, Life Cycle Assessment, Membrane Fouling, Protein

Abstract

The increased demand for food production to nourish the rapidly growing human population raises serious sustainability issues for the food sector. Indeed, conventional food production lines involve processes having significant environmental burden. Hence, the present study aims to demonstrate an environmentally sustainable way of food production. The milk protein was chosen as a model food ingredient due to its exceptional role in the human diet. The proposed innovative way of milk protein production includes bipolar membrane electrodialysis coupled with ultrafiltration (EDBM-UF). The crucial problem during EDBM-UF of milk, such as different types of membrane fouling, was successfully solved. Moreover, the life cycle assessment of the novel EDBM-UF protein production process was carried out and compared to conventional acid/base process. Additionally, a sensitivity test of electricity supply at different geographical locations of the world was performed since electricity is the main energy source for the EDBM-UF process and it could be derived from different sources (renewable and non-renewable). The assessment results demonstrate that the proposed electromembrane process has significant environmental benefits compared to the conventional process using chemicals independently from the electricity supply mix from all considered geographical locations. Thus, EDBM-UF could become a perspective industrial technology taking into account environmental concerns and promoting the development of healthy human society.

1. Introduction

The world population is growing each year. In 2017, we have 7.4 billion people and the population will reach more than 9 billion by 2050. Moreover, 70 % of the population will be urban compared to 49 % today[1]. The population growth and urbanization raise serious challenges for the agri-food sector since there will be a 70 % increase of the global food demand by 2050[1]. To satisfy the demands of the growing population, the food industry should significantly increase its productivity. How can it be performed? The simple expansion of the traditional supply chains and related infrastructure would lead to harmful consequences on the environment due to an increased pressure of the agri-food industries on the eco-systems of our planet, human health and natural resources. Eco-design of the agri-food systems is therefore necessary and inevitable to minimize the unwanted consequences. Eco-design is based on a sustainable processing providing healthy food to meet current food needs while meeting the need to supply food for present and future generations with minimal negative impact on the environment[2].

The present paper is about protein production. Proteins are considered as one of the most important food components due to their ability to furnish essential amino acids for synthesis of organ and tissue proteins and other nitrogen-containing compounds for the normal growth and functionality of organism. Moreover, proteins are an important source of bioactive peptides having anticancer, immunomodulatory, antimicrobial, hypotensive, cytomodulatory, antidiabetic, opioid and other properties improving human health and emotional conditions[3, 4]. The above-mentioned benefits of protein intake in human diets lead to the tremendous increase in the demand for food protein production[5]. The current study focus on the production of proteins from skim milk since dairy proteins have several advantages compared to vegetable ones such as higher protein efficiency ratio, biological value, net protein utilization and digestibility[6]. This paper aims to present technological aspects related to the development of a novel eco-designed process for protein production and the evaluation of its environmental impacts compared to the traditional protein production process.

Firstly, the innovative process for skim milk protein production will be presented. This process consists of production of milk caseins and whey proteins via electrodialysis with bipolar membrane (EDBM) coupled with ultrafiltration (UF). The EDBM-UF process does not use any hazardous chemicals and does not generate wastes as conventional technologies using acids, fermentation or ion-exchange resins[7, 8]. EDBM module comprises a particular bipolar membrane allowing the production of H^+ and OH^- ions from water under the application of current. Thus, milk can be acidified in the EDBM module and caseins can be precipitated and then separated from whey proteins[8]. The base generated by bipolar membrane could be used for the subsequent conversion of insoluble caseins into their soluble form called caseinates instead of using chemically produced base. The implication of EDBM process is limited by the presence of membrane fouling, which is the major problem of all membrane processes[9]. Indeed, cleaning procedures and membrane replacement cost up to 47 % of the overall process expenses[10]. There are two types of fouling occurring during milk electroacidification: protein fouling (clogging) inside the EDBM cell and mineral fouling called scaling on cation-exchange membranes. Recently, the protein fouling problem was solved by coupling an EDBM module with an ultrafiltration (UF) module[8]. Indeed, UF membrane hampers the penetration of protein fractions inside the EDBM module significantly increasing the performance of milk electroacidification. However, the scaling problem, which hampers the industrial application of EDBM-UF process, remains unsolved despite the attempts to inhibit formation of minerals by applying pulsed electric fields, changing the hydrodynamic conditions and other methods [8, 11-13]. Knowing the mechanism of scaling formation on ion-exchange membranes, it is clear that the main promoter of mineral precipitation on the membrane surface is the alkaline environment. Indeed, OH^- ions generated by the bipolar membrane or by water splitting phenomenon, occurring on ion-exchange membranes thanks to development of concentration polarization, could interact with Ca^{2+} and Mg^{2+} ions (present in milk and released from casein micelles during acidification) forming insoluble hydroxides. Moreover, HCO_3^- ions present in milk[11, 14] could be modified into CO_3^{2-} ions and could be found in a form of $CaCO_3$ precipitate on cation-exchange membrane[8, 14]. Hence, in this work, a new design of EDBM module will be studied aiming to avoid the high concentration of OH^- ions in the compartments containing Ca^{2+} and Mg^{2+} ions and to prevent scaling formation on cation-exchange membranes.

Secondly, the results of the proposed EDBM-UF process will be used to evaluate the environmental profile of sodium caseinate manufacturing by performing a Life Cycle

Assessment (LCA). LCA is a tool that quantify the use of resources (e.g. fuels, water, land, etc.) and emissions (water, soil and air pollutants) throughout the whole life cycle of the evaluated product, service or process and characterize their adverse effects into relevant impact categories[15, 16]. It provides comparative metrics to evaluate the most environmentally harmful steps of the production chain. In this research, we will compare the newly developed EDBM-UF process against conventional acid/base process, identify environmental hotspots along each life cycle and perform a sensitivity analysis on electricity supply since EDBM-UF uses electricity as a main energy source. This latter evaluation will inform on the impact variability of using both EDBM-UF and acid/base technologies in different regions of the world, each supplied by a distinct electricity mix (renewable and nonrenewable)[17].

2. Experimental section

2.1 Configuration of electrodialysis and ultrafiltration modules

The EDBM module (Fig.1) used was a laboratory scale cell (Model MP, 100 cm^2 of effective surface) from ElectroCell Systems AB Company (Täby, Sweden). The tested cell consists of six compartments separated by three Neosepta CMX-SB cation-exchange membranes, one Neosepta BP-1 bipolar membrane and one Neosepta AMX-SB anion-exchange membrane: all these membranes manufactured by Astom Ltd. (Tokyo, Japan) are food grade membranes. This configuration was compared with the control one described in the literature[8] and consisting of five compartments separated by two anion-exchange membranes, one cation-exchange membrane and one bipolar membrane (Fig.A1). The four electrolytes: milk ultrafiltered fraction (MUF), containing mainly lactose and minerals (e.g. Ca^{2+}, Mg^{2+}, K^+, Cl^-, $P_xO_y^{n-}$), 2 g/l NaCl (KCl for the control configuration) (500 ml, 150 ml/min) and 20 g/l NaCl (500 ml, 500 ml/min) were circulated using three centrifugal pumps. The anode, a dimensionally stable electrode (DSA), and the cathode, a 316 stainless steel electrode, were supplied with the MP cell. The UF module (Fig.1 and A1) was equipped with a spiral wounded membrane with a molecular weight cut-off of 10 kDa and a surface of 2,13 m^2 (GE Water and Process technologies, Vista, USA). The UF system was run at room temperature (22±1°C) under a pressure of 25 psi.

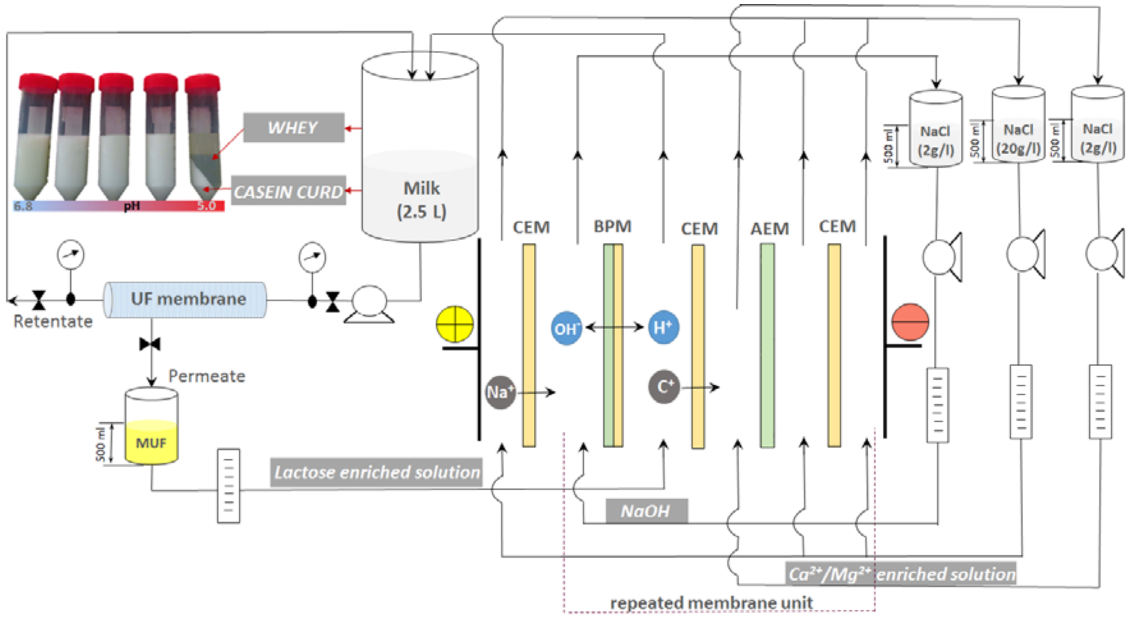

Fig. 1. Scheme of the six-compartment bipolar membrane electrodialysis coupled with ultrafiltration. The final products are indicated inside the grey squares. C^+ represents migrating cations.

2.2 Protocol

EDBM was carried out as a batch process using a constant current density of 20 mA/cm^2 generated by a Xantrex power supply (Model HPD 60-5SX; Burnaby, Canada). The permeate from the UF module (MUF) passed directly to the EDBM cell and electroacidification was stopped when pH in the UF reservoir reached 5.0 in order to obtain fully precipitated casein fraction[8]. Moreover, three co-products were generated after EDBM-UF milk electroacidification (Fig.1):

- NaOH solution (consisted of OH^- ions generated by BPM and Na^+ ions migrated through CEM);
- lactose enriched solution (consisted of lactose and minerals separated from milk by UF membrane);
- Ca^{2+}/Mg^{2+} enriched solution (consisted of Ca^{2+}/Mg^{2+} ions migrated through the CEM from lactose enriched solution (MUF)).

Three replicates of each EDBM-UF treatment were performed. During each treatment, 1.5 ml-samples of the acidified milk solution were taken at every 0.4 pH unit decrease. The time required to reach the final pH value, the anode/cathode voltage difference and the temperature were recorded as the treatment progressed. After electroacidification, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were carried out on CMX-SB membrane separating the MUF and $Ca^{2+/}Mg^{2+}$ enriched solution (Fig.1) to evaluate the presence and composition of membrane scaling.

2.3 Life cycle assessment

The life cycle assessment (LCA) was carried out according to ISO 14044[18] to evaluate the potential environmental impacts associated with the production of protein (caseinate) powder from skim milk of two different scenarios: 1) electromembrane treatment (scenario I) and 2) chemical treatment (scenario II) (Fig.2). Moreover, the sensitivity test of electricity mix supply at different regions of the world was performed since electromembrane process uses electricity as a main energy source, which can have significant differences in environmental profile depending on production process (Supplementary materials). The function defined for both evaluated processes focuses on the production of sodium caseinate powder chosen as the main milk protein product. The functional unit (i.e. the reference to which the environmental impacts of a scenario are related) was defined as being the production of 1000 kg eq. of sodium caseinate powder from skim milk at the dairy factory gate, ready to be delivered.

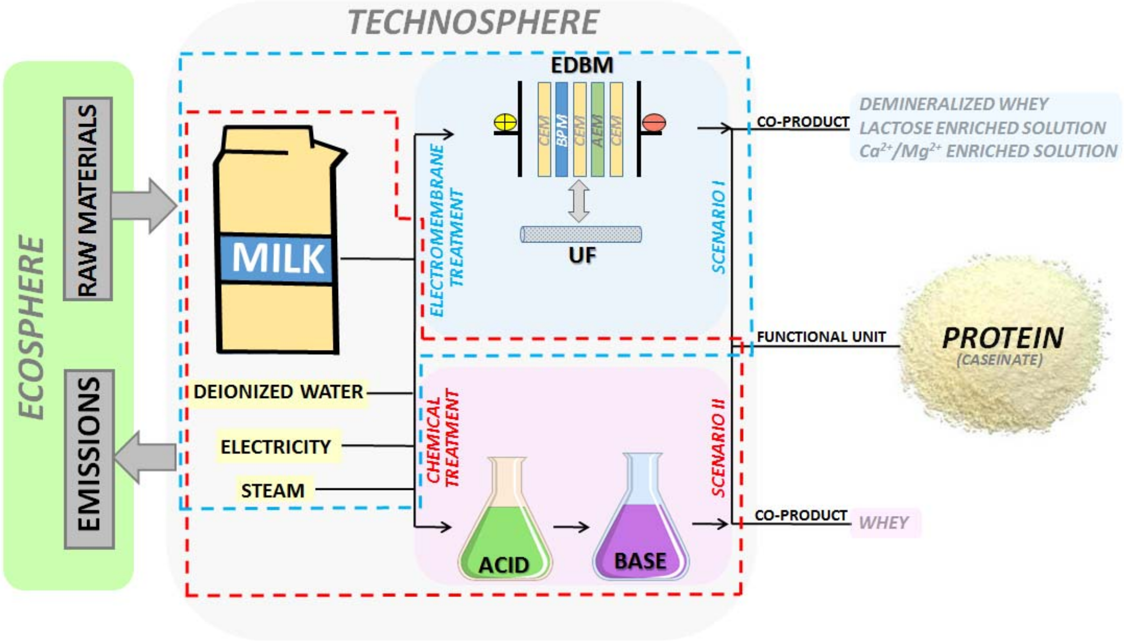

Fig. 2. Scheme of Life Cycle of both processes of milk protein (caseinate) production.

Similarities and differences of both studied systems for caseinate powder production from skim milk[19] with their respective life cycle stages are presented (Fig.3): electromembrane processing (scenario I) and acid/base processing (scenario II). The casein precipitation process of scenario I occurs through the electrogeneration of H^+ ions by EDBM-UF system (data from the present experiment), whereas it is obtained by chemical precipitation via addition of inorganic acid for scenario II (data from literature). Note that electricity supply is initially considered for a Quebec context (more than 99 % from hydropower[20]). It is known that electrically precipitated casein has higher purity (91.4 – 95.0 %)[12, 21] compared to the chemically precipitated casein (83.0 - 85.0 %)[12, 22]. This fact is due to the use of a strong acid during chemical acidification, which can affect the integrity of caseins and whey proteins and trigger their interactions[23, 24]. Moreover, the ionic strength of chemically acidified milk is significantly higher than the one of electroacidified milk leading to possible contamination with ions of precipitated casein[12]. After precipitation, caseins are centrifuged and washed several times. The whey is separated from the casein curd after the first centrifugation. After centrifugation/washing step, the casein curd is resolubilised by NaOH. At this step, the alkali generated by EDBM-UF or conventional alkali is used. Eventually, the sodium caseinate solution is dried to obtain the caseinate powder. Data for the EDBM-UF acidification step were generated from the experimental part of the present paper assuming the industrial scale of EDBM-UF modules (see Additional materials). All data concerning other processing steps were taken from the multiple literature sources[12, 19, 25-29]. The detailed description of the reference flows quantification is given in the Additional materials section. The cleaning-in-place operations were out of consideration for the present study.

The life cycle impact assessment (LCIA) of both scenarios was performed using the Impact 2002+. The climate change impact category was updated with the IPCC 2013 characterization factors[30] to identify the environmental hotspots of caseinate powder manufacturing. All impacts were attributed to the same functional unit (production of 1000 kg eq. of sodium caseinate powder). The cut-off approach was applied to deal with the multifunctional character of caseinate powder production. Therefore, no environmental burdens are associated to the co-products generated by the respective product systems described in Fig.3; they are all attributed to the caseinate powder. This approach is justified by the impossibility, at that stage of the development, to define the market values of the different co-products. The open-LCA software (GreenDelta, Berlin, Germany) with ecoinvent 3.2 database were used to carry out the LCA[31].

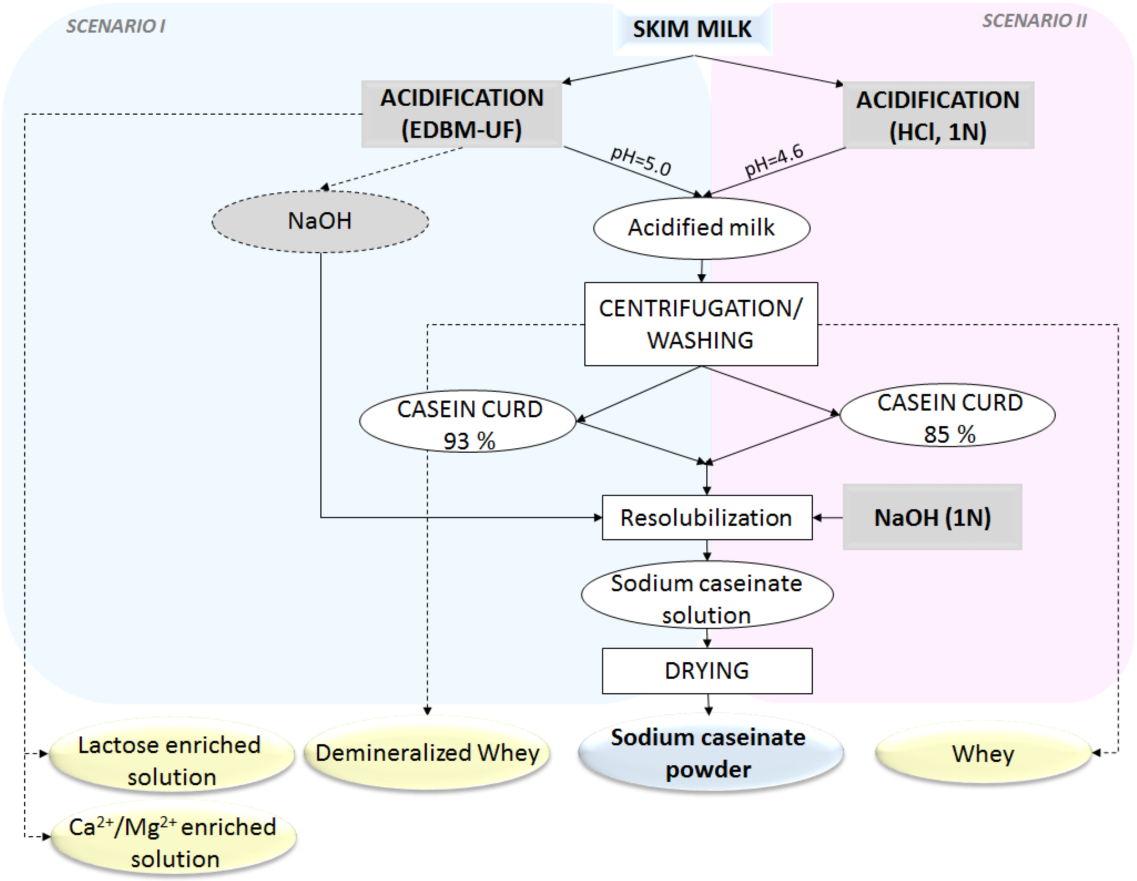

Fig. 3. Description of sodium caseinate powder production by EDBM-UF (scenario I) and acid/base (scenario II) treatments.

3. Results and discussion

3.1 Skim milk electroacidification and membrane fouling

Images obtained from scanning electron microscopy and EDS-X-ray spectra demonstrate that original non-treated CMX-SB membrane (Fig.A1) has a flat homogeneous surface. This membrane contains carbon, oxygen, chlorine and sulfur coming from the membrane polymeric matrix and ion-exchange groups, sodium coming from ion-exchange groups as a counter-ion, and gold and palladium elements from the covering layer serving for the improvement of the membrane surface conductivity and consequently image quality. However, CMX-SB membrane after skim milk electroacidification in a five-compartment EDBM module contains a crystalline deposit on its surface (Fig.4A). This fact could be understood from the EDS-X-ray spectrogram indicating the appearance of high intensity peaks of Ca and Mg elements. Indeed, it is known that milk contains Ca^{2+} and Mg^{2+} ions, which could be found as mineral fouling (scaling) on the surface and inside CEM in the carbonate and/or hydroxide forms. The CEM after the treatment of MUF in EDBM module having new six-compartment design does not contain any visible deposit on its surface (Fig.4B). Moreover, EDS-X-ray does not indicate any scaling agents (Ca and Mg elements). The differences between the results obtained from SEM and EDS-X-ray analyses could be understood from the mechanisms of membrane scaling formation. There are several mechanisms affecting membrane scaling formation such as concentration of scaling ions, pH, temperature, hydrodynamic conditions and water splitting phenomenon occurring in ED systems approaching or exceeding limiting currents[9]. The literature dedicated to the scaling problematic during milk electroacidification revealed that the main factor affecting the formation of CMX-SB scaling presenting in $CaCO_3$, $Mg(OH)_2$ and $Ca(OH)_2$ forms is an alkaline pH of concentrate stream (alkali in Fig.4A Ca^{2+}/Mg^{2+} enriched solution in Fig.4B)[8, 12].

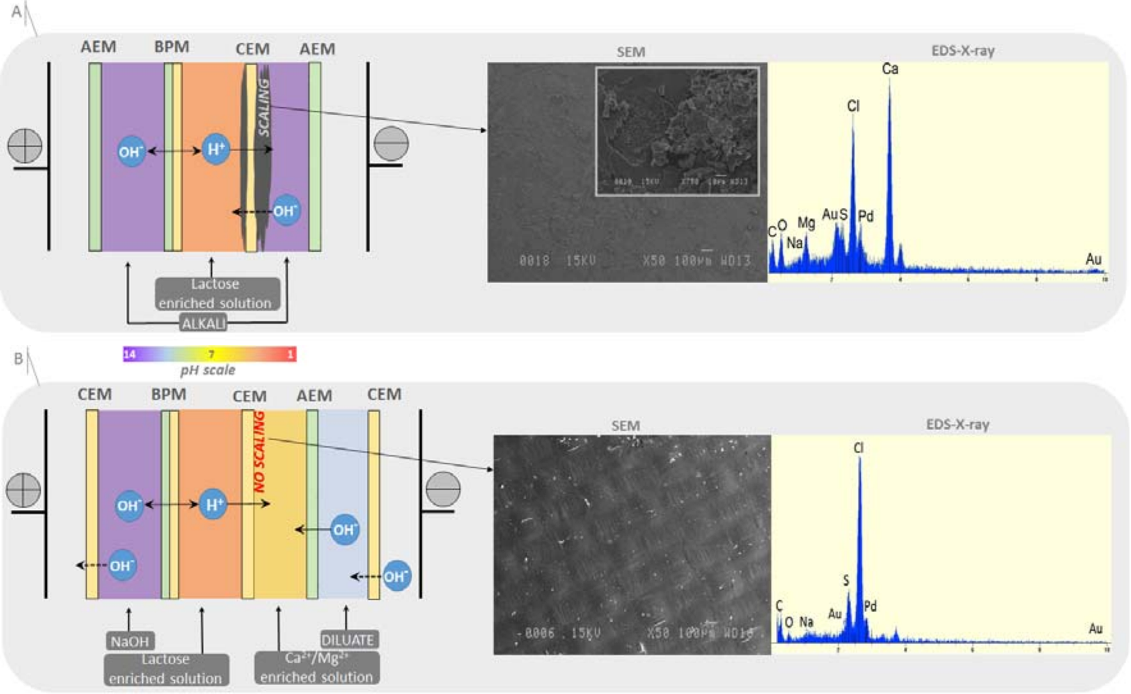

Fig.4. Scheme of both EDBM configurations tested for skim milk electroacidification with respective Scanning Electron Microscopy (SEM) images and Energy Dispersive X-ray Spectroscopy (EDS-X-ray) images of CMX-SB membrane: A) conventional five-compartment stack and B) new six-compartment stack design.

Recent works attempted to prevent fouling formation by application of pulsed electric fields, addition of potassium ions and changing the hydrodynamic conditions inside EDBM cell [8, 11]. Indeed, pulsed electric fields can decrease the concentration polarization and water splitting as well as could prevent the nucleation and crystal growth of membrane scaling[9]. Moreover, addition of K^+ ions having much higher ionic mobility compared to Ca^{2+} and Mg^{2+} ions[32, 33] would inhibit the migration of scaling ions and scaling formation. Additionally, the increase of solution flow rate inside EDBM cell would inhibit the attachment and growth of scaling. All above methods demonstrated a high efficiency for scaling inhibition (up to 50 %) though they could not completely prevent the membrane scaling formation. Thus, the new design of the EDBM cell was proposed to answer this problematic. Indeed, additional CEM membrane was installed into EDBM cell to prevent the migration of OH^- ions generated by the BM towards the concentrate stream (Fig.4B) and consequently to prevent the occurrence of alkaline pH near the surface of CMX-SB membrane contacting with acidified milk fraction MUF. The application of the proposed EDBM cell design allowed the prevention of pH growth above the neutral values in the Ca^{2+}/Mg^{2+} enriched solution during milk electroacidification (Fig.5). One could notice that during the first 20 min of electroacidification, pH in the Ca^{2+}/Mg^{2+} enriched solution remains acidic. This fact is due to the migration of H^+ ions generated by BM from acidification compartment towards the concentration stream. However, after 20 min, pH increases slightly to values higher than 7.0 and remains constant until the end of the treatment. The pH increase relates to two phenomena. Firstly, there is a leakage of OH^- ions generated by the BM through the CEM due to the fact that membrane permselectivity is less than 100 percent and highly mobile OH^- could penetrate even through the membrane having cationic selectivity[34]. Secondly, during milk acidification, there is a release of weak anions (mainly phosphates and citrates)[35] increasing the milk buffering capacity and consuming a large part of free protons generated by the BM. Hence, leakage of OH^- ions and reduced migration of H^+ ions create a neutral pH in the concentrate stream, which is unfavorable for scaling formation on CEM. Hence, the CEM after milk electroacidification in this special six-compartment EDBM configuration looks like the original one (Fig.4B and A1). The new six-compartment design of the EDBM stack allows complete elimination of membrane scaling, which is the crucial breakthrough in skim milk electroacidification due to the significant improvement of the process efficiency and decrease in process costs[9].

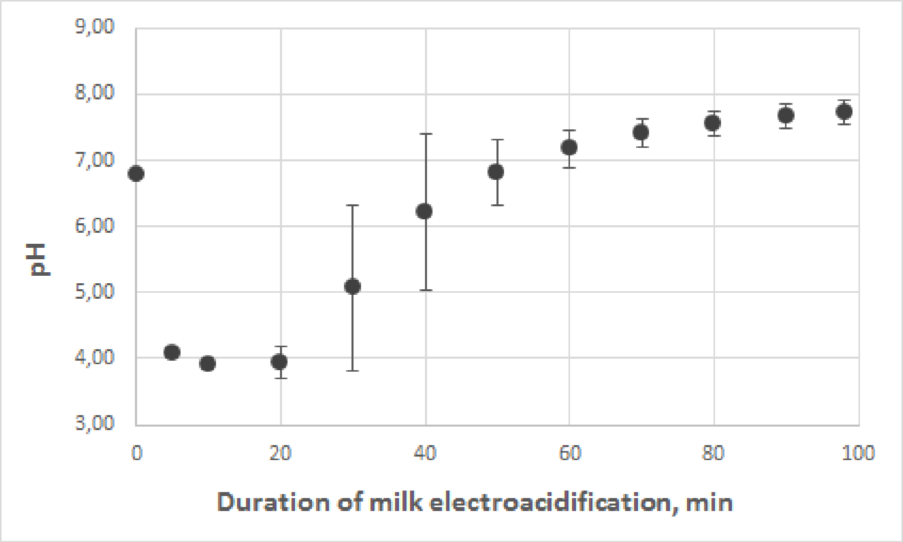

Fig.5. pH evolution in the concentrate compartment of EDBM cell (Ca^{2+}/Mg^{2+} solution in Fig.1) during skim milk electroacidification.

The proposed EDBM-UF process has several important advantages apart the possibility to produce caseins without addition of chemicals. Indeed, EDBM-UF process generates several co-products such as a partially demineralized whey, a solution enriched in lactose, a solution enriched in Ca^{2+} and Mg^{2+} ions and a NaOH solution (Fig. 1). Could these co-products be valorized? Definitely, they do have important values. Whey proteins possess high nutritional value and could be used in different food sectors (e.g. dairy, confectionary, infant formula, meat, etc.), pharmaceutical sector (e.g. tablets, inhalers, drugs) and nutraceutical sector (e.g. bioactive peptides, probiotics, prebiotics)[36, 37]. EDBM-UF process derives whey fraction with low mineral content due to demineralization in EDBM module. Moreover, this whey fraction contains less lactose due to its separation by UF membrane. These advantages of the EDBM-UF whey fraction positively affect its following transformation (e.g. reduced risks of fouling on filtration membranes and evaporators) and properties (e.g. bioactivity and functionality). The same situation happens with the lactose-enriched solution, which could be further transformed to lactose having food and pharmaceutical applications[38]. Ca^{2+}/Mg^{2+} enriched solution could be used directly as a stabilizer of sterilized milk, cheese and yogurt or Ca^{2+} and Mg^{2+} ions could be precipitated from the EDBM concentrate stream and used as food supplements [39, 40]. Finally, NaOH generated in the basification compartment of the EDBM module could be used as a solubilizing agent for casein and in the cleaning operations of dairy equipment. Hence, one could see that EDBM-UF allows obtaining several valuable co-products along with the main casein product, while in the case of conventional chemical there are just two products: casein and whey with high mineral, lactose and water contents.

Solving the main problem of electromembrane process for casein production, membrane fouling, along with the generation of valuable co-products allows the industrialization of the proposed innovative approach. However, knowing the current global tendencies focused on the improvement of sustainability of food production lines, the next part will be dedicated to the estimation of environmental impacts of the proposed EDBM process and its comparison to conventional process using chemicals.

Life cycle assessment

The life cycle assessment profile of the sodium caseinate powder production by conventional (acid/base) process and the innovative (EDBM-UF) process demonstrates that this latter has about 10 % less impacts on all damage categories compared to acid/base process (Fig.6A). More than 95 % of the overall impacts of the sodium caseinate powder production are related to the skim milk supply. For instance, the greenhouse gas emissions for the production of milk at farms are mainly due to methane release during enteric fermentation, to nitrous oxide emissions from the usage of nitrous fertilizers and manure and to carbon dioxide emissions from tractors and trucks[41]. The on-farm operations significantly affect non-renewable energy use (i.e. animal feed production, drying fodder, milking, ventilation, etc.), water consumption and acidification (mainly due to ammonia fertilizers use). The high impact intensity of milk production allows concluding that the caseinate production process consuming more milk is likely to have a higher environmental burden. Indeed, the acid/base process of caseinate production demands 3723 L more of skim milk compared to EDBM-UF process, which is due to the lesser purity of chemically precipitated casein curd[12]. To facilitate the interpretation, Fig.6B focuses on the results that only takes into account the additional milk required by the acid/base process compared to EDBM-UF process ($\Delta = \text{milk}_{\text{HCl-NaOH}} - \text{milk}_{\text{EDBM-UF}}$), i.e. excluding the equal amount of milk supplied to both systems. The higher efficiency of electromembrane precipitation process, i.e. quantity of precipitated casein / quantity of skim milk, reveals to be the key parameter for an improvement of eco-design compared to the chemical process: 93 % vs 85 % for EDBM-UF process compared to acid/base process, respectively. The next hot spot of the caseinate powder manufacturing process is the steam flux for the drying of sodium caseinate solution. However, the quantities of steam to produce 1000 kg eq. of caseinate powder were equal for both studied scenarios (Tab.A1). The reasons of relatively high impacts allocated to steam relate to its production, which implies combustion of non-renewable energy sources (76 % of natural gas and 24 % of oil) resulting in CO_2, SO_2, NO_x emissions, ozone depletion, marine and fresh water eutrophication, etc. These results corroborate with other investigations of milk protein powder production[42-44] reporting the necessity of optimizing steam consumption by improvement of heat recovery and condensate return, elimination of steam leaks, insulation of pipes and steam lines, improvement of equipment design and eventually, the use of renewable energy sources (e.g. solar and geothermal energy).

Fig.6. Relative contributions (in %) of caseinate powder manufacturing by EDBM-UF and acid/base technologies to the impact categories: climate change (IPCC 2013), human health (Impact 2002+), ecosystem quality (Impact 2002+) and resources depletion (Impact 2002+). The A row reports the results including all processes needed to fulfill the functional unit (production of 1000 kg eq. of sodium caseinate powder). The B row reports results of the same scenarios assessed in A excluding the equal amount of skim milk supplied in both systems and therefore, only accounting for difference of skim milk impacts between acid/base and EDBM-UF technologies.

Conclusions and perspectives

- This research work demonstrated the feasibility to manufacture casein (the main milk protein) by an innovative electromembrane process (EDBM-UF) without any membrane fouling meaning the substantial improvement of the process efficiency and decrease of its costs;

- EDBM-UF acidification of skim milk allows obtaining, in addition to the casein main product, several valuable co-products such as demineralized whey, lactose enriched solution and Ca^{2+}/Mg^{2+} enriched solution having a great potential for the food and pharmaceutical sectors. Moreover, EDBM-UF process generates NaOH, which could be used to solubilize the casein or in the cleaning operations of milk manufacturing equipment;
- A Life Cycle Assessment of the electromembrane process demonstrated that this novel process has the potential to reduce the environmental burdens for caseinate powder manufacturing by about 10 units of percentage compared to the conventional chemical (acid/base) method, mainly due to a more efficient precipitation process, i.e. higher quantity of precipitated casein per quantity of skim milk. Nevertheless, milk production accounts for more than 95 % of the overall impact of caseinate powder production;
- The performed sensitivity analysis assuming an electricity supply from the region with the most carbon intensive electricity mix (Asia without China) confirmed the conclusion about the environmental preference of EDBM-UF process over acid/base process.

Thus, future studies should focus on further improving the eco-efficiency of the EDBM-UF process by better characterizing the co-products of caseinate production (NaOH, lactose solution and Ca^{2+}/Mg^{2+} enriched solution) and therefore offering the opportunity to allocate the environmental burdens of the process across the valuable co-products.

Supplementary materials

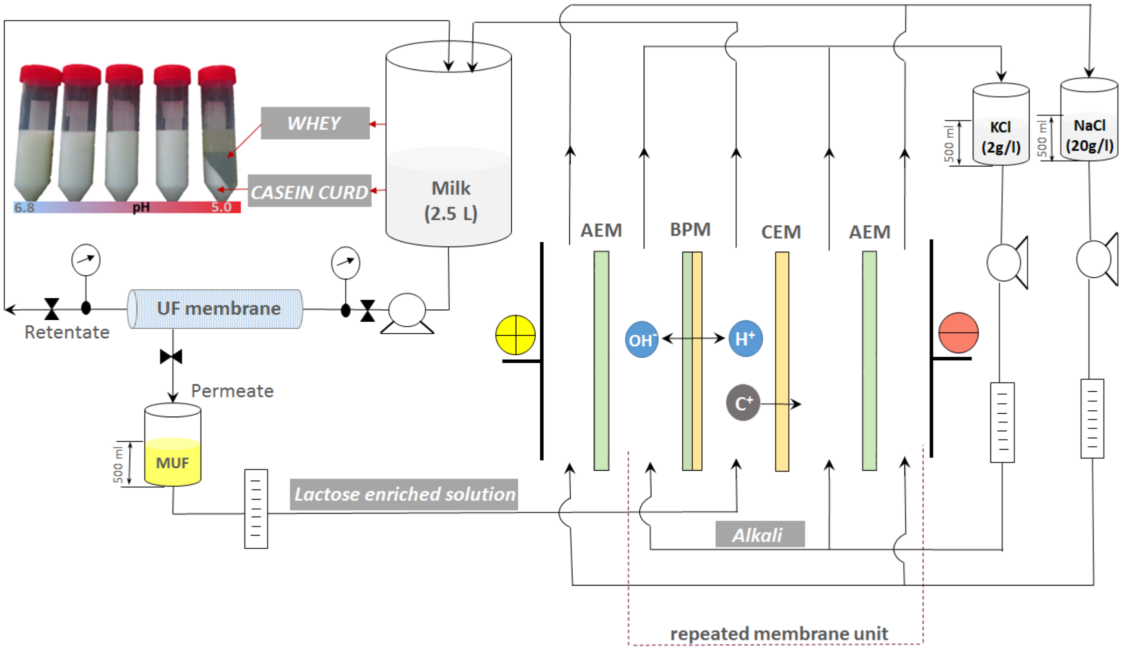

Fig.A1. Scheme of five-compartment bipolar membrane electrodialysis coupled with ultrafiltration. The final products are indicated inside the grey squares. C$^+$ represents migrated cations.

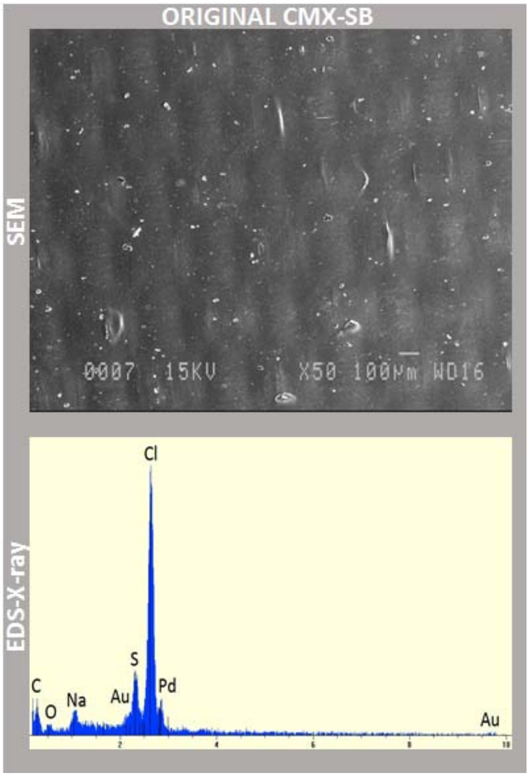

Fig.A2. Scanning Electron Microscopy (SEM) images and Energy Dispersive X-ray Spectroscopy images of original CMX-SB membrane.

Table A1. The quantities of references flows for EDBM-UF and acid/base processes of caseinate powder manufacturing scaled up to fulfill the functional unit, i.e. to produce 1000 kg eq. of caseinate powder.

	Incoming reference flows	**Process***	**Unit**	**Amount**
Electromembrane treatment	Skim milk	A	kg	39098
	Deionized water	A, CW	kg	30529
	NaCl	A	kg	182
	Polysulfone	A	m^2	$6,07\cdot10^{-02}$
	Polyvinyl chloride	A	kg	$3,26\cdot10^{-02}$
	Styrene	A	kg	$7,51\cdot10^{-02}$
	o-Diethylbenzene	A	kg	$4,89\cdot10^{-03}$
	m-Diethylbenzene	A	kg	$4,89\cdot10^{-03}$
	Trimethylamine	A	kg	$3,89\cdot10^{-06}$
	Sulfuric acid	A	kg	$8,43\cdot10^{-06}$
	Anode	A	kg	$9,10\cdot10^{-05}$
	Polypropylene	A	kg	$9,10\cdot10^{-05}$
	Steel	A	kg	$9,10\cdot10^{-05}$
	Ultrafiltration module	A	items	$9,10\cdot10^{-05}$
	Electricity	A, CW, R, D	kWh	1245
	steam	R, D	kg	5882
Acid/Base treatment	Skim milk	A	kg	42821
	Deionized water	A, CW, R	kg	14753
	HCl (30 %)	A	kg	206
	NaOH (50 %)	R	kg	42
	Electricity	A, CW, R, D	kWh	370
	steam	R, D	kg	5882

*A stands for acidification process, CW for centrifugation/washing process, R for resolubilisation process and D for drying process.

Acidification process

The quantity of skim milk for the production of 1000 kg eq. caseinate powder were calculated taking into account the caseinate powder composition[19] and the purity of casein curd obtained after acidification process[12]. The quantity of deionized water consumed at acidification step for EDBM-UF treatment was calculated based on experimental data described in section 2.1, which includes water for the preparation of NaCl solutions of 2 g/L and 20 g/L concentrations. The deionized water consumed at the acidification step for acid/base treatment includes water for the preparation of 1.0 N HCl solution from 30 % solution. Quantity of NaCl needed for the preparation of solutions (2 g/L and 20 g/L) for EDBM module was calculated from the experimental data described in section 2.1. Polysulfone represents the basic material for the UF membrane and its quantity was calculated taking into account that the UF module includes 100 m^2 of membrane area, membrane lifetime is 3 years and there is 549557 kg of caseinate powder produced annually (5 days per week, overall 2080 hours). The polyvinylchloride, styrene and divinylbenzene (obtained by endothermic dehydrogenation of o-diethylbenzene and m-diethylbenzene[25]) represent the polymeric matrix of IEMs incorporated in EDBM module. These membranes are prepared by paste method and Mizutani et al. described the contribution of each above-mentioned component to the overall membrane polymeric matrix[26]. It was assumed that industrial EDBM module consists of 200 m^2 of CEM, 100 m^2 of AEM and 100 m^2 of BPM having a lifetime of one year. The weights of dry membranes were measured and were taking into account during calculations of incoming fluxes related to the IEMs. The trimethylamine and sulfuric acid represent the components of ion-exchange groups[26], which are fixed on the polymeric matrix of IEMs. Their quantities were calculated based on the membrane lifetime, dry weight and ion-exchange capacity. The anode, polypropylene (material of intermembrane gaskets) and steel (material of cathode) represents the materials of EDBM module, having a lifetime of 20 years as well as UF module. The electricity flux at the acidification step for EDBM-UF treatment consists of the power consumed by the EDBM module (858 kWh) and power consumed by pumps of EDBM (1.36 kWh) and UF modules (16.58 kWh). The electricity consumed during conventional acidification comprises only mixing tank power consumption (2 kW) considering an acidification time of 10 min. The quantity of HCl was determined concerning 1.60 mol of acid per kg. of casein obtained after acidification[12].

Centrifugation-Washing process

The deionized water consumed for the washing of casein curd after acidification process represents 25 % of the incoming acidified milk[27]. The electricity consumption was calculated based on the power consumption of the centrifuge-decanter (55 kW) and washing tank (1.5 kW) considering the four centrifugation-decantation steps of 10 min each and three washing steps of 20 min each[28].

Resolubilisation process

The deionized water consumed during resolubilisation step for the acid/base treatment includes water for the preparation of 1.0 N NaOH solution from 50 % solution. The quantity of NaOH were determined based on the assumption of 0.5 mol of NaOH per kg. of casein solids[19]. The electricity consumption for both treatments comprises the consumptions related to the grinding operations of casein curd on the colloid mill (27 kW) during 20 min and dissolution of casein curd in NaOH solution in the dissolution tank (2 kW) during 45 min[28]. The steam consumption for heating of the sodium caseinate solution (up to 65 °C) to reduce its viscosity was calculated based on specific heat (4.0 kJ/kg°C), temperature difference (45 °C), specific enthalpy of steam evaporation (2108.1 kJ/kg) and mass of sodium caseinate solution.

Drying process

The electricity and steam consumptions for the both treatments were calculated from Hui et al.[29] considering that the moisture of the caseinate powder is 3.8 %[19]. The air consumption is not taken into account due to its recycling during powder production.

Geographical sensitivity test of electricity supply mix

Results of Figure 6 are contextualized in the Canadian province of Quebec, where 95.3 % of electricity production is from hydropower, which makes this province a leader in terms of sustainability of electricity production in comparison to other provinces and countries[20]. On Figure 6 electricity (included in "others") accounts for an insignificant share of environmental impacts when comparing acid-base and EDBM-UF processes. However, how will the eco-profile change in different geographical locations with different electricity production mix? Considering that EDBM-UF process requires about three times more electricity (1245 kWh) than acid/base process (370 kWh) for the production of 1000 kg eq. of caseinate powder, are the conclusions still maintained in a different geographical context?

To answer these questions, a sensitivity analysis was performed taking into account different geographical localization of the electricity mix supply as an inventory flow. The results of sensitivity test demonstrate that sustainable leader of the caseinate production is Quebec using hydroelectricity as an energy source having the lowest emissions as compared to other considered regions (Fig.A3). Moreover, EDBM-UF process releases 8.9 units of % less of CO_2 eq. as compared to acid/base process. One could notice that countries of Eastern Europe have very similar environmental impacts with difference between the both studied scenarios is 8.7 units of %. In this region, electricity is mainly produced from natural gas, hydropower and nuclear power having relatively low emissions. For instance, in Russian Federation, 50.1 % of electricity is produced from natural gas, 17.1 % from hydropower, 16.3 % from nuclear power and just 15.2 % and 0.1 % from coal and oil respectively[17]. Similar impacts (8.6 units of % difference between both scenarios) were demonstrated for countries of South America using almost the same sources of energy as in Eastern Europe. The emissions associated with caseinate manufacturing in Western Europe are slightly higher as compared to above regions, which leads to decrease of differences between EDBM-UF and acid/base processes to 8.3 units of %. This could be related to the fact that electricity production in Western Europe is quite diversified. For instance, in France more than 70 % of electricity comes from nuclear power while in Norway it mainly comes from hydropower (96.1 %)[17]. More than 40 % of German electricity is derived from coal as in Greece and Denmark, which is associated with significant environmental issues[17]. However, these issues are addressed to the development of the electricity production from renewable sources. Indeed, there is relatively wide implementation of renewable energy sources in certain countries of Western Europe such as Denmark (46 %), Germany (21 %), Iceland (29 %), Italy (21 %), Spain (26 %), etc[17]. Thus, the diversification of electricity production in Western Europe with the aim of environmental burden decrease could explain the relatively low impacts of electromembrane process for the caseinate production. The use of non-renewable energy sources in North America, Oceania, Africa and Persian Gulf countries (mainly coal and natural gas) for the electricity production leads to the higher environmental burden during caseinate manufacturing. In these regions, the differences between EDBM-UF and acid/base technologies are about 7.5 units of %. The least favorable regions for caseinate manufacturing from a sustainable point of view are China and Asia. For instance, in China with the largest electricity production industry (5719 TWh/year)[45] the main energy source is coal (> 70 %). Consequently, the differences between both studied scenarios of protein manufacturing are just about 6 units of %.

The similar trends could be observed for the ecosystem (6.9 – 8.9 units of %) and resources (4.6 – 8.9 units of %) impact categories between EDBM-UF and acid/base processes at different geographical locations (Fig.A.4). Though the general trends for the human health (5.3 – 8.0 units %) are similar to above categories, there is one particular region where the EDBM-UF process has 9.0 units of % higher impacts than acid/base one (Fig.A4). This region is Asia (without China) where the electricity production is associated with the important impacts on human respiration due to the emissions of inorganic pollutants from coal power production.

Thus, the sensitivity test revealed that the novel electromembrane process of caseinate production has less environmental burden compared to conventional process using chemicals no matter the electricity supply mix.

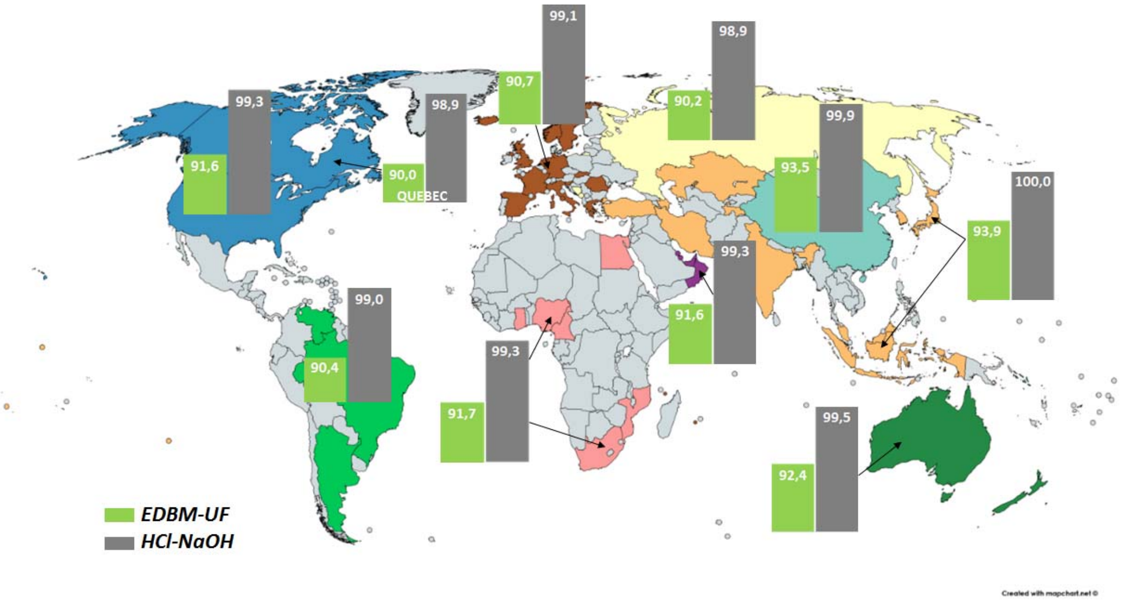

Fig.A3. Relative contributions (in %) of caseinate powder manufacturing by electromembrane and acid/base processes to the climate change (IPCC 2013) concerning the geographical localization of electricity inventory flow.

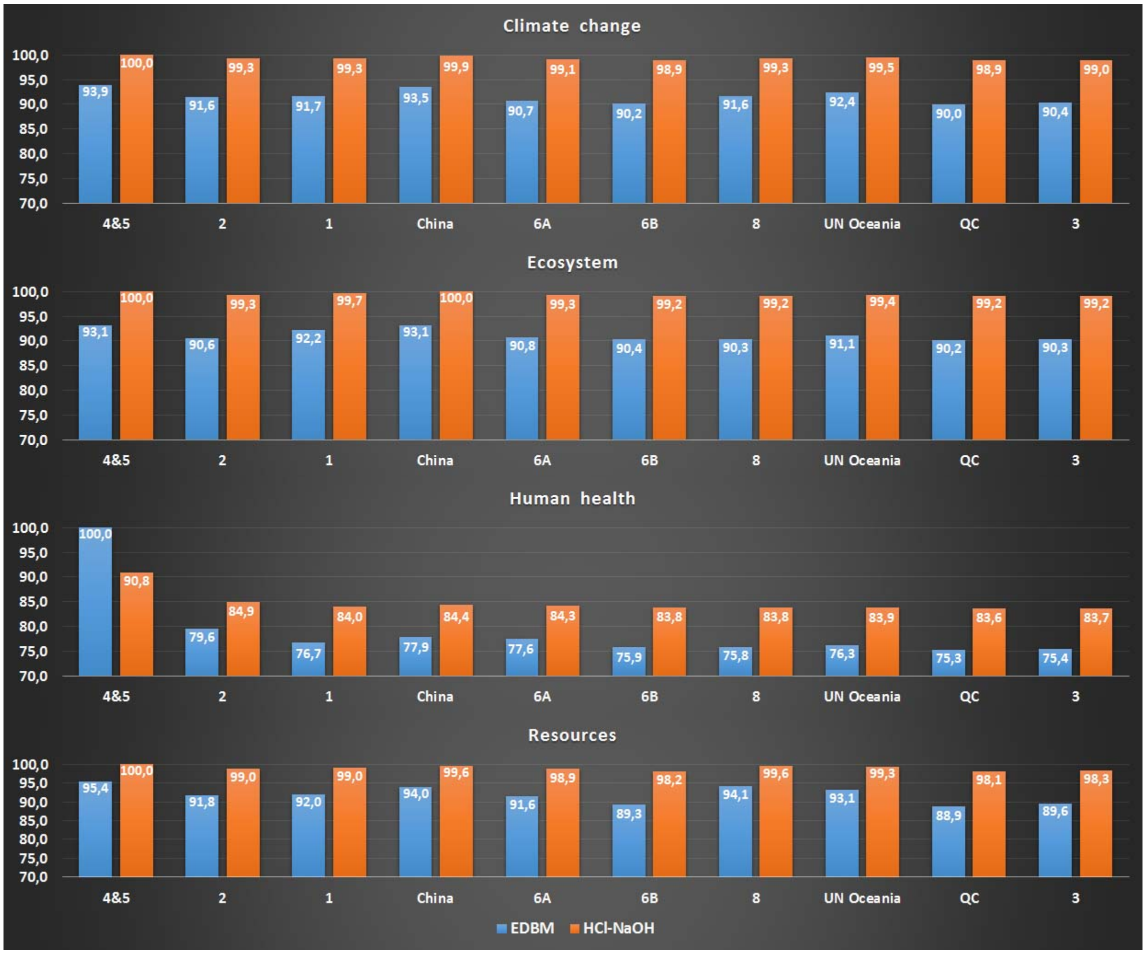

Fig.A4. Relative contributions (in %) of caseinate powder manufacturing by electromembrane and acid/base processes to the impact categories: climate change (IPCC 2013), human health (Impact 2002+), ecosystem quality (Impact 2002+) and resources (Impact 2002+) at different geographical locations of electricity production. Definition of areas: 4&5 – Azerbaijan, India, Indonesia, Iran, Japan, Kazakhstan, Malaysia, Tajikistan, Turkey; 2 – Canada (without Quebec), USA; 1 - Cameroon, Egypt, Ghana, Mozambique, Nigeria, South Africa; 6A - France, Germany, Greece, Iceland, Italy, Netherlands, Norway, Spain, Sweden, United Kingdom, Romania, Slovakia and Slovenia; 6B - Russia, Montenegro, Bosnia and Herzegovina; 8 - Bahrain, Oman, Qatar, UAE; UN Oceania – Australia, New Zealand; 3 – Argentina, Brazil, Venezuela.

References

1. Report “How to feed the world in 2050?” Food and Agricultural Organization of United Nations (FAO), 2009.

2. Policy No. 200712: Toward a Healthy, Sustainable Food System, American Public Health Association (APHA), 2007.
3. R. Hartmann and H. Meisel, *Current Opinion in Biotechnology*, 2007, **18**, 163-169.
4. H. Korhonen and A. Pihlanto, *International Dairy Journal*, 2006, **16**, 945-960.
5. G. Wu, J. Fanzo, D. D. Miller, P. Pingali, M. Post, J. L. Steiner and A. E. Thalacker-Mercer, *Annals of the New York Academy of Sciences*, 2014, **1321**, 1-19.
6. J. R. Hoffman and M. J. Falvo, *Journal of Sports Science & Medicine*, 2004, **3**, 118-130.
7. D. M. Mulvihill and M. P. Ennis, in *Advanced Dairy Chemistry—1 Proteins*, eds. P. F. Fox and P. L. H. McSweeney, Springer US, 2003, DOI: 10.1007/978-1-4419-8602-3_32, ch. 32, pp. 1175-1228.
8. S. Mikhaylin, V. Nikonenko, G. Pourcelly and L. Bazinet, *Green Chemistry*, 2015.
9. S. Mikhaylin and L. Bazinet, *Advances in Colloid and Interface Science*, 2016, **229**, 34-56.
10. V. D. Grebenyuk, R. D. Chebotareva, S. Peters and V. Linkov, *Desalination*, 1998, **115**, 313-329.
11. S. Mikhaylin and A.-V. Sion, *Innovative Food Science & Emerging Technologies*, 2016, **33**, 571-579.
12. M. P. Mier, R. Ibañez and I. Ortiz, *Biochemical Engineering Journal*, 2008, **40**, 304-311.
13. J. Balster, I. Pünt, D. F. Stamatialis, H. Lammers, A. B. Verver and M. Wessling, *Journal of Membrane Science*, 2007, **303**, 213-220.
14. L. Bazinet, D. Montpetit, D. Ippersiel, J. Amiot and F. Lamarche, *Journal of Colloid and Interface Science*, 2001, **237**, 62-69.
15. S. Hellweg and L. Milà i Canals, *Science*, 2014, **344**, 1109.
16. G. Rebitzer, T. Ekvall, R. Frischknecht, D. Hunkeler, G. Norris, T. Rydberg, W. P. Schmidt, S. Suh, B. P. Weidema and D. W. Pennington, *Environment International*, 2004, **30**, 701-720.
17. The World Bank IBRD-IDA, *World Development Indicators: Electricity production, sources, and access*, 2014.
18. I. O. f. Standardization, *ISO 14044: Environmental Management - Life Cycle Assessment - Requirements and Guidelines*, ISO, 2006.
19. C. R. Southward, in *Dairy Processing Handbook*, Tetra Pak Processing Systems AB, Lund, 1995, ch. 20.
20. Centre international de référence sur le cycle de vie des produits procédés et services (CIRAIG), 2014.
21. L. Bazinet, F. Lamarche, D. Ippersiel and J. Amiot, *Journal of Agricultural and Food Chemistry*, 1999, **47**, 5291-5296.
22. J. W. Fuquay, P. F. Fox and P. L. McSweeney, *Encyclopedia of dairy sciences*, Academic Press, 2011.
23. B. Ribadeau-Dumas and R. Grappin, *Lait*, 1989, **69**, 357-416.
24. Z. Haque, M. M. Kristjansson and J. E. Kinsella, *Journal of Agricultural and Food Chemistry*, 1987, **35**, 644-649.
25. D. H. James and W. M. Castor, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
26. Y. Mizutani, R. Yamane, H. Ihara and H. Motomura, *Bulletin of the Chemical Society of Japan*, 1963, **36**, 361-366.
27. P. Segalen, M. Boulle and G. Gwozdz, *Laits et produits laitiers*, 1985, **2**, 147-155.
28. O. V. Dymar and S. I. Chaevsky, Institute of Meat and Dairy Industry, Minsk, 2007.
29. Y. H. Hui, *Food drying science and technology: microbiology, chemistry, applications*, DEStech Publications, Inc, 2008.
30. O. Jolliet, M. Margni, R. Charles, S. Humbert, J. Payet, G. Rebitzer and R. Rosenbaum, *The International Journal of Life Cycle Assessment*, 2003, **8**, 324.
31. G. Wernet, C. Bauer, B. Steubing, J. Reinhard, E. Moreno-Ruiz and B. Weidema, *The International Journal of Life Cycle Assessment*, 2016, **21**, 1218-1230.

32. S. Koter, P. Piotrowski and J. Kerres, *Journal of Membrane Science*, 1999, **153**, 83-90.
33. G. Saracco, *Chemical Engineering Science*, 1997, **52**, 3019-3031.
34. G. Pourcelly, *Russian Journal of Electrochemistry*, 2002, **38**, 919-926.
35. Y. LE Graet, F. GAUCHERON, Eacute and RIC, *Journal of Dairy Research*, 1999, **66**, 215-224.
36. J. De Wit, *European whey products association, Brussels*, 2001.
37. G. W. Smithers, *International Dairy Journal*, 2008, **18**, 695-704.
38. J. A. Hourigan, E. V. Lifran, L. T. T. Vu, Y. Listiohadi and R. W. Sleigh, in *Advances in Dairy Ingredients*, Wiley-Blackwell, 2013, DOI: 10.1002/9781118448205.ch2, pp. 21-41.
39. P. Walstra, P. Walstra, J. T. Wouters and T. J. Geurts, *Dairy science and technology*, CRC press, 2005.
40. D. A. Straub, *Nutrition in Clinical Practice*, 2007, **22**, 286-296.
41. International Dairy Federation (IDF), *Environmental / Ecological Impact of the Dairy Sector: Literature review on dairy products for an inventory of key issues List of environmental initiatives and influences on the dairy sector. Bulletin no.436*, Brusels, 2009.
42. The UNEP Working Group for Cleaner Production in the Food Industry, *Eco-efficiency for the Dairy Processing Industry*, Environmental Management Centre,, Sydney, 2004.
43. C. A. Ramírez, M. Patel and K. Blok, *Energy*, 2006, **31**, 1984-2004.
44. International Dairy Federation (IDF), *Energy Use in Dairy Processing, Bulletin no.401*, Brussels, 2005.
45. Electricity information, International Energy Association OECD/IEA, 2016.