Modern Processes in Food Engineering: A Coupled Process for Processing Sea Buckthorn Fruits

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Keywords: food engineering, electroosmosis, sea buckthorn, anode juice, mathematical modelling

Recently, the electrotechnologies based on effect of electric field on one's basic processes from food engineering have gained a real interest. The processing of some natural products by pressing them in a DC electric field is known as electroosmosis under pressure. The particularization of this process for products separation from *Sea buckthorn* fruits is the aim of this paper. This particularization is due to the fact that the products of these fruits or their derivatives highlights high therapeutic activity acting as antioxidant[1], immunomodulator[2], anticancer[3], cardioprotective[4], hepatoprotective[5], antistress[6], antibacterial, antiviral[7] and respectively radioprotective[8] agents and also because the adding of new knowledge to a problem is always welcome. In this processing case (electroosmosis under pressure) the carotenoids, the polyphenols, the flavones, the enzymes (amylase, protease, lipase, etc.) and other compounds from the processed fruits are distributed between the juice separated at the cathode, the pulp from the processed bed and the juice separate at the anode. This distribution is experimentally established using a specially designed device and characteristic analytical methods. The process dynamics is characterized by experimental curves showing the time evolution of juice extraction ratio and by temperature dynamics in the pulp. A consistent modelling part is developed in order to cover most of experimental investigation and to show how it can be used to process scale-up.

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Process Intensification using Microwaves and Ultrasound

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The use of microwave energy in chemical laboratories was first described in 1986 by Gedye [1] and by Giguere [2] in organic synthesis and by Ganzler [3] in the extraction of biological matrices for the preparation of analytical samples. Due to the fact that the microwave radiation is nonionized, the interaction with materials occurs by their heating. Some advantages of microwave heating over conventional systems are[4]:

- Volumetric heating: heating does not take place by transfer from a surface but to the volume of the reaction mixture;
- Selective heating - the components of a heterogeneous system can heat up differently even if the size of the components is very small;
- Rapid energy transfer - very high power densities can be obtained which produce very high heating rates.

Because of these particularities, microwave heating is increasingly used in the synthesis and processing of materials. However, the overall process rate is often limited by mass transfer. Ultrasound can be used to improve the mass transfer. Power ultrasound which is capable of influencing chemistry and processing, generates cavitation bubbles when passes through the liquid. There are many thousands of such bubbles in the liquid some of which are relatively stable but others expand further to an unstable size and undergo violent collapse to generate temperatures of about 5000°K and pressures of the order of 2000 atm. If the bubble collapses close to or on a solid surface the collapse is not symmetrical and results in a microjet of liquid being directed towards the surface of the material at speeds of up to 200 m/s. These jets are of course the underlying reason why ultrasounds are so effectives in increasing mass transfer.
The combination of these two types of irradiations — electromagnetic and mechanical — and their application to chemical reactions is really interesting.
Both microwave irradiation and ultrasound definitely meet the Process Intensification rules through the improvement of energy transfer, the reduction of energy consumption, the reduced volumes of reactors/plants, the improved product quality, the ease of process automation as well as remote reaction control
The main question about the combined technology is how the two separate technologies can be combined. There are two approaches:

- Use separate reactors one using ultrasound and another using MW with a recirculating pump to allow the liquid to be transferred from one reactor to another.
- Use a single reactor with both US and MW inside.

The paper describes the main types of equipment that make it possible to simultaneously use of ultrasounds and microwaves.

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Pareto-optimal Operating Policies of a Mechanically Agitated Continuous Reactor used for the Oxidation of D-Glucose on co-Immobilized Pyranose Oxidase and Catalase

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When developing an industrial enzymatic process, one essential engineering problem concerns the choice of the reactor optimal operating policy based on à-priori knowledge of the process kinetics and enzyme inactivation characteristics. For a multi-enzymatic system, involving complex interactions among enzymes that exhibit optimal activity on different parametric domains, and a high-order deactivation, this problem requires an extended analysis. The engineering problem becomes difficult when a multi-objective optimization problem is formulated. An elegant option developed in this paper is to obtain sets of Pareto optimal solutions, also called Pareto-optimal fronts, each one generated for the case of at least two adverse objectives. Then, the final choice of the enzymatic reactor operating policy results from the comparative analysis of these fronts. Exemplification is made for the case of the oxidation of D-glucose (DG) to 2-keto-D-glucose (kDG) in the presence of P2Ox (oxygen 2-oxidoreductase) and catalase, continuously operated in a three-phase-fluidized-bed reactor (TPFB) with co-immobilized enzymes on alginate beads (Fig. 1left).
To perform the TPFB optimization, a dynamic ideal model was adopted from literature[1,2] corresponding to an isothermal, perfectly mixed reactor of constant volume, with vigorous aeration and mechanical stirring, fed with substrate solution, and including suspended solid particles (spherical beads) with immobilized enzymes. The current model also considers P2Ox activity decay due to their chemical interactions, but also due to its leaking following the hydrodynamic stress, and its inherent denaturation over time.
The optimal operating policy choice is that requiring minimum P2Ox amount but ensuring an imposed reaction conversion and maximum reactor productivity under various technological constraints (Fig. 1right).

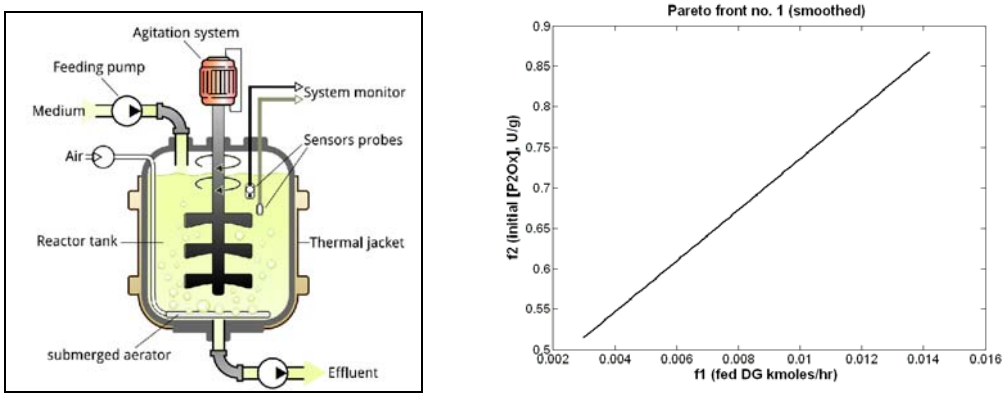

Fig. 1. The TPFB scheme (left). Pareto-optimal front (right) of the continuous TPFB to get MORE THAN 30% DG-conversion under specified nominal conditions (co-immobilized P2Ox and catalase enzymes, 30°C, pH=6.5, 19 h hydraulic residence time, for an initial substrate $[DG]_o$ = 250 mM). The Pareto-optimal front was generated for the following two contrary objectives: minimum of the initial P2Ox enzyme on the support (f2), and maximum of the processed DG molar flow-rate, (f1).

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Setting Optimal Operating Policies of a Fluidized Bed Bioreactor used for Mercury Uptake from Wastewaters by using Immobilized *P. putida* cells

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A model-based analysis of a three-phase continuously operated fluidized-bed bioreactor (TPFB, Fig. 1) is developed in order to determine the multi-objective optimal and sustainable operating policy of the TPFB used for removing mercury ions from wastewaters. More specifically, the analysis is focused on finding the optimal feeding policy of alginate porous beads of known particle size containing immobilized biomass (*P. putida* bacteria) that minimize the biomass consumption, while keeping a quasi-constant high mercury removal conversion, under quasi-stable reactor performances.

To simulate the TPFB reactor performances and to derive the optimization problem solution, an extended dynamic ideal model of the bioreactor was adopted[1], including a simple Michaelis-Menten kinetics of the bioprocess derived from a structured extended model[2-4], thus allowing its use for bioprocess optimization. The model includes the main characteristics of the bioprocess on the solid support, but also terms for the biomass growth, biodegradation, and its partial leakage and washout. The model accounts for the solid-liquid-gas interfacial transport of the mercury, by means evaluating the particle effectiveness and by solving the mass flux equality at solid-liquid-gas interface during the transient regime. To solve this complex multi-objective optimization problem, the "weighting function method" has been used, by associating to each criterion suitable weighting factors, the obtained optimal feeding policies with immobilized biomass (some being plotted in Fig. 2) being dependent on the relative importance given to each objective.

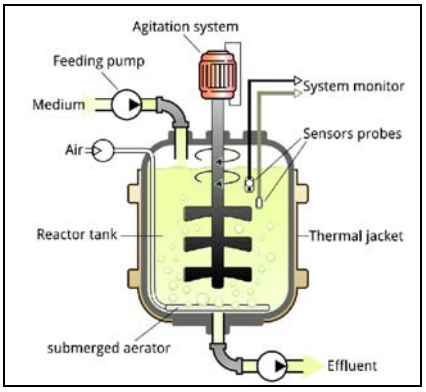

Fig. 1. The TPFB scheme.

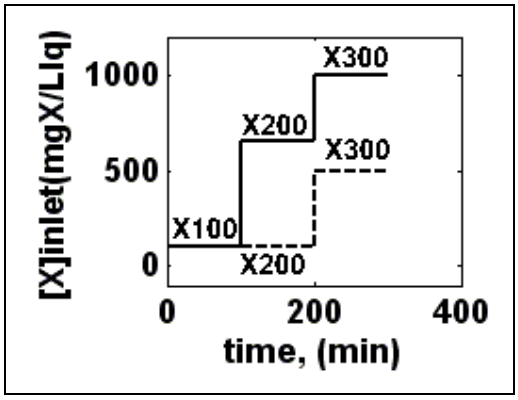

Fig. 2. Optimal feeding policies of the TPFB.

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Identification and Characterization of Environmental Pollution Sources of Natural Radionuclides and Heavy Metals from the Aries River Basin

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The present work is performed to obtain information on the pollution sources of natural radionuclides and heavy metals that can affect water quality in Aries River.

Potential sources of pollution with radionuclides are geological exploration perimeters[1,2] uranium ores located on tributaries of the Aries River (Arieşeni – Galbena, Gârda, Avram Iancu and Lupşa) or even on its valley. Potential sources of heavy metal pollution are mining perimeters which are located on tributaries of the river Aries namely Roşia Poieni mining, Roşia Montană and Baia de Aries.

Radiation sources are sources of radiation in the water and in the case of sediments. Natural radioactive series are the most widespread of radionuclides: potassium - 40 (K^{40}), uranium - 238 (U^{238}) and thorium - 232 (Th^{232})[3]. The majority of radionuclides have a low solubility in water and tend to be adsorbed, therefore, accumulate in the sediment. Ra^{226} and U_{nat} content in soil is between 5 and 850 ppm for U_{nat} and for Ra^{226} from 0.05 to 400 Bq/g; values over levels of exclusion of 16 ppm for Unat and 0.040 Bq/g for Ra^{226} provided in Radiological safety rules on operational radiation protection in the mining and preparation of uranium and thorium NMR 01, CNCAN.

Investigation of heavy metals in water and sediments can be used to estimate the anthropogenic impact of mining industries and the risks posed by discharges of waste on ecosistemelor[4,5,6]. It is therefore important to measure the concentrations of heavy metals in water and sediments[7]. Sum of the concentrations of metal ions contained in mine water is below 2 mg/L.

To determine the extent of contamination by heavy metals and natural radionuclides of Aries river, it is necessary to know the processes of migration and concentration of contaminants in river water and sediments.

Keywords: uranium, thorium, environmental pollution, radionuclides

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Aluminium Pigments Encapsulated in SiO_2 Inorganic Nanostructures

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Aluminium pigments are widely used in the paints industry. Traditionally, aluminium pigments are used in solvent-borne formulations. The concerns about the human health and environment have pushed the industry to develop new environment-friendly products, such as water-based coatings. The problem is that aluminium pigment reacts with water and a large amount of hydrogen is released. This is a very dangerous reaction which also damages the metallic appearance. A method to avoid this reaction is encapsulation of aluminium pigments in polymer matrices.

This study focusses on encapsulation of aluminium pigments with a sol-gel process using tetraethoxysilan as inorganic precursor, water and a basic catalyst. The new products were characterized by TEM, SEM, EDAX, FTIR and TGA. The water stability and the optical properties were also tested. As a result, the aluminium pigment is encapsulated in a matrix of inorganic polymer, which greatly enhances the resistance to water, while preserving the optical properties.

Aspects Concerning the Computation of the Separator Serving an Oil Well

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The fluids produced from the well are a mixture of oil, gas, water and solids. These fluids pass through separators, which may be either two or three phase. The purpose of the separators is to split the flow into desirable fractions in order to obtain components for the advanced stage of separation. The design of the separator is based on the specific gravity difference between the oil gas and the liquid and solid phases. The design criterion take into accout that the suspended solids settles to the bottom of the separator as a sediment layer, the oil will rise to top of the separator, and the wastewater will be the middle layer between the oil on top and the solids on the bottom[1,2]. The retention time is typically five minutes, allowing gas to bubble out, water to settle at the bottom and oil to be taken out in the middle. The pressure is often reduced in several stages (high pressure separator, low pressure separator, etc.) to allow controlled separation of volatile components. In gravity separation, the well flow is fed into a horizontal vessel. In a two-phase separator, oil and water are sent for further separation as a single liquid stream whereas, in a three-phase separator, oil and water are separated in the vessel into separate streams. The treatment of the crude must be such that it meets the required specifications. Further processing takes place to recover the oil from the produced water in a procedure called de-oiling. This procedure of emulsified oil–water mixtures can be done by gravity and utilizing thermal and chemical techniques. The standard of cleanliness of disposed water depends of the method used for disposal: waterflooding, residual injection or river disposal. Either way, the target of impurities is below 100-200 parts per million. The gas leaving the separators is treated to remove water and any condensate present by cooling, known as dew-point conditioning, i.e. the temperature at which liquids condense out of the gas. Solids tend to collect in the separators, which are periodically cleaned during a planned shutdown when major maintenance work is undertaken.The scope of this papper is to propose a calculation and working design based on hidrodinamic processes and mass transfer principles for primary separation of oil wells components, that are produced from the reservoir.

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Extraction of Seaweed Biomolecules from the Romanian Black Sea (*Cystoseira barbata*)

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Historically, seaweed has been used as food, both for humans and their domesticated animals, as a nutrient-rich fertilizer or as a source of gelling agent. Recently, seaweed is found interesting in medicine and biotechnology as pharmaceuticals, cosmetics, fertilizers in agriculture, pigments and antioxidants. Brown seaweed is cultivated industrially for its alginate. Fucoxanthin from brown seaweed has potential as a food pigment whilst possessing antioxidant activity along with phlorotannins.

Cystoseira barbata is the main brown seaweed found in the Black Sea and is fairly common in the Mediterranean Sea. It is part of the Sargassaceae family from the Fucales order. It is rich in alginate and fucoidan and could be a source of valuable polyphenols (phlorotannins), pigments and proteins. Despite its potentially valuable composition, it is not currently valorized which is also the case for other species of red and green seaweed which are abundant in the Black Sea.

In the current work, we focus on the extraction and characterization of biomolecules from *Cystoseira barbata* recovered from the Romanian seaside of the Black Sea. Different procedures are performed to selectively extract proteins, alginates, fucoidans and pigments (fucoxanthin). A procedure widely used in literature is applied to extract alginates and fucoidans in a stepwise manner[1]. Proteins are separated via acidic and alkaline extraction[2]. Different solvents were tested for polyphenols extraction (phlorotannins, fucoxanthin).

Efficient extraction and purification of compounds from algae is a critical step when attempting to valorize them. In the context of valorization of natural products in seaweed, extraction methods are very important and optimized solutions should be found for various valorization pathways. The extraction procedures used for separating biomolecules from *Cystoseira barbata* are also optimized for maximum extraction yields.

Different analytical methods were employed for the quantification of proteins (Bradford assay; total nitrogen content; amino acid profile). Polysaccharides were quantified and characterized by using: phenol-sulfuric acid method, HPAEC, FTIR, NMR and HPSEC. Finally, polyphenol were estimated using the Folin–Ciocalteu reagent and fucoxanthin concentration was determined by HPLC.

In this work, we have presented optimized solvent extraction methods for biomolecules from *Cystoseira barbata* recovered from the Romanian seaside of the Black Sea. The next step is to propose cheap formulations for various industries (cosmetics, food industry and pharmaceutics).

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Ultrafiltration with Membrane Surface Clogging in Batch Processing of Some Primary Algae Extracts

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Algae (especially microalgae) are an abundant source of HVAB (high value added biomolecules) such as antioxidants, pigments, polyunsaturated fatty acids, polysaccharides and proteins which are or could become a sustainable feedstock for applications in pharmaceuticals, nutraceuticals or food industry. Apart from the intrinsic value of these compounds, algae are also expected to be a good feedstock for biofuels in the near future. Despite all the possible applications related to algae, their use at an industrial level is not yet achievable mainly due to the high costs related to separation and purification.
Ultrafiltration is a method which has already been employed for use in the food industry or for obtaining high purity streams of complex biological entities such as viruses or proteins. Its main advantage over classical methods is that the separation does not depend on the processing temperature.

We consider the application of ultrafiltration to simultaneously recover the valuable phycocyanin pigment whilst concentrating a protein extract from Spirulina (*Arthrospira platensis*). Although the separation is performed at pilot scale and rates of separation are good enough, working at industrial levels requires dealing with the decrease in permeate productivity, a phenomenon which is frequently associated to clogging effects.

The first step in the current work is to quantify the total protein concentration in the extracts by evaluating the total nitrogen content to which it is linked by a correlation factor. This was also determined by linking the amino acids profile to the total nitrogen content performed by elemental analysis. Gel chromatography has been employed to assess the size distribution of proteins found in the extracts.
In ultrafiltration of proteins and other biochemicals, the clogging effect is due to adsorption and gel formation both of which lead to a decrease in productivity. We attempt to understand this effect by a series of ultrafiltration experiments in which the effect of important parameters is evaluated (concentration in the retentate, transmembrane pressure and tangential flow rate) and linked to the increase in the overall resistance to permeate flow of the system. The resistance in series model is considered for explaining flux decline[1]. A stochastic model with two elementary processes featuring the local locking and unlocking the filtration surface by microparticles will be checked for time decrease of permeate flow rate[2].

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Fed-Batch Biodiesel Production: Experimental Results and Modelling in Transesterification of Waste Vegetable Oils to Biodiesel

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Keywords: fed-batch system; transesterification kinetic model; oil conversion, biodiesel, green process.

Biofuels and green energies production shifted for many states from protecting climate actions and sustainability actions to securing own energy resources. Securing energy resources first, fuels or electric energy, and securing energetic non-dependency gives the strength then to participate to global efforts made in respect with sustainable development or environmental protection. Biodiesel as second most produced and used biofuel is made using more than twenty techniques and technologies, only three of them being considered conventional: oil transesterification using homogeneous acid catalysts, homogeneous base catalyst (more than 60 % of commercial biodiesel) and homogeneous acid-base catalyst[1]. The remained technologies implies reactors using ultrasounds, microwaves, membranes, or reactive distillation, super (sub) critical techniques, enzymes and non-catalytic processes. In this work fed-batch system was studied as a novel technique for biodiesel production along with modelling the kinetic for transesterification reaction to convert waste vegetable oils to biodiesel[2]. While batch system implies all reagents to be initially fed then reaction to take place until completion, for this fed-batch system we opted to feed catalyst and methanol first allowing *in situ* methoxide formation and secondly oil feeding corresponding to a pre-calculated debit flow. Experimental results showed high yields when the reactions went under similar conditions with commercial-like biodiesel in terms of reaction temperature, catalyst loadings and methanol to oil molar ratio and allowed us to gather data to develop a kinetic model. The model for waste vegetable oils transesterification reaction either homogeneously or heterogeneously catalyzed is used to represent the chemical reaction kinetics. A kinetic model was solved assuming an isothermal process and the reaction mixture perfectly stirred. The dynamic of species concentration and the expressions for the feed flow dynamic analyzed led to the conclusion that controlling the process using these technique makes scaling–up this kind of process a viable one.

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Unconventional Methods for Enhancing the Fermentation Process

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Bioethanol, the most widely used biofuel, can be obtained by the fermentation of glucose. In order to reduce production costs, new methods for enhancing the fermentation process must be identified.
Microwaves are mostly used for the destruction of microorganisms (food sterilization at low temperatures) [1, 2]. Few information are available regarding the possibility to enhance biological processes through exposure to microwaves [3, 4, 5].

The fermentation process of glucose with *Saccharomyces cerevisiae* under continuous exposure to microwaves was studied. A multimode applicator was used, in which the microwaves are provided by a solid state microwave generator with a maximum power of 20 W. This type of construction allows the exposure of the fermentation broth to controlled small doses of microwaves. Microwave irradiation, the cooling and stirring of the reaction mixture were carried out simultaneously, in order to maintain the temperature constant during the fermentation process. Temperature distribution in the reactor was verified both experimentally and by process modelling using Comsol Multiphysics®.

The effects of microwave irradiation on fermentation rate and yeast cell growth were observed during the fermentation process, at different glucose and yeast concentrations. The optimal specific absorption rate (SAR = 25 W/kg) was identified, at which the fermentation rates were up to 40 % higher than those obtained in the conventional process carried out at the same conditions but in the absence of microwaves.

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Sustainability in Chemical Engineering

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A comprehensive definition of sustainability is as[1] *the optimal growth path that maintains economic development while protecting the environment and optimizing the social conditions with the boundary of relying on limited, exhaustive natural resources*. Therefore, sustainability clearly does not mean to preserve, but to develop responsibly. There are three dimensions constituting sustainability: economic, environmetal and social developments which are considered the three pillars carrying this concept. All these three parts are equally important in sustainable development. They are not independent of each others; on the contrary, there is manifold interaction between them. Nowadays the concept of sustainability is imposed in all human activity fields, especially in industrial domains. Chemical industry, as a huge materials and energy consumer, and with a strong ecological impact, could not remain outside of sustainability requirements.

Current chemical practices must be transformed into new paradigms in sustainable chemistry. Some of these new paradigms that will be exposed in this work are[2]:
- Tailorable, *e.g.* genetically engineered, renewable feedstocks supply the building blocks for material synthesis;
- Thermoprocessible plastics produced by simple modifications of oxygenated biomaterials;
- Materials held together by non-covalent forces that can be disassembled under specific conditions;
- High level computations used to predict new catalytic systems;
- Accurate computational approaches to predicting the properties of novel materials to reduce the development effort;
- The future chemical plant will consist of modular microreactors that can be rapidly assembled in multiple combinations to create new processes;
- Highly selective, nanomaterials-based separations methods avoid the need for distillation.

As a result of these new paradigms, new researches in a number of specific areas are necessary. Some examples are:
• Supplying the building blocks for material synthesis by research into tailorable, e.g. genetically engineered, renewable energy feedstocks.
• Increasing alternative fuel use by searching for thermoprocessible plastics produced by simple modifications of oxygenated biomaterials.
• Lessening present energy conversion inefficiencies by developing single solvent, e.g. near-critical water.
• Developing catalysts with environmentally friendly metals (not precious metals or heavy metals) or non-metal catalysts.
• Establishing design rules for nanomaterials.

The new main principle of research must be: “research is the conversion of money into knowledge, while innovation is the conversion of knowledge into money”.

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Hydrodynamic Cavitation – Equipment and Uses

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Cavitation is a phenomenon characterised by the formation of bubbles or cavities in a liquid either by exposing it to ultrasonic waves (acoustic cavitation), or by passing the liquid itself through a smaller section (hydrodynamic cavitation), for example a plate with multiple small orifices, usually known as a Venturi section. The bubbles formed alternate through compression and expansion cycles, and if their diameter reaches a specific diameter they implode, leading to the formation of powerful microjets which achieve high local pressures and temperatures[1].

In the last two decades, acoustic and hydrodynamic cavitation were both studied in terms of their potential for disrupting the biological activity of living cells, Harrison and Pandit obtained the first cavitation reactor which can be used for this purpose, using a choke valve. Recent literature studies followed the applications of ultrasound in the regeneration of adsorbents and the drying / dehydration of food, processes which consist mainly of mass and heat transfer. A common use for cavitation has been the degradation of organic compounds in wastewater treatment, due to the formation of highly oxidative hydroxyl radicals by the dissociation of water molecules under the high temperatures and pressures achieved through cavitation[2, 3].

The goal of this paper is focusing on the potential uses of acoustic and hydrodynamic cavitation in the fuel and biofuel industry, by either improving biodiesel/bioethanol productivity through cavitation assisted processes, or by developing stable fuel – biofuel blends for use in current vehicles. The high temperatures and pressures obtained by cavitation lead to an increase in mass transfer due to the formation of more stable emulsions and a greater dispersion of the two phases which would eliminate the main limiting factor in biodiesel production. The jets formed during the bubble collapse could also improve mass transfer through the cells' membrane in bioprocesses like bioethanol fermentation. For this purpose hydrodynamic cavitation has been obtained using a device which consists of a high speed rotor connected to a set of plates with a specific geometry, and a centrifugal pump for the circulation of the liquid through the space between the moving plates.

A better understanding of the phenomenon of cavitation may allow a better control over its effects and routing them towards carrying out chemical reactions and physical processes with high efficiency and lower power, making possible the development of certain technologies around using cavitation, which are normally limited by long reaction times and high degree of complexity[4, 5].

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Simulation and Control of a Municipal Wastewater Treatment Process using SuperPro Designer Simulator

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The basic function of the wastewater treatment plant is to speed up the natural processes by which water purifies itself. In earlier years, the natural treatment process in streams and lakes was adequate to perform basic wastewater treatment. As population and industry grew to their present size, increased levels of treatment prior to discharging domestic wastewater became necessary.

A wastewater treatment plant was simulated using SuperPro Designer Simulator on the base of Bardenpho process for nitrogen removal[1,2]. The Bardenpho process does a better job in terms of NO3-N removal as well as in terms of overall nitrogen removal[2]. In the Pro-Designer flowsheet two anoxic and two aerobic stages were used as separate process units. In reality, all four stages are accommodated by the four initial tanks[2]. More specifically, one of the four tanks (25% of total volume) houses the first anoxic stage, two other tanks (50% of total volume) house the first aerobic stage, 80% of the fourth tank (or 20% of the total volume) houses the second anoxic zone, and the remaining 20% of the fourth tank (or 5% of the total volume) houses the second aerobic stage. The reaction stoichiometries and kinetics were assumed the same as in an example from the SuperPro Designer library[2].

It was simulated an increase of the ammonia concentration in the input of the process which lead to an effluent ammonia concentration in discharge above the legal, maximum admitted value. In order to control this situation it was increased the residence time of anoxic and/or aerobic bio-oxidation stages and the effluent ammonia concentration decreased under the maximum admitted value. It was investigated the effect of this control on the total operating cost.

A similar investigation was realized for the case of the increasing of nitrate concentration in the input of the process.

This application indicates the abilities of the simulator to control a wastewater treatment process in order to maintain the effluent pollutants concentrations in the limits of accepted values. Wastewater discharges are one of the key factors of European policy, given that they come mostly from human activities and can lead to negative impacts on aquatic ecosystems and human health.

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Heterologous Expression, Purification and Primary Characterization of an Alcohol/Aldehyde Dehidrogenase Suitable for 1,4 Butanediol Production

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1,4-butanediol (BDO) is an important intermediate molecule that is used as a starting material for the production of important polymers such as polyesters and polyethers. We designed and carried out a simple heterologous pathway for this non-natural compound in metabolically engineered *Escherichia coli*. The designed biochemical pathway leading to BDO production is starting from succinyl-CoA, which can be converted into 4-hydroxybutyrate by a heterologous enzyme, the double specificity alcohol/aldehyde dehydrogenase adhE2 from *Clostridium acetobutylicum*. The carboxylic group of 4-hydroxybutyrate can be activated by the native enzyme of *E. coli*, succinyl-CoA synthetase (sucCD) and in the final step the 4-hidroxybutyryl-CoA will be converted to 1,4-butanediol by the same alcohol/aldehyde dehydrogenase or by the malonyl-CoA reductase *from Chloroflexus aurantiacus* (mcr).

The aim of the study was to express this alcohol/aldehyde dehydrogenase from *Clostridium acetobutylicum* in *E. coli* BL21 (DE3) Star host strain using the co-expression vector pETDuet1. The His6-tagged adhE2 was purified using affinity chromatography on Ni-NTA resin, and the activity of the purified protein was studied on different substrates by spectrophotometry.

KEYWORDS

BDO, enzyme activity, heterologous expression, adhe2, *E.coli*

Proteomimetic SMAC Peptides: Cloning, Heterologous Expression with Fusion Partner, Purification and Interaction with Inhibitor of Apoptosis Proteins

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Present work highlights cloning, heterologous expression and purification of proteomimetic SMAC peptides. Genes of active part of Second Mitochondria-Derived Activator of Caspases (SMAC) protein was cloned into pET-19b ubiquitous fusion partner containing expression vector. Successful shake flask expression was achieved in *E. coli BL21 (DE3) Rosetta* cells using M9 minimal medium. The recombinant peptide-fusion protein was purified by immobilized Ni-affinity chromatography. The fusion partner was hydrolyzed with Ubiquitin carboxyl-terminal hydrolase (YUH1) enzyme. Interaction with Inhibitor of Apoptosis Proteins (IAP's) were carried out on Ni-NTA beads and detected by Western Blot.

Keywords: SMAC mimetics, heterologous expression, fusion partner, immobilized Ni-affinity chromatography, protein-peptide interaction, Western Blot.

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Palladium and Copper Catalysts for Furfural Hydrogenation

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It is well known that the world fossil fuels reserves will be eventually depleted, which is forcing humanity to look for alternative liquid fuels for transportation[1,2]. One of the most viable oil replacement alternatives is the conversion of biomass to furan derivatives that are precursors for many chemicals and can be used as biofuels. Furfural, along with its sister molecule 5-hydroxymethyl furfural (HMF), are biomass derived heterocyclic aldehydes commonly used as solvents for extraction of lubricating oils, as fungicides and weed killers, and as source for the production of tetrahydrofuran – an important industrial solvent. However, because of its high oxygen content, furfural has a low reciprocal solubility with petroleum hydrocarbons, thus, in order to be used as a component or additive for commercial gasoline, its oxygen content has to be decreased. Selective hydrogenation of furfural is the easiest and most efficient way to convert furfural and HMF into compounds with increased potential to be used as components or additives for automotive gasoline[3-6].

The main objective of the research presented here was to design an efficient catalyst for the selective hydrogenation of furfural to oxygenated furan derivatives having a high octane number and good stability. Palladium and copper based catalysts supported on alumina carriers with controlled acidity were synthesized. Introduction of copper aimed to improve the hydrogenation performance of the carbonyl group of furfural, while the palladium is employed for the saturation of the furan cycle. The acid strength distribution and textural characteristics (surface area, pore volume, pose size distribution) of the synthesized catalysts were characterized by diethyl-amine temperature programmed desorption, and nitrogen adsorption measurements, respectively. Their catalytic performance in furfural hydrogenation was assessed in a laboratory setup using a continuous flow fixed bed reactor operated isothermally.

Preliminary results indicated that the Cu content influenced the hydrogenation of the carbonyl bond, while higher Pd loading favored hydrogenation of both the furan ring and the carbonyl group, thus enabling control of the hydrogen consumption in the process. These results are promising for the design of an optimized catalytic system for the hydrogenation of furan derivatives.

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Sodium Citrate as a New Possible Complexing Agent for the Bioscouring Treatment of the Cellulosic/Lignocellulosic Fabrics

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The cellulosic/lignocellulosic fabrics are usually subjected to a pretreatment for the removing of all compounds which could negatively affect the further specific technological processes as whitening and dyeing. During the scouring process the physical parameters of the fabrics are improved. A classical scouring process implies the use of an alkaline media and high temperatures. To reduce the environmental impact, enzyme treatment (bioscouring) could be successfully applied. The treatment consists in utilisation of a pectinase mixture along with a complexing agent and a surfactant. There were also attempts to combine the alkaline and the enzymatic methods to improve the efficiency of the process, to make it more ecological and economic[1].

In the literature is underlined the important role of the chelating agent for accelerating the impurities removal from the fibres and the degradation of the pectic structure. The action mechanism consists in removing of calcium from the pectin structure. The enzymes activity is facilitated by the calcium removal[2, 3].

As chelating agent is usually use the EDTA, in our study we have obtained good results using sodium citrate. This reagent could be considered as a viable alternative, more eco-friendly, for the bioscouring treatment.

The bioscoring treatment was applied on 50 % of cotton- 50 % of flax, fabrics. The reaction was made in 0.1 M phosphate buffer of pH 8 and ultrasound media. The samples were immersed in an aliquot containing the commercial pectinolytic product Beisol Pro, Denimcol Wash-RGN as a surfactant provided by CHT Bezema Company and sodium citrate as complexing agent. The reaction was conducted by varying the time and enzyme concentration.

All the parameters determined after bioscouring treatment (weight loss, hydrophilicity, tensile strength and elongation at break) showed values comparable to treatment conducted using EDTA as a complexing agent.

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Mathematical Modelling of Molecular Distillation

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Molecular distillation is a thermal separation technique based on decreasing boiling point when pressure is reduced. At very low pressures the mean free path of molecules becomes comparable with dimensions of the separation space. This technique is suitable for low volatility heat sensitive compounds. An example is represented by polyunsaturated fatty acids (PUFA) esters with low molecule alcohols.

This technique is based on the evaporation of the compounds of the mixture to be separated from a heated falling film, and then condensation on a cooled surface situated at a lower distance, compared to the mean free path of the more volatile compounds. In this paper KDL5 laboratory pilot plant is considered, with minimum operating pressure as 0.1 Pa. Thus some compounds from feed mixture remain mainly in the heated film (heavy product), while the other compounds form the light product condensing as a liquid film on the cooled surface. The feed mixture is obtained by high vacuum fractionation in a DSL5 laboratory pilot plant operating at pressure as 1 Pa. Molecular distillation is performed in a KDL5 laboratory pilot plant at pressure as 0.1 Pa. Under these conditions, the volatility of PUFA has reasonable values at temperature which do not affect the thermal stability [1].

This paper presents the mathematical model and the solution method for a molecular distillation separation problem using Modelling Testbed (MoT) tool[2], a component of the Integrated Computer Aided System (ICAS). Main assumptions of the physical model are: two dimensional steady state model, the liquid film on the evaporation wall is much thinner than his diameter, the flow in the vertical direction is laminar, re-evaporation is neglected, no diffusion in the axial direction and the flow in radial direction is neglected [3].

The mathematical model is based on mass, heat and momentum balances for multi-component mixtures, resulting in a set of partial differential algebraic equations. Appropriate boundary conditions are considered. The constitutive equations include models for critical and physical –chemical properties. These are estimated by group contribution method (Lydersen Method), implemented in ProPRED component of ICAS. Model equations are implemented into MoT; this involves model translation, solution and analysis [4]. A first step is to convert model equations from text-mode to a form accepted by the computer. The variables are classified as explicit (the composition, the thickness film profile etc.), parameter (vapor pressure, heat of evaporation etc.), unknown, known (system pressure, feed temperature etc.) and dependent (velocity profile, temperature profile). A detailed analysis of the model is presented based on model structure. From the modelling results, some macroscopic variables can be computed and compared with experimental findings. In this respect the flowrate / quantity of heavy fraction and light fraction are used obtaining reasonable agreement. Future interest will be to evaluate relations between mean free path and operating variables.

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Hybrid Separation Techniques for Butanol Recovery from the ABE Process

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Biobutanol is an alternative fuel with characteristics similar to petro-fuels. Compared to ethanol - a more popular additive (up to 5% in gasoline) - butanol enjoys lower water miscibility, flammability and corrosiveness, while having the advantage of being able to directly replace gasoline in car engines without needing any modifications. Moreover, it can be produced by fermentation (ABE process) from a wide variety of waste biomass feedstock that does not compete with food, so it avoids food versus fuel issues. However, the ABE production via fermentation is facing great challenges due to the very low concentration owing to the severe butanol toxicity to microorganisms. One way to address this problem is development of more efficient downstream processes for butanol recovery.

In this contribution, several hybrid separation techniques for butanol recovery from the ABE fermentation process are analysed. The most promising alternative (in terms of reduced capital cost and low energy requirements) couples enhanced distillation in a dividing-wall column with liquid-liquid separation and heat integration by means of a vapour recompression system. Another option involves a suitable mass separation agent used in a process which combines liquid-liquid extraction and distillation. The third option is to couple a gas stripping column with liquid-liquid separation and distillation to improve butanol recovery. For each process analysed, a simulation model is developed using Aspen Plus. An economic evaluation is achieved by calculating the capital and operating costs. Finally, the controllability of the processes is assessed by performing rigorous dynamic simulation in Aspen Plus Dynamics.

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A Kinetic Study of Glycerol Acetylation Process

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One of the research directions in the last decade is the development of novel technologies for glycerol valorization, a high amount byproduct resulting in the biodiesel synthesis. Its valorization through esterification with acetic acid leads to mono-, di- and tri- glycerol acetates, chemical compounds with several practical applications (cosmetics, food industry, fuel additives, application in cryogenics, raw materials for synthesis of biodegradable polymers)[1,2].

The acetylation of glycerol with acetic acid is a reversible transformation, usually carried out in liquid phase, both in homogeneous and heterogeneous acid catalysis.

In the present work it was investigated the acetylation process using sulfuric acid and ion exchange resins (Amberlyst 35) as catalysts. The experiments have been carried out both in semi-batch system, using toluene as a carrier for the water resulting from the reaction, and in a closed batch system. Temperatures in the range of 80-120ºC, glycerol to acetic acid of 1:3 – 1:9, reaction times up to 5 h, and catalyst to glycerol mass ratios 0.01-0.04:1 have been implemented in the experimental work. In the semi-batch system there were obtained practically total glycerol conversion, whereas in the batch system, even if the conversion were relatively high (>90 %), they depend significantly on the operating conditions, especially on the reactants molar ratio. The maximum selectivity is obtained in respect to diacetin, in the range 60 – 95 %, and the selectivity for the other reaction products is in the range of 5- 40 % for monoacetin and up to 5 % for triacetin. With the increase of acetic acid/glycerol molar ratio, the selectivity in monoacetin is decreasing, whereas the selectivities in di- and triacetin are increasing.

The equilibrium composition dependence on the operating conditions was evaluated theoretically by a thermodynamic study. Given that the behavior of the reaction mixture is strongly non-ideal, the liquid phase activity coefficients were evaluated using UNIFAC method, based on group contribution approach. Because the literature is lacking some of the physical and thermodynamic properties of the glycerol esters (enthalpies, free enthalpies, heat capacities, vaporization enthalpies), these have been determined using published estimation methods. The calculated reaction enthalpies values are evidencing that the glycerol acetylation process is slightly exothermal. There were calculated the equilibrium compositions in different operating conditions, and the calculated equilibrium conversions were over 95 %. These conversion values are in good agreement with the experimental results obtained in batch system.

Based on the experimental investigations, there have been developed kinetic models both for homogeneous and heterogeneous catalysis processes and their parameters were estimated using nonlinear regression techniques. Their adequacy was tested by comparison with experimental data.

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CO_2 as a Source to Obtain Synthetic Natural Gas

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Romania, a country with a tradition over a century in the natural gas and oil industries, has one of the world's most pure methane deposits (up to 99.9% CH_4). The usage of methane gas has been steadily increased due to its energy, technological and sustainability advantages. Ussually, 1 Nm^3 of methane gas is energetically equivalent with 1.313 t of anthracite or about 0.9 t of crude oil. However, when burning methane, large amounts of CO_2 are released. To ensure a favourable carbon foot print, different methods for recovery and transformation into valuable products are investigated in last decades. One of them concerns transformation into valuable fuel gases.

In this work, a sustainable plant is presented, consisted into two main parts: CO_2 capture from flue gases by absorption in alkaline solutions, and then methanisation with hydrogen. The whole process, based on chemical reactions, thermodynamic models for electrolits and nonideal systems, as well as kinetic models for heterogenous catalysed reactions, is implemented in Aspen Plus process simulator. Two design alternatives are proposed: a) chemical absorption+desorption+metanisation and b) chemical absorption+ desorption+metanisation+heat exchangers network optimisation.

Sustainability is proved by economical analysis and environmental impact assessment for both alternatives. Economically, second alternative shows the possibility of reducing by 66% utilities consumption, by generating medium pressure and low pressure steam. Form environmentalpoint of view, second alternative demonstrates that CO_2 emissions are considerably reduced (by over 64%) by optimizing the heat exchanger network.

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TAME Synthesis Pilot Plant Modelling and Experiments

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Tert-Amyl-Methyl-Ether (TAME) is a gasoline additive used to increase the octane number. This project develops a model in *gPROMS® ModelBuilder* to simulate the behaviour of a laboratory pilot plant fixed bed catalytic pre-reactor for TAME synthesis. The chemical reactions describe the addition of methanol to 2-methyl 1-butene (2M1B) and to 2 methyl 2-butene (2M2B) to obtain TAME, as well as the isomerization between the 2 isoamylenes. The reactions take place in liquid phase with cationic exchange resin as catalyst as fixed bed (e.g. Amberlyst 35 wet). Parameterization of the pre-reactor is performed modifying space velocity, temperature and molar ratio (Methanol:Isoamylenes). The pressure in the pre-reactor is ~6 bar to avoid vaporization of components at reaction temperature[1]. Results are analyzed by gas chromatography.

The model is structured into three thermodynamic sub-models (activity coefficients, thermodynamic properties and transport properties) and two sub-models for the equipment (tubular reactor, cooling jacket). Partial differential equations for the conservation balances and boundary conditions are considered for the tubular reactor model. The jacket is considered as a perfectly mixed vessel and the heat balance at the thickness of the wall is neglected. A general model, named *cooled tubular reactor*, connects two sub-models (the tubular reactor and the jacket model). Regarding properties calculation, *Multiflash®* can be used as an external data base to be useed the *Foreign Object* feature in *gPROMS®*. This feature has integrated methods to calculate activity coefficients, physical properties and transport properties. TAME is not in *Multiflash®* database. Consequently, sub-models for the properties calculation are developed in this contribution. The first step is to implement the NRTL thermodynamic model to calculate activity coefficients[2], as a sub-model inside the tubular reactor model in *gPROMS®*. Then liquid phase density, viscosity, molar heat capacity, thermal conductivity are calculated with models from *SIMULIS®*. To be sure that the implementation is correct hand calculations in Excel® are compared with results obtained from the model implemented in *gPROMS®* and with *SIMULIS®* results. *Multiflash®* is used only for the cooling jacket sub-model. The chemical thermodynamic model is taken from literature[3]. The kinetic model is pseudo-heterogeneous Eley-Rideal type expressed with activities[4]. Diffusion coefficients and thermal conductivity are calculated with specific models for turbulent flow, both axially and radially. All these models are merged in the *gPROMS®* project of TAME synthesis reactor. Simulations under the same conditions as the pilot plant pre-reactor parameterization are performed for model validation.

Data obtained from *gPROMS®* project simulation are processed using *gRMS®* and *Microsoft Excel®*, to present temperature and composition profiles in dynamic and steady states.

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