IProPBio Workshop Series
Valuable products from residual biomasses towards a greener society (ProGreS)

BOOK OF EXTENDED ABSTRACTS

ProGreS 2nd WORKSHOP

From biomass characterization to process synthesis

May 16-17, 2022, Lisbon, Portugal

IProPBio

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Contents

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Practical Information

Conference location

Address

ISEL – Instituto Superior de Engenharia de Lisboa

R. Conselheiro Emídio Navarro, 1

Building A

1959-007 Lisboa, Portugal

Google Maps: [link](#)

GPS Coordinates: 38.75691186259142, -9.116494150002076

Metropolitan Map

Welcome Message

Following the success of the first project workshop *ProGreS: Biomass selection, characterization, and valorisation*, hosted by the Bulgarian Academy of Sciences in September 2019, we welcome you in Lisbon for the second workshop *ProGreS: From biomass characterization to process synthesis*.

This event is hosted and organized by the Instituto Superior de Engenharia de Lisboa (ISEL) and the Instituto Superior Técnico (IST). The initial workshop schedule has been postponed due to the limitations in travelling and in organizing physical events necessary to contain the spreading of the Corona virus. A fact that deeply affected our IProPBio project. Research and Innovation Staff Exchange (RISE) projects have their foundation in research exchanges and being prevented from travelling delayed our activities and deliverables. It is however a pleasure to share with you that the IProPBio activities have been extended until October 2023.

The Organising committee of the current ProGreS workshop are pleased to offer you a remarkable scientific programme giving the opportunity to open fruitful scientific and technological discussion about relevant challenges in achieving the goals of a more sustainable society.

We acknowledge the special contribution as a keynote lecture from Professor Rafiqul Gani, as well the contributions of the members of the IProPBio consortium. Moreover, we are grateful for the complementary participation from Institute of Food Science Research CIAL(UAM - CSIC), Secil - Companhia Geral de Cal e Cimento, S.A., LNEG - Laboratório Nacional de Energia e Geologia and Centro de Estudos Florestais, Instituto Superior de Agronomia/Universidade de Lisboa. All participants and contributions will open new horizons and improve the final outcome of this meeting.

The Organizing Committee gratefully acknowledges all authors for their contributions and all sponsors for their financial support.

We wish you an excellent conference both scientifically and socially, and an enjoyable stay in Lisboa.

16 of May, 2022
ProGreS 2nd WORSHOP
Organizing and Scientific Committee

Conference Programme

MONDAY, MAY 16		
09h00 – 09h30	Welcome and Opening session	
Session 1 CHAIRPERSON: Henrique Matos		
09h30 – 10h30	**Keynote:** Sustainable process synthesis, design, and analysis: Challenges and opportunities	Rafiqul Gani
10h30 – 11h00	Integrated design of biorefineries based on spent coffee grounds	M. Taifouris
11h00 – 11:30	Coffee break & poster session	
Session 2 CHAIRPERSON: José Coelho		
11h30 – 12h00	Some thoughts on the various P's of biomass valorization: *Arctium lappa* as a generic example	S.M. Stefanov
12h00 – 12h30	Functionalization of agro-industrial wastes with lanthanum at room temperature for the removal of arsenic	D.I. Mendonza-Castillo
12h30 – 14h00	Lunch	
Session 3 CHAIRPERSON: Massimiliano Errico		
14h00 – 14h30	Circular bioeconomy principles applied to an industrial biomass liquefaction plant	M. Mateus
14h30 – 15h00	A propylene glycol-organosolv process for efficient lignin and hemicellulose removal and recovery	L.C. Duarte
15h00 – 15h30	A novel and efficient method for the synthesis of methyl (R)-10-hy-droxystereate and FAMEs from sewage scum	C. Pastore
15h30 – 17h00	Coffee break & poster session	
19h30	Gala dinner	

TUESDAY, MAY 17

Session 4 CHAIRPERSON: Rui Filipe

09h30 – 10h00	ANTIVIRAL MEDICINALS: Process flowsheet and mass and energy balances	M. Papadaki
10h00 – 10h30	Design of experiments as a tool to optimize microwave assisted extraction of phenolic bioactives from spent coffee grounds propane	J.A.P. Coelho
10h30 – 11h00	Lipids extraction from sewage sludge using ethyl butyrate for a sustainable production of biodiesel	C. Pastore
11h00 – 11:30	Coffee break & poster session	

Session 5 CHAIRPERSON: Paula Robalo

11h30 – 12h00	Modelling and simulation of supercritical CO_2 extraction of oil from grape seeds and spent coffee grounds	R.M. Filipe
12h00 – 12h30	Integrated renewable production of sorbitol and xylitol from switchgrass	M. Martín
12h30 – 13h00	Round table discussion & Closing session	
13h00 – 14h30	Lunch	

Session 6 CHAIRPERSON: Massimiliano Errico

14h30 – 17h00	Research, Innovation and Exchange Committee meeting

Keynote

Sustainable process synthesis, design, and analysis: Challenges and opportunities

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Keywords: Process synthesis; Process design; Sustainability; Process systems engineering

In a world with increasing population and finite natural resources that are not uniformly distributed, the challenge for modern society is to satisfy the demands for new and improved products and their sustainable manufacturing (Martin et al., 2022). With data showing increased emissions of greenhouse gases resulting in rapid rise of earth's temperature and other negative developments, urgent action is necessary to tackle the energy-water-environment-health-food nexus through sustainable alternatives. Improvements in orders of magnitude are needed in technologies currently being employed in the conversion of resources to products that sustain modern society. It is, however, questionable if the currently available technologies and/or methods and associated tools for their development are able to deliver the needed improvements. Opportunities therefore exist for chemical and biochemical engineering and related disciplines to deliver truly innovative solutions by managing this complexity (Li et al., 2022 and Mongkhonsiri et al., 2021). The lecture will highlight the challenges and the opportunities within chemical and biochemical engineering and especially within process systems engineering to tackle the challenges through the development of a new class of systematic methods and computer-aided tools (Tula et al., 2019), where integration of ideas-disciplines, hybrid model-data analytics, design techniques based on the 'define-targets and match-targets" paradigm, and a systematic multi-scale analysis-solution approach play important roles. Results from case studies illustrating the main concepts and highlighting aspects of sustainable process synthesis, design and analysis will be presented.

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Oral Presentations

Integrated design of biorefineries based on spent coffee grounds

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Keywords: product design, circular economy, sustainable processes, integrated crop and livestock systems, beef cattle, nutrient recovery.

Introduction

Energy, food, and reduction of waste are three of the most important challenges to be faced by the population in the 21st century (Sridhar et al., 2021). The circular economy is born as a solution to motivate waste treatment through economic, environmental, and social benefits (European commission, 2020). Among consumer products, coffee is the second most important product after petroleum. Spent coffee grounds (SCG) are one of the most produced wastes during the production of soluble coffee (Murthy & Madhava Naidu, 2012). This residue has a series of high value-added products, such as polyphenols, polymers, and nutrients, that can be used to produce food supplements, fertilizers, bio components, and additives for industry and agriculture (Rajesh et al., 2020). Even though studies have addressed the valorization of this waste, there is a knowledge gap in the techno-economic comparison between the different alternatives. In this work, an optimization framework is proposed to select the best option to transform SCG from an economic point of view. This design constitutes a step prior to the start of the construction of a biorefinery.

Process description

The superstructure considers three processes and two sub-processes. They are modeled using first principles, such as mass and energy balances, phase equilibria, experimental yields, and empirical rules of thumb. They can be seen in Figure 1.
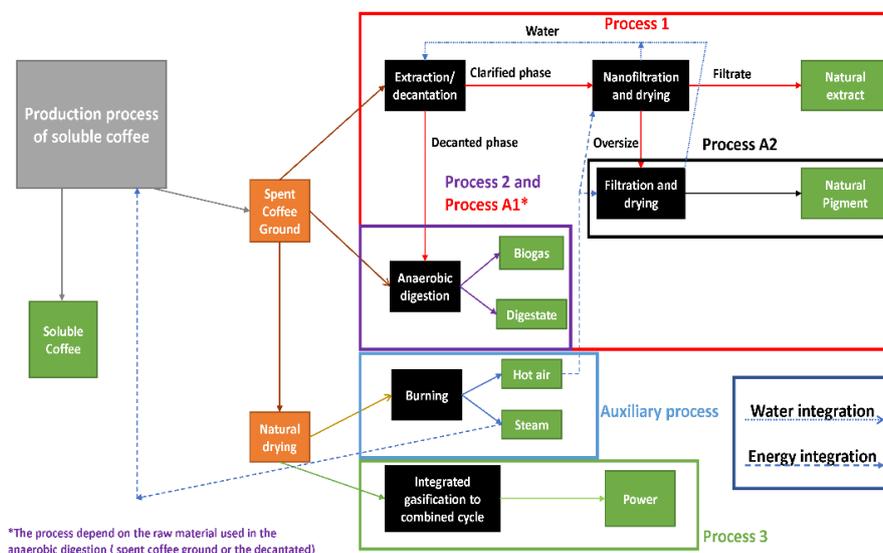

Figure 1. Superstructure for the use and integration of spent coffee grounds.

Process 1 consists of an extraction-filtration system to produce natural extract. The extraction uses citric acid as solvent, while the filtration system uses a nanofiltration membrane to separate the caffeine from the rest of the phenolic components. The permeate is dried by reverse osmosis and flue gas, obtaining a caffeine-enriched powder (natural extract). The reject is dried by flue gas to produce a powder with tannins, that can be used as brown pigment. Both products can be sold directly. Process 2 uses SCG to produce biogas and digestate by anaerobic digestion. The digestate is filtered to reduce the water concentration and the biogas is upgraded to produce power. Finally, in Process 3, SCG is introduced into an integrated combined gasification cycle to directly produce power. In addition, it is necessary to send a fraction of SCG to a boiler to produce flue gas and steam to supply energy to the rest of the processes. Even though the selection of the process is addressed from an economic point of view, the integration of water and energy reduces the environmental impact of the facilities.

Results and conclusions.

A soluble coffee production process, that produces 40000t/year of SCG, is considered to test the methodology. Two processes are economically viable, natural extract production and power production (Process 1 and 3, respectively). However, there is a large difference between the profit of Process 1 (65M€/year) and Process 3 (1.73M€) due to the high value of natural extract and pigment. Although natural extract is more valuable than pigment (70€/kg vs. 28€/kg), its amount is smaller (9.85 times). Therefore, natural pigment is the most profitable product that can be obtained from SCG. Regarding costs, the operating and investment costs are 4.59 MM€/year, and 13.97 MM€, respectively. The distribution of the operating cost can be seen in Figure 2.

Figure 2. Operating cost of the Process 1.

41 % of the SCG must be sent to the boiler to produce flue gas and steam. Part of this steam is used to supply 7% of the total energy of the soluble coffee production process. 32.6% of the water is saved through water integration. A sensitive analysis is performed to explore the effect of the variability of prices and demands of the two most important products, natural extract, and pigment. The results show that the uncertainty in the prices and demands of these products results in a strong variability in profit, with values in the range of 0.6M€/year and 6.9M€/year. Therefore, a detailed market analysis is necessary before making the final decision

Acknowledgments

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Some thoughts on the various P's of biomass valorization: *Arctium lappa* as a generic example

Stefan M. Stefanov[1,*], Damian E.L. Fetzer[2], Ariádine Reder Custódio de Souza[2], Marcos L. Corazza[2], Fabiane Hamerski[2], Dragomir S. Yankov[1] and Roumiana P. Stateva[1]

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Keywords: Circular bioeconomy, *Arctium lappa*, Biomass valorization, Biorefinery.

Circular bioeconomy (CBE) follows the principles of circular economy, but the feedstock used is biomass. Processes using biomass can be economically viable when the loop in the CBE framework is closed. To realize that goal, an advanced approach to the design of smart green biorefineries should be used. It should be based on the integration of environmentally benign and predominantly mild, innovative processes and techniques, that will allow obtaining from the biomass high quality value added products with a wide spectrum of applications without damaging one or more of the extracts, particularly those that are heat sensitive. Moreover, the recovery methods applied should be selective towards the target compounds.

The aspects of an effective biomass valorization are numerous and versatile. In what follows we will discuss briefly just few of them, namely: biomass **P**otential and **P**erspectives, and **P**rofitability prospects and **P**roblems. Those issues will be outlined on *Arctium lappa* seeds and roots biomass valorization forecasts and outlooks, used as a generic example.

Figure 1. Burdock roots (left) and seeds (right).

Potential of the biomass: *Arctium lappa* or simply burdock is the largest plant of the *Asteraceae* family. It is native to Eurasia, but has spread to the Americas, and in many countries it is treated as a weed/invasive species. Burdock biomass production, collection and preparation require low investment cost and can be obtained in great quantities (for example burdock roots are up to 1 m in length, with a weight of about 450 g). Still, at present, regardless of the plethora of various positive effects of burdock secondary metabolites on human health and wellbeing, the species' biomass remains highly neglected and underused. The unlocking of its huge potential could be realized *via* a smart one-source-multiproduct biorefinery targeted at its integral valorization. However, what is needed (but was missing till present) for the design and possible realization of such biorefinery is *quality new trustworthy data and information*. The latter should specify key technologies, operating conditions and solvents for the sustainable recovery from the biomass of extracts rich in valuables. To fill that gap, advanced techniques - extraction using compressed fluids (CO_2 and propane), pressurized liquid extraction (single and multistep), and different polarities co-solvents were applied for the first time by Stefanov et al. (2022), to recover oils and extracts from burdock seeds and roots biomass. They were evaluated by yield, total phenolic content and antioxidant activity, and quali- and quantified by a number of analytical methods (GC-FID, GC-MS, LS-MS/MS).

The new data gathered allow analyses of the **Perspectives** of burdock biomass. For example, *Arctium lappa* seeds oils contain substantial amounts of the essential linoleic acid – 61.2 %

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(regardless of the method used to recover the respective oils), which situates burdock seeds oils fifth among vegetable oils being inferior only to safflower, grape, *Silybum marianum*, and commensurable with sunflower. High content of sugars (not detected in the seeds oils), namely fructose and sucrose, are registered in the roots but the quantities depend on the extraction method applied. Taking into consideration that burdock seeds oils have a high index of unsaturation (about 1.5. *vs* about 1 for spent coffee grounds' oil) they can be used as an appropriate source of unsaturated fatty acids suitable for the cosmetic and food supplement industries. On the other hand, the roots extracts composition marks a distinct industrial opportunity and perspective that is worth of further exploration, namely using the roots biomass as sustainable carbohydrate biorefinery platform alternative to the lipid one for biofuels. A different perspective of application is outlined if the profile of bioactives detected in the roots extracts is examined: It is demonstrated that they are very rich in phenolic acids – outstanding high quantities of chlorogenic, as well as gentisic, and syringic acids, to name just a few, are detected. Also, different subgroups of the secondary metabolites flavonoids are registered. That specifies the roots as a very rich source of compounds with diverse chemical complexities and perspective applications in pharmaceutical, cosmetic, and nutraceutical industries.

The data obtained allows addressing one additional issue: What are the profitability prospects of integrating the techniques examined into a technically and economically viable, scalable and sustainable biorefinery platform for burdock biomass valorization with a possible zero waste? What are the problems facing that endeavor?

Profitability and Problems: Although the techniques we have studied are relatively expensive to implement industrially, they are sustainable and promising due to the use of GRAS solvents (CO_2, water, and/or ethanol), and the possibility to tune operational parameters in such a way as to enhance the recovery of target compounds. With regard to the latter *sequential* PLE should be named particularly as it not only maximizes extraction yields but the integration of several steps in which solvents with gradually increasing polarity are used allows recovery of extracts with different compositions and applications. Therefore, within the frame of profitability and depending on whether the biomass valorization is focused at a group of compounds or at a particular bioactive favored, the process performance and techno-economic parameters must be studied. For example, as a very rough heuristic rule for a process to be economically profitable the product selling price should be over USD 170/kg. Furthermore, payback period, net present value, and internal rate of return have to be evaluated as well.

In that context it should be noted that the choice and economic evaluation of the best performing route among all complex alternative biorefinery designs is far from trivial. For example, if epicatechin gallate is chosen as a target compound (very high price - USD 210.00 for $0.5 \cdot 10^{-3}$ kg, and a wide spectrum of health benefits), the most efficient technique for its recovery from the roots is PLE with water. But, how much will the subsequent separation (and purification) of the single desired product cost? Maybe it will be more profitable to use PLE with ethanol and recover an extract rich in caffeic, syringic, cinnamic and gentistic acids? Though the price of the pure constituents are not that high (e.g. caffeic acid – USD (80-100)/kg, syringic acid about USD 460/kg), still the health benefits of such extracts are enormous and they might find application in the food, pharmaceutical and cosmetic industries, without requiring intrinsic separation and purification steps?

The above illustrates only one of the challenges facing the design of a sustainable, economically attractive and profitable biorefinery. Other major problems and bottlenecks that should be considered when designing different alternatives are: *i*) Availability of reliable experimental data; *ii*) Knowledge of the thermodynamics and kinetics of the processes involved, which requires robust models that can be used to predict and calculate the phase behavior of the complex strongly non-ideal systems under consideration; *iii*) Availability of information on the thermophysical parameters of the mixtures' pure constituents; *iv*) Robustness of the design procedures and global optimization techniques applied; *v*) Alternatives for valorization of the biorefinery residual waste (residual cake), etc.

The residual cakes possible utilization merits some additional comments: In order to comply with the CBE from cradle to cradle (zero waste) concept, utilization of the residual cakes is a must. For burdock oil cakes (seeds) and just solid cakes (roots) a range of methods must be analyzed and explored with the goal to produce added-value products and bioenergy resources. Those include for example different heat treatments (e.g. pyrolysis) for the generation of bio-oil, syngas, etc. Also, based on whether any valuables are quanti- qualified in the residual cakes other routes for their valorization can be suggested.

In summary – Can one be smart about a weed? Yes, by introducing cutting-edge technical solutions for the valorization of the abundant, underused and highly neglected biomass of various weeds (such as *Arctium lappa*); solutions, which are capable of generating Back to Earth Alternatives. That, however, requires a lot of experimental efforts, analytical methods knowledge, and proficiency in systematic analysis, modelling, design and optimization of flowsheet alternatives. In short – a consortium of scientists with diversified know-how and expertise are needed to fully devise and implement the smart one-source-multiproduct biorefinery of the future.

Acknowledgements

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Functionalization of agro-industrial wastes with lanthanum at room temperature for the removal of arsenic

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Keywords: adsorption, arsenic, biomass functionalization, lanthanum.

The preparation of adsorbents using renewable organic residues (i.e., lignocellulosic wastes) as feedstock is an alternative to improve the cost-effectiveness tradeoff of adsorption (Sharma et al., 2022). Frequently, these adsorbents are obtained from the biomass pyrolysis/carbonization to avoid operating drawbacks related to microorganism growth in the adsorption equipment (Landin-Sandoval et al., 2020). However, the biomass thermochemical conversion affects the adsorption capacities of final adsorbents because the thermal treatment promotes the degradation of their surface chemistry (Steiner et al., 2016). As consequence, the resulting materials could have a relative low adsorption capacities in comparison with other adsorbents, which could be a limitation for their application at large industrial scale. To face this problem, raw biomass and/or carbon-based adsorbents are often functionalized (using different organic and inorganic agents) to improve their adsorption capacities (Aryee et al., 2021). But, the high energy consumption associated with this synthesis stage and its cost could also limit the large-scale application of functionalized adsorbents. Hence, it is necessary to explore new alternatives to reduce the energy costs associated to adsorbent activation with the aim of making feasible the large-scale implementation. Considering this background, this study has focused on the synthesis of lanthanum-based adsorbents using macadamia nutshells, avocado seeds and cauliflower stems as feedstock and their application for the arsenic removal. Arsenic was selected as a study case since it is dangerous for human beings even at low concentrations, so it is cataloged as a priority water pollutant (Kumar et al., 2020).

Functionalization step was carried out in presence of atmospheric air at room temperature using lanthanum solutions. Arsenic adsorption experiments were carried out in batch conditions at 30 and 40 °C, and pH 7. Chemical composition of biomasses was determined according to the methodology reported by Landin-Sandoval et al. (2020). The functionalized adsorbents were characterized before and after the adsorption process by FTIR and XRD. Results showed that the performance of tested adsorbents shows the next trend: cauliflower stem > avocado seed > macadamia nutshell.

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Circular bioeconomy applied to an industrial biomass liquefaction plant

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Keywords: Biomass, Bio-oil composition, Liquefaction, Pilot-plant

A biorefinery is a facility for the synergetic processing of biomass into several marketable biobased products (food and feed ingredients, chemicals, materials, minerals, CO_2) and bioenergy. In this context, biomass is an interesting alternative to fossil fuels and an important source of several added-value compounds. This work describes the use of liquefaction as a process to produce a bio-oil from which several compounds can be extracted in a biorefinery perspective. Therefore, a study of the influence of biomass composition on the chemical composition of the liquefaction products was carried out at a laboratory scale. Furthermore, results of several liquefaction experiments carried out in a pilot plant of Secil-Pataias are also presented (Braz et al., 2019 and Nunes et al., 2018).

The behavior of softwoods (Maritime Pine sawdust, and Pine nut shells), hardwoods (Eucalyptus sawdust, Peach stone shells, Olive stones, Olive bagasse, Spent Coffee Grounds, and cork residues), herbaceous (*Miscanthus*, Thistle, and Rice husk) and aquatic biomass (*Ulva lactuca*) was studied at laboratory scale. The condensates recovered during liquefaction were characterized. Furfural was the main component with concentrations above 50g/L for *Miscanthus*. The characterization of the bio-oils revealed that the main water-soluble compounds are monosaccharides (glucose and xylose) and aliphatic acids (acetic, formic, and levulinic acid). The analysis of the solid residues showed that they are mostly comprised by precipitated lignin, residual polysaccharides (cellulose) and ash. The influence of the reaction time on the composition of the liquefaction products of pine sawdust revealed that the decomposition or repolymerization of sugars and aliphatic acids may occur. Bio-oils produced at an industrial level from cork and eucalyptus residues were also characterized and showed to be similar in composition to the bio-oils produced at the laboratory scale.

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A propylene glycol-organosolv process for efficient lignin and hemicellulose removal and recovery

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Keywords: Biomass fractionation; Delignification; Lignocellulosic biomass; Non-volatile solvent; Organosolv process

The use of organosolv processes has been receiving an increase attention within the biorefinery framework. Typically, these processes are based on the use of a mixture of a high vapour pressure solvent (e.g. ethanol, acetone) and water. The use of such solvents presents several implementation hindrances, most noteworthy linked to safety and economic issues. As such, the use of lower vapour pressure solvents that allows for operation at, cheaper, near atmospheric pressure, even at moderately high temperatures may present significant advantages. Furthermore, the preferable solvent should be non-toxic, less flammable and less hazardous and it should be derived from biomass, turning it into a green sustainable solvent in agreement with the circular bio-based economy strategy and improving the overall economic performance of the biorefinery. Unfortunately, the choice of such solvents is limited (Carvalheiro et al, 2019).

Among the potentially relevant solvents, Propylene-glycol (PG) presents many of the desired traits, but its use is still poorly studied.

In this work, this innovative organosolv pre-treatment is explored using lignocellulosic residues as model feedstock.

Under mild conditions (up to 160 ºC, and 3 hours reaction time), PG-based organosolv was able to sustain a significant delignification (58% of the total lignin) together with a 57% removal of the initial feedstock xylan. Furthermore, the cellulosic fraction remained quantitatively mostly intact. PG composition had a significant impact on the process selectivity, with higher water content enabling higher hemicellulose removal as compared to delignification.

In order to further improve process performance, the effects of sodium hydroxide and sulfuric acid catalysts were also evaluated. Alkali-catalyzed PG pretreatment yielded slight superior selectivity for lignin, presenting a higher delignification and a lower recovery of hemicellulose in the liquid stream.

Additionally, both uncatalyzed and catalysed processes enhanced the enzymatic digestibility of the remaining cellulose-enriched fraction. Nevertheless, sulfuric acid catalysis enabled a superior performance and an increase (40%) on glucose yield for the enzymatic saccharification was estimated. Further process intensification routes are also presented and discussed.

North Portugal Regional Operational Programme (Norte 2020) under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).The authors gratefully acknowledge Céu Penedo and Belina Ribeiro for laboratory help.

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A novel and efficient method for the synthesis of methyl (R)-10-hydroxystearate and FAMEs from sewage scum
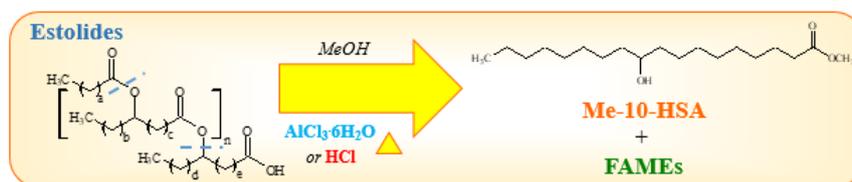
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Keywords: sewage scum, methy-10-hydroxystearate, FAMEs, biodiesel, estolides

Introduction

Hydroxy fatty acids (HFAs) are valuable raw materials widely used for several industrial applications, including resins, polymers, cosmetics, biofuels, biolubricants and additives in coatings and paintings. Since its first discovery, 10-(R)-hydroxystearic acid (10-HSA) has attracted great industrial interest. It is the natural precursor of γ-dodecalactone, component of taste and aroma used in foods and consumables as medical products, toothpastes and perfumes. Moreover, it is used in manufacturing of lubricants and cosmetics for its chemical properties similar to those of ricinoleic acid. In recent years, different studies have been carried out for the production of 10-HSA, based on the enzymatic hydrolysis of vegetable oils from bacteria and other microorganisms. However, their applicability on industrial scale is limited for a series of drawbacks including: i) the specificity of substrate, which can be a problem for the conversion of some feedstocks; ii) the instability of the enzymes in the organic solvents, that are often required for the solubilization of reacting substrate or recovery of final product; iii) their excessive cost. As well, the use of edible oils used for human consumption, represents a non-sustainable choice from an economic and environmental point of view. The development of new solutions for the production of 10-HSA or its derivatives, especially if based on the use of non-edible feedstocks could be a really challenging goal not only for economic reasons, but also for environmental and ethical concerns. Sewage scum can be used as a source of energy or resources, thus replacing non-renewable resources, with a considerable environmental impact. In particular, a great attention has been devoted to the lipid fraction (up to 36-50% of dry weight), which can be used for the production of biodiesel and biolubricants (di Bitonto et al., 2020). Lipids extracted from sewage scum are mainly constituted by Free Fatty Acids (FFAs, 45-55%), calcium soaps of fatty acids (25-30%) and estolides (10-15%). These last, mainly used as lubricants, can be further converted into methyl-10-hydroxystearate (Me-10-HSA) and FAMEs, representing a valuable source (Figure 1).

Figure 1. Schematic process for the conversion of estolides into Me-10-HSA and FAMEs.

In this work, a novel method was proposed for the synthesis of Me-10-HSA and FAMEs by direct conversion of lipids extracted from sewage scum with methanol. $AlCl_3 \cdot 6H_2O$ and HCl were used as catalysts. The best operative conditions were determined through a response surface methodology on a Box–Behnken factorial design of experiments with the aim of maximize the production of methyl esters.

Material and methods

Sewage scum

Sewage scum was collected from wastewater treatment plants (WWTPs) of Polignano a Mare (12000 Population Equivalent, PE) located in South of Italy.

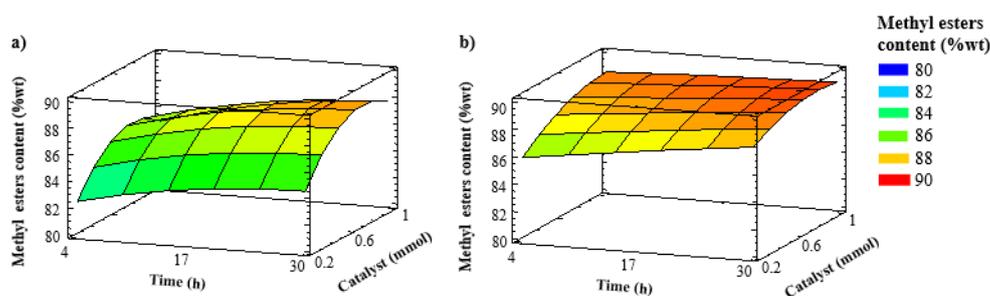*Recovery and activation of lipid fraction*

Sewage scum was heated at 353 K and then centrifuged at 4000 rpm for 3 min, obtaining a three phasic-system: (i) an upper brown oily phase constituted of lipids, (ii) an aqueous intermediate phase and (iii) a lower wet solid phase. The oily phase was recovered and stored at 4 C°. Finally, extracted lipids were activated by adding the stoichiometric amount of formic acid respect to the starting calcium soaps (20-30%), obtaining a final product mainly composed of FFAs (75-80%) and estolides (10-15%). Activated oil was recovered as clear oil after centrifugation (4000 rpm, 1 min) at 353 K (Pastore et al., 2014).

Conversion of activated lipids into methyl esters (Me-10-HSA and FAMEs)

In a typical reaction, 0.1 g of activated lipids from sewage scum were placed with 1 mL of methanol and 0.02 mmol of catalyst, in a glass Pyrex reactor of 15 mL. The reaction was carried out for 4 h at 80 °C. Then, the system was cooled and the catalyst recovered by centrifugation. The organic phase was recovered by evaporation of methanol under nitrogen flow. Finally, methyl esters (Me-10-HSA and FAMEs) were determined by gas-chromatography using methyl-heptadecanoate as internal standard.

Analysis of results

To achieve the highest yield of methyl esters, a three-step approach was used to study the effects of the process variables on the conversion of lipids extracted from sewage scum. Temperature (80, 100 and 120 °C), reaction time (4, 17 and 30 h), methanol (1, 3 and 5 mL) and amount of catalyst (0.2, 0.6 and 1 mmol) respect to the starting lipid fraction) were selected as the independent variables (factors), while the methyl ester content (%wt) was selected as the dependent variable (response). Then, the analysis of variance (ANOVA) significance check for the mathematical model describing the functional relationship between factors and the response was performed, and finally, the multi-response optimization was applied. The results are reported in Figure 2.

Figure 2. Response surface plot of the combined effects of time and catalyst (temperature = 100 °C, methanol = 3 mL) using a) $AlCl_3 \cdot 6H_2O$ and b) HCl as catalysts.

In both cases, a complete conversion of extracted lipids from sewage scum was observed. In particular, using $AlCl_3 \cdot 6H_2O$ as catalyst (0.76 mmol), a methyl esters content of 89.6%wt was obtained at 115 °C after 30 h with 3.9 mL of methanol. Instead, using HCl (1 mmol), a methyl esters content of 90%wt was achieved at 120 °C with a reduced amount of methanol (2.1 mL), after only 4 h of reaction. However, compared to the use of conventional acid catalysts as HCl, $AlCl_3 \cdot 6H_2O$ can be easily recovered by centrifugation and reused for several cycle of reaction. At the end of the process, Me-10-HSA (10%wt) was isolated by column chromatography and analyzed by NMR. A high enantiomeric excess (ee >92%) of R-enantiomeric form was observed, further confirming the validity of the synthesis process.

Conclusion

In this work, a novel and efficient method was proposed for the synthesis of Me-10-HSA and FAMEs from sewage scum. This process will significantly improve the recovery and reuse of sewage sludge in the production of biofuels and biochemicals.

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ANTIVIRAL MEDICINALS: Process flowsheet and mass and energy balances

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Keywords: COVID-19 formulations, plant extracts, plant-extracts processes, natural medicinals quality

Medicinal plants have been searched, researched and used for ages. A great variety of plant roots, leaves, flowers, tree barks, kernels and all different plant segments pose ample medicinal properties, which have been proven very effective in treating and preventing disease, while they can substantially strengthen body's immune system. Presently, research on the field is fast growing and effort is focusing in recovering, refining and adapting old knowledge with new technological advances. The variety and the volume of medicinal products and food-supplements of plant origin are rapidly expanding. However, medicinal properties of plants are very sensitive to the conditions of treatment of the raw material and the choice of employed processes for their formation. In contrast to the synthetic medicines, plant extracts function through synergies and the role of the so called "active ingredient" is not *per se* applicable as a term. The study of synergies renders research and the development of protocols of quality products production complex and the large scale bulk production of such formulations questionable. Collective experience of the past has to be carefully considered before radical modifications of processes are implemented.

The difficult conditions which the world came upon with COVID-19 pandemic urged the society to rapidly respond and elaborate on effective solutions. Simultaneously, it also provided opportunities for the development of natural medicinal antivirus products principally for the prevention but also for the effective mitigation of the effects of the consequences of the disease.

Towards that direction a number of formulations employing the combination of compounds of well-known properties have been formed and tested.

In this work we demonstrate the process of development of such formulations and the restrictions and the problems of its bulk production.

Between others, a sequence of process involves the following stages: Collection of the plants, selection of the appropriate plant-segments, cleaning, quality analyses, stabilisation, drying, maceration, three stages of percolation, formation of mother tincture, quality analyses, pH adjustment, dilution and appropriate mixing of different compounds for the effective result.

A few of these stages can be the same or can be easily adjusted, irrespectively of the plant. However, some stages have to be adjusted and modified according to the kind of the plant, its origin and the period of collection. This mainly affects the quantity of solvents employed in the stages of percolation. Plants develop more valuable ingredients when they grow under conditions of stress. As such, cultivation under strictly controlled conditions, which would restrict the variation between different batches of the same kind does not appeal as an attractive option.

Consequently, the differences in the raw materials employed must be faced by adaptation of the process conditions to the plant quality.

Typical plants employed for the COVID-19 antiviral treatments involve grapefruit seeds, *astragalus propinquus*, echinacea, green tea, tea tree leaves, *Arctium lappa L., Hydrastis Canadensis* and additionally well purified propolis. The selection and proportion of the extracts of those plants which will be used in a formulation depend on the health history of the patient and the medications they potentially receive.

Main solvents employed are distilled water and pure ethanol. Temperatures up to 55 °C and separations assisted by gravity. The processes employed are labour intensive and require lengthy treatments. However, mass and energy resources use are minimal. The residual mass can be employed as an effective fertilizer and/or biocides. Those processes result in practically zero pollution.

In this work typical flowsheets are shown accompanied by relevant mass and energy balances.

Acknowledgements

Design of experiments as a tool to optimize microwave assisted extraction of phenolic bioactives from spent coffee grounds

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Keywords: Spent coffee grounds, Microwave extraction, Antioxidant activity, Response surface methodology.

Introduction

Phenolic compounds are secondary metabolites that are found in many plants foods and beverages. They are of great value due to their health-beneficial antioxidant properties and potential protection against inflammation, blood clots, heart disease, and certain cancers, improvement of brain function, and blood sugar levels, etc. It has been demonstrated that spent coffee grounds (SCGs), the primary biowaste of the production of instant coffee and coffee beverage preparation, contain many important compounds, among which polyphenols and antioxidants (Coelho et al. 2019, 2020; Kovalcik, Obruca, and Marova 2018). Hence, SCGs, as a biomass, possesses an immense potential for valorisation because of the huge quantities produced worldwide, and its richness in high value bioactives. Among the available techniques for SCGs valorisation, microwave assisted extraction (MAE), combined with green solvents like water and ethanol, has proved to be one of the most promising and a viable alternative to conventional and other green extraction techniques (e.g. sub- and supercritical fluid extraction, pressurized liquid extractions, accelerated fluid and ultrasound-assisted extraction, etc).

In view of the above, the aim of our work was twofold: (*i*) to study the MAE of phenolic compounds from SCGs by applying design of experiments and (*ii*) to identify and quantify the extracts according to the lipidic and fatty acid profiles. To achieve the first goal, two different design of experiment methods (DOE) were combined and applied to optimize the process, namely a Fractional Factorial Design (FFD) and, subsequently, a Central Composite Design (CCD). As a result, a mathematical model representing the interrelationships among the independent process parameters and responses was designed. As independent parameters ratio of ethanol to water in the solvent mixture, microwave irradiation power, irradiation time, and solvent to SCGs ratios were chosen, while the yield, total phenolic content (TPC), and antioxidant activity (AA) by the DPPH assay method were used as response functions. To accomplish the second objective, the composition of certain extracts was analyzed by NMR, while the fatty acid profile was determined by GC-FID.

Materials and methods

The SCGs were obtained from a local coffee shop in Bulgaria. The biomass was oven-dried at 105 °C and stored frozen in a refrigerator until used. The MAE of the SCGs samples were performed using a CEM Discover SP microwave reactor (2.45 GHz, 300 W) equipped with a non-contact infrared temperature sensor. Temperature was controlled by the variable microwave irradiation and the samples were cooled by nitrogen current at the end of extraction. The microwave irradiation ranged from (60 to 120) W and was adjusted to stabilize the temperatures at 75 °C for different extraction times. The resulting suspension (solvent+extract) was filtered,

and the solvent evaporated in a rotary evaporator (Büchi, model R-205). The extract was stored at -18 ºC until further use and analyses.

Results and discussion

The process parameters optimization by DOE was performed into two steps: Firstly, a 2^{4-1} two level FFD was used and ratios "solvent to solute" (A) and "ethanol to water" (B) were identified as the significant experimental factors. Then, CCD was applied to analyse the effects of the significant variables on the three responses - yield, TPC, and AA. The final models for the responses in terms of coded factors are represented by eqs. 1-3, respectively.

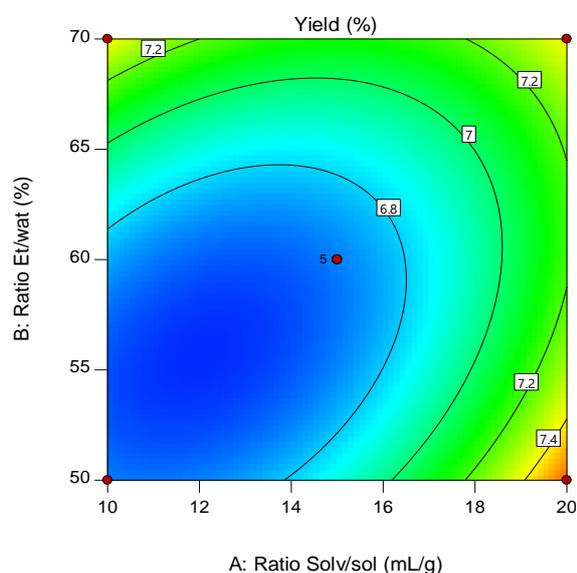$$Yield = 6.71 - 0.2172 * A + 0.1150 * B - 0.2075 * (AB) + 0.2530 * A^2 + 0.2855 * B^2 \tag{1}$$

$$Polyphenols = 136.02 - 0.7199 * A - 19.45 * B \tag{2}$$

$$DPPH = 38.35 - 2.38 * A - 3.42 * B + 1.43 * (AB) + 3.00 * A^2 + 1.42 * B^2 \tag{3}$$
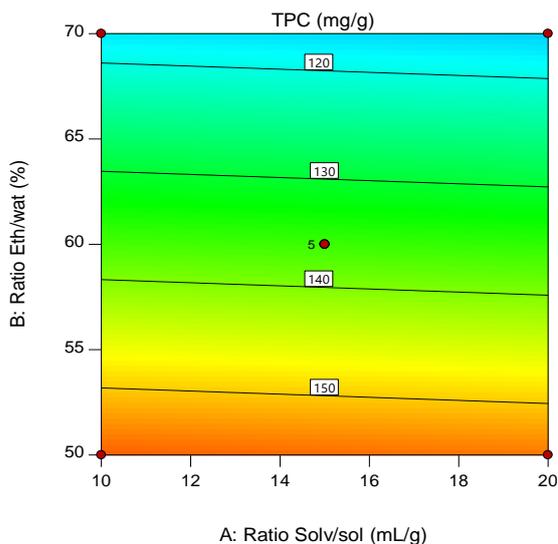
Response contour plots showing the effect of A and B ratios on the yield, TPC and AA of SCGs extracts are displayed in Figures 1 and 2, respectively.

The impact of B ratio, identified as the most significant experimental parameter, on the extracts FAME composition was examined. It was revealed that palmitic, linoleic, oleic and stearic acids are the most abundant. It should be noted that the highest composition of DUFA (41.8) was registered at the highest value of the B ratio, while, for MUFA and SFA, the opposite trend was observed. As could be expected, the polyunsaturated/saturated ratio UI increased with the increase of the ethanol percentage.

Figure 1. CCD, response contour plots showing the effects of the two principal independent variables on the extracts yield.

Our study demonstrated that the influence of the factor of principal significance – ethanol:water ratio on the extraction process responses yield, TPC, and AA is substantial. While low ratio values (decrease of ethanol percent in the solvent mixture) decreased considerably the yield, it positively affected the TPC and AA of the extracts obtained. The significant impact of the variations of the % of ethanol in the solvent mixture on the compositions of the lipids, caffeine, pentacyclic diterpenes of the kaurene family, and FAME was also confirmed by the NMR and GC-FID analyses of the extracts recovered. The results of our study provide reliable and trustworthy data that can be used to design a strategy for the optimum performance of MAE of SCGs.

Figure 2. CCD, response contour plots showing the effects of the two principal independent variables on the TPC.

Figure 3. CCD, response contour plots showing the effects of the two principal independent variables on the AA.

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J. P. Coelho, R.M. Filipe, M. Paula Robalo, S. Boyadzhieva, G. St Cholakov, and R.P. Stateva, 2020, Supercritical CO_2 Extraction of Spent Coffee Grounds. Influence of Co-Solvents and Characterization of the Extracts, Journal of Supercritical Fluids, 161, 104825

A. Kovalcik, S. Obruca, and I. Marova, 2018, Food and Bioproducts Processing Valorization of Spent Coffee Grounds: A Review, Food and Bioproducts Processing, 110, 104–19

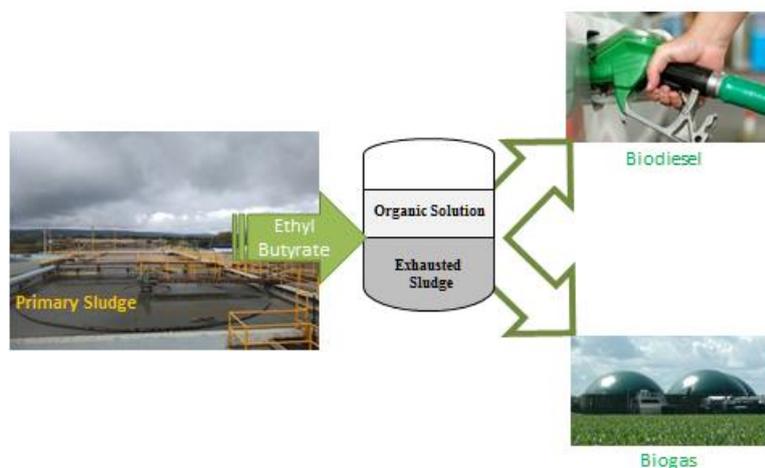# Lipids extraction from sewage sludge using ethyl butyrate for a sustainable production of biodiesel

V. D'Ambrosio[1], L. di Bitonto[1], A. Angelini[1], A. Gallipoli[1], C.M. Braguglia[1], C. Pastore[1,*]

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Keywords: Biodiesel, Sewage sludge, Ethyl Butyrate, Biosolvent, FAMEs

Urban sewage sludge generated in wastewater treatment plants are considered as a waste and their treatment and disposal represents the 50-60% of total cost in a wastewater treatment plant (Spinosa et al. 2011). Thanks to their abundant lipid content, sewage sludge could be considered as viable alternative lipid feedstock for the production of biodiesel. Two different approaches have been typically investigated: the direct alcoholysis on dry or wet sludge (di Bitonto et al. 2019) and the two-step lipid extraction followed by transesterification/esterification reaction (Olkiewicz et al. 2014, 2015; Pastore et al. 2013). The two-step process results the best option in terms of profitability and energetic consume, but present also some drawbacks. The solvents contaminate the starting feedstock, so that, besides formation of biodiesel, a new waste is always generated, which consists of residual material containing organic solvent or mineral acids or both. Management of this new special waste could damper the economic balance and increase the environmental impact of the process.

Figure 1. Rationale of the study.

In this work we have investigated the possibility of using ethyl butyrate as a green solvent to extract lipids from sewage sludge, for the following production of biodiesel (Figure 1). Extraction conditions were optimized using the desirability function applied on the response surface methodology analysis of a Box–Behnken factorial design of experiments. Then, lipids were recovered and reacted with methanol and $AlCl_3 \cdot 6H_2O$ in order to achieve fatty acid methyl esters.

The optimization of the extraction conditions was carried out by using a Box-Behnken factorial design of 27 experiments, selecting solvent to sludge weight ratio (0.25, 0.625 or 1), acid to alkalinity molar ratio (0, 1 or 2), temperature (25, 47.5 and 70°C) and extraction time (1, 4 and 7h) as variable factors and the recoverability of esterifiable lipids (%) as response.

The statistical analysis of the model was then carried out by the analysis of variance (ANOVA), considering a P-value of 0.05 as a suitable threshold for checking the statistical significance of

the model and identifying the significant parameters of the model. The main statistics associated to the model were determined.

At the end of this study, the optimal conditions were identified and experimentally tested: when extraction of lipids from centrifuged PS was carried out with ethyl butyrate (solvent to sludge weight ratio = 1), at 70 °C and 7 h, without any use of acid, a recovery of 90±4% of esterifiable lipids was obtained, showing no significant difference from the value predicted by the model (93.7%).

The extracted lipids were then efficiently converted into biodiesel through a direct esterification promoted by $AlCl_3·6H_2O$ (obtaining a FAMEs yield of about 70 % of the maximum yield obtainable) and the sludge resulting from the extraction with ethyl butyrate, differently from the one obtained by using hexane, was found anaerobically digestible, without any inhibition. Finally, an economic evaluation of the extraction process was conducted, resulting economically feasible if performed on centrifuged sludge (TS:15-20% wt) with a high content of esterifiable lipids (20% wt of TS).

Acknowledgements

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Modelling and simulation of supercritical CO₂ extraction of oil from grape seeds and spent coffee grounds

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Keywords: supercritical CO_2 extraction, extraction kinetics, mathematical modelling, biomass valorisation.

The effective use of waste biomass and vegetal material as renewable resources of high added value compounds with applications in food, cosmetics, pharmaceutical industries, biodiesel production, etc. is receiving increased attention. Grape seeds and spent coffee grounds are two examples of waste biomass with huge potential for circular production in sustainable biorefineries.

Seed biomass from *Vitis vinifera* L. contains typically (8–15) %$_{mass}$ of oil, which is rich in esters of long chain polyunsaturated fatty acids (PUFAs), and antioxidants (Bail et al., 2008; Fernandes et al., 2013). It represents about (20-25) % of the biomass generated by the wine industry but is usually considered a disposable material.

Spent coffee grounds (SCG) are one of the main biowastes in the production of instant coffee and after coffee brewing. The world coffee production in 2019-2020 was estimated at 169.34 million 60 kg bags. Around 91 % of the coffee becomes wasted after extraction, so the importance of its further valorisation is obvious.
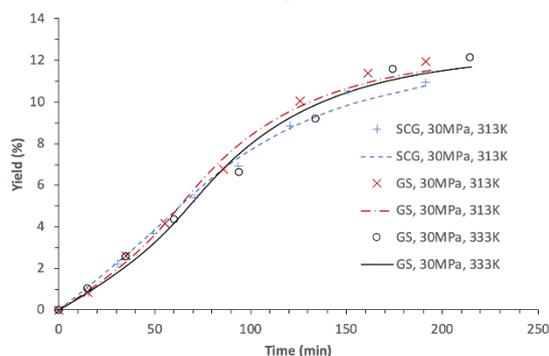
This work reports the simulation of the kinetics of supercritical extraction of oils from grape seeds and from spent coffee grounds with a model, advocated originally by Sovová and Stateva (2015), using gPROMS ModelBuilder (PSE, 2020).

A rigorous thermodynamic framework is applied to calculate the solubility in the supercritical solvent of the oils recovered from grape seeds and SCG. The calculation of the solubility of all the compounds present in the oil is not trivial or even possible not only due to the lack of some of their measured properties but also to the dimension of the task. To overcome this situation, different approaches for modelling the experimentally determined oil composition are tested. For instance, the oil mixture can be represented by one or several of the dominant compounds identified in it. Another approach uses as a model a single virtual molecule, the chemical structure of which has the potential to take into account all compounds in the actual oil composition (Coelho et al., 2020).

The critical properties, required by the thermodynamic model, are estimated using some of the known group contribution methods. Non-integer descriptors are applied for the virtual chemical structure. Second order polynomial functions are fitted to the solubility data for the kinetics model (Coelho et al., 2018). The oil solubility in pure $scCO_2$ is then predicted applying either the Predictive Soave-Redlich-Kwong (PSRK) or SRK cubic EoS.

The partition coefficient K (kg solid matrix/kg CO_2) is an unknown parameter of the dynamic model and was estimated using gPROMS ModelBuilder parameter estimation capabilities.

Figures 1 and 2 depict some representative results at *T* = (313.15 and 333.15) K and *P* = (30 and 40) MPa. The extraction profiles for both biomasses examined follow similar trends for the pressure and temperatures conditions used, and the solubilities (evaluated by the initial slope at the beginning of the extraction) are comparable. This can be explained since the triacylglycerides extracted from both oils have similar compositions of the fatty acids profiles, but the spent coffee grounds have a higher content of lower molecular mass esters (C16:0 is ≈ 33 %, against ≈ 7.7 % in grape seed oil).

Figure 1. Experimental (symbols) and simulated (lines) results at P = 30 MPa for SCG and grape seeds (GS).

Figure 2. Experimental (symbols) and simulated (lines) at P = 40 MPa for SCG and grape seeds (GS).

This difference can elucidate the behaviour observed at 40 MPa and 313 K: when the density of the scCO$_2$ increases, the solubility of the grape seeds oil is lower, when compared to the SCG. Another explanation for the differences observed at the higher pressure may be the particle size, 0.273 mm for the SCG and 0.620 mm for the grape seeds. The smaller particle size and the larger surface contact area between the spent coffee grounds particles and the solvent, favors the release of the oil into the particles surface, improving the mass transfer phenomena.

The fitting accuracy results, evaluated with absolute average relative deviation, AARD, show a good qualitative and quantitative agreement between the experimental and simulated extraction yield curves, despite the very complex nature of the systems examined. Furthermore, the results obtained can be used in the design of biorefineries implementing supercritical extraction processes for the sustainable valorization of the huge amounts of the easily obtainable waste generated from wine and coffee processing.

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Integrated renewable production of sorbitol and xylitol from switchgrass

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Keywords: Biorefinery, process and product design, superstructure optimization

The chemical industry is undergoing a transformation towards a more sustainable future starting from the use of renewable instead of fossil resources, which constitutes the 7th principle of green chemistry[1]. Biomass has emerged as a rich raw material towards the production of energy and chemicals. The US department of energy (Holladay et al., 2007) lists Xylitol and Sorbitol as the top 12 high value-added building block intermediate chemicals that can be produced from renewable biomass resources, while the EU has included them both as part of the map of potential value chains based on sugars since there already exist commercial markets with the potential to replace petrochemicals (Dusselier et al., 2014).

This work deals with the design of integrated facilities for the production of xylitol and sorbitol from lignocellulosic biomass (Figure 1). On the one hand, xylitol can be obtained from xylose via fermentation (Srivani and Pydi Setty, 2012) or catalytic hydrogenation (Rafiqui and Mimi Sakinah, 2013). On the other hand, sorbitol is obtained from glucose, but preferably from fructose, also via fermentation (Silveira and Jona, 2002) or catalytic hydrogenation (Ribeiro et al., 2017). Fructose can be obtained from glucose via isomerization (Illanes et al., 1992). Thus, a superstructure of alternatives is formulated to process switchgrass, corn stover, wheat straw, and other agricultural and forestry residues. Different pretreatments, such as dilute acid or AFEX for the fractionation of the biomass are evaluated. Next, after hydrolysis, the C5 and C6 sugars are processed separately for which a catalytic stage or a fermentation one are considered. Glucose is to be isomerized before it can be processed. Finally, crystallization in a multistage evaporator system is used for purification. The biorefinery is modeled using first principles and surrogate models for each one of the operations.
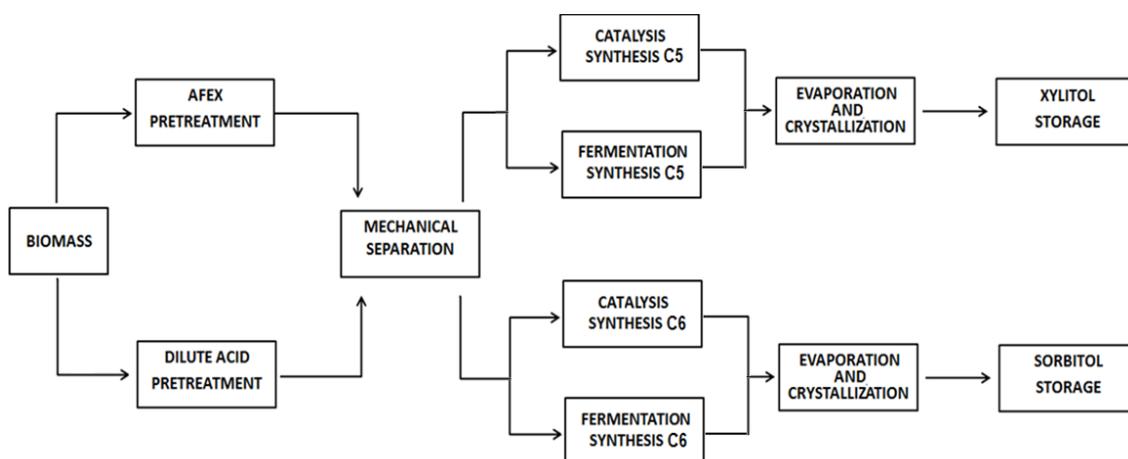

Figure 1. Superstructure for the renewable production of xylitol and sorbitol.

Pretreatments, ammonia recovery column, and crystallizers are modeled with simulations and/or experimental data using total and component mass flow rates, mass fractions, and stream temperatures. AFEX and Dilute Acid pretreatments use response surfaces based on experimental data to determine performance. Process simulators are used to determine ammonia recovery. The dilute acid pretreatment depends on the operating temperature, T; acid concentration, %; use of an added enzyme, Enz, and residence time, t (Shi et al., 2011).

$$Y_{cellu}, Y_{Hemi} = f(T, \%, Enz, t) \tag{1}$$

The yield of sugars from the AFEX process depends on the operating temperature, T; of water and ammonia added per kg of biomass, NH_3, added or Added, and residence time, t (Garlock et al., 2012). Moreover, a surrogate model is developed to evaluate the effect of the feed composition on the operating conditions of the column that recovers ammonia.

$$Y_{cellu} = f(T, NH_{3,added}, Wa_{added}, t) \tag{2}$$

Xylitol and sorbitol production can be developed with a catalytic or fermentative process. For the catalytic process, xylitol production occurs between 100-120 °C and 40-60 bar for 3-4 h. The model to determine the conversion is developed using the kinetics results from the literature (Ngoc Pham et al., 2016). Sorbitol production is carried out at 100-140 °C, 40-60 bar.

In the fermentation process, xylitol production is carried out operating at 30°C and 1 bar with a conversion of 92% using ammonia and hydrogen as reagents (Mountraki et al, 2017). In the case of sorbitol production, a first step of the isomerization of glucose into fructose is needed. From experimental data, a correlation to predict the conversion of fructose into sorbitol is developed.

$$X_{(fructose)} = -1.40 \cdot 10^{-6} (\text{concentration}(g \cdot L^{-1}))^2 + 8.70000 \cdot 10^{-4} (\text{concentration}(g \cdot L^{-1})) + 0.819 \tag{3}$$

Finally, a crystallization step is used to purify the xylitol and sorbitol produced. The model of each crystallizer is developed using mass and energy balances. The pressure in the evaporation chamber depends on the steam generated in the previous chamber and on the composition of the mixture to be concentrated. The solubility of sugars is determined by correlations based on data from the literature (Zambé et al., 2001), along with boiling effects. S represents steam, s condensed stream, F feed, E evaporated water, L liquid product, and C crystals.

$$
\begin{aligned}
&F_j \cdot x_{j,f,i} = C_{j,i} + L_j x_{j,l,i} && \forall j \in \{effects\}, i \in \{X,S\} \\
&H_S + H_F = H_s + H_E + H_L + H_C \\
&H_i = \sum_i f_i \cdot \Delta h_{i,f} + F \int_{T_{ref}}^{T} c_p(X,T) dT
\end{aligned}
\tag{4}
$$

An NLP problem is solved for each one where the objective function consists of simplified production costs. Each NLP consists of around 2700 eqs and 3800 variables and it was solved with GAMS requiring 12.5 s of CPU-time

As a complementary study, the optimal biomass design was performed. Among all of the components, hemicellulose and cellulose are selected because they are the sources of sugars. Thus, the optimal biomass is the one that provides the closest composition with existing biomass.

The optimization of the system suggests the use of dilute acid and the catalytic system. A system of 3 crystallizers is selected because it allows obtaining higher performance. For a facility that produces 145 kt/yr of xylitol and 157.6 kt/yr of sorbitol, the investment adds up to 120.74 M€ for a production cost of 0.28 €/kg of products.

Integrated facilities operate at their optimum for specific biomass compositions. This framework also allows evaluating the best use of each biomass used depending on its composition, as long as the models for the pretreatments are valid. The inverse engineering of biomass was also performed resulting in a composition of 15% water, 20% cellulose, 40% hemicellulose, 15% lignin, and 5% ash. The closest biomass corresponds to *Sargassum* (brown algae), which is capable of producing 230.5 kt/yr of xylitol and 116 kt/yr of sorbitol with investment and

production costs of 120.5 M€ and of 0.25 €/kg of products, respectively. From the production cost point of view, comparing up to 8 biomasses, corn stover, forest residues like a birch, pine and spruce, hybrid poplar, sugar bagasse, and wheat straw, corn stover is chosen as the best option, resulting in a production capacity of 181 kt/yr of xylitol and 202 kt/yr of sorbitol, while the investment adds up to 112 M€ for a production cost of 0.22€/kg.

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Poster Presentations

Book of Extended Abstracts of the ProGreS 2nd Workshop: From biomass characterization to process synthesis
May 16-17, 2022, Lisbon, Portugal

P1

Thermodynamic analysis of the extraction of antioxidants from rice husk biomass

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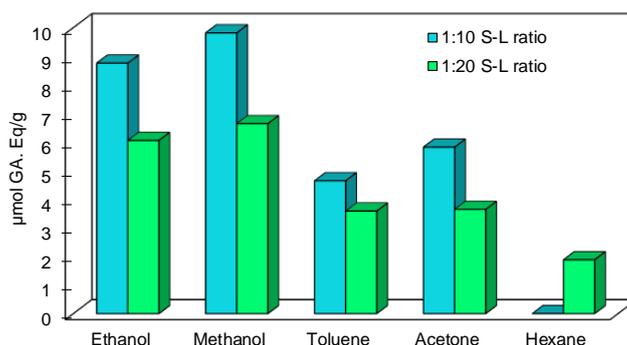[1] *Instituto Tecnológico de Aguascalientes, Aguascalientes, 20256, México*

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Keywords: Biomass, Polyphenols, Taguchi, antioxidant, extraction.

Residual biomass is the most abundant and economical renewable resource on the planet generated from different human economic activities. Biomass structure can contain a wide spectrum of value-added compounds that can be recovered, purified and used in several industrial sectors (Kircher et al., 2015). One of these compounds that has attracted a significant attention corresponds to polyphenols because they have a variety of beneficial properties for human health such as their antioxidant capacity (Abidin et al., 2013). Due to the importance of polyphenols, different extraction methods have been used and studied for their recovery including the solid-liquid (S-L) extraction (Abidin et al., 2013). The performance of S-L extraction is mainly influenced by the solvent type and its polarity as well as operating temperature, S-L ratio and extraction time (Sridhar et al., 2021). Therefore, it is paramount to study the effect of the operating conditions involved in S-L extraction and to determine their optimal values. This study reports the extraction of these antioxidants from rice husk biomass using different organic solvents.

Rice husk biomass was characterized to determine ash, oil and moisture content, the composition of simple and complex sugars, the structural carbohydrates and lignin in the biomass. Preliminary studies were carried out to determine the most efficient organic solvents for polyphenol extraction. Therefore, the extractions were carried out with ethanol, methanol, acetone, hexane and toluene. The content of total polyphenols (TPC) for the different extraction conditions was quantified with a UV-VIS instrument using the Folin-Ciocalteu reagent. TPC was reported as an average in µmoles of gallic acid equivalent per g of biomass. The results of the preliminary studies are presented in Figure 1, where it was observed that the solvents with the highest extraction yields were ethanol, methanol and acetone.

Figure 1. Average total polyphenol content obtained from solid-liquid extraction using rice husk with different organic solvents.

The best conditions for the extraction of these compounds were identified via experimental designs. Results showed that the best solvents for the extraction of polyphenols (antioxidants) from rice husk were solvents with polar nature.

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P2

Application of artificial neural networks and group contribution models for calculating the surface tension of organic acids

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Keywords: Surface Tension, Organic Acids, Fatty Acids, Group Contribution, Artificial Neural Network

Two approaches based on Group Contributions (GC) and Artificial Neural Network (ANN) were applied and tested to estimate the surface tension of organic acids. These models used the molecular weight and structure, critical temperature and operating temperature as input variables. The group contributions models were based on the empirical correlation proposed by Jasper (1972) and on the van der Waals principle of corresponding states. 870 experimental data of 70 organic acids (including aliphatic, aromatic, dicarboxylic and polyfunctional acids) were employed to determine the model parameters and to test the model performance. The group contributions were obtained using the Simulated Annealing-Quasi Newton hybrid method implemented in MATLAB® software. On the other hand, the ANN parameters were determined using five training techniques for various ANN structures via the minimization of the objective function implemented in the Deep Learning Toolbox simulation package of MATLAB®. The summary of model performance is shown in Table 1 including a comparison with other models reported to estimate the surface tension of organic acids.

Table 1. Performance of different thermodynamic models for the calculation of the surface tension of organic acids.

Model	Statistical metrics			
	RMSE	AAD±DE	|PD| min	|PD| max
Group contribution (this study)	**1.61**	**2.67±3.79**	**1.07E-05**	**45.20**
Group contribution + ANN (this study)	**1.60**	**2.24±3.86**	**5.69E-03**	**50.55**
Brock and Bird (1955)	10.90	38.28±20.45	0.153	175.55
Pitzer (1995)	13.60	48.31±21.99	0.022	264.70
Di Nicola and Moglie (2011)	8.21	28.11±16.81	0.018	119.50
Gharagheizi et al. (2011)	4.70	15.79±8.34	0.093	54.12

The models developed in this study showed $R^2 = 0.98 – 0.99$ with average modelling errors of $2.67 – 5.1\%$. The group contribution model outperformed those models based on the principle of corresponding states. The application of ANN improved the predictions of group contribution models, thus reducing the errors for the calculation of surface tension. Also, these models were more reliable for the calculation of the surface tension of organic acids than other models reported in the literature.

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P3

New iron-based catalysts to obtain biofuels via transesterification

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Keywords: biodiesel, heterogeneous catalyst, transesterification, FAME.

Biodiesel is one of the most promising alternatives as a substitute for conventional fossil fuels due to its low toxicity, biodegradability and renewability (Mohadesi et al., 2020). The biodiesel production via the transesterification of vegetable oils relies on the catalyst type, which has a significant impact on the process performance. Heterogeneous catalysts with magnetic properties have great potential for this application due to their easy separation from the reaction mixture thus implying additional benefits in terms of environmental impacts and production costs (Quah et al., 2020). Therefore, this study has focused on the preparation of heterogeneous catalysts with magnetic properties and their application in oil transesterification to produce biodiesel.

The coconut endocarp was used as lignocellulosic support in the preparation of heterogeneous catalysts with magnetic properties. This biomass was functionalized with iron to identify the best route to obtain the catalyst where different experimental conditions were tested. These samples were used in the transesterification of safflower oil and methanol at 60 °C under stirring for 2 h. The catalysts and support were analyzed via XRD and FTIR.

The results showed that the catalysts performance in the oil transesterification achieved FAME formation from 93.58 to 97.49%. The catalyst prepared under the best experimental conditions had a FAME formation of 98.13%. The lifetime and reuse of the catalyst was evaluated in 3 reaction cycles after washing with methanol where a FAME formation of 66.7% was obtained after 3rd cycle. The reaction kinetics were quantified at 50, 60 and 70 °C to determine kinetic constants and activation energy. The kinetics showed a fast FAME formation at 2 h and, after this time, the formation was slow. The process was endothermic, and the experimental data were adjusted to the pseudo-first and -second order models. The pseudo-first order model was the most suitable to describe the reaction kinetics ($R^2 = 0.95$–0.99) and the calculated activation energy was 34.37 kJ/mol thus indicating a chemically-controlled reaction (Sharma et al., 2019). FTIR and XRD characterization confirmed the effective modification of coconut endocarp with iron moieties, which contributed to generate magnetic properties in the catalyst.

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A. Sharma, P. Kodgire, S.S. Kachhwaha, 2019, Biodiesel production from waste cotton-seed cooking oil using microwave-assisted transesterification: Optimization and kinetic modeling, Renewable and Sustainable Energy Reviews, 116, 109394

P4

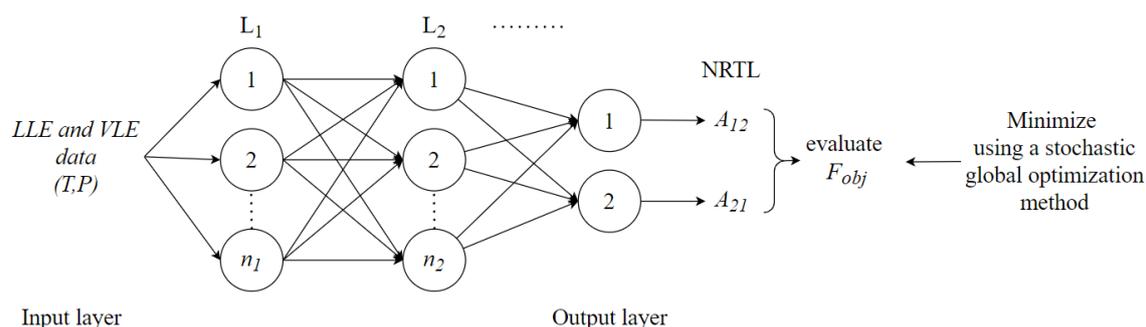# LLE and VLE modeling using NRTL and artificial neural networks

O. Del-Mazo-Alvarado[1], A. Bonilla-Petriciolet[1,*]

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Keywords: parameter estimation, NRTL, artificial neural networks, phase equilibrium.

Separation operations are relevant for industrial processes due to their cost and energy consumption. Wakeham and Stateva (2004) stated that between 70 and 90% of the energy cost in chemical facilities can be associated with these units. The design of separation systems is based on the description of the phase equilibrium behavior of the mixture under analysis. In this regard, mathematical models and numerical algorithms play a major role to achieve an accurate phase equilibrium description. A wide variety of thermodynamic models has been developed with the common objective of describing the thermodynamic behavior of pure component and mixtures. Some well-known models are cubic equations of state (e.g., Soave-Redlich-Kwong or Peng-Robinson) and activity coefficient models (e.g., Wilson or NRTL). In particular, the NRTL equation has been identified as a suitable model to describe non-ideal mixtures (Reynel-Ávila et al., 2019). However, this local composition model is unable to accurately describe the phase equilibria of some particular systems (Bollas et al., 2009). The selection of model binary interaction parameters is a key step in phase equilibrium calculations. Marcilla et al. (2017) provided a detail discussion on this subject regarding liquid-liquid equilibrium (LLE) modeling, while Lopez-Zamora et al. (2021) addressed the vapor-liquid-liquid equilibrium (VLLE) analyzing different thermodynamic models and binary interaction parameters. The parameter estimation of thermodynamic models is a global optimization problem where several objective functions can be employed. In this work, different data processing formulations were assessed for determining the binary interaction parameters of NRTL for binary systems with LLE and VLE calculations. A hybrid data regression framework based on NRTL and an artificial neural network model was also proposed, see Figure 1.

Figure 1. Schematic representation of the simultaneous modeling strategy using artificial neural networks and NRTL for binary systems with LLE and VLE data.

Selected binary systems showing both LLE and VLE data were modeled using NRTL with the binary interaction parameters obtained from tested objective functions. Homogeneous and heterogeneous azeotrope calculations were also performed to evaluate the capabilities of this thermodynamic model. Overall, the hybrid approach showed the best modeling results, which was attributed to the flexibility provided to NRTL by the application of artificial neural networks. This study emphasizes on the relevance of binary interaction parameters for phase equilibria calculations where the model parameter identification is not a trivial task even for binary mixtures.

The use of machine learning algorithms can contribute to enhance the performance of thermodynamic models to achieve better results in VLE and LLE calculations.

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Optimization of the adsorption properties of a biochar for the recovery of methyl ethyl ketone

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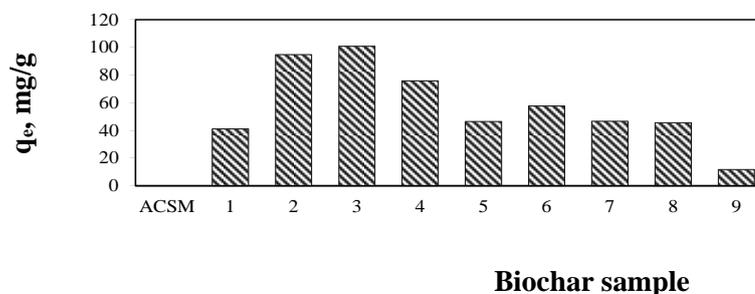
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Keywords: Methyl Ethyl Ketone, Adsorption, Avocado seed

Methyl ethyl ketone (MEK) is a compound derived from petroleum and can be also obtained from the biomass processing. This chemical can be used as alternative biofuel and for other industrial applications (Burke et al., 2016). MEK can be also found as pollutant in the waste effluents from relevant manufacturing industries. Different separation methods for the recovery/removal of MEK have been used (Ma et al., 2018). Specifically, activated carbon-based adsorption has been recognized as an effective and a reliable method to recover this organic compound (Alalm and Nasr, 2018).

Particularly, the lignocellulosic biomass can be used as a precursor to prepare carbon-based adsorbents due to their composition, processing versatility and physicohemical properties (Bhagat et al., 2020). From a biotechnological point of view, there is a wide variety of lignocellulosic resources available for their conversion into value-added bioproducts (Iqbal et al., 2013). In this direction, the avocado seed is a mexican biomass that can be considered as an attractive precursor for the preparation of biochars. These adsorbents can be utilized for the recovery of benzene, trichlorethylene, MEK, chloroform, acetone, ethanol and other relevant chemicals (Tang et al., 2016). These carbon-based adsorbents can be modified with several agents to improve their adsorption capacities. Thus, this paper reports the use of avocado seeds to prepare biochars tailored with H_2SO_4 for the recovery/removal of MEK in aqueous solution.

Different adsorbents were obtained using experimental designs to optimize the pyrolysis conditions and acid functionalization of biochars. These adsorbents were tested in the MEK adsorption at pH 6 and 30 °C. MEK concentrations in the adsorption studies were quantified with gas chromatography. Samples of these adsorbents were characterized, before and after the adsorption process, to analyze their surface chemistry. Figure 1 shows the adsorption capacities of MEK for different biochars.

Figure 1. MEK adsorption capacities of different biochars prepared from avocado seeds.

The adsorption capacity of the carbon-based adsorbents without acid modification was around 5 mg/g. MEK adsorption capacities of functionalized biochars ranged from 11.63 to 100.83 mg/g. These modified adsorbents showed an increase up to 1916% in their MEK adsorption capacities. Surface chemistry of these adsorbents indicated that the presence of oxygenated functionalities played a relevant role in the MEK adsorption.

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P6

Preparation of new cellulose-based catalysts for biodiesel production

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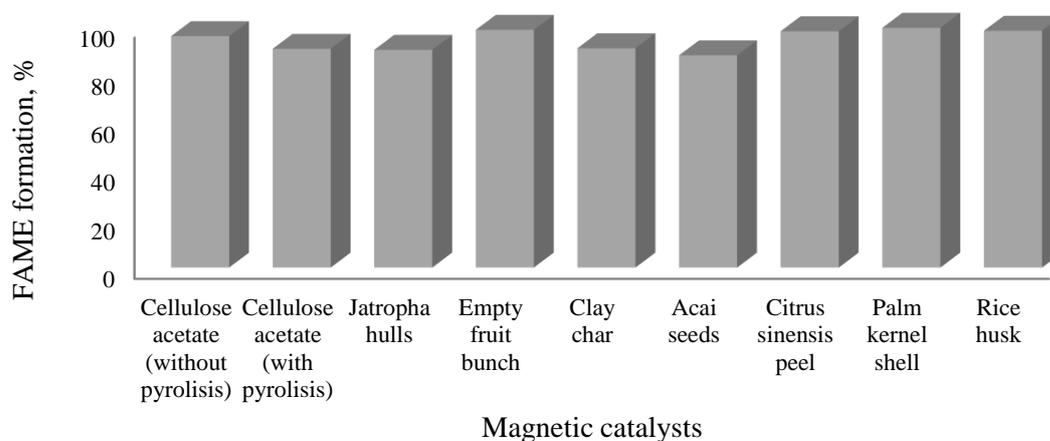
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Keywords: magnetic catalyst, transesterification, biodiesel

This paper reports the preparation of magnetic catalysts derived from cellulose acetate fibers obtained from cigarette filter wastes. The support was functionalized with iron particles that were synthesized using iron sulfate salt as metal precursor and sodium hydroxide as precipitating agent. It is noteworthy that the cigarette filters are classified as toxic, non-biodegradable and one of the most abundant waste worldwide (Pu et al., 2019). The catalysts were applied in soybean oil transesterification reactions for biodiesel (FAME) production. Two preparation routes were proposed to obtain carbon-based catalysts (with pyrolysis) and catalysts from cellulose acetate (without pyrolysis) using the cigarette filter wastes previously washed with NaOH and deionized water at boiling temperature. The best conditions for the preparation of these catalysts were identified via the Signal/Noise ratio analysis. These catalysts showed better FAME formation percentages compared to carbon-based catalysts where FAME formation up to 95.96% was obtained. Reaction kinetics of transesterification to obtain biodiesel were also studies at different temperatures where an endothermic process was identified. Reaction rates were calculated including the estimation of the activation energy. Surface chemistry of these catalysts was analyzed to explain their physicochemical properties.

Figure 1 shows the comparison of the FAME formation percentage obtained with the best catalysts prepared in this study with respect to those obtained with different carbon-based magnetic catalysts reported from Jatropha hulls (Zhang et al., 2017), empty fruit bunch (Ibrahim et al., 2019), clay char (Cong et al., 2020), acai seeds (Araujo et al., 2021), *Citrus sinensis* peel (Changmai et al., 2021), palm kernel shell (Goh et al., 2021), rice husk (Hazmi et al., 2021).

Figure 1. Comparison of FAME formation obtained via oil transesterification with different catalysts.

This study proved that the transesterification of soybean oil using magnetic catalysts derived from cigarette filter wastes was feasible. The magnetic properties of these materials allowed the separation of the catalyst at the end of the reaction without using additional equipment. These catalysts are promising for biodiesel production.

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Framework of phase stability benchmark problems to assess the performance of stochastic global optimization methods

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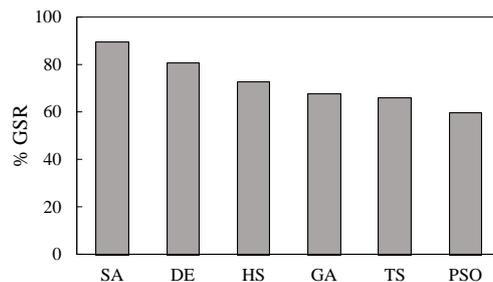
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Keywords: phase stability analysis, global optimization, benchmark problems.

Thermodynamic calculations are essential for estimating and predicting properties of pure components and mixtures involved in the design, simulation, operation and control of separation processes. The phase stability analysis is a fundamental step in phase equilibrium calculations in multicomponent and multiphase systems. This analysis allows to evaluate if a mixture is thermodynamically stable or not under certain operating conditions (Bonilla-Petriciolet and Segovia-Hernández, 2010). This problem can be formulated using an optimization approach via the global minimization of the tangent plane distance function (TPDF). This function is highly non-linear, non-convex and multivariable (Bhargava et al., 2013; Ivanov et al., 2013). Therefore, these calculations must be performed with reliable methods.

Different optimization methods have been used to solve the phase stability problem. The performance of these algorithms has been evaluated by solving a given set of stability problems. However, the properties and characteristics of these problems have not been evaluated and it is not clear whether they are adequate to compare, evaluate and identify the advantages and limitations of the available optimization methods. It is necessary to have a set of benchmark problems for a reliable evaluation of these methods in order to identify and propose improvements. An appropriate benchmark problem set should have different characteristics, e.g.: an adequate number of problems, problems with different levels of resolution complexity, as well as verified and confirmed solutions (Beiranvand et al., 2017). The selection of an inappropriate set of benchmark problems can lead to wrong conclusions about the algorithm (Zhigljavsky and Zilinskas, 2008). Therefore, this paper reports a set of phase stability problems that has been characterized and classified according to their resolution complexity.
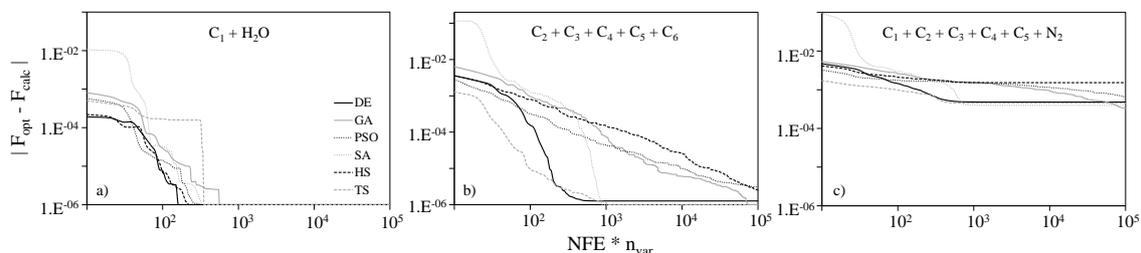
A literature review was carried out in order to identify phase stability problems that have been solved with optimization techniques. Different stochastic global optimization methods (SGO) were employed in this study: Harmony Search (HS), Genetic Algorithm (GA), Particle Swarm Optimization (PSO), Simulated Annealing (SA), Tabu Search (TS) and Differential Evolution (DE). These methods were applied to carry out a numerical characterization and classification of 35 phase stability problems according to different metrics associated with the algorithm performance.

For illustration, Figure 1 shows the global success rate (GSR) of the different methods employed to resolve the set of selected phase stability problems. These problems were classified into three categories according to their resolution complexity. In summary, 54, 20, and 26% of the problems were identified in the low, medium and high complexity categories, respectively.

Figure 1. Global success rate of stochastic optimizers for the phase stability problem categorization.

Figure 2 shows the convergence profiles of the SGO methods for three different problems belonging to the low, medium, and high resolution complexity categories, respectively. SA and DE methods were the most competitive and robust techniques to perform the global minimization of TPDF. A subset of phase stability problems was proposed with suitable characteristics (e.g., appropriate size, problems from low to high resolution complexity) that can be used to allow a fair comparison and evaluation of current and new SGO methods. The results of this study highlight the relevance of developing and improving SGO algorithms to reliably perform the phase stability analysis.

Figure 2. Convergence profiles of stochastic optimizers in the global minimization of TPDF. a) low, b) medium, and c) high resolution complexity.

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P8

Prediction of the mean activity coefficients of ionic liquids using a group contribution-based e-NRTL model

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Keywords: Group Contribution model, Ionic Liquids, e-NRTL, activity coefficients

Extraction processes require the intensive use of solvents, which are generally not environmentally friendly. Ionic liquids have been applied as alternatives to traditional solvents. They are classified as a new class of solvents with unique properties as a melting point below 100 °C, negligible vapor pressure, thermal and chemical stability (Vallet *et al.*, 2022). Therefore, the ionic liquids are considered "green solvents" and have been utilized for electrochemistry, spectroscopy, mining, catalysis, materials science, and other applications (Díaz-Álvarez *et al.*, 2012). The process design involving ionic liquids requires the analysis and modeling of their thermodynamic properties, which are difficult to find in the literature. In particular, the calculation of activity coefficients is an important thermodynamic property to be modeled and predicted. This paper reports the development of a predictive e-NRTL model based on group contribution approach to calculate the mean activity coefficients of ionic liquids. In particular, the binary interaction parameters of this model were determined via the group contribution approach. A database of 1250 experimental data of the activity coefficients of 56 quaternary ammonium salts at different concentrations was used. A predictive e-NTRL model was proposed and tested. Results showed that this alternative model can be effective for the prediction of this relevant thermodynamic property.

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P9

A heterogeneous metal-organic based catalyst for oil transesterification to obtain biodiesel

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Keywords: Biodiesel, Transesterification, Metal-organic compounds.

Biodiesel represents an ecological energy alternative due to its low toxicity, lubricating properties, renewability, biodegradability and lower greenhouse gas emissions than fossil fuels (Mansir et al., 2018; Gumahin et al., 2019). This biofuel is mainly obtained via the lipid transesterification in the presence of a catalyst (Al-Zuhair et al., 2017). Different heterogeneous catalysts can be utilized for this purpose including metal-organic compounds. In particular, they are porous materials consisting of coordinated covalent bonds of metallic ions or groups and organic molecules called ligands (Yoon et al., 2012). Several methods for the synthesis of metal-organic compounds have been described in the literature where solvothermal synthesis has attracted attention (Dhakshinamoorthy et al., 2016).

The objective of this study was to synthesize heterogeneous catalysts derived from metal-organic compounds and to evaluate their catalytic performance in biodiesel production via oil transesterification. These catalysts were obtained using a solvothermal process and chemically modified with potassium hydroxide. The synthesis procedure was carried out according to a Taguchi experimental design to identify the best conditions. The catalysts were evaluated in the transesterification of commercial safflower oil with methanol oil at 60 °C for 4 h under stirring. The results indicated that 99.15% of FAME formation was obtained for the best catalyst. Finally, a physicochemical characterization with XRD and FTIR of the best catalysts was carried out before and after impregnation with KOH solution with the aim of explaining their performance and surface chemistry.

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P10

Assessment of hydrochar-based catalysts for the biofuels production

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Keywords: biodiesel, catalyst, hydrothermal carbonization

Biodiesel has been considered as the main candidate to replace conventional petro-diesel in the future due to its benefits including the good performance in internal combustion engines that generates low emissions of polluting gases into the atmosphere. It is also environmentally friendly, non-toxic, biodegradable and sustainable (Naylor and Higgins, 2017; Muhammad et al., 2021). Biodiesel is mainly produced through the transesterification process that consists of the reaction between lipids and an alcohol in the presence of a catalyst (Tabatabaei et al., 2019). Catalysts play a leading role in the transesterification of lipids because they allow to overcome the reaction energy barrier due to the decrease of activation energy and, in turn, it favors the formation of products in a short reaction time (Abdullah et al., 2021). Recently, solid catalysts obtained from the hydrothermal carbonization (HTC) of lignocellulosic biomass have shown excellent performance in the production of biodiesel (Abdullah et al., 2021). Therefore, the present study has focused on the preparation and evaluation of carbon-based catalysts via HTC of coconut endocarp, macadamia nutshell and orange peel biomass and their functionalization with KOH or H_2SO_4 for their application in the production of biodiesel.

The synthesis of the heterogeneous catalysts was developed under different hydrothermal conditions where Taguchi experimental designs were applied to identify the best preparation conditions. The functionalization stage was carried out at room temperature and continuous stirring via the mixing of hydrochars with KOH or H_2SO_4 at the different concentrations. The performance of these heterogeneous catalysts was evaluated in the transesterification of a commercial safflower oil at 60 °C during 4 h. The content and profile of FAME present in the biodiesel samples was quantified by gas chromatography. Finally, a physicochemical characterization of biomass, hydrochars and catalysts was carried out using FTIR and XRD analytical techniques to determine their functional groups and crystalline structures. Results showed that the raw hydrochars achieved poor performance (FAME < 2%) in the transesterification due to their lack of catalytic properties. Acidic catalysts also achieved low FAME conversions (< 30%) because they required more drastic reaction conditions compared to alkaline catalysts (Tabatabaei et al., 2019). KOH-modified hydrochars showed FAME conversions higher than 93%.

In summary, the catalysts prepared through HTC from lignocellulosic biomass and chemically treated with KOH offer high catalytic activity, thus favoring the biodiesel production process from an economic and environmental point of view. The selection of the preparation route is paramount to obtain suitable and competitive catalysts to be used in biodiesel production.

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P11

Preparation of new adsorbents from lignocellulosic wastes via hydrothermal carbonization and pyrolysis and their application in the mercury removal

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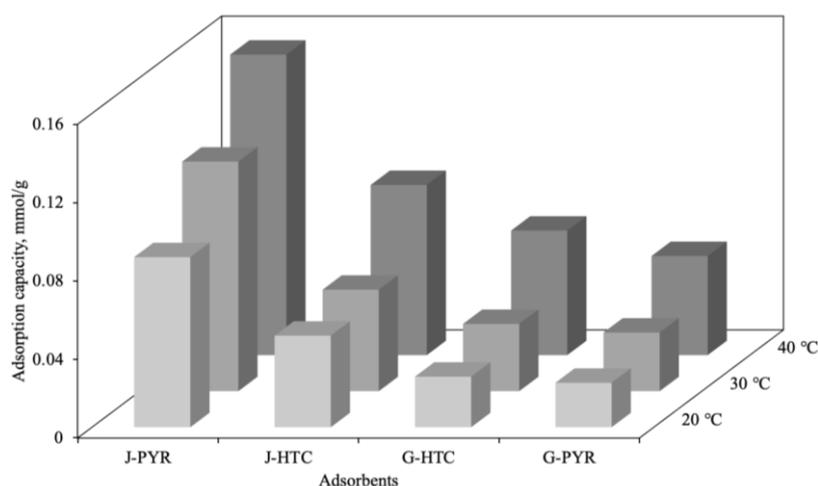
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Keywords: hydrothermal carbonization, lignocellulosic biomass, mercury depollution, pyrolysis.

This study has focused on performing a comparative study of hydrothermal carbonization (HTC) and pyrolysis (PYR) routes for the preparation of carbon-based adsorbents from lignocellulosic wastes and their application in the removal of mercury from aqueous solution. This pollutant was selected as a case of study because it is considering a toxic and hazardous water pollutant with a significant impact on human health (WHO, 1991; Arias et al., 2017; Liu et al., 2020; Zúñiga-Muro et al., 2020; Fasae et al., 2022). Therefore, the properties of adsorbents obtained from HTC and PYR using jacaranda fruit (J) and guava seeds (G) as precursors were analyzed and compared to determine the advantages and disadvantages of these biomass thermochemical transformation routes. Four adsorbents were obtained (J-PYR, G-PYR, J-HTC, G-HTC) at different conditions and a comparative analysis of their adsorption performance was carried out via batch adsorption studies at 20, 30 and 40 °C and pH 4. These adsorbents were characterized by XRD, FTIR and SEM before and after the mercury adsorption. Overall, the adsorbents prepared from jacaranda fruits showed higher adsorption capacities than those obtained from guava seeds, see Figure 1. Also, the mercury adsorption with these adsorbents was endothermic. Results reported in this study contribute to the valorization of alternative Mexican biomass for the preparation of new adsorbents to be applied in water depollution.

Figure 1. Mercury adsorption capacities of carbon-based adsorbents obtained by pyrolysis (PYR) and hydrothermal carbonization (HTC) using guava seed (G) and jacaranda fruit (J) as precursors. Adsorption conditions: 20, 30 and 40 °C.

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Valorization of Mexican residual biomasses for the oil extraction and biodiesel production

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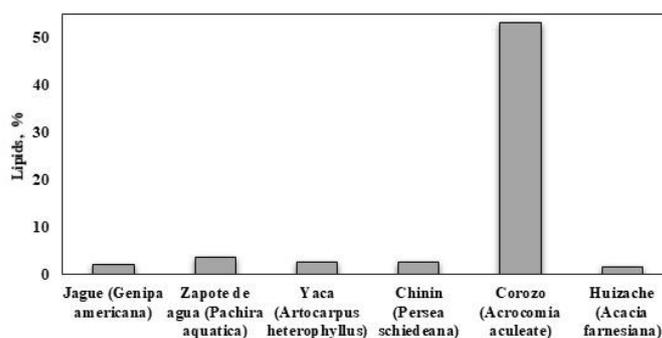[1] Instituto Tecnológico de Aguascalientes, 20256, México

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Keywords: biomass, valorization, lipids, biodiesel

The imminent depletion of traditional fuels has been the main impulse to intensify the research on finding alternative sources of green energy. This is the case of producing biofuels derived from vegetable oils that are not associated with the food chain (Raheem et al., 2020). Biodiesel is considered as an environmentally friendly biofuel energy source since it is non-toxic, renewable and biodegradable (Gaurav et al., 2019). Mexico has a wide agricultural diversity that generates several wastes that could be used as raw lipidic source for biodiesel production. In particular, the valorization of biomass wastes provides relevant information about the content of value-added components that can be obtained and utilized in biorefineries. This study has focused on the evaluation of lipid content of different forest biomass from the state of Tabasco, Mexico, with the aim of establishing their potential for biofuels production. Jague (*Genipa americana*), Zapote de agua (*Pachira aquatica*), Yaca (*Artocarpus heterophyllus*), Chinin (*Persea schiedeana*), Corozo (*Acrocomia aculeate*) and Huizache (*Acacia farnesiana*) were used in this study. Lipid extraction studies were done with these forest wastes and hexane. Results of lipid extraction varied from 1.6 to 53 wt%, see Figure 1. It was evident the potential to use the corozo seed as raw source of lipids. The other biomass with low lipid content (1.6-3.44%) could be also used for other applications considering that they are wastes with no commercial value.

Figure 1. Results of extraction of lipids contained in the residual biomass.

The oil extracted from the corozo seed was characterized where the acidity index and acid value was determined. The acidity index and acid value were 5.44% and 0.014 g KOH/g. The fatty acids profile of the corozo oil was identified via a derivatization reaction. Results indicated that the lauric acid (47.63%) and oleic-linoleic acid (17.63%) were the main fatty acids present in the oil followed by myristic acid (13.68%), capric acid (11.47%) and palmitic acid (7.22%), respectively.

Once the oil was characterized, different routes were studied to obtain biodiesel via esterification and transesterification where the best reactions conditions were identified. It was concluded that the corozo seed is a mexican biomass with a great potential to be used in the production of biodiesel.

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P13

Antioxidant properties of prickly pear waste

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Keywords: peel waste, soxhlet extraction, antioxidant activity, high-value added product

Large quantities of fruit and vegetable peel waste are produced every year, which are usually disposed in the environment. However, peel waste represents one of the main sources of antioxidant molecules, including terpenes, phytosterols, phenolic compounds, and peptides. Peels and pomace of fruits such as prickly pear are the main waste of the agro-food industry, which might contain a greater amount of bioactive ingredients with beneficial properties than the edible portion. The Prickly Pear Cactus (*Opuntia ficus-indica L.*) is a species of the genus *Cactus* of the *Cactaceae* family. Fruit, cladodes, and flowers have been historically used in folk medicine because of their nutritional properties, beneficial activities, and economic value. The fruit of *Opuntia ficus-indica* is usually consumed fresh. According to past reports, the discarded outer coating (peel) of this fruit constitutes nearly 45% to 50% of its total weight. Thus, millions of kilograms of fruit peels are discarded yearly with potential adverse effects, on the environment, whereas they could be repurposed due to the presence of beneficial active compounds.

The current study investigated the main constituents of the unused parts (fruit peel) of *Opuntia ficus-indica* and identified the total phenolics content (TPC), total flavonoid content (TFC) and antioxidant activity (AA). Specifically, Soxhlet extraction was conducted using different solvents (Ethanol, Methanol, and Ethanol-Water mixture) and afterwards the values of TPC, TFC and AA among the different extracts were assessed. According to the current findings the methanolic and ethanol-water extracts from the peel of prickly pear displayed the highest TPC, TFC and AA values. In conclusion, prickly pear waste could be considered as a high-value added product with potential pharmaceutical and therapeutic purposes, since it appears to contain beneficial compounds exerting antioxidant activity.

P14

Kinetic modeling of Baru (Dipteryx alata volgel) seeds oil extraction using compressed propane

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Keywords: Baru seed, Compressed propane, Solvent free oil; Extraction kinetics, Mathematical models

Introduction

Dipteryx alata Vogel (Fabaceae) called baru is a widely distributed tree species in the Cerrado Biome, central Brazil in South America. The higher value of the wood established extinction risk of the specie (Collevatti et al 2013). The fruit, specifically the quality of the seeds, is the main reason why there is increasing demand in the market, due to the high amount of oil (40%). The characteristics as such: unsaturated fatty acids, presence of tocophenois, antioxidant activity, and so on prove the importance of the oil in the food and pharmaceutical industries (Fetzer et al 2018).

Correlation of experimental data on extraction of natural matter applying mathematical models are important tools for scaling laboratory data up to industrial level, to make estimates of viability or to design processing equipment (Grosso et al 2010). These two models are based on differential mass balances and presented a stronger physical meaning, including mass transfer coefficients in fluid and solid phases or in just one phase. They consider the characteristics of the plant matrix, specifically the particle size and the bed porosity. These models reflect the mechanisms behind the extraction process.

A discussion of the modelling of our data on compressed propane extraction of baru seeds oil was carried out. The results obtained at different extraction conditions using two (Sovová, 1994) or one adjustable parameter (Sovová, 2005), provided a good agreement between the model curves and the experimental data, which evidence the capability of these models.

Methodology and Results

Compressed propane extraction of oil from samples of baru seeds, were performed in the Laboratory of kinetic and thermodynamic apply, for its acronym in Portuguese LACTA, Brazil. It was carried out in the flow apparatus, at temperatures 293 and 333K, pressures at 2.0 and 10.0 MPa, particle size (ϕ) from 0.50 to 1.70 mm and flow rates of 2.0×10^{-3} kg·min^{-1} of propane. Around 32 g baru seeds was weighed and loaded into the extraction vessel of the extractor. After 10 min of static time elapsed, the dynamic extraction took place. The extract was collected every 5 minutes.

The mathematical models used are based on some general assumptions as discussed before (Grosso et al 2010), and the objective function was defined as the average absolute relative deviation (AARD) represented to yields, between the experimental and calculated values attained for the models. The mathematical models applied are based in the basic and usual general assumptions (Grosso et al 2010)., and a differential mass balance equation considering plug flow can be used:

$$\frac{\partial C}{\partial t} + \frac{u}{\varepsilon}\frac{\partial C}{\partial h} + \frac{(1-\varepsilon)}{\varepsilon}\frac{\rho_s}{\rho_f}\frac{\partial q}{\partial t} = 0 \tag{1}$$

where the yields of extraction can be calculated by:

$$e = \frac{Q}{t}\int_0^t C(h=H)dt \tag{2}$$

The assumption of homogeneous concentrations in both phases represents the initial condition, as well as the boundary condition are:
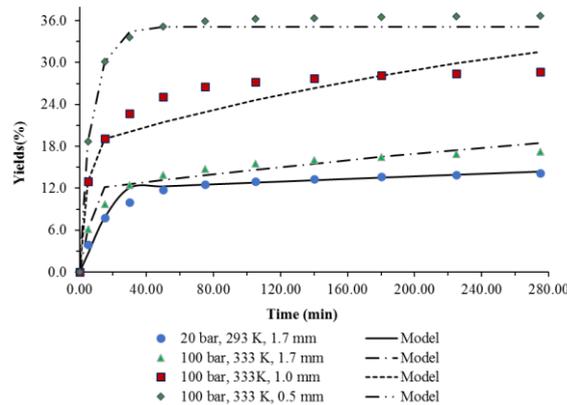
$$q(h, t=0) = q_0 \quad and \quad C(h, t=0) = C_0 \tag{3}$$

$$C(h=0, t) = 0 \tag{4}$$

Two models were applied the Sovová 1994 and Sovová 2005, where the distinctions are in the solid phase differential mass balance equation containing the term for mass transfer rate. The parameters used in both model and the results obtain are presented in Table 1.
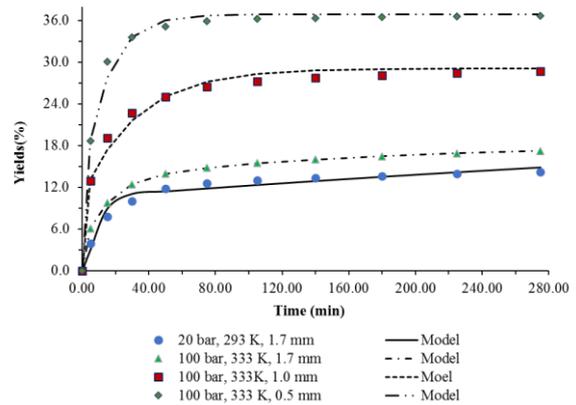
Table 1. Extraction conditions and initial conditions for fluid(C_0) and mass transfer coefficients to the models and respective AARD (%).

P(MPa)	T(K)	ϕ (m)*10^3	u (m.s^{-1})	ρ (kg.m^{-3})	C_o(kg/kg)*10^1	Sovová 1994 k_s x10^7(m.s^{-1}) / k_f x10^7 (m.s^{-1})	Sovová 2005 k_s x10^7 (m.s^{-1})
2.0	293.2	1.7	1.08E-04	503.31	2.00	0.0279 / 2.19 (6.3%)	0.0576 (7.0%)
10.0	333.2	1.7	1.19E-04	513.05	3.30	0.0725 / 3.63 (5.7%)	0.128 (6.2%)
10.0	333.2	1.0	1.19E-04	513.03	7.00	0.0579 / 1.91 (4.9%)	0.807 (3.3%)
10.0	333.2	0.5	1.19E-04	513.03	8.00	1.89 / 3.31 (2.7%)	1.07 (1.9%)

In Figures 1 and 2 it can be observed that the yield of oil was influenced by the density of the compressed propane. The change of temperature and pressure from, 293K and 20 bar, to 333 K and 100 bar, corresponded to a density rise from 503.31 to 513.03 kg.m^{-3}, induced a slightly increase in the extraction yield.

Figure 1. Extraction curve of Baru oil yield as a function of time to different conditions of pressure (bar), temperature (k) and particle size ϕ (mm) at constant flow rate 2.0x10^{-3} kg·min^{-1}. Points are experimental results and lines obtained with Sovová model (1994).

Figure 2. Extraction curve of Baru oil yield as a function of time to different conditions of pressure (bar), temperature (k) and particle size ϕ (mm) at constant flow rate 2.0x10^{-3} kg·min^{-1}. Points are experimental results and lines obtained with Sovová model (2005).

More significatively are the decrease of particle size to the same pressure and temperature, where the increase of the contact surface between the particles and the solvent is reduced, resulting in

the release of the oil into the particles surface and improving the mass transfer phenomena. A maximum of 36.7 % with 0.5 mm particle size with compressed propane and 39.76 % compared with Soxhlet was obtain. A global yield decrease was achieved when 1.7 mm particle size is used, namely with Soxhlet 23.98 % or lower values with compressed propane.

From figures is possible to identified that the model Sovová 2005 presents better results when compare with the model from 1994. In fact, the AARD to the more recent model presents values from 1.9 to 7.0%, and to the first proposed model, values between 2.9-6.3% were achieved. Model Sovová 1994, considers both transport resistances, in the fluid, and in the solid phases, where a fluid phase (kf) and solid phase (ks) mass transfer coefficient was determined. This model was initially intended for the extraction of vegetable oils. Moreover, in the model of Sovová 2005 an overall *kf* and *ks* mass transfer coefficient, was determined, presented better results to the experimental results.

Conclusions

For the experimental conditions studied it can be concluded that the extraction was controlled by internal diffusion, and the internal mass transfer coefficient, *ks*, changes significantly with pressure, temperature and mainly with particle size (from order of values of 10^{-9} to 10^{-7} m.s^{-1}). *ks* is much more important that *kf* considering the change of values in the models and it looks that the solute-matrix interaction plays a key role in the extraction process.

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P15

Revalorisation of avocado industrial wastes to produce a food antioxidant ingredient

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Keywords: avocado, side-streams, polyphenols, antioxidant

Introduction

Avocado is one of the worldwide most cultivated tropical fruit (Martín, 2021). Over the years, its cultivation was intensified due to a considerably increase of consumers demand (FAO, 2018). The world's leading producer of avocados is Mexico and around 70% of the production takes place in Latin America and the Caribbean. In Spain, the cultivated hectares increased noticeably in recent years (Orús, 2022). Avocado is presented as a fruit with health benefits, together with attractive organoleptic qualities, named as "green gold". The most cultivated variety in 1950 was *Fuerte*, but *Hass* variety production gained market and become in 1970 the most popular worldwide (Dreher et al., 2013).

Many avocado-derived products are highly demanded by consumers, such as guacamole, avocado spread or crushed avocado pulp. Each kg of processed fruit generates around 25-30% of side-streams, specifically shells and bones. These side-streams are currently used for the production of biofuels, avocado oil, or simply are discarded at a cost (Natural Tropic, 2022). Skins and bones represent, respectively, 3-14% and 10-26% by weight of the fruit (Páramos et al., 2020). Besides oil production, antioxidant polyphenols can be recovered from these agrifood side-streams, to produce a food antioxidant ingredient as a profitable opportunity to circular economy.

In this work, dry and fresh avocado skins were extracted using methanol and ethyl acetate solvents, assessing two different methods, i.e. pressurized liquid extraction (PLE) and ultrasound assisted extraction (UAE). The avocado skins were the industrial by-product of a local guacamole production industrial unit. The extracts were studied in order to assess the content of phenolic compounds and their antioxidant activity.

Materials and methods

Avocado skins (*Hass* variety) were provided by the Eurobanan Group Company (Madrid distribution Centre). The avocado skins were subjected to a first drying (45°C, 1.5 h) employing a tray dryer (Edibon, model SBAN, Spain) up to 40% moisture. A second drying was carried out in an oven to obtain samples with less than 15% w/w water. Then, skins were ground with a Grindomix GM 200 model blade mill in particles with sizes between 500 and 250 μm.

The UAE extraction was carried out with both fresh and dried skins using an ultrasonic device (Branson Digital Sonifier 550 model, Danbury, USA) (20 kHz and 550 W). The ratio skin/solvent (methanol and ethyl acetate) was 1/10 (w/v) and extractions were accomplished during 15 min at 55°C. A 30 min extraction assay using methanol was also carried out, to analyse the influence of time. PLE experiments (Accelerated Solvent Extractor, Dionex Corporation, ASE 350, USA) were accomplished during 20 min, using dried avocado skins, filling the cell with a ratio 1/4 (w/w) skin/sand, and methanol or ethyl acetate at temperatures in the range 50-200°C. All extraction experiments were done by duplicate. After extraction, the UAE extract was vacuum filtered and in both UAE and PLE extracts the solvent was removed by evaporation under vacuum.

The Folin-Ciocalteu method (Singleton et al., 1999) was used to quantify the total phenolic compounds content (TPC) and the DPPH assay (Brand-Williams et al., 1995) was utilized to

evaluate the antioxidant capacity of the samples. The reaction was carried out at room temperature in the dark for 2 h, and the absorbance was measured at 515 nm the for DPPH assay and at 760 nm for the TPC determination, using a Genesys 10S UV-Vis spectrophotometer (Thermo Fischer Scientific Inc., USA). A calibration curve was used to determine the concentration of DPPH in the reaction medium. Trolox was used as standard, and results expressed as EC_{50} (µg/mL) (50% of maximum effect concentration). All analyses were done in triplicate.

Results and discussion

In UAE experiments (Table 1), higher extraction yield was obtained using fresh skins than using dried skins, both with methanol or ethyl acetate solvents. In the processing of dried skins with methanol, an increase of yield from 4.80% to 6.34% was observed (1.3-fold increase) when increasing time from 15 to 30 min. Nevertheless, similar TPC values were determined in both samples (c.a. 24 mg GAE/g). Concerning the extraction of phenolic compounds a significant increase of TPC values was observed with fresh skins and ethyl acetate solvent.

Table 1. UAE of avocado skins: yield (mass recovered / mass of dry matter processed) and content of total phenolic compounds (TPC).
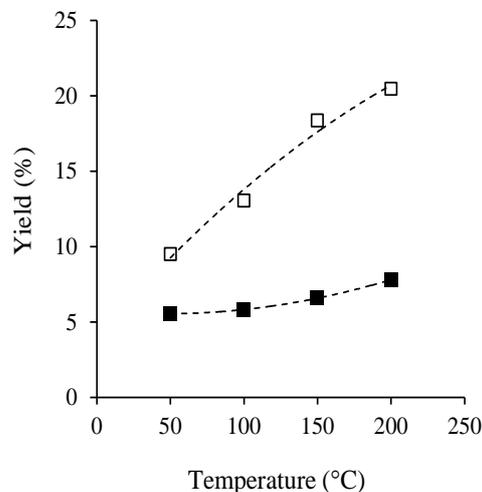
Solvent	Vegetal matrix	Time (min)	Yield (%)	TPC (mg GAE/g)
Methanol	Dried skins	30	6.34	23.80 ± 1.44
Methanol	Dried skins	15	4.80	24.51 ± 0.67
Methanol	Fresh skins	15	28.06	19.89 ± 0.46
Ethyl acetate	Dried skins	15	4.78	20.94 ± 1.78
Ethyl acetate	Fresh skins	15	7.05	50.45 ± 6.40

PLE assays were accomplished with dried skins and, as expected, the extraction yield increased with increasing temperature, particularly using methanol as the solvent (Figure 1). Furthermore, yields obtained with methanol were always higher than the yields obtained with ethyl acetate solvent.
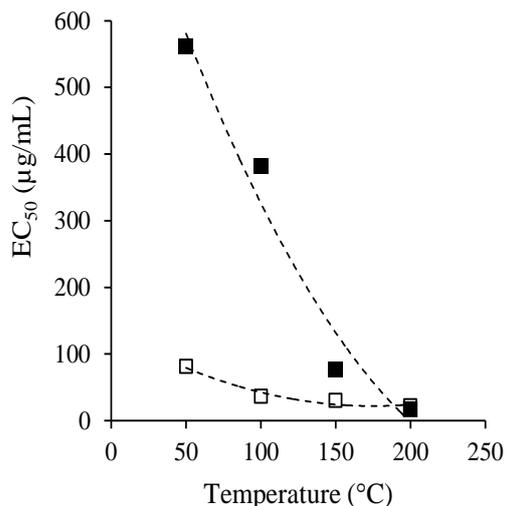
Concerning the extraction of phenolic compounds, the TPC values increased with increasing temperature in the range 50-200°C, with values from 20.4 to 98.4 mg GAE/g in the case of ethyl acetate and from 25.8 to 102.3 mg GAE/g with methanol solvent. That is, despite yields were higher with methanol, similar concentrations of phenolic compounds were obtained with methanol or ethyl acetate solvents.

Nevertheless, the antioxidant capacity of the extracts was rather different and dependent of the extractive solvent used, as can be deduced from Figure 2, in which the EC_{50}

values (µg/mL) obtained are depicted as a function of the extraction temperature.

Figure 1. PLE yields obtained in the extraction of dried avocado skins with (□) methanol and (■) ethyl acetate.

Figure 2. IC$_{50}$ values (µg/mL) of PLE extracts obtained from dried avocado skins with (□) methanol and (■) ethyl acetate.

Despite the EC$_{50}$ values decrease with temperature, this effect is much noticeable in the case of ethyl acetate. With methanol EC$_{50}$ values are rather similar, denoting a similar antioxidant capacity of all the methanolic extracts obtained. But in the case of using ethyl acetate as solvent, only the extracts produced at the higher temperatures (150°C and 200°C) resulted with low EC50 values, and similar to the values obtained for the methanolic extracts.

Conclusion

Side-streams of avocado processing, such as skins, can be used to produce a food antioxidant ingredient. PLE extraction with ethyl acetate, a GRAS and admitted by FDA for safety use in food, can produce at high temperatures (150-200°C) an extract with similar antioxidant activity than the extracts obtained with toxic methanol. The chemical analysis of the extracts will elucidate the phenolic compounds that mainly contribute to antioxidant activity.

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Valorization of *Equisetum arvense* leaves for production of high value products

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High-value added products extracted from plants have been used for their valuable properties and as medicinal alternatives. *Equisetum arvense*, also known as Horsetail, is a native plant of the northern hemisphere, distributed throughout Canada and USA -except the southeast-, Europe and Asia. This plant contains many biologically active compounds such as phenolic acids, flavonoids, alkaloids, phytosterols, tannins and triterpenoids. According to the literature data, it has been widely applied in folk medicine and its extracts has been used for the treatment of various ailments since it possesses anti-inflammatory, antidiabetic, antibacterial, antifungal and anticonvulsant activities among others. The present study applied the Soxhlet extraction, using different solvents (Ethanol, Methanol, Water and Ethanol-Water mixture), in order to investigate and compare the total phenolics content (TPC), total flavonoid content (TFC) and antioxidant activity (AA) of *Equisetum arvense* leaves' extracts. The current findings revealed that the methanolic, ethanolic and ethanol-water extracts from the *Equisetum arvense* leaves demonstrated significant TPC, TFC and AA values. Consequently, *Equisetum arvense* leaves' extracts should be further investigated since they could potentially constitute a high-value added product for pharmaceutical and other medicinal applications.

Hydrothermal based pre-treatments for upgrading algal biomass in a biorefinery framework

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Keywords: (very dilute) acid hydrolysis; Algal biomass; Autohydrolysis; Biomass fractionation

The use of algae as a bioresource for biorefineries is an increasingly important topic within the blue bioeconomy framework. Both micro- and macroalgae have several advantages in their use when compared to the most established and common lignocellulosic biomasses. On top of the plethora of bioproducts, than can be obtained (biofuels, pigments, protein, amino acids, fatty acids, and speciality chemicals), these aquatic biomasses both present extremely interesting properties, especially their high productivity and carbon fixation potential than can sustain their sustainable exploration. Furthermore, microalgae, have the advantage of being able to efficiently aid in wastewater treatment and of having an unparalleled versatility to accommodate manipulations in their chemical composition, enabling the control of the production of the targeted compounds by changing the composition of culture medium and other abiotic culture parameters. Macroalgae, on the other hand, are very efficient bioremediation for oceanic habitats, and their ability to be produced in multi-trophic aquaculture systems is a strong logistic trait concerning their recollection and utilization.

To take full advantage of both these types of algae, in the biorefinery framework, it is imperative for the biomass to be fractionated and for all the different compositional fractions to be recovered and valorised, similarly to what has been extensively described for land plants. Unfortunately, many of the proposed fractionation strategies described in the literature for algae (e.g. Dominguez et al. 2019) are laborious, expensive, and tend to focus on a single fraction and/or added-value product forsaking considerable amounts of the produced biomass.

An alternative approach is the use of mild biomass fractionation pre-treatments, such as hydrothermal treatments (autohydrolysis) and dilute acid hydrolysis that has been proved relevant and viable methodologies for the production of added value hemicellulosic oligosaccharides with wide potential for market applications (Lopes et al., 2019; Moniz et al., 2016). Furthermore, these methodologies also present several operational and economic advantages, most noteworthy by facilitating the upgrade of the remaining fractions (polysaccharides, protein, ash, and others), but their use for upgrading algal biomass is not yet comprehensively studied.

In this work, the application of such methodologies in algal biomass treatment is dealt with in detail to provide the comparative data for the production of oligosaccharides from *Ulva lactuca* and *Scenedesmus obliquus*, as representative of macro-, and microalgae, respectively. Autohydrolysis and very dilute acid hydrolysis (0.5% sulfuric acid) were carried out at mild temperatures (140ºC-190ºC), exploring both the isothermal (up to 300 min) and non-isothermal operational modes. For the experiments carried out in simple batch reactors, data obtained show very promising results for both algae types, with the recovery of sugar being mainly in oligomeric form (84-97%), with maximum total sugar yields of 50 and 63% for micro- and macroalgae, respectively. The treatments carried out for *Ulva lactuca* testing fully controlled STR reactors, enable to reach high oligosaccharide yields of 10.6 and 16.6 g/100 g initial biomass for

autohydrolysis and dilute acid hydrolysis, respectively. At the optimal oligosaccharides production conditions, the residual solid fractions are enriched in protein and still present a relevant amount of potentially upgradable glucan.

These results provide a promising outlook on the innovative application of these pre-treatments to algal biomass, not only for the production of oligosaccharides and also for other applications e.g. biofuels, food and feed industries

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