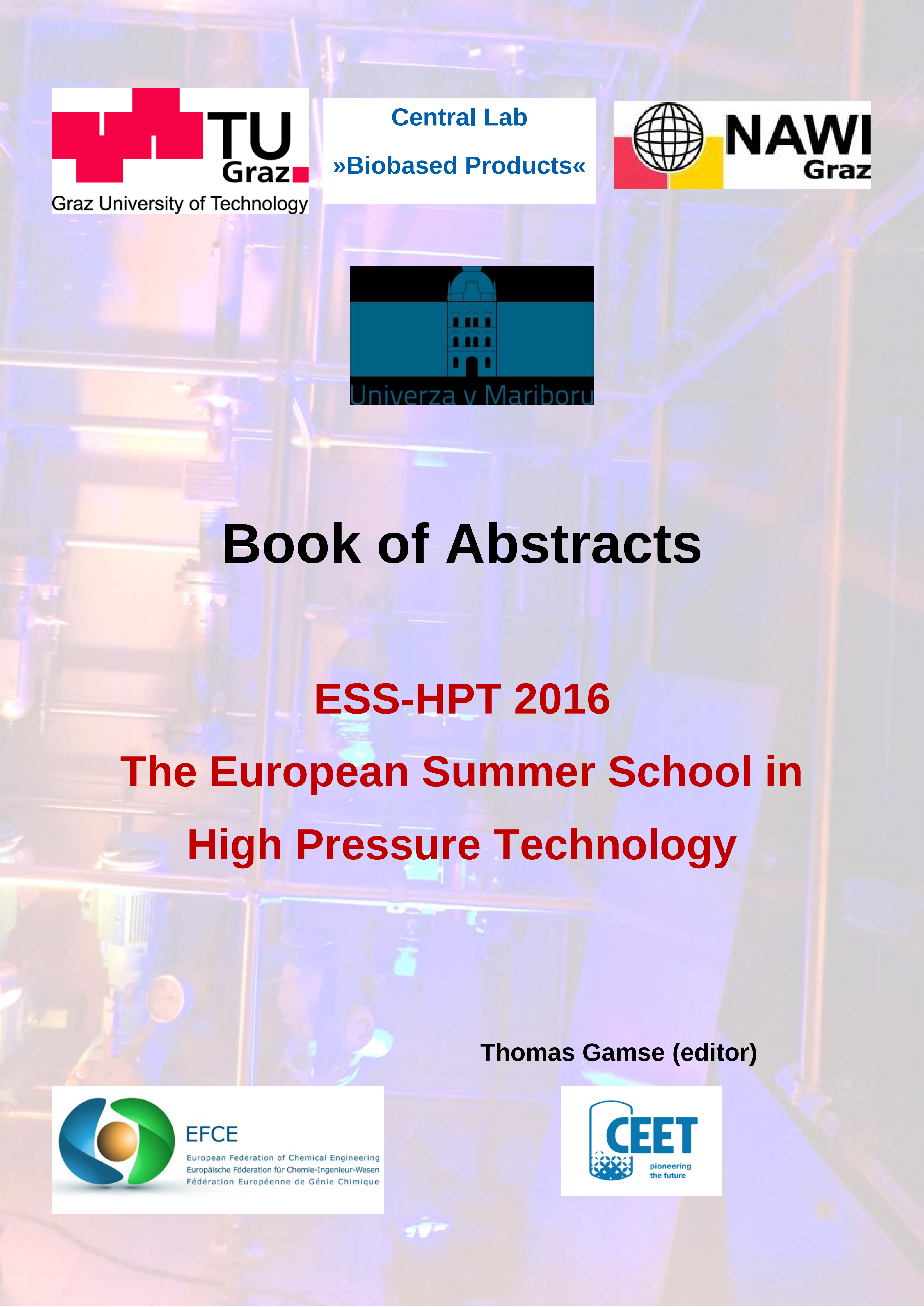

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Book of Abstracts

ESS-HPT 2016

The European Summer School in High Pressure Technology

Thomas Gamse (editor)

EFCE
European Federation of Chemical Engineering
Europäische Föderation für Chemie-Ingenieur-Wesen
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Impressum

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Editor: Thomas Gamse
Layout: Thomas Gamse
Cover: Thomas Gamse

© 2016 Verlag der Technischen Universität Graz

www.ub.tugraz.at/Verlag

ISBN (e-book) 978-3-85125-479-2

DOI 10.3217/978-3-85125-479-2

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Preface

The European Summer School in High Pressure Technology (ESS-HPT) is the continuation of many years of high pressure intensive courses. The history of this very successful series of courses started in 1995, when the first intensive course took place in Monselice, Italy. Most of these Intensive Courses were supported by SOCRATES and later Life Long Learning, as shown in following overview:

SOCRATES IP "Current Trends in High Pressure Technology and Chemical Engineering
- 1995 Monselice / Italy
- 1996 Nancy / France
- 1997 Erlangen / Germany

SOCRATES IP "High Pressure Technology in Process and Chemical Engineering"
- 1999 Abano Terme / Italy
- 2000 Valladolid / Spain
- 2001 Maribor / Slovenia and Graz / Austria

SOCRATES IP "High Pressure Chemical Engineering Processes: Basics and Applications"
- 2002 Graz / Austria and Maribor / Slovenia
- 2003 Budapest / Hungary
- 2004 Barcelona / Spain

SOCRATES IP "Basics, Developments, Research and Industrial Applications in High Pressure Chemical Engineering Processes
- 2005 Prague / Czech Republic
- 2006 Lisbon / Portugal
- 2007 Albi / France

Life Long Learning IP "SCF- GSCE: Supercritical Fluids – Green Solvents in Chemical Engineering
- 2008 Thessaloniki / Greece
- 2009 Istanbul / Turkey
- 2010 Budapest / Hungary

EFCE Intensive Course "High Pressure Technology - From Basics to Industrial Applications"
- 2011 Belgrade / Serbia

Life Long Learning IP "PIHPT: Process Intensification by High Pressure Technologies – Actual Strategies for Energy and Resources Conservation
- 2012 Maribor / Slovenia and Graz / Austria
- 2013 Darmstadt / Germany
- 2014 Glasgow / Great Britain

Unfortunately the financial support for these Intensive Programmes was cancelled within ERASMUS+. The EFCE Working Party "High Pressure Technology" decided in September 2014 to go on with this course in the form of a Summer School.

ESS-HPT "The European Summer School in High Pressure Technology"

ESS-HPT 2015	Maribor / Slovenia and Graz / Austria
ESS-HPT 2016	Maribor / Slovenia and Graz / Austria

The ESS-HPT will take place every year within the first 2 weeks of July at University of Maribor, Slovenia and Graz University of Technology, Austria.

All participants have to give an oral presentation and the abstracts of these presentations, which are peer-reviewed by the EFCE WP Members, are published in this book of abstracts.

The editor

Thomas Gamse
Organiser of ESS-HPT 2016

Many thanks to our sponsors, NATEX Prozesstechnologie GesmbH and Tourismusverband Stadt Graz,

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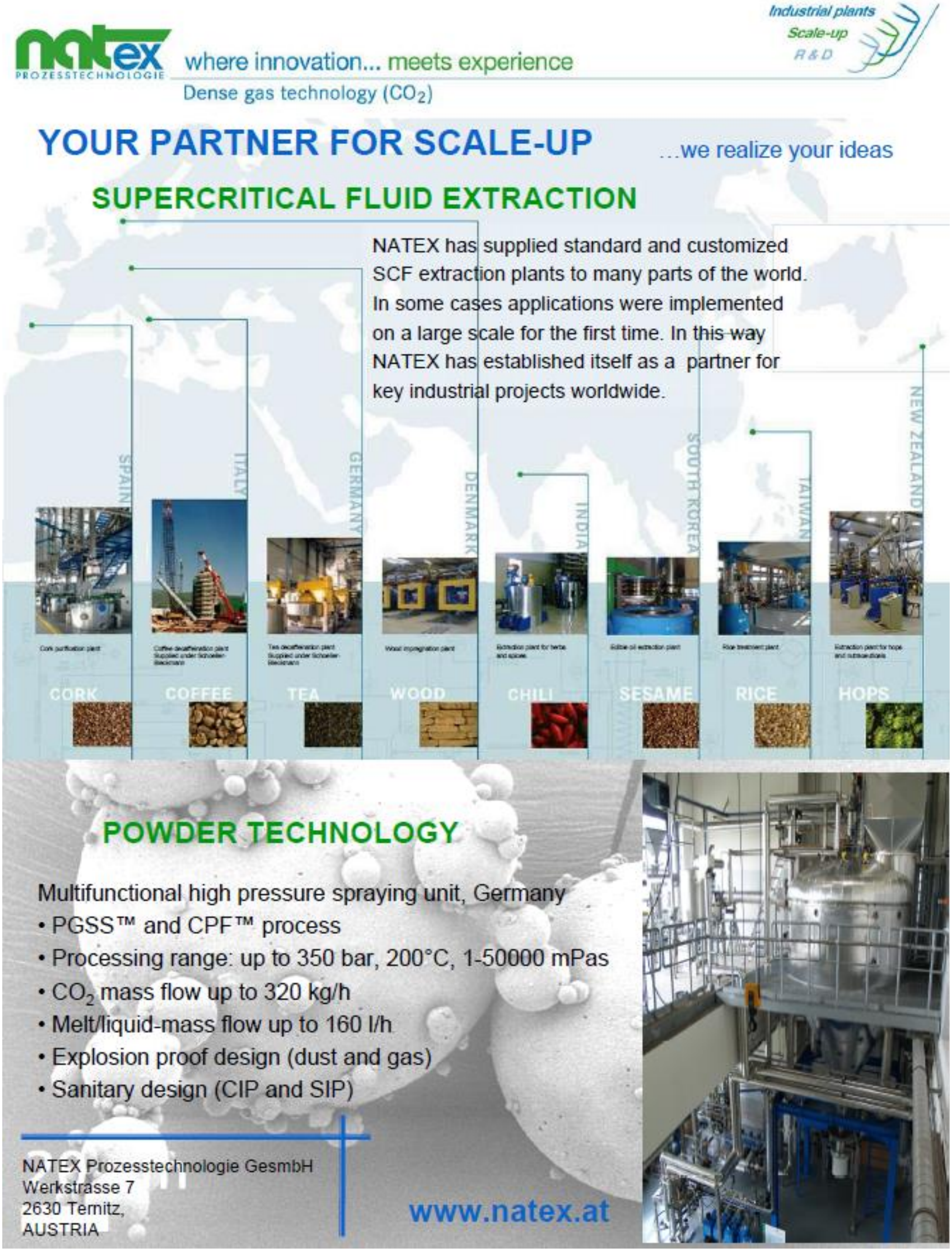
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Experimental and theoretical solubility studies on the high-pressure absorption of small molecules

Kirsten Grübel

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Introduction

The oxidation of organic compounds is an important branch of industrial chemistry for the production of basic chemicals which are widely used as major intermediates in commercial organic synthesis for fabrication of plastic detergents, paints, or as cosmetic and food additives. From an ecological and economical point of view it is evident to develop environmentally benign industrial technologies using harmless and renewable resources to overcome pollution of the ambience and to lower the costs in production by recyclable substrates. The aerobic oxidation of ethanol, utilizing O_2 from air as a benign oxidizing agent, became increasingly important due to the sustainable extraction of ethanol from biomass by fermentation of corn and sugar canes, emphasizing the role of ethanol as an environmentally friendly feedstock for the production of acetic acids and ethyl acetates [1]. Furthermore, oxygen is readily available and an inexpensive reactant bearing high atom efficiency and the catalytic oxidation of alcohols with pure oxygen as an oxidizing agent produces water as the main by-product. Unfortunately, little is known about the reaction mechanisms, the underlying thermodynamics and the role of O_2 on the selectivity of individual elementary reaction steps. Progressing computational methods to describe gas-solubility and phase behavior of complex multinary systems still rely on experimental data. But reliable data are not sufficient over a wide temperature and pressure range [2,3].

However, it is evident to gain a comprehensive knowledge on the underlying thermodynamics and the high-pressure dissolution properties of N_2 and O_2 into the liquid phase which will provide information on the requirements of the catalyst, help to optimize reaction conditions, and thus, improve efficiencies in industrial alcohol oxidation processes.

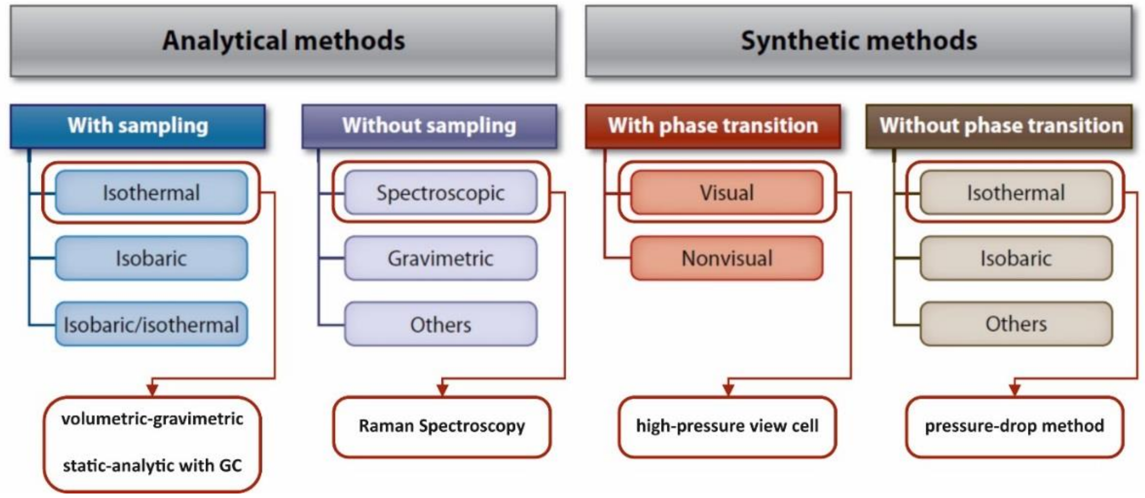

Figure 1: Classification of experimental methods for phase equilibria investigations [4]. Highlighted Methods show potentially suitable methods within the framework of this thesis.

Within the scope of this project, the solubility of the air components N_2 and O_2 in the volatile organic solvent ethanol will be analyzed under high pressure and temperature. The multitude of techniques to investigate phase behavior and gas solubilities under high pressure are divided into two main classes, characterized by means of the fixed quantities (see figure 1). The techniques where the composition of the overall system have been “synthesized” and the concentrations of the components are well defined, are embraced by the term *synthetic methods*. Investigations of the gas solubility and phase behavior of the system are conducted by altering pressure and/or temperature in the high-pressure device. In contrast, in the *analytical methods*, the composition of the system is unknown and has to be determined from samples withdrawn from equilibrium state of the system at constant temperature and pressure.

The variety of methods and experimental setups arise from the different properties of the system components and the thermodynamic value to be examined. The methods utilized in this project to study solubility properties of the gaseous air compounds (N_2 and O_2) in ethanol and the results of these measurements will be compared to each other, to validate the most appropriate method to achieve adequate experimental solubility data.

Experimental

First experiments were made according to the analytic-isothermal method with volumetric-gravimetric analysis of the withdrawn samples. The schematic representation of the experimental apparatus depicted in figure 2, shows the high-pressure autoclave, filled with degassed ethanol and pure nitrogen. The ethanol is degassed by a combination of gas substitution and vacuum refluxation for several hours. After attainment of the thermodynamic equilibrium at the desired temperature and pressure in the autoclave, the sample is withdrawn into a cooling trap in order to condensate the liquid ethanol content, which can be weighted afterwards. The total volume of the withdrawn sample can be recorded by a connected gasmeter. From these data and by means of the equation of state of nitrogen, the content of nitrogen dissolved in the pressurized ethanol can be calculated.

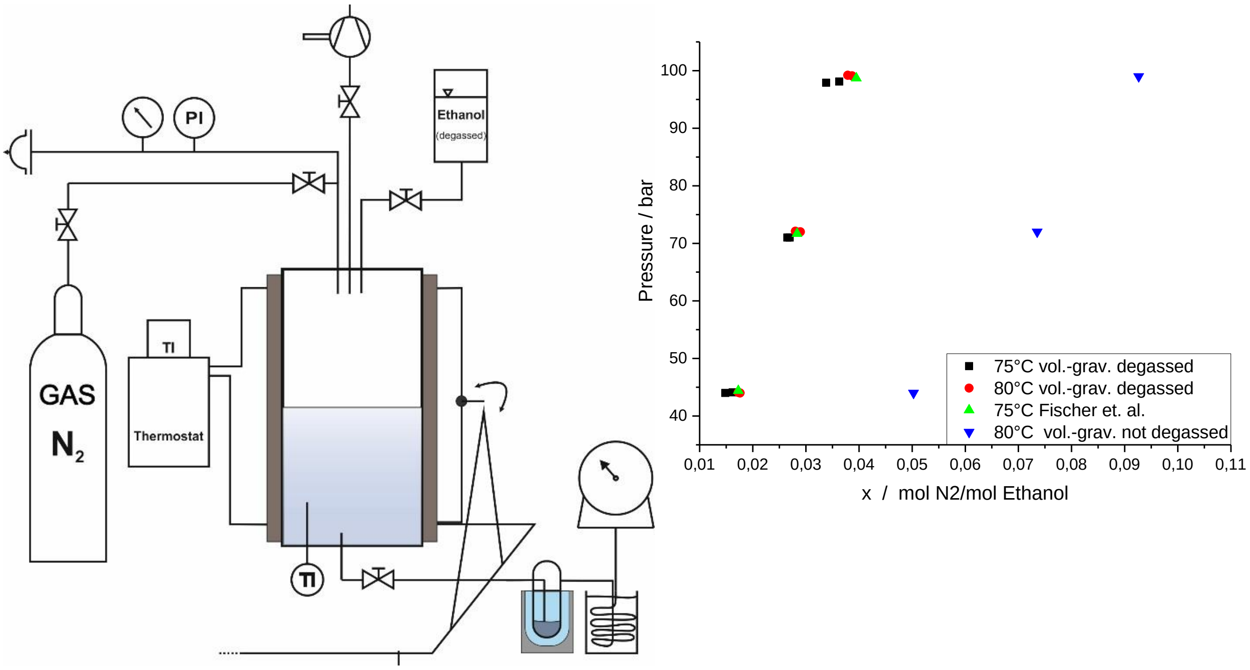

Figure 2: Schematic representation of the experimental apparatus for the analytic-isothermal method with volumetric-gravimetric analysis of the withdrawn samples; diagram depicts results of measurements with degassed and non-degassed ethanol in comparison to literature data from Fischer et al [5].

The selection of experimental data (75 °C and 80°C isotherms) in the diagram in figure 2 reveals that the utilized method, using *degassed* Ethanol as solvent, yields reproducible nitrogen in ethanol solubility data which are in good agreement with the rare reliable experimentally determined high pressure solubility data found in literature [5]. In further consideration, the isotherms show a distinct and linear pressure dependence and a slight temperature dependence of the solubility of nitrogen in ethanol, indicating an increase of the solubility by increasing pressure and/or temperature. The constructed apparatus for the analytic-isothermal method and the volumetric-gravimetric analysis of the withdrawn samples is a fast and facile method to repetitious quantify solubility properties of binary systems of gases in polar organic solvents.

Outlook

Examinations over a wider temperature and pressure range in the described apparatus will be performed, to gain a diversified data base for further investigations. Furthermore, the apparatus will be extended by a gas chromatograph in order to analyze more complex ternary and quaternary systems. This enables the quantification of oxygen solubility in organic solvents by pressurizing with air, which will be a further approach to describe the phase properties of the real technically used system in ethanol oxidation reactions.

Yet another method, which is promising to contribute to investigations of gas solubility in ternary and multinary systems, is Raman spectroscopy of pressurized systems in high pressure view cells. This technique comes into mind, especially when aqueous ethanolic solutions are considered to be analyzed. A comprehensive knowledge of nitrogen and oxygen solubility in ethanol, water and aqueous ethanolic solutions is beneficial in order to identify the role of oxygen in heterogeneously catalyzed aqueous aerobic alcohol oxidation and to design tailor-made catalysts for optimal reaction conditions and selectivity.

Acknowledgement

This work is supported by the Cluster of Excellence RESOLV (EXC 1069) funded by the Deutsche Forschungsgemeinschaft.

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Intensification of Batch-Distillation Processes for Production of Alcoholic Beverages

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Abstract

Methanol is formed during the production of alcoholic beverages, especially during the alcoholic fermentation of pomaceous fruits. It is hazardous to health and therefore an undesired congener in alcoholic distillates. At the CEET the separation of methanol in the foreshots is investigated experimentally as well as with common simulation tools. Besides methanol the separation of other harmful volatiles, e.g. acetaldehyde and ethyl acetate is investigated in order to gain high quality fruit distillates. The proof of concept was already shown in experiments and simulations.

Introduction

During production of alcoholic beverages, especially the alcoholic fermentation of pomaceous fruit e.g. apples and pears, formation of methanol is an issue that has to be considered because of its hazardeous properties. Since the middle lamella which binds adjacent fruit cells, consists of methylated polygalacturonic acid, i.e. pectin (Fig.1), the formation of methanol is unavoidable during natural fruit specific enzymatic digestion. Furthermore pectin methyl esterase is commonly added to fruit mash in order to gain an enhanced yield of ethanol [1,2,3]. While methanol in principle is not toxic to human beings, the effect of its metabolites formaldehyde and formic acid can cause severe injuries to health, e.g. blindness or acidosis and can even cause death. Thus the separation of methanol from distilled alcoholic beverages has to be explicitly taken into account.

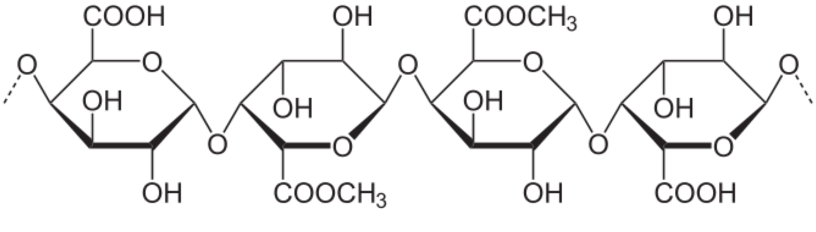

Figure 1: structure of pectin (partially methylated polygalacturonic acid)

Against the widely shared notion including the Austrian federal ministry of health [4, 5] it is not possible to separate methanol by distillation using common batch-distillation equipment although it can be separated from ethanol in the ternary system methanol/ethanol/water [6]. No matter if multi-stage columns or single-stage pot stills are used [7].

Simulation and experimental investigation

To investigate the separation of the ternary system methanol/ethanol/water by distillation

in batch mode, dynamic simulations with Aspen Hysys of single-stage batch distillation as well as the experimental investigation in laboratory scale were carried out.
The results of the simulation are depicted in fig. 2, which shows the mole fraction of methanol and ethanol, the distillate temperature and the liquid level in the still versus batch-distillation time. It can be seen that the ratio of methanol to ethanol in the distillate increases with distillation time which points out, that methanol cannot be separated in the foreshots [8].

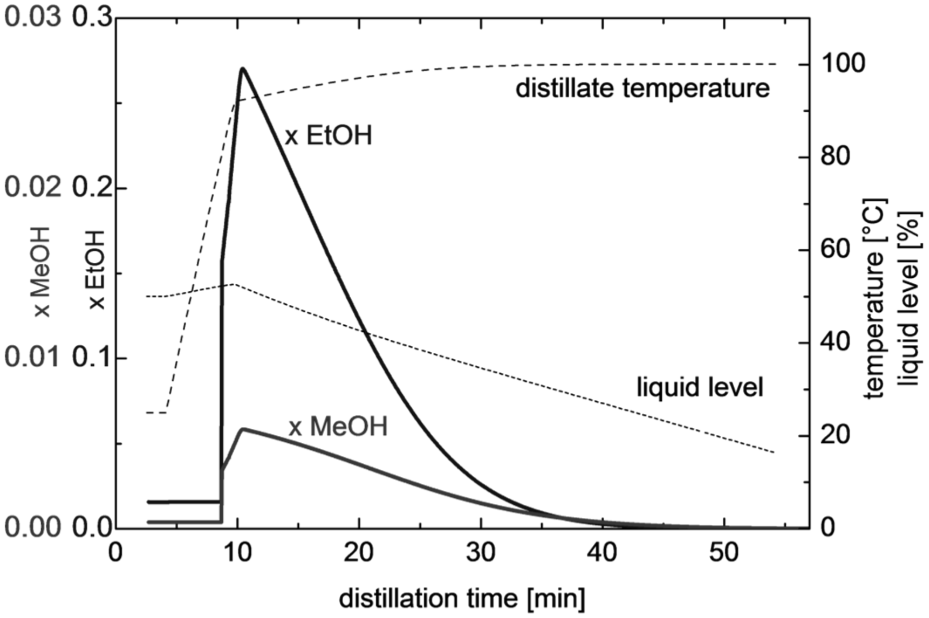

Fig. 2: Course of methanol and ethanol vs. batch-distillation time

The simulation results were validated in a single-stage laboratory batch distillation. As can be seen in fig.3 the ratio of methanol to ethanol is increasing with distillation time (= equivalent to distillate temperature) independent of the reflux ratio r. To separate methanol in the foreshots it seems obvious to increase the separation efficiency. For this reason the column was packed with Raschig rings and the separation was investigated under same conditions with variing reflux ratios. Fig. 4 shows that the ratio of methanol to ethanol is decreasing with increasing distillation time. Thus, methanol can be separated in the foreshots under appropriate conditions.

Optimization of the separation

At the CEET a new approach to batch distillation was developed to improve common pot stills used for the production of alcoholic beverages. Therefore an extension of common lyne arms was installed to a pot still, realized with an optional bypass, the so called “Löffler fork” which provides the possibility to route the vapor via an additional randomly packed lyne arm (fig. 5). Further the bypass lyne arm enables enhancement of internal reflux, due to a coaxial heat exchanger, which is used as dephlegmator. To accumulate methanol in the foreshotes the separation efficiency at the beginning of the distillation process is increased using the bypass lyne arm. After foreshots separation the common lyne arm is used to gain the heart cut as desired product, since the bypass lyne arm would increase the ethanol concentration but would decrease the flavourings in the distillate.

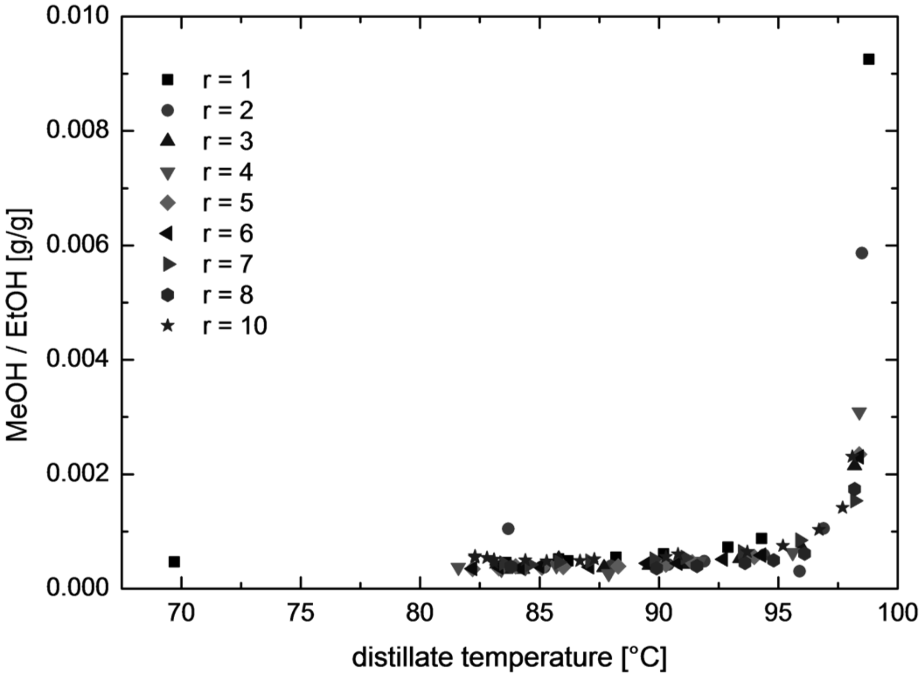

Fig.3: Ratio of methanol to ethanol vs. distillate temperature – laboratory-batch distillation column without internals

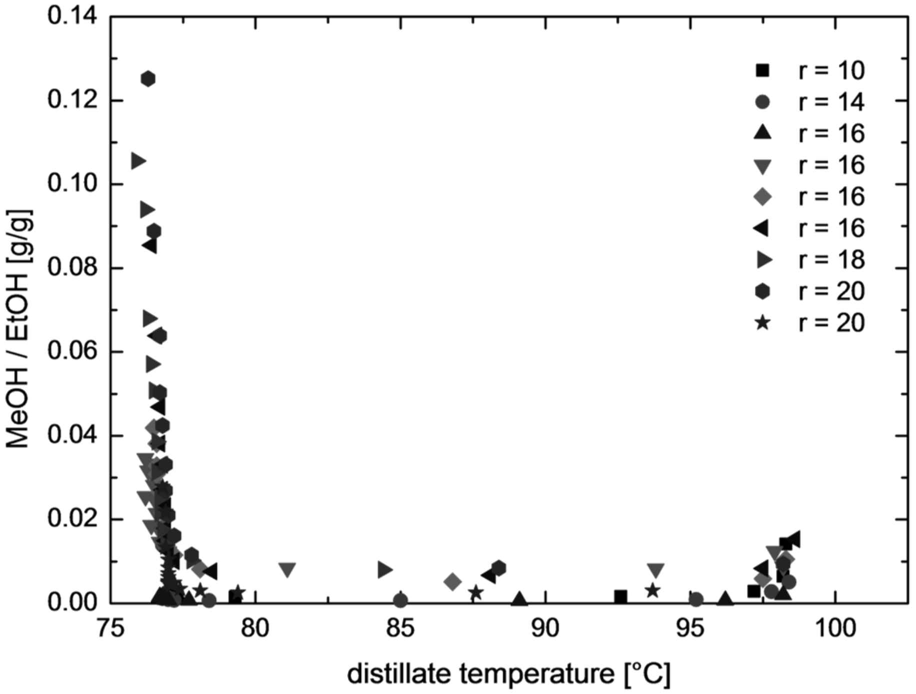

Fig.4: Ratio of methanol to ethanol vs. distillate temperature – laboratory-batch distillation column with Raschig rings

Fig.5: The „Löffler fork“: optional bypass of common lyne arms realized with randomly packed column

Outlook

Besides methanol other components hazardous to health, e.g. acetaldehyde and ethyl acetate, are formed during the alcoholic fermentation of fruit mashes [9, 10]. Furthermore higher alcohohls, so called fusel alcohols are formed during the fermentation of amino acids [3, 9]. Sufficient separation of these components from the target product has been investigated using synthetic systems in experiments as well as with common CAE software tools. Based on the results of the current research efficient and simple improvements of pot stills, especially in the field of application of small distilleries will be realized by constructive modifications of existing equipment.

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In situ Raman Monitoring of Dense CO_2 Drying of Biological Matrices

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Introduction

This work represents an early research stage during which an already widely used spectrographic technology, Raman spectroscopy (RS) ([1]), is flanked to an innovative drying process, dense carbon dioxide (DCO2) drying ([2]), the aim of the work is to prove RS effectiveness on on-line monitoring the water content of different test-samples during the DCO2 process. Fruits and piglet oesophagus were chosen as test–samples because they had been already selected within two distinct projects in which Prof. Spilimbergo and her group have been already involved in for a couple of years.

The first research project is Future food, an European project supported within the Horizon2020 Research and Innovation Programme, involving several European academic and industrial partners; it investigates dense carbon dioxide drying as a new process, addressing both the need for more ecologically sound food chain as well as the increasing wishes of European consumers for high quality minimally processed foods.

The second research project concerning oesophageal substitute for clinical purposes, has been founded by Ca.Ri.T.Ro. and Telea Biotech. The use of decellularized matrices in tissue engineering has become extremely significant for organ/tissue reconstruction.

Two different Raman apparatus have been used with suitable excitation wavelengths of 532 nm and 785 nm. Thanks to this study, Raman potential to on-line monitor drying kinetic curves has been demonstrated. These preliminary results could be exploited to identify the optimal drying operational conditions both at laboratory and industrial scale.

Experimental

Fig.1 shows the principal components of the “green” and “red” Raman apparatus used in the experimental measurements: a spectrometer (QE65000 Ocean Optics, spectral range from 535 to 705 nm for the ‘green’ and from 833 to 1148 nm for the ‘red’ apparatus), a laser source, lenses (A), a dichroic mirror (B) and a long pass filter (C). . The “red” Raman sensor (785 nm) was applied at a laser power of less than 500 mW measured at the sample surface, which was the maximum for that source. At this power, no degeneration of tissue was observed from the detected Raman signals and from the visual inspection of the fruit tissue. For the measurements with the green laser (532 nm), the power was reduced to a maximum of 250 mW.

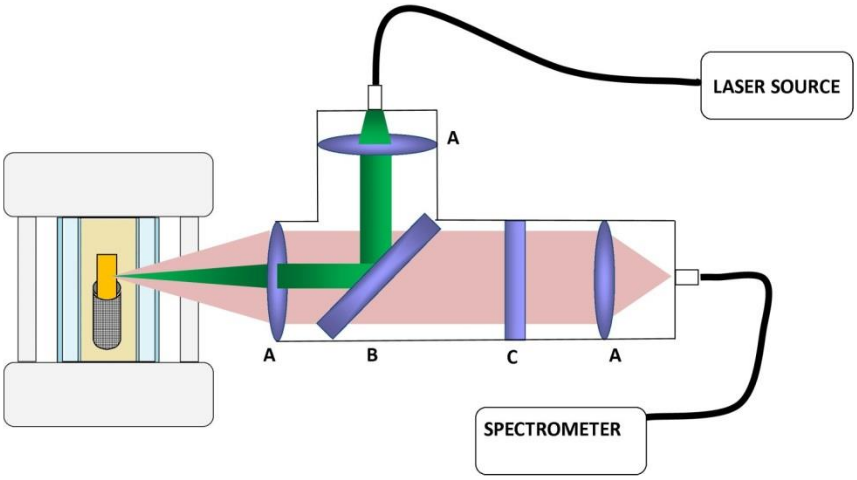

Figure 1:Raman apparatus scheme. Lenses(A),dichroic mirror(B))long pass filter(C)

Two fruit types were considered as test samples for DCO2 drying: mesocarp pieces of mango (Mangifera indica) and endocarp films of seedless persimmon (Diospyros kaki). The samples were positioned inside the sapphire vessel in a sample holder able to keep the sample still and to preserve the optical accessibility to the sample surface for the entire experiment. During all the drying experiments performed, 10 MPa, 313 K and 190 g min-1 were chosen as set-up condition for pressure, temperature and flowrate. To avoid the detector saturation with background disturbs, short acquisition time was preferred. For the “green” Raman sensor the spectra were acquired within a maximum of 10 seconds, while for the red sensor within a maximum of 2 seconds every 120s. After DCO2 drying, the samples were transferred in an oven (60°C) for 12h to ultimate the dehydration. As far as oesophagus drying is concerned, the objects measured were pieces of the cervical section of decellularized oesophagus from white domestic piglets, aged from 12 to 16 weeks and weighted from 25 to 40 kg provided by Institute of Child Health, University College London Fig.3.4. Two different approaches were used: in the first one the piece of oesophagus was dried directly by DCO_2, while, in the second approach, an earlier stage of water/ethanol substitution followed by the ethanol removal phase in the vessel chamber was performed. The use of two drying procedure was decided to probe RS with the same approach presented by Zambon et al. ([3]).

Summary

For wavenumbers larger than 2800 cm^{-1}, is possible to see that the Raman spectra have in both cases a peak representing the carbon-hydrogen (C-H) stretch vibration and a broad Raman band representing the water stretch vibration.

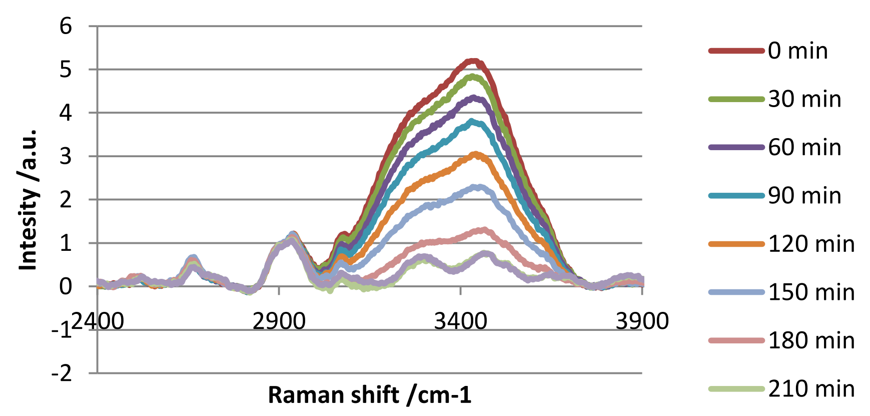

Figure 2:water band evolution during kaki drying

Fig 2 shows spectra acquired during the kaki dehydration process at increasing time with the the green apparatus. Each spectra was normalized with respect to the C-H peak to enable further calculation. On this purpose, the integral between 3110 and 3770 cm^{-1} was assigned to the Raman signal intensity of water (I_{water}) and the integral between 2800 and 3770 cm^{-1} to the Raman signal intensity of water plus C-H ($I_{water} + I_{C-H}$). Assuming that the number of C-H bonds did not change during the drying process and that it was representative of the dry fruit matrix, the ratio between I_{water} and $I_{water} + I_{C-H}$ is proportional to the ratio of the mass of water contained inside the fruit (m_{water}) and the entire mass of the fruit, given by the mass of the water plus the mass of the dry fruit ($m_{water} + m_{C-H}$).

$$\frac{I_{water}}{I_{water} + I_{C-H}} \propto \frac{m_{water}}{m_{water} + m_{dry\ Fruit}} \quad (1)$$

Weighing the mass of fruit slices before drying, after DCO$_2$ drying and after complete drying in an oven, m_{water} and $m_{dry\ Fruit}$ can be quantified, where a relative water content of 100% is related to the not treated fruit slice and 0% indicates that the sample after oven are completely dried. Fig.3 reports the drying kinetics computed from the ratio of intensities $I_{water}/(I_{water} + I_{C-H})$ expressed in term of relative water content. The drying curve shows an unexpected behavior compared to the usual thermal drying kinetics curve, which at the beginning presents a steep negative slope that flattens towards the end. The curves start flat, get steeper and get flat again. The shape of the initial “flat” part of the drying curve is related to the fact that in the first part of the DCO_2 drying mechanism, CO_2 has to penetrate inside the fruit matrix, and once it is penetrated, the more CO_2 is contained inside the fruit, the faster water can be detracted and so the curve becomes steeper. When some water is detracted, DCO_2 can penetrate into the fruit, enhancing the removal of the remaining water.

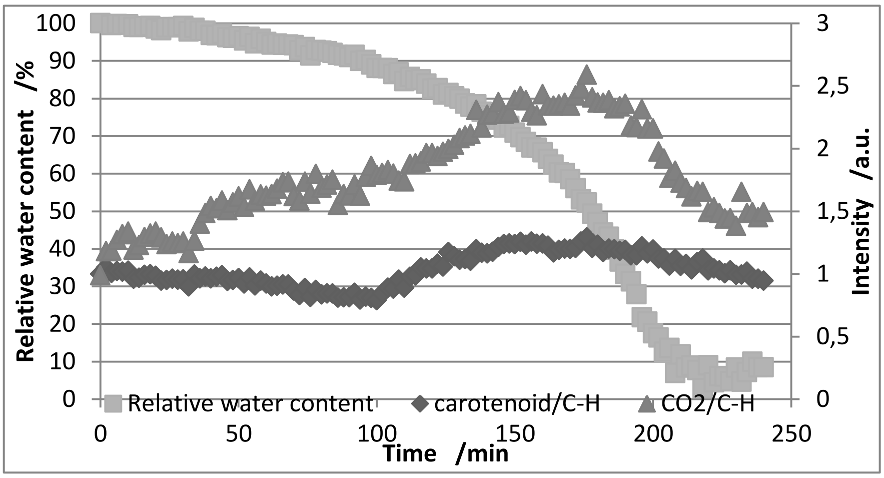

Figure 3: DCO_2 drying kinetics of kaki slice measured

At later drying times, the water concentration gradient between the inside of the fruit slice and the bulk DCO_2 gets smaller: this decelerates the removal of water again and flattens the drying curve. The oesophagus drying resulting drying curve is similar to the one presented by the fruit drying experiment. Moreover, the process time needed to reach a water relative content below 10% was similar for pieces with similar initial weight and total water content. In the case of oesophagus drying starting from ethanol saturation, the drying curve does not present a flat initial behaviour but a steep negative slope, probably because of the high ethanol-CO_2 mutual solubility, unfortunately, it was not possible to use the C-H peak as internal reference as in the dehydration experiments, since it was affected from ethanol.

Acknowledgment

The experimental studies have been performed at High Pressure Laboratory thanks to the stay in Padova of Ing. A. Bräuer, head of School of Advanced Optical Technologies (S.A.O.T.) at the Friedrich-Alexander-Universität in Erlangen-Nürnberg (FAU) invited by Prof. S. Spilimbergo.

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Dissolution/Hydrolysis and Repolymerization of Lignin Using Ultrafast Reactors in Supercritical Water

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Introduction

The pretreatment of lignocellulosic biomass is an important initial step in biorefinery operation. The pretreatment separates the principal components of biomass (cellulose, hemicellulose and lignin), degrades the extended polymer to smaller compounds, and occasionally causes other chemical transformations depending on the pretreatment method. Efficient biomass fractionation is actually one of the major challenges posed to the biorefinery, because the complex structure of the plant cell wall and the high crystallinity of cellulose make the feedstock recalcitrant to separation into its components. It is important to stress that the structure of the isolated lignin stream is dependent on the isolation method employed. Consequently, isolation/pretreatment methods that result in consistent types of lignin of high quality and purity are highly desirable (Zakzeski et al., 2010).

Lignin is a nature’s dominant aromatic polymer, derived from the radical polymerization of substituted phenyl propylene units. Characterization and structural analysis of lignin has become almost a subdiscipline of its own, with several textbooks written on the topic. The pretreatments methods for chemical analysis and studies based on NMR have allowed the identification and quantification of residues, groups and bonds in the structures of lignin. Although these studies have greatly improved our knowledge of the lignin, the proto-lignin structure in plants is still unknown (Ragauskas et al, 2014). The lignin structure depends on the biomass from which is derived. The lignin composition varies in the proportion of coumaryl, coniferyl and sinapyl alcohols. For example, the softwood lignin has around 90% of sinapyl alcohol, while the hardwood lignin contains the same proportion of coniferyl alcohol and sinapyl alcohol, exiting exceptions. Figure 1 shows a general structure of lignin.

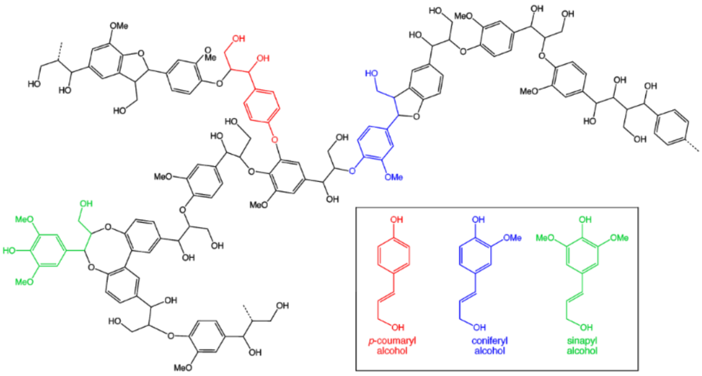

Fig. 1. Structure of lignin

The necessary pretreatments to carry out the lignin depolymerization and analysis break the structure into low molecular weight molecules. This change in the structure and the different structure of lignin depending on its biomass source, limit the knowledge about the depolymerization mechanisms.

The use of pressurized fluids has been proposed as a clean technology to integrate the depolymerization-reaction-separation processes. Particullary, supercritical water has proved to be a good solvent to process biomass feedstock due to its unique properties. Supercritical water (SCW) refers to the state of water under pressure and temperature conditions above its critical point (374 ºC, 22.1 MPa). Near its critical point, water drastically changes its physical properties by simply modifying the pressure and temperature. This behavior is a promising alternative to control the selectivity in chemical reactions. The main variations in the properties of water can be summarized as follows: (1) in the surroundings of the critical point, the dielectric constant decreases by increasing the temperature, increasing in this way the solubility of organic compounds and (2) the ionic product of water varies from 10^{-10} to 10^{-22} when changing the temperature from 300 °C to 400 °C at 25 MPa, changing the benefited reaction mechanism from ionic to free-radical. In addition, the hydrothermal processing presents the following advantages: (1) the direct use of the raw material regardless of its water content, which implies an important energy saving; (2) the same reaction medium can be used for the transformation of different biomass fractions; (3) mass transfer limitations can be reduced or avoided, thus reaction rates are faster (Cantero et al., 2015). Thus, these unique properties of water and the advantages of being a non-expensive and environmentally friendly solvent, make water an excellent reaction medium to hydrolyze lignin.

Experimental

The continuous pilot plant used to carry out the lignin hydrolysis is shown in Figure 2. It was design to operate up to 400ºC and 30 MPa using a sudden expansion micro-reactor (SEMR) (Figure 3). The lignin solution is continuously compressed and pumped up to the operation pressure of 25 MPa, remaining at room temperature until the inlet of the reactor. The reaction starts and stops by sharp temperature changes, in order to avoid heating and cooling slopes that could lead to uncontrolled reactions. Heating is achieved by mixing the compressed room temperature lignin solution with a stream of hot pressurized water in a T junction, in order to reach the target temperature of the reaction. This cooling method is more effective than the conventional heat transfer methods because the temperature change is instantaneous. This allows the precise evaluation of the reaction time without diluting the products. The reactor was thermally isolated. The short time needed to start and stop the reaction, along with the small reactor volume, make the micro reactor isothermal, allowing a constant and homogenous reaction rate through the whole reactor, which makes it possible to consider it as isothermal. The reactor outlet stream is driven to a heat exchanger (HE-1) after the decompression valve to pre-heat the supercritical water stream. In order to ensure the cooling of the sample, a cooler was set after HE-1. Key parameters in the conversion rate of lignin in SCW are pressure, temperature, and residence time. Thus, several experiments will be performed to evaluate the kinetic of lignin hydrolysis and for studying the depolymerization of lignin as a function of these operating parameters. The residence time is controlled by changing the inlet flow to the reactor and the reactor volume. The residence time will range from 4 ms to 1 s, the pressure in the reactor from 25 to 30 MPa, and experiments at different temperatures between 300 and 400ºC will be carried out.

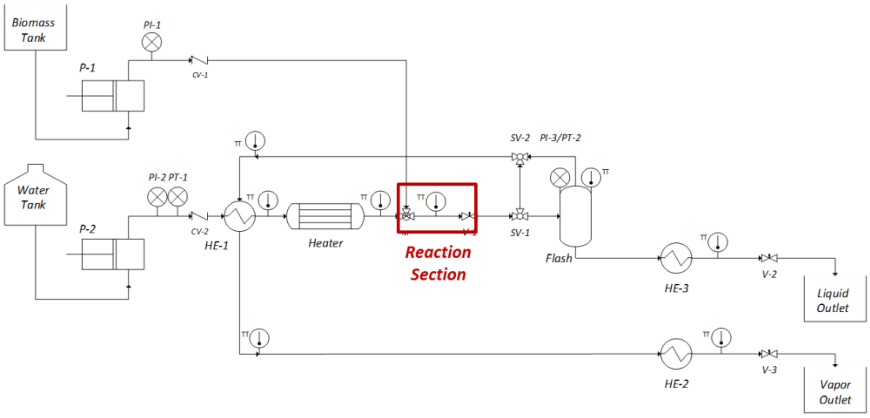

Fig. 2. FastSugars Pilot Plant. Ultra-rapid hydrolysis of lignin.

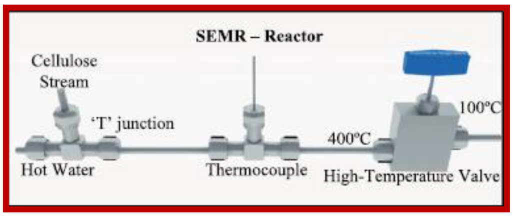

Fig. 3. Sudden expansion micro-reactor used in the ultra-rapid hydrolysis of lignin

Moreover, the study of the reaction mechanisms of lignin in sub and supercritical water will be carried out using a visual cell. In regard to the characterization and analysis methods, techniques such as FT-IR, NMR, GPC, HPLC, TOC, and elemental analysis will be carried out to characterize the different fractions obtained after the hydrolysis of lignin in sub and supercritical water and to determine the conversion of lignin and the yield of the hydrolysis process.

Summary

The pretreatment of lignocellulosic biomass to separate its main components (cellulose, hemicellulose and lignin) is an important initial step in biorefinery operation. The structure of the isolated lignin stream is dependent on the isolation method employed. Consequently, isolation/pretreatment methods that result in consistent types of lignin of high quality and purity are highly desirable. The use of pressurized fluids has been proposed as a clean technology to integrate the depolymerization-reaction-separation processes. Particullary, supercritical water has proved to be a good solvent to process biomass feedstock due to its unique properties. Although there are a lot of studies which have greatly improved our knowledge of the lignin, the proto-lignin structure in plants is still unknown. In this work, the kinetic study to describe the disolution/hydrolysis and polymerization of lignin in sub and supercritical water will be carried out, designing ultrafast reactors and using experimental devices in the range of times in which hydrolysis and polymerization take place, considering kinetic data, mass transfer, hydrodynamic and phase behaviour.

Acknowledgment

Thanks to the Spanish Ministry of Economy and Competitiveness for the Project CTQ2013-44143-R.

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Treatment of Biomass Waste with Subcritical Water for Obtaining Various Products

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Subcritical water, which represents water at temperatures between its boiling point (100 ˚C) and its critical point (374 ˚C) under sufficient pressure that keeps it in liquid state, is a benign and environmentally friendly processing medium, with many advantages compared to conventional techniques. The utilization of water for the processing of biomass represents the key for a sustainable chemical industry and a better opportunity for production of chemicals.

Conversion of cellulose is a highly attractive topic since it is a representative biomass compound that can undergo various chemical transformations at subcritical conditions to obtain various products. Within the processes of cellulose treatment with subcritical water, many different types of reactions occur. These include the dissolution and hydrolysis to primary hydrolysis products and their further repolymerization, condensation and the pyrolysis to form char, gases and oils. First products from cellulose are oligosaccharides. With further contact of the medium with the formed oligosaccharides however, the further degradation into simple monomer sugars, particularly glucose, is possible. Rearrangement or decomposition of glucose and other monomer sugars leads to the occurrence of various products, such as: 5-hydroxymethylfurfural (5-HMF), pyruvaldehyde, 1,3-dihydroxyacetone, glycol-aldehyde, glyceraldehyde, erythrose and 1,2,4-trihydroxybenzene. With further increase of temperature and reaction time, the isomerization, fragmentation and repolymerization of these small compounds into liquid oils, gases and char can occur. The yield of gases below the critical point of water is generally not high.

The main task of the present work was to focus on the description of the mechanisms of cellulose degradation under subcritical water conditions and the influence of reaction parameters on the reaction course, which shows the formation of various products. The experiments were carried out in a batch reactor at temperatures between 250 °C and 350˚C at different residence times. At the end of each experiment, water- soluble (WS), acetone-soluble (AS) and solid residue (SR) fractions were obtained. The main products formed in WS and AS fractions were determined by high performance liquid chromatography (HPLC).

The future work will be based on the research of cellulose containing materials, such as paper waste. This can be useful for industries, which do not utilize the by-products formed in the production facility. As a consequence this would eliminate the problems of their disposal, as well as increase the profitability of the process.

Change of Microstructural Properties of TiO_2 Thin Films at Crystallization in Supercritical CO_2 Environment

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Introduction

Titania films are materials of great interest for various applications such as the dye-sensitized electrodes used in solar energy conversion [1] or gas sensors [2]. TiO_2 forms three crystalline phases (rutile, anatase, brookite), of which anatase is most investigated because of its high photocatalytic activity. Due to its chemical stability, strong oxidation activity and non-toxicity, anatase can be used in environmental applications, such as self-cleaning surfaces and coatings [3] air- and water-purification [4] or for the decomposition of organic compounds [5]. The use of TiO_2 for a given application depends not only on the phase composition, but also on hydrophilicity, specific surface area, crystallinity and crystallite-size. These properties can be significantly influenced by the preparation method used.

Calcination (thermal treatment, TT) is the most commonly used method for transforming amorphous titania to anatase [6]. Nevertheless, this simple approach has some disadvantages, such as recrystallization, excessive sintration, crystallite growth and a decrease in the specific surface area. Furthermore, the properties or photocatalytic performance cannot be easily managed. Therefore, it is important to develop a method by which the structural, textural and physicochemical properties can be better controlled.

Matějová et al. utilized supercritical carbon dioxide with the addition of water and methanol to obtain the nanocrystalline and of pure titania with high specific surface area [7]. The advantage of this combination of solvents consists not only in their low price and availability, but mainly in their chemical universality to dissolve broad range of compounds showing different polarity.

Based on this knowledge, we utilized a combination of supercritical CO_2, water and organic solvents for the preparation of crystalline and pure nanostructured TiO_2 without any subsequent thermal processing. The effect of temperature (40–150 °C) and type of modifiers (water, ethanol, methanol, acetone) on microstructure and purity of

TiO_2 thin films were examined. The prepared thin films were characterized with respect to the (micro)structural properties by Raman spectroscopy. The most promising thin films were analyzed by means of X-ray diffraction to determine the crystallite size and the phase composition.

Experimental

Thin films of titanium dioxide were prepared by applying a solution on the soda-lime glass by dip-coating. The solution was obtained by sol-gel techniques controlled within reverse micelles of a nonionic surfactant Triton X-114 in cyclohexane. The molar composition of the titanium solution was as follows: cyclohexane : Triton X-114 : water : $Ti(OCH_2(CH_3)_2)_4$ = 11: 1:1:1.

Air dried glasses with deposited thin films were fixed in a steel holder and immersed in the high pressure column (volume 150 mL; inner diameter 30 mm) filled in the bottom part with glass beads serving as solvent flow distributors. The column was connected with stainless steel capillaries and placed into the air-conditioned box. The SFC experiments were carried out in apparatus Spe-ed SFE (Applied Separations, USA) whose schema is shown in Figure 1.

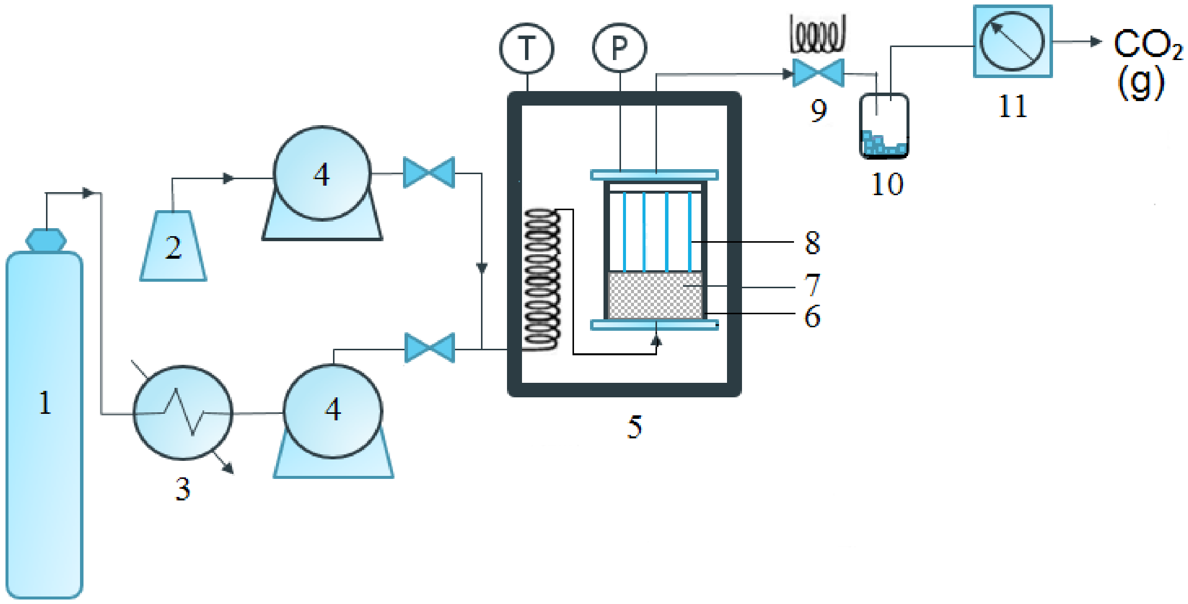

Figure 1. Illustration of experimental set-up: (1) CO_2 pressure bottle, (2) bottle with modifier, (3) cooling bath, (4) high pressure pumps, (5) air-heated box, (6) high pressure column, (7) glass beads, (8) glasses with deposited TiO_2 thin films, (9) micrometer valve, (10) separator and (11) gas meter.

The thin film crystallization was performed under a constant pressure of 30 MPa and temperatures of 40 and 150 °C by pure or modified $scCO_2$. As a $scCO_2$ modifiers water (30 wt.%), ethanol (10 wt.%), acetone (10 wt.%), methanol (10 wt.%) and the mixture of water+ethanol in ratio 1:1 (10 wt.%) were tested. The volume of $scCO_2$ passed through the high pressure column was 100 g. The effects of temperature, type of modifier and experimental design on crystallinity, crystal size and purity were investigated. SFC conditions are given in Table 1.

Table 1. Experimental design and conditions of supercritical fluid crystallization.

Experiment Nr.	Temperature, °C/$scCO_2$ modifier			
	1st step		2nd step	
1	150	-		
2	150	water		
3	150	ethanol		
4	150	water+ethanol		
5	40	ethanol	150	water
6	40	methanol	150	water
7	40	acetone	150	water
8	40	water	150	ethanol

Thin films prepared with pure $scCO_2$ (Exp. 1) were amorphous as expected. The crystallization of TiO_2 thin film was achieved by the treatment with 100 g of water modified $scCO_2$ at 150 °C (Exp. 2). Ethanol as $scCO_2$ modifier (Exp. 3) was ineffective for crystallization, however resulted in the removal of almost all precursor organic substances. At combination of $scCO_2$, water and organic solvent (Exp. 4-8) the best results in the terms of crystallization and the purity of thin films achieved.

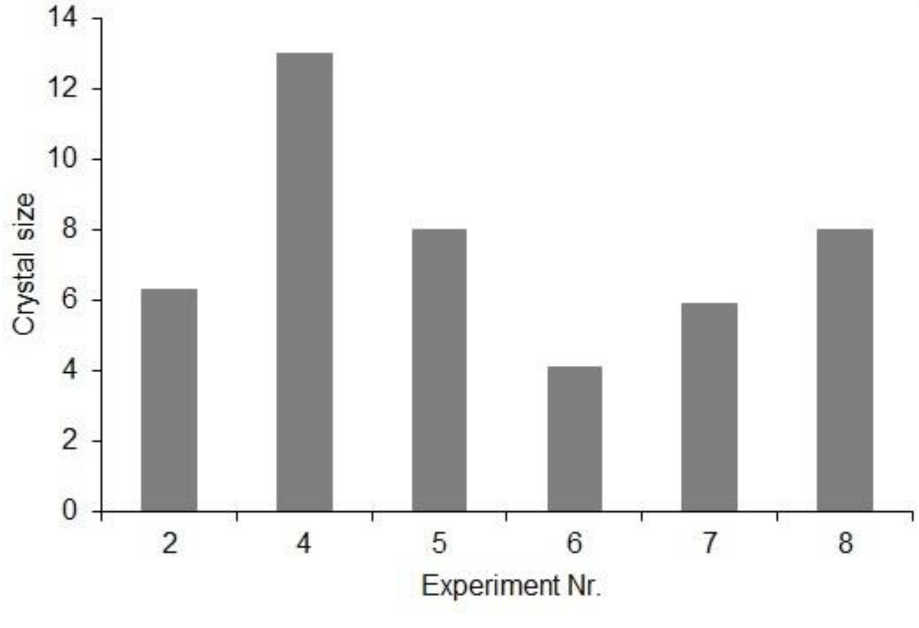

Figure 2. TiO_2 anatase crystal size of thin films processed by SFC by different conditions (see Table 1).

As apparent from Figure 2, if organic solvent as a modifier $scCO_2$ was used in the first step, the size of the crystal increased in the order of methanol-acetone-ethanol. The order of steps in the combined crystallization where in one step was $scCO_2$ modified by water and the second by ethanol (Exp. 5, 8) did not influence the anatase crystal size. When mixture of water and ethanol in a ratio of 1:1 (Exp. 4) as a modifier of $scCO_2$ in one step was used, the largest dimension of the crystals of 13 nm obtained.

Summary

We have successfully used pure and water modified supercritical carbon dioxide (SFC) in a flow regime to direct preparation of highly pure nanocrystalline TiO_2 thin films. The utilization of water (30 wt. %) as $scCO_2$ modifier at optimal SFC conditions - temperature 150 °C, pressure 30 MPa, amount of $scCO_2$ 100 g led to the direct crystallization of films and simultaneously, the purity of TiO_2 films was significantly improved. The addition of organic solvent to water modified $scCO_2$ resulted in the nanocrystalline TiO_2 thin films of high purity. The anatase crystals with the size in the range of 4.1 to 13 nm were obtained.

Acknowledgment

The financial support of the Grant Agency of the Czech Republic (project no.14-23274S) is gratefully acknowledged.

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Supercritical Fluid Extraction of Ethanol from Aqueous Solutions by the Use of Micro-Devices:
Study of the Influence of the Capillary Length

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Introduction

Ethanol (C_2H_5OH) has a large importance in the chemical industry and is mainly used for alternative fuel production, in the food industry, the pharmaceutical industry and for cosmetic productions. It is mostly produced by the sugar fermentation process; although it can be manufactured by chemical processes or as a by-product of some chemical processes[1]. However, the main challenge facing ethanol production is the separation of high purity ethanol, because the final product contains water[1].

Distillation is the most common process used to separate liquid mixtures. Nevertheless, some mixtures present properties, which make it difficult or even hinder the total separation of the components. Especially for systems with very close boiling points or systems with an azeotropic point, i. e. water and ethanol. In these cases, a liquid-liquid extraction can be used as an alternative separation process achieving better results.

Supercritical CO2 (scCO2) has many properties, which makes it an interesting solvent choice for the extraction of liquid mixtures.

Water and ethanol extraction using a supercritical fluid has several advantages over conventional separation processes: according to Furuta et al.5 the azeotropic point could be broken at certain extraction conditions (333.2 K and 10.1 MPa) [2].

In the last decades, micro devices have gained much attention as a promising alternative to conventional reactors, allowing higher mass-transfer rates and product yields and increasing process safety as well. A significant intensification of mass and heat transfer can be achieved, resulting in considerable reductions in operating times. Micro devices have been successfully applied to extraction, chemical synthesis and biotechnology[3].

Experimental and Results

The experiments were performed considering three different feed concentrations (10, 50 and 90 w% of ethanol) and with two different micro-devices: a tee-junction and a multi-lamination micro-mixer. The main aim was to study the influence of the capillary length between outlet of the micro mixer and inlet to the first separator on the extraction efficiency. In capillary systems, the residence time can be varied over a wide range without changing flow patterns. Frequently, in reaction studies with micro reactors altering the flow rate changes the residence time. In multiphase systems, the variation of the flow rate to alter the residence time results in a change of the flow patterns and it consequently changes the reaction conditions. Thus, it is much better to change residence time by varying the capillary length at a constant flow rate[3]. Therefore, three different lengths of 3, 20 and 65 cm were tested for each feed concentration.

K factor versus Residence time

Moreover, the efficiency of the mixing process and its influence on the extraction process, were analyzed with both micro-mixers. For the following results, **TE** is referring to the tee junction and **MM** to the HPIMM micro-mixer and the lengths **L1, L2** and **L3** have the respective length of 3, 20 and 65 cm.

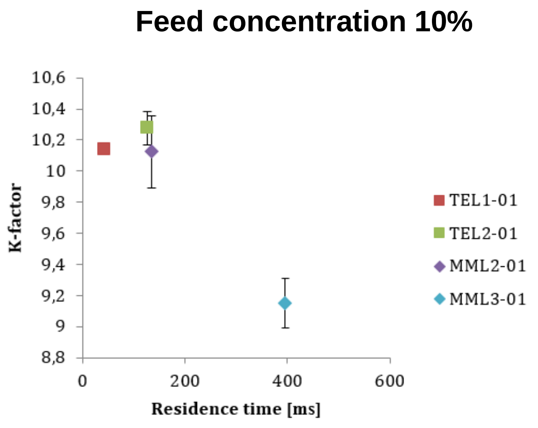
Feed concentration 10%

Figure 1: K- factor as function of residence time

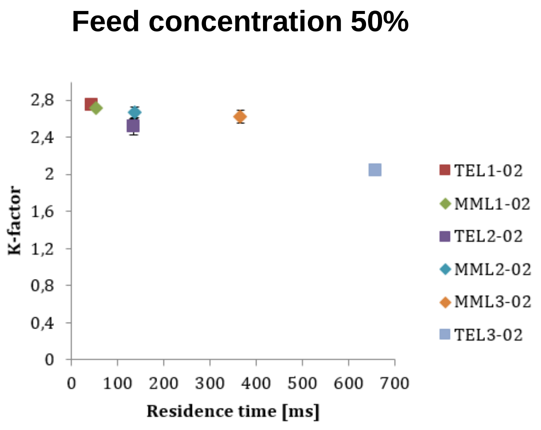
Feed concentration 50%

Figure 2: K- factor as function of residence time

From Figs. 1-3, it can be concluded that the influence of the residence time on the K-factor is negligible. Especially considering that in the experiments in which a more noticeable difference is observed (such as, experiments MMEL3-01 and TEL3-02) the solvent-to-feed ratio is lower than 16 due to problems with the HPLC pump. Moreover, the standard deviation was calculated for every experiment, however in most of the cases it was so small, that it is not shown on every result.

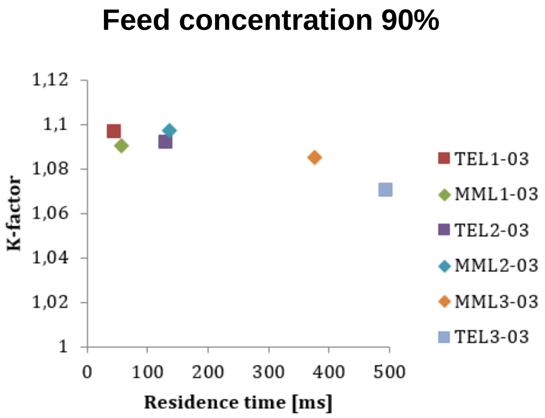

Figure 3: K- factor as function of residence time

Summary

In this research, the efficiency of an extraction process using the system water, ethanol and supercritical CO_2 were investigated. During the experiments, two different micro devices and three different capillary lengths were tested with three different feed concentrations, to study the mixing process and the effect of the residence time.

The experimental conditions of the process, such as temperature (333.2K) and pressure (10.1MPa) were chosen according to the literature, where it was stated that at those conditions it was possible to break the azeotropic point. The present solvent to feed ratio was chosen based on the literature and previous experiments.

For every sample obtained, the density was measured and afterwards the mass fraction of the ethanol was determined from tabulated data. Every result presented in this work is the average value of the several samples taken during each experiment.

By comparing the experimental results with a model of the phase behaviour of the ternary mixture, it was possible to see that for every experiment the equilibrium was achieved, even in those with a different solvent to feed ratio. Since *Peng-Robinson* was chosen as the equation-of-state the extract line of the model is not as precise as the raffinate line, because this equation is better used for a gas liquid equilibrium.

The residence time had a negligence influence on the results; however further experiments about the flow pattern are necessaries. Moreover, according to the efficiency, neither the micro-device nor the capillary length affected the overall efficiency of the extraction process in this work.

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Investigation of Cavitation Induced Degassing

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Introduction

Most liquid flows in technical applications are gas loaded. When the liquid pressure drops below the vapour pressure of the liquid vapour cavitation may occur. Since the solubility of a gas in a liquid depends on pressure and temperature, additionally a sudden pressure drop can lead to degassing. This process seems to be expedited by the cavitation process. Since gas diffusion is a slow process in comparison to cavitation these bubbles may stay in the system for some time. [1] Remaining gas bubbles in flowing liquids affect the performance of hydraulic systems e.g. due to reduction of the sonic speed. The aim of the present investigation is to understand the correlation between vapour cavitation and the effect of degassing in liquids. The experimental results of a detailed parameter study, in particular of the gas content, will be used for developing a model of an effective diffusion-coefficient for cavitating flows.

The occurrence of cavitation in a system depends on the inlet, outlet and vapour pressure, p_i, p_o and p_v respectively, of a system. A non-dimensional parameter, the cavitation number K, mentioned by Nurick [2], can be used to describe the flow conditions.

$$K = \frac{p_i - p_v}{p_i - p_o} \tag{1}$$

The tendency for the liquid to cavitate is increased by lowering K. For a constant inlet pressure the cavitation number decreases by lowering the outlet pressure. For every system and inlet pressure, a critical K describes the limit between cavitating and non-cavitating conditions. These critical cavitation conditions are related to the so called choked flow. [3]

Most orifice flows can be described by the Bernoulli equation. The mass flow $\dot{m}$ depends on the pressure difference, the cross-sectional area A, the density ρ and the discharge coefficient C_D.

$$\dot{m} = C_D \cdot A\sqrt{2\rho \cdot (p_i - p_o)} \tag{2}$$

Due to mass flow choking the mass flow curve can change to a constant mass flow for higher pressure differences. Iben et al. [3] called the transition point, from Bernoulli regime to choked flow regime, Critical Cavitation Point (CCP).

Experimental

A setup (figure 1) for experimental investigations of flow cavitation for variable flow conditions is constructed to observe the occurrence of cavitation depending on the mass of dissolved gas in the liquid.

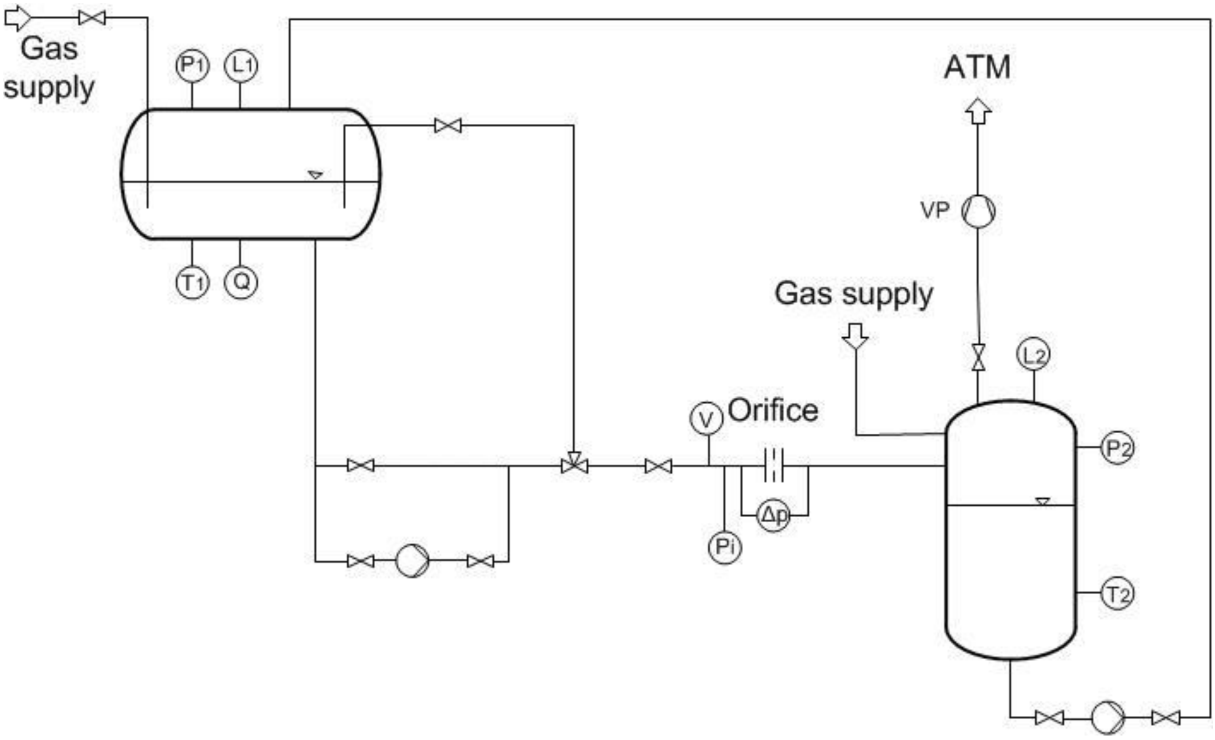

Figure 1: Experimental setup

The main components of the setup are two vessels designed for a pressure range from 0 to 10 bar. In the first vessel, water can be saturated with air at a known pressure and temperature. The pressure in the second vessel can be increased with air pressure or lowered by using a vacuum pump. A liquid flow through the connecting pipe (29 mm inner diameter) is induced by a pressure difference between these two vessels. The variation of the two parameters upstream pressure and downstream pressure can be realized independently. Pressure reduction in the pipe can be achieved with an orifice. Due to the pressure drop at the orifice, cavitation and air release can be observed for conditions beyond the CCP.

In a first step the hydraulic characteristics of the setup are identified. Therefore experimental data for mass flow curves using an orifice with a bore diameter of 3 mm is generated. For a fixed inlet pressure the outlet pressure is reduced. The pressure drop over the orifice and the mass flow are measured for different outlet pressures P_2. The results for the inlet pressure P_i = 7.2 bar are presented in figure 2. Squaring the ordinate values leads to a linear correlation between the mass flow and the pressure drop in the Bernoulli regime (see eq. 2).

The measurements are carried out three times to examine the reproducibility of the results. It can be seen that the squared mass flow increases linearly with increasing pressure difference until approximately 4.7 bar. For higher pressure differences, there is no further mass flow increase. The results lead to the conclusion that mass flow choking can be achieved with the presented experimental setup.

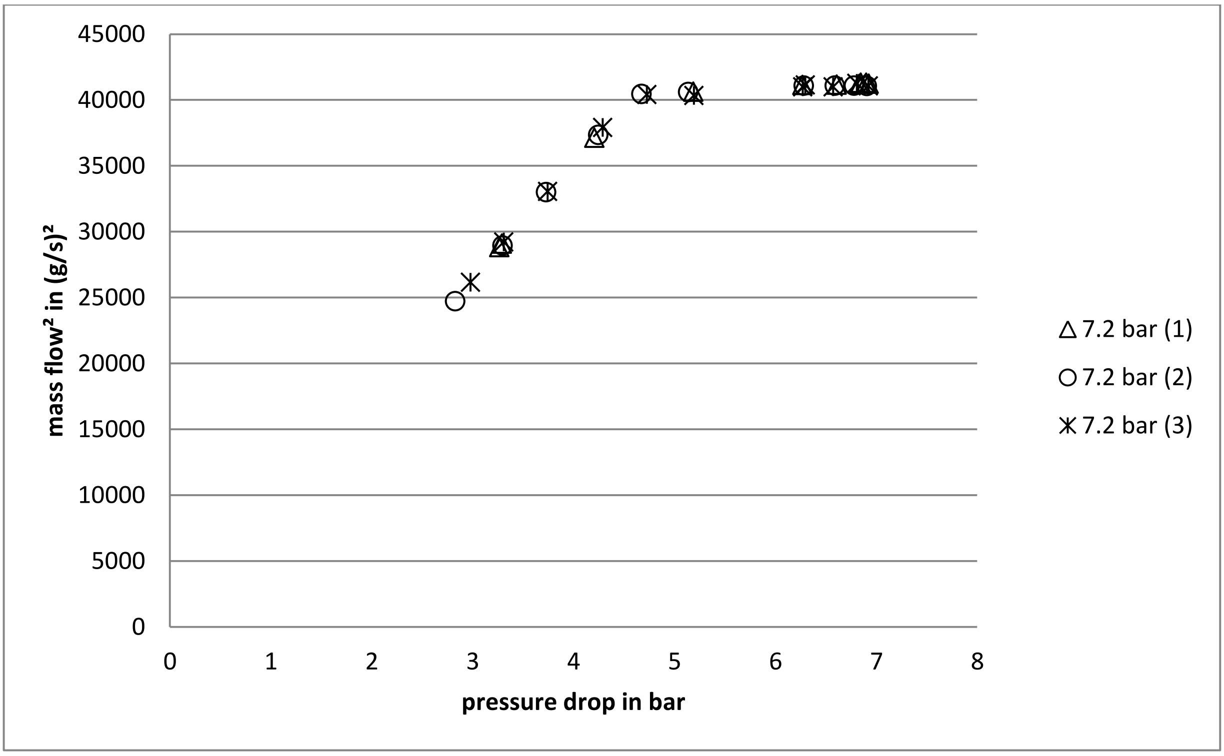

Figure 2: Experimental results for the mass flow curve (inlet pressure P_i = 7.2 bar)

Outlook

In further experiments, optical access to the flow will be realized using a Plexiglas pipe. This section can be installed upstream or downstream of the orifice position allowing the observation approximately 500 mm of the pipe. Recordings with shadowgraphy imaging are supposed to give information about the volume fraction of gas and vapour in the flow. Due to detailed monitoring of the dependence of gas/vapour fraction on dissolved gas mass in the upstream liquid, a connection between degassing and cavitation may be found.

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Influence of the Transfer to Polymer on the Molecular Topology of LDPE

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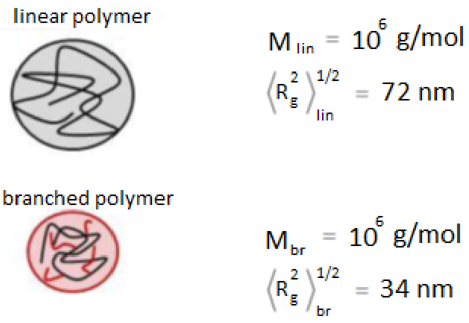
Low density polyethylene (LDPE) is mostly used for packaging, but also for many products in automotive, electronics and constructions. Its European demand is 17.2 % relating to all plastics [1]. LDPE consists out of only one monomer so the different macroscopic properties of the product are given through its microscopic structure. This implements its branching density consisting of short and long chain branches (SCB and LCB) and the molecular weight distribution. The molecular topology is mainly influenced by the so called transfer to polymer reaction step, which is part of free radical polymerization kinetics. Through this reaction an active radical transfers its radical functionality to a “dead” polymer and reactivates it so a long chain branch grows on the reactivated position.

In the industry simulation is a common tool to predict the polymer topology. It is a fast and inexpensive possibility to analyze the influence of parameter changes on the products properties. A stochastic approach to describe the reaction sequence for each generated polymer molecule is called Monte Carlo method. The reaction kinetics are correlated to reaction step probabilities in order to follow the evolution of the exact polymer topology. Every reaction model has to be validated using experimental data. This work focuses on the optimization of the reaction step of the transfer to polymer reaction. In order to analyze the topology gel permeation chromatography (GPC) with a multi-angle light-scattering detector was used. This way the radius of gyration $R_{g,\text{branched}}$ for each mass fraction was analyzed (Fig. right[3]) and correlated to the radius of gyration of a linear molecule with the same molecular mass $R_{g,\text{linear}}$. The ratio $R_{g,\text{branched}}/R_{g,\text{linear}}$ is called contraction-factor and was compared to the simulated contraction-factor. This value is correlated to the branching density of the polymer and for this it can be used to compare topologies of the PE-polymers.



In order to validate the simulation by the experimental data different evaluation methods [2] (Zimm and Debye) were compared using the molecular weight distribution, average molecular weight M_w and the radius of gyration R_g. Even though both methods use the same mathematical and phenomenological assumptions, they do not deliver the same results. The unique difference in this methods is the plot on the y-axis. The R_g and M_w is determined by fitting the detector data polynomial, whose order also influences the resulting values. In order to determine the most reliable combination of evaluation method and fitting order several samples have been analyzed using different flow rates and comparing the resulting calculated values. The comparison to simulation data has been done with the most reliable combination of an evaluation method and fitting order. This work has shown, that using a preferred position for the transfer to polymer is representing the experimental data in a better way and its changing has an influence on the polymer topology. This shows that the Monte Carlo Simulation is a good way to investigate kinetic and topological effects on the product.

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Nanoencapsulation of Liquid Lipophilic Bioactive Compounds by Supercritical Fluid Extraction of Emulsions

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Introduction

Bioactive compounds used in the pharmaceutical, cosmetic and nutraceutical or food industries present low solubility in water and high sensitivity to a great variety of physical and chemical factors which could cause loss of biological functionality, chemical degradation and premature or incomplete release. For these reasons, these compounds require frequently innovative technical approaches, such as the encapsulation of the bioactive compound within secondary material (polymeric shell) which protects and stabilizes the core. Up to now, many encapsulation techniques like spray drying, extrusion, solvent evaporation or solvent extraction, among others have been developed. However, these conventional techniques still present several disadvantages (particle sizes bigger than 20 µm, use of organic solvents, high temperatures or vaccum) which affect product quality [1]. On the other hand, the scale up of these technologies is difficult.

Since the 80’s, multiple processes of particle formation with supercritical fluids have been developed to overcome the drawbacks of the conventional processes. Supercritical Fluid Extraction of Emulsions (SFEE) is one of the latest supercritical fluid technologies for micro- and nanoparticle formation [2]. It is a combination of the conventional emulsion precipitation methods with the supercritical antisolvent processes. This new technique uses supercritical CO_2 to extract rapidly the organic phase of an emulsion, in which a bioactive compound has been previously dissolved. By removing the solvent, the solute precipitates, generating a suspension of particles of that compound in water. Produced particles have controlled size and morphology, due to the use of the emulsion, which acts as a template and to the fast kinetics of the supercritical CO_2 extraction. So far, most of the work done was related to solid pharmaceutical compounds encapsulated in PLGA (poly(lactic-co-glycolic acid)). Nevertheless, this method is a promising technology to produce nanoparticles encapsulating bioactive compounds for the nutraceutical and food industries.

Experimental

The first step to produce nanoparticles by SFEE was to generate an O/W emulsion, in whose organic phase the bioactive compound and the polymer were previously dissolved.

The SFEE process could be understood as a liquid-supercritical fluid extraction and consequently bubble, spray or packed columns can be used for nanoparticle production by this technology. Fig. 1 shows the available supercritical fluid extraction equipments for SFEE.

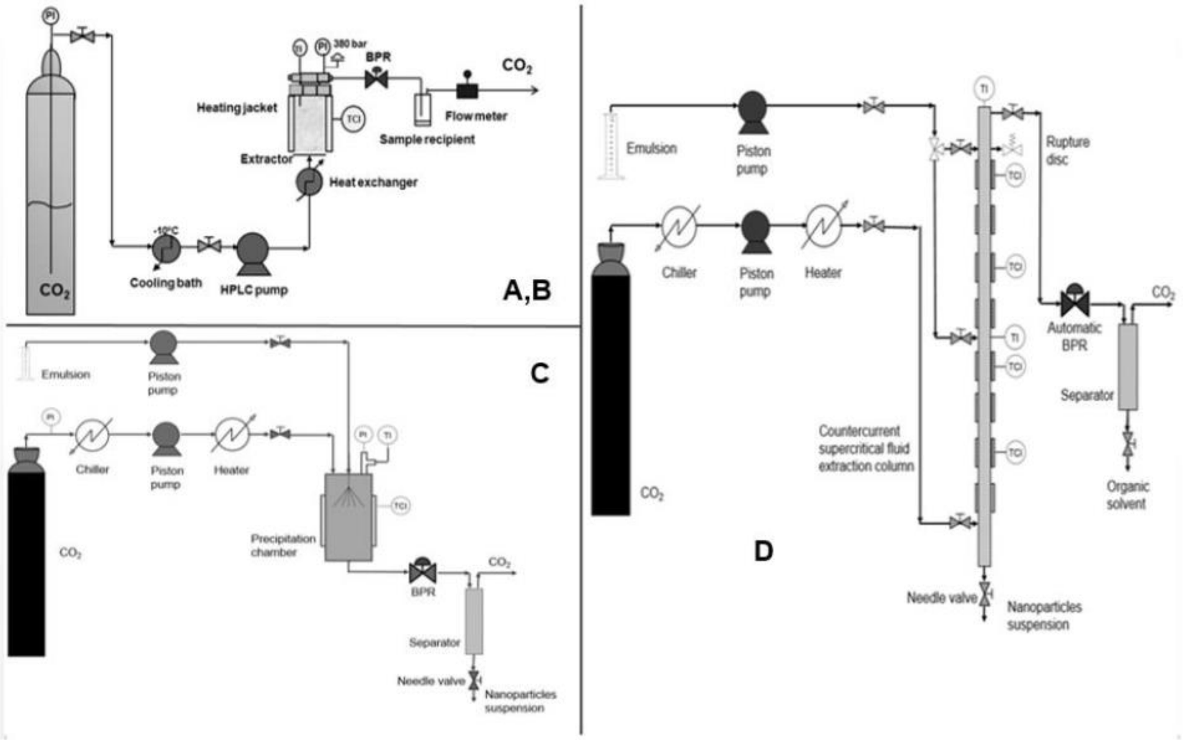

Fig. 1. Supercritical fluid extraction equipments for SFEE. A, B, bubble column with or without gas redistributor; C, spray column; D, packed column.

In order to carry out the process, the emulsion and a CO_2 stream were contacted under certain pressure and temperature conditions to extract completely the organic solvent without extracting the bioactive compound. Particle formation was based on the precipitation of the encapsulating polymer when the organic solvent was extracted from the emulsion by the supercritical CO_2.The result of the process was a suspension of nanoparticles in water. A scheme of this process is shown in Fig. 2.

Finally, in order to evaluate nanoparticles quality, it was necessary to study the following parameters: encapsulation efficiency (amount of bioactive compound entrapped inside the particle), usually measured by HPLC; particle size distribution, studied by dynamic light scattering; residual concentration of organic solvent was measured by headspace gas chromatography; and morphology was studied by electron microscopy.

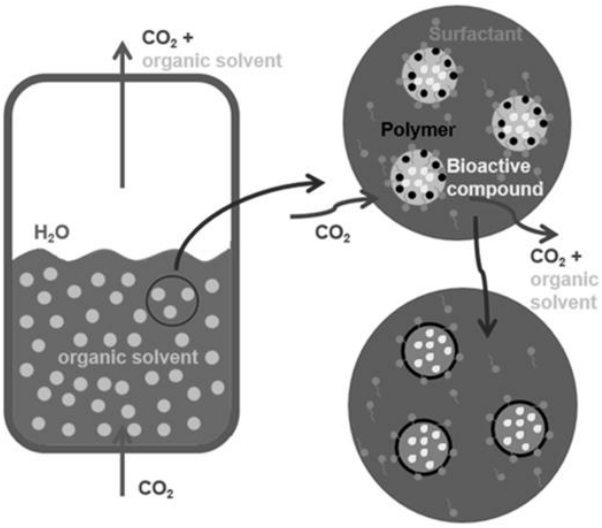

Fig. 2. Scheme of the fundamentals of nanoparticles formation by SFEE.

<u>Encapsulation of vitamin E in polycaprolactone by SFEE</u>

The encapsulation of vitamin E in polycaprolactone was done using this technology [3].

An O/W emulsion was formulated using vitamin E as a model compound, polycaprolactone as a polymer, acetone as organic solvent, Tween 80 as a surfactant and water. This emulsion was subjected to SFEE and the nanoparticles suspension was recovered and analyzed.

Obtained particles had very high encapsulation efficiency (around 90%), narrow particle size distribution (polydispersity index around 0.24-0.54) and sizes at the nanoscale (between 8 and 276 nm), which could be controlled thanks to the emulsion formulation. The residual concentration of organic solvent was very low (50 ppm), adequate for food and pharmaceutical use. Morphological analysis showed non-aggregated, spherical nanocapsules. In Fig. 3 images of the obtained particles with an emulsion (A) and with a microemulsion (B) are shown. Stability test showed that nanocapsules remained unchangeable even at long storage times (6 and 12 months).

Nonetheless, such promising results were obtained using a bubble column where only 5 g of emulsion were treated and long operation times (240 min) and high amount of CO_2 (100 kg/kg) were required. In order to increase production capacity and reduce CO_2 consumption, other configurations, spray and packed column, were experimented [4]. The spray column did not provide enough contact time to extract completely the acetone and particle quality was affected due to the depressurization in the nozzle. The best results were obtained with the packed column, where CO_2 consumption was highly reduced without compromising particle quality. Even if an optimization on packing type, height and hydrodynamics was still needed in order to increase acetone extraction yield.

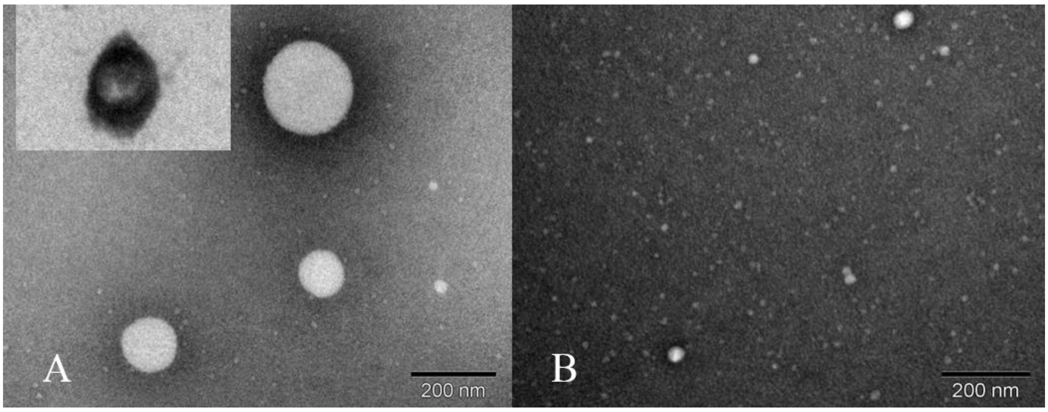

Fig. 3. ***A***, TEM image of the nanoparticles obtained from an emulsion, on the upper left corner a cut nanoparticle of vitamin E is shown. ***B***, TEM image of the nanoparticles obtained from a microemulsion.

Summary

Supercritical Fluid Extraction of Emulsions is a new particle formation technology with supercritical fluids, useful for the nanoencapsulation of liquid lipophilic compounds for the food or nutraceutical industries.

Acknowledgment

Cristina Prieto thanks the Complutense University of Madrid for an UCM predoctoral grant.

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Development of a Lignin Recovery Process Targeting its Formulation and Application into Consumer Goods

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Abstract

Lignocellulosic materials are the most promising feedstock as natural renewable resource, and due to this, offer many advantages as a substrate in a biorefinery. For the profitable utilization of these materials under the biorefinery concept, all three constituents – cellulose, hemicellulose, and lignin - must be converted into valuable products. Regarding to this, the first two components have a clearer fate in the market since they can be readily converted into biofuels and bulk chemicals, however; lignin´s potential remains under development since it was considered as a waste instead of a valuable by-product. Methods for lignin production are very diverse, and thus are the physicochemical and biochemical properties of the obtained ligneous products; most common processes are Kraft and Sulfite processes from the paper industry and Organosolv, Steam Explosion, and Liquid Hot Water (LHW) in pilot scale. The operating conditions of these processes can drastically affect the molecular weight, chemical structure and functional groups in the generated lignin product; thus, affecting its homogeneity and particle size distribution (PSD), both desired properties for further industrial applications. PSD is of great interest since it has a direct impact on biological behavior and technical properties, for instance on the bioavailability, flowability, and solubility in pharmaceutical excipients, and on the adhesive strength in adhesive masses.

Current LHW process at the Institute of Thermal Separation Processes of Hamburg University of Technology does not generate lignin with a homogeneous and/or desired PSD. Follow-steps should be incorporated to the current process in order to homogenate the lignin particle size, targeting the functional properties of homologous materials in the market. Additionally, an option is to skip current 5 steps process to reach homogeneous PSD in lignin and use the spray drying technology and gas anti solvent methods, both allowing to dry solutions and suspensions and form particles in a single-step process (see figure1). Moreover, the final characteristics of the product can be tailored depending on the desired applications.

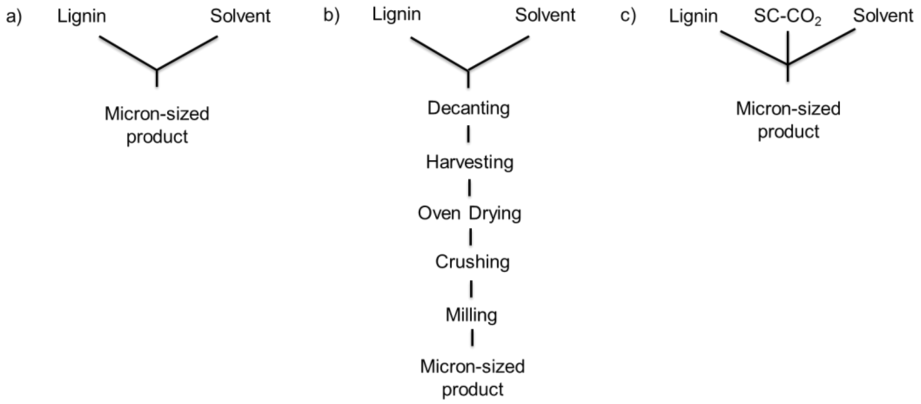

Figure 1. Number of steps in the different lignin-drying and particle formation methods. Spray drying (a), conventional drying and comminution (b) and gas anti solvent method (C).

Spray drying is the process in which the product of interest is dissolved in a common solvent (mostly water) and the resulting solution is atomized into a drying chamber through a nozzle (see figure 2). The hot drying gas is introduced to the chamber that evaporates de solvent, thus; reducing droplets to dried solid particles.

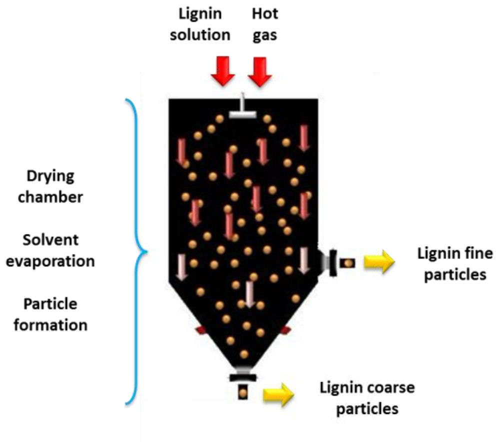

Figure 2. Schematic spray drying process for the particle formation and drying of lignin in a single-stage process.

As for lignin, conditions for drying ranging from 180-200 °C of temperature, nozzle pressures of 1-1.5 bar and feeding rates of 75-100 mL/min are being tested and first results showed that two major fractions are obtained in the case of lignin, a coarse fraction (D90: 82 µm) and fine fraction (D90:28 µm) when treated at 190 °C, 1.1 bar and 65 mL/min. Further studies have to be done in order to optimize the parameters and tailor the final characteristics of lignin according with the final intended application. The parameters mentioned above are believed to have the greater effect on the particle formation and thus; in the particle size, water content and morphology.

In relation to the use of supercritical fluids for the gas anti solvent process, this latter takes advantage high dissolution power of supercritical CO_2 (SC-CO_2), and its tunable solvation properties. With high solubilities of supercritical fluids in organic solvent, a volume expansion occurs when the two fluids make contact, leading to a reduction in solvent density and parallel fall in solvent capacity. Such reductions cause increased levels of supersaturation, solute nucleation and particle formation (see figure 3). First attempts using EtOH as solvent have render lignin particles with a particle size of 40 µm; however, more research is needed to tailor the properties of lignin in SC-CO_2, as the evaluation of different solvents, as well as variation of pressure and temperature during the process.

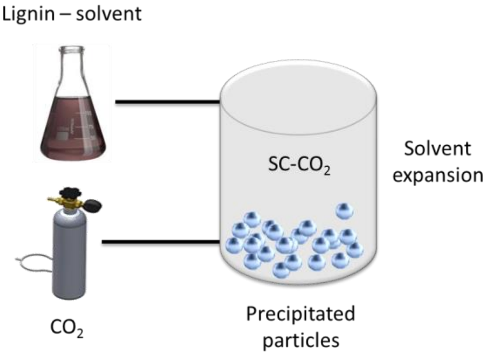

Figure 3. Gas anti solvent process for lignin particles formation.

The ambition of evaluating these two methods is to prepare powdered lignin with directed or targeted properties, especially particle size, in a single stage and scalable process that simultaneously eliminates many of the limitations of current particle preparation methods.

Alkaloid Concentration Control in Cat's Claw (*Uncaria tomentosa* [Willd.] DC) Extracts with Conventional Dynamic Maceration

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1 Introduction

In recent years much more interest for the natural food productions has grown up due to the pursuit of healthy eating, and the increasing demand of natural health products. Cat's claw (*Uncaria tomentosa* [Willd.] DC) is a woody vine from Amazonas and is a traditional medicinal indian herb. It is recommended for the treatment of arthritis and as general immune system booster. Anticancer and antiviral effects are also reported, which makes it well known around the world. The medical effects of the plant are due to pentacyclic alkaloids (POA), triterpenes, flavonoids and tannins, which can be found in the bark. The use and marketing of the herb and its' extracts are legal in many countries (e.g.: USA, Austria), while in other countries such as Hungary, application of cat's claw is restricted, due to its high alkaloid content. The aim of the research was to control the alkaloid concentration in the extracts with conventional extraction methods, which can be the basis for further product development and standardization.[i]

2 Experimental

During our research milled cat's claw bark was used and the following solvents were applied for extraction: water, ethanol, 50:50 water – ethanol with and without citric acid. Conventional dynamic maceration was performed, alkaloid concentration and the yield corrected with citric acid were selected as target parameters.

Citric acid (E330) is a typical component of the final products in food industry, and in nutraceutical supplements as an acidity regulator additive and preservative effects. We chose the citric acid to control the pH of the extraction solvent, because the acid pH is beneficial for extracting the basic alkaloids.

At first the effect of drug – solvent ratio was investigated, where the 1 g drug:20 ml solvent ratio has shown the best results, due to the filterability of the mixture, in addition the extract concentration was high.

Regarding extraction temperature 70 °C is the most effective, because at this temperature both alkaloid concentration and corrected yield were the highest. The extraction time in 0.5 to 2 hours range didn't show any influence on the extraction efficiency, furthermore three steps were sufficient. Effects of the solvent composition and citric acid concentration on alkaloid concentration and yield were studied by a 3^2 experimental design (Figure *Figure 1.*).

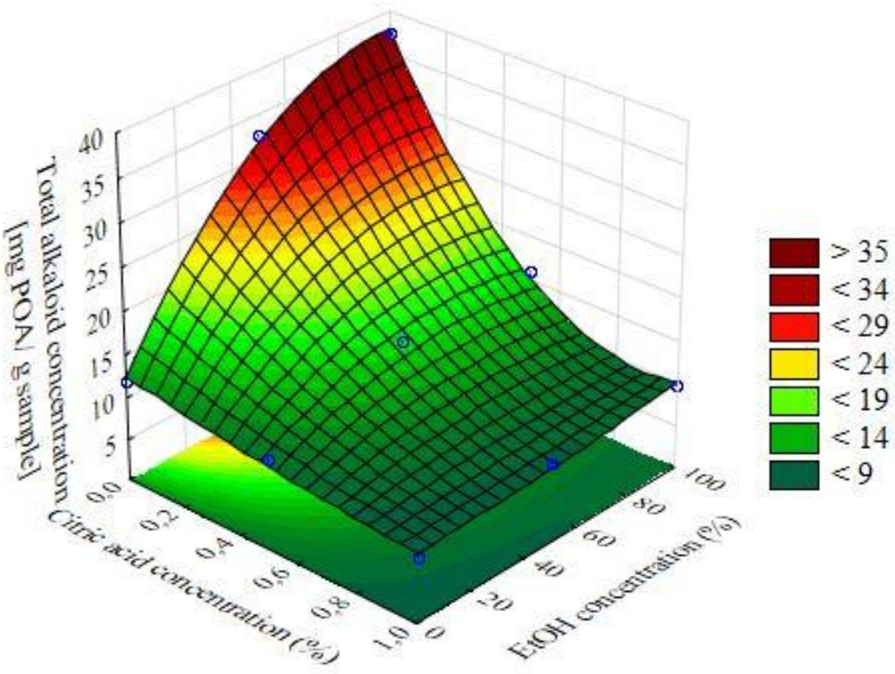

Figure 1. The total (1.+2.+3. steps) alkaloid concentration as function of citric acid mass percent and alcohol volume percent. Three step extraction (1 h mixing each, 1g:20 ml drug to solvent ratio, 70 °C)

Considering the alkaloid concentration in the extract, the highest value was obtained with 100 % ethanol and 0 m/m% citric acid. In addition, with the application of citric acid the yield increased, but the alkaloid concentration decreased. If more concentrated citric acid solution is used in extraction solvent, it results in more citric acid in the extract after evaporation of the solvent. Thus dilution effects have a major role, alkaloid recoveries (mg alkaloid in the extract/ g dry raw bark) were less emphatically affected. Based on the experimental design it can be observed that by using citric acid the alkaloid concentration can be efficiently controlled within 5 – 37.3 mg POA/ g extract. The highest alkaloid concentration can be achieved by using citric acid free absolute ethanol. The maximal corrected yield (excluding citric acid mass) was achieved at 1 – 1.2 mass percent citric acid content in 50:50 water – ethanol solvent.

In Figure 2. the antioxidant activities of the different extracts (free radical scavage activity in terms of inhibition concentration 50) are plotted.

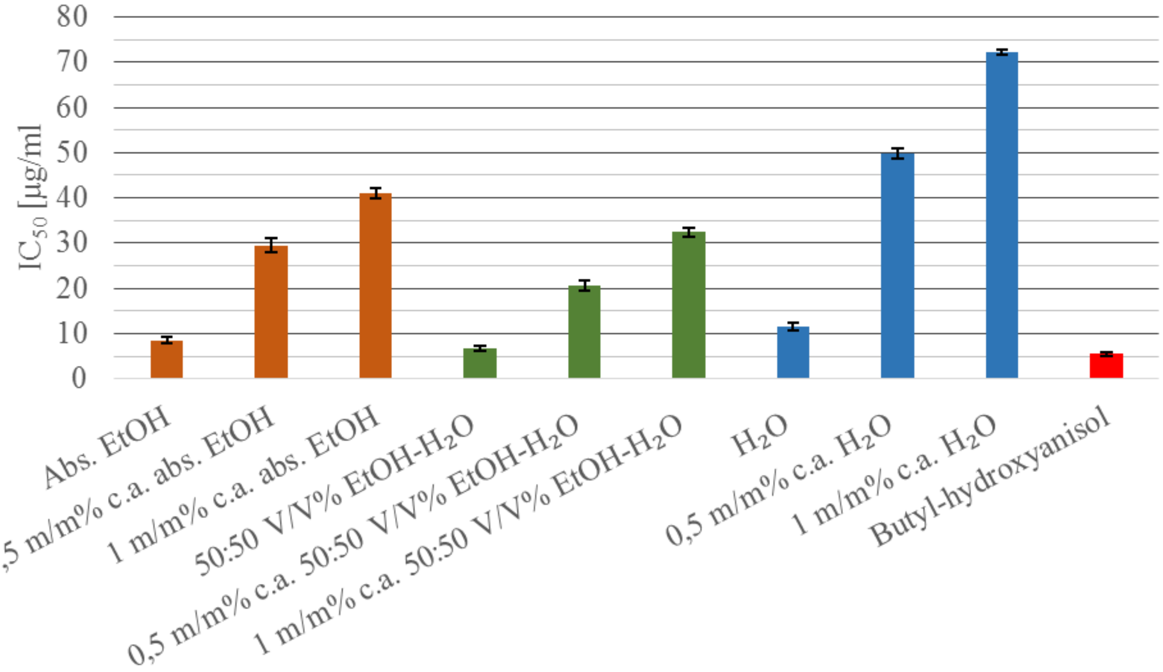

Figure 2. The 3^2 design extracts' antioxidant activity (70 °C, 1h, 1. step, c.a.= citric acid)

A synthetic antioxidant molecule, butyl hydroxyanisol (BHA), was used as reference. By increasing citric acid concentration in the extraction solvent the antioxidant activity is reduced (the IC_{50} increases). It is interesting to note, that in the food industry citric acid is considered as an antioxidant molecule, although mainly to maintain the color of the products, but our results show, that the citric acid content extracts have lower scavenger ability, than the citric acid free extracts. Furthermore we can say, that the 50:50 water-ethanol solvent' extract has almost the same antioxidant ability (IC_{50}= 6,7 ± 0,5 µg/ml) the BHA (IC_{50}= 5,55 ± 0,4 µg/ml).

3 Summary

We can control the alkaloid concentration in the cat's claw extracts with different ethanol and citric acid containing solvents suitable for the production of nutraceutical products. The highest yield and concentration was found on 70 °C extraction temperature. The range of the alkaloid concentration, where we can control is 5 – 37.3 mg POA/ g extract.

Some of the extracts possess almost the same free radical scavenger ability (IC_{50}= 6,7 ± 0,5 µg/ml), as the synthetic reference components (BHA: IC_{50}= 5,55 ± 0,4 µg/ml).

The results of the investigations may allow an alkaloid standardized product development at relatively low cost and easy to implement with industrial scale technique.

4 Acknowledgement

The research work was supported by Marie Curie DoHiP European Project (Training Programme for the Design of Resource and Energy Efficient Products by High Pressure Processes). E. Székely thanks the János Bolyai Research Fellowship of the Hungarian Academy of Sciences.

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Development, Extraction and Improvement of Phytochemicals for Dye Applications by Non-Polluting Technology

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Introduction

Phytochemicals are biologically active chemical compounds, present in some plants, and a very attractive and studied area of modern chemistry because of their health benefits.

Polyphenols, Carotenoids, Glucosinolates and Isothiocyanates are secondary metabolites of plants (with remarkable properties as antioxidant and/or natural dye activities) and examples of phytochemicals investigated because of their potential application in pharmaceutical, cosmetic and alimentary products.

However, these types of compounds have elaborate structures. This implies that their synthesis reactions are complicated and expensive. In this case, a viable alternative is extraction. Particularly, a large amount of potential sources of phytochemicals is wasted daily in residues from the food industry, fruits and vegetables that are naturally rich in activity compounds. Recovery of these compounds would add additional value to the process, but it can be complex due to the properties of these waste matrixes. For this reason, it is necessary to develop efficient methodologies for extraction and to improve their application.

Moreover, recent studies have demonstrated the efficiency of antioxidants compounds for treatments or prevention of diseases like atherosclerosis, cholesterol and diabetes. However, these compounds have the disadvantage of not being soluble in water. Improving bioavailability of these compounds require application of formulation processes like Supercritical Anti Solvent (SAS), Particle Gas Saturated Solvent (PGSS), Supercritical Fluid Extraction of Emulsions (SFEE) and microencapsulation, which have been show to be quite efficient. Additional advantages of supercritical extraction methods are related to lower processing time, the high yield and the mild conditions of temperature, which reduces degradation.[1]

In this context, this project proposes to perform: plants selection (prioritizing native plants of Brazilian flora); extraction of compounds (such as polyphenols, carotenoids, flavonoids and anthocyanins) by microwave assisted extraction; formulation of compounds by encapsulation with SAS and PGSS techniques; and application essays, which takes into account the effects of dissolution of these compounds in the body by in vitro tests, studying their behavior and biological activity.

Plants selection

Classified as superfood, Açaí berry shows interesting characteristics as a potential phytochemical source.

Açaí is a black-purple berry obtained from Euterpe Oleracea mart. palm, typically found in Amazon Rainforest and strongly present in the diet of Brazilians, especially in north and northeast regions. This product is actually expanding out to North and South America and Eastern Europe.

Although the fruit provides health benefits, it also causes environmental problems. During the season, a processing company produces 40 tons of residue per day. Until now, the environmental impact has been minimized by the use of the waste seed of the fruit as ceramic oven feed or handicraft to perform bijouterie, but these applications do not make use of the valuable phytochemicals present in the waste.

Extraction techniques

In literature, it is possible to find a large number of extraction methods; certainly, one extraction technique or another will be more adequate depending on the characteristics of the sample (procedure, type, size, among others characteristics). Maceration is a simple and classic methodology that has been successfully applied to obtain bioactive compounds when combined with Microwave-Assisted Extraction (MAE) intensification. This procedure is actually in use by the High Pressures Processes (HPP) group of the University of Valladolid to extract polyphenols and anthocyanins from similar samples.

Maceration is normally performed using a dried plant as a matrix. In the case of large-scale matrix, the current literature recommends to decrease the size of granules to obtain a more homogeneous raw material. The starting material is placed in the extractor glass to soak with a mixture of water and organic solvent. The process takes place under room temperatures, an advantage when it is compared with other classic extraction methods, which require elevated temperatures for a large period of time.

However, the maceration procedure requires many hours to obtain a low yield of extract by itself. In this way, microwave energy can be applied as a previous step in this traditional extraction process to enhance solid-liquid diffusion.

MAE is an efficient pre-treatment to reduce the time spent in the maceration procedure because it acts in the slow diffusion step of the extraction process. Microwave provides energy able to heat the intracellular water; this hot water increases the pressure inside of vegetal-cell and causes the cell-wall to rupture, finally releasing the internal content, and drastically accelerating the diffusion step[2].

The aim of this present project is to perform the extraction of bioactive compounds and, as previous commented, the extraction method depends on the sample. MAE and maceration will be used as a starting point. The results will determine the possible application of other techniques such as Supercritical Fluid Extraction (SFE), Subcritical Water Extraction (SCWE), Ultrasound-Assisted Extraction (UAE), or also ultrasound/microwave Assisted Extraction (UMAE), among other methodologies efficient in this kind of extraction[3].

Formulation and Application assay

According to literature, in the pulp of Euterpe Oleracea mart. berry some important compounds are present, such as Anthocyanins (Cyanidin, Peonidin, Pelargonin), Flavonoids (Homo-Orientin, Orientin, Catequin Epicatechin, p-cumárico), Prothocyanidins, and some other interesting products (Vanilic, Ferulic, and Gallic Acid, and Resveratrol).[4] These compounds, present in natural pulp, are expected in low concentration in açaí waste. Moreover, their low solubility in water is a restraint for future application.

In order to solve this problem, this paper proposes to analyze different alternatives to increase the solubility of these compounds in water as well as their bioavailability, performing a formulation with polymeric surfactants by different processes (SAS, PGSS, SFEE and microencapsulation). Selected samples obtained in the formulation will be check by in vitro tests, for example to evaluate the products dissolution in simulated gastrointestinal fluids and the ORAC antioxidant activity of extracts[5].

Summary

The present project proposes to make use of Açaí production waste as a source of Phytochemical compounds, especially Anthocyanins and Polyphenols. The main focus of this work is divided in four principal steps: (1) selection of plant, to find a partner able to supply Açaí Berry and its waste, and material characterization; (2) Sample preparation for Extraction by microwave assisted extraction, to quantify and to qualify extracted compounds; (3) formulation of extracted compound; and, (4) Application assay.

At present, the efforts have been focused on moving Açaí berries and its waste from the industry-partner (Brazil) to University of Valladolid (Spain). The main problem is governmental bureaucracy.

Acknowledgement. R Buratto thanks Ciências sem Fronteira - CAPES/CNPq Brasil for a Phd fellowship.

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Measurement of Thermophysical Properties under Pressure

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One of the most important polymers produced nowadays is LDPE (low-density polyethylene) with a production volume of over 33 billion tons a year. To understand and therewith control the respective process, knowledge of the heat balance and also the kinetics during the reaction is required. To test new ideas and concepts in this regard for an already existing plant, modelling represent a useful and safe instrument. Models of LDPE plants go back to correlations of thermophysical parameters such as heat capacity, viscosity or density. However these correlations and their respective data sets are partly determined at atmospheric pressure and have not been evaluated further since their introduction in the last century. [1]

The current goal of research is generating exact thermophysical data of polymers, gases and supercritical fluids at process conditions of LDPE (3500 bar and 300 °C). Here the main focus lies on the heat capacity of the reaction mixture in the LDPE production containing ethene and polyethylene.

In order to determine heat capacities thermal analysis, represented by calorimetry, can be used. By default regular DSC devices are utilized, which however are not suitable for calorimetric experiments at high pressures. Measurements at these conditions can only be realized with special devices exhibiting high sensitivity; one of those being the transitiometer. This special calorimeter monitors heat flows while varying pressure, temperature or volume. [2]

Using the transitiometer two different methods were tested to determine heat capacities: The “classical” three-step method and the method of small temperature steps. Applying the three-step method, the heat capacity of LDPE at various pressures in a temperature range from 50 °C to 170 °C was examined. At the current stage, however, a definite conclusion about the pressure dependence of the heat capacity cannot be given and further research will be needed.

In addition the heat capacities of the liquids toluene, acetone and hexane at 1000 bar were studied. Using the method of small temperature steps it was operated at temperatures between 40 °C and 55 °C. The values for heat capacities obtained in this way show deviations from 10 % to 20 % to extrapolated literature data measured under similar experimental conditions. [3]

The next target is to improve the precision of the transitiometer for measuring heat capacities. A possibility to achieve this is averaging the heat flows of several measurements at identical experimental conditions. Another approach is to develop a new cell with an increased internal volume, whereby a higher amount of sample substance can be applied during the measurement. Although this decreases the maximum applicable pressure, it is a promising approach towards precise measurements of thermophysical data at high pressures.

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Turbidity Control – Designing a Flotation Cell

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Introduction

Biomass may cause a negative effect in the extraction process. Depending on the properties in the wastewater and the process temperature turbidity in the raffinate- or extract phase can occur. The main problem is that wastewater in the raffinate phase has not a high purity, therefore another separation process is necessary. Previous experiments using electro coalescence were performed in order to split the emulsion and to eliminate the turbidity. [1] Moreover a flotation cell for aqueous emulsion will be designed in lab-scale to compare this experiment with the previous one.

Methodical approach

In flotation cell, the density difference between solid particles is artificially increased. These happened by catching the particles from the rising gas bubbles. The rate of ascent of the gas-charged particles is usually much faster than the natural rate of descent of unladen particles. [2]

Because of the variety of flotation equipment, the first step for the designing of the flotation cell is a fundamental literature research. There are three mainly applications: Electro-Flotation, DAF (Dissolved air flotation) and IAF (Dispersed air flotation). The big difference between these procedure is how the gas bubbles are formed and depending on the forming, also the size of the bubbles is different. The finest Gas bubbles can be produced with electrolyse (d< 50 µm). The water dissociates by voltage in O_2 and H_2 gas-bubbles. [3] In the DAF the gas bubbles are formed by the reduction of pressure. The supersaturated water is going through a nozzle and forms a cloud of small gas bubbles (d = 30-100 µm) which slowly rise to the top. IAF is a combination of a mechanical agitator and air injecting system. Using this technique, the gas-bubbles are formed mechanically (d = 40- 100 µm). [4]

Further parameters need to be studied in order to decide which, application is the best option. After the final decision the flotation cell will be constructed.

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Virtual Learning on Packed Bed Systems

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Introduction

For scientist the investigation of phenomena and effects is the main aspect of their everyday work. Having a look on the curricula of academic study programs, the gain of theoretical knowledge is usually only one aspect of the study process. Especially in the field of natural sciences hands on labs are used to impart lab workflows, gaining awareness for lab safety and show impressive effects in a real context. With the progress of technology over the past 15 years the much older classic hands on lab gets a virtual alternative. A virtual or remote lab can be accessed more flexible as a classic hand on lab. A remote lab, as shown in Fig. 1, can be used in the classic context as well as in some new scenarios with flexible settings due to the world wide access through the internet.

Fig. 1.: Setup of a remote experiment: Lab equipment <-> LabServer <-> User

Dealing with the advantages and disadvantages of remote labs in comparison to the classic hands on lab it is important to clarify the differences, some are shown in Tab. 1.

Hands on Lab	Virtual and Remote Lab
• Access time scheduled (group and assistance)	• Scheduled individual
• Usually small groups (2-4 Students)	• single or multiple users possible
• Support, moderation and reflection by an assistant	• Support, guidance and reflection via virtual interaction with a PC
• Using real lab environment with all potential and restrictions of that facility	• Worldwide access over the internet

Tab. 1.: A collection of differences between hands on and virtual or remote labs

Installing a remote lab is a process, which contains several loops of optimization but starts in the planning phase, where things need to be set. The context in which the remote lab will be used is of same importance as the content that is going to be imparted. There for a didactical scheme needs to be designed. To bring this concept to a real remote experiment, the remote setup has to be designed. That includes choosing the Hardware and Software components that full fill the needs of a highlight accessible, remotly operated plant.

Experimental

For the field of process technology at the Ruhr University Bochum, the understanding of unit operation processes is as much important as the knowledge about the technical solutions to realize this operation. A common content for our process engineering students is the process of catalysis. Therefor a remote tube reactor experiment was designed and setup, see Fig. 2. Before students are allowed to operate the hardware remotely, a virtual preparation needs to be passed. Once the students reflect their preparation, the access to the remote plant is granted. With the main idea of individual exploring, the students can operate a flow process that emulates the flow through a packed bed catalyst within a range of parameters. At this point, a good balanced User interface is needed to allow discovering plant behaviour without damaging the lab equipment.

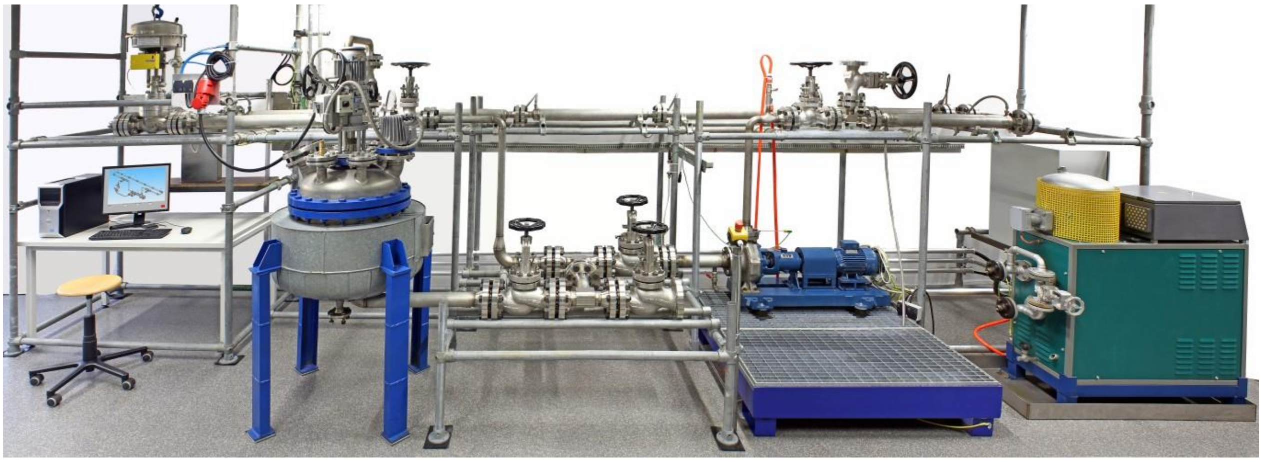
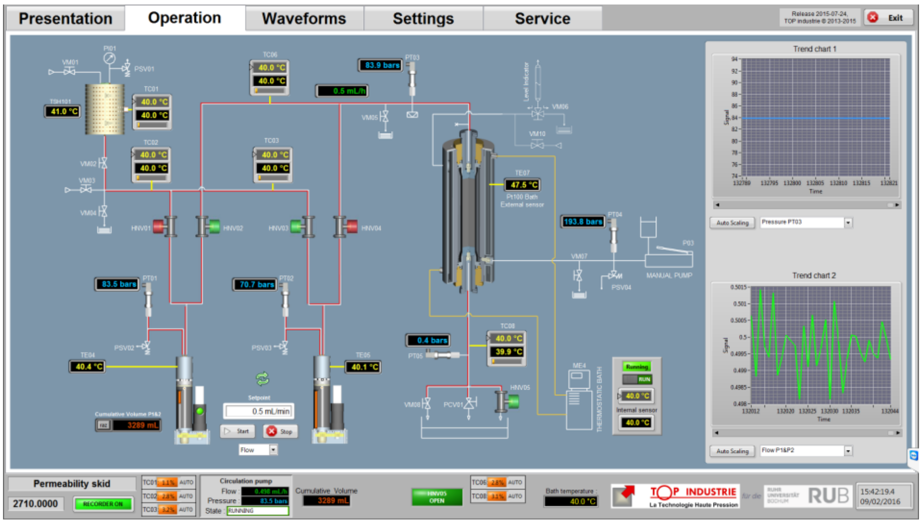


Fig. 2.: Remote setup of packed bed tube reactor for a catalysis process

With Labview as Software environment it is managed to observe the plant functions and guarantee a faultless operation. The designed user interface allows the students to control and observe plant parameters, see Fig. 3.



Flow : 0.498 mL/h
Pressure : 83.5 bars
State : RUNNING
Cumulative Volume 3289 mL
Bath temperature : 40.0 °C

Fig. 3.: LabView Interface with adjustable parameters, parameter observation and data acquisition

In the case of our remote tube reactor setup, the students have to operate a catalyses process with a backed bed catalysis and adjust the mode of operation in the most efficient way, in behalf of process rate in the catalysis and energy efficient of the technical equipment (pump and pipe system). As the students will run this plant many hours, the packed bed catalyst is substitute by uniform glass spheres (see Fig. 4) and the process fluid is no complex chemical, that need to be deposed after each experiment, but just simple water.

Fig. 4.: Glass spheres (3mm) that replace a real catalyst, to emulate real flow behaviour through a tube reactor

By performing this remote lab, the students gain experience in different fields of process technologies. To support the understanding of the flow through a particle bed, an Ansys Simulation has been setup. By investigating the flow process in a visual way, different flow behaviours can be observed. The focus can by on the distinction between turbulent and laminar flow in such a packed bed. Therefor a simplified model of the packed bed is used for the simulation (see. Fig. 5). The packed bed here is extremely reduced in the length, otherwise it is possible that several hours, sometimes even days or weeks, are necessary to produce a convergent solution.

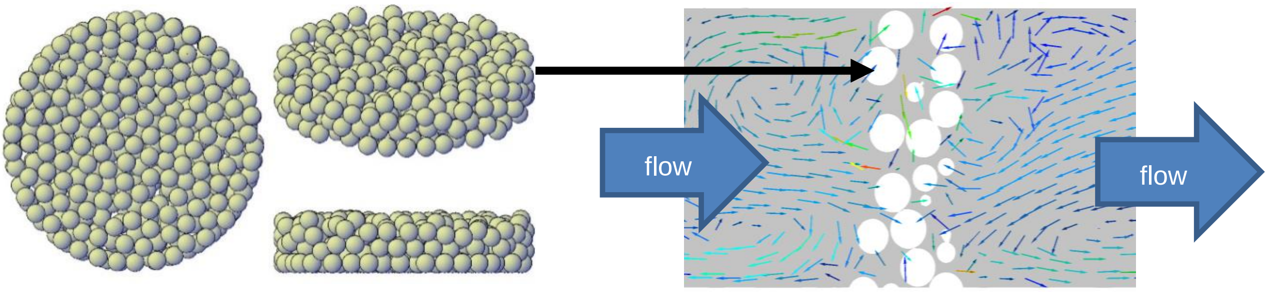


Fig. 5.: reduced packed bed (429 Spheres, 3mm) to 40mm diameter and 10mm length.

If the results of the simulations should be used in the students' learning process, it is necessary to simulate this flow process in a range of settings in which the results are most significant.

Summary

Education nowadays has can choose from a wide range of tools and use them in a way that was unthinkable 20 or 30 years ago. This remote tube reactor plant is not the only experiment but part of a larger experiment pool that is set up at the Ruhr University Bochum. A Step by step implementation into the existing curriculum allows all involved persons to gain experience with the virtual or remote way of education. There are plans to use our virtual and remote lab pool for the preparation of student's exchange with participants all over the world, preparing for a stay at the Ruhr University Bochum.

Determination of Physical Properties of Cellulose Dissolving Ionic Liquids in Combination with Co-Solvents

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The project in which I am involved consists on the determination of physical properties of mixtures of co-solvents such as dimethyl sulfoxide (DMSO) of CO_2 with cellulose dissolving ionic liquids (ILs). Ionic liquids are promising solvents for biomass processing, but their higher viscosity is a limitation to their extensive use in this field. The use of co-solvents such as DMSO or CO_2 can decrease viscosities of these ILs.

As a first step of my work, densities and viscosities of mixtures dimethyl sulfoxide + 1-allyl-3-methylimidazolium chloride mixtures have been experimentally determined. Densities were measured at temperatures T = [293.15, 373.15] K and molar fractions of dimethyl sulfoxide x_{DMSO} = 0, 0.05 0.1, 0.15, 0.25, 0.5, 0.75, 0.9 and 1 at pressures P = [0.1, 35] MPa with a vibrating tube densimeter. It was found that density increase with ionic liquid concentration and with pressure and decrease with temperature. Excess molar volumes were calculated resulting in negative values

Densities and viscosities at atmospheric pressures were measured with a Stabinger viscometer. Viscosity increases with the ionic liquid concentration and decreases with temperature.

Introduction

Ionic liquids are substances composed totally of ions that are liquid at room temperature. They are considered as green solvent due its negligible vapor pressure. They outstand for its high solvation capacity and their properties can be changed by selecting different cation and anion. It is known that, imidazolium based ionic liquids with acetate, chloride or alkylphosphate anions stand out for their capacity of dissolving cellulose, one of the most abundant substances on earth, whose treatment can lead to obtain high added-value substances [1]

The main inconvenience for the development of these processes is the high viscosity of ILs [2], therefore, ionic liquids are often used in combination with co-solvents in order to reduce the viscosity, or enhance the transport properties [3]. The most frequently used so far co-solvent is dimethyl sulfoxide (DMSO), but CO_2 can also be an attractive option. CO_2 it is an abundant and inexpensive gas, without environmental limitations that presents high solubilities in ionic liquids. It is able to decrease viscosity and melting points of ionic liquids, and it can be separated from them easily by depressurization.

The objective of my thesis is to determine and model physical properties of some cellulose dissolving ILs with DMSO and CO_2 in order to improve biomass processing using ILs. In this work the first step of my work is presented. The experimental determination of densities and viscosities of mixtures DMSO + 1-allyl-3-methylimidazolium chloride (AmimCl) at temperatures T = [293.15, 373.15] K and molar fractions of dimethyl sulfoxide x_{DMSO} = 0, 0.05 0.1, 0.15, 0.25, 0.5, 0.75, 0.9 and 1 at pressures P = [0.1, 35] MPa with a vibrating tube densimeter.

Experimental

Densities of these mixtures at various temperatures and pressures, from atmospheric to 35 MPa were performed in a vibrating tube densimeter (VTD) model Anton Paar DMA 514, connected to it a frequency meter Anton Paar DMA 60. In Figure 1 the installation scheme is shown.

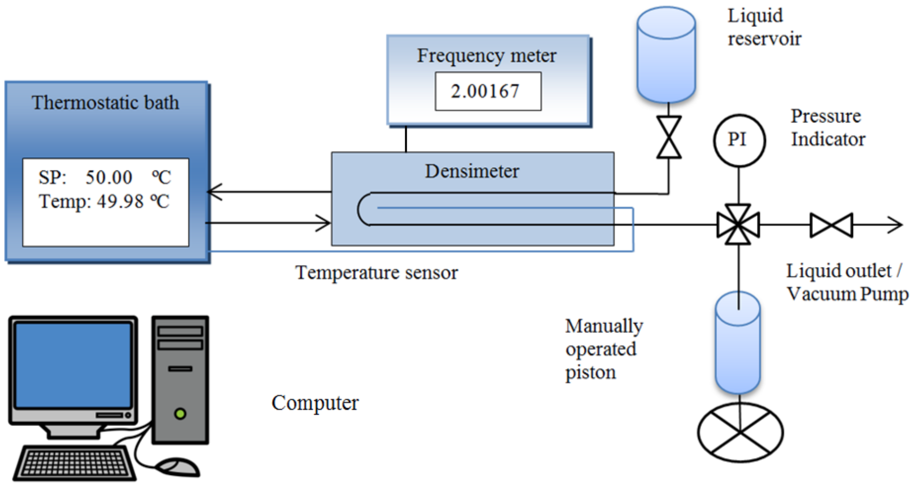

Fig. 1.: Installation scheme.

To determine densities and viscosities at atmospheric pressure, a Stabinger viscometer (SVM 3000 model) was used. The measurements with this device are limited to atmospheric pressure. However, this equipment can measure the density, temperature and viscosity of the fluid.

Results

In Figure 2 some of the density data obtained at different pressures are presented. It is observed that density decrease with DMSO molar fraction and increase with pressure.

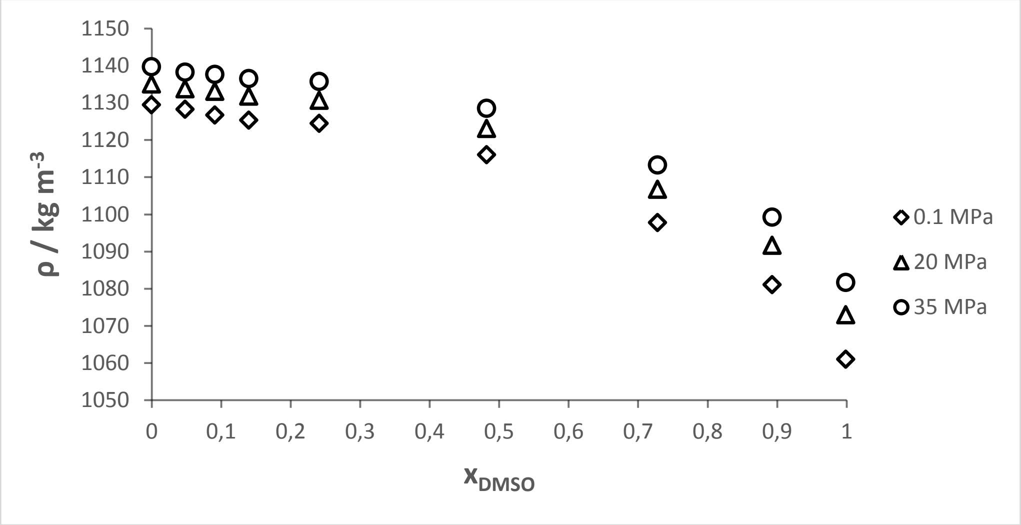

Fig. 2.: Densities of mixture at 333.15 K and different pressures.

In Figure 3 the viscosity results are displayed. It is observed that viscosity decreases with temperature and concentration of DMSO.

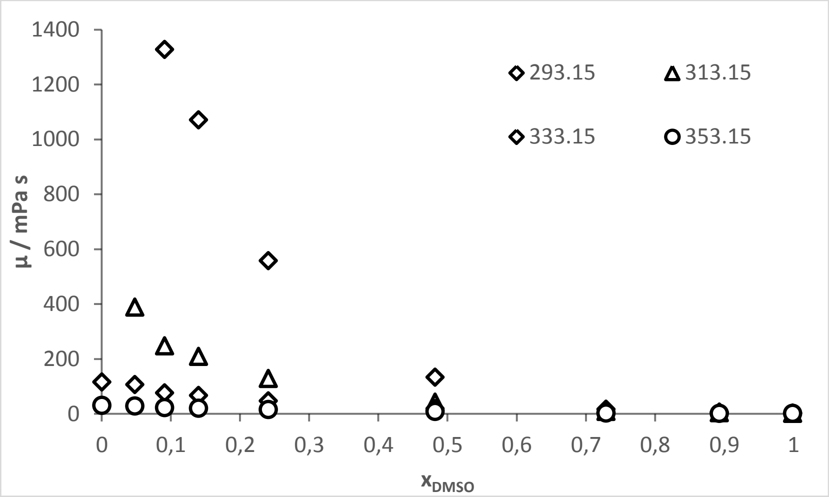

Fig. 3.: Viscosities of binary mixtures DMSO + AmimCl at atmospheric pressure.

Excess molar volumes were calculated from the experimental data. Calculated results are presented in Figure 4.

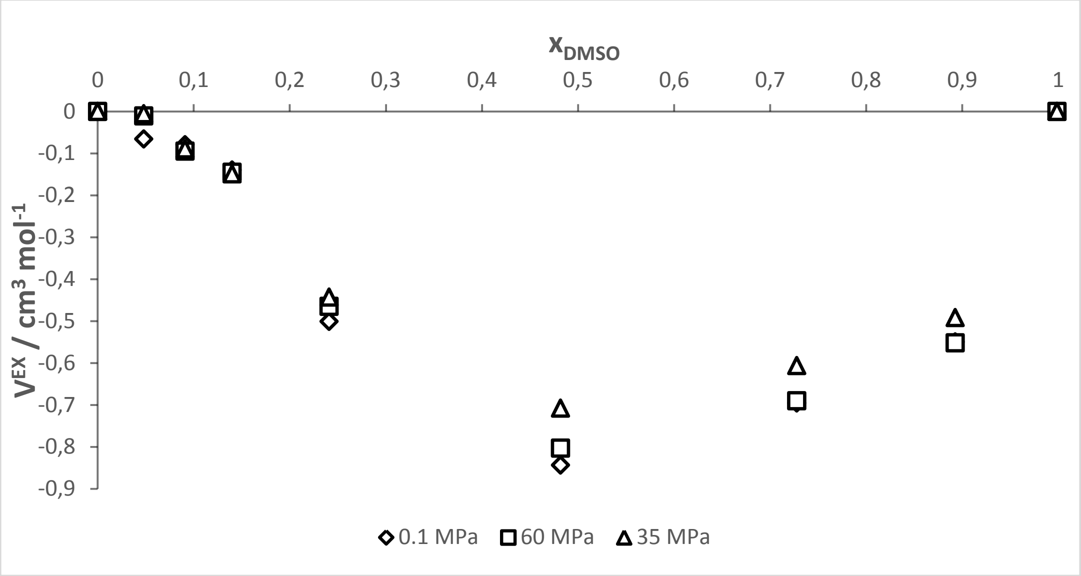

Fig. 4.: Excess volume at 353.15 K and different pressures

As it can be seen from Figure 4 that there is a minimum of excess volume at x_{DMSO} = 0.5 molar fraction, increasing with the pressure.

Conclusions

In this work density, viscosity and excess molar volume of mixtures of DMSO + AmimCl are experimentally determined at a wide range of conditions. It is observed that density and viscosity of the mixture decrease with the concentration of DMSO and with temperature and density increase with pressure. Negative values of molar fraction are obtained.

Acknowledgment

The author acknowledge funding to Junta de Castilla y León for project VA295U14 and MINECO for project ENE2014-53459-R.

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Preparation and Characterization of Nanoporous Micro Particles as Potential Carrier for Pulmonary Drug Delivery using Supercritical Fluid Technology

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The majority of anticancer drugs are administrated intravenously, in which high doses of toxic drugs are employed, causing severe adverse side effects on healthy organs due to the systemic drug distribution. On the other hand, oral delivery of lung anticancer agents is usually compromised by poor bioavailability due to degradation during the first-pass metabolism.

Recently, there has been increasing interest in pulmonary drug delivery. The attractiveness of this route comes from its outstanding features such as: The large absorptive surface of lungs; the epithelial layer of the peripheral lung is (100 m^2) and it is very thin (0·2–0·7 µm), making it an ideal site for high blood perfusion with perfect sink conditions for particles deposition. Compared to oral and parenteral routes it also has many advantages such as: avoidance of the first-pass metabolic degradation, minimal systemic adverse effect due to limited penetration of inhaled drug(s) into the systemic circulation, high therapeutic ratio, increased selectivity and the ability to permeate large molecules such as proteins (1,2) .

However, to achieve an efficient delivery, there is a requirement to design a formulation with appropriate aerodynamic properties composed of biocompatible excipients.
Deposition of particles in the respiratory tract depends on particles size, morphology and geometry, along with surface properties. (3)

Particle size plays an important role in deposition phenomena. Furthermore, breathing frequency and the holding of breaths, humidity, air velocity and tidal volume also are vital factors influencing the deposition.

To reach the lower respiratory tract, particles need to have aerodynamic diameters between 0.5 - 5μm, particles larger than 5μm usually deposit in the oropharynx where they are easily cleared. On the contrary, particles smaller than 0.5μm may not deposit at all because they move by Brownian motion, settle very slowly and could be exhaled. (4)

Porous micro particles considered a good choice for the delivery of drugs to the lungs because they are light and inhaled deeply into the lungs. However, proper aerosol properties are expected to be delivered with porous particles of relatively large physical diameter.

This study aims to prepare and characterize porous micro particles as potential carrier for pulmonary anti-cancer drug delivery using supercritical fluid technology. Therefore, the maximum treatment efficiency and lowest systemic side effects would be achieved by the administration of high doses of lung anti-cancer to the lung tumor tissues via the inhalation.

Full physicochemical characterization for the prepared carriers will be performed. Loading the prepared carrier with a model drug will also be done followed by determination of loading efficiency, *in-vitro* drug release and stability study.

Due to its safety, accessibility and biodegradability, alginate and other biodegradable polymers will be used as the polymeric material.

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Preparation of Aerogels Based on AS Lignin and Chemical Modified AS Lignin

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As the crude oil and the petrochemical raw materials will become scarce in the following decades, lignocellulosic materials represent a potential new feedstock for the industry for the production of goods. There are several approaches targeting the utilization of renewable resources to produce bulk chemicals and materials by means of extraction or biotechnological processes. As one of these approaches, the biorefinery concept aims to produce multiple valuable products from biomass, including bioethanol, chemicals and biodegradable materials, to name a few. In order to accomplish this goal, lignocellulosic biomass is split up in its major three components, cellulose (production of bioethanol), hemicellulose (bulk chemicals) and lignin (considered majorly as a waste). The main insoluble compound left after the separation of the polysaccharides is lignin, a highly branched aromatic polymeric network of phenylpropanoids. Lignin represents a very promising resource, because it is the second most abundant biomass and therefore exists in an inexhaustible amount, which makes it a sustainable source. Due to the complex structure of lignin, depending on its source, extraction method and degradation processes, lignin is classified in different types. One of the environmentally friendliest processes is the liquid hot water (LHW) pretreatment.[i] In this process, biomass is pretreated with water at about 200 °C and 30 bar, in the first step the hemicelluloses are removed and the pretreated material is subsequently hydrolyzed.[ii] The Lignin obtained after enzymatic hydrolysis is called Aquasolid lignin (AS lignin) and is the major part of the solid residue the final hydrolysis. Due to the fact that these processes avoid chemical treatment, lignin fragments obtained have a natural structure and high molecular weight. This polymeric network has several functional groups, such as OH-groups, and offers curing or crosslinking possibilities, as well as its use in adhesive masses, filler or blending compound. One of the highest valuable applications of AS Lignin networks is its use for the construction of thermal insulation materials based on porous materials, as the case for aerogels.

Aerogels are dried gels that are featured by low density, high surface area and low thermal conductivity, due to their porosity. A typically route to aerogel is the formation of a sol followed by a curing step and subsequent supercritical drying of the obtained gel in order to avoid collapsing of the network. Lignin-based aerogels have been produced in water. CHEN et. al. described the synthesis of a resorcinol-lignin-formaldehyde resins, which are supercritically dried after the solvent exchange of the aerogel is performed.[iii] Moreover, SMIRNOWA et. al. described the synthesis of lignin-based aerogels using lignin and an epoxy-hardener in aqueous sodium hydroxide.[iv] Nevertheless, the low reactivity and the low solubility of the lignin limited the processability of the gel formation and the solvent exchange to an organic solvent was required, which affected the properties of the resulting aerogel.

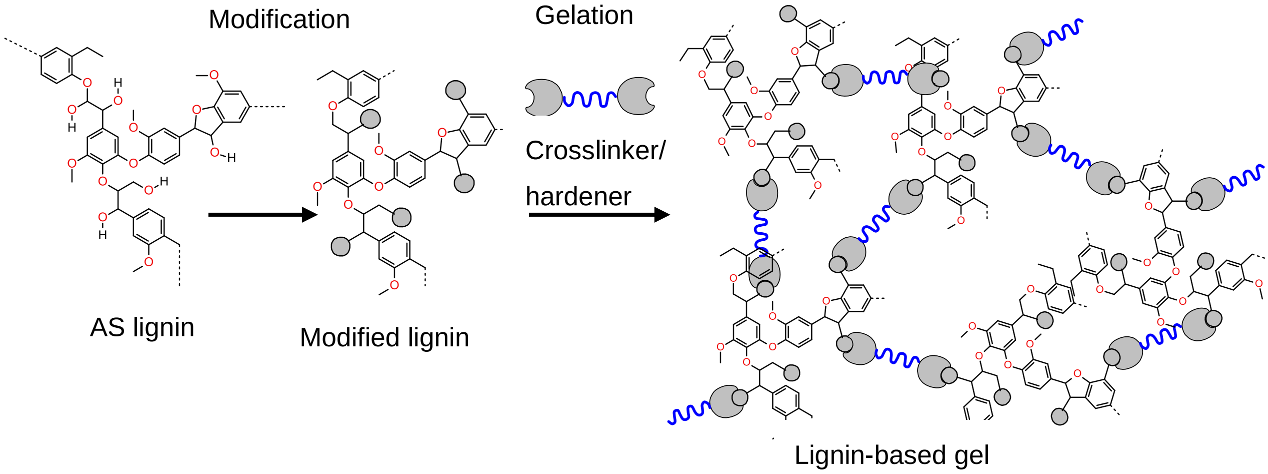

Figure 1. Schematically reaction path to lignin-based gels via modification of lignin and the crosslinking to a network.

In this work the chemical modification of AS lignin from wheat straw to increase the solubility and reactivity, as well as different crosslinking approaches to the targeted aerogels are investigated. Moreover, structure-properties relationships of the obtained AS lignin and the modified lignin and the optimization of the process parameters are intended to investigate. Especially, if the modification of the AS lignin provides a certain solubility in organic solvent, solvent exchange step can be skipped, thus rendering in a less time consuming and more efficient process for Lignin-based aerogel formation.

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Determination of Transfer Constants for Gaseous CTAs

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Due to their wide range of applications and their adjustable properties, polymers have become the material of choice in many areas. With a market share of almost 30 % with respect to the production volume, polyethylene is one of the most important synthetic polymers. Its properties are dominated by its polymeric microstructure which can be adapted to match customer needs. Amongst others, the microstructure highly depends on the process conditions: Low-density polyethylene (LDPE) is produced by radical high-pressure polymerization, while high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) are synthesized at medium-pressure using catalysts. This explains the huge portfolio of applications in which polyethylene is used, including foils, package materials or medical implants.[1,2]

For a radical polymerization, one way to control a polymer's molecular weight distribution (MWD) and therefore its microstructural properties is to add chain-transfer agents (CTAs) to the polymerization. CTAs act as modifiers by lowering average molecular weight as they transfer a radical functionality from one polymer chain onto another.[3,4] In order to evaluate CTAs, the transfer constant C_{tr} is used, which is defined as the ratio between the rate coefficient of the chain-transfer and the propagation reaction $C_{\mathrm{tr}}=k_{\mathrm{tr}}/k_{\mathrm{p}}$. In general, there are two established ways to determine transfer constants: the Mayo method and the chain-length distribution method (CLD method). While the Mayo method uses solely the molecular weight averages in order to obtain transfer constants, the CLD method takes the whole MWD into account. Both techniques are based on an idealized kinetic polymerization scheme and require therefore several experimental requirements in order to provide reliable results.[3,4]

In the 1960s and 1970s Mortimer[5] determined the transfer constants of many CTAs with regard to the polyethylene high-pressure synthesis. To this day, these transfer constants are used to rate the transfer activity of the respective CTAs. However, the absolute values may be questioned since Mortimer did not strictly fulfill the corresponding requirements, such as low conversion. Therefore, a reevaluation of this transfer constants is of current interest and can help to achieve a better understanding of transfer reactions.

Within this work, the transfer constants of gaseous chain-transfer agents, in particular methane and ethane, are determined with regard to the high-pressure polyethylene synthesis using the Mayo and the CLD method. The respective experiments are carried out in a continuously operated high-pressure polymerization mini-plant including a 100 mL autoclave reactor at a pressure of 2000 bar and temperatures between 180 °C and 240 °C. The activation energies of both CTAs are calculated by observing the temperature dependence of $C_{\mathrm{tr.}}$ In order to fulfill the requirement of small conversions, no initiator is used to start the polymerization, but it is taken advantage of the intrinsic background conversion. The CTAs are dosed via a mass flow controller before a three-stage membrane compressor. The MWDs of the polymer samples are measured by high-temperature size exclusion chromatography.

With this experimental setup it is possible to determine even very small transfer constants successfully using both evaluation methods.

We gratefully acknowledge the support of Saudi Basic Industries Corporation for this work.

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Investigation of Polycarbonate Modification with Copper Nanoparticles via Supercritical Fluid Impregnation

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Introduction

Polymer nanocomposites are one of the most promising composite materials. Different nanometric scale compounds can enhance the properties and expand the applications of several polymers [1]. When such nanoparticles are homogeneously distributed inside the polymeric matrix, the properties of nanocomposite material are superior to that of the original polymer. Polymers can be modified with nanoparticles to gain many unique properties such as catalytical, electrochemical, mechanical, magnetic, optical and biological ones [1]. All these characteristics make these materials interesting in wide range of applications. The conventional production processes of these materials have some drawbacks such the control of size, loading and distribution of the particles within the polymer.

This study focuses on to carry out nanoparticle modified polymers by the use of supercritical carbon dioxide ($scCO_2$). $ScCO_2$ is a suitable supercritical fluid for polymer impregnation; it is environmentally friendly, relatively cheap and not toxic. Because of its low surface tension, it can penetrate throughout the whole polymer matrix therefore it enhances the impregnation efficiency. Due to its relatively low critical pressure and temperature (73.9 bar and 31.1°C), the usage of $scCO_2$ does not require very special equipment and extraordinary security regulations [2]. In addition, CO_2 is a by-product of many processes so there is no need of extra CO_2 production for the impregnation.

The conventional way to product metallopolymer nanocomposites through supercritical impregnation is carried out by a 3-steps process. First an organometallic complex (metallic precursor) synthesis is needed. The aim is to produce a compound soluble in $scCO_2$. This stage could be very expensive due to the high cost of the reagents and for the difficult purification of the final complex. Nevertheless, these syntheses can often be realized only with a low amount of yield. Successively, the complex and the polymer are placed in the supercritical media where the impregnation step occurs. The resulting product consists in an organometallic complex impregnated polymer. After this stage the metallic precursor has to be converted into metal nanoparticle. This can be done by different reduction steps [3].

In our work, the copper impregnation of polycarbonate in $scCO_2$ was investigated, by using three different copper complexes. First, the commercially available copper hexafluoroacetylacetonate hydrate ($Cu(hfac)_2*xH_2O$) was used. We have also synthesized two other copper complexes in our lab; the primary and the secondary copper dithizonate ($Cu(HDz)_2$ and CuDz, respectively). Besides, we tried to carry out the impregnation in two distinct step; first, the impregnation of PC with the dithizone, a molecule which reacts copper, and as a second step, impregnation of this product with a solution containing copper ions. By this we wanted to investigate if the copper complex formation can take place *in situ* in the polymer phase.

Experimental

$Cu(hfac)_2$ and dithizone were ordered from Sigma-Aldrich Austria. Carbon dioxide (purity >99.5%) was supplied from Linde Gas GmbH. Polycarbonate (PC) samples (LEXAN 121 resin) were kindly provided by the Saudi Arabian Basic Industries Corporation (SABIC) in pelletized form. Other reagents (such as solvents, washing ethanol) were obtained also from Sigma-Aldrich Austria. Impregnation experiments were carried out in a batch mode by using the high pressure apparatus shown in figure 1.

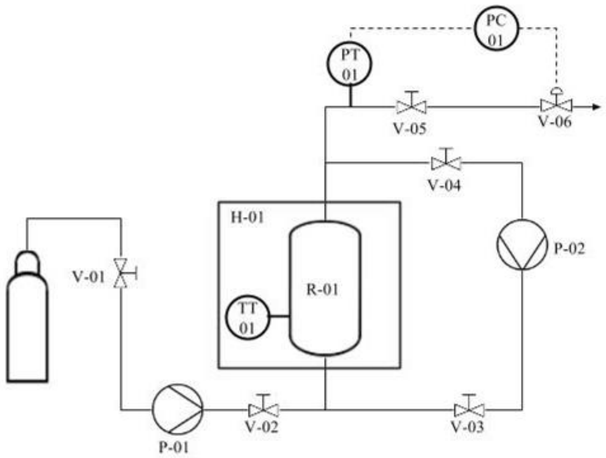

Fig. 1: Experimental plant scheme

The pump P-01 is a pneumatic pump (Haskel ASF 100) used to reach the experimental pressure. To maintain the CO_2 in liquid form during the compression the pump is cooled by a cooling system that keeps it below 3°C. The vessel is placed inside an oven (H-01) that controls the temperature of the experiment. A pressure control system (PC-01, PT-01) is installed to the apparatus. It is used during the depressurization to achieve the linear decompression of the vessel. A gear pump (P-02) is used to mix the volume of the vessel when the experiment is running. The samples were analysed with ICP-OES to investigate the copper load, and with UV-VS spectrophotometry to determine the dithizone content. Measurements with Scanning Electron Microscopy (SEM) were performed in order to characterize the system.

Results

By using the commercially available copper complex ($Cu(hfac)_2$) and the complexes, which were synthetized by our lab, we did not achieve satisfactory results; all the samples were below or just slightly above the detection limit of the ICP-OES (4ppm). By using $Cu(hfac)_2$ it is believed that the unsuccessful impregnation was due to the relatively high solubility of the complex in the $scCO_2$ therefore its low partition coefficient between the polymer and the fluid phase. Unlike CuDz, $Cu(HDz)_2$ was found to be soluble in $scCO_2$ according to our observations carried out in a high pressure view cell. However, impregnation by using $Cu(HDz)_2$ was not successful; presumably the high molecular weight or size of the complex limited the impregnation.

However, by using the 2-steps impregnation process, a successful impregnation was performed. First, a dithizone impregnated polycarbonate (DPC) was produced by using only $scCO_2$ as a solvent and also in ethanol-CO_2 mixture under supercritical conditions. A concentration between 0.0055 and 0.1786 mg/g of dithizone in the polymer was reached, depending upon the applied temperature, pressure and the ethanol content in the vessel.

The second step was an impregnation of the DPC with copper ions dissolved in water or in ethanol in $scCO_2$ media. The aim was to carry out the complexation between copper and dithizone inside the polymer matrix. Copper nitrate trihydrate $Cu(NO_3)_2{*}3H_2O$ was used as copper source; the pH of the solution was varied by adding KOH or HNO_3 to the system. Copper ions are not soluble in $scCO_2$ though the impregnation was successful. A similar result was achieved and patented by Perman *et al.* [4]. It was discovered that even additives that are substantially insoluble in a supercritical fluid can be impregnated in the polymer even if there is not compatibility with the substrate. This is realized by contacting the polymer with a liquid carrier (where the additive is soluble) and in presence of the supercritical fluid. It is supposed that sorption and the swelling induced by the fluid in the polymer allows the addictive to penetrate the matrix.

The best results were obtained in a slightly basic solution. The copper load reached is up to 235 ppm but the samples turned out to be highly inhomogeneous. Measuring different pellets of the same sample may result in remarkably different copper load. This phenomenon could be related to the poor mixing performance. Since water and $scCO_2$ present in two distinct phases it is really complicated to ensure an effective mixing. By this mixing does not affect in the same way on all the pellets. To support this hypothesis an experiment was carried out at the same conditions but without the mixing device (gear pump). The measured copper load results to be very low but homogeneous in those pellets.

Some samples were analysed by SEM that determined an almost equal impregnation through the entire polymer pellet and a variable particle size between 5 and 400nm.

Summary

A copper impregnation was performed successfully on polycarbonate with a 2-step impregnation. However, the copper load in the samples turned out to be highly inhomogeneous. Measurement performed with Scanning Electron Microscopy has shown the presence of clusters of copper deeply and equally spread in the polymer pellet. Further analysis will be performed to investigate the oxidation state of the copper inside the polymer and for better understanding the chemistry of the process.

Acknowledgment

This work was financially supported by the Marie Curie Initial Training Networks (ITN) via “DoHip – Training Program for the Design of Resource and Energy Efficient Products by High Pressure Processes”, project number PITN-GA-2012-316959. Simone Schiavo would like to thank the ERASMUS program for financial support.

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Pressure Dependence of the Hydrogenation of Carbon Dioxide to Hydrocarbons under Supercritical Conditions

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Introduction

The actual supply of energy by burning fossil fuels leads to a rise of CO_2-concentration in the atmosphere, which is correlated with climate changes.[1] It is a political and economic aim to reduce anthropogenic CO_2 emissions. One strategy that could solve this problem is to use CO_2 in a circular process: CO_2 and solar H_2 are converted to long chain hydrocarbons (for example diesel) by Fischer-Tropsch synthesis. Those liquid fuels can be burned with O_2 to pure CO_2 and H_2O. The obtained CO_2 is reused in the circular process and again converted to fuels. Compared to gaseous fuels (for example methane), diesel has advantages in terms of transportation and storage (high energy density).

For an industrial application todays catalysts for the CO_2 hydrogenation need to be improved to reach the required activity and selectivity towards the desired products. Beside the development of new catalysts and catalytic systems the influence of the reaction conditions need to be investigated.

This contribution deals with the pressure dependence of the hydrogenation of CO_2 under supercritical conditions.

Experimental

A batch reactor was used for the hydrogenation of CO_2 to hydrocarbons. Self-made Fe/Cu/La/K catalysts were prepared by co-precipitation. The experiments include two steps: the reduction of the calcined catalyst in pure H_2 and the reaction with a mixture of H_2 and CO_2 (molar ratio 3:1). Liquid CO_2 was fed into the reactor while H_2 was added in gaseous form. The initial pressure was varied in the range of 40-176 bar (at room temperature). Reactions were carried out at 325 °C. Gaseous products were analyzed by FTIR-spectroscopy, liquid products via GC-MS.

Results and Discussion

The pressure variation shows no significant influence on product selectivities in the considered range. In contrast to the selectivities the conversion is strongly influenced by the reaction pressure (see Fig. 1). If the initial pressure is raised from 40 to 75 bar, conversion is more than two times higher. This is maybe due to a change of thermodynamic behavior. At 75 bar initial pressure the reaction mixture is assumed to be supercritical. The application of supercritical conditions reduces mass transport limitations in heterogeneous catalyzed reactions leading to optimized catalyst activity. This fact is known from literature. Further increase of reaction pressure leads to decreasing conversion. This could be caused by decreasing diffusibility due to rising density.[2]

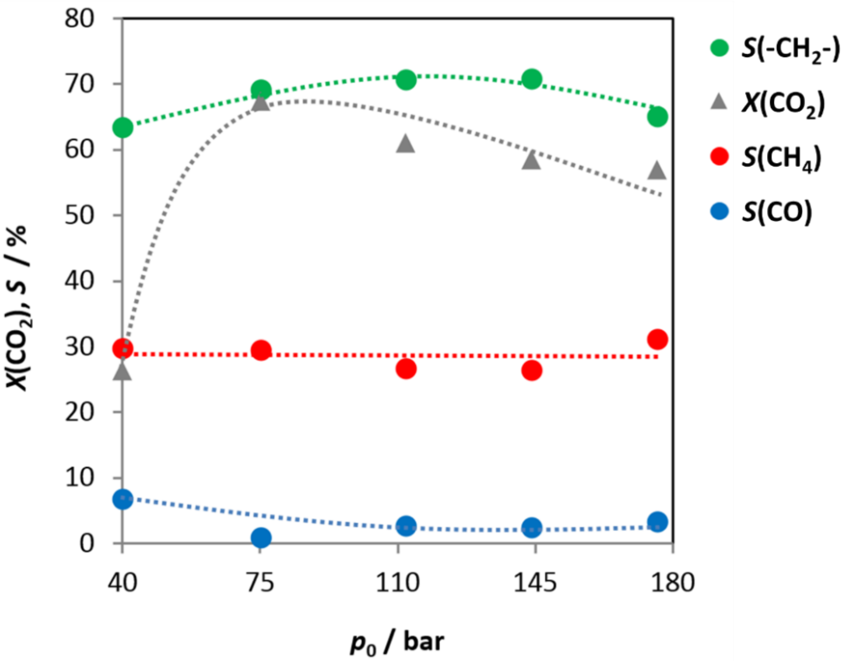

Fig. 1. Influence of pressure on the hydrogenation of CO_2 at Fe/Cu/La/K catalysts, $H_2/CO_2=3$, 325 °C, $t_{Rkt}=15$ h, batch reactor.

In further experiments the pressure range will be extended. In addition experiments will be carried out in a continuous setup.

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Chemical Recycling of CO_2 through Hydrothermal Conversion in a Continuous Flow Reactor

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Introduction

In the past two centuries, the industrial and economic development of our society is resulting in changes in the Earth´s atmosphere. The rise in emissions of greenhouse gas is causing an increase of global average temperature. Atmospheric CO_2 levels have increased by more than 40 percent since the beginning of the Industrial Revolution, from about 280 parts per million (ppm) in the 1800s to 400 ppm today.

So the development of methods for the abatement of CO_2 emissions is an urgent task. As a complement for capture and storage technologies that consider CO_2 as a residue, utilisation of technologies that consider CO_2 as a resource has the advantage of generating an added value, but their development still is in an early stage.

Among the different carbon dioxide conversion technologies proposed, the hydrothermal reduction of CO_2 has shown the potential to selectively convert carbon dioxide into valuable products such as formic acid, methane and methanol, favoured by the increased reactivity of CO_2 in hydrothermal conditions(1). These conditions are in water at high temperature and pressure, using metals, such as zinc or nickel, as reductors. It is necessary to bring the reaction to those conditions, to break the stability of CO_2. Best results so far were obtained using Zn as reductor at temperatures of around 300ºC at basic media [2]. The formed key product is formic acid, but with different metals and residence time different products can be obtained. This is supposed that formic acid acts like an intermediate for formation other compounds [2].

However, current research on this technology is limited to discontinuous or semicontinuous process layouts that show limitations for commercial applications in terms of productivity, equipment durability and energy efficiency. For a scalable, cost-effective deployment of this technology, a fully continuous reactor design is required, but to accomplish this goal several challenging scientific and technical questions must be solved, including: controlling reaction conditions for the selective generation of the desired products; incorporating the metal regeneration cycle in the process; and integrating the hydrothermal reduction reaction with CO_2-production process.

The objective of my thesis is developing a continuous CO_2 hydrothermal reduction process. To do so, the kinetics of the process will be studied and modeled. A continuous laboratory facility will be designed and used for testing different technological solutions.

Our goal in a first stage of the project is evaluate chemical paths and kinetics in batch, of the reduction of CO_2 in hydrothermal media using Zn as a reductor in the reaction:

$$\mathrm{Zn} + CO_2 + H_2O \Rightarrow \mathrm{HCOOH} + \mathrm{ZnO}$$

Experimental

Commercial metallic zinc powder with average grain sizes of 10 μm with a purity of at least 98 wt% was obtained from SIGMA-ALDRICH. The carbon dioxide source in the experiments was sodium bicarbonate ($NaHCO_3$). The reagent was purchased from COFARCAS.S.A. with a purity of 100wt%. This bicarbonate is dissolved in water Milli-Q.

Experiments were carried out by using batch reactors consisting of tubing with two end fittings, giving an inner volume of approx. 15 ml. A known amount of sodium bicarbonate solution was introduced in each reactor, filling approx. half of the volume of the reactor. Then the reactors were introduced in an oven at the reaction temperature. After a fixed reaction time the reactor is extracted from the oven and suddenly cooled down to room temperature by introduction in cold water. Total organic carbon and HPLC analysis of the liquid phase were carried out, while solid was analyzed by XRD to determine the Zn oxidation to ZnO. Experiments in a temperature range from 275ºC to 350ºC were perfomed at residence times from 10 to 180 minutes.

Pilot plant

The second stage of the project is the building a pilot continuous facility where a continuous process for the hydrothermal reduction of CO_2 can be performed. The facility will be based on a tubular reactor with cooling by sudden expansion of the effluent. The feed flow capacity will be of 0.2 – 2 kg/h.

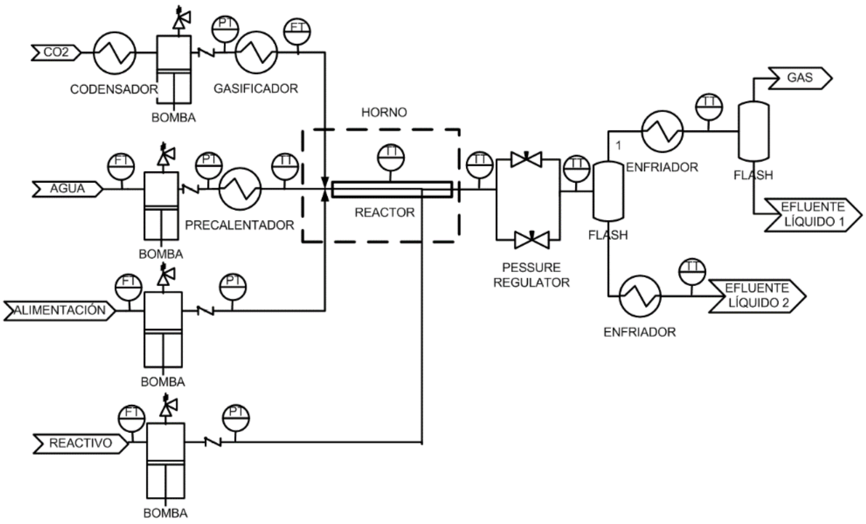

Fig. 1.: Continuous System Diagram

Results

Fig. 2 shows the effect of temperature on the yield of formic acid. As shown in the figure, formic acid yield decreased when increasing temperature. The ratio Zn/$NaHCO_3$ was 5 and bicarbonate concentration was 42 g/L.

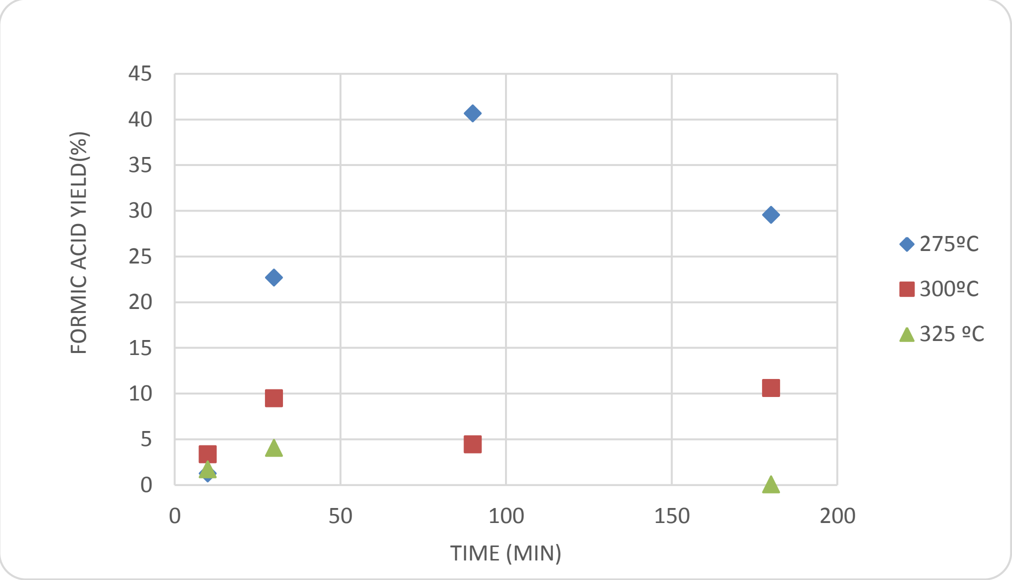

Fig. 2.: Temperature effect on the yield of formic acid with stainless steel reactors

Conclusions

Our research suggests the better conditions to improve formic acid selectivity and productivity are at temperatures less 300ºC and time residence between 30 and 90 minutes. These conditions will be tested in the pilot continuous facility.

Acknowledgment: This research has been financed by the Spanish Ministry of Economy and Competitiveness through project ENE2014-53459-R, "AQUA-CO2NV".

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Continuous Flow Generation and Use of Chlorine for Organic Synthesis

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Chlorine is a very powerful and one of the cheapest oxidizing and chlorinating agents.[1] Although often used for disinfection and bleaching, it has been scarcely used in organic synthesis as reagent for oxidation or chlorination reactions.[2] This is due to the severe safety and regulatory restrictions derived from its high toxicity, and the strongly exothermic reactions usually observed with organic compounds.[3] Moreover, the presence of free chlorine leads to by-product formation, mainly over-oxidized products and chlorinated derivatives.

An alternative to the hazardous use and storage of cylinders of chlorine gas is its generation “in situ” from safe sources such as sodium hypochlorite (NaOCl) and hydrochloric acid (HCl) (Equation 1). These methods are typically used for the preparation of small amounts of chlorine in a lab scale,[2] but are not of practical use for larger scale production using traditional batch methods.

$$2HCl + NaClO \rightleftharpoons Cl_2 + NaCl + H_2O \qquad \text{(Equation 1)}$$

Herein we present a continuous flow procedure for the generation and use of free chlorine for organic synthesis. The chlorine gas is generated from cheap, safe, and readily available reagents (diluted HCl and NaOCl), extracted into an organic phase ($CHCl_3$), and separated from the aqueous phase using a semipermeable membrane in a continuous fashion. Under continuous flow conditions, the toxic reagent can be produced “on demand” and immediately consumed, minimizing any risk of exposure. Moreover, continuous flow reactions can be readily scaled to production quantities without major modifications of the setup.

Our chlorine generator consisted of three peristaltic pumps, which continuously mixed HCl and NaOCl in water, and $CHCl_3$ (Figure 1). The Cl_2 generated was thus extracted to the organic phase, and separated using a hydrophobic membrane. The organic substrate and other reactants can be introduced in-line into the reactor, and the mixture quenched before the reactor output. In this manner, the free chlorine is confined within the reactor.

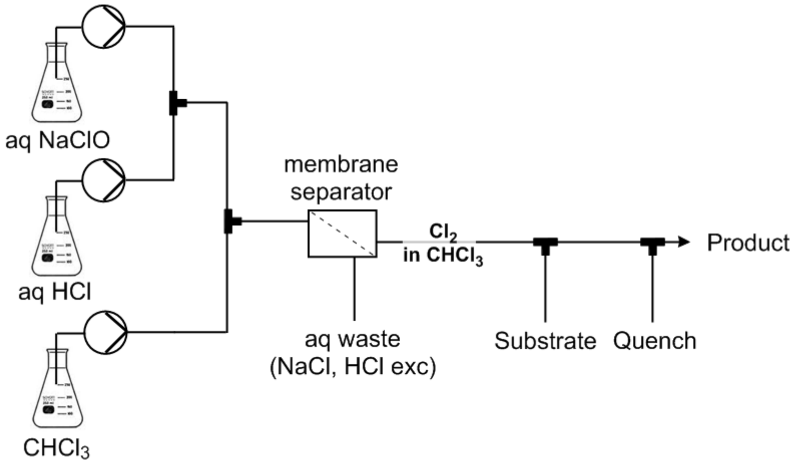

Figure 1. Setup for the continuous generation and use of Cl_2

Our system has been tested for several organic transformations of interest, including the selective oxidation of secondary alcohols using the Cl_2:pyridine complex, as well as the synthesis of sulfonyl chlorides from thioethers (Figure 2). Photochemical chlorination of benzylic compounds has also been accomplished by coupling the chlorine generator with a continuous flow photoreactor equipped with an UV lamp.

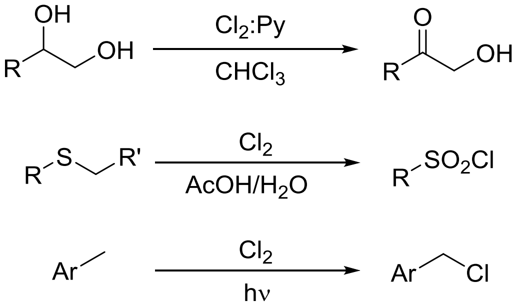

Figure 2. Chemistry examples using the in situ generated Cl_2

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CO_2-Intensified Chromium Contaminated Wastewater Free Tanning of Skins

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1 Introduction

Tanning of leather is one of the oldest human technologies. Nowadays, about 7 million tons of skins are converted to over 2000 km^2 of leather every year. The turnover of the leather industry in the year 2011 was approximately US $69 billion. Europe is the second largest tanning region after China. According to estimations the costs of environmental protection measures in European tanneries account for 5 % of their turnover [1, 2, 3].

The leather production process from raw skin to leather goods is divided into a lot of different working steps like washing, unhairing, liming, pickling, tanning, dyeing etc. of which tanning is in the focus of this work. In 1858 tanning with chromium salts was developed by Knapp [4]. Because of the high performance of chromium tanned leather, 90 % of all leather products are tanned by chromium-(III)-salts at present [5]. In the conventional chromium tanning process skins are treated for 12 h in rotating drums by using approximately 70 wt.-% of water and 6 to 8 wt.-% of chromium tanning agent based on the weight of the skins. The annual consumption of chromium-(III)-salt in the leather industry is 500,000 tons. However, 30 to 50 % of the chromium applied in the tanning process is lost with the wastewater and causes pollutions of high concern [1, 6].

The new CO_2-intensified tanning process described in the following combines advantages of the conventional chromium tanning, high performance and quality, with the possibility of saving process time, chromium tanning agent and water, especially wastewater. This work is focused on the saving of chromium tanning. The process principle, the influence of pressure and time is described elsewhere [7].

2 Experimental

2.1 High pressure tanning reactor

The main part of the PLC-controlled “pilot-scale plant” is a horizontal autoclave with a volume of 20 liter. Inside of the autoclave a rotatable basket can be used for tanning comparable to conventional tanning procedures. To improve the movement of the skin samples during the tanning procedures eight metal pikes were vertically installed inside the basket over it´s full length. The motion affects the mass transport and the distribution of the tanning solution. The maximum working parameters of the equipment are 320 bar, 80 °C and 20 rpm.

2.2 Materials

2.2.1 Skin

For the test series bull skins with a surface area of approx. 7 m^2 were used. For the high pressure tanning the skins were conventionally prepared in a tannery. Skin is divided into several parts like neck, side, croupon etc. The part with the highest quality and the most regular structure is the croupon. For each experiment eight equally sized parts were taken out of the croupon. Before the samples were placed in the high pressure autoclave their water content was reduced by samming.

2.2.2 Tanning solution

The tanning solution consisted of water and a conventional chromium tanning agent. The quantity of the tanning agent was calculated based on the weight of the skin samples before they were sammed. The amount of used water was equal to the amount of water which was removed from the skin by samming.

2.3 Quality assessment

2.3.1 Shrinkage temperature

Measuring the shrinkage temperature (T_S) is the most common method used in the leather industry for quality assessment of chromium tanned skin. Chromium tanned skin has to be resistant to the temperature of 100 °C without degeneration. In this work the T_s was assessed by using common equipment from the leather industry. The heating medium was water. After the tanning process defined parts of the tanned samples were punched out. The samples were placed firmly with an interlock on one side of the apparatus. The other side was connected by a yarn using a hook. A weight tightened the system. The sample was subsequently submerged into the heating medium. The water was heated. When the leather sample was shrunken the corresponding temperature was documented. After each experiment the T_s of four different samples were measured and the standard deviation was determined.

2.3.2 Emission spectroscopy

In addition to the T_s the chromium oxide (Cr_2O_3) content of the tanned skin is common to assess its quality. For this test series the chromium content was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). After each experiment the Cr_2O_3-contents of four different samples were analyzed and the standard deviation was determined. A Cr_2O_3-content of at least 3 wt.-% indicates a high leather quality.

2.4 Results

For the test series four experiments by varying the quantity of tanning agent between 2 and 3.5 wt.-% based on the weight of the skin were performed. During each trial the whole tanning solution, which was used, was absorbed by the skins. Thus, no wastewater was left. The duration of the process including depressurization was 3.5 h. The maximum pressure was 30 bar. The temperature was 20 °C in the beginning of the process and heated up to 45 °C at the end of the process.

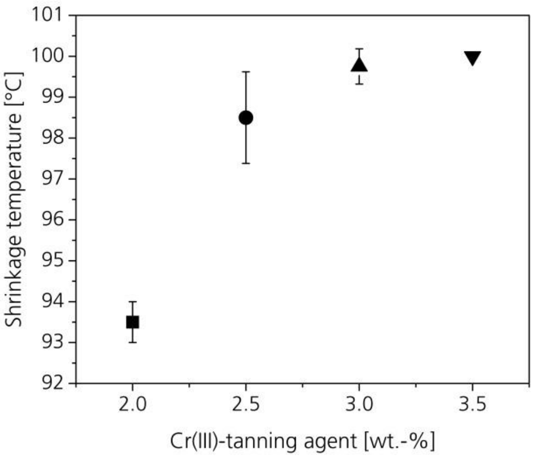

Figure 1: Influence of the quantity of the used Cr(III)-tanning agent on the shrinkage temperature of the tanned skin

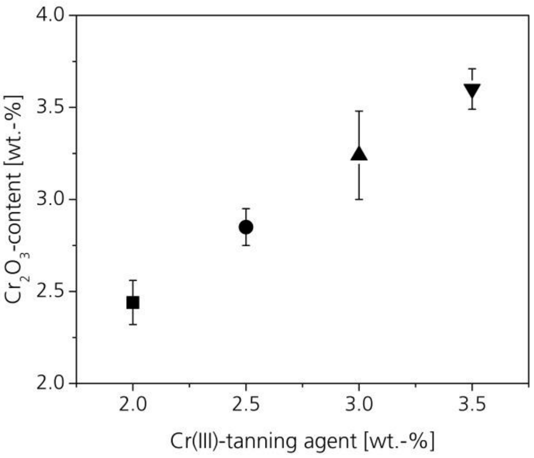

Figure 2: Influence of the quantity of the used Cr(III)-tanning agent on the Cr_2O_3-content in the tanned skin

Figure 1illustrates the influence of the quantity of used tanning agent on the T_s of the tanned skins. It is shown that 2 wt.-% of tanning agent are insufficient to reach a high quality because all analyzed samples degenerated between 93 and 94 °C. An increase in the quantity of tanning agent results in a higher quality. By using 3 wt.-% just 1 of 4 samples was not resistant against a temperature of 100 °C. At a consumption of 3.5 wt.-% all analyzed samples reached a T_s of 100 °C.

Figure 2 shows the results regarding the analytics of the Cr_2O_3-content in the tanned skin. It can be seen in the diagram that an increase in the quantity of the tanning agent leads to an increase in the Cr_2O_3-content in the tanned skin. By using 3 wt.-% of tanning agent a Cr_2O_3-content of at least 3 wt.-% was reached in every analyzed sample.

3 Summary

By comparing the conventional and CO_2-intensified tanning process the results demonstrate that by using dense CO_2 the amount of tanning agent can be highly reduced. The most important difference between the processes is that in conventional tanning a high excess of tanning solution has to be used whereas in the CO_2-intensified process just the amount of solution that can be absorbed by the skins is needed. Professional European tanneries use a minimum of 6 wt.-% of tanning agent based on the weight of the skin. By using dense CO_2 a high quality can be achieved with the consumption of 3 to 3.5 wt.-%. Thus, a saving of approx. 50 % can be achieved. Furthermore, chromium contaminated wastewater caused by the tanning step is totally avoided. To sum up it can be noted that the newly introduced tanning process carries a great potential for environmental protection. Furthermore the process has the potential to decrease costs because of the enormous savings regarding the consumption of tanning agent and wastewater treatment.

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