Foto di Giuseppe Maria Lacitignola – Cortesia di SISSG (Società Italiana per lo Studio delle Sostanze Grasse)

"Qualità ed Autenticità Tecnologie e Sottoprodotti"

Sala degli Affreschi dell'Università di Bari 'Aldo Moro'

18-19 Ottobre 2018 - Bari

Si è tenuto a Bari nella prestigiosa Aula Magna dell'Università "Aldo Moro" nelle date 18-19 Ottobre 2018 il Convegno organizzato da La Società Italiana per lo Studio delle Sostanze Grasse (SISSG) "***Qualità ed Autenticità Tecnologie e Sottoprodotti".***

L'evento era rivolto ad un vasto pubblico di accademici, ricercatori, associazioni, operatori del settore e delle macchine per tecnologie olearie.

Sono stati trattati temi relativi alle sostanze grasse intese nel senso più ampio del termine, non limitando la discussione al solo olio di oliva.

II Convegno era strutturato secondo diverse sessioni consecutive:

- Sottoprodotti
- Sostenibilità e Prodotti da Forno
- Analitica ed Autenticità
- Fonti Alternative
- Contaminanti
- Tecnologia
- Shelf Life

Per ogni sessione era prevista una Keynote Lecture ad invito, per mezzo della quale si intendeva introdurre la tematica della sessione stessa, seguita da presentazioni di iniziative di ricerca sullo stesso argomento. Numerosi sono stati gli interventi e gli argomenti di discussione emersi a margine delle presentazioni scientifiche

Il programma dell'evento è stato molto apprezzato dai più di 130 partecipanti, che si sono poi ritrovati per la cena sociale al Teatro Petruzzelli in una cornice di eleganza e buon gusto, ospiti della locale sezione del Rotary Club al Circolo Unione.

Le presentazioni complete, limitatamente a quelle degli Autori che hanno fornito la liberatoria alla diffusione, sono raccolte come di consueto nell'Area Riservata del sito *www.sissg.it* e accessibili mediante password ai soli Soci SISSG.

Pubblichiamo di seguito gli abstracts delle presentazioni orali e dei poster presentati al Convegno, suggerendo gli interessati di contattare direttamente gli Autori per maggiori dettagli.

SESSIONE UTILIZZAZIONE E VALORIZZAZIONE DEI SOTTOPRODOTTI DELLE FILIERE OLI E GRASSI ALIMENTARI

Valorizzazione dei sotto-prodotti della filiera olearia: da scarto a risorsa

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Nel mondo sono coltivati più di 8 milioni di ettari di olivi e circa il 98% di questi nel bacino del Mediterraneo. La produzione dell'olio di oliva è inevitabilmente fonte di sottoprodotti e scarti, rappresentati prevalentemente da acqua di vegetazione, sansa di olive e foglie e rametti. Le quantità dei suddetti sotto-prodotti sono particolarmente elevate, basti pensare che per le acque di vegetazione il volume è compreso tra 0,5 e 2 m^3 per tonnellata di olive. La quantità di foglie che arriva in frantoio, invece, è aumentata drasticamente in seguito all'utilizzo della raccolta meccanizzata.

Scarti e sottoprodotti, dunque, costituiscono un problema per l'impatto ambientale e quindi per tutto quello che è correlato allo smaltimento. Allo stesso tempo, però, essi rappresentano una fonte importante di molecole potenzialmente bioattive che possono essere recuperate ed utilizzate in vari settori, da quello bio-medico a quello alimentare.

Diversi autori hanno indagato sulle tecniche di estrazione più appropriate per recuperare svariate molecole, quali polifenoli, tocoferoli, steroli, ecc. Ampio spazio viene dato alle tecniche di estrazione cosiddette "green", di cui alcune prevedono l'impiego di ultrasuoni, microonde, fluidi supercritici, pressurizzazione. Svariati sono, inoltre, i loro impieghi tra i quali, in primo luogo, quello in ambito farmaceutico (integratori e altri fitorimedi), per l'alimentazione animale, come ammendanti per l'agricoltura e in ultimo anche l'impiego negli alimenti al fine di ottenere prodotti nutraceutici o di incrementare la shelf-life sfruttando la loro azione come antiossidanti e/o antimicrobici.

L'interesse nel recuperare le suddette molecole da sottoprodotti e scarti dell'industria olivicolo-olearia per formulare alimenti funzionali e fitorimedi nasce dalla lunga serie di evidenze scientifiche inerenti gli studi in ambito biologico. Test *in vitro* ed *in vivo*, infatti, hanno evidenziato le numerose potenzialità dei composti bioattivi estratti da foglie di olivo, sansa e acqua di vegetazione, tra cui proprietà antiossidanti e anti-fungine, così come la capacità di contrastare la proliferazione cellulare in alcune cellule tumorali, la nefrotossicità e la genotossicità.

Sulla base di queste evidenze, appare chiaro che scarti e sottoprodotti dell'industria olearia mostrano realmente le potenzialità per lenire un problema grave legato al loro smaltimento, nonché creare nuove opportunità di utilizzo per essere considerate realmente una risorsa.

Prodotti ad uso alimentare dagli scarti oleari: ipotesi di produzione di un "aceto di oliva" dalle acque di vegetazione

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Università degli Studi del Molise - Campobasso, Dipartimento di Agricoltura, Ambiente e Alimenti

Gli scarti di lavorazione delle industrie olearie (acque reflue, foglie e sansa) si prestano a varie forme di riciclaggio. Numerosi e recenti studi hanno riguardato il possibile riutilizzo dei sottoprodotti oleari per scopi alimentari, come, per esempio, produzione di pasta o paté di olive, polvere di olive, bevande a base di foglie, integratori e additivi antiossidanti a base di estratti fenolici. In questo studio, è stata indagata la possibilità di produrre dalle acque di vegetazione (AV) una soluzione simile-aceto, denominata "aceto di oliva", da poter consumare direttamente o come ingrediente in salse e condimenti agro-dolci.

La ricerca è stata condotta in scala di laboratorio, in annate successive, su volumi di 5-10 litri di AV prelevate da impianti oleari tradizionali a presse. Le AV sono state utilizzate tal quale o diluite. Fermentazione alcolica e acetificazione sono state condotte in condizioni variabili di temperatura, inoculo e zuccheraggio. Raggiunto un significativo livello di acidità totale (≥ 4% in acido acetico), l'aceto di oliva è stato filtrato su carta, imbottigliato e caratterizzato da un profilo chimico-microbiologico.

L'aceto di oliva prodotto si presenta limpido e stabile nel tempo. Il soddisfacente grado di acetificazione è stato ottenuto attraverso due differenti percorsi. Nelle tesi inoculate con lieviti starter, la formazione di acido

acetico seguiva la fermentazione alcolica per ossidazione biologica dell' etanolo. Nelle tesi senza inoculo, la produzione di acido acetico era dovuta a ceppi microbici indigeni, apparentemente incapaci di metabolizzare il saccarosio aggiunto. Alla fine del processo, a parità di acido acetico formato, i prodotti avevano diversa composizione, soprattutto riguardo gli zuccheri residui. In entrambi i casi, l'aceto di oliva, comparato con altri aceti commerciali, si caratterizzava per un elevato contenuto di sostanze minerali (ceneri ≥ 2%) e fenoli totali (≥ 3 g/L), tra cui soprattutto idrossitirosolo (1,0 g/L). In conclusione, l'aceto di oliva dalle acque di vegetazione pare essere un fattibile e promettente prodotto nutraceutico.

La produzione e l'utilizzo del biogas da sottoprodotti dell'industria olearia: dagli oneri di smaltimento alle opportunità di reddito delle Aziende

G. Bratta

Distretto Pugliese delle Energie Rinnovabili 'La Nuova Energia' - Bari

Nello scenario nazionale della green-economy e della sostenibilità ambientale e produttiva del territorio, il recupero e la valorizzazione energetica delle biomasse residuali della filiera olivicola-olearia possono consentire di trasformare materiali di scarto in prodotti energetici permettendo la *produzione di energia rinnovabile* da biomasse senza l'utilizzo di suolo agricolo per fini energetici.

I sottoprodotti sono ancora lontani dalla piena valorizzazione.

Gli ostacoli alla valorizzazione energetica dei sottoprodotti olivicolo-oleari sono di varia natura e vanno dalle difficoltà burocratiche ed autorizzative, alle problematiche nello sviluppo di piani di approvvigionamento affidabili e di lungo periodo a partire da una materia prima notevolmente dispersa sul territorio, nonché alla difficile interazione tra il mondo agricolo (da sempre abituato ad orizzonti temporali di investimento e contrattuali molto brevi) e quello industriale-energetico, che necessita di lunghi orizzonti temporali ed elevata affidabilità degli approvvigionamenti per garantire la redditività degli investimenti.

Le nuove tecnologie di estrazione, oltre a fornire un olio di migliore qualità, permettono anche importanti benefici ambientali, eliminando la necessità di aggiungere grandi quantità d'acqua al processo e limitando il problema dello smaltimento delle acque di vegetazione.

Nel settore oleario la destinazione energetica degli scarti oleari, soprattutto se accompagnata da tecnologie innovative, che riducono il consumo di acqua e migliorano la qualità dell'olio, può rappresentare un effettivo aumento di valore per tutta la filiera, grazie al loro utilizzo negli impianti di biogas e biometano.

La filiera del biometano diviene quindi oggi un naturale completamento della filiera agroalimentare, ed offrire interessanti opportunità di sviluppo permettendo di realizzare un'economia circolare e ambientalmente virtuosa.

Molecular basis of antihypertensive effect of bradikinin: functional involvement of renal aquaporins

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Bradykinin (BK) is one of the most important peptide regulating vascular tone, water, and ionic balance in the body, playing a key role in controlling blood pressure. Interestingly, patients with essential hypertension excrete less BK than do normotensive subjects. To elucidate the mechanism by which BK regulates renal water transport, AQP2-transfected collecting duct CD8 cells, expressing the BK receptor (BK2), were used as experimental model. In CD8 cells, BK pretreatment impaired forskolin-induced AQP2 translocation to the apical plasma membrane. To clarify the signal transduction cascade associated with this effect, we first investigated whether BK induced increase in citosolic calcium, via the G protein Gq known to be coupled to BK2 receptor. Spectrofluorometry employing fura-2-AM revealed that 100 nM BK elicited a significant increase in Cai (from 72.8 ± 7.4, to 310.7 ± 43.4 nM, n=6, $P<0.001$) which was abolished by the receptor antagonist HOE-140. In renal cells, Gq coupled receptors may activate Rho and its downstream effectors. In CD8 cells it has been shown that forskolin-induced AQP2 translocation is associated with a decrease in Rho activity and depolymerization of F-actin which facilitates the translocation of AQP2 to the plasma membrane. Interestingly, BK treatment in CD8 cells resulted in a significant increase in Rho activity, as assessed by selective pull down experiments. In agreement with these data, BK induced a significant increase of F-actin content as assessed by actin polymerization assay and by immunofluorescence experiments. BK effects on actin assembly were abolished by the BK2 agonist HOE-140. We conclude that the diuretic effect of bradykinin may in part be explained by impairement of AQP2 translocation *via* activation of Rho and F-actin formation.

SESSIONE OLI E GRASSI IN PRODOTTI DA FORNO

Transition towards a Sustainable Oils & Fats future

L. de Gruijter
Bunge Loders Croklaan - Wormerveer, The Netherlands

Fats and oils are an essential part of a healthy and nutritionally balanced diet for humans and livestock. As the world population heads towards 10 billion, consumption of vegetable oils are expected to rise by around one sixth by 2030 and one third by 2050. The way we're producing and consuming fats and oils is often associated with unsustainable practices. Biodiversity, climate change and human rights in the supply chains are some of the sustainability challenges surrounding the production of oils & fats. Especially palm oil is currently much debated and subject to NGO campaigns. At Bunge Loders Croklaan, we recognize the critical role we play in the global food system and leverage our position to address sustainability challenges in our production chains. Via our Sustainable Palm Oil Sourcing Policy and No Deforestation Policy for Grains & Oilseeds we work towards fully traceable, transparent and sustainable product supply chains.
The presentation takes in consideration the sustainability challenges in the oils & fats production supply chains with a focus on the palm oil supply chain. It will discuss the industry efforts to tackle these challenges. In addition, Bunge Loders Croklaan, one of the biggest tropical oils & fats processors in Europe, will present its strategy.
The presentation will set out the challenges the world will have anticipating the future demand for vegetable oils and fats. It will illustrate how the global population is growing; the demand for oils & fats will increase and how the industry could respond to this increasing demand in a sustainable way.
Main Topics:
- Increasing demand for oils & fats by global world population
- Environmental impact of production of oils & fats
- Sustainability challenges in oils & fats industry, specifically for palm oil
- Industry collaboration & Bunge Strategy to address the challenges around sustainable production
- The way forward to improve sustainability along oils & fats supply chains

Future Proofing of Fats and Oils used in the production of Fillings and Doughs for the Bakery Industry

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Bunge Loders Croklaan - Wormerveer, The Netherlands

Fats and Oils play an important role in the processing and product characteristics of Doughs and Fillings used throughout the European Bakery industry.
With the ever demanding requirements by consumers for Nutritious, Clean Label and Sustainable Baked products, manufacturers want to ensure that they provide long lasting solutions that maintain the high quality and value of their Baked products.
This presentation will cover the following topics:
- The characteristics of Fats and Oils required in the production of high quality Dough and Filling Fats.
- Raw materials used in formulating Dough and Filling Fats.
- Role of hard and soft fats in laminated doughs.
- Role of Fats and Oils in Crystallization and melting behavior of fats required to give 'Great' tasting fillings.
- The consequences of the substitution of hard fats and liquid Oils on the quality of Doughs and Fillings.
- Bunge Loders Croklaan's Sustainable, Nutritious Low contaminant Filling and Dough Fat products that address the consumers concerns now and into the future.

Use of inulin based emulsion filled gel as fat-replacer in formulation for shortbread cookies

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The study aims to evaluate the impact of different percentages of butter replacement, in formulations for shortbread cookies, with an emulsion filled gel (EFG) made by inulin and extra virgin olive oil.
A physical chemical and sensory investigation was conducted during a 60 days shelf life.

Four different formulations of cookies were tested containing 0, 20, 40 and 50% of butter replacement with EFG. The samples were stored in a thermostatic chamber at 25°C and 40% humidity and after 0, 7, 15, 30 and 60 days from the production were analyzed in terms of:

- Chemical composition: proteins (Kjieldahl), lipids (Soxhlet), ash (muffle), carbohydrates (for difference) fatty acids (GC-FID)
- Moisture content: gravimetric method, oven at 105°C for 5' (AOAC method n. 925.09)
- Water activity: hygrometer (Aqualab Decagon series 4 TEV)
- Hardness: penetration test, 3 mm cylindrical probe (TA-TX2i Texture Analyser)
- Volume: Rapeseed displacement (AACC method n.10-05); caliber
- Colour: colorimetric parameters (L *, C, ° h) (Minolta Colorimeter CM2600d).
- Sensory analysis: quantitative analysis of descriptors (QDA) on an 10 cm scale (0 = low intensity, 10 = very high intensity) with a panel of 15 people.
- Thermal behavior: differential scanning calorimeter (DSC Q100 TA Instrument)
- Proton molecular mobility: free induction decay (FID), transverse (T_2) and longitudinal (T_1) relaxation times (low resolution (20 MHz) ^{1}H NMR spectrometer - miniSpec, Bruker Biospin)

Statistical differences among samples and times of storage were evidenced by ANOVA bivariate test coupled with Tukey post hoc ($p<0.05$) (SPSS v25.0).

Increasing the EFG percentage in cookies more carbohydrates (fiber), unsaturated fatty acids and water content were observed. Despite the high water content and water activity of the EFG richest formulations, higher values of hardness were registered for these samples in comparison to the others, as also perceived by the panelists during the sensory analysis, probably due to initial gluten formation. Increasing the EFG content, the cookies showed higher heights and lower diameters after cooking, developing a browner color because of a boosted Maillard reaction due to the presence of inulin. The change of chemical composition and the interactions of the molecules in the different formulations were also visible by the results of the thermal analysis and ^{1}H NMR mobility which resulted very valuable tools for a better understanding of the properties and stability of the products. All the cookies showed a good stability during the considered storage period, with the ones containing 50% EFG as the most stable among all. This formulation would allow to obtain a product that could meet a high consumer satisfaction, having also potential health properties due to the reduced saturated fats content in comparison to the control.

Study of the antioxidant potential of tyrosyl oleate in a real lipid matrix

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The aim of this research was the study of the antioxidant potential of a lipophenol, tyrosyl oleate, obtained from the reaction between oleic acid and tyrosol. The antioxidant effect of tyrosyl oleate was studied in tarallini, typical Italian bakery product, was carried out through the study of the oxidation process.

The reaction between tyrosol and oleic acid was carried out according to Fernandez et al. (2012) and after purification through chromatographic column, different percentage of tyrosyl oleate were used in tarallini formulation. Formulation of tarallini was made according to the traditional recipe using wheat flour, salt and sunflower oil to obtain the control sample (CS); based on sunflower oil content 1, 4 and 7% of tyrosyl oleate was added (1TO, 4TO and 7TO). The oxidation process was studied, immediately after the formulation through an accelerated oxidation analysis using the Oxitest® instrument (Riciputi, 2017). Then at different storage time (T0, T15, T30, T37 and T45) peroxide value, spectrophotometric analysis according to Shantha & Decker method (1994), Oxidized Fatty Acids (OFA) (Verardo et al., 2010) and volatile compounds (Marzocchi et al., 2017) originated from lipid oxidation, with innovative gas chromatographic techniques, were determined in the different samples.

Analysis by Oxitest® allowed to discriminate between the control sample and the three samples with tyrosyl oleate; in fact, already in 1TO sample the IP value was more than twice (13.58 h) of CS (6.10 h); in the 4TO and 7TO samples the IP value reached 22.34 h and 25.28 h, respectively. For the peroxide value, at T0 and T15 all the samples did not show significant differences ($p<0.05$) having all the values under the legal limit of 20 meqO_2/ kg of fat. At T30, instead, CS and 1TO exceed the legal limit (79.6 and 49.0 meqO_2/ kg of fat, respectively), while 4TO and 7TO registered a peroxide value of 17.3 and 16.1 meqO_2/ kg of fat. These two samples exceed the legal limit after 45 days of storage (T45); so, in the worst condition (sunflower oil and storage at environmental conditions) the addition of tyrosyl oleate can slow down the lipid oxidation process. CS registered significant higher ($p < 0.05$) OFA content rather than all the samples with tyrosyl oleate (0.60 mg FA/100 mf FAME); 7TO sample showed the significantly lowest values than 1TO and 4TO at T30 (0.41,

0.37 and 0.31 mg FA/100 mg FAME, respectively). The concentration of volatile compounds originated from lipid oxidation increased with the increasing of shelf life. Tarallini made with tyrosyl oleate shown a significantly lower concentration of these compounds than CS for all the storage time; hexanal, the major representative compound of lipid oxidation, was the preponderant compound. Considering that the tarallini were made with one of the most oxidable oil, sunflower oil, and stored at room temperature without any modified atmosphere; the presence of tyrosyl oleate allows to counteract lipid oxidation and extend the shelf life of tarallini added with it.

SESSIONE: ANALITICA DELLE SOSTANZE GRASSE

On the authenticity of olive oils and possible identification of virgin olive oils in extra virgin olive oil

C. Mariani - *Milano*

A well-known Italian researcher a few years ago on a well-known book on olive oil reported that the problems related to the analysis and authenticity of olive oils were attributable to fraudulent mixtures with Hazelnut oils, with second centrifugation oils obtained from old pomace and oils subjected to mild deodorization.
To these problems I would also add the problem of desterolized, especially those obtained by cold condition.
In this key note I will show some experiences that allow a reduction of the mentioned problems

Olea europaea L. Biophenols: a past overview, present and future

P. Rovellini
Innovhub-SSI, Area Oli e Grassi – Milano

The aim of this presentation will be to do an overview of the most important results obtained from the past researches developed and regarding the Olea europaea L. biophenols, a report of the present state, highlighting research controversies and relative uncertainties and presenting at the end an outlook of the biophenols future research. Numerous published studies have put in relevance a lot of their biological properties suggesting as they could be contribute to human health and prevent diseases. Sometimes the concept to cure with aliments is contested, sometimes they are considered antioxidant, sometime as prooxidant, there are deep industries interests, the health and nutritional claim influence the brand choice.

Stable isotope ratio analysis for verifying the authenticity of vegetal oils

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The remarkable price disparity among vegetable oils generates a commercial temptation to fraud. In particular, adulteration may comprise the dilution of expensive oils with cheaper ones or a false declaration of origin. However, at the moment the officially recognised methods do not allow detection of these kinds of adulterations. There is therefore a need of developing of new analytical tools.
Stable isotope analysis of H(^{2}H/^{1}H), C (^{13}C/^{12}C), and O (^{18}O/^{16}O) in bulk oil or in sub-components can be a good choice for adulteration detection, because the three isotopic ratios change with the botanical origin (type of oil) and with the climatic and geographical characteristics of the location where the plant grew up.
The C isotope ratio of bulk oil is determined by EA-IRMS (Elemental Analyser-Isotope Ratio Mass Spectrometry) directly on the raw sample without any need of pre-treatment. The analysis of H and O stable isotope ratios of bulk dehydrated oil is performed via TC (Termal Conversion)/EA-IRMS. The isotopic values of many specific oil components, such as glycerol, sterols, aliphatic acids, fatty acids and *normal*-alkanes (*n*-alkanes) are performed using GC-C-IRMS.
The C stable isotope ratio analysis of bulk oil allows the detection of the addition of C_4 plant oil, such as maize oil, to other edible oils. Using compound specific carbon stable isotope ratio analysis, it is possible to identify other types of adulteration, such as the addition of pomace oil to virgin olive oil, or to distinguish different types of vegetal oil.
By combining the stable isotope ratio of C with H and O it is possible to characterize oils on the basis of the geographical origin, because these two ratios in oil are related with those of the local meteoric water.
Focus is pointed on olive oil, sesame oil, rapeseed oil and *Camelina sativa* oil.

NMR applied to olive oil authenticity and traceability control

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The need of a scientific tool for EVOOs geographical origin assessment by scientific methods represents a hot topic issue, since the EU Regulation 182 of 6 March 2009 (on the compulsory labeling of EVOOs with the geographical origin of the olives in all European countries) still lacks an official validation methodology. The same is for the EU Regulation 1151/2012, which seek to improve the EU quality policy for agricultural products by increasing coherence of various quality schemes. This recent Regulation includes measures to support agricultural and processing activities, as well as the farming systems associated with high-quality products, marketed under a PDO, PGI, in line with EU rural development policy objectives.

^{1}H-NMR-based metabolomic profiles were studied by chemometric analyses, in order to assess cultivar composition and geographical areas origin of EVOOs, in particular for PGI and 100% Italian blend EVOO production, mainly from Apulia and Tuscany regions.

Our results confirmed the need of suitable ^{1}H NMR metabolic profiles database of monocultivar genetically certified EVOO samples for cultivar and/or geographical origin assessment by suitable multivariate analyses (MVA).

SESSIONE FONTI ALTERNATIVE DI OLI E GRASSI

Opportunities and constraints of farming insects: a global overview

P. Vantomme
FAO Forestry Department - Roma

Trends towards 2050 predict a steady population increase to 9 billion people. Particularly the demand for animal proteins, fats and oils in our food and feed uses is exploding. “New” plant and animal species as alternative sources of proteins, fats and oils are being investigated such as: algae (*Spirula*), Moringa, medusae and jelly fish or even laboratory-made artificial meat. However, farming “insects” appears the most promising. Insects are part of the traditional diets already of approximately 2 billion people worldwide. Insects can contribute to food security given their high nutritional value (proteins, fats, fibres), low emissions of greenhouse gases (GHG), low requirements for land and water, and the high efficiency at which they can convert feed into food. The majority of insects consumed in developing countries today are harvested in nature. In western countries, the disgust factor to consider insects as food, combined currently with their limited availability on the market and a lack of regulations governing insects as food and feed are major barriers for their further expansion. The overall contribution of edible insects to livelihoods is difficult to estimate by lack of reliable statistics. However, the biggest opportunity may well lay in the production of insect biomass as feedstock for animals as it can be combined with the bioprocessing of organic waste. Considering the immense quantities of insect biomass needed to supplement current feed ingredients, automated mass rearing facilities that produce stable, reliable and safe products are being developed. For this to occur significant technological innovations, changes in consumer food preferences, insect-encompassing food and feed legislation, and progress towards more sustainable food production systems are needed.

Uso degli insetti in alimentazione animale

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L’aumento della popolazione mondiale e i cambiamenti delle abitudini alimentari determinano un incremento della domanda di proteine di origine animale con un conseguente incremento della richiesta di materie prime destinate alla produzioni di mangimi.

Attualmente le fonti proteiche più utilizzate in mangimistica provengono essenzialmente da coltivazioni industriali (soia, colza, girasole) e dalla pesca (farine di pesce) ritenute sovente ecologicamente ed economicamente poco sostenibili.

Gli insetti rappresentano una delle alternative ritenute più promettenti in quanto ricchi di nutrienti (proteine, grassi, vitamine e sali minerali). La loro produzione è ritenuta sostenibile in termini di consumo di terra e di acqua, di emissioni di gas serra e di efficienza alimentare. Gli insetti dimostrano inoltre un elevato livello di accettabilità da parte di pesci e monogastrici terrestri poiché fanno parte della loro dieta naturale.

Risultati molto promettenti sono stati ottenuti includendo le farine di insetti nelle diete per le specie avicole, suinicole e di acquacoltura.
L'utilizzo delle farine di insetti in acquacoltura è stato recentemente autorizzato a livello europeo (Reg. (UE) 2017/893) mentre per avicoli e suini al momento il divieto permane.

SESSIONE CONTAMINANTI

Quality parameters and content of processing contaminants in olive oils

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The presence of fatty acid esters of 3-monochloropropan-1,2-diol (3-MCPDE) and glycidol (GE), two classes of processing contaminants formed during refining of vegetable oils and fats, attracts significant attention of chemists, food technologists, toxicologists and other professionals. Over the past decade, the occurrence of these compounds was mapped extensively in a variety of edible oils. However, occurrence data available for olive oil are relatively limited.
Therefore, the SISSG (Italian Society for Study of Fatty Materials) carried out a sample collection comprising authentic virgin, lampante and refined olive oils and crude and refined olive pomace oils. Apart from gathering information on refining conditions, other chemical parameters and legal quality indices (free acidity, peroxide value, fatty acids composition incl. trans isomers, UV absorption) were recorded and they fell within established limits. Furthermore, the diglyceride content was measured according to the IOC (International Olive Council) method, as one of major precursors of 3-MCPDE/GE. The analysis of 3-MCPDE, 2-MCPDE and GE, performed according to the Official AOCS method Cd29a-13 (currently also ISO 18363-3:2017), showed a large variation in the content of these compounds. In several cases the levels exceeded a recently established regulatory limit for GE (EU Regulation 2018/290).
In this speech the major findings are discussed in the context of oil processing and occurrence of these processing contaminants in other vegetable oils and fats.

Mineral oils in vegetable oils: an update

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Mineral oils are widespread environmental and processing contaminants of petrogenic origin. Chemically, they are complex mixtures of saturated (MOSH) and aromatic hydrocarbons (MOAH), giving gas chromatographic traces characterized by the presence of humps of unresolved peaks. Sample preparation before GC analysis must aim to separate the hydrocarbons from the bulk of the fat (and other possible interference), and to pre-separate MOSH and MOAH, which have different toxicological relevance. The former are of concern mainly because of their bioaccumulation potential in human tissues, while the latter are suspected carcinogens, so that their presence in food should be avoided. Vegetable oils are particularly prone to contamination with mineral oils and different sources of contamination have been identified.
The official method for MOSH and MOAH determination in vegetable oils is the and fats (BS EN 16995:2017) basically reproduce the on-line HPLC-GC-FID method developed at the Official Food Control Authority of the Canton of Zurich.
The aim of the presentation is to give a critical overview on possible sources of contamination and analytical methods for MOSH and MOAH determination in vegetable oils. Both on-line and off-line approaches, will be discussed, with a particular focus on the need to introduce a sample enrichment step to reach adequate sensitivity and a sample purification step to eliminate the interference by olefins. The potentiality offered by microwave-assisted saponification (MAS), and by automated solid phase extraction, will be also discussed.

Maximum Residue Limits of pesticide residues in olive oil

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The olive tree is one of the most important and ancient crops in the Mediterranean area where
95% of the olive oil in the world is produced. Furthermore the olive oil represents one of the major component in the Mediterranean diet.

The olive tree can be attacked by a large variety of pests, resulting in a reduction in the quality and quantity of the olive fruit and olive oil produced. Most plant protection products (PPP) used on the olive trees are insecticides, acaricides and fungicides. The traces pesticides leave in treated crops are called “residues”.
A Maximum Residue Level (MRL) is the highest level of a pesticide residue that is legally
tolerated in or on food or feed when pesticides are applied correctly (Good Agricultural Practice, GAP). The European Commission fixes MRLs for all the possible combinations food-pesticide and these data can be consulted in the MRL database on the European Commission website.
The MRL values of pesticide residues are established in olives (as all crops) by the Regulation (EC) 396/2005 and subsequent updates.
To calculate MRLs in olive oil are used processing factors indicate in the coordinated multiannual control programme of the European Union applied at MRLvalues on olives.

3-MCPD, 2-MCPD e glicidolo negli oli vegetali: aspetti tecnico-analitici, aspetti normativi e ricorrenza nei campioni reali.

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3-MCPD, glicidolo, contaminanti di processo, oli vegetali raffinati

E’ a partire dal maggio 2016, quando una Scientific Opinion di EFSA (fonte EFSA Journal del 3/05/16) indicò la potenzialità del rischio per la salute umana di 3-monocloropropan-1,2-diolo (3-MCPD), 2-monocloropropan-1,3-diolo (2-MCPD) e Glicidolo (GLY) nelle forme libere ed esterificate, che queste sostanze sono diventate oggetto di attenzione da parte del settore agroalimentare. Esse rientrano tra i “contaminanti di processo” ossia sostanze che si sviluppano a seguito di processi di lavorazione/trasformazione per la produzione di alimenti e/o ingredienti alimentari. Nello specifico, 2-, 3-MCPD e Glicidolo si formano durante i processi che comportano il passaggio dell’alimento ad alte temperature, in presenza di un certo contenuto di cloro.
Il 26 febbraio 2018 è stato dunque pubblicato il Regolamento (UE) 2018/290, che modifica il regolamento (CE) n. 1881/2006 introducendo i tenori massimi di Glicidil Esteri degli Acidi Grassi (espressi come Glicidolo) negli oli e nei grassi vegetali, nelle formule per lattanti, nelle formule di proseguimento e negli alimenti a fini medici speciali destinati ai lattanti e ai bambini nella prima infanzia. Il Regolamento è entrato in vigore il 19.03.2018**.**
Dopo uno studio collaborativo l’American Oil Chemistry Society (AOCS) ha convalidato e adottato, per la determinazione di questi contaminanti di processo in oli alimentari di origine vegetale, tre metodiche (Cd29a-13, Cd29b-13, Cd29c-13) sono state indicate come metodi normalizzati AOCS raccomandati da EFSA. A partire dal 2015 Chemiservice ha intrapreso lo studio di queste metodiche. La sperimentazione è stata condotta su oli vegetali alimentari raffinati e grezzi, oltre che su oli di oliva applicando il metodo AOCS Cd 29a-13. Per un ristretto gruppo di campioni di oli vegetali è stato applicato anche il metodo AOCS Cd 29b-13.
Per il metodo AOCS Cd 29-13 vengono riportate alcune scelte sperimentali, i risultati della validazione ed i controlli qualità eseguiti in routine. Viene riportata una statistica dei livelli di 3-mcpd e glicidolo dei campioni analizzati nel periodo gennaio-settembre 2018 suddivisi per tipologia di olio. Dallo studio dei risultati, raccolti nel 2018 e suddivisi per tipologie di olio, emerge, per quanto riguarda il 3-MCPD, che i valori più alti si riscontrano negli oli di palma, avocado, riso, a seguire negli oli di sansa. Per quanto riguarda il Glicidolo possiamo dire che i valori più alti per questo contaminante sono stati ottenuti negli oli di palma, avocado e di riso.

Mitigazione/contenimento/dinamica dei contaminanti, Glicidil estere, 2 e 3MCPD e pesticidi

R. Baldini
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Tipo di contaminanti presenti nei vari olii edibili. Formazione dei contaminanti durante i processi di raffinazione. Alcuni principi fisici fondamentali dell’ apprendimento del concetto dell’ applicazione delle tecniche da adottare. Valutazione di soluzione tecniche impiantistiche atte a contenere e a mitigare i contaminanti. Valutazione impatti economici delle tecnologie e ricerca della soluzione tecnica idonea.
Possibili applicazioni industriali da adottare, vantaggi e risultati ottenibili.

Gli ultrasuoni combinati con lo scambio termico per un simultaneo incremento della resa e della qualità dell'olio extra vergine di oliva

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Progettare e costruire un reattore in scala industriale per la somministrazione di ultrasuoni a bassa frequenza ed alta potenza combinato con uno scambiatore di calore, con un livello di maturità tecnologica (TRL) 9 (pronto per il mercato). Questo innovativo dispositivo, unico nel suo genere, collocato tra il frangitore ed il decanter, può rendere il processo di estrazione effettivamente continuo, riducendo i tempi di lavoro, incrementando la capacità lavorativa, migliorando le rese, determinando un incremento dei composti minori. Il processo, per efficienza del processo, garantisce una lavorazione sostenibile ed un rapido ritorno dell'investimento, migliorando la competitività delle aziende olearie ed il giusto reddito ai frantoiani.

Partendo dalla sperimentazione pilota in laboratorio che ha consentito di quantificare l'energia specifica e le opportune frequenze di utilizzo degli ultrasuoni, la progettazione si è avvalsa di una simulazione 3D, statica e dinamica, condotta in ANSYS Fluent. Per la prima sono stati descritti numericamente i fenomeni indotti dai trasduttori sonicanti in una condotta in cui la pasta di olive scorre. Con tale strumento di progettazione si può ottimizzare la geometria, gli spessori, la posizione dei trasduttori, le pressioni di esercizio. Lo scambio termico è stato dimensionato invece con le equazioni di letteratura per l'efficiente riscaldamento o raffreddamento della pasta olearia.

L'effetto meccanico della cavitazione acustica, descritto dalle simulazioni, rompe le cellule passate integre al frangitore, libera ulteriori quote di olio e composti minori. Inoltre, moti vorticosi impressi alla pasta dai transitori di pressione, determinano la coalescenza delle goccioline lipidiche. L'impianto, denominato sono-heat-exchanger, nelle prove sperimentali condotte in numerosi frantoi, si è dimostrato efficiente, ovvero in grado incrementare le rese e il contenuto di sostanze antiossidanti, ed efficace, in quanto raggiunge questi obiettivi in maniera sostenibile.

Sustainable filtration systems for the stabilization of the extra virgin olive oil

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Some strategies and hotspots for extra virgin olive oil (EVOO) stabilization are briefly reviewed in the present work. Further, an innovative stabilization solution is described. The oily must escaping the decanter centrifuge has a veiled appearance due the presence of residual water and solid fragments of the processed olive fruits. These fractions have the potential to affect the EVOO quality traits (sensory, volatile, and biophenolic profiles) during the storage time (shelf-life). Specifically, also the development and survival of yeasts during the storage period have been related to the presence of solids and water and detrimental effects on the sensory characteristics of EVOO have been highlighted. This calls for the oily must clarification and some new strategies could be implemented.

Vertical centrifugation and/or filtration are two common techniques adopted for oily must clarification. Both of them have some operative/quality benefits and drawbacks. The possible inert blanketing of the vertical centrifuge has been investigated aiming to protect the EVOO from oxidation. Furthermore, recently some small sized transformation plants have implemented the EVOO filtration in-line with the decanter centrifuge, thus removing the vertical centrifugation step. Hence, the addition of a steel pre-filter before the conventional plate filter-press has been investigated to improve the overall sustainability of the system. Finally, high pressure processing (HPP), an emerging food preservation technology, has been tested on turbid EVOO to inactivate yeasts naturally occurring in the oil.

Inert centrifugation was found effective in protecting EVOO from oxidation, even if this solution cannot avoid the losses of biophenols because of the use of process water. The implementation of the steel pre-filter before the filter-press improves the filtration cycle by doubling its duration and, thus, halving consumption of filtration sheets and the oil losses in the sheets. HPP allows yeasts inactivation, thus preserving the EVOO volatile profile, despite the persistence of turbidity.

Centrifugation and stabilization of turbidity: the Alfa Laval experience

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The vertical centrifuge in the extra virgin olive oil industry is widely used for oil purification at a final stage of extraction process. The obtained oil should be commercialized directly as turbid or sent to settling and/or filtration. Parameters like temperature, flow rate, water dilution, interface position, discharge interval and cleaning, are important to have optimal purification, reduction of water consumption and consequent loss of olive oil quality. A recent research showed that, a specific adjustment of vertical centrifuge allows to obtain a stable "veiled" oil reducing the formation of deposits at the bottom of the oil bottles. "Veiled" oils obtained by centrifugation, compared to filtered ones showed, by the same research, no negative effects on the oxidative stability and with a higher phenolic concentration at the end of storage period. The production of stable "veiled" oils by proper centrifugation could be a potential application to satisfy the important market segment which associate turbidity with genuineness of extra virgin olive oil.

Riduzione dell'impatto ambientale delle Acque di Vegetazione

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Presentazione della soluzione di Alfa Laval per il trattamento delle acque di vegetazione provenienti dai frantoi al fine di ridurne l'impatto ambientale

Utilizzo di evaporatori continui con scambiatori a piastre funzionanti sottovuoto e alimentati a vapore o tramite ricompressione meccanica per separare acqua a basso contenuto inquinante dal flusso principale.

Descrizione del principio di funzionamento dei suddetti evaporatori e delle principali caratteristiche tecniche e costruttive evidenziandone i provati benefici.

L'evaporazione sottovuoto consente di estrarre acqua a basso contenuto inquinante da inviare all'impianto di trattamento riducendone i costi operativi e, allo stesso tempo, consente di ridurre drasticamente il volume dell'acqua di vegetazione residua da destinare a un trattamento dedicato o all'eventuale estrazione di sottoprodotti.

SESSIONE SHELF LIFE

Uncertainties, pitfalls and perspective in shelf life assessment of food undergoing lipid oxidation

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Shelf life is a finite length of time after production and packaging during which the food product retains a required level of quality under well-defined storage conditions. Food companies are required by law to attribute a shelf life to their products under defined storage conditions. Beyond this requirement, manufacturers have also to deal with the more debatable concept of secondary shelf life. The latter is the period after pack opening during which a food/ingredient maintains an acceptable quality.

The growing need for increased food sustainability boosts the industry demand for more accurate primary and secondary shelf-life prediction methodologies. Currently, many shelf-life determinations of commercial shelf-stable products are based on trial-and-error methods, which could pose risks resulting in brand damage (overestimation) or food waste (underestimation).

Defining the exact shelf life of a shelf stable food is a still a challenge. This is especially true for foods suffering oxidation. Primary and secondary shelf life issues relevant to foods undergoing oxidation will be critically discussed, underling possible uncertainties and pitfalls of present assessment methodologies and highlighting future research needs

Olive oils storage and best before date: risk factors, innovative quality controls and guidelines

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It is well known that, during the conservation of the edible oils, the oxidation processes favors the accumulation of free radicals, the generation of off-flavour, the loss of antioxidants, the lowering of sensory, health qualities, category, product value and consumer acceptability.

The objective of this presentation is to summarize the best practices for the storage of olive oils and olive-pomace oils, from the production and before the consumption, with the aim to carefully maintain, as longer as possible, the own composition and characteristics defined by the regulation, given that that the oils must address the legal parameters all the time they remain on the market, from production to the final consumption.

The presentation takes into consideration the different phases of the olive oil preparation after the extraction and before the final consumption, discusses and addresses the most important aspects of proper or incorrect transportation or storage and suggest some possible new levers and tools to follow and asses the quality in terms of oxidation.

The presentation follows step by step the oil from the phase preceding the bottling, till the act of purchase by the consumer in the small shop or the supermarket. The time that elapses and the conditions are commented, selecting the critical aspects crucial for the quality of the oil at destination. Each phase is discussed and some hypotheses of new systems to follow the quality are also suggested.

- **ABSTRACTS - POSTERS**

SESSIONE ANALITICA ED AUTENTICITA'

Application of chemical and thermal analysis for the evaluation of traceability of italian extra virgin olive oil

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The aim of this work, supported by AGER foundation (Project "SOS Sustainability of the Olive Oil System", grant no. 2016-0105), is to select chemical (fatty acids) and thermal predictors, obtained by means of differential scanning calorimetry (DSC), able to discriminate among extra virgin olive oils (EVOO) belonging from different minor cultivars of different Italian regions. The use of DSC as complementary technique to those traditionally employed in this sector will be thus proposed.

Thirteen extra virgin olive oils belonging from minor olive cultivars of three different Italian regions were analyzed: two from Apulia (Oliva Rossa, Cima di Melfi and Bambina), three from Sardinia (Corsicana da Olio, Semidana and Sivigliana), three from Abruzzo (Dritta, Tortiglione and Gentile de L'Aquila) and four from Calabria (Ottobratica, OttobraticaCalipa, Tonda di Filogaso, Ciciarello).

For each of the selected cultivars the drupes were harvested at three different ripening times, at intervals of 15 days, starting about one month before the traditional harvest time.

For each sample fatty acids were determined as FAMEs by capillary GC analysis after alkaline treatment. The results were expressed as area normalization in percent (%).

Thermal properties upon cooling and heating were measured by means of DSC Q100 (TA Instruments, New Castle, DE,USA) in a range of temperature from 30 to - 80°C and vice versa at a scanning rate of 2°C/min. Temperatures and enthalpies of the transitions were recorded.

ANOVA and Principal component analysis (PCA) were conducted by means of the Statistical Software SPSS (version 25) to discriminate or find relationships among the samples according to specific variables. The

experimentation has been conducted over two crop years.
Several differences were evidenced between the analyzed EVOOs, with good correlations between the chemical and thermal measurements. Saturated and monounsaturated fatty acids resulted respectively related to the onset temperatures of the cooling and heating transitions, being instead enthalpy not discriminating among the samples. PCA analysis helped in identifying the variables able to separate the oils according to their cultivar and geographical origin.
DSC resulted to be a useful tool to obtain a unique fingerprint of the oils, useful to identify their botanical and geographic origin.
The experimentation will be conducted over three years, to confirm the data and open a good way for the characterization and thus recover and valorization of the minor olive cultivars, botanical heritage of the Italian regions.

Fast and green FT-IR classification of extra virgin olive oil based on ethyl ester content

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Ethyl esters are mandatory parameters to be checked for extra virgin olive oil commercial classification. Their determination is complex, time consuming, and expensive. Moreover, many toxic solvents are required. Thus, our aim was the development of a model based on FT-IR spectroscopy able to classify virgin olive oils in two classes: extra and non-extra products.
A set of 119 virgin oils were analysed for the content of ethyl esters; besides, their FT-IR spectrum was collected (6 per sample), in the range 4000-600 cm^{-1}, with a 4 cm^{-1} resolution. After averaging, spectra were subjected to smoothing and Standard Normal Variate (SNV) pre-treatments and used to develop classification models by means of Linear Discriminant Analysis (LDA). The 30 variables most relevant for discrimination were selected by applying the Select algorithm implemented in V-Parvus software. Models were validated by internal and external validation.
Preliminary results showed good classification ability of the developed model. An average correct classification of 98%, 92%, and 88% for calibration, cross-validation and prediction, respectively, was obtained. At this point, the method seems to be useful for fast screening purposes. In future perspectives, sample set broadening and use of the selected variables for the development of regression models for the quantification of ethyl esters could be considered.

La spettroscopia NIR per determinare il grado di maturazione delle olive: confronto tra uno spettrofotometro VIS/NIR e uno FT-NIR

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Negli ultimi anni, nel settore olivicolo è cresciuto l'interesse verso lo sviluppo di metodiche analitiche alternative a quelle tradizionali, più rispettose dell'ambiente e in grado di fornire risposte rapide e applicabili anche in campo. In questo contesto, la spettroscopia NIR si rivela uno strumento efficace. L'obiettivo di questo lavoro è stato lo sviluppo di applicazioni basate sulla spettroscopia vis-NIR e FT-NIR per monitorare la maturazione delle olive in campo. La rapida valutazione dell'indice di maturazione è infatti determinante per individuare il momento più opportuno per la raccolta delle olive, al fine di ottenere una buona resa produttiva e una buona qualità dell'olio.
Questo lavoro è parte di un progetto AGER (Progetto Agroalimentare e Ricerca), denominato "Sustainability of the Olive-Oil System - S.O.S.", il cui obiettivo è quello di migliorare e rafforzare la sostenibilità della filiera dell'olio extravergine di oliva in Italia.
Sono state analizzate cinque cultivar di olive (Cima di Melfi, Oliva Rossa, Corsicana, Semidana e Sivigliana) raccolte a diversi stadi di maturazione. Le olive sono state classificate in base all'indice di maturazione utilizzando due metodi diversi e sono stati inoltre acquisiti gli spettri vis-NIR (400–1023 nm), con strumento da campo, e FT-NIR (900–2560 nm) mediante spettrometro da banco. Dopo pretrattamento mediante smoothing, i dataset ottenuti da ciascuno strumento (1020 spettri) sono stati analizzati mediante Principal Component Analysis (PCA). Sugli spettri pretrattati mediante smoothing, Standard Normal Variate (SNV) e trasformazione in derivata

prima è stato poi applicato il metodo di classificazione Partial Least Square – Discriminant Analysis (PLS-DA), con l'obiettivo di creare modelli in grado di classificare correttamente le olive in 4 classi di maturazione:
Classe 1 - olive totalmente verdi; Classe 2 - olive con meno del 50% di superfice invaiata; Classe 3 - olive con più del 50% di superfice invaiata; Classe 4 - olive totalmente invaiate.
Sono stati elaborati due dataset, uno completo, contenente gli spettri di tutte le olive analizzate, e un dataset specifico per le olive della cv. Cima di Melfi (180 spettri).
Dall'analisi qualitativa, mediante PCA, si è individuato un andamento dei campioni di olive analizzati in funzione dell'indice di maturazione (PC1) e una suddivisione per provenienza e/o varietà (PC2). Per quanto riguarda la classificazione, i migliori valori di accuratezza in validazione sono stati registrati per gli spettri acquisiti nel vis-NIR e pretrattati mediante SNV, sia per la classificazione delle 1020 olive totali (95.20±4.88%), sia per quelle appartenenti alla cv. Cima di Melfi (92.33±5.86%). Con gli spettri FT-NIR si sono registrati dei valori di accuratezza inferiori, pari a 84.41±6.11% per gli spettri totali (pretrattamento di smoothing) e a 82.98±7.65% per quelli della cv. Cima di Melfi (pretrattatamento SNV).
La classificazione delle olive in campo mediante applicazione della spettroscopia NIR appare quindi possibile in modo rapido, accurato ed oggettivo.

Confronto tra l'impatto ambientale dell'analisi tradizionale e mediante spettroscopia nir sull'oliva

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Le analisi che tradizionalmente si effettuano sulle olive richiedono l'utilizzo di molteplici strumentazioni, lunghi tempi di analisi, l'utilizzo di solventi potenzialmente dannosi, sia per la salute umana che per l'ecosistema, e la distruzione del campione. Le stesse analisi effettuate con una tecnologia ottica, non distruttiva (spettroscopia nella regione del visibile e vicino infrarosso, Vis-NIR), permettono la stima dei parametri di interesse, in modo molto rapido, con una sola lettura, anche condotta dagli addetti alla raccolta. L'unico aspetto laborioso è la costruzione di robuste calibrazioni. Il grande vantaggio sarebbe un ridotto impatto ambientale della tecnologia ottica, la cui valutazione, a confronto con i metodi tradizionali, è lo scopo di questo lavoro. Esso è parte di un progetto AGER (Progetto Agroalimentare e Ricerca), denominato "Sustainability of the Olive-Oil System - S.O.S.", il cui obiettivo è quello di migliorare e rafforzare la sostenibilità della filiera dell'olio extravergine di oliva in Italia.

Le analisi tradizionali per la valutazione qualitativa delle olive individuate come riferimento sono state: contenuto di acqua, olio e fenoli totali. Il confronto è stato effettuato per le stesse determinazioni mediante analisi ottica.Il metodo Life CycleAssessment (ISO 14040:2006, ISO 14044:2006), è stato applicato per valutare l'impatto ambientale mediante un preciso schema di esecuzione. L'approccio utilizzato (*from cradle to grave),* ha considerato tutti gli input e output di ogni analisi, tenendo conto della strumentazione necessaria per l'esecuzione (estrazione materie prime, costruzione, utilizzo e smaltimento), dei solventi utilizzati (ottenimento solvente, utilizzo e smaltimento), delle risorse energetiche necessarie. Inoltre, per la strumentazione Vis-NIR sono state considerate le analisi necessarie per la calibrazione dello strumento. I dati raccolti sono stati elaborati con il software SimaPro.
Il confronto tra l'impatto ambientale delle analisi tradizionali e quello delle analisi ottiche ha evidenziato un netto vantaggio nell'applicazione della strumentazione ottica la quale, non solo garantisce la non distruzione del campione e un risultato in tempi brevi ma, ha un impatto sull'ambiente 36 volte inferiore rispetto alle analisi tradizionali di riferimento. Se le maggiori voci di impatto ambientale per le analisi tradizionali sono la corrente elettrica, la strumentazione e le sostanze chimiche, per l'analisi non distruttiva, l'impatto ambientale è dettato maggiormente dalla necessità di calibrare lo strumento, attività che richiede di effettuare su un relativamente elevato numero di campioni (500 per la calibrazione iniziale, 200 per il mantenimento) sia le analisi tradizionali che le letture ottiche (Vis-NIR).

Validation of an off-line SPE-GC-FID method for the determination of n-alkanes in vegetable oils

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The main objective of the work was the validation of a rapid and solvent-sparing off-line SPE-GC-FID method

for the determination of endogenous n-alkanes in vegetable oils and comparison with the on-line LC-GC-FID method. The distribution of n-alkanes may be a very good fingerprint useful to distinguish between different vegetable oils and to determine adulteration of high quality oils with other cheap and low-quality oils.
For n-alkane evaluation, a suitable mixture of internal standards was added to an aliquot of the sample, then SPE cartridge packed with silver silica gel was carried out and n-alkanes were eluted with n-hexane. The analytical determination was performed by capillary GC, applying large volume injection with the retention gap technique. Solvent and matrix-matched calibration curves were obtained in the range 0.05-50 µg/g and repeatability was assessed by performing 6 replicate analysis on the same extra virgin olive oil.
The method showed good performance characteristics: the linearity coefficients (R2) obtained with the minimum square method were equal to 0.99; recoveries in matrix ranged from 86 to 99%, being practically quantitative at the lower spiking level. Different oils showed typical n-alkane profiles. Also the amount of total n-alkane differed significantly: the highest concentration was found in an extra virgin avocado oil (595 µg/g), while the rest of the samples revealed amounts ranging from 6 µg/g (refined palm olein oil) to 95 µg/g (desterolized and deodorized high oleic sunflower oil). Results obtained were comparable to those obtained with the on-line method. The off-line method was only slightly less repeatable (RSD 5.4%) than on-line method (RSD 2.8%).

Two dimensional gas chromatography: a powerful tool for discriminating VOCs in monovarietal and commercial extra virgin olive oil

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The unique and special flavour of EVOO can be attributed to VOCs such as the C6 and C5 aldehydes, which are responsible for green aromatic notes, but also terpenes and sesquiterpenes, which tend to generate greater aromatic complexity in quality oils. 15 monovarietal EVOOs produced from different cultivars (purchased directly from producers) were compared with 25 blended commercial EVOOs (purchased in national grocery stores). The aim of the study was to demonstrate the possibility of discriminating between these two classes of samples based on VOC composition.
Extra virgin olive oil VOCs were analysed with HS-SPME-GCxGC-TOF-MS. A total of 1254 putative compounds were detected, with 123 being significantly different in monovarietal and commercial oils. Compound identity was confirmed with Kovats retention index and by comparing spectra compounds to NIST 2.0, Wiley 8 FFNSC 2 (Chromaleont, Messina, Italy).
Principal component analysis (PCA) showed clear separation between the two classes of samples. Specifically, commercial samples were more influenced by compounds such as alcohols, acids (acetic acid and formic acid) and other acetates frequently responsible for certain unpleasant notes. The monovarietal samples were more influenced by compounds deriving from LOX pathways (aldehydes C6 and C5), as well as terpenes and sesquiterpenes, such as valencene, copaene and o-cimene for example, which generally generate pleasant wood, green and lemon notes.
Furthermore, differences in the composition of monovarietal samples were evaluated. Two varieties (Casaliva and Ottobratico) were clearly distinguished from the rest of the monovarietal samples, underlining that the cultivar and pedoclimatic conditions can influence VOC composition.
The preliminary results show that HS-SPME-GCxGC-TOF-MS is a fast and very powerful tool for revealing differences between the aroma of various EVOO classes.
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Stable isotope ratio analysis for characterizing PDO extra-virgin olive oil 'Garda'

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PDO extra-virgin olive oils are premium products with higher quality which command a higher price. Stable isotope ratio analysis of $^{13}C/^{12}C$, combined with or without analysis of $^{18}O/^{16}O$ and $^{2}H/^{1}H$ proved to be a good tool for characterising geographical origin, as isotope ratios change according to latitude, suggesting distance from the sea and environmental conditions during the growing of plants (water stress, atmospheric moisture and temperature) as co-factors of variability. Objective of this study was to define the stable isotope ratio profile of the PDO extra-virgin olive oil 'Garda'.

Around 80 samples of extra-virgin olive oil produced in the area of Garda Trentino (Italy) were collected in 2 seasons (2016 and 2017) and analysed.
The C isotope ratio of bulk oil has been determined by EA-IRMS (Elemental Analyser-Isotope Ratio Mass Spectrometry) directly on the raw sample without any need of pre-treatment. The analysis of H and O stable isotope ratios of bulk dehydrated oil has been performed via TC (Termal Conversion)/EA-IRMS. The H and C isotopic values of the four main fattyacids (linoleic, oleic, palmitic and stearic acids) have been performedusing IRMS coupled with GC (Gas Chromatography), after transesterification of oil.
The Garda PDO extra-virgin olive oil has very characteristic and typical H, C and O stable isotope ratios, because it is produced in an area with a unique microclimate. On this basis, it can be distinguished by the extra-virgin olive oils produced in the Mediterranean areas.
The H and C stable isotope ratios of the main fatty acids can be further markers of geographical traceability.
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SESSIONE CONTAMINANTI

MOSH/MOAH negli oli extravergini di oliva: aspetti tecnico-analitici e ricorrenza nei campioni reali

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I MOSH (MineralOilsaturedHydrocarbons) e MOAH (MineralOilaromaticHydrocarbons fanno parte della vasta e complessa classe di composti degli Oli Minerali. Le cause che portano alla presenza di oli minerali MOSH e, in parte dei MOAH negli oli vegetali, sono molteplici: contaminazione ambientale in campo (gas di scarico, fumi di combustione presenti nell'atmosfera), contaminazione da materiali da imballaggio in diretto contatto con semi/frutti oleaginosi durante le fasi di stoccaggio/trasporto, trattamento con particolari pesticidi. Negli oli vegetali, un'ulteriore particolare causa della loro presenza è dovuta anche ai processi di pressione (oli lubrificanti), raffinazione (passaggio su terre decoloranti) e confezionamento. Occorre considerare che attualmente mancano indicazioni normative ufficiali relative ai limiti massimi dei livelli degli oli minerali tollerabili negli alimenti; manca un metodo ufficiale standardizzato per la distinzione tra le varie frazioni di oli minerali.
Il Laboratorio Chemiservice si avvale dell'applicazione di un metodo validato internamente e accreditato presso l'ente di accreditamento italiano ACCREDIA che si è rivelato perfettamente in linea con i metodi di analisi citati dall'EFSA, sia sotto il profilo della procedura analitica sia sotto il profilo delle prestazioni. Principio del metodo: l'olio, addizionato di opportuni standard di riferimento interni (C40-tetracontano e perilene) e surrogati viene frazionato mediante cromatografia su colonna di gel di silice idratato; se ne ricavano due frazioni contenenti rispettivamente i MOSH e i MOAH che vengono analizzate mediante gascromatografia in colonna capillare con rivelazione a ionizzazione in fiamma (GC-FID).
Nel periodo compreso tra settembre 2017 e gennaio 2018 sono stati analizzati quasi 200 campioni di olio extravergine di oliva. Dai dati raccolti si evince che quasi il 40% dei campioni analizzati presentano concentrazioni di MOSH superiori a 10 mg/kg con un valore medio di 12,9 mg/kg.
MOAH (C10-C35) - Dai dati raccolti si evince che quasi la metà dei campioni analizzati presentano concentrazioni di MOAH superiori a 1 mg/kg con un valore medio di 1,5 mg/kg.
Nella presentazione viene riportato un aggiornamento di tali valutazioni estendendo il periodo di acquisizione dei dati a giugno 2018. Presenti anche valutazioni su oli prodotti/commercializzati in paesi extra Europei.

Fitofarmaci negli oli vegetali: aspetti tecnico-analitici, aspetti normativi e ricorrenza nei campioni reali

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I residui di pesticidi sono presenti negli alimenti e nei mangimi a causa dell'uso di prodotti fitosanitari su colture o prodotti alimentari utilizzati per la produzione di alimenti e mangimi. Al fine di garantire un livello elevato di protezione del consumatore, a livello europeo sono fissati i limiti di legge, i cosiddetti "livelli massimi di residui" o "LMR". Gli LMR definiscono la concentrazione massima di residui di pesticidi consentiti negli alimenti e nei mangimi. Tali limiti normativi sono stabiliti dal regolamento (CE) n. 396/2005. Attualmente sono in vigore LMR armonizzati per oltre 500 pesticidi. Per i pesticidi non menzionati esplicitamente nella legislazione sui LMR è

applicabile un LMR di default di 0,01 mg / kg, un livello pari al limite di quantificazione (LOQ) ottenibile con i metodi analitici utilizzati per l'applicazione dell'MRL. Il regolamento (CE) n. 396/2005 fornisce inoltre il quadro giuridico per le attività di controllo dei residui di antiparassitari che devono essere svolte dagli Stati membri al fine di far rispettare gli LMR.
L'oggetto è la presentazione del quadro normativo comunitario e nazionale vigente in relazione ai limiti massimi di residui (LMR) nei semi e frutti oleaginosi e possibilità di applicazione ai prodotti trasformati. Panoramica sulla normativa vigente in alcuni dei paesi maggiori importatori di olio di oliva provenienti da agricoltura convenzionale. Cenni ai metodi analitici normalizzati applicati nel laboratorio Chemiservice. Statistica sull'incidenza dei fitofarmaci negli oli di oliva e in altri oli vegetali alimentari di maggior interesse commerciale.
Per la determinazione della concentrazione delle sostanze attive nell'olio di oliva e negli oli vegetali destinati al consumo umano sono stati utilizzati due metodi diversi entrambi normalizzati. Per un gruppo ristretto di campioni sono stati messi a confronto i risultati ottenuti con i due metodi
Risultati: Valutazione dei risultati analitici di più di 3000 campioni per anno per un periodo compreso tra il 2015 e il 2017. Quasi il 99 % degli oli di oliva analizzati sono risultati conformi ai limiti legali; nel periodo 2015-2016 circa il 50 % dei campioni non presentavano livelli quantificabili di fitofarmaci, nel 2017 la percentuale di campioni con tracce di fitofarmaci non quantificabile è scesa a circa 35%.
Applicazione di entrambi i metodi analitici ad un gruppo di campioni di oli vegetali: le due metodiche hanno restituito a risultati confrontabili statisticamente; presentazione dei vantaggi e degli svantaggi dell'applicazione delle due metodiche. Esposizione delle problematiche sia legate all' applicazione della normativa comunitaria ai prodotti trasformati sia alla non-armonizzazione delle normative vigenti in paesi di importazioni non comunitari.

SESSIONE: OLI E GRASSI IN PRODOTTI DA FORNO

Study of the antioxidant potential of tyrosyl oleate in a real lipid matrix

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The aim of this research was the study of the antioxidant potential of a lipophenol, tyrosyl oleate, obtained from the reaction between oleic acid and tyrosol. The antioxidant effect of tyrosyl oleate was studied in tarallini, typical Italian bakery product, was carried out through the study of the oxidation process.
The reaction between tyrosol and oleic acid was carried out according to Fernandez et al. (2012) and after purification through chromatographic column, different percentage of tyrosyl oleate were used in tarallini formulation. Formulation of tarallini was made according to the traditional receipt using wheat flour, salt and sunflower oil to obtain the control sample (CS); based on sunflower oil content 1, 4 and 7% of tyrosyl oleate was added (1TO, 4TO and 7TO). The oxidation process was studied, immediately after the formulation through an accelerated oxidation analysis using the Oxitest® instrument (Riciputi, 2017). Then at different storage time (T0, T15, T30, T37 and T45) peroxide value, spectrophotometric analysis according to Shantha& Decker method (1994), Oxidized Fatty Acids (OFA) (Verardo et al., 2010) and volatile compounds (Marzocchi et al., 2017) originated from lipid oxidation, with innovative gas chromatographic techniques, were determined in the different samples.
Analysis by Oxitest® allowed to discriminate between the control sample and the three samples with tyrosyl oleate; in fact, already in 1TO sample the IP value was more than twice (13.58 h) of CS (6.10 h); in the 4TO and 7TO samples the IP value reached 22.34 h and 25.28 h, respectively. For the peroxide value, at T0 and T15 all the samples did not show significant differences ($p<0.05$) having all the values under the legal limit of 20 meqO_2/ kg of fat. At T30, instead, CS and 1TO exceed the legal limit (79.6 and 49.0 meqO_2/ kg of fat, respectively), while 4TO and 7TO registered a peroxide value of 17.3 and 16.1 meqO_2/ kg of fat. These two samples exceed the legal limit after 45 days of storage (T45); so, in the worst condition (sunflower oil and storage at environmental conditions) the addition of tyrosyl oleate can slow down the lipid oxidation process. CS registered significant higher ($p < 0.05$) OFA content rather than all the samples with tyrosyl oleate (0.60 mg FA/100 mf FAME); 7TO sample showed the significantly lowest values than 1TO and 4TO at T30 (0.41, 0.37 and 0.31 mg FA/100 mg FAME, respectively). The concentration of volatile compounds originated from lipid oxidation increased with the increasing of shelf life. Tarallini made with tyrosyl oleate shown a significantly lower concentration of these compounds than CS for all the storage time; hexanal, the major representative compound of lipid oxidation, was the preponderant compound. Considering that the tarallini were made with one of the most oxidable oil, sunflower oil, and stored at room temperature without any modified atmosphere; the presence of tyrosyl oleate allows to counteract lipid oxidation and extend the shelf life of tarallini added with it.

SESSIONE UTILIZZAZIONE E VALORIZZAZIONE DEI SOTTOPRODOTTI DELLE FILIERE OLI E GRASSI ALIMENTARI

Waste and by-product from olive oil production as source of functional compounds

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A large amount of wastes and by-products are generated during olive oil production process such as olive leaves and pomace. Since the importance of some molecules from vegetables, particularly from olives, has been highlighted, olive leaves and pomace are potential rich sources of phenolic compounds, endowed with a wide array of biological activities and also of valuable lipophilic molecules. If the olive leaves are a good source of oleuropein and flavonoids, the olive pomace represents a good source of β-sitosterol, squalene and terpenic compounds. For these reasons our aims are the extraction and the use in foods and in biological systems of the above-mentioned compounds.

The extracts obtained from olive leaves were characterized for the phenolic profile by UHPLC-ESI-MSnwhereas the lipophilic molecules from olive pomace were detected by gas chromatography after saponification and derivatisation. The foods (salty snacks and olive-based paste) enriched with olive leaves extracts (OLE) were monitored with antioxidant activity assays, volatile compounds determination and microbiological analyses. Intracellular ROS (Reactive Oxygen Species) content was evaluated with the fluorescent probe dihydrorhodamine-123 in epithelial cells exposed to OLE.

The salty snacks added of OLE showed a significantly lower level of volatile compounds originated from lipid oxidation and an increased antioxidant activity (which improved the oxidative stability of snacks) than control snack without OLE. OLE influenced the microbial growth in olivebased paste during storage. The pre-treatment of epithelial cells with OLE lowered the intracellular ROS content.

Technological functionality of olive leaves phenolic extracts

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Most of olive by-products, such as olive leaves, are still undervalued despite their high potential as a source of functional compounds. However, to incorporate such compounds as active ingredients in complex food systems, it is of primary importance the knowledge of their technological functionality which represented, thus, the objective of this work. To this aim, three olive leaves phenolic extracts obtained by either pure water or two different water:ethanol ratios (Eth0, Eth30, Eth70), were characterized for some technological properties such as surface activity at the air/water interface, emulsifying capacity, water/oil holding ability and flow behaviour.

The surface tension was evaluated by means of a tensiometer and a dose-dependent curve was obtained for each phenolic extract at pH 4.5 and pH 7. The emulsifying activity was evaluated by measuring the particle size and distribution of oil-in-water model emulsions: the dispersed phase, represented by sunflower oil, varied from 5% to 20% (w/w) while two buffered solution at pH 4.5 and 7 were used as continuous phase. A concentration of 0.3% (w/v) of each extract was added to the water phase. The flow behavior was investigated by means of a rheometer equipped with concentrical cylinders while water and oil holding capacity (WHC/OHC) were determined by previous solubilization of each extract either in water or in oil followed by centrifugation.

The phenolic extracts exerted a significant surface activity showing a typical dose-dependent behavior; in particular the extracts Eth30 at pH 4.5 and Eth70 pH 7 resulted to be the most surface active. Surface properties were affected by pH. Such results were confirmed also by the emulsifying capacity: the model emulsions enriched with Eth30 at pH 4.5 showed a monomodal particle size distribution with a mean diameter of 5 μm and higher resistance towards physical instability when compared to the other systems. No significant differences were observed in their flow behavior while WHC and OHC were higher for the Eth70 extract.

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Catalysts development for biomass conversion into chemicals and fuels

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In this communication we describe our approach to solving the problem of the simultaneous *trans*-esterification of lipids (that require a basic catalyst) and esterification of FFAs (that require an acid catalyst), using mixed

oxides *ad hoc* prepared. New mixed oxides based on calcium, cerium and aluminium have been used as catalysts in the reaction of *trans*-esterification of oils of different composition and quality, namely: i) extra virgin olive oil as a test case (low acidity) and ii) non-edible oil (high acidity). Among the several catalysts used, 12CaO $7Al_2O_3$ $7CeO_2$ has shown unprecedented properties in terms of activity and resistance in the simultaneous *trans*esterification/esterification.
In this work we have prepared new mixed oxides based on ceria loaded with calcium oxide or alumina either separately or in combination, by using a dry-technique that avoids the use of water and the formation of large volumes of waste water. The different acid-base properties in function of the composition allow to produce catalysts able to convert directly in one pot process a low quality oil rich in FFAs into a valuable product. The choice of ceria as acidic support was suggested by our previous experience on its use in catalysis.
Al_2O_3 was selected for its stabilization properties. As we have already shown in combination with CeO_2, Al_2O_3 modulates the oxidative properties of the latter towards organics by interacting with the surface and making more difficult the surface oxygen-transfer. In this work, each oxide has been used alone to show its catalytic capacity towards the same substrate, and couples of oxides or quaternary oxides have been used. CaO Al_2O_3 has also been used, that may not be considered a real mixed oxide. CaO CeO_2 and CaO Al_2O_3 CeO_2 oxides with variable composition have been tested in order to demonstrate the effect of the acid and basic components on real mixtures of lipids and FFAs.
The new mixed-oxides catalysts used in this work are quite adaptable to convert bio-oils of different composition lipids-FFAs. A further improvement is represented by the catalytic extraction that
avoids the preliminary extraction of bio-oil and produces FAMEs and glycerol quite pure for further
applications. The catalyst 12CaO $7Al_2O_3$ $7CeO_2$, is active especially in the conversion of biooils with high FFAs content. It can be easily prepared by HEM and calcined at 823 K, that reduced the environmental impact of catalyst preparation. It is easily recovered and can be re-used several times reducing the environmental impact of the catalyst disposal. The fact that the whole process does not use water is another quite positive aspect, as water use and processing is a quite sensitive parameter in industrial processes. As an additional benefit, bio-glycerol produced in this way is salt-free and water-free, that reduces the need of costly and high energy purification techniques, making it more easily usable in further conversion technologies such as the biotechnological conversion into added value chemicals and monomers for polymers (e.g. 1,3-propandiol), an application that is salt sensitive. The excess methanol used in the conversion of lipids and FFAs is not wasted as it can be easily recovered and re-used.

SESSIONE TECNOLOGIE PER GLI OLI ED I GRASSI

Industrial demonstration of megasonics technology for enhanced oil recovery

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The goal of research was to demonstrate the effects of high-frequency ultrasoundstreatment, post malaxation, on olive oil quality and extractability, in an industrial oliveoil mill context.
A megasonic system was developed to verify the effects of high frequency ultrasoundtechnology in an olive oil extraction process, post malaxation. Megasonic system wasdesigned for scale up trials employing 9 kJ/kg (600 kHz) ultrasound energy inputs.Trials with Barnea and Picual varieties were conducted in a single processing line, withand without megasonic application, using batches of 3.6 ton of olives.The experimental tests were carried out in Australia at the Boundary Band mill (Boort,VIC – Australia).
The results shown a significant improvement of the extractability. Additional trialsinvolving the megasonic treatments of pastes, previously malaxedwith enzymesaddition, trials concerning the malaxation reduction tine from 90 to 60 min, also shownpositive effects of the megasonics technology in an industrial setting.

Combined machines by using ultrasounds, microwave and heat exchanger to improve the olive paste conditioning: impact on olive oil quality and yield

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In this paper an industrial combined plant assembled by a low frequency ultrasound device, a microwave apparatus and a heat exchanger were employed and implemented inan industrial olive oil plant to improve the conditioning of the olive paste.
Four different conditioning conditions were compared to the traditional one. The extractability index (E), rheological parameters and olive oil quality were determined.
The use of heat exchanger only for olive paste conditioning leads to a low value ofextractability.
By placing the heat exchanger and the traditional malaxer in series, it is possible toobtain the same quantitative performances, reducing the conditioning time from 40 minto 20 min. By using a microwave system in series with a heat exchanger, it is possibleto reduce the conditioning time considerably to just 4 min, obtaining an entirelycontinuous process. Combining heat exchanger, microwave, ultrasound a slight increaseof extractability was found. Finally, the use of alternative conditioning technologies,alone or in combination, are able to save the lipophilic antioxidant furniture while, onthe contrary, brought to a reduction of hydrophilic antioxidant. The cavitation effect ofultrasound is able to overcome this drawback.

Design and testing of a full-scale scraped surface heat-exchanger for the thermal conditioning of olive paste coupled with a passive malaxer

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The aim of the project was to design and test a low-cost and high-efficiency system composedby a scraped heat-exchanger coupled with passive malaxers. The developed systemis useful to warm up and knead the olive paste simultaneously. Respect to the heat-exchangers already commercialized, this prototype is equipped with a scraping blades that increase the convective movements, reducing the process time, optimizing the sustainability of the continuous olive oil extraction system. The innovative device, placed downstream the crusher, was dimensioned to allow a fast worming up the olive paste reducing the malaxing time. The passive hermetic malaxer is a cylindrical thank equipped with rotating blades. Respect to the traditional malaxer, the passive one is built excluding the water jacket simplifying the constructive aspects. Both the heat exchange and the passive malaxers are thermally insulated to avoid any possible thermal losses towards the external environment, including all the pipes through which the olive paste passes when already heated. The thermal conditioning allows both cooling and warming.
The thermal power transferred to the olive paste can be calculated knowing its mass flowrate, the specific heat capacity and the difference of temperature between outlet and inlet.
Assuming that the thermal losses towards the external environment are negligible thanks to the efficient thermal insulation, the amount of heat power transferred to the oil paste can be considered equal to the amount of heat power taken from the water stream. The thermal power to be exchanged between the oil paste and the water flux needs to be achieved by using an appropriate heat transfer surface area. In fact, the value of the thermal power is equal to the global heat exchange coefficient multiplied by the overall heat transfer surface area and the logarithmic mean temperature difference. With regard to the global heat exchange coefficient, it depends on the convective coefficients of water and olive paste. The convective coefficient of olive paste depends on scraper velocity. This consideration depends on the knowledge that the Nusselt number can be retrieved according to the Reynolds number. The thermal power loss from the passive malaxer can be evaluated by means of the Fourier's Law.
The innovative low cost device (TRL9) allows a fast worming up the olive paste reducing the malaxing time and with a minor energy employment, assuring satisfactory oil yields.