Green Chemistry from desktop to industrial renewable cell growth scaffolds, materials, and platform chemicals

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The high rates of global development produce anthropogenic changes that added to natural ones decrease life, ecosystems and natural resources with excessive land use and waste generation. Agriculture is one of the pillars of our increasing world population society and countries which have large agricultural resources, such as Spain, also produce vast amounts of residues, that can produce environmental hazards on the environment. A way of overcoming environmental issues found in this research group, given the agricultural use of land in our country, is the transformation of agricultural residues into renewable and enormously valuable materials and substances, closing in this way an industrial cycle, reaching at the same time solutions for economic and environmental problems, with the added bonus of avoiding other that are often non-renewable ones. The developed processes avoid the use of toxic substances and achieve maximum reduction of energy expenditure, i.e., by using renewable vs. conventional energy demanding ways of activation. Some processes implemented in our research group are base don materials capable of competing with commercial ones, i.e. for immobilization of enzymes for biodiesel and nutraceuticals production, developing renewable biomaterials to be used as matrices for regenerative medicine, conversion of liquid wastes to fine chemicals and bio hydrogen, avoiding the need to use petroleum derivatives, design of non hazardous catalysts prepared from own Company`s wastes for environmental protection or multivalorization of fruit juice processing wastes into chemicals, pectin and biomaterials for tissue engineering of hard and soft tissues.

Projects: "Systems for recovery of aqueous effluents with contaminants valorisation and reduction of wastes"(IDI-20091139), "Valorisation of agriresidues as biomaterials for dental implants" (IPT-2011-1935-310000), Applications of biodiesel waste with catalysts produced from own company´s residues" (IDI-20121298), "Valorisation of Spanish agriresidues for advanced uses" (PIE 201460E105), "Preparation of biomedical materials from industrial wastes" (PIE 201480E103).

Articles in SCI: Sustainable Materials and Biorefinery Chemicals from Agriwastes. M.A. Martin-Luengo, M. Yates, M. Ramos, et al. Resource Management for Sustainable Agriculture, 3, 49-84ISBN 978-953-51-0808-5. Synthesis of p-cymene from limonene, a renewable feedstock. Appl. Cataly B: Env., 81 (2008) 218-224 Renewable fine chemicals from rice and citric sub product: Ecomaterials. Appl. Catal. B: Env. 106 (2011) 488-493. Multivalorization of apple pomace towards materials and chemicals. Waste to wealth. Journal of Cleaner Production 143 (2017) 847. Three pathways to cleaner platform chemicals: Conventional, microwave and solar transformation of a by-product from the orange juice manufacturing process. Journal of Cleaner Production, 168 (2017) 746. Beverage waste derived biomaterials for tissue engineering. Green Chemistry 19 (2017) 4520.

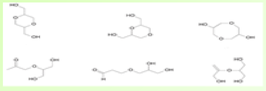
Patents: M. Yates, M.A. Martín-Luengo, et al. Procedure to obtain multifunctional and renewable materials from sunflower oil production residues" (P201130303), "Procedure to obtain immobilized enzyme on material derived from agri residue" (P 201330114), "Preparation of biocompatible materials from beer production residues (P200803331, WO/2010/058049).

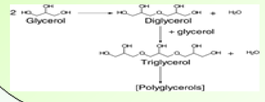
FROM BIODIESEL WASTE TO COMMODITIES

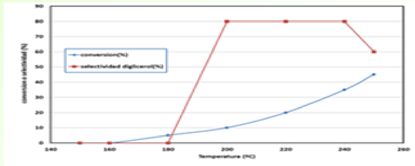
Renewable energies are considered as one possible solution to world energy crisis, being biodiesel one of the most studied. Biodiesel production generates ca. 10% glycerol as a sub product, this leading to a fall in glycerol prices, making the search for its industrial applications a necessity. Etherification is a promising alternative, since glycerol ethers can be used as such or with slight modification as platform chemicals for cosmetics, food additives, lubricants, monomers for polymerisation processes, fuel additives, etc.

A biodiesel producing company contacted our group with the aim to valorise glycerol. The residues of this industry were transformed into catalysts to produce glycerol ethers. The catalysts prepared in this way are in fact Ecomaterials and their origin makes them competitive with commercial ones. Production of ethers with more than three glycerol molecules competes with di-ethers and thus control of the selectivity is important. Etherification of glycerol with acid catalysts was found to be difficult to control, however, the catalytic transformation of glycerol into ethers, carried out with basic catalysts allows more controllable results. A bibliographic search showed alkaline and alkaline earth oxide catalysts that achieved interesting conversions with selectivities to di- and tri-glycerols, at 220 ºC (20 h) giving rise to higher glycerol conversions on the more basic catalysts: 5 % (MgO), 58 % (CaO), 80 % (SrO) and 80 % (BaO). Furthermore, the use of heterogeneous catalysts derived from the agriresidues, compared to homogeneous bases has the added bonus of being easily separated from the reactants and products for reuse with the corresponding economic benefits and by carrying out the reaction in the absence of solvent, in this work only filtering the catalyst was needed, with evident economic and environmental advantages.

The conditions used for glycerol etherification were chosen with catalysts from sunflower oil production agriresidues (RP45), given their composition of alkaline (26 % K) and alkaline-earth cations (5 % Mg, 7 % Ca) make them of basic nature. Adsorbed acetic acid indicated that RP45 contained basic centres of low (100-200 ºC), medium (200-500 ºC) and high basicity (550-650 ºC) and can catalyse Knoevenagel condensation reactions.







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Three pathways to cleaner platform chemicals: Conventional, microwave and solar transformation of a by-product from the orange juice manufacturing process

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Highlights

- Cleaner production of platform chemicals from limonene a by-product of orange juice industry.
- Design of economic low toxicity catalysts.
- Comparison of conventional, microwave and solar activations.
- Solar activation favours countries with high amounts of sunlight.
- Using orange peel oil versus purified limonene improves the economy and sustainability of the process.

Multivalorization of fruit wastes

This research used an industrial waste from juice production as RRM to develop materials that can be utilized as biocompatible scaffolds for osteoblasts and chondrocytes growth, employed in tissue engineering, valuable extracts that can be used as nutraceuticals and pectin. All of these have much higher value than the original raw material, pectin can be priced up to 1 euro/g, chlorogenic acid is *ca.* 120 euros/g, caffeic acid 3-5 euros/g and especially the scaffolds that are usually made by synthetic methods using non RRM materials with high fabrication costs and sold at prices higher than 100 euros/g, while the residues used here have prices lower than 100 euros per ton. Therefore there are clear environmental and financial incentives in transforming this wastes into valuable substances and materials.

The procedure consists in sequential extractions of antioxidants, pectin and finally the preparation of a biocompatible material, giving priority to the latter due to its importance as a renewable scaffold for tissue engineering.