Development of an innovative biorefinery process by the one-pot fractionation of defatted cardoon

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Significance and Relevance

The one-pot fractionation of defatted cardoon through biphasic organosolv process was conducted under the efficient microwave heating that allowed the separation and recovery of each biomass fraction. Subsequently, these fractions were characterized and valorized according to the Green Chemistry principles to provide high-quality lignin, to be employed as an antioxidant and in materials formulation, furfural, which is a relevant platform chemical and butyl levulinate, which can be advantageously adopted as bio-blendstock in mixture with Diesel or gasoline. Thus, for the first time, the complete exploitation of the waste defatted cardoon was successfully performed, contributing to developing the biorefinery process.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion; Sustainable and clean energy production and transport.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Since 2020 the European Union, by subscription of the Green Deal, fixed the aim of carbon neutrality by 2050. For this purpose, it is fundamental to reduce the net carbon emissions, and one possible strategy is the replacement of fossil resources with renewable ones.[1] Under this perspective, lignocellulosic biomass represents a valid renewable resource because it can be converted into a plethora of valuable chemicals and fuels. Among the biomasses, cardoon is an interesting feedstock being a perennial herbaceous crop that can grow on marginal lands. Up to now, the seeds of the cardoon flower have found applications for bio-diesel production, whilst the cardoon residues (defatted cardoon) are generally pretreated by the steam explosion, which is mainly focused on cellulose exploitation leading to hemicellulose degradation and recovery of low-quality lignin.[2] However, from the perspective of a biorefinery scheme, all the biomass fractions should be valorized, thus minimizing the waste. On this basis, the present work investigated the one-pot fractionation of defatted cardoon through the biphasic (*n*-butanol/water) organosolv process to recover and valorize each biomass fraction. Then, to effectively develop a biorefinery process, the recovery and characterization of lignin, and the conversion of hemicellulose and cellulose to furfural and butyl levulinate, respectively, were performed. Noteworthy, the *n*-butanol adopted for the butanolysis of cellulose was recovered by the lignin separation step, thus reducing the total amount of employed solvent according to the Green Chemistry principles. Lastly, also the solid by-product (char) deriving from the butanolysis step was characterized to propose its possible applications, thus effectively valorizing all the products of the proposed process.

Materials and Methods

The organosolv process was performed adopting the biphasic system *n*-butanol/water acidified with diluted H_2SO_4 under microwave heating with the monomodal reactor CEM Discover S-class System. Thus, at the end of the pretreatment, lignin was solubilized in the organic phase, hemicellulose was depolymerized to give mainly xylose that was recovered in the aqueous phase, and cellulose was recovered within the solid residue (cellulose-enriched residue). Lignin was then isolated by vacuum removal of the solvent and its quality was evaluated by optical microscopy, FT-IR and elemental analysis characterizations. Xylose present in the aqueous phase was directly converted to furfural under microwave heating employing H_2SO_4 as catalyst. The chemical compositions of defatted cardoon and cellulose-enriched residue were determined by the NREL procedure[3] to evaluate the effective removal of lignin and hemicellulose. The cellulose-enriched residue was then converted to butyl levulinate under microwave heating employing H_2SO_4 as catalyst and as solvent/reactant *n*-butanol recovered by the lignin separation step. Finally, the solid char deriving from the butanolysis step was characterized by FT-IR and elemental analysis techniques.

Results and Discussion

The organosolv process was investigated studying the influence of temperature and acid loading on lignin and hemicellulose removal The increase of both temperature and acid loading positively affected the effectiveness of the pretreatment leading to the highest lignin and hemicellulose removals of 72 and 97 wt%, respectively, and to the contemporary enrichment of cellulose within the solid residue, which reached 74 wt%. Moreover, these conditions promoted hemicellulose depolymerization leading to an aqueous phase enriched in xylose that was quickly converted to furfural up to a yield of 52 mol%. The optimization of cellulose-enriched solid residue butanolysis was optimized reaching the highest yield of 46 mol%, higher than that reached starting from not pretreated defatted cardoon (36 mol%), thus proving the effectiveness of the organosolv approach. A char yield of 6 wt% was ascertained under the optimized butanolysis conditions and the characterization of this by-product highlighted a promising higher heating value that made it a potential solid fuel. To prove the effectiveness of butyl levulinate as bio-blendstock, it was added as bio-blendstock to Diesel/gasoline and tested in real engines, leading to a decrease of polluting emissions without affecting the engine performance. Last but not least, very pure lignin was recovered from the organic phase, as proven by FT-IR and elemental analysis characterizations.

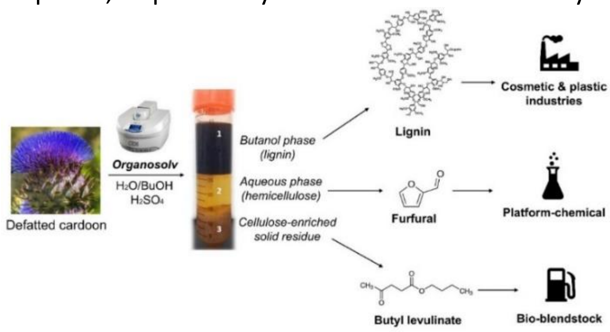

Figure 1. Scheme of the developed biorefinery scheme.

In conclusion, the complete exploitation of all the defatted cardoon fractions to give a valuable bio-fuel, a platform chemical, and lignin, employable as an antioxidant and in materials formulation, was successfully performed.

References

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