VALORIZATION OF AN EXPLOTED WINE LEES RESIDUE INTO VALUABLE PRODUCTS VIA SUPERCRITICAL WATER HYDROLYSIS

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Wine lees are water-waste residues generated during maceration and fermentation steps of the vinification process and they constitute a source of high value compounds, such as polyphenols, mainly anthocyanins (AC). The exploitation of these dregs could contribute to the development of new wine-related products and could also lead to a sustainable growth of the wine industry due to the concentration of AC is 10 times higher in wine lees than in grape skins [1]. After the recovery of the polyphenols from wine lees, a wet solid waste remains with poor chemical potential. This residue can be recycled by a hydrolysis step. Supercritical water (SCW) has proved to be a suitable environment-friendly media for biomass hydrolysis due to its unique properties, such as a high diffusivities or low dielectric constant [2]. This hydrolysis produces a liquid product rich in sugars that can be used as feed in a fermentation step afterwards. However, the yield of this last step would be lower with wine lees than with conventional biomasses since its cellulosic fraction only constitutes 18%.

The main objective of the hydrolysis of the wine lees residue is to obtain reduced sugars which are essential chemical building blocks in the so-called biorefinery cycle. A continuous pilot plant was used to carry out the hydrolysis of wine lees in SCW. This facility was based on a continuous reactor with instantaneous heating and cooling that allowed precise control of the reaction time and therefore, high recovery of sugars was achieved and avoiding sugar degradation reactions. A wine lees-water suspension (10% w/w) was continuously fed to the reactor using a pump at a flow rate of 1 kg/h and processed under 380-395ºC and 25MPa at different reaction times, between 0.056 and 0.076s. A brown liquid was obtained after the hydrolysis step, rich in hexoses (extraction yield of 50%) such as cellobiose, glucose and fructose. It was also observed that increasing the reaction time and temperature favored the degradation of the recovered sugars into pyruvaldehyde and glycolaldehyde.

References

[1] Á.Peralbo-Molina and M.D.Luque de Castro, “Potential of residues from the Mediterranean agriculture and agrifood industry,” Trends Food Sci. Technol., vol. 32, no. 1, pp. 16–24, 2013.

[2] D.A.Cantero, L.Vaquerizo, C.Martínez, M.D.Bermejo, M.J.Cocero, “Selective transformation of fructose and high fructose content biomass into lactic acid in supercritical water” Catal. Today 2015, 255: 80-86.

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WCCE10 ECCE11 ECAB4 1st - 5th October, 2017 Barcelona, Spain
10th World Congress of Chemical Engineering
Paper-ID: 27976

1 INTRODUCTION

Wine lees are water-waste residues generated during maceration and fermentation steps of the vinification process and they constitute a source of high value compounds, such as **polyphenols**, mainly anthocyanins (AC) which concentration is 10 times higher in wine lees than in grape skins. Further, the exploitation of these dregs could contribute to the **development of new wine-related products** and could also lead to a sustainable growth of the wine industry. After the recovery of the polyphenols from wine lees, a wet solid waste remains with poor chemical potential. This residue can be recycled by a hydrolysis step:

Freeze-dried wine lees

- **Solid-liquid** conventional extractions.
- **MW** pre-treatments.
- **US** pre-treatments.
- **Enzymatic** pre-treatments

Anthocyanin extraction

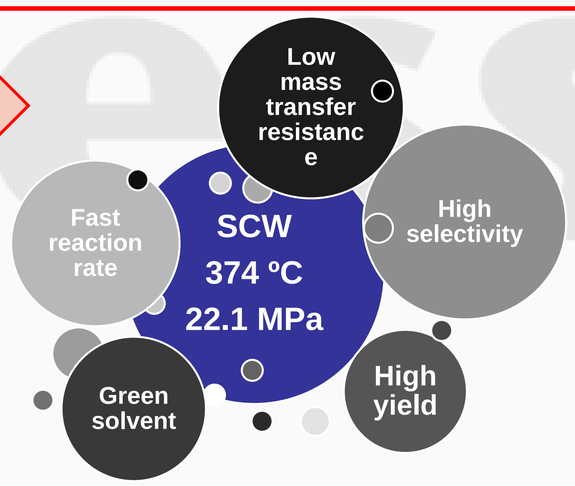
Liquid → Rich in **polyphenols**

Solid → **Super critical water** (SCW) **hydrolysis**

SCW is a promising solvent to process biomass feedstock due to its unique properties.

Reducing sugars

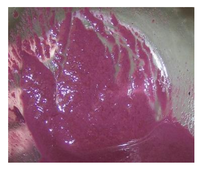
- Chemical building blocks
- Feedstock for fermentation
- Etc.



WineSense project:

Research on Extraction and Formulation Intensification Processes for Natural Actives of Wine

Wine lees compositions:



- Tartaric Acid: ~ 12%
- Proteins: ~ 20%
- Lipids: ~ 4%
- Sugar and pigments: ~ 10%
- Alimentary fiber (cellulose, pectin, lignin, hemicellulose, polyphenols) : ~ 25%
- Others: ~ 30%

Biorefinery Concept

Biorefineries are the industries of the future capable of replacing the current petrochemical-based industry by transforming biomass into marketable products and energy

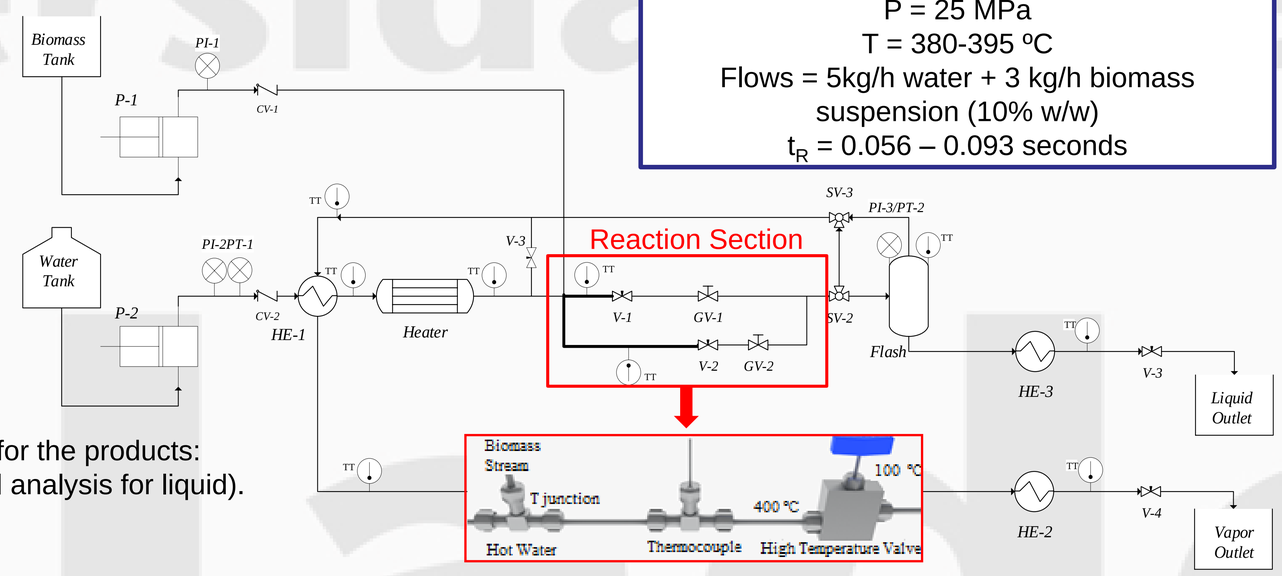
2 EXPERIMENTAL SET-UP AND METHODS

The continuous pilot plant is designed to operate up to 400 ºC and 30 MPa using a micro-reactor.

The wine lees-water suspension is pumped up to 25 MPa and instantaneously heated to 380-395 ºC by mixing it with a supercritical water stream. Then the effluent is is suddendly depressurized to stop the reaction.

The reaction is started and stopped by sharp temperature changes, to avoid uncontroled degradation reactions providing in this way an effective method to control the reaction time (t_R).

Operating conditions
P = 25 MPa
T = 380-395 ºC
Flows = 5kg/h water + 3 kg/h biomass suspension (10% w/w)
t_R = 0.056 – 0.093 seconds



Analysis

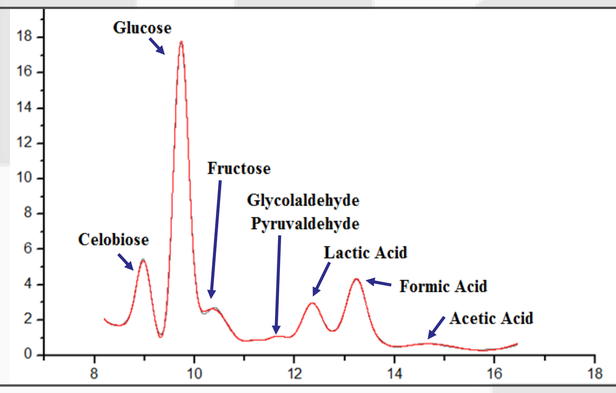
1) Compositional analysis for raw material:
- ✓Soxhlet extraction (extractive fraction).
- ✓Acid hydrolysis (insoluble lignin and ash content).
- ✓UV- Vis Spectrophotometry (soluble lignin).
- ✓HPLC analysis (cellulose and hemicellulose fractions).

2) Compositional analysis for the products:
- ✓ HPLC (compositional analysis for liquid).

3 RESULTS AND DISCUSSION

List of experiments at different temperatures and reaction times with results of obtained C-6 sugars (ppm), degradation compounds (ppm) and yield transformation (%).

T^a (°C)	t_R (s)	C-6 sugars (ppm)	Degradation (ppm)	Yield (%)
380	0.093	2528	2316	64
395	0.053	2793	3605	70
395	0.076	2446	3817	62



HPLC profile of the liquid obtained after the SCW hydrolysis.

C-6 sugars:
- *Cellobiose*
- *Glucose*
- *Fructose*

Degradation compounds:
- *Glycolaldehyde*
- *Pyruvaldehyde*
- *Lactic Acid*
- *Formic Acid*
- *Acetic Acid*

4 CONCLUSIONS

- **Supercritical water hydrolysis** showed yields up to 60% in terms of conversion of C-6 sugars, but the concentration of degradation products were in the same order of magnitude. Furthermore the initial carbohydrate content in wine lees, which is much less than the carbohydrate content that can be found in the usually processed raw materials for this purpose, makes them a not profitable feedstock for this process.
- The control of **reaction time** was the **key factor** to stop the reaction before sugars degradation, allowing high selectivity to sugars just by controlling the reaction time. If temperature is increased, the yield and the concentration of sugars increase and the degradation compounds do too. At a temperature of 395 ºC, the higher the reaction time, the higher the degradation.

ACKNOWLEDGMENTS: The authors thank the Marie Curie Industry-Academia Partnerships and Pathways actions (FP7-PEOPLE-2013-IAPP-612208),Junta de Castilla y Leon and FEDER 2014-2020 under project VA040U16 and Ministerio de Economía y Competitividad Spain (CTQ2015-64892-R)for funding. Soraya Rodríguez Rojo acknowledges Junta de Castilla y Leon and FEDER 2014-2020 for her postdoctoral contract. Rut Romero Díez thanks Junta de Castilla y León for her research fellowship.