OPTIMISATION OF 5-HYDROXY METHYFURFURAL (5-HMF) PRODUCTION FROM BIOMASS THROUGH HETEROGENEOUS CATALYSIS

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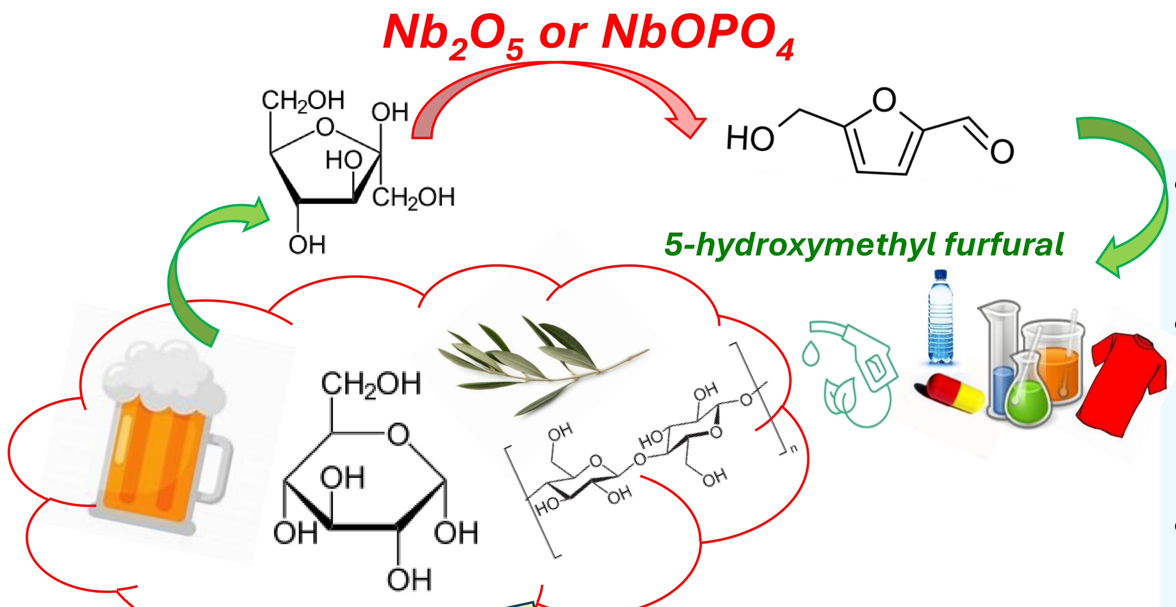
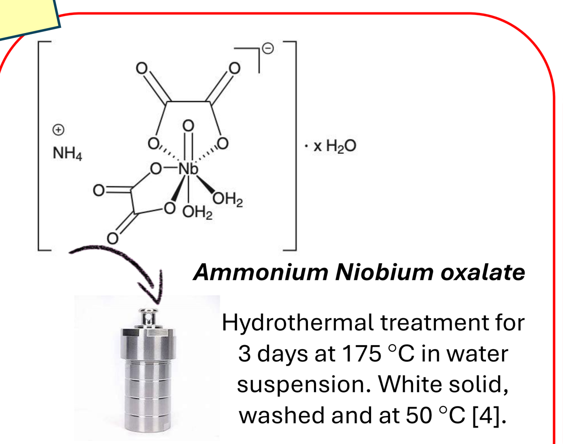


Real biomass is composed of different compounds, being often a complex structure. The releasing of simple carbohydrates from its matrix could be challenging. The valorization presented in this work is related to the **hexose's conversion contained in biomass,** essentially glucose, which suffers an acid **catalytic conversion into furans.**

- Cellulose, olive leaves and brewery wastewater are appealing source of sugars to obtain 5-hydroxymethyl furfural (5-HMF).
- In this work two home prepared Nb based materials Nb_2O_5 and $NbOPO_4$ have been prepared, characterized and used as catalysts for the conversion of the carbohydrates deriving from brewery wastewater, cellulose and olive leaves into 5-HMF;
- 5-HMF is a precursor of several compounds for the chemical industry and may be obtained through lignocellulosic biomasses or hexoses sugars through acid catalysis [1-3];
- Glucose was studied preliminary as substrate to test the ability of the home prepared Nb based solids to obtain 5-HMF. Once the experimental parameters for the catalytic reaction in the presence of Nb_2O_5 or $NbOPO_4$ were optimized (by software Design-Expert 13) fructose, microcrystalline cellulose, brewery wastewaters and olive leaves were used as initial substrates to obtain 5-HMF.

EXPERIMENTAL

Preparation of the heterogeneous acid catalysts

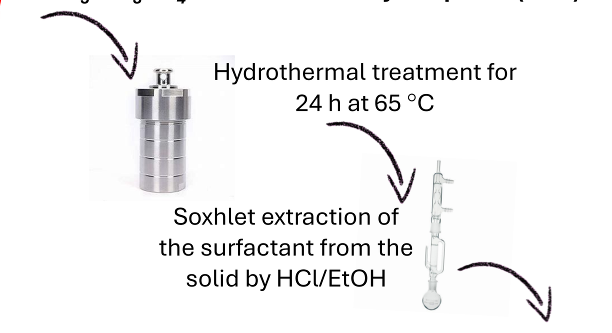


Ammonium Niobium oxalate

Hydrothermal treatment for 3 days at 175 °C in water suspension. White solid, washed and at 50 °C [4].

Nb_2O_5

***$NbCl_5$ + H_3PO_4* + Sodium dodecyl sulphate (SDS)**



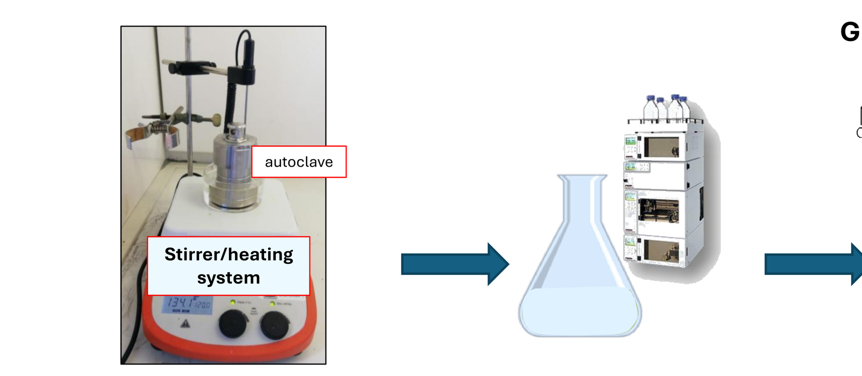
Hydrothermal treatment for 24 h at 65 °C

Soxhlet extraction of the surfactant from the solid by HCl/EtOH

Solid washed, dried at 50 °C and calcined at 500 °C [5].

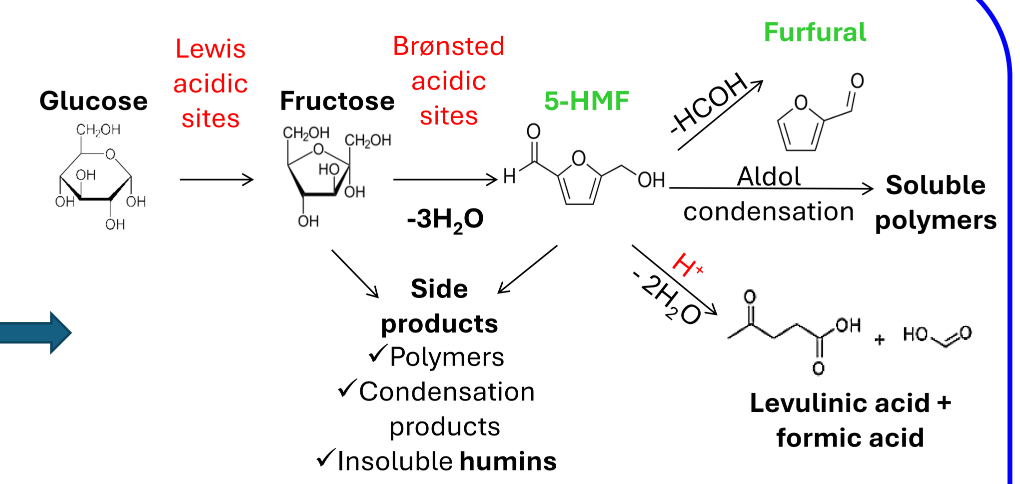
$NbOPO_4$

Catalytic hydrothermal reaction



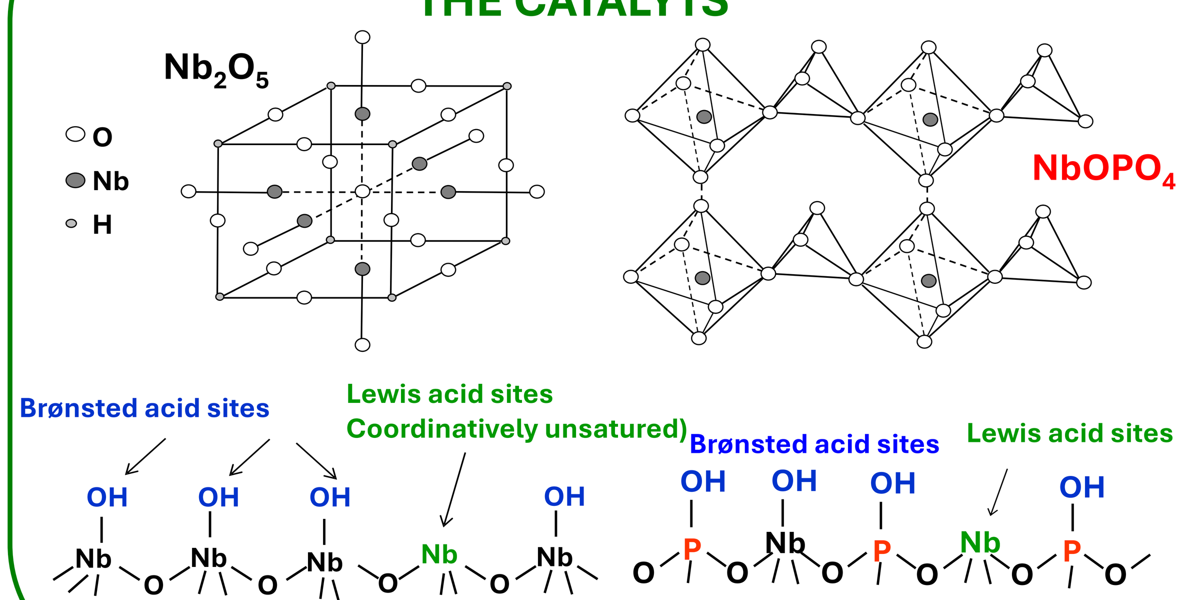
25 mL of **6g/L** of total sugars (hexoses + pentoses) aqueous solution. Catalyst amount, temperature, and reaction time were varied during experimental trials

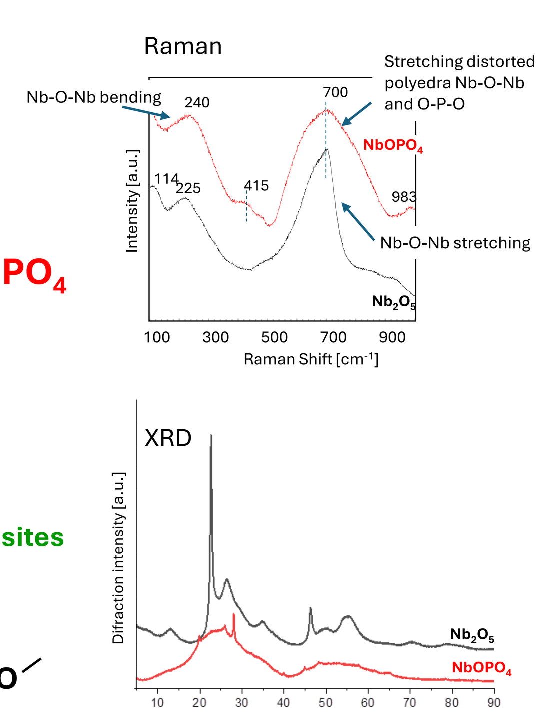
The obtained suspension was filtered. **The species in solution were analysed by HPLC**



Scheme of the catalytic reaction for 5-HMF production from the glucose in the presence of Nb_2O_5 or $NbOPO_4$ as acidic catalyst

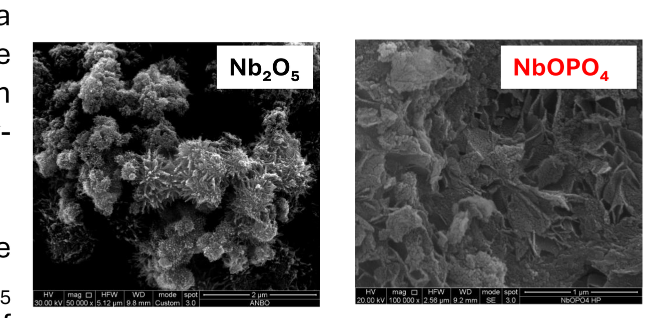
PHYSICO-CHEMICAL CHARACTERISATION OF THE CATALYTS





The structures consist of distorted NbO_6, NbO_7 and NbO_8 hydrated polyhedra (Brønsted acid sites). Both samples are poorly crystalline, nevertheless both possesses small crystals of low-temperature orthorhombic crystal phase.

The $NbOPO_4$ sample presented higher pore volume and diameter values than Nb_2O_5 attributed to the 2D lamellar structure of $NbOPO_4$ capable of occlude neutral molecules, as water.



SEM micrographs show that Nb_2O_5 is composed of agglomerates of needle-shaped nanoparticles (sea urchin shape), ranging from 200 to 500 nm with needle sizes ranging from 6 to 10 nm.

$NbOPO_4$ shows a layered microstructure resulting from the two-dimensional architecture of the solid. The platelets are clustered in a three-dimensional nanostructured composition. The thin nanosheets show a thickness ranging from 10 to 50 nm.

Specific surface area and acid properties of the catalysts determined by NaOH 0.01 M titration

Catalyst	Specific surface area [$m^2 \cdot g^{-1}$]	Acid sites by NaOH titration [mmol H^+ g^{-1}]	Surface density of Brønsted acid sites $\times 10^3$ [μmol H^+ m^{-2}]
$NbOPO_4$	106	4.5	42.2
Nb_2O_5	237	1.8	7.6

$NbOPO_4$ is more acidic than Nb_2O_5

VALORISATION OF BIOMASS

Experimental design based on **Design-Expert 13 software** for the heterogeneous catalytic experiments has been applied to individuate the optimal experimental conditions. Results are expressed as percentual yield to 5-HMF using glucose as starting substrate

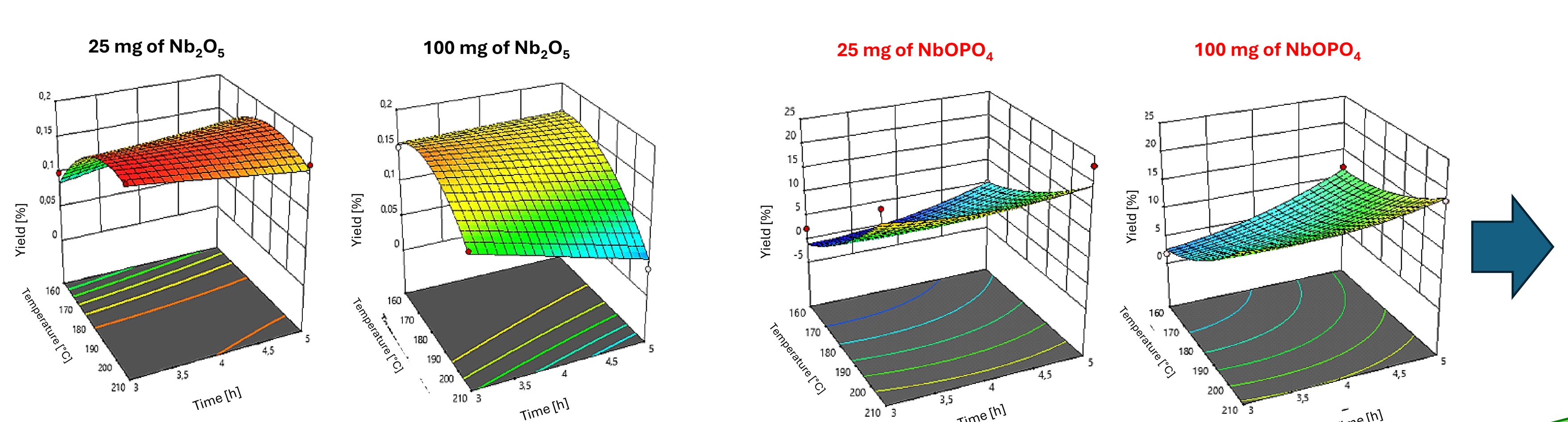
Two experimental designs on a model solution of **glucose 6 g/L (33mM)** by varying:

Catalyst: Nb_2O_5 or $NbOPO_4$

Temperature: 143 - 227 °C

Reaction time: 2.3-5.7 h

Amount of catalyst: 0-125.6 mg



The best results for the catalytic GLUCOSE valorization to 5-HMF determined the optimal conditions to be applied for all the alternative initial substrates to valorise in the presence of Nb_2O_5 or $NbOPO_4$.

OPTIMAL CONDITIONS for both catalysts:
Temperaure: 210 °C
Time: 3 hours
Amount of solid catalyst: 25 mg

The sugars measured in complex matrices (beer wastewaters and olive leaves) were measured with the Dubois method [6] which measures total sugars, not distinguishing between hexoses and pentoses. We can therefore say that the experiments were conducted with an initial quantity of total sugars equal to 6 g/L

Brewery wastewaters

11.2 g/L of sugars

Brewery wastewater was filtered (0.45 μm) and diluted in the reaction vessel to have a final concentration of 6 g/L of total sugars

Olive leaves

33.4 % in weight of sugars

Olive leaves were Soxhlet-extracted, dried, mortar-crushed, sieved to 60 μm, and suspended in water to obtain 6 g/L of total sugars in the reaction vessel

Results on various substrates at the optimal conditions

	Glucose		Fructose		Brewery wastewaters		Cellulose		Olive leaves	
	Conversion [%]	Yield in 5-HMF [%]	Conversion [%]	Yield in 5-HMF [%]	Conversion [%]	Yield in 5-HMF [%]	Conversion [%]	Yield in 5-HMF [%]	Conversion [%]	Yield in 5-HMF [%]
Nb_2O_5	87.9	18.8	98.5	25.8	50.4	75.1	100	1.50	100	2.63
$NbOPO_4$	74.0	22.4	98.8	28.4	81.0	80.8	94.3	4.10	100	3.63

The initial concentration of total sugars (hexoses + pentoses) was adjusted to 6 g/L for all of the substrates

CONCLUSIONS

- Two acidic nanostructured materials were prepared and physico-chemically characterized to be used as catalysts: Nb_2O_5 and $NbOPO_4$.
- Catalytic reactivity tests were carried out with glucose, fructose, beer wastewaters, cellulose and olive leaves as substrates in order to obtain 5-HMF.
- A preliminary catalytic study was conducted with the aim of obtaining the best operating conditions in the presence of Nb_2O_5 or $NbOPO_4$ using 6 g/L of glucose as starting substrate to obtain 5-HMF. Experimental tests concluded that the optimal conditions are the following: temperature 210 °C for 3 h of reaction and 25 mg of catalyst.
- $NbOPO_4$ gave better results than Nb_2O_5, demonstrating that the choice of catalyst plays a crucial role. The best results obtained with $NbOPO_4$ can be related to the higher acidity of the phosphate compared to the oxide.
- Different substrates give different results, in fact fructose and brewery wastewaters were the most suitable substrates giving higher yields and selectivity's in 5-HMF.
- Cellulose and olive leaves, gave significantly lower yields in 5-HMF. This result can be attributed to the complex structure, which limits their conversion.

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