BI-FUNCTIONAL ZEOLITIC SOLID CATALYSTS IN AGRICULTURAL RESIDUES FRACTIONATION

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1. Introduction

► Annual production of cereal crops in Greece: 2 million tones

✓ Annual straw production: 630,000 tn (30% straw yield)

✓ Majority is derived from hard wheat (55%) and soft wheat (21%)

► Wheat straw is typically utilized as animal feed

✓ Typically priced very low, at ~50€/tn

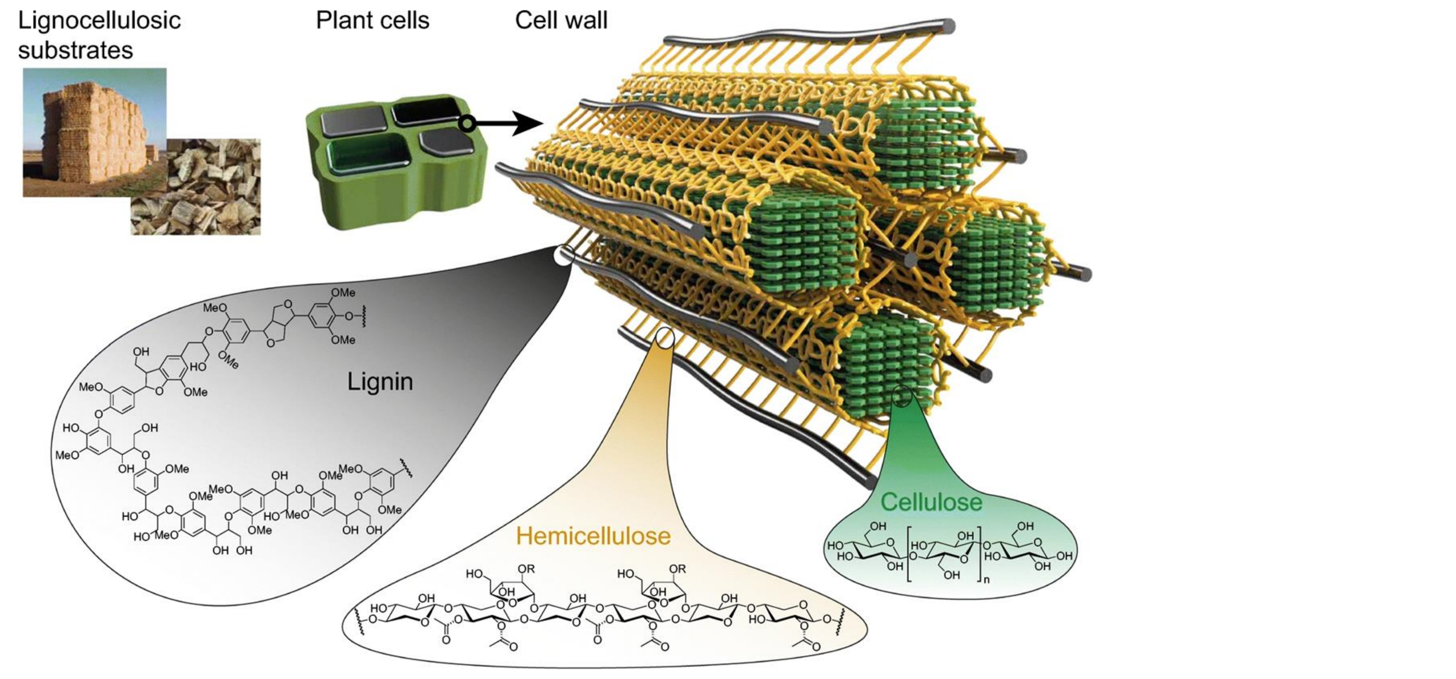
✓ Large quantities are abandoned in the fields due to low selling price

► ***Straws are primarily composed of cellulose, hemicellulose & lignin***

✓ Cellulose and hemicellulose are sugar biopolymers

✓ Lignin is a unique source of renewable aromatic chemicals

► ***Organosolv pre-treatment*** can ***fractionate lignocellulosic feeds*** like wheat straw into cellulose, hemicellulose and lignin streams



► CERTH has developed an organosolv oxidation (***OxiOrganosolv***) process for the fractionation of lignocellulosic feeds is carried out in an oxygen-rich atmosphere, in the ***absence of soluble acids*** that are typically employed in organosolv fractionation:

✓ Does not require the handling of large volumes of acid wastes

✓ Does not necessitate the use of corrosion-resistant reactor materials

✓ ***Low formation of byproducts*** that hinder the cellulose conversion to valuable products

2. Scope of the study

► Investigate the ***solid catalyst-assisted OxiOrganosolv pre-treatement*** of wheat straw

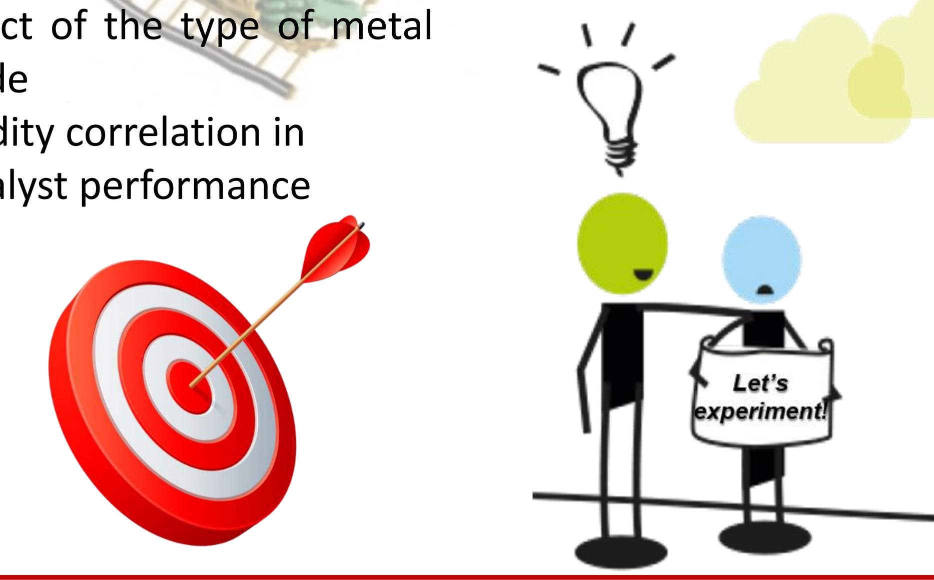
✓ ***Reduce severity*** of OxiOrganosolv conditions

✓ Ability to ***recover and re-use*** solid catalyst

► Study the ***effect of physicochemical characteristics of the catalysts in the wheat straw fractionation*** efficiency during OxiOrganosolv process

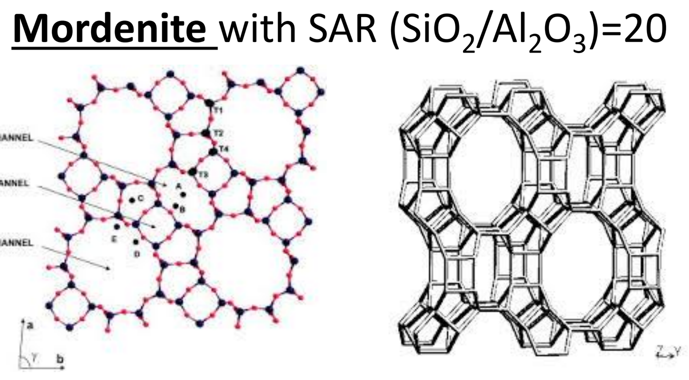
✓ Effect of the type of metal oxide

✓ Acidity correlation in catalyst performance



3. Catalysts

► <u>Mordenite</u> with SAR (SiO_2/Al_2O_3)=20



► <u>Metal oxides supported on Mordenite-20:</u>

- NiO/MOR SAR 20, Cu2FeO/MOR SAR 20

- Modified via wet impregnation method in order to ***induce bi-functionality of acid-redox properties***

► <u>Bulk metal oxides:</u>

- Fe_2O_3, CuO, NiO, Cu2FeO

- Synthesized via decomposition method or co-precipitation method

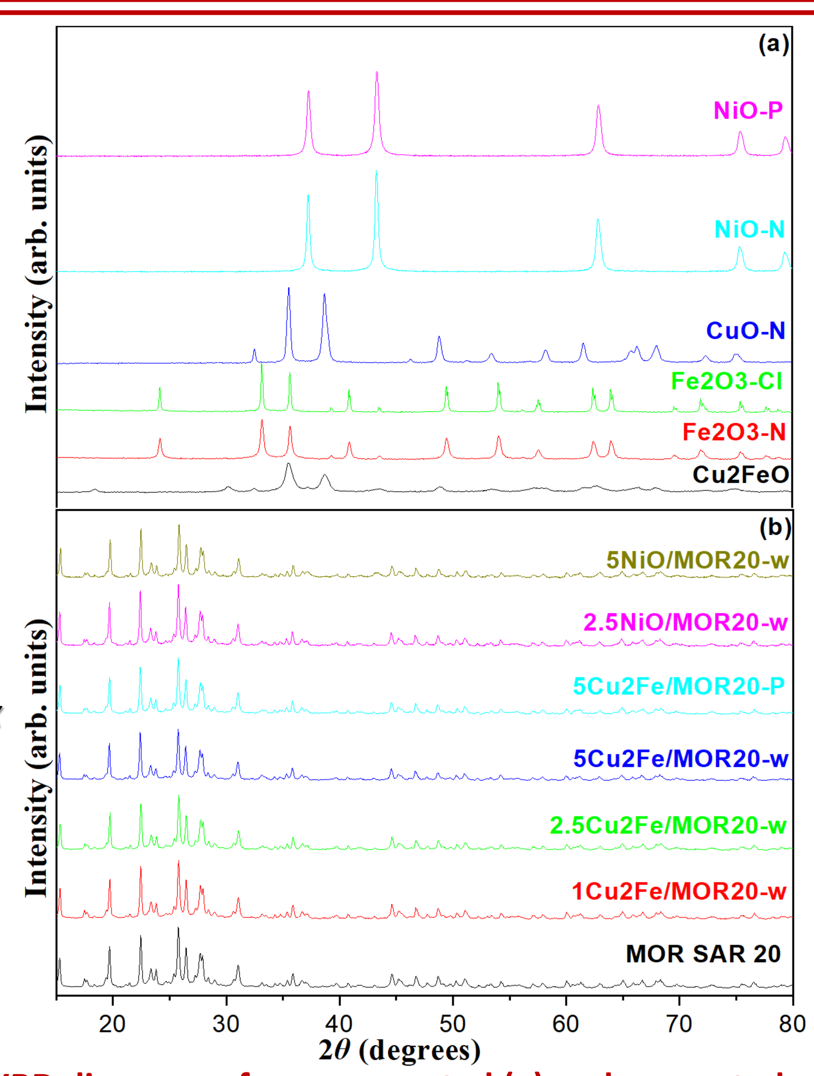


Figure 1: XRD diagrams of non-supported (a) and supported metal oxides (b)

Table 1: Elemental and acidity characteristics

Catalyst	ICP method (wt. %)				FTIR pyridine (μmol/g)			
	Al	Cu	Fe	Ni	Brönsted	Lewis	Total	B/L
MOR SAR 20	3.9	-	-	-	384.4	141.8	526.2	2.71
1Cu2Fe/MOR20-W	3.77	0.7	0.5	-	227.6	160.1	387.7	1.42
2.5Cu2Fe/MOR20-W	3.66	1.8	1	-	156.6	176.7	333.3	0.89
5Cu2Fe/MOR20-W	3.5	3.5	3.2	-	123.5	247.5	371.0	0.50
5Cu2Fe/MOR20-L	3.53	1.7	1.8	-	96.5	201.9	298.4	0.48
2.5Ni/MOR SAR 20	3.52	-	-	2.6	90.3	152.4	242.7	0.59
5Ni/MOR SAR 20	3.45	-	-	4.5	66.7	172.3	239.0	0.39

► All metal oxides showed representative XRD patterns for their respective crystal structures (Figure 1a), while both non-modified Mordenite and supported catalysts revealed typical patterns of MOR zeolite structure (Fig. 1b)

► Among bulk metal oxides, the ***highest surface area was noticed for the bimetallic Cu_2FeO*** synthesized via co-precipitation method (Table 2)

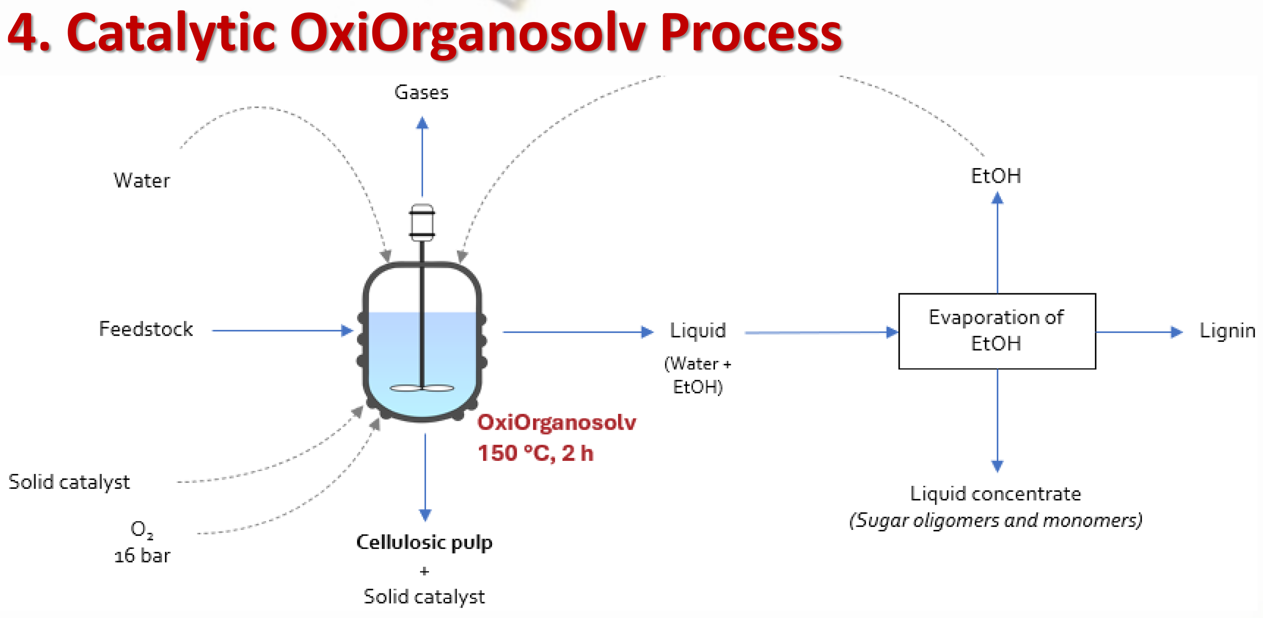
► ***Deposition of metal oxides*** on the surface of the zeolite caused a ***reduction in the total surface area*** mainly due to the partial coverage of its microporous from metal oxide crystals, retaining however the typical porosity characteristics of the initial non-supported Mordenite (Table 2)

Table 2: Porosity characteristics

Catalyst	Total surface Area	Micro-pore volume	Meso-macro-pore volume	Textural volume	Total Pore volume
	m^2/g	ml/g			
MOR SAR 20	540	0.180	0.046	0.061	0.287
1Cu2Fe/MOR20-W	532	0.176	0.049	0.088	0.313
2.5Cu2Fe/MOR20-W	514	0.170	0.047	0.092	0.309
5Cu2Fe/MOR20-W	502	0.166	0.047	0.072	0.285
5Cu2Fe/MOR20-L	510	0.168	0.052	0.080	0.300
2.5Ni/MOR SAR 20	524	0.173	0.055	0.083	0.312
5Ni/MOR SAR 20	485	0.163	0.055	0.076	0.280
Cu2FeO	24	0.000	0.049	0.111	0.160
Fe2O3-N	14	0.000	0.017	1.605	1.622
Fe2O3-Cl	0.8	-	-	-	-
CuO-N	0.7	-	-	-	-
NiO-N	3.2	-	-	-	-
NiO-P	15	0.000	0.021	0.165	0.186

► The reduction of the microporous noticed for the supported catalysts, particularly at a high degree of metal oxide loading, also ***affected negatively the number of Brönsted acid sites***, due to the partial coverage of its microporous, while in parallel ***Lewis acidity was increased*** (Table 1)

4. Catalytic OxiOrganosolv Process



► ***Feedstock:*** Wheat straw

Extractives, wt.%	Cellulose, wt.%	Hemi-cellulose, wt.%	Lignin, wt.%	Ash, wt.%
15.5	39.9	22.9	16.6	3.1

► Carried out in a 1 L autoclave reactor under continuous stirring:

Reaction medium: water:ethanol (50:50)

Temperature: 150 °C, **Oxidant:** 100% O_2

Time: 2 h, **Pressure:** 16 bar

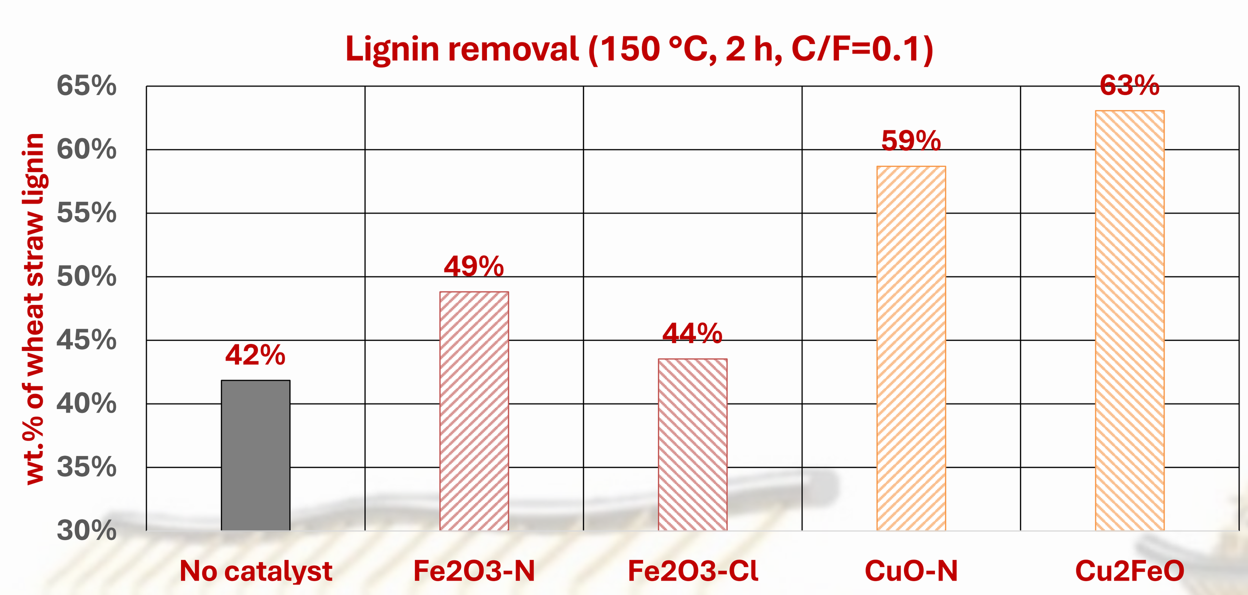
Catalyst/Feed Ratio: 0.1 and 0.5

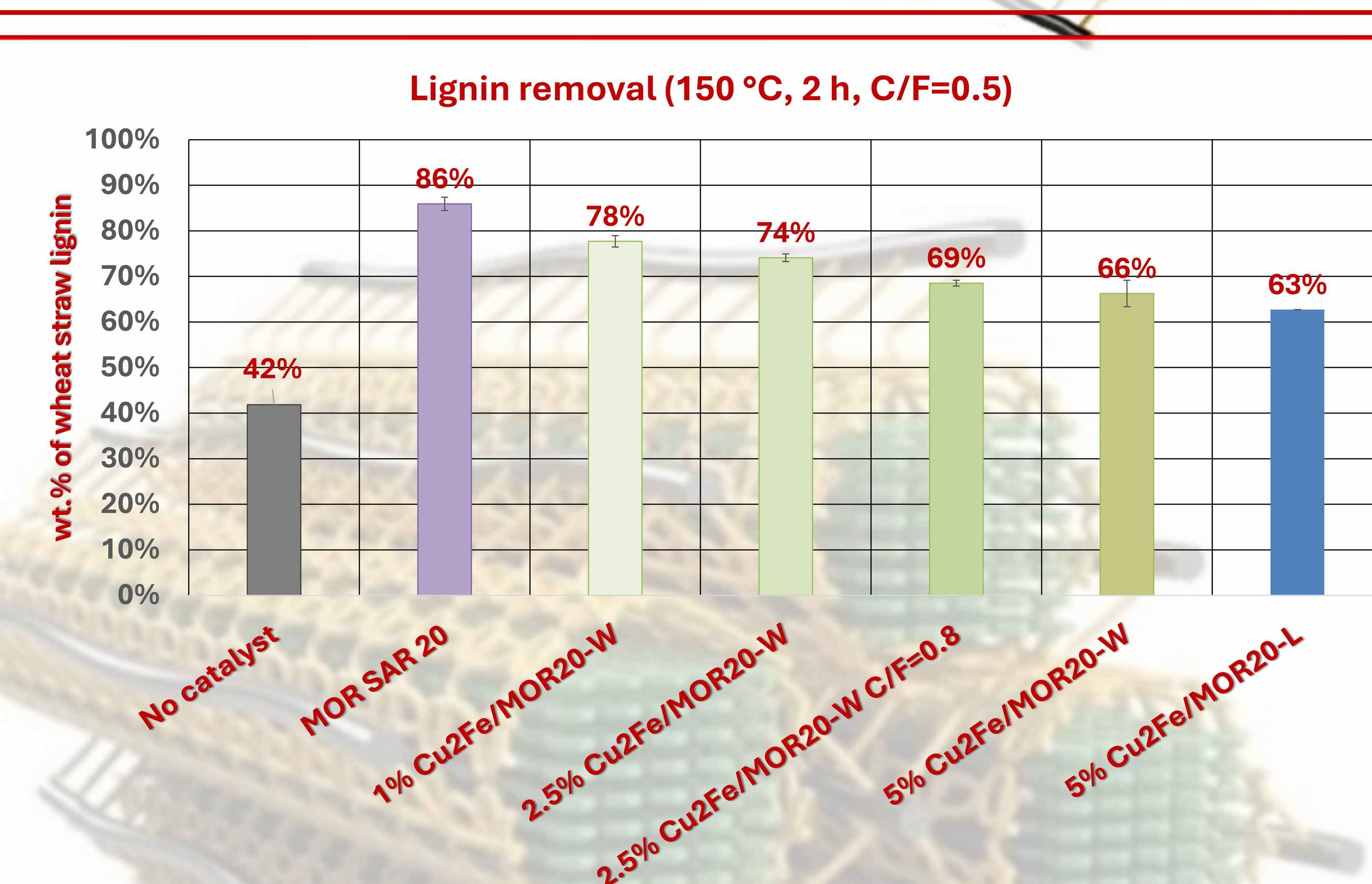
► ***OxiOrganosolv products***:

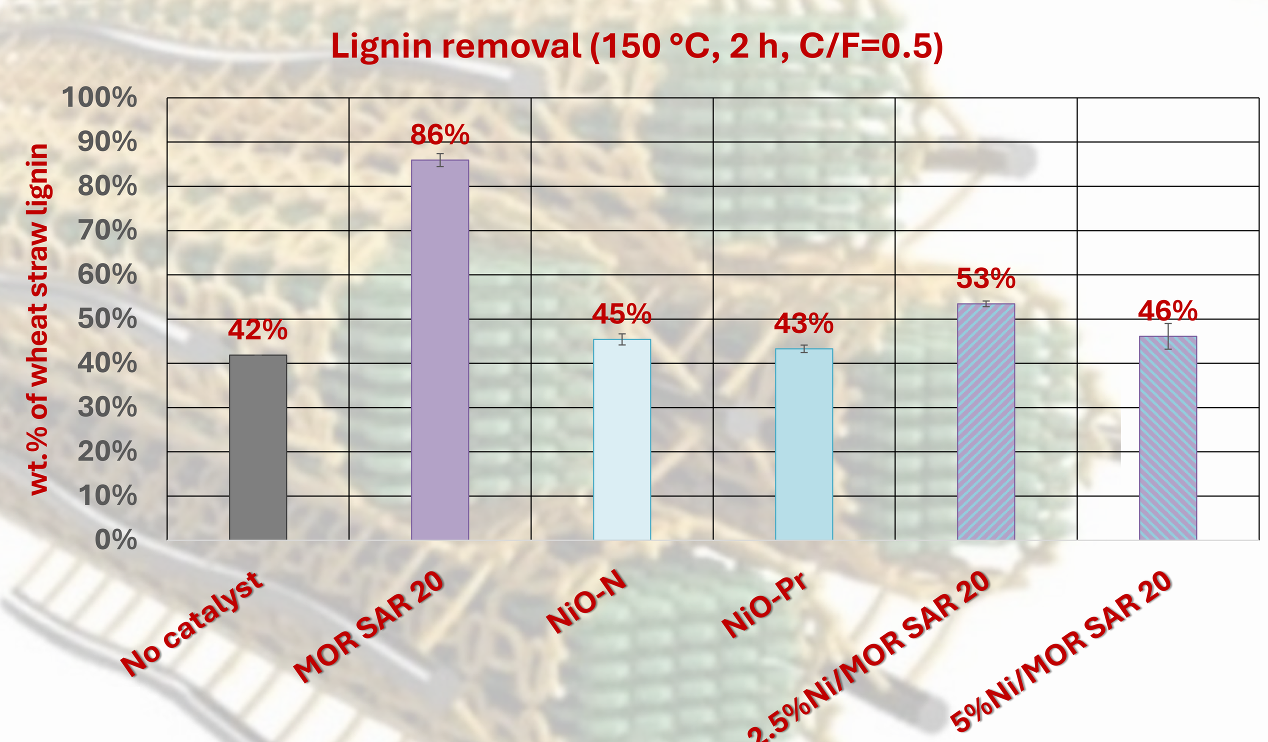
✓ Cellulose-rich solid fraction (pulp)

✓ Liquid fraction containing hemicellulose sugar monomers and oligomers

✓ Lignin residue







► ***All solid catalysts*** were active in wheat straw fractionation achieving ***increased biomass delignification*** compared to the non-catalytic OxiOrganosolv at the same temperature (150°)

► Among bulk metal oxides, ***the highest value of lignin removal*** was performed in the case of bimetallic ***Cu_2FeO*** reaching up to 63% due to its redox properties

► Regarding zeolites, ***non-modified Mordenite showed the highest catalyst performance*** due its high number of ***Brönsted acid sites*** which ***favors lignin (and hemicellulose) removal resulting to a cellulose-rich solid fraction of 62%***

5. Conclusions

► ***Solid catalysts increased the delignification of wheat straw*** compared to the non-catalytic OxiOrganosolv at the same temperature

► ***Brönsted acid sites seem to enhance the effectiveness of the catalyst*** achieving higher degree of delignification

► Modification of Mordenite with redox metal oxides affected negatively the catalyst performance due to the ***reduced active Brönsted acid sites*** provoked from the partial coverage of the microporous zeolitic surface area from the Lewis acid metal oxides

► Best performing catalyst was the non-modified zeolite of ***Mordenite type with SAR 20*** showing ***high number of Brönsted acid sites*** reaching up to ***86% of lignin removal***

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