# Oxidative Organosolv Fractionation of Lignocellulosic Biomass Assisted by Solid Catalysis and Biochemical Sugars Conversion

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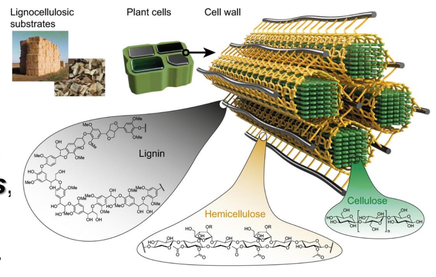
## 1 INTRODUCTION

► Biorefineries aim to convert renewable lignocellulosic biomass to sustainable fuels and chemical products.



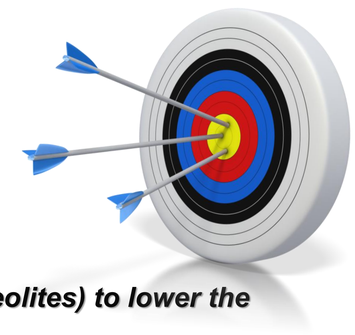

► A crucial step in this process is the ***pretreatment of the biomass***, which separates it into cellulose, hemicellulose, and lignin streams.

► CERTH has developed an ***innovative organosolv pretreatment method known as OxiOrganosolv*** (OOS).

► OOS effectively fractionates lignocellulosic biomass under oxidising conditions, eliminating the need for soluble acid catalysts typically required in conventional organosolv processes. The optimal conditions for this method were 175 °C, 2 h, a 50:50 water-to-organic solvent ratio, and a 16 bar, 100% oxygen atmosphere [1].

### *Objective*

► Reduce the intensity of the OOS conditions to ***make the process more energy-efficient and cost-effective***.



### *Approach*

► We utilised ***solid acid catalysts (zeolites) to lower the reaction temperature to 150 °C***.

► We screened various zeolite catalysts.

► We studied the catalyst-to-feed (C/F) ratio effect with the optimum zeolite.

► We ***recovered*** and characterised the catalyst to investigate changes in its properties

## 2 EXPERIMENTAL

**Feedstock:** Hard wheat straw (WS) collected from fields in Northern Greece

| Feedstock | Extractives, wt.% | Cellulose, wt.% | Hemicellulose, wt.% | Lignin, wt.% |
|---|---|---|---|---|
| **Wheat straw** | 15.5 | 39.9 | 22.9 | 16.6 |

**Catalysts:** Four different zeolitic types (Mordenite, Y, Beta and ZSM-5) with varying Al content (SAR: 5-300)

| Catalyst* | Surface area, $m^2/g$ | Micropore surface area, $m^2/g$ | Brønsted acid sites, µmol/g | Lewis acid sites, µmol/g | Total acid sites, µmol/g |
|---|---|---|---|---|---|
| **H-Y(5)** | 880 | 764 | 385 | 146 | 531 |
| **H-Y(12)** | 870 | 713 | 263 | 184 | 447 |
| **H-Y(30)** | 885 | 641 | 184 | 83 | 267 |
| **H-Y(60)** | 908 | 610 | 118 | 32 | 150 |
| **H-Beta(25)** | 609 | 423 | 229 | 177 | 406 |
| **H-Beta(75)** | 679 | 443 | 133 | 81 | 214 |
| **H-Beta(300)** | 651 | 488 | 68 | 5 | 73 |
| **H-MOR(20)** | 540 | 478 | 384 | 142 | 526 |
| **H-ZSM5(30)** | 410 | 260 | 214 | 87 | 301 |

*The silica-to-alumina (SAR) ratio is indicated in parentheses

**Experimental setup:** OOS runs were carried out in a 975 mL autoclave reactor (**Fig. 1**).

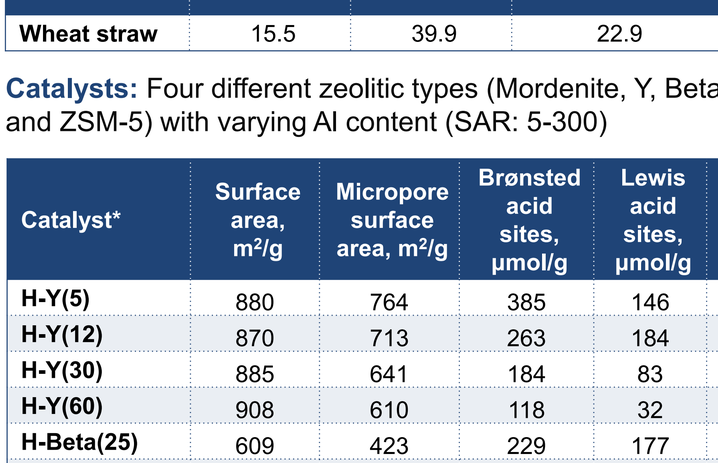



**Fig 1**. Schematic representation of the OxiOrganosolv experimental setup and procedure.

**Product characterisation:** NREL method [2] (**Pulp** composition)

► Acid hydrolysis of pulp followed by ion chromatography (cellulose and hemicellulose content) and UV-Vis spectroscopy (acid-soluble lignin content). Acid insoluble lignin content determined from acid hydrolysis residue.

## 3 RESULTS

### *Screening of different zeolites*

►The zeolites were screened at 150 °C employing a C/F ratio of 0.1.

► Results were compared to non-catalytic runs at the same temperature.

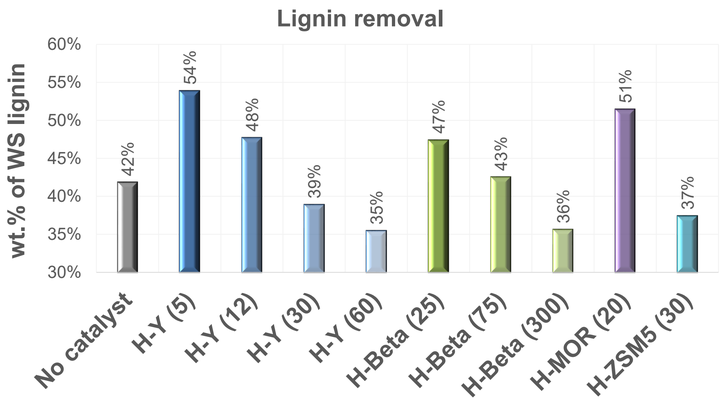



**Fig 2**. Effect of solid acid zeolites on the degree of lignin removal.

### *Effect of C/F ratio*

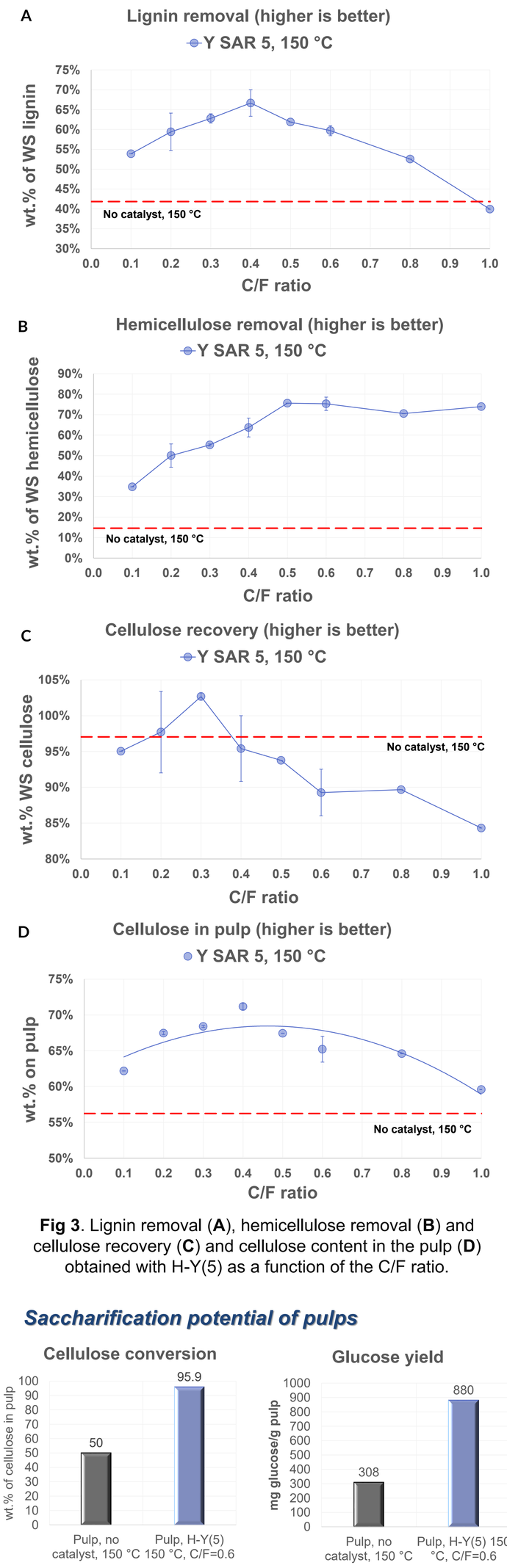


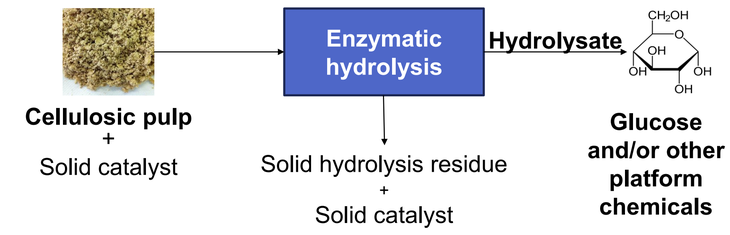

**Fig 3**. Lignin removal (**A**), hemicellulose removal (**B**) and cellulose recovery (**C**) and cellulose content in the pulp (**D**) obtained with H-Y(5) as a function of the C/F ratio.

### *Saccharification potential of pulps*




**Fig 4**. Cellulose conversion (**A**), and glucose yields (**B**) obtained from the enzymatic hydrolysis of non-catalytic and catalytic OOS pulps.

### *Catalyst recovery and characterisation*




► The pulp was enzymatically hydrolysed to produce fermentable sugars, and the catalyst was recovered with the hydrolysis residue.

► Organic residues were removed from the catalyst by calcination in air at 600 °C for 3 h.

**Table 1**. Properties of fresh vs. recovered Y SAR 5 catalysts.

| Property \ Catalyst | H-Y(5) (fresh) | H-Y(5) (recovered) |
|---|---|---|
| **Surface area, $m^2/g$** | 918 | 745 |
| **Micropore surface area, $m^2/g$** | 882 | 631 |
| **Pore volume, $cm^3/g$** | 0.378 | 0.391 |
| **Micropore volume, $cm^3/g$** | 0.333 | 0.240 |
| **Brønsted acid sites, µmol/g** | 385 | 211 |
| **Lewis acid sites, µmol/g** | 146 | 159 |
| **K, ppm** | 0 | 10,400 |
| **Na, ppm** | 0 | 12,800 |
| **Ca, ppm** | 0 | 3,800 |
| **Mg, ppm** | 0 | 718 |

## 4 CONCLUSIONS

► At C/F=0.1, several ***zeolites facilitated lignin removal compared to the non-catalytic OOS*** run (**Fig 2**).

✓ Lignin removal correlated with SAR (**Fig 2**).

► H-Y significantly increased hemicellulose removal due to the ***promotion of acid hydrolysis*** (**Fig 3B**).

► Cellulose recovery maintained at about 100% up until C/F=0.4. At higher C/F ratios, cellulose hydrolysis started to occur, reducing recovery (**Fig 3C**).

► ***Pulps with up to 71.2% cellulose content obtained with H-Y(5)*** at C/F=0.5 (**Fig 3D**).

► Enzymatic hydrolysis of the ***catalytic OOS*** pulp resulted in ***higher cellulose conversion and higher glucose yields compared to the pulp obtained from the non-catalytic OOS*** (**Fig 4**).

► The ***recovered catalyst*** exhibited ***reduced surface area and acidity due to its contamination with alkali and alkaline earth metals*** (**Table 1**)

## REFERENCES

[1] K.G. Kalogiannis, et al., **Bioresource Technol.**, 313 (2020), 123599.

[2] A. Sluiter et al., **Determination of Structural Carbohydrates and Lignin in Biomass**, NREL 2008

## ACKNOWLEDGEMENTS

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