

SOLID ACID CATALYSIS IN AGRICULTURAL RESIDUE FRACTIONATION

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ABSTRACT

We have explored the incorporation of solid catalysts in an oxidative organosolv process (OxiOrganosolv) that uses a pressurized oxygen atmosphere instead of soluble acid catalysts for the fractionation of lignocellulosic biomass (wheat straw) into cellulose, hemicellulose and lignin streams. A range of catalysts was first screened, including different zeolite types with variable silica-to-alumina ratios (SAR) and Cu and Fe metal oxides, and the results were compared to the OxiOrganosolv treatment of wheat straw without a catalyst. The catalyst-to-feed (C/F) ratio was then optimized with a promising catalyst to produce pulps with increased cellulose content. Finally, a catalytic OxiOrganosolv pulp was enzymatically hydrolyzed to assess its saccharification potential. Most catalysts tested, especially the most acidic ones, increased the removal of hemicellulose and lignin from wheat straw, enriching treated feedstock (pulp) in cellulose. The optimum lignin removal and most cellulose-rich pulps were obtained at C/F ratios of about 0.4-0.5 with a Y zeolite with SAR 5. During enzymatic hydrolysis, a significantly higher portion of the cellulose in the catalytic OxiOrganosolv pulp could be converted compared to the corresponding pulp from the non-catalytic OxiOrganosolv, resulting in a majorly increased glucose yields.

KEYWORDS: Lignocellulosic biomass, organosolv, fractionation, catalysis, zeolites

INTRODUCTION

Biorefineries convert low-value biomass into diverse products like heat, power, and chemicals, akin to petroleum refineries processing crude oil. Initially, biomass undergoes pretreatment and is fractionated into cellulose, hemicellulose, and lignin with minimal waste to extract maximum value from the feedstock. Organosolv processes fractionate biomass with minimal degradation in a mixture of water, organic solvent, and a soluble acid catalyst. Recently, we reported a modified, more feedstock-flexible oxidative organosolv process (OxiOrganosolv) that uses a pressurized oxygen atmosphere instead of acid to produce cellulosic streams (pulp) with near-zero cellulose degradation and superior saccharification potential compared to conventional organosolv processes^[1].

In this work, we explored the use of solid catalysts in the OxiOrganosolv process to catalyze the fractionation of wheat straw at a reduced temperature of 150 °C, compared to the usual 175 °C. Various zeolites (Y, Beta, ZSM-5, Mordenite) with different silica-to-alumina ratios (SAR), and Cu and Fe metal oxides were initially screened at 150 °C with a catalyst-to-feed (C/F) ratio of 0.1. A promising catalyst was further tested to fine-tune the C/F ratio, aiming to produce high-purity cellulosic pulps. The cellulosic pulp was then enzymatically hydrolyzed to assess its saccharification

potential, which was compared to the saccharification potential of a pulp from the non-catalytic OxiOrganosolv of wheat straw at the same reaction temperature.

METHODOLOGY

The feedstock used in this work was straw from hard wheat collected from fields in Northern Greece. Its composition was 39.9% cellulose, 22.9% hemicellulose, 16.6% lignin, 15.5% extractives and 3.1% ash. The catalysts used for the catalytic OxiOrganosolv runs are listed in **Table 1**, along with their textural and acidic properties. The zeolites (Y, Beta, ZSM-5, MOR) were commercial samples purchased from Zeolyst. The Fe and Cu oxides were prepared from thermal degradation of iron(III) nitrate nonahydrate (Fe₂O₃-N), iron(III) chloride hexahydrate (Fe₂O₃-Cl) και copper(II) nitrate trihydrate (CuO-N) at 500 °C under air, using a heating rate of 5 °C/min. The mixed Fe-Cu oxide was prepared via controlled precipitation followed by calcination at 500 °C (Cu₂FeO). The catalysts were characterized by N₂ physisorption to determine their textural properties, and Fourier-transformed infrared spectrometry coupled with *in situ* pyridine adsorption to determine the number and type of their acid sites.

The OxiOrganosolv runs were carried out in a 975 mL stirred autoclave reactor. The reactor was loaded with 25 g of wheat straw, 250 g of water, 250 g of EtOH, and the appropriate quantity of catalyst to achieve the target C/F ratio (0-1). The reactor was pressurized with O₂ gas at 16 bar and heated to the reaction temperature. After the reaction temperature was reached, the reactor was kept at these conditions for 2 h, after which it was cooled down and depressurized. The reactor pressure at the end of each run was recorded to calculate the volume of reaction gases, and a

Table 1. Textural and acidic properties of the catalysts used in this work.

Sample	Surface area, m ² /g	Micropore Surface area, m ² /g	Pore volume, cm ³ /g	Micropore volume, cm ³ /g	Brønsted acid sites, μmol/g	Lewis acid sites, μmol/g
Y SAR 5	918	918	0.378	0.333	385	146
Y SAR 12	882	882	0.481	0.276	263	183
Y SAR 30	36	36	0.521	0.248	184	83
Y SAR 60	870	870	0.552	0.233	118	32
Beta SAR 25	609	389	1.063	0.167	229	177
Beta SAR 75	679	443	0.940	0.178	133	81
Beta SAR 300	651	488	0.549	0.191	68	5
ZSM-5 SAR 30	n.d.	n.d.	n.d.	n.d.	214	87
MOR SAR 20	528	491	0.281	0.190	432	105
Fe ₂ O ₃ -N	14	0	1.622	0	n.d.	n.d.
Fe ₂ O ₃ -Cl	1	0	-	0	n.d.	n.d.
CuO-N	1	0	-	0	n.d.	n.d.
Cu ₂ FeO	24	0	0.160	0	n.d.	n.d.

sample of the gas was collected in a sampling bag and analyzed using gas chromatography. The treated biomass (pulp)-catalyst mixture and the liquid reaction medium containing the dissolved lignin and hemicellulose products were separated by vacuum filtration. The pulp-catalyst mixture was homogenized by grinding in a mortar. The homogenized mixture was calcined at 600 °C in air to remove the organic substrate and measure the amount of catalyst in the mixture. The composition of the pulp was then determined after hydrolysis of the homogenized mixture and analysis of the products using ion chromatography to determine the cellulose and hemicellulose content, and UV-Vis spectrometry to determine the lignin content. Details on the analysis methods can be found in our previous work^[1].

To compare their saccharification potential, pulps produced from the non-catalytic and catalytic OxiOrganosolv were hydrolyzed enzymatically in Erlenmeyer flasks using a previously reported method^[1].

RESULTS AND DISCUSSION

Initially, different catalysts were screened for the catalytic OxiOrganosolv treatment of wheat straw at 150 °C and C/F=0.1. The results of the screening runs are presented in **Figure 1**, compared to results from the non-catalytic OxiOrganosolv of wheat straw at the same temperature. Almost all catalysts proved effective and increased the removal of lignin (**Figure 1A**) and hemicellulose (**Figure 1B**) from wheat straw, resulting in most cases in pulps with increased cellulose content (**Figure 1D**). In most cases, cellulose recovery was around 100%, indicating minimal cellulose degradation (**Figure 1C**). Interestingly, a trend was observed with the SAR of the zeolites; zeolites with low SAR and,

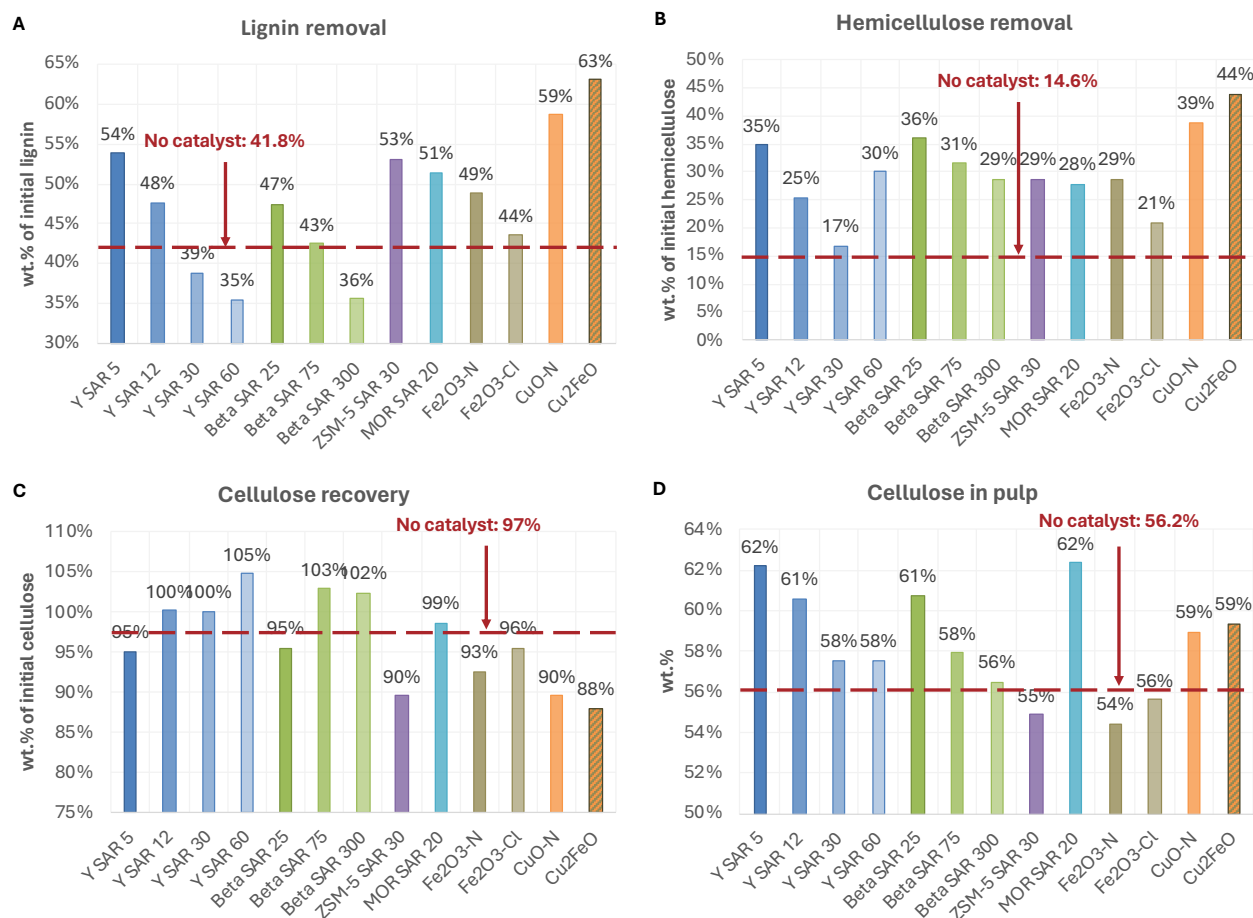


Figure 1. Lignin removal (A), hemicellulose removal (B), cellulose recovery (C), and cellulose content (D) in the pulps produced from the OxiOrganosolv of wheat straw with different catalysts at 150 °C and C/F=0.1.

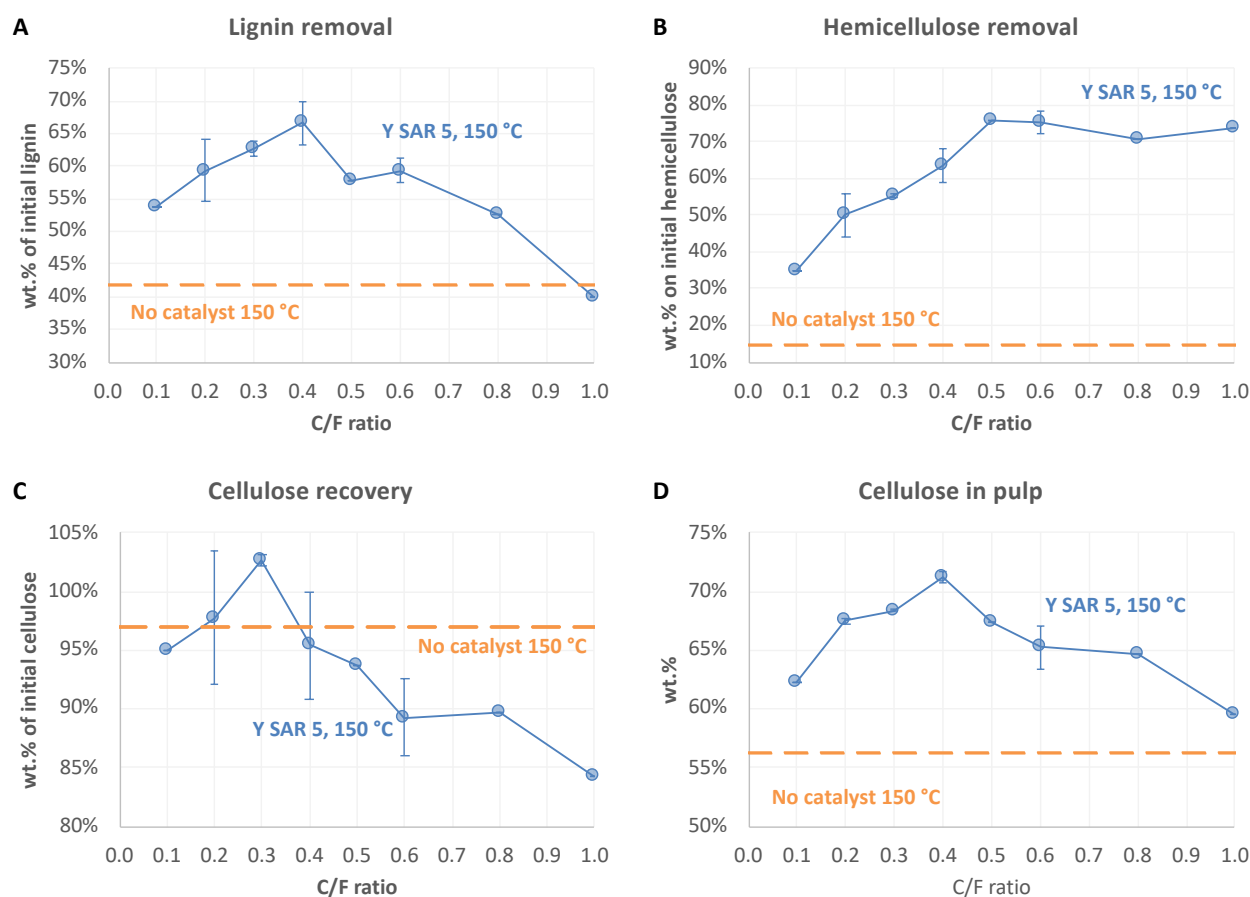


Figure 2. Lignin removal (A), hemicellulose removal (B), cellulose recovery (C), and cellulose content (D) in the pulps produced from the OxiOrganosolv of wheat straw with USY SAR 5 at 150 °C as a function of the C/F ratio.

therefore, higher acidity were more effective than their higher SAR counterparts, indicating that the acidity of the catalyst was pivotal for the fractionation of wheat straw.

Based on the catalyst screening, the Y SAR 5 catalyst was chosen to optimize the C/F ratio. Catalytic OxiOrganosolv runs were carried out at 150 °C at C/F ratios ranging from 0.1 to 1. The results are presented in **Figure 2** and compared to the non-catalytic OxiOrganosolv treatment of wheat straw at 150 °C. As the C/F ratio increased, lignin (**Figure 2A**) and hemicellulose (**Figure 2B**) removal increased up to a C/F ratio of ca. 0.4-0.5. Increasing the C/F ratio further resulted in reduced lignin removal, while the removal of hemicellulose plateaued. It is hypothesized that the high amount of catalyst in the reactor at C/F ratios >0.5 impeded the mass transfer of oxygen and reduced the oxidation reactions of lignin, resulting in reduced lignin removal. The recovery of cellulose was between 95% and 100% at C/F ratios up to 0.5, but then started to decrease and reached ca. 85% at C/F=1. This was attributed to the acidity of the catalyst, which, at high loadings, started to hydrolyze the cellulose. Correspondingly, the highest cellulose content in the pulps produced was obtained using a C/F ratio of ca. 0.4. Beyond this C/F ratio, the cellulose content in the produced pulp decreased due to the reduced lignin removal and due to the hydrolysis of cellulose that took place at high catalyst loadings. Compared to the non-catalytic OxiOrganosolv at 150 °C, using the Y SAR 5 catalyst at C/F=0.4-0.6 significantly increased the removal of lignin and hemicellulose, resulting in more cellulose-rich pulps, with a cellulose content up to 70%.

A pulp produced from the catalytic OxiOrganosolv of wheat straw (Y SAR 5, C/F=0.6, 150 °C) was enzymatically hydrolyzed to assess its saccharification potential, which was compared to the saccharification potential of a

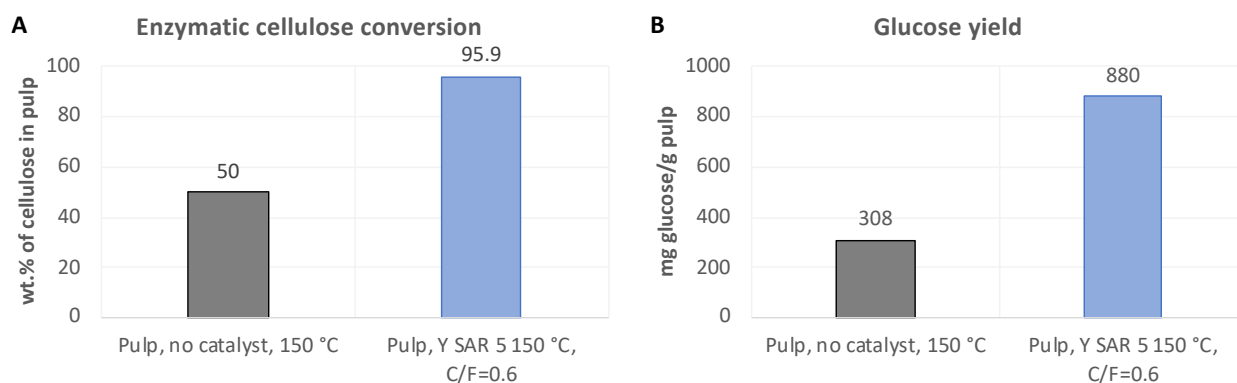


Figure 3. Comparison of the cellulose conversion (A) and the glucose yield (B) from the enzymatic hydrolysis of a non-catalytic OxiOrganosolv (150 °C) pulp and a catalytic OxiOrganosolv pulp (Y SAR 5, 150 °C, C/F=0.6).

pulp produced from the non-catalytic OxiOrganosolv of wheat straw at 150 °C. Almost 96% of the cellulose in the pulp from the catalytic OxiOrganosolv was enzymatically converted, compared to only 50% of the cellulose in the pulp from the non-catalytic one (**Figure 3A**). Consequently, the glucose yield from the catalytic OxiOrganosolv pulp was significantly higher (**Figure 3B**). This was despite the fact that catalyst was present in the pulp from the catalytic OxiOrganosolv, which did not negatively impact its saccharification potential. After hydrolysis, the catalyst could be easily recovered from the solid hydrolysis residue for reuse.

Our future efforts will focus on catalyst stability and reuse, and on the synthesis and testing of bifunctional acid-redox catalysts to further optimize the catalytic OxiOrganosolv.

ACKNOWLEDGMENTS

The research project NanoHybrid is implemented in the framework of H.F.R.I.'s call "Basic research Financing (Horizontal support of all Sciences)" under the National Recovery and Resilience Plan "Greece 2.0" funded by the European Union – NextGenerationEU (H.F.R.I. Project Number: 015795).



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