Acetalization of furfuraldehyde with argan nut shells carbon catalysts

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Introduction

Furfuraldehyde has been identified as a crucial molecule derived from biomass that can be used in a wide range of reactions including hydrogenation, oxidation, reductive amination, decarbonylation, nitration, and acetalization [1]. Several reports refer to the use of solid catalysts in the acetalization of furfural to produce furfural diethyl acetal products. These products have industrial application as solvent in organic reactions and is an important material in the perfume industry. Traditionally, these reactions are catalysed by strong inorganic acids such as H_2SO_4, with all the environmental and process drawbacks. In this context, the performance of novel activated carbon-based catalysts derived from argan nut shells, an abundant biomass waste in Northern Africa, was evaluated as catalysts on furfural diethyl acetal production. Activated carbon was synthesized via chemical activation, using H_3PO_4 as an activating agent (ACH sample). ACH was subjected to HNO_3 treatment to modify its surface chemistry and named as N-ACH.

The catalytic tests were conducted on the reaction of acetalization of furfuraldehyde under different conditions. The results demonstrated that both catalysts exhibited excellent catalytic potential for furfuraldehyde acetalization. However, the oxidized carbon presented the higher activity since N-ACH surface was significantly enriched with oxygenated acidic groups compared to ACH surface.

Experimental methods &materials

1. Preparation of the catalysts

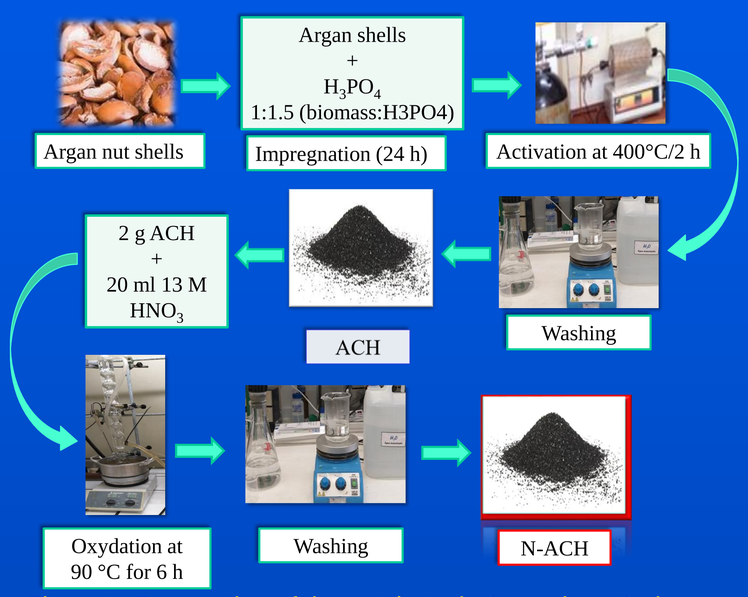

Figure 1: Preparation of the catalysts (ACH and N-ACH)

2. Characterization of the catalysts

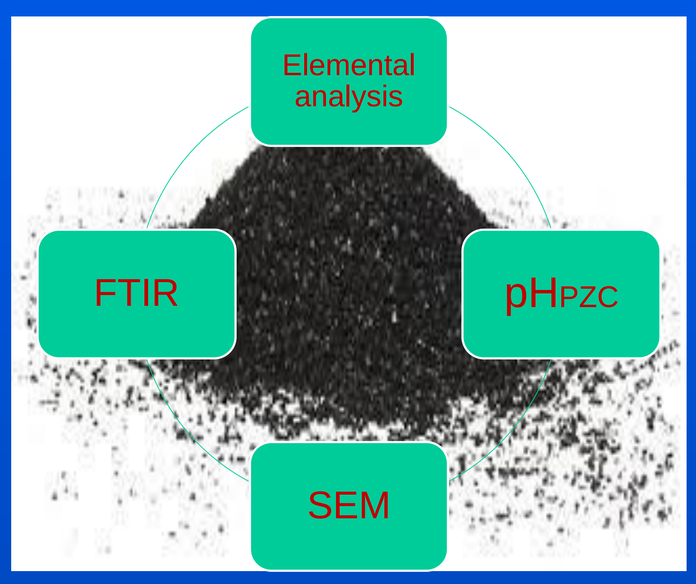

Figure 2: Analysis methods

3. Catalytic experiments

- A mixture of catalyst (ACH or N-ACH) with 12 ml of ethanol and 0.25 ml of undecane was placed in a reaction flask at the desired temperature.
- Addition of 2.4 mmol of 2-furfuraldehyde 99% (v/v) started the reaction.
- Samples were stirred in high-rate values (1000 rpm) for 7 h. Blank experiments without catalyst were also performed in the same conditions.
- Samples were taken periodically and analysed by GC-FID, using a KONIC HRGC-5000B instrument.

Figure 3: Catalytic experiments

Results & Discussion

1. Catalyst characterization

Table1: Elemental composition and pHPZC of biomass, ACH and N-ACH samples

	ANS	ACH	N-ACH
Elemental analysis			
C (wt. %)	47.8	59.1	54.65
H (wt. %)	6.54	4.39	2.06
N (wt. %)	0.33	<02	1.70
S (wt. %)	<0.03	<0.03	0.02
O* (wt. %)	45.26	36.57	41.57
pH_{PZC}	n.d	6.0	2.8

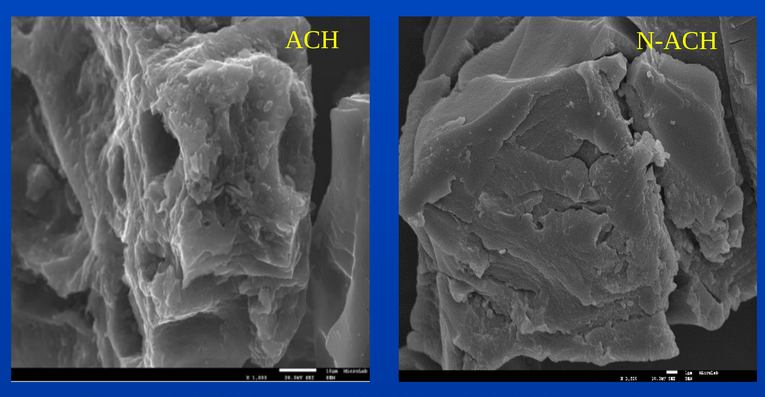

Figure 4: SEM images of ACH and N-ACH samples

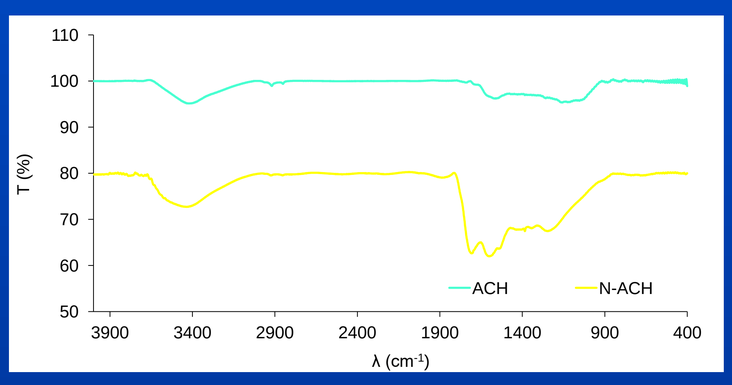

Figure 5: FTIR spectra for ACH and-ACH

2. Catalytic study

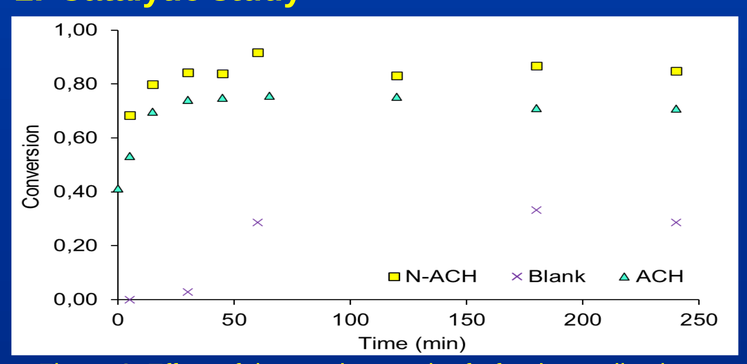

Figure 6: Effect of the catalyst on the furfural acetalization with ethanol. Reaction conditions: 100 mg of catalyst, 45 °C, 2.4 mmol furfuraldehyde, 12 mL ethanol

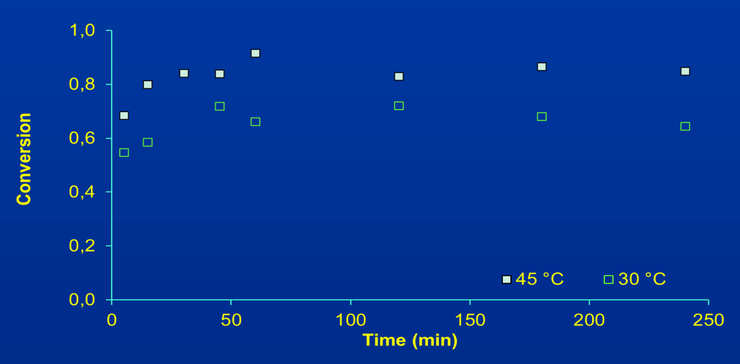

Figure 7: Effect of the temperature on the furfural acetalization with ethanol. Reaction conditions: 100 mg of N-ACH catalyst, 2.4 mmol furfuraldehyde, 12 mL ethanol.

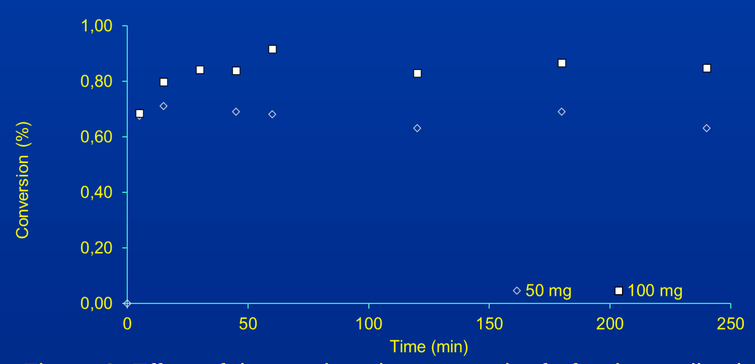

Figure 8: Effect of the catalyst dosage on the furfural acetalization with ethanol. Reaction conditions: temperature 45 °C, 2.4 mmol furfuraldehyde, 12 mL ethanol.

Conclusions

This work reports herein two eco-sustainable and recyclable porous carbons able to efficiently catalyze the synthesis of furfural diethyl acetal with very high selectivity under mild conditions, contributing to the valorization and circular economy of this platform biomass derived molecule. The biomass derived carbon ACH obtained through a chemical activation process using H3PO4 as activation agent resulted in a carbon with some oxygen groups incorporated in the surface. Although the pHPZC and XPS (reported in [2]) did not indicate a very strong acidity, in the tested conditions this carbon already revealed catalytic activity demonstrating the possibility of a direct catalyst synthesis. The posterior treatment with HNO_3 was meant to introduce more acidic groups in the carbon surface. Although successful in the surface oxidation it led to diminished textural properties, which probably was responsible for the mild overall success of the procedure over the catalytic behaviour.

Acknowledgements

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References

[1] Castellanos-Blanco, N., Taborda, G., and Cobo, M.: An efficient acetalization method for biomass- derived furfural with ethanol using γ-Al2O3-s upported catalysts. ChemistrySelect (2020).

[2] Mokhati, A. et al.: Nanoporous carbons prepared from argan nutshells as potential removal agents of diclofenac and paroxetine. J. Mol. Liq (2021).