NMR analysis of oilseed residues

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VALREO

- the VALREO project (https://valreo.fkkt.um.si) aims to transform vegetable oil production facilities into sustainable biorefineries by converting industrial residues into high-value products and renewable energy, following circular economy principles.
- VALREO investigates green innovation by valorizing agro-industrial waste, integrating biochemical and thermochemical processes, and enhancing sustainability in food and energy sectors.
- expected Outcomes: Development of bio-based products such as e.g. hydrochar, volatile fatty acids, enzymes, and bioactive compounds, with applications as adsorbents, biocatalysts, and biofertilizers to close the resource loop.

INTRODUCTION

- lignocellulosic biomass (LB) is a promising feedstock for the production of various bio-based eco-friendly products including biochemicals and biofuels
- LB mainly consists of three types of biopolymers: cellulose, hemicellulose and lignin
- in order to optimize pretreatment process and further (bio) conversion into bio-based products it is necessary to unveil its composition
- many different analytical methods and approaches were used to study properties and composition of lignocellulosic samples
- in this work we demonstrate the power of NMR spectroscopy in solution and in the solid state as a valuable tool for investigating lignocellulosic residues from the vegetable oil industry: pumpkin oil cake (PC) and hemp pomace (HP)

RESULTS AND DISCUSION

Oilseed cakes

- important by-products after oil production from various nuts and oilseeds
- wide range of applications (animal feed, organic fertiliser in agriculture, substrate source for the cultivation of microorganisms and the production of enzymes)
- high calorific value and high fat content (solid and liquid biofuels)

NMR spectroscopy

- the influence of Thermomyces lanuginosus on the chemical structure of biopolymers and lipids from hemp pomace during solid-state fermentation (SSF) was studied using solution and solid state NMR
- after SSF, the hemp pomace was subjected to milling and subsequent isolation of biopolymers (lignin, cellulose, hemicellulose) and lipids.

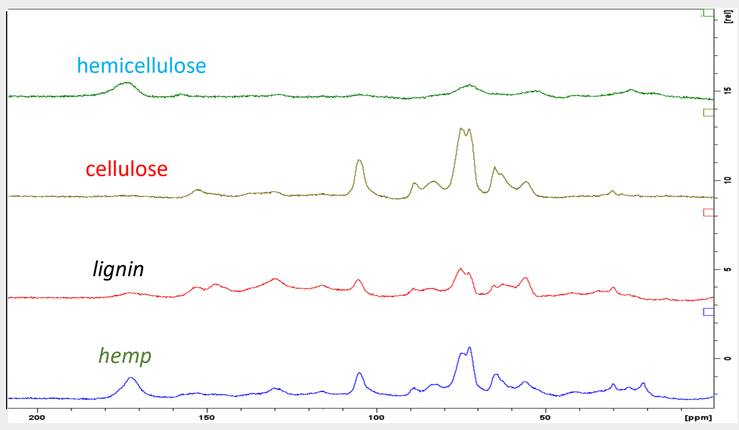

Figure 1. Typical ^{13}C CP MAS NMR spectra of hemp, lignin, cellulose and hemicellulose

Sample	N_{TG}* %	$N_{1,2DG}$* %	$N_{1,3DG}$* %	N_{FA}* %	L_n* %	L* %	U* %	M_U* %	S+M* %
PC	88.43	7.31	4.14	0.14	4.77	31.14	36.29	0,38	63.71
HC	90.86	6.88	-	2.26	8.58	28.25	40.48	3.65	59.52

Table 1. Percentages of glyceride components and fatty acids and acyl group of PC and HC raw samples.

Sample	L_n* %	L* %	U* %	M_U* %	S+M* %
SS	4.78	35.28	41.08	1.02	58.92
PC	4.77	31.14	36.29	0,38	63.71
HC	8.58	28.25	40.48	3.65	59.52
SS 250^{0}C	5.98	29.17	37.57	2.42	62.43
PC 250^{0}C	6.24	20.57	30.01	3.20	69.99
HC 250^{0}C	10.52	27.53	43.03	4.93	56.97
PC-SS 1:1	6.84	18.86	35.60	9.9	64.40
PC-SS 1:3	13.47	15.77	32.16	2.92	67.84
PC-SS 3:1	10.76	12.91	29.78	6.09	70.22
HC-SS 1:1	8.67	18.04	28.74	2.03	71.26
HC-SS 1:3	8.13	16.13	36.63	12.37	67.37
HC-SS 3:1	7.65	10.75	33.84	15.44	66.16

Table 2. Percentages of fatty acids and acyl groups of analysed samples

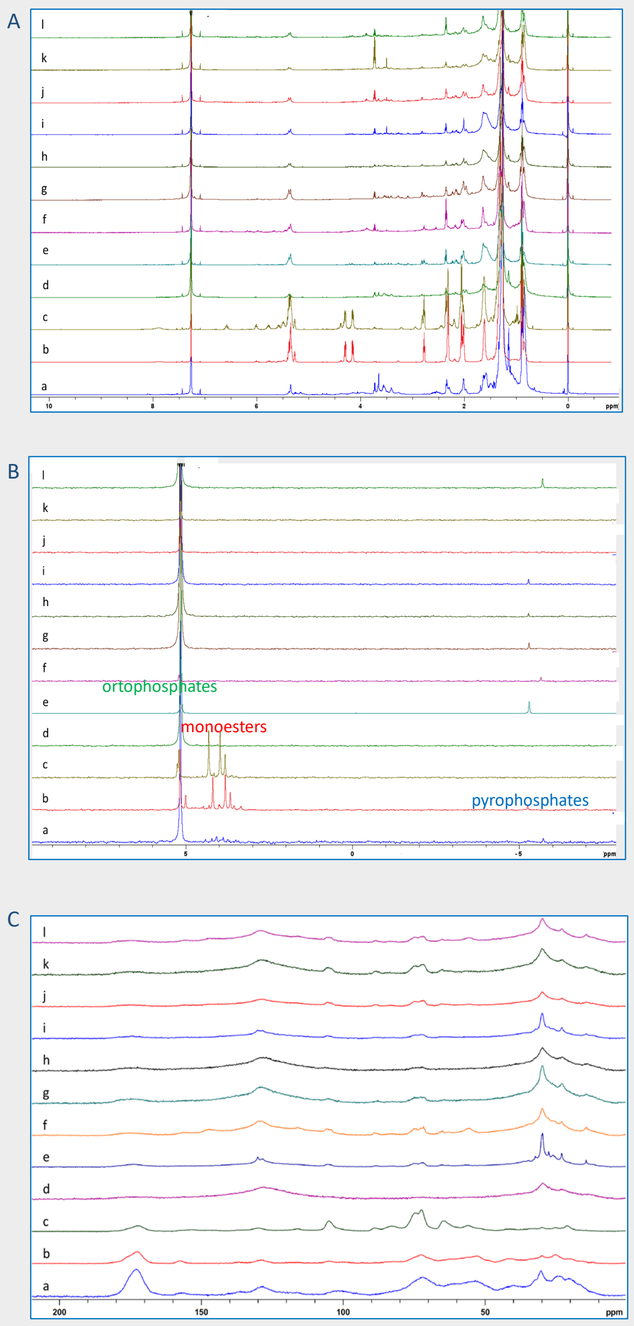

Figure 2. A) ^1H NMR spectra of samples (a) SS, (b) PC, (c) HC, (d) SS 250, (e) PC 250, (f) HC 250, (g) PC-SS 1:1, (h) PC-SS 1:3, (i) PC-SS 3:1, (j) HC-SS 1:1, (k) HC-SS 1:3 and (l) HC-SS 3:1 in $CDCl_3$,

B) ^{31}P NMR spectra of (a) SS, (b) PC, (c) HC, (d) SS 250, (e) PC 250, (f) HC 250, (g) PC-SS 1:1, (h) PC-SS 1:3, (i) PC-SS 3:1, (j) HC-SS 1:1, (k) HC-SS 1:3 and (l) HC-SS 3:1 in D_2O

C) ^{13}C CP MAS NMR spectra of the samples (a) SS, (b) PC, (c) HC, (d) SS 250, (e) PC 250, (f) HC 250, (g) PC-SS 1:1, (h) PC-SS 1:3, (i) PC-SS 3:1, (j) HC-SS 1:1, (k) HC-SS 1:3, (l) HC-SS 3:1

Acknowledgment: This research was conducted within the Project of the Croatian Science Foundation "Valorisation of residues from the vegetable oil industry based on a biorefinery approach – VALREO) (HRZZ-IPS-2023-02-6614). Part of this research was performed using resources from the Division of Analytical Chemistry, University of Zagreb, Faculty of Science funded by the European Regional Development Fund (infrastructural project CIuK, grant number KK.01.1.1.02.0016).

- the hydrothermal co-carbonization (co-HTC) of residues from the vegetable oil industry (pumpkin oil cake – PC, hemp oil cake – HC) and sewage sludge (SS) was investigated by NMR
- the co-HTC was performed at 250 °C and a treatment time was 5 h
- the influence of the mass ratio of the feedstocks (1:1, 1:3 and 3:1) on the properties of the HTC products were investigated
- the results are given in Table 1.-4. and Figure 1.

Sample	Ortophosphate (~5.20 ppm)/%*	Monoester (3.15-5.10 ppm)/%*	Pyrophosphate (~-5.60 ppm)/%*
SS	87.57	11.08	1.37
PC	25.09	72.76	2.15
HC	20.05	79.95	-
SS 250^{0}C	100	-	-
PC 250^{0}C	80.12	-	19.88
HC 250^{0}C	64.35	-	35.65
PC-SS 1:1	99.45	-	0.55
PC-SS 1:3	99.63	-	0.37
PC-SS 3:1	98.85	-	1.15
HC-SS 1:1	100	-	-
HC-SS 1:3	100	-	-
HC-SS 3:1	98.04	-	1.86

Table 3. ^{31}P NMR assignments and percentages of phosphates.

References

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CONCLUSION

- NMR spectroscopy is a valuable tool for investigating complex mixtures such as lignocellulose
- NMR can provide new insights into the chemical changes and nutrient transformation
- the results demonstrate that SSF with Thermomyces lanuginosus is an effective strategy for modifying and enhancing the chemical profile of biopolymers and lipids in hemp pomace, highlighting its potential for value-added biorefinery applications
- an increase in the carbonyl group content in lignin was noticed
- in lipid samples, a significant reduction in mono-, di-, and triglycerides occurred during fermentation time, accompanied by an increase in glycerol and unsaturated fatty acids
- fungal treatment substantially influenced the phosphorus-containing compounds present in the hemp pomace
- the co-HTC of SS with oil cakes resulted in improved fuel properties of the hydrochar
- obtained results revealed new insights into the production, properties and potential applications of hydrochars obtained from the co-HTC of oily waste and SS