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Introduction

At present, sustainability and the reduction of the carbon footprint are two most important issues in the industrial sector and in society in general. The production of environmentally friendly and sustainable materials has become a priority in many industries. Obtaining hemicelluloses, lignin, nanocelluloses or other high value-added materials from high-yielding forest species can be an efficient and sustainable way of producing materials with improved properties.

In this work, *Robinia Pseudoacacia* was subjected to cold alkaline extraction (CAE) with and without ultrasound, the main objective being to obtain a liquor rich in hemicelluloses. The CAE could be a first stage of a cascading biorefinery.

Experimental

SAMPLES PREPARATION AND CHARACTERIZATION: Samples were stored and dried after chipping; Furthermore, its composition was obtained by standard TAPPI analysis.

COLD ALKALINE EXTRACTION: The modeling and optimization of the process was proposed, based on a central composition factorial design with a total of 16 experiments. Operating ranges: soda concentration 80-120 g.L⁻¹; operating time 30-90 min and temperature 20-40 °C. At the same time, with or without the simultaneous application of ultrasound.

LIQUOR PHASE: Precipitation of Hemicelluloses with ethanol.
SOLID PHASE: The composition was obtained by standard TAPPI analysis and was subjected to a thermogravimetric and calorific value study.

ADDITIONAL TREATMENTS TO INCREASE THE YIELD OF THE CAE:

1. Decrease in splinter size by 80% of the size originally.
2. Reduction of the chip size by 80% of the original size and impregnation with water for 24 hours.
3. 80% sliver size reduction, water impregnation for 24h and wet milling.
4. Size originally, impregnation with water for 24h and wet milling.

Results and discussion

Chemical Composition	Robinia Pseudoacacia	Eucalyptus Globulus	Tagasaste
α Cellulose (%)	47,05±2,8	42,8±2,0	38,9±3,4
Klason Lignin (%)	19,59±1,2	21,2±0,9	19,8±1,9
Xylan (%)	18,83±0,6	17,1±0,3	19,9±1,3
Araban (%)	2,2±0,2	0,7±0,1	0,6±0,3
Acetyl groups(%)	1,35±0,1	3,5±0,1	4,4±0,6
HHV, KJul/kg	18362±102	19326±84	19592±28

Table 1. Chemical composition of the biomass under study together with other reference biomasses.

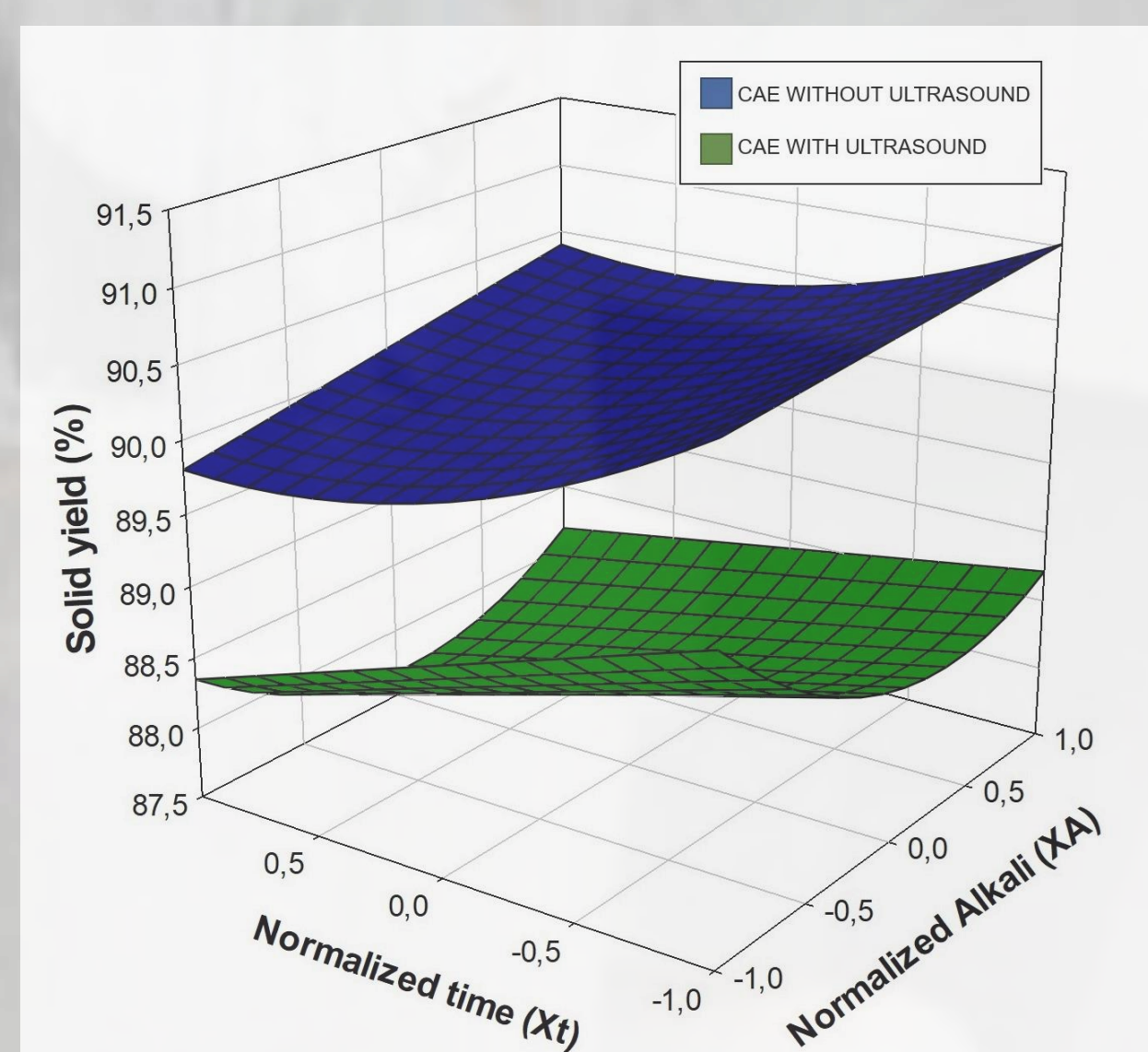


Figure 1. The variation in solid yield as a function of alkali concentration and time in the CAE processes with and without ultrasound.

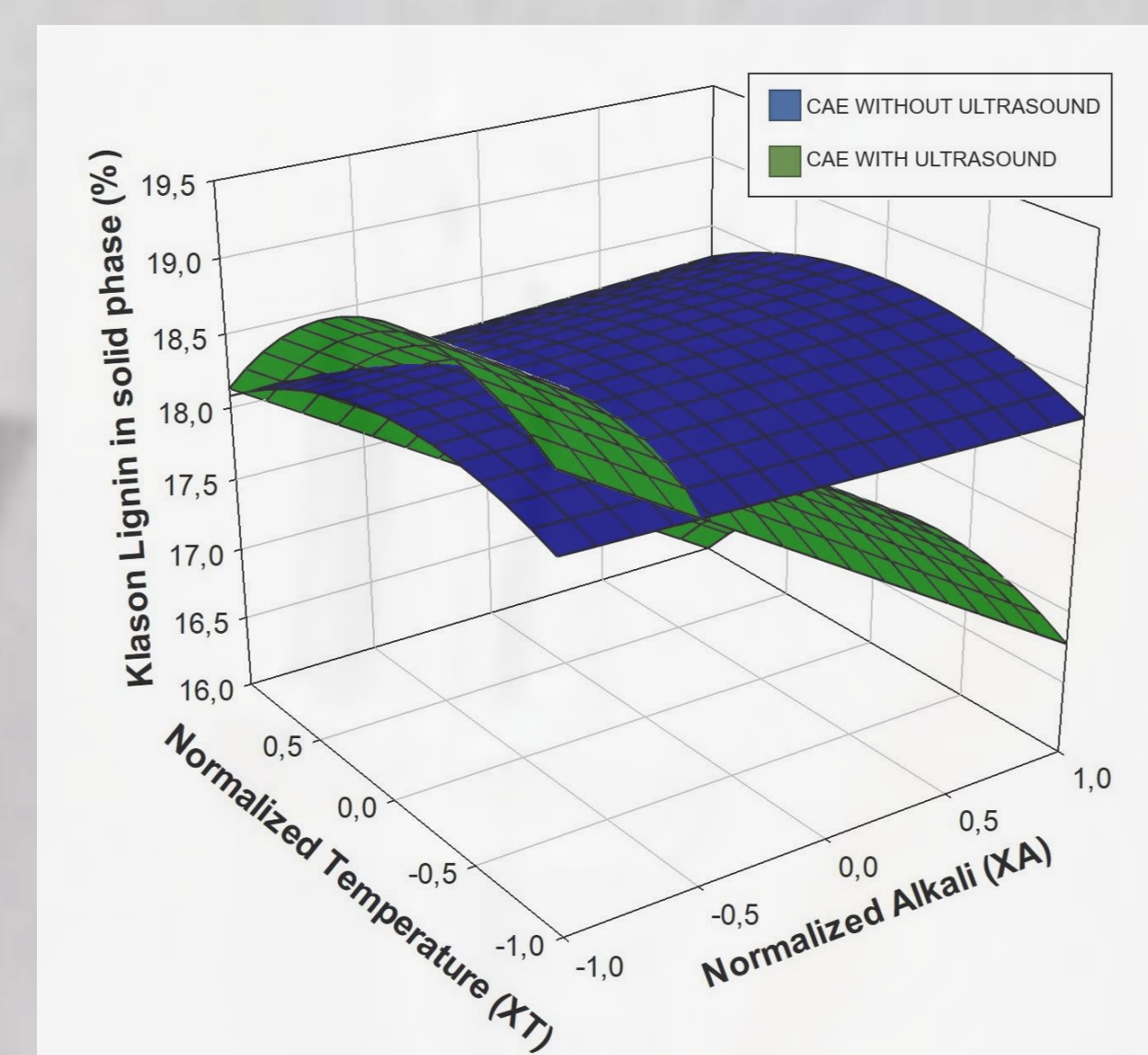


Figure 2. The variation in Klason lignin content in the post-CAE solid phase as a function of alkali concentration and temperature, with and without ultrasound.

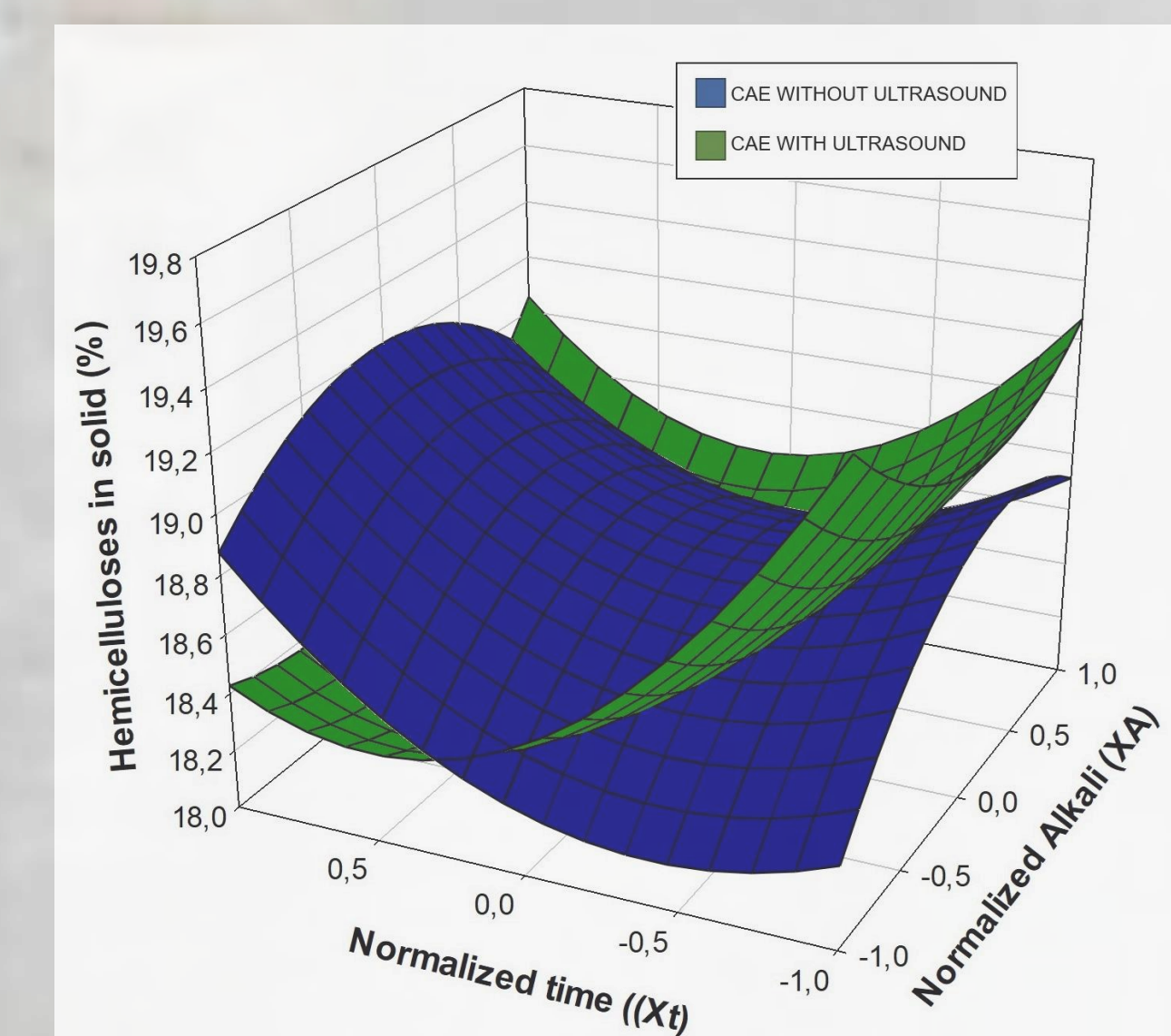


Figure 3. The variation in hemicelluloses content in the post-CAE solid phase as a function of alkali concentration and time, with and without ultrasound.

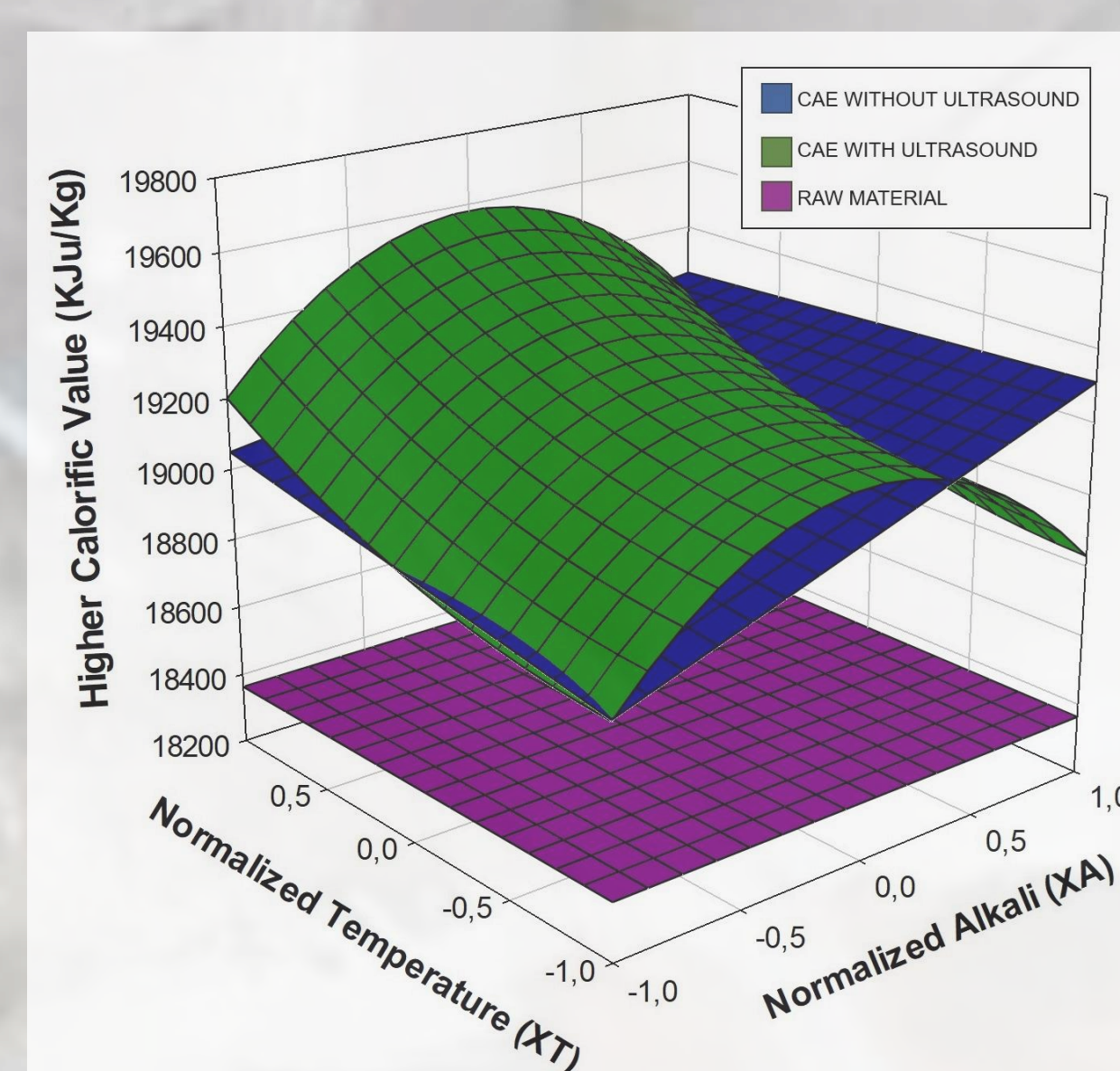


Figure 4. The variation of higher calorific value of post-CAE solid phase as a function of alkali concentration and temperature, with and without ultrasound.

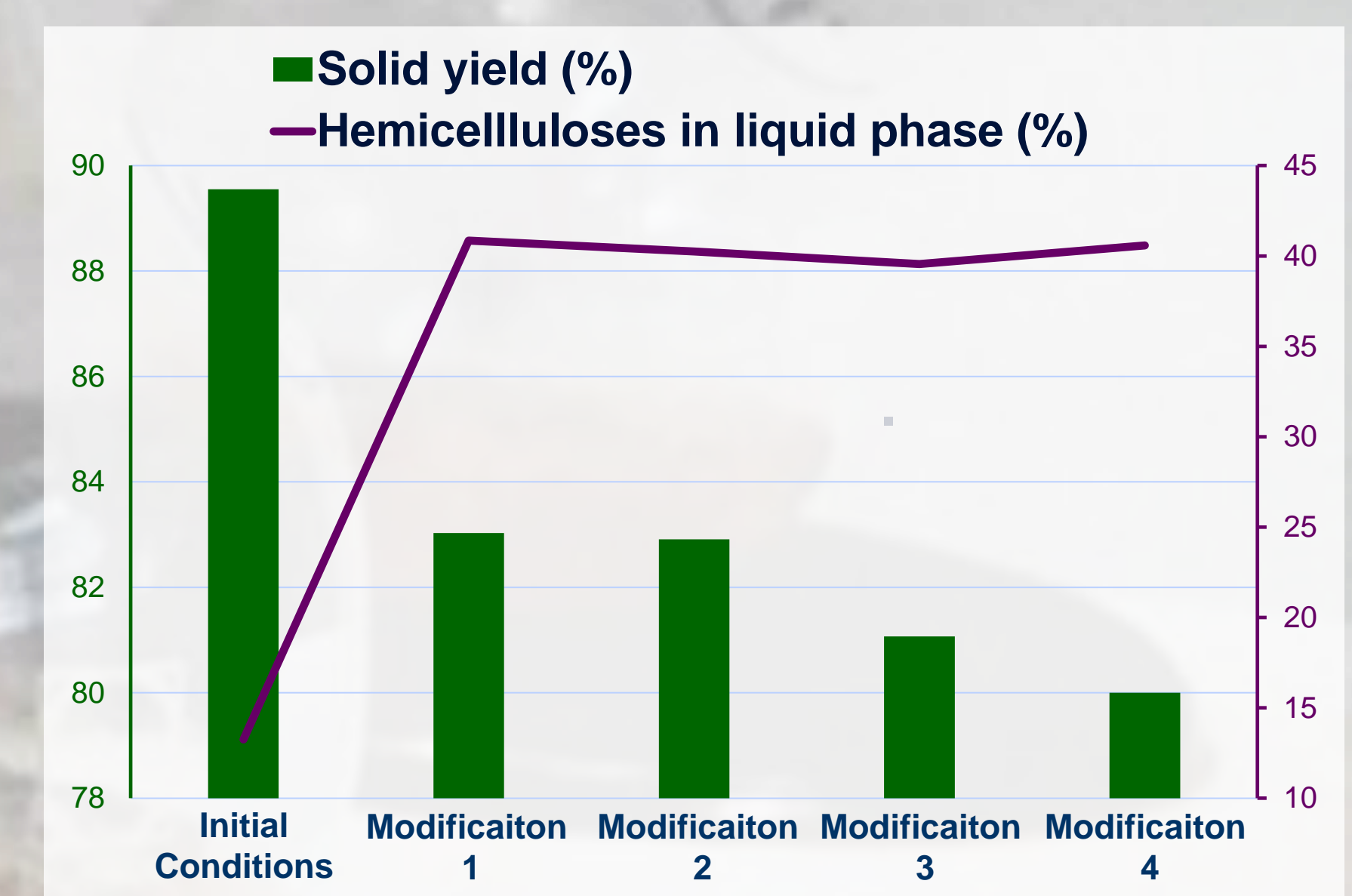


Figure 5. Variation of solid yield and hemicellulose extraction in the liquid phase as a function of additional treatment at the optimum conditions of the CAE process with ultrasound.

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Conclusions

- Based on the results obtained throughout the entire experimental design of the CAE process, in the case where ultrasound was not applied, the temperature variable predominantly affected hemicellulose extraction, whereas when it was applied, it was the time variable.
- The simultaneous application of ultrasound with CAE resulted in the treatment exhibiting greater selectivity for the hemicellulosic fractions, especially for the major component, xylan.
- The optimal point for the CAE treatment of *Robinia Pseudoacacia* was selected due to its lower solid yield (indicating higher extraction yield in the liquid phase) with ultrasound, as well as for operating conditions involving the lowest alkali concentration (80 g.L⁻¹), lowest temperature (20°C), and longest operating time (90 min). At this point, a balance was achieved between maximum extraction of total hemicelluloses and low extraction of glucose in the liquid phase.
- The introduction of additional variables to the ultrasound-assisted CAE treatment, under the conditions selected as optimal, increased the yield of polysaccharide extraction in the liquid phase. Some of these measures achieved a reduction in solid yield from 89.55% to 80% and even triple the extraction of the hemicellulosic fraction into the liquid phase.
- With the CAE treatment, in addition to obtaining a high-value liquid, a solid material suitable for energy purposes is also obtained. These post-CAE solids exhibit an increased calorific potential compared to the calorific value of the raw starting material, owing to the selective retention of the cellulose fraction. Furthermore, it was demonstrated that the post-CAE solids with ultrasound exhibited a greater increase in calorific value, specifically increasing from a value of 18362 KJ.kg⁻¹ for the raw material to a maximum value of 19328 KJ.kg⁻¹ for the post-treatment solid.