ISGC 2022

N°1398 / PC
TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Reductive Catalytic Fractionation of non-conventional lignocellulosic biomass

AUTHORS

Diego MONTESDEOCA / UNIVERSITÉ CATHOLIQUE DE LOUVAIN, PLACE LOUIS PASTEUR, LOUVAIN-LA-NEUVE
Damien DEBECKER / UNIVERSITÉ CATHOLIQUE DE LOUVAIN, PLACE LOUIS PASTEUR, LOUVAIN-LA-NEUVE

PURPOSE OF THE ABSTRACT

Introduction: Globally, agro-industrial activities generate significant amounts of biomass since substantial parts of the crops become waste during harvesting or processing. The accumulation of these agricultural wastes amounts to 2 billion tons worldwide [1], which is a cause for concern since inadequate disposal practices are likely to provoke adverse effects on the environment or even harm human health.

On the other hand, concerns around the gradual depletion of fossil resources and the negative impact on the environment due to the use of petroleum products have driven the search for alternative and sustainable feedstocks for the supply of energy, chemicals, and materials.

At present, a promising strategy that embraces waste valorization to produce valuable products with potential use as fuels or platform molecules is the reductive catalytic fractionation (RCF) of lignocellulosic biomass, which is essentially solvolysis followed by reductive hydrogenation that allows obtaining stable phenolic monomers from lignin and leaving the cellulosic part almost intact [2], thus making it possible to exploit the biomass components integrally.

Research on RCF is extensive but focused exclusively on woody feedstocks, with little information about using lignocellulosic biomass from less conventional (yet abundant) sources.

In this work, 4 types of abundant and cheap biomass from Ecuadorian agro-industries (sugarcane bagasse, rice husks, cocoa pod, and banana rachis) were subjected to catalytic conversion through this lignin-first biorefinery approach.

Experimental part: Biomass was characterized following standard protocols for dry matter and ash, extractives in water and ethanol, structural carbohydrates, and acid-insoluble lignin (AIL) [3].

Typical RCF conditions were applied, 3 g of biomass, 0.3 g of Ru/C, 120 mL of methanol, 30 bar H2 (reductive agent), heating up to 200 °C for 3h, aiming to obtain the yield of phenolic monomers.

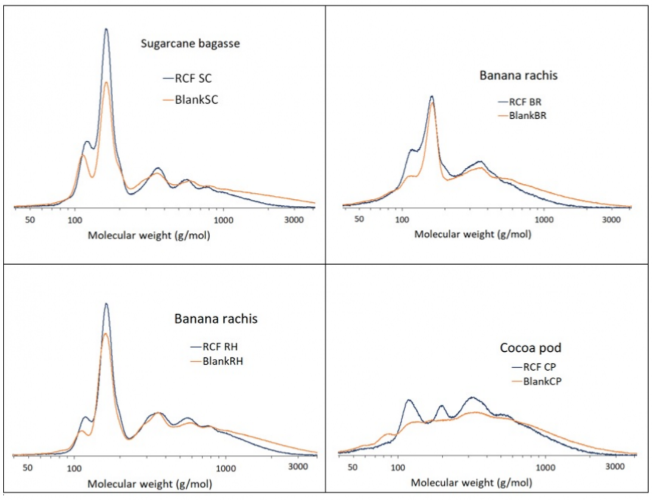
The outlet streams from RCF were fully characterized to gain insights into cellulose and hemicellulose retention in the residual pulp, and especially the fractionation level of lignin into its monomers in the lignin oil.

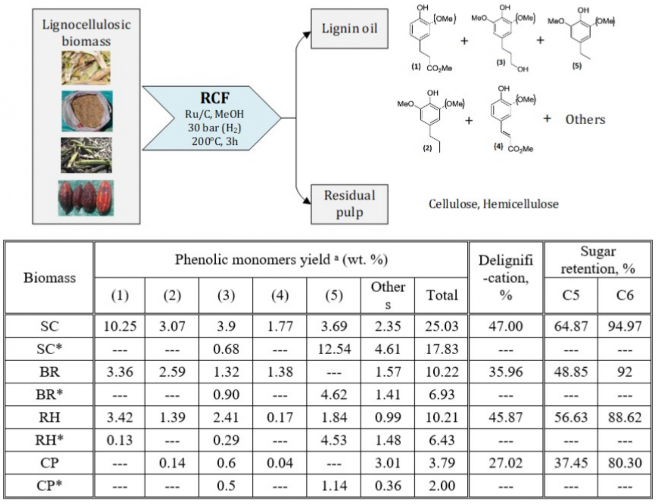
Results and discussion: Gel permeation chromatography (Fig. 1) was used to evaluate the molecular weight distribution of lignin oils obtained during RCF reactions and blank experiments (without the catalyst). Two main peaks are observed at 120 and 150 g/mol, representing the formation of phenolic monomers, followed by 1 to 3 smaller peaks between 330 and 800 g/mol, likely corresponding to phenolic dimers and trimers. Finally, a tail extending from 900 g/mol reveals the presence of some condensation products. In the presence of the catalyst, the peaks of monomers, dimers and trimers are more intense, while the high molecular weights tail is less pronounced. This confirms the crucial role of the hydrogenation catalyst that stabilizes the products of depolymerization against re-condensation.

To further sustain these findings, lignin oils were characterized by GC-MS and GC-FID, showing the presence of several phenolic monomers that account for total yields of 4-25% (based on the initial Klason lignin). In the lignin oils (Fig. 2), the major phenolic compounds identified correspond to units of propyl-, propanol-, and ethyl-substituted guaiacol/syringol, which is consistent with results obtained in RCF reactions applied to woody biomass [2]. Additionally, units of methyl hydrocoumarate/hydroferulate derived from coumaric/ferulic acid were significantly present, which is explained by the herbaceous nature of biomass from rice, sugarcane, and banana. In the blank experiments, the monomers yields dropped to 2-18%, mostly prevailing unsaturated molecules of methyl coumarate/ferulate and propenyl guaiacol/syringol.

Cocoa pod biomass results are somewhat unexpected with the lowest yield of phenolic monomers (3.79%). The high content of ash and extractives could cause this low yield.

FIGURES





Biomass	Phenolic monomers yield ª (wt. %)							Delignifi -cation, %	Sugar retention, %	
	(1)	(2)	(3)	(4)	(5)	Other s	Total		C5	C6
SC	10.25	3.07	3.9	1.77	3.69	2.35	25.03	47.00	64.87	94.97
SC*	---	---	0.68	---	12.54	4.61	17.83	---	---	---
BR	3.36	2.59	1.32	1.38	---	1.57	10.22	35.96	48.85	92
BR*	---	---	0.90	---	4.62	1.41	6.93	---	---	---
RH	3.42	1.39	2.41	0.17	1.84	0.99	10.21	45.87	56.63	88.62
RH*	0.13	---	0.29	---	4.53	1.48	6.43	---	---	---
CP	---	0.14	0.6	0.04	---	3.01	3.79	27.02	37.45	80.30
CP*	---	---	0.5	---	1.14	0.36	2.00	---	---	---

FIGURE 1

Comparison of GPC chromatograms of the lignin oils obtained after RCF and blank reactions for sugar cane bagasse, banana rachis, rice husks, and cocoa pod.

SC=sugarcane bagasse, BR=banana rachis, RH=rice husks, CP=cocoa pod

FIGURE 2

Phenolic monomers yields from reductive catalytic fractionation of non-conventional biomasses

SC=sugarcane bagasse, BR=banana rachis, RH=Rice husks, CP=cocoa pod, (a) Based on the initial Klason lignin, * Blank experiments

KEYWORDS

Biomass | Lignin | Reductive catalytic fractionation | Biorefinery

BIBLIOGRAPHY

[1] R. Millati et al., Elsevier B.V., Chapter 1, pp. 1-22, 2019.
[2] T. Renders et al., Curr. Opin. Biotechnol., vol. 56, pp. 193-201, 2019.
[3] A. Sluiter et al., Natl. Renew. Energy Lab., LAP, pp. 3-17, 2012.