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OrganoCat Fractionation of Empty Fruit Bunches from Palm Trees into Lignin, Sugars, and Cellulose-Enriched Pulp

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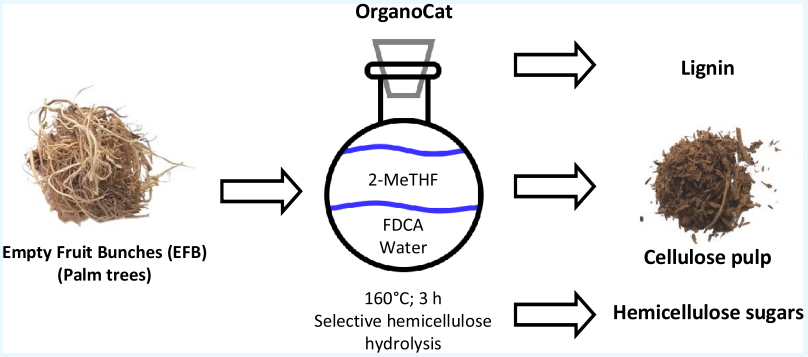
Supporting Information



ABSTRACT: The palm oil industry produces large amounts of empty fruit bunches (EFB) as waste. EFB are very recalcitrant toward further processing, although their valorization could create novel incentives and bio-economic opportunities for the industries involved. Herein, EFB have been successfully subjected to the OrganoCat pretreatment—using 2,5-furandicarboxylic acid as the biogenic catalyst—to fractionate and separate this lignocellulosic material into its main components in a single step. The pretreatment of EFB leads to the deacetylation and depolymerization of noncellulosic polysaccharides and to the partial delignification of the cellulosic fiber. The OrganoCat processing of EFB yielded 45 ± 0.5 wt % cellulose-enriched pulp, 20 ± 0.7 wt % extracted lignin, 3.8 ± 0.2 wt % furfural, and 11 ± 0.6 wt % hydrolyzed sugars. The obtained EFB-pulp showed high accessibility to cellulases, resulting in a glucan conversion of 73 ± 2% after 72 h (15 ± 2% after 1 h) with commercial cellulase cocktail (Accellerase 1500). Overall, the results suggest that the treatment of the EFB material using OrganoCat may create promising paths for the full valorization of EFBs.

1. INTRODUCTION

Palm oil has become an important raw material for the production of food additives, for other nonedible bio-based materials like detergents, lubricants, and so forth, also for biofuels. The biorefining of palm oil, extraction, and upgrading, is thus well-established.[1−3] However, the sustainability and life-cycle assessment of the palm oil industry has been often challenged because of the replacement of rain forests and other high biodiversity areas by large palm tree plantations.[4,5] On the other hand, the palm oil production facilities—plantations and biorefining—represent an important source for employment, (bio)economy, and assets for many (sub)tropical areas. A compromise between development, ecosystem preservation, and bioeconomy thus appears necessary. Recent studies have assessed the actual available land for the sustainable development of palm plantation for oil production by appraising several parameters such as climate, soil quality (or lack of), topography of the area ("ease" of cultivation), and accessibility of the land for logistics (e.g., penalizing "remote areas" because of higher costs).[4] On that basis, sustainability criteria have

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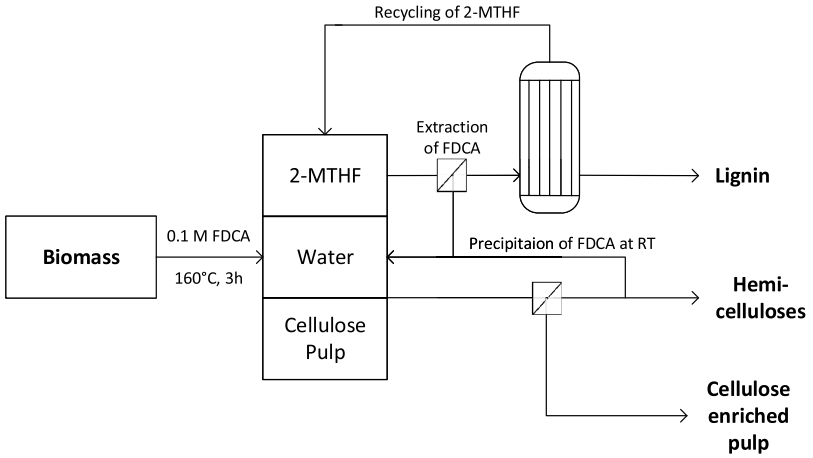

Figure 1. Conceptual approach of the OrganoCat process,[22−24] using water and 2-methyltetrahydrofuran (2-MTHF) as a biphasic solvent system involving FDCA as the biogenic catalyst.[25]

been set, concluding that up to 17% of the total potential arable land (for palm trees) can be sustainably harvested for palm oil production, accounting for 233 MHa worldwide.[4] While several areas would still have "sustainable room" for further extension of the plantations, other regions have already exceeded their potentially available sustainable land for palm trees. Hence, for such regions, no further palm plantations should be established in line with sustainability, bioeconomy, or biorefineries.[4]

By increasing the economic outcomes of the already present palm tree plantations, sustainability might be more properly targeted without compromising the elimination of further biodiversity-rich areas that must be preserved for future generations. An option is to holistically valorize the by-products, for example, lignocellulosic residues, that are generated in a palm oil biorefinery. Thus, once palm kernels have been harvested for palm oil production, the lignocellulosic residues—the so-called empty fruit bunches (EFB)—, may be pretreated to render lignin, hemicellulose, and cellulose, broadening the benefits for the palm tree biorefinery.[1] EFB is usually burned in incinerators of palm oil mills, which generates energy, but also environmental pollution.[6] Multiple approaches to process EFB have been proposed aiming for different valorization strategies, for example, fuels,[7,8] fibers,[9,10] fermentable sugars,[11−13] or even nutraceuticals.[14,15] Moreover, residual lignin may be valorized as well.[16]

Depending on the envisaged product, different pretreatment strategies have been assessed for EFB, such as use of alkali,[7,13,16−18] acid,[13,18,19] hot water or steam,[11,20] ionic liquids,[21] or direct pyrolysis.[10] In this work, the full valorization of EFB is envisaged by successfully applying the OrganoCat technology[22−25] (Figure 1), using the biogenic acid 2,5-furandicarboxylic acid (FDCA) as the recyclable catalyst. FDCA is being evaluated as the potential monomer for bio-based plastic materials and is thus available in large quantities. In the present context, FDCA offers advantages during its recovery and reuse, as it is highly thermostable at the OrganoCat temperature operational range (140−160 °C).[25] Furthermore, the combination of a biogenic pretreatment involving FDCA and 2-methyltetrahydrofuran (MTHF) with the valorization of EFB may lead to strong synergies, leading researchers to pursue activities with environmental and economic benefits.

Albeit the current price of FDCA is still high, Dessbesell et al. have recently described synthetic pathways that may hold potential to decrease FDCA market prices down to 1.8 US$ kg^{-1}, for example, when produced from high-fructose corn syrup.[26] Moreover, the recyclability of FDCA as the catalyst in OrganoCat has been successfully shown by Weidener et al., showcasing the quantitative recovery of the acid.[25] Thus, upon optimization, FDCA may become an economically viable catalyst for pretreatment processes and for other biorefinery-based conversions.

The OrganoCat concept has shown to be effective at high biomass loadings—up to 400 g L^{-1}—, and preliminary economic assessments are promising.[24] A range of plant materials have been successfully pretreated by this process, such as beech wood,[22−25] mate tea, phragmites, rice,[24,27] or biomass from energy plants like *Sida*, *Miscanthus*, *Szarvasi*, and *Silphium*.[28] The obtained lignin and cellulosic fractions are delivered without major degradation because of mild processing conditions. The resulting fractions can be used for further chemical or biotechnological processing to deliver novel materials with high (bio)economic impact. In this respect, the application of OrganoCat to EFB holds potential to enable novel synergies and a higher value generation in palm oil biorefineries. Moreover, the used solvent (2-MTHF) and catalyst (FDCA) are potentially biogenic, and thus could be synthetized in biorefineries directly in-house.

2. RESULTS AND DISCUSSION

Using multiscale analytics including chemical, spectroscopic, and enzymatic methods, the composition of the original EFB lignocellulosic material and the composition of the fractions obtained from OrganoCat were characterized in detail. An overview of different components measured before and after the treatment is depicted in Figure 2.

As depicted in Figure 2 (left column), the composition of EFB raw material accounts for a 31.9 ± 0.3 wt % of cellulose, 18.2 ± 0.5 wt % of lignin, and 14.8 ± 1.2 wt % of hemicelluloses. Starch and ASR were extracted prior to the analysis with ethanol, methanol, and chloroform to remove lipids, pigments and other small molecules, followed by an enzyme cocktail containing amylase and amylopectinase to remove specifically starch (9.2 ± 0.1 wt % in total). In addition, EFB also contained 6.0 ± 0.3 wt % acetyl groups and some nondetermined material, which include residual moisture

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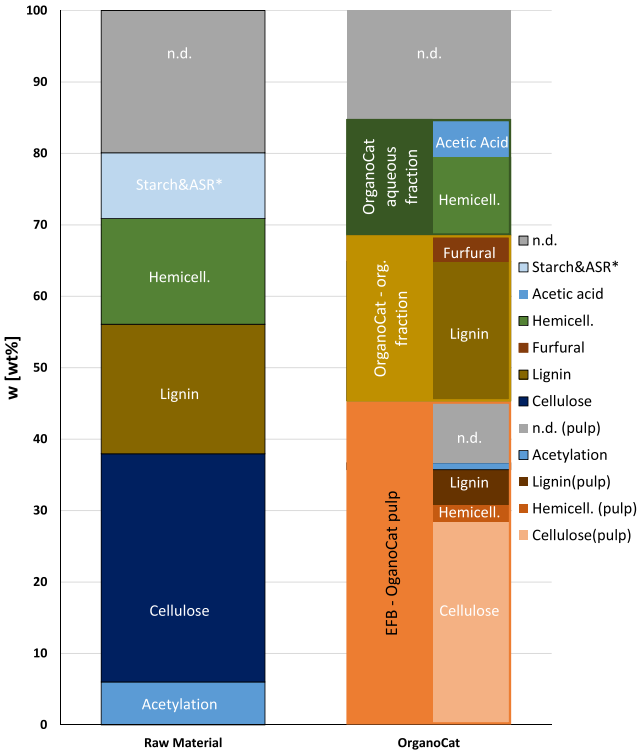

Figure 2. Analysis of EFB samples before and after applying the OrganoCat pretreatment. The material was dried until constant weight before analysis. Left bars show the initial composition of EFB raw material; right bars show the composition of fractions obtained; hydrolyzed hemicelluloses and acetic acid detected in the aqueous fraction are grouped as "OrganoCat aqueous fraction"; products, obtained in the 2-MTHF phase are labeled as "OrganoCat-organic (org.) fraction"; the label "EFB-OrganoCat pulp" shows the composition in cellulose, hemicellulose, and lignin content. N.d.—not determined. ASR—alcohol insoluble residue. * Weight loss due to pretreatment/extraction with EtOH/MeOH/chloroform (removing alcohol soluble residue, ASR) and enzymatic destarching (removing starch).

(6.6−12%) and ashes (1.7−3.4%).[29−31] Gratifyingly, the OrganoCat process enabled the selective depolymerization of most hemicelluloses resulting in different sugar monomers in the aqueous fraction (10.8 ± 0.6 wt %, Figure 2, right column). Moreover, the remaining OrganoCat pulp contained mainly cellulose, 28.5 ± 1.0 wt %, with some remaining lignin (4.9 ± 0.3 wt %) and entrapped hemicellulose (2.3 ± 0.1 wt %). The organic phase contained mainly lignin (19.5 ± 0.7 wt %) with low amounts of furfural (3.8 ± 0.2 wt %) formed during the dehydration of xylose during the pretreatment. Some of the compounds found in the ASR-fraction are expected to be extracted in the OrganoCat organic fraction. Nondetermined material after the OrganoCat process include residual moisture and ashes, derived from the raw material.[29−31]

To calculate the acetic acid release, the degree of *O*-acetylation in EFB raw material and in the pulp was measured as well as free acetic acid in the hydrolysate. The degree of acetylation decreased from 6.0 ± 0.3 wt % in the raw material to 1.1 ± 0.2 wt % in the OrganoCat pulp material. This is in line with the measured acetic acid content in the hydrolysate (5.2 ± 0.1 wt %) and consistent with other works.[11] Regarding xylan, *O*-acetylation changes from 63 ± 2 mol % in the raw material to 26 ± 4 mol % in the OrganoCat pulp. Acetate in the solid material originates from the hemicellulose xylan, where it is esterified at the O-2, O-3, and/or O-2,3 position, or from lignin, which may be γ-acetylated.[32] Here, the position of the *O*-acetyl substituent on xylan was assessed. In the raw material, acetylation in the 2-position, 3-position, and 2,3-position was 15 ± 2, 40 ± 1, and 8 ± 1 mol %, respectively, whereas in the pulp, the numbers were 10 ± 1, 12 ± 1, and 4 ± 2 mol %, respectively. This suggests that *O*-acetates in the 3-position on xylan were deacetylated at a higher rate (*O*-acetylation reduced by 69%) than in the 2-position (*O*-acetylation reduced by 34%) or in the 2,3-position (reduced by 48%). Thus, the OrganoCat pretreatment (with FDCA) leads to a major reduction in polymer *O*-acetylation. Based on the amount of xylan present in the EFB material and the degree of acetylation of xylan, the majority of acetyl groups released during the OrganoCat process are derived from xylan, as also described for angiosperm trees by Lu et al.[32] The reduction in hemicellulose acetylation is known to improve cellulose hydrolysis, enhancing subsequent valorization steps.[29,33]

With respect to the hemicellulose fraction, a detailed analysis of the sugar monomers found in the aqueous phase was conducted (Figure 3). For comparison, the monosaccharide composition present in the raw material and in the pulp are depicted as well.

The most common sugar present in EFB raw material hemicellulose is xylose (Figure 3, blue bars). Consistent with the previous literature[22−25] this is mostly due to the presence of the hemicellulose xylan, which is hydrolyzed by the OrganoCat process, as can be observed in the OrganoCat hydrolysate (Figure 3, orange bars). However, the solid product stream (Figure 3, grey bars)—the cellulose enriched OrganoCat Pulp—contained some residual hemicellulosic

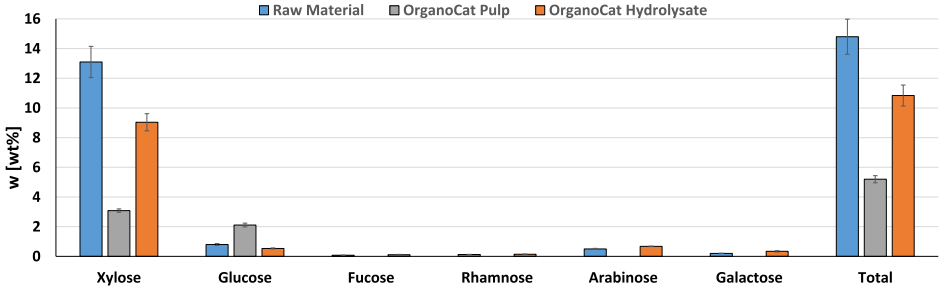

Figure 3. Monosaccharide composition of hemicelluloses in the raw material (blue bars), residual hemicelluloses in the cellulose-enriched OrganoCat pulp (grey bars) and in the aqueous OrganoCat hydrolysate (orange bars) present in wt %. Hemicelluloses of raw material and OrganoCat Pulp were hydrolyzed into their monosaccharides with trifluoroacetic acid.[34] In the OrganoCat hydrolysate, the monosaccharides were detected after removal of the catalyst FDCA.

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sugars. Here, a set of OrganoCat parameters was chosen to avoid degradation of the OrganoCat fractions. A fine-tuning strategy of the OrganoCat, specifically adapted to the envisaged application, might improve the solubilization of hemicelluloses and lignin but might cause higher content in sugar degradation products such as furfural.[25]

Lignin makes up a significant part of EFB raw material. After the OrganoCat pretreatment, the extracted components were isolated from the organic phase upon evaporation of 2-MTHF, leading to a yield of 18.2 ± 0.5 wt % of the initial biomass weight, containing mostly lignin and presumably some pigments and lipids (ASR). Based on the data, approx. 73% of the initial lignin content in the raw material was extracted from the biomass and recovered in the organic phase as a novel raw material from EFB. Figure 4 depicts the ratio of lignin

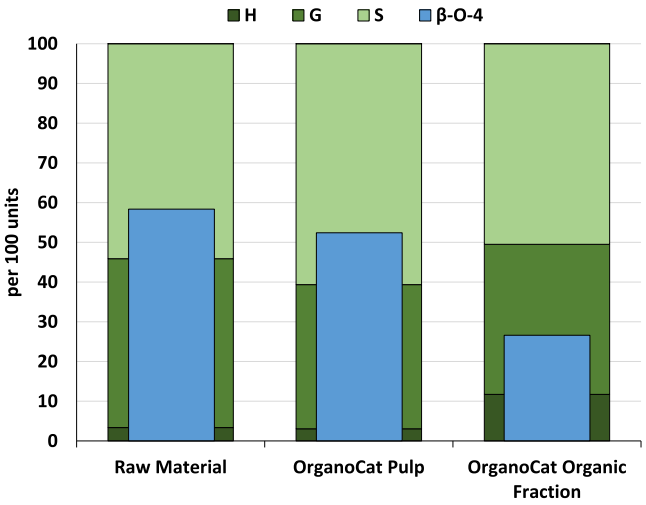

Figure 4. NMR-analysis of lignin fraction in EFB raw material, OrganoCat Pulp and OrganoCat Organic Fraction. Amounts of *p*-hydroxyphenyl (H-), guaiacyl (G-), syringyl (S-) groups are given per 100 units. The blue bars indicate how many H-, G-, and S-groups are connected via *β-O*-4 linkage.

monomers—*p*-hydroxyphenyl group (H), guaiacyl group (G), and syringyl group (S)—and the relative amount of *β-O*-4-linkages. Here, it has been analyzed in detail (Figure 4) to give a thorough characterization of the changes occurring during pretreatment.

The H/G/S ratio of the raw material was 3:43:54 (resulting in a ratio of 1:12.6:16) and the S/G ratio 1.27, which is more comparable to lignin from grasses such as rye or wheat straw[35] than lignin from beech wood or other sources.[36] H-unit overestimation in the whole material, and the lignin fraction discussed below, is probably produced because of the presence of *p*-hydroxybenzoic acid acylating palm lignin at the gamma position. In the raw material, 53 ± 3 mol % of the monomers are connected by a *β-O*-4-linkage, which only changes slightly in the OrganoCat pulp after processing (48 ± 3 mol %). The extracted OrganoCat lignin, however, shows a significant decrease in *β-O*-4-linkages, resulting in 24 ± 1 mol % of the S- G- and H-groups being connected by a *β-O*-4-linkage. In addition, the number of H-groups rises from 3.4 ± 0.3 mol % in the raw material to 11.7 ± 1.0 mol % in the extracted lignin suggesting that extracted lignin reacts further during the OrganoCat treatment. This observed change in H-units might be caused partially by conversion of S- and G-units to H-units and also by the liberation of *p*-hydroxybenzoic acid from acylated *γ*-hydroxyls of lignin side-chains, as described by Lu et al.[32] The changes of lignin during the OrganoCat process have been observed to be time-dependent, and thus, at shorter reaction times (up to 1 h pretreatment), lignins with a higher amount of *β-O*-4-linkages can be obtained, enabling the generation of different materials depending on the final application.[25] A trade-off in lignin yield and (higher) proportion of *β-O*-4-linkages could be thus reached in line with the emerging concepts of "Lignin-first" biorefineries.[37−39]

With respect to the EFB-pulp, visual differences compared to the raw material were observed (Figure 5). During the

Figure 5. Visual changes along the OrganoCat process. (a) Original EFB raw material (b) obtained EFB OrganoCat pulp.

OrganoCat process, lignin is not only extracted into the OrganoCat org. fraction, but some of the remaining lignin also relocates by absorbing to the OrganoCat pulp surface. Thus, the partially delignified material appears to be of a darker color than the untreated raw material as observed also in other biomasses.[22−25] The processiblity of the EFB-cellulose pulp was assessed by determining the glucose yield upon enzymatic digestion. Here, an industrial, commercially available enzyme mix was used (Accellerase 1500, Figure 6).

The OrganoCat process increases the glucose yield after 72 h (orange dots) 8-fold compared to the original raw EFBs (blue dots), indicating a superior depolymerization of the cellulose fibers in the residue. The achieved maximal conversion rate (∼73%) is somewhat lower than values observed in other studies using pretreated materials (up to 80%).[13,17] This may be due to the residual lignin still present in the pulp (Figure 2) or due to the use of cellulase cocktails with different bias toward polysaccharides (e.g., more or less effective enzymes). In any case, higher conversion rates may also be achieved by tailoring OrganoCat process conditions to further enhance delignification[25] as well as by designing new cellulase variants or enzyme cocktail mixtures with higher selectivity to EFB raw material properties.

3. CONCLUSIONS

The successful proof-of-concept of the OrganoCat pretreatment applied to EFB has been shown and was characterized in-depth. The approach enables the production of soluble sugars (mostly xylose), soluble lignin (e.g., in EtOH, 2-MTHF, acetone, DMSO), and a solid cellulose-enriched pulp. Because of significant delignification and deacetylation, the obtained pulp is highly accessible to cellulases for its hydrolysis to glucose as fermentable sugars. Overall, the OrganoCat pretreatment renders three different fractions of the EFB lignocellulosic materials with potential valorization in palm tree biorefineries. Thus, treating the waste material EFB with the OrganoCat process may contribute to open additional commercial options of the palm oil industry.

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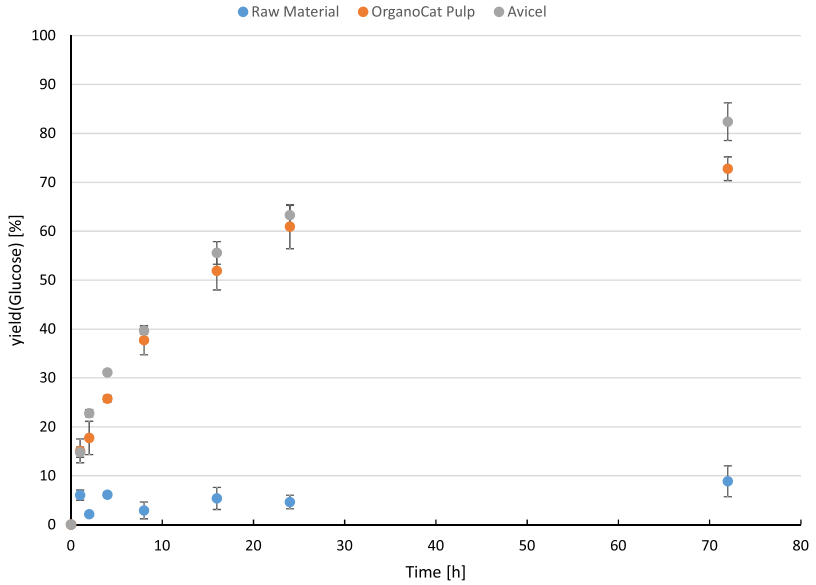

Figure 6. Enzymatic hydrolysis of EFB raw material (blue dots), OrganoCat pulp obtained from EFB after the OrganoCat process (orange dots). For comparative purposes, commercial crystalline cellulose (Avicel, grey dots) was used. Glucose yields were calculated based on the cellulose content of each sample.

4. EXPERIMENTAL PART

4.1. Materials and Methods. All chemicals were purchased at Sigma-Aldrich, Carl Roth, and CGI. They were used without further modification. Empty fruit bunches (EFB) from a palm oil plantation in Sabah (Borneo/Malaysia) were kindly supplied by Autodisplay Biotech GmbH, Düsseldorf. The material was dried in an oven at 50 °C until constant weight (24 h).

4.2. OrganoCat Pretreatment. Reactions were conducted in triplicates. In a 300 mL Parr high pressure reactor, with glass inlay 3000 mg EFB and 468 mg (3 mmol) of FDCA were suspended in 30 mL ultra-pure water and 30 mL 2-MTHF. The reactor was closed and heated to 160 °C for 3 h. After cooling the reactor to room temperature, the reactor was opened, the liquid phases were separated by decantation and the aqueous phase was filtered to isolate the cellulose enriched pulp. The sugar concentrations were determined in the aqueous phase via IC and HPLC. The solid residue was washed with distilled water until neutral pH and dried until constant weight. Lignin was obtained by evaporation of 2-MTHF. The amount of residual FDCA and furfural in the lignin was determined via ^{1}H NMR using mesitylene as the standard.

4.3. Lignocellulose Analysis. Every analysis was conducted in triplicates. EFB raw material was chopped into slices of approx. 1 cm and subsequently grinded to fine powder using a ball mill M 400 (Retsch, Haan, Germany) in a 50 mL metal beaker (30 s^{-1}, 2 min). Alcohol insoluble residues (AIR) were prepared and destarched as described elsewhere.[34] The weight loss during the procedure including removal of starch was calculated and is defined as ASR and starch. The remaining destarched alcohol-insoluble residues (d-AIR) were used for the subsequent analysis of noncellulosic polysaccharide composition, crystalline cellulose content, and acetyl bromide soluble lignin (ABSL) as previously described.[34] The acetate content of d-AIR was determined using an acetic acid kit (catalog #K-ACETRM, Megazyme, Wicklow, Ireland), following an adapted version of the procedure described by Schultink et al.[40] AIR material (2 mg) was mixed with 200 μL water and saponified by addition of 200 μL 1 M NaOH. Samples were incubated at 25 °C with 600 rpm shaking frequency, followed by neutralization with 200 μL 1 M HCl. The material was pelleted by centrifugation for 10 min at 14 000 rpm and the total acetic acid content of the supernatant was determined with the acetic acid kit.

4.4. Analysis of OrganoCat Product Streams. Every analysis was conducted in triplicates. The obtained aqueous fraction was cleared from FDCA via precipitation at 5 °C and subsequently analyzed by high-performance anion-exchange chromatography with pulsed amperometric detection to determine the monosaccharide yield, as described elsewhere.[28]

4.5. Saccharification Test. Every reaction was conducted in triplicates. Hydrolysis of raw material, Avicel, and OrganoCat pulp obtained from the OrganoCat pretreatment was carried out in an Eppendorf ThermoMixer Comfort using 1.5 mL Eppendorf vials. For each reaction, 20 mg of pulp and 10 μL Accellerase 1500 (60 FPU mL^{-1} and 82 CBU mL^{-1}, Genencor, the Netherlands) were dissolved in 1 mL of citrate buffer (pH = 4.5) and shaken at 50 °C for a specific time. Afterward, samples were heated to 90 °C for 10 min. The glucose concentration was determined using a glucose (HK) assay kit obtained from Sigma-Aldrich and a BioTek PowerWave HT UV−vis spectrometer. Glucose yields were calculated based on cellulose content as determined in the lignocellulose compositional analysis.

4.6. NMR Analysis. Measurements of OrganoCat lignin were conducted with a Bruker Ascend 400 (400 MHz) spectrometer. Dried lignin (approx. 100 mg) was dissolved in DMSO-d_6. ^{1}H−^{13}C-Heteronuclear single quantum coherence (HSQC) measurements were performed to identify different linkages present in the lignin. Mesitylene was used as an internal standard to quantify furfural and 5-HMF in the extracted lignin fraction.

Analysis of EFB raw materials and pulp samples (3 replicates each):

For the NMR analysis, EFB raw biomass was destarched. The destarched raw biomass and OrganoCat produced pulp

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materials were milled separately using a Retsch PM 100 CM ball mill, as described previously.[41] The above ball-milled material (25 mg) was dissolved in 0.75 mL of deuterated dimethyl sulfoxide DMSO-d_6 containing 10 μL of 1-ethyl-3-methylimidazolium acetate (EMIM(OAC)) and stirred for 2 h at 60 °C. Two dimensional (2D) $^{13}C-^{1}H$ HSQC nuclear magnetic resonance (NMR) spectra were measured on a 600 MHz Bruker NMR spectrometer using the following parameters. Experimental conditions: pulse program: hsqcetgpsisp.2, NS: 384, interscan delay: 1 s, TD1: 2048 and TD2: 256 data points, temperature: 25 °C. The chemical shifts were referred to the solvent DMSO-d_6 peak (δ_H 2.49 ppm, δ_C 39.5 ppm). The $^{13}C-^{1}H$ cross peaks were identified and quantified as described.[41]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01371.

Material composition obtained before and after applying OrganoCat pretreatment to EFB samples; monosaccharide composition of hemicelluloses in the raw material, in the OrganoCat pulp, and in the aqueous OrganoCat hydrolysate; HSQC-analysis of the OrganoCat pulp; enzymatic hydrolysis of EFB raw material, cellulosic pulp obtained from EFB after the OrganoCat process and Avicel; expansion of HSQC NMR spectrum of EFB pulp and EFB raw material; and expansion of HSQC NMR spectrum of extracted OrganoCat lignin (PDF)

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Notes

The authors declare no competing financial interest.

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