SUNLIBB

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Deliverable 5.7
"Design of the best catalytic approach to generate lignin breakdown products"

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D5.7 SUNLIBB - University of Sheffield
Design of the best catalytic approach to generate lignin breakdown products

This deliverable presents the results of an experimental process that combines TiO_2 and laccase to degrade lignin in single- and dual-step processes.

Results.

GC-MS was used for the identification and quantification of the intermediate compounds in lignin. The main identified compounds were organic acids: acetic acid, malonic acid, succinic acid, butylated hydroxytoluene, vanillin, veratric acid, and palmitic acid. The photodegradation of phenolic compounds by TiO_2 begins with 'OH radical attack on the phenyl rings, producing catechol, resorcinol, and hydroquinone. Subsequently, the phenyl rings in these compounds break up first to give malonic acid and then short-chain organic acids, such as maleic, oxalic, acetic, and formic acids, before finally yielding CO_2. In the reactions observed here, TiO_2/UV yielded some organic acids, such as succinic, palmitic, and acetic acids. This implies that the phenolic compounds in the lignin molecule were decomposed in this reaction. These organic acids were also found by others who used a hydrothermal oxidation process to degrade alkali lignin. However, in their case, the hydro-thermal reaction was carried out at a higher temperature and the alkali lignin that they used had a lower molecular weight than the lignin tested in this work in SUNLIBB (thus potential energy saving here).

In contrast, the compounds that we identified from the degradation by laccase were substantially different from those observed from lignin and photocatalytic lignin degradation. For example, several polysaccharides were detected in the extracted samples sourced from the biocatalytic reaction, as well as from the single- and dual-step processes. The peaks obtained were D,L-arabinose, methyl α-D-glucopyranoside, hexose (D-galactose), hexopyranose, D-glucose, and glucopyranose. These monosaccharides could be carbohydrate derivatives from the laccase molecule. The carbohydrate moiety of the majority of laccases consists of mannose, *N*-acetylglucoamine, and galactose at about 10-20% for fungal laccases. In comparison of the concentrations of intermediate compounds in lignin with laccase (standard), it was noted that the amount of palmitic acids significantly decreased for the biocatalytic and dual-step process but were the same concentrations as found in the single-step process. Furthermore, the amount of stearic acid that considerably decreased in the single- and dual-step processes was unchanged in the biocatalytic process. These compounds were also found in Kraft ~~lignin degradation mediated by *Bacillus* sp.~~ (accession number AY 952465), as reported elsewhere. The occurrence of these compounds indicates that lignin was degraded.

Figure 1 shows the amount of identified intermediate compounds from lignin in each category from experiments conducted in the absence of H_2O_2. The results show that there was a similar amount of fatty acid in all treated lignin samples. It was ca. 15%, while it was only ca. 10% in the lignin standard samples. The highest amount of organic acids was obtained in the photoreaction process at ca. 20%. We found industrially useful organic acids, including succinic, acetic, and lactic acids.

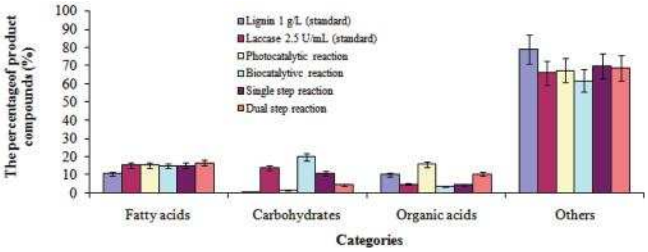

Figure 1. Amount of intermediate compounds from lignin by category from experiments conducted in the absence of H_2O_2.

Figure 2 depicts the amount of identified product compounds derived from lignin in each category from experiments conducted in the presence of H_2O_2. The maximum amount of fatty acids and carbohydrates was found in the dual-step reaction process, at ca. 25 and 20%, respectively, while the lowest amount of fatty acids and carbohydrates was obtained in the bioreaction at 10% and was negligible for the photoreaction process, respectively. The photoreaction process, in contrast, produces the maximum amount of organic acids at 23%. The majority of the organic acids was malonic, succinic, acetic, and lactic acids, which can be very useful for the chemical industry and as a feedstock for biofuel processes.

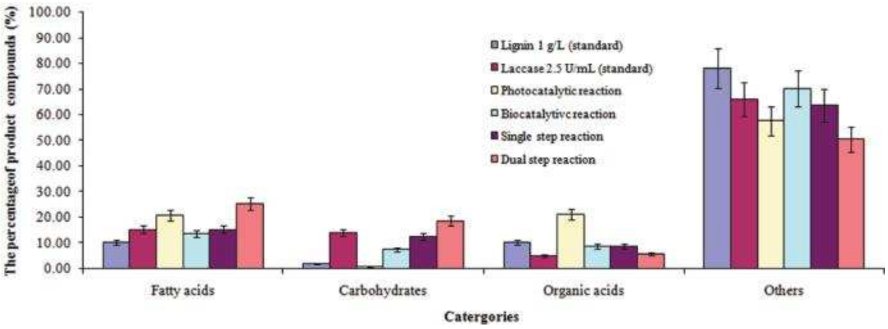

Figure 2. Amount of intermediate compounds from lignin in each category from experiments conducted in the presence of H_2O_2.

Conclusions

The results satisfy the hypothesis that there would be increased lignin degradation using a combination of TiO_2 and laccase processes, rather than using only one process. The results also show that this combination of photocatalytic and biocatalytic reactions is best performed as a two-stage process, with TiO_2 first and laccase second, because this configuration was much more successful than a single-step process. The investigation also shows that laccase requires a supply of oxygen to produce high degradation success rates. Primarily for practical reasons, H_2O_2 was chosen. In addition to these main conclusions, GC−MS analyses identified and quantified the lignin breakdown products. Of these data, perhaps the most interesting was that TiO_2 used in the presence of H_2O_2 yielded a significant quantity of succinic and malonic acids. These byproducts of the main reaction have the potential to be used to produce a variety of useful chemicals. More details are available in the published paper (Kamwilaisak & Wright, 2012) and supplementary materials.

References

Kamwilaisak, K. & Wright, P.C. (2012) *Investigating laccase and titanium dioxide for lignin degradation.* Energy Fuels 26:2400-2406