Reductive depolymerization of lignin into valuable products

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Summary

The utilization of lignin in industries is primarily restricted to the role as waste material for energy recovery, despite the existence of a great number of potential applications. A possible solution could be the extensive introduction of high-quality lignin-based products exceeding the properties of the petroleum-based one. Another option could be the development of new processes to directly produce high-added value products from lignin, limiting the exploitation of fossil resources.

For these reasons, the aim of this PhD thesis was to overcome the principal issues concerning lignin valorisation.

The state-of-the-art strategies involve catalytic depolymerization to achieve an aromatic rich bio-oil through different processes, such as acid/base hydrolysis, pyrolysis, hydrotreating (hydrodeoxygenation, hydrogenation, hydrogenolysis), oxidation and gasification. Among them, reductive processes have proven to increase bio-oil yield in milder conditions: in fact, H_2 and H-donor can quench reactive intermediates, reducing side reactions that might result in char formation.

Therefore, in this thesis emphasis was placed on reductive depolymerization of Kraft lignin with the intention of focusing on more sustainable catalytic processes. Indeed, along with harsh reaction conditions, highly expensive noble metals are typically required since they exhibit higher efficiency in depolymerization strategies. However, lignin from Kraft process (50 Mt/year produced worldwide) contains 1-3% of sulphur, therefore the exploit of robust catalysts is required to avoid poisoning.

Consequently, attention was focused to exploit new strategies to minimize the cost of the catalyst and the overall process. Principal achievements are listed below:

I. Molybdenum and copper-based catalyst were chosen as non-noble catalysts to depolymerise Kraft lignin at mild condition (T < 250 °C). Mo was selected as the active phase due to its robustness against sulphur poisoning, while Cu is a cheap and effective catalyst employed in several biomass valorisation processes. Mo and Cu were supported on acid Al_2O_3 to further enhance the overall activity in the process.

Catalysts proved to be effective in the reductive depolymerization, in particular when oxidation state of metals was 0, while oxidized forms of metals proved to be less active in achieve high bio-oil yield. Optimizations of the process (timing, catalyst loading, solvent selection) were performed aiming to minimize solid by-products (char, and oligomers) and increase bio-oil yield (85 wt.% achieved with Cu/Al_2O_3 and 88 wt.% when Mo/Al_2O_3 was used).
Moreover, calorific value and oxygen/carbon ratio were evaluated and compared to lignin, achieving a reduced O/C ratio and a doubled heating value compared to the Kraft lignin.

II. Following the result obtained with Mo and Cu catalyst, commercial zeolite Y was selected as a cheaper catalyst and tested in lignin depolymerization, aiming to avoid the issues related to metals (poisoning, sintering, leaching). Zeolite's high acidity resulted in bio-oil production of 85 wt. %, while the combination of H_2 atmosphere and a water/ethanol solvent mixture reduced char formation to only 3 wt.%. The calorific value of the bio-oil was also evaluated (27 MJ/kg). Therefore, Cu/Zeolite Y catalyst was synthesized to further upgrade bio-oil obtained from zeolite Y, resulting in a new aromatic rich oil with a lower O/C ratio and a higher calorific value (43 MJ/kg), similar to the diesel fuel (47 MJ/kg).

III. As stated before, principal challenge concerning lignin valorisation is catalyst recovery, as a successful separation from solid by-products may allow it to be reused several times. In this regard, a magnetic core-shell catalyst ($Pd/Al_2O_3@Fe_3O_4$) was synthesized and tested in the microwave-assisted reductive depolymerization of 4-benzyloxyphenol (4-BOP) as a lignin model compound. Indeed, the last decade has witnessed MWs as an efficient alternative approach in biomass process intensification. In fact, this technology generates high-energy microenvironments in the reaction system, enhancing mass transfer and promoting a more efficient conversion, minimizing the production of undesirable by-products. The core-shell structure was confirmed by TEM, TGA and XPS analysis. $Pd/Al_2O_3@Fe_3O_4$, thanks to the easily recovering by an external magnet, together with the excellent conversion (97%) of 4-benzyloxyphenol and selectivity toward toluene (60%) has proven to be an ideal catalyst for the reductive depolymerization of lignin into high-added value products. Furthermore, it was also reused four times with no loss of catalytic activity.

IV. Finally, to adhere to the principles of sustainability, Pd/RHA catalyst was synthesized aiming to combine the valorisation of rice husk biomass waste, rich in SiO_2, with the valorisation of lignin waste. Reductive depolymerization of 4-BOP was performed in a MW reactor using formic acid as the reducing agent, aiming to avoid the risks associated to the use of high H_2 pressure. Different solvents and reaction conditions were performed, and total conversion, together with high selectivity toward toluene and hydroquinone, was achieved.