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## Hydrothermal liquefaction of by-products from the second-generation bioethanol industry

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Unlike first-generation bioethanol, second-generation bioethanol (2GB) does not compete with edible biomass and it can be produced from residual biomass from other industries. In this sense, pinewood is a lignocellulosic material that can be used to produce 2GB.

To produce 2GB from pinewood, only the sugar fraction is used, leaving a phase rich in lignin. This phase is forming a slurry with high water content, so the use of valorization methods that do not involve drying the material is recommended. In this work, hydrothermal liquefaction (HTL) is used to valorize this lignin-rich slurry. HTL consists of subjecting the biomass to moderate temperatures (250-400 °C) and high pressures (5-20 MPa) [1] in a water environment and/or organic solvents, to be transformed into a hydrochar (carbonaceous solid), an aqueous phase rich in organic compounds, a gaseous phase, and a biocrude (oily liquid), the latter being the main product.

The objective is to evaluate the effect of the HTL process conditions on the biocrude yield and its low heating value (LHV). The process parameters studied were temperature (250-350 °C), percentage of ethanol (0-100 %), and liquid phase:dry slurry ratio (L:S; 3:1-9:1) applying a central compound experimental design.

The materials and methods used in this work were a Parr 4575 reactor of 0.5 I capacity which was heated employing a tubular furnace. Once the reaction temperature was reached, it was maintained for 90 min, then the reactor was cooled. The tests were carried out in an inert atmosphere and the test pressure was self-generated by the water vapour pressure and the gases produced.

Once cold, the liquid and solid products were mechanically recovered and subsequently, the interior of the reactor was washed with acetone. The hydrochar was obtained by filtration and washed with acetone until a colourless solution was obtained. The biocrude was recovered as heavy and light biocrude. The light biocrude was obtained by vacuum evaporation of the recovered liquid phase, while the heavy biocrude was obtained by vacuum evaporation of the washing acetone.

As the main results, it was determined that the L:S ratio and the ethanol percentage are relevant parameters in the biocrude yield, while the range of temperatures studied had a lower effect on it. In the case of light biocrude, the yields obtained were 3-25.7% depending on the reaction conditions with LHV of 16.1-26.1 MJ kg<sup>-1</sup>. The yield of this biocrude improved at 9:1 L:S ratios and 100% ethanol in the medium. For the heavy biocrude, the yield varied between 2.4-20.8% with a LHV of 23.4-33.3 MJ kg<sup>-1</sup>; its yield increased when working with the ethanol-water mixture in the medium and a 9:1 L:S ratio.

In conclusion, it was possible to valorize the slurry rich in lignin through HTL obtaining a maximum yield of total biocrude of 41.3% at 350 °C, 50% of ethanol, and L:S 9:1. In addition, it was possible to identify the production of some compounds of industrial interest such as phenols and benzaldehydes.

## References

1. Leng, L., et. al. (2020). Nitrogen in bio-oil produced from hydrothermal liquefaction of biomass: A review. Chemical Engineering Journal, 401, 126030.