**Hydrothermal Liquefaction of Lignocellulosic Ethanol Lignin-Rich Co-Product.**

Edoardo Miliotti1\*, Stefano Dell’Orco1,2, Giulia Lotti1, Alberto Bini1, Andrea Maria Rizzo1, Luca Rosi1,3, David Chiaramonti1,2

*1 RE-CORD, Viale Kennedy 182, 50038, Scarperia e San Piero, Florence, Italy; 2 Department of Industrial Engineering, University of Florence, Viale Morgagni 40, 50135, Florence, Italy; 3 Chemistry Department “Ugo Schiff”, University of Florence, Via della Lastruccia, 3-13 50019 Sesto Fiorentino, Florence, Italy*

*\*Corresponding author: edoardo.miliotti@re-cord.org*

**Highlights**

* Temperature is the most significant factor for light and heavy biocrude yield.
* B/W is not a significant factor for light and heavy biocrude yield.
* Good biocrude and low solids yields were achieved without catalysts or capping agents.

**1. Introduction**

Residual/dedicated lignocellulosic biomass will be the future main feedstock for sustainable biofuel production, now dominated by lipids, which are criticized, since they rely on food and mainly on imported palm oil. The major effort in the EU focuses on developing new industrial energy chains to produce truly sustainable biofuels/bioenergy from lignocellulosic material. The lignocellulosic ethanol route has achieved full industrial scale worldwide and, consequently, a very wet lignin-rich co-product is made available at the production site in considerable amount and affordable costs [1], whose current use is combustion for heat and power generation. However, being lignin the most abundant renewable source of aromatics in nature, its valorization represents a very attractive opportunity for green chemistry. Several studies addressed the economic valorization of lignin-rich streams (LRS) from lignocellulosic ethanol production, highlighting the importance of co-product valorization to achieve commercial competitiveness [2,3]. Hydrothermal liquefaction (HTL) is a thermochemical process, which can convert biomass into a biocrude by using hot compressed water [4,5]. It is a wet process, which does not require feedstock drying, as it is generally required by other technologies like gasiﬁcation and pyrolysis. As such, HTL is an attractive approach for the conversion of wet biomass into a liquid intermediate for chemicals and biofuels. HTL generates biocrude as main fraction, along with gaseous products, solids, and an aqueous-phase byproduct. Different behavior in pyrolysis of lignin from different origin was demonstrated in an international round-robin [6] and to date, most of the known HTL studies addressed lignin from pulp and paper or high-purity model compounds [7,8], both of them structurally different from lignocellulosic ethanol LRS, which still needs further investigation. The present work aims at partially filling this gap by preliminary assessing the viability of converting this material.

**2. Methods**

The LRS was characterized and then processed in a custom-made batch test bench. Two solvent extraction methods were investigated and compared for the extraction of a light and a heavy biocrude fraction. A full factorial design of experiment (5 % significance level) was performed, investigating the influence of process parameters on product yields, biocrude elemental composition, molecular weight and carbon balance. Investigated temperature, time and biomass-to-water mass ratio (B/W) were, respectively, 300, 350 and 370 °C, 5 and 10 min, 10 and 20 % w/w. The biocrudes were analyzed in terms of CHN, ash content, GPC and FT-IR.

**3. Results and discussion**

The feedstock, as received, contained a high amount of moisture (~70 % w/w on wet basis) and nearly 54 % w/w of lignin on dry basis. The total biocrude yields ranged from 39.8 to 65.7 % w/w. Temperature was the main parameter determining a different distribution between the light and heavy fractions: at 300 °C the higher amount of heavy biocrude was recovered, while at 350 and 370 °C the yield of the light fraction increased, reaching 41.7 % w/w at 370 °C. Instead, B/W ratio did not cause a significant effect on light and heavy biocrude yields. A relatively low amount of solid residue was observed (from 11.4 to 19.5 % w/w), even without catalysts or capping agents. Feedstock carbon content was mainly recovered in the biocrude (up to 77.6 % w/w): the distribution between the light and heavy fractions followed the same trend as the yields. The typical aromatic structure of the LRS was also observed in the biocrudes, indicating that mainly hydrolysis depolymerization occurred. The weight-average molecular weight of the total biocrude was strictly related to process temperature, decreasing from 1146 at 300 °C to 565 g mol-1 at 370 °C.

**4. Conclusions**

LRS was converted without catalysts or capping agents in light and heavy biocrude with a relatively low amount of solid residue. Concerning the biocrudes yields, temperature was the most significant parameter. The elemental analysis suggests that the light biocrude was mainly produced by decarboxylation rather than dehydration, which was more evident for heavy biocrude and solids. The aromatic structure typical of lignin was preserved in the biocrudes, indicating the feedstock was mainly subjected to hydrolysis depolymerization. The decreasing values of the molecular weight with temperature indicated that a consistent fractionation occurred.

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