High Yield of Biocrude and High Energy Recovery from Noncatalytic Hydrothermal Liquefaction of Black Liquor.

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INTRODUCTION

- Hydrothermal liquefaction (HTL) is an efficient thermochemical conversion technology using Sub- and Supercritical water (200–400°C, 10–25 MPa) to convert wet biowaste into high-quality bio-crude with a High yield, up to 55%.
- The costly and time-consuming drying process is not required for HTL.
- The feedstock of this study, Black liquor is a major by-product of the kraft pulping process containing lignin, hemicellulose, sodium hydroxide (NaOH), and sodium sulfide (Na_2S).

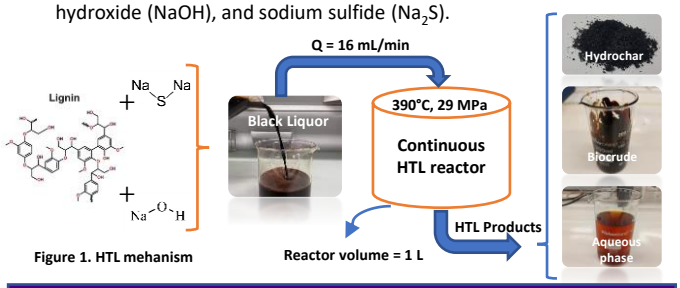

Figure 1. HTL mechanism

OBJECTIVE OF THE STUDY

- Investigation of the biocrude yield and energy recovery from the continuous HTL of black liquor.
- Analyzing the HTL products including biocrude, aqueous phase, and hydrochar based on the following table.

- **HHV = Higher Heating Value**

MATERIALS AND METHODS

- **Material:** Black liquor with 4 wt.% Lignin concentration.
- **Operating conditions:** The HTL experiment was conducted at SINTEF, Trondheim, Norway using a 1-liter continuous flow reactor to convert BL to biocrude with the following operational conditions;
  T = 390 °C, P = 28~30 MPa, Q = 16 mL/min, residence time = ~62.5 min.

RESULT AND DISCUSSION

✓ **Elemental analysis of isolated lignin from black liquor (PL), Hydrochar, and Biocrude:**

Table 1. Elemental Analysis

Sample	N	C	H	S	O	Ash	HHV
PL	0.47	53.64	5.8	4.85	35.4	0.08	29.556
Hydrochar	0.25	48.4	3.208	0.972	21.44	25.72	23.14
Biocrude	0.412	80.247	7.135	1.127	8.88	2.3	37.52

❖ The oxygen content and ash content of the produced biocrude are quite low it is while the HHV of the biocrude is high, which indicates the high quality of the produced biocrude from Black liquor.

Higher heating values (HHV) were calculated according to Boie's formula:
HHV = 0.3516 C +1.16225 H + 0.1109 O + 0.0628 N

✓ **Total Organic Carbon (TOC) analysis (Aqueous phase):**

Table 2. TOC Analysis

Sample	Total Organic Carbon (TOC)	Total carbon (TC)	Inorganic Carbon (IC)
Aqueous phase	24600	32820	8214

❖ The aqueous phase has roughly high TOC content which means a significant amount of chemicals were produced and transferred to the aqueous phase during the HTL process.

RESULT AND DISCUSSION

✓ **TGA analysis (Bio-crude & Hydrochar):**

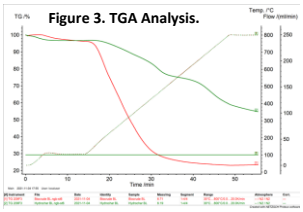

Figure 3. TGA Analysis.

Table 3. TGA Analysis

Sample	Moisture	VM	FC
Biocrude	5	71	24
Hydrochar	4	35	61

- **VM = Volatile Matter**
- **FC = Fixed Carbon**

50 °C to 800 °C under N_2 atmosphere for 90 min (ramp of 10 K/min).

✓ **GC-MS analysis (Bio-crude):**

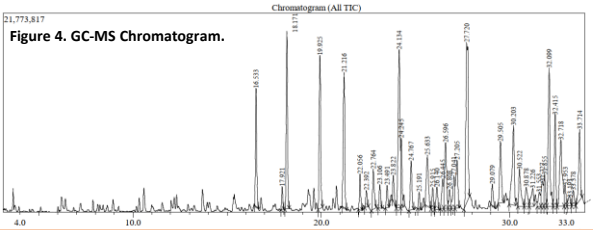

Figure 4. GC-MS Chromatogram.

48.2% of the volatiles are related to phenols, ketones are the second most abundant compound with 15.38%.

✓ **The Biocrude Yield and Energy Recovery: (4)**

$$\text{Biocrude Yield} = \frac{\text{Mass}_{\text{biocrude}}}{\text{Mass}_{\text{Precipitated Lignin in the BL}}} \times 100\%$$

$$\text{Energy Recovery} = \frac{\text{HHV}_{\text{biocrude}} \times \text{Mass}_{\text{biocrude}}}{\text{HHV}_{\text{PL}} \times \text{Mass}_{\text{PL}}} \times 100\%$$

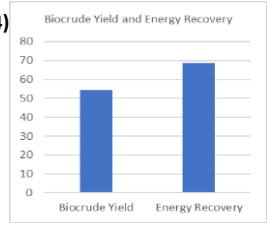

Figure 5. Biocrude Yield & Energy Recovery.

CONCLUSION

- ❖ Biocrude has a rather low oxygen content and high HHV.
- ❖ Phenols and ketones are the most abundant compounds in the biocrude.
- ❖ Volatile matter content of Biocrude and hydrochar were 71 and 35% respectively and the Fixed carbon contents were 24 and 61% respectively.
- ❖ The TOC content of the aqueous phase was high and further analysis is required to investigate the organic and inorganic compounds.
- ❖ Biocrude yield and energy recovery were 54.25% and 68.46%, respectively.

REFRENCES

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FUNDING AND CONTACT

This project has received funding from the European Union Grant Number 884111.

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