Comparison of hydrothermal liquefaction and pyrolysis of cellulosic ethanol lignin: bio-oils characterization and energy analysis

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Abstract

There are social problems for the production of biofuel from first-generation feedstock related to the competition with agricultural land, fresh water uses and food vs. fuel issues. For these reasons, in Renewable Energy Directive to 2030 (RED II) the contribution of biofuel from "high indirect land-use change" was limited to 2019 consumption. The second-generation biofuels produced from lignocellulosic feedstock, such as forestry and agricultural residue, or from waste and industrial co-products are exempted from this limitation. The aim of the work is a comparison between two different processes for the valorization of lignin-rich stream from 2nd generation ethanol taking into account the chemical and physical characteristics of the two bio-oils and the energy balance of the processes. Hydrothermal liquefaction (HTL) and intermediate pyrolysis processes were performed in two continuous small-scale pilot plant (inlet flowrate 1 – 2 kg/h). The HTL process was performed in a plug flow reactor, while the intermediate pyrolysis in a screw reactor.

Material and methods

Feedstock

- Lignin-rich stream from 2nd generation ethanol plant
- 69.7 wt.% w.b. moisture content

Test conditions

Operating conditions	HTL	Intermediate pyrolysis
Pretreatment	Drying and milling	Drying and milling
Inlet mass flow	1 – 2 kg/h	1 – 2 kg/h
Temperature	350°C	450°C
Residence time	10 min	5 min
Biomass/water ratio	5 wt.%	-
Catalyst concentration	0.05 g/L (NaOH)	-

Bio-oil characterization

- Elemental analysis, GPC, KF, ICP

Aqueous phase characterization

- HPLC, TOC and pH

Bio-char characterization

- Proximate and ultimate analysis

Energy balance

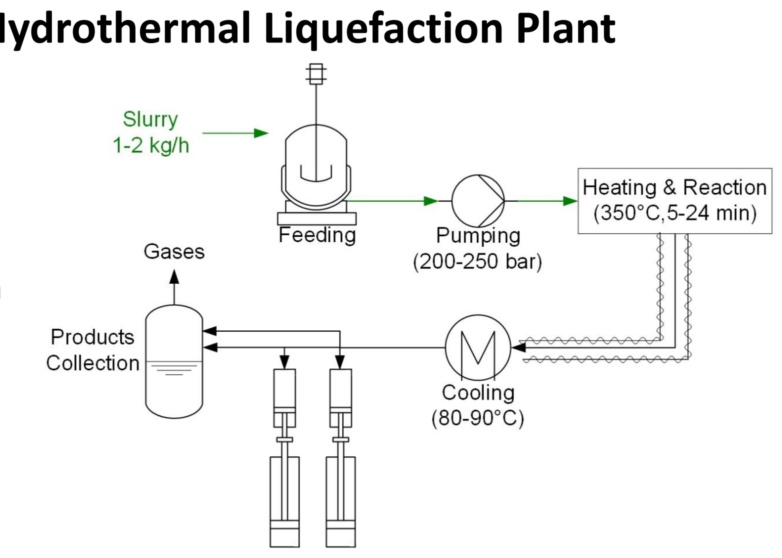
- Biomass-to-water ratio in HTL = 20%
- Heat for pyrolysis = 1.2 MJ/kg dry
- Thermal losses were neglected

- $\eta_{th} = \frac{W_{bio-oil}}{W_{th\ in}} = \frac{m_{bio-oil} \cdot HHV_{bio-oil}}{W_{th\ in}}$
- $\eta_{th} = \frac{W_{bio-oil}}{W_{ch}} = \frac{m_{bio-oil} \cdot HHV_{bio-oil}}{m_{LRS} \cdot HHV_{LRS}}$
- $\eta_{plant} = \frac{W_{bio-oil}}{W_{LRS} + W_{th\ in}} = \frac{m_{bio-oil} \cdot HHV_{bio-oil}}{m_{LRS} \cdot HHV_{LRS} + W_{th\ in}}$

Experimental Setup

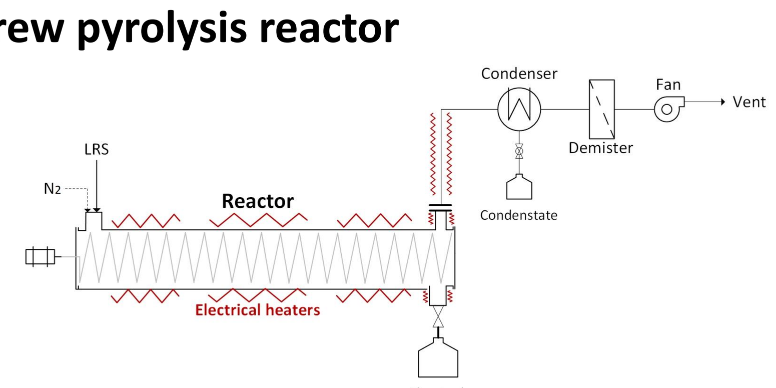
Continuous Hydrothermal Liquefaction Plant

- Electrical heating
- Plug flow reactor
- Custom-made double pistons depressurization system

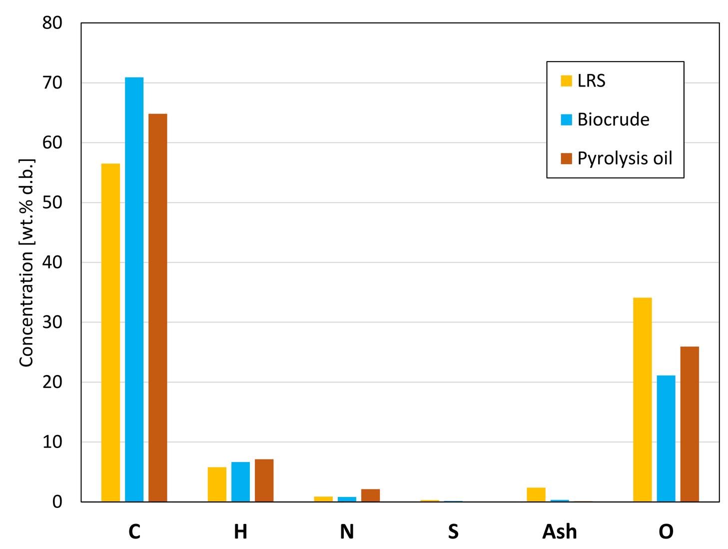


Screw pyrolysis reactor

- Electrical heating
- Screw reactor
- Pyrogas condensation system



Bio-oil characterization

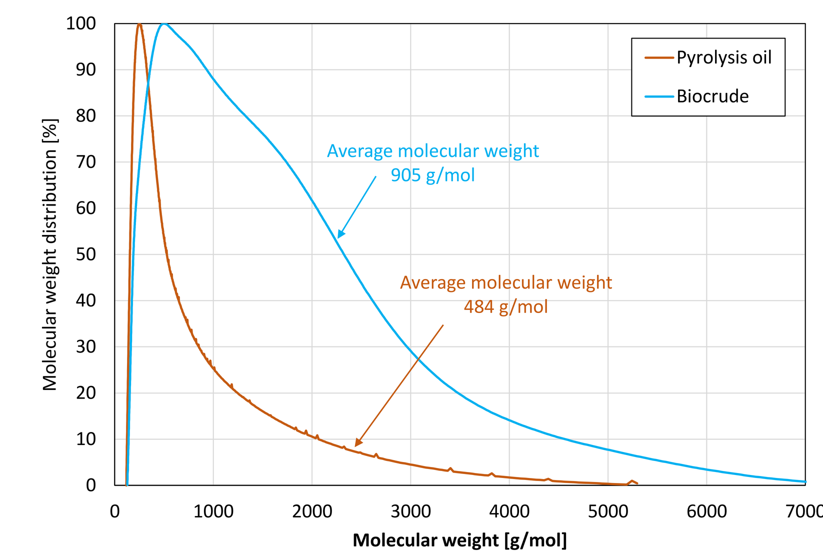


	C	H	N	S	Ash	O	Water Content	HHV
	[wt%db]	[wt%db]	[wt%db]	[wt%db]	[wt%db]	[wt%db]	[wt%wb]	[MJ/kg db]
HTL Oil	70.91	6.67	0.82	0.16	0.33	21.11	11.6	30.4
Inter. Pyrolysis Oil	64.83	7.11	2.12	0.00	0.12	25.94	2.0	28.4

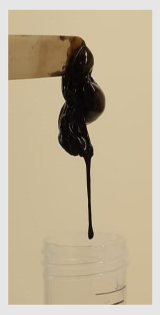
Values are reported on a dry basis; * by difference, *a* evaluated with: HHV = 0.3491·C + 1.1783·H - 0.1034·O - 0.0211·Ash + 0.1005·S - 0.0151·N

Element [mg/kg]	Al	Ca	Fe	K	Mg	Na	P	Si	Zn
Lignin-rich stream	267	2710	345	772	195	5040	370	259	13
HTL Oil	197	1666	312	263	446	840	1138	138	29
Inter. Pyrolysis Oil	13	64	32	144	21	45	u.d.l.	97	9

u.d.l.= below detection limit

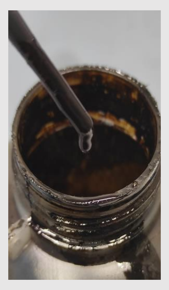


HTL bio-oil



- Higher molecular weight
- Polydispersity index (PDI) = 1.89
- Almost solid at ambient temperature
- Higher carbon content and HHV
- Lower water and oxygen content

Inter. Pyrolysis bio-oil



- Lower molecular weight
- Polydispersity index (PDI) = 1.50
- Lower inorganics concentration
- Higher hydrogen content

Co-products

Char

	C	H	N	Ash	O	Fixed carbon	O/C	H/C	HHV
	[wt%db]	[wt%db]	[wt%db]	[wt%db]	[wt%db]	[wt%db]	-	-	[MJ kg-1db]
HTL Hydrochar	64.4	5.01	1.46	7.37	21.5	93.30	0.25	0.93	26.0
Pyrolysis Biochar	81.0	3.50	1.60	8.60	5.30	70.40	0.05	0.52	31.6

Biochar:
- Higher yield
- Higher carbon content and HHV
- Lower oxygen content

Hydrochar:
- Higher oxygen and fixed carbon content
- Higher H/C ratio

Aqueous phase (AP)

Concentration [g/l]	HTL AP	Inter. Pyrolysis AP
Acetic acid	0.89	18.4
Propionic acid	0.51	1.2
Lactic acid	1.96	0.0
Glycerol	0.00	8.2
Glutaric acid	0.08	1.6
Glycolic acid	2.05	0.0
Catechol	0.20	4.4
Benzoic acid	0.00	0.4
3-methyl-1,2-cyclopentanedione	0.00	0.6
Phenol	0.46	4.3
Guaiacol	0.27	0.3
Syringol	0.41	0.3
Methanol	3.40	45.6
Acetic acid	0.89	18.4
TOC	7.71	24.8
pH [-]	5.2	4.9

Higher concentration of organics in intermediate pyrolysis AP:
- Reaction water

Similar detected compounds:
- Lactic and glycolic acid not converted in HTL process due to lower temperature

Higher methanol production in inter. pyrolysis:
- Demethylation reaction
- Demethoxylation reaction

Biochar Management

Combustion → Provide the heat for drying and pyrolysis

Agricultural application → Soil improver

HTL AP Management

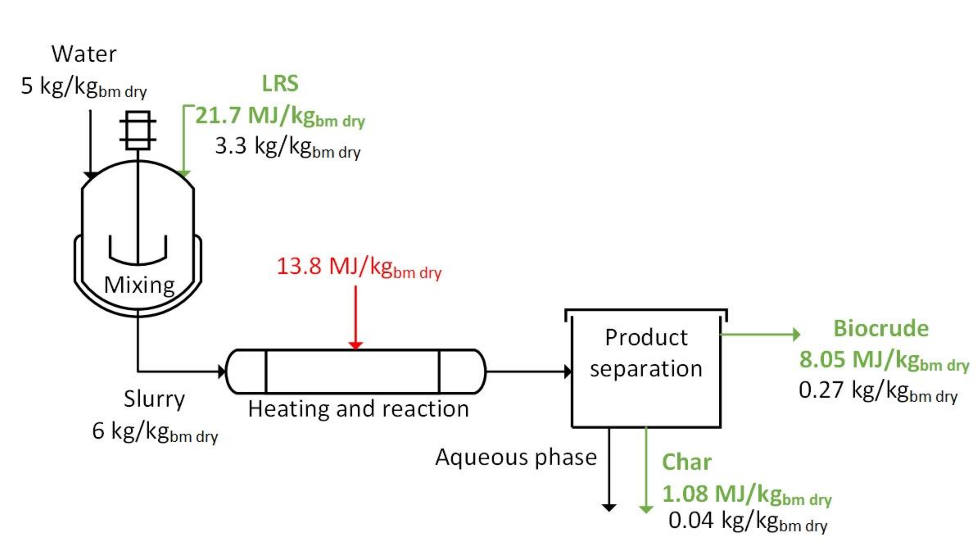
Partial recycle in inlet slurry → Increase process efficiency

Aqueous phase reforming (APR) → H_2 production

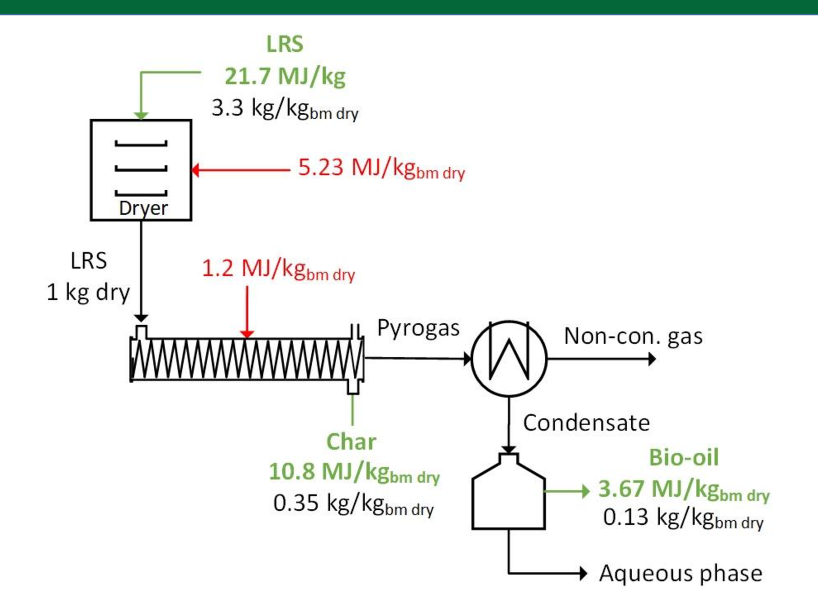
Supercritical water gasification (SWG) → Syngas

Anaerobic digestion → Biogas

Energy balance



	HTL	Int. Pyrolysis
LRS chemical energy [MJ/kg$_{bm\ dry}$]	21.7	21.7
Bio-oil chemical energy [MJ/kg$_{bm\ dry}$]	8.05	3.67
Char chemical energy [MJ/kg$_{bm\ dry}$]	1.08	10.8
η_{th} [-]	58%	52%
η_{ch} [-]	37%	16%
η_{plant} [-]	23%	12%



Conclusions

- The results of proximate and ultimate analysis showed that HTL bio-oil had higher carbon content and HHV, lower oxygen and water content
- The molecular weight of HTL bio-oil is considerably higher than intermediate pyrolysis oil and consequently it is almost solid at ambient temperature
- The biochar produced in intermediate pyrolysis process could be used to provide the required heat for the reaction or as soil improver
- The HTL AP management is one of the main problems for industrial scale-up of the process and the main investigated solution are APR, SWG and anaerobic digestion
- Despite the high energy consumption for biomass drying, the total specific thermal energy required for intermediate pyrolysis process is lower than HTL process
- Due to the higher bio-oil yield and HHV, the HTL process exhibited higher thermal, chemical and plant efficiency

Contact & Information

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