Hydrothermal Processing of Waste into Value

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Background

Hydrothermal liquefaction (HTL) is a promising method for production of valuable products (drop-in biofuels and chemical building blocks) by conversion of mixed biomass feedstocks, e.g. lignocellulosic waste, in near- and supercritical water (T=374 °C, p=22.1 MPa) [1].

Fallopia japonica, also known as japanese knotweed, is a resistant and invasive species of lignocellulosic biomass. It can grow over a wide range of soil types, pH, salinity, and temperatures, thus making it an ideal feed in a sustainable HTL process.

Highlights

HTL of Fallopia japonica at T=280 °C, 300 °C, and 320 °C, p=18 MPa, 20 MPa, and 22 MPa, in the presence of a catalyst (K2CO3) and co-solvents (tetralin and acetone).

1. *Innovative reactor system*
2. *Co-solvents*
3. *Solid-phase microextraction*
4. *Multivariate data analysis*

AIM : REACTION MECHANISMS

Analysis

Complex HTL products

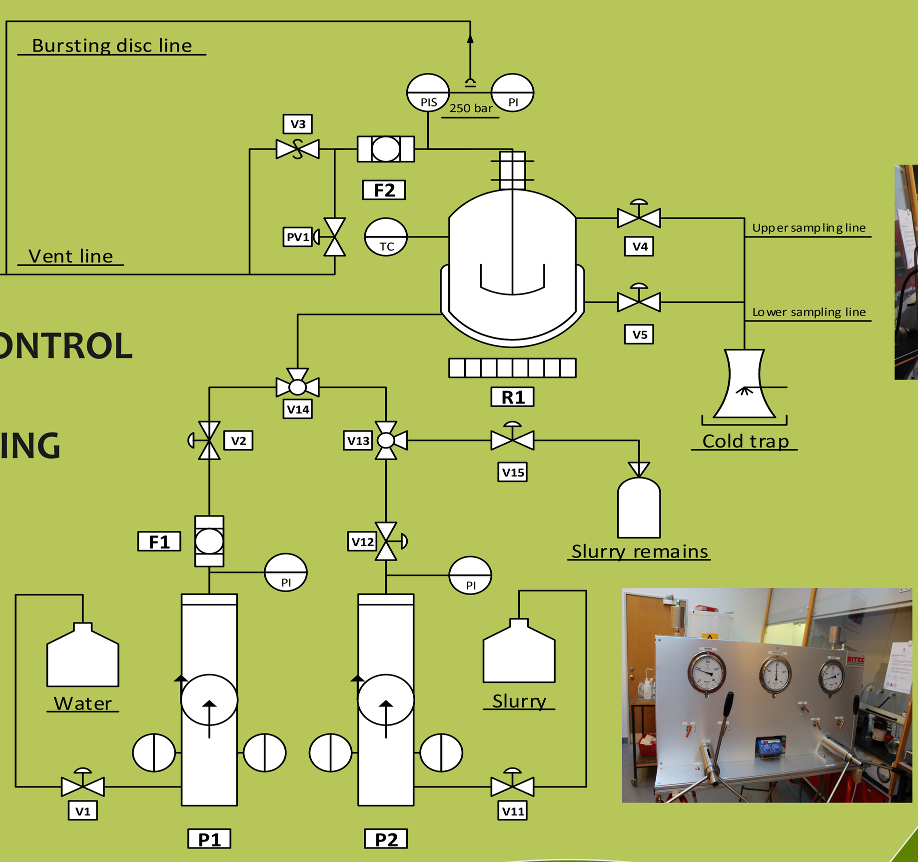
HTL products were separated by centrifugation into water soluble (WSO) and water insoluble (WIO) fractions and characterized by yields (dry biomass basis), total organic carbon (TOC) and CHNS analysis (carbon balance), solid-phase microextraction (SPME) combined with gas chromatography mass spectroscopy (GCMS). The results were compared by univariate and multivariate statistics.

SPME instead of LLE

SPME is a solvent-free sample preparation method based on equilibrium between a fiber and the sample, alternative to the exhaustive liquid-liquid extraction (LLE) method [2].

Semi-batch reactor

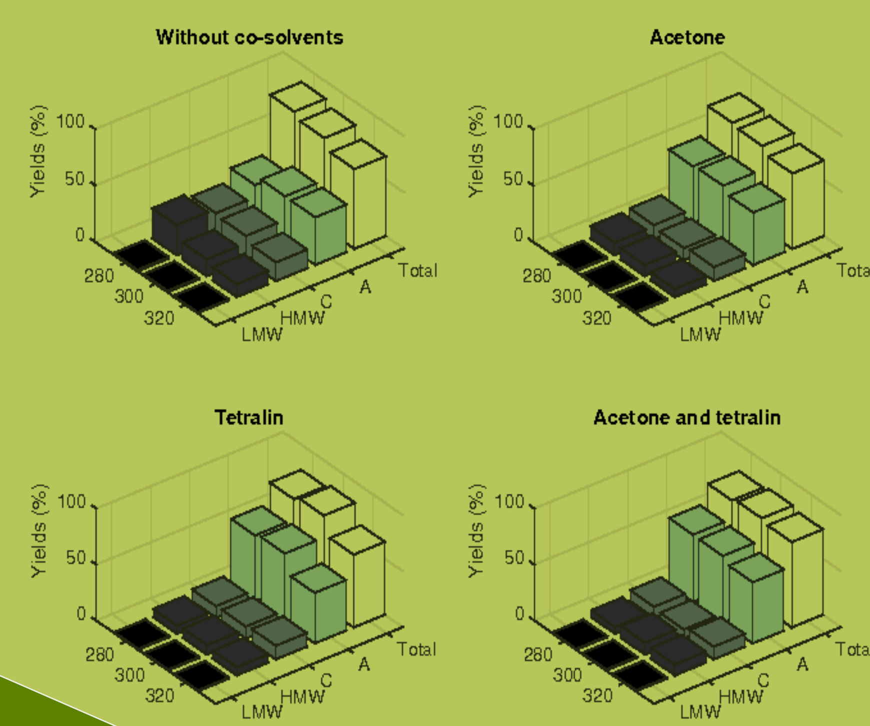
1) TEMPERATURE AND PRESSURE CONTROL
2) PRECISE BIOMASS INJECTION
3) INSTANTANEOUS BIOMASS HEATING
4) PRODUCTS QUENCHING
5) STIRRING



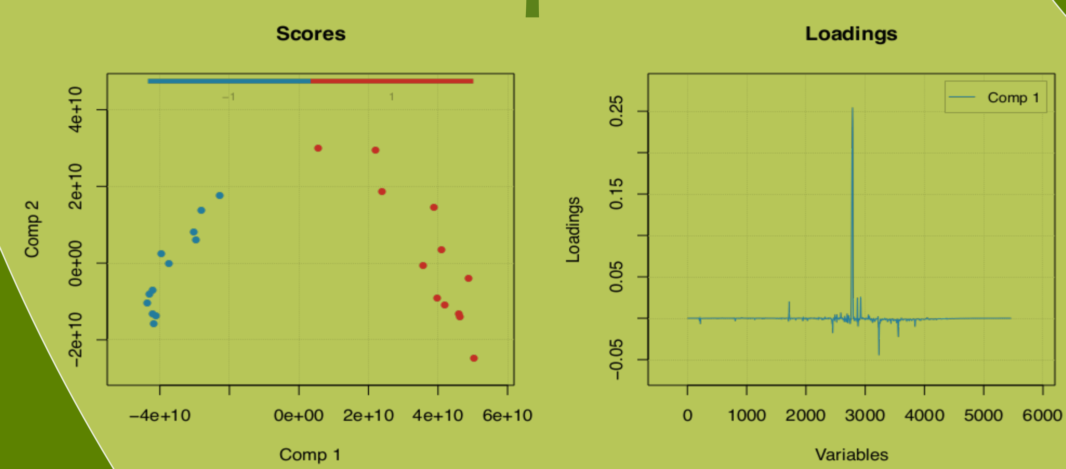
SPME & GCMS

Distribution of species:

1) Low molecular weight aliphatics
2) Cyclic derivatives
3) Aromatics
4) High molecular weight compounds



Tetralin presence



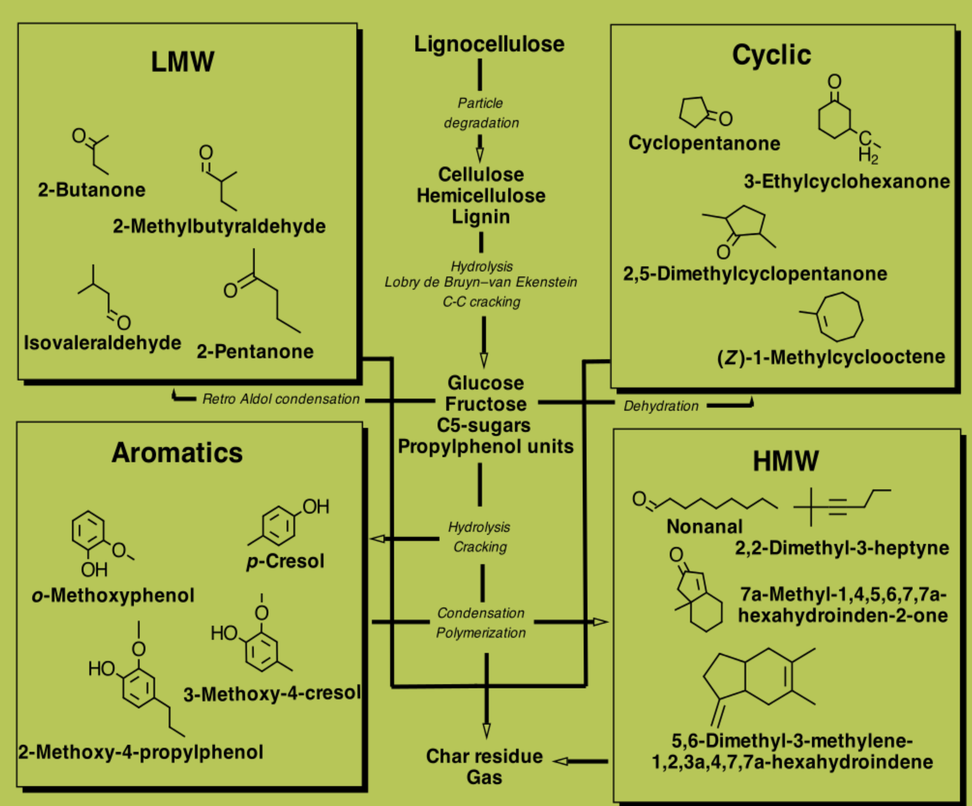
Key compounds

Variable	RT (min)	Identification	Loadings
2429-2453	9.91-9.99	2-Cyclopenten-1-one, 3,4,5, trimethyl-	-
2860-2869	11.48-11.50	Creosol	+
2912-2920	11.68-11.71	Phenol, 4-methoxy-	+
3225-3231	12.83-12.85	2H-Inden-2-one, 1,4,5,6,7,7a-hexahydro-7a-mehytl-, (S)-	-
3550-3557	14.02-14.05	Phenol, 2-methoxy-4-propyl	-
3835-3838	15.07-15.08	Bicyclo[4.3.0]non-3ene, 3,4,-dimethyl-7exo-methylene	-

Yields and C-balances

1) ***WSO: 54-68 wt. %***
Increase with co-solvents
2) ***WIO: 9-44 wt. %***
Decrease with temperature
3) ***Gas products: 6-36 wt. %***
Increase wih temperature
4) ***C-recovery: 54-103 %***
Decrease with temperature

Reaction mechanisms



MDA - PCA

Multivariate Data Analysis
Principle Component Analysis

INPUT: Chromatographic SPME-GCMS data for WSO.

The score plot shows the samples with and without tetralin (red and blue, respectively). The loading plot shows the variables (RT values) responsible for the shift in reaction mechanisms explained by PC1 (68.94%).

Conclusions

Without co-solvents

High yields of cyclic compounds, especially at low temperatures (280 °C), indicating the dominance of dehydration over retro-aldol condensation. High yields of HMW compounds.

Addition of co-solvents

Shift toward cyclization of glucose and degradation of lignin resulting in an increased production of aromatics, especially for tetralin and at moderate temperatures (300 °C).

Increasing temperature

Decreasing amounts of cyclic and HMW compounds and formation of gaseous products.

Acknowledgements

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References

[1] S.S. Toor, L. Rosendahl, A. Rudolf, Hydrothermal liquefaction of biomass: A critical review of subcritical water technologies, Energy 36 (5) (2011) 2328-2342

[2] J. Pawliszyn, Handbook of solid-phase micro-extraction, Elsevier, 2011