Development of a kinetic model for HTL conversion of waste biomass

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Anne ROUBAUD*[,a], Geert HAARLEMMER[a], Morgane BRIAND[a], Pascal FONGARLAND[b]

*Corresponding author: anne.roubaud@cea.fr

[a] CEA LITEN, Université Grenoble Alpes 38054 Grenoble cedex 9, France

[b] CP2M, CPE, Université Claude Bernard, Lyon, France

Introduction

New process routes are now being developed to obtain cost-effective biofuels from low cost and abundant biogenic residues and waste fractions. The kind of resources that can be considered are biogenic wastes, in particular food wastes and agro-industrial wastes. These wastes have a high humidity (> 50%wt) and are composed of cellulose, hemicellulose and lignin as any lignocellulosic biomass but also lipids and proteins. This type of resource is well suited for an HTL conversion into intermediate bio-oil that can be further upgraded to obtain a fuel. Hydrothermal liquefaction (HTL) converts biomass compounds under hot compressed water into a biocrude. This biocrude is an oily material containing bio-oil and char. Developments started in the 1980's in Europe [1] and in the United States [2]. The conversion takes place at temperatures between 300 and 400°C and at pressures above the saturation pressure to ensure that water remains in the liquid phase, typically above 100 bar. Under these conditions the ionisation of water increases while its polarity decreases, favouring depolymerisation and dehydration of biomass biopolymers to produce hydrophobic compounds. This process is well adapted for wet resources avoiding an energy consuming step of drying. Our previous work on HTL of agro-industrial residues has shown that the biochemical composition of the initial matter is the major parameter influencing conversion efficiency and quality of the product [3].

Objectives and methodology

The objective of this work is to develop a simulation tool in order to predict the HTL product distribution in term of aqueous phase, gas phase, bio-oil and bio-char for an organic waste based on it biochemical composition and the conversion conditions (temperature and residence time). Experiments were performed for too different resources at different residence time and temperature. This study was done with Blackcurrant pomace is a residue of juice production, were sourced from "Les Vergers de Boiron" in France, and Brewers' Spent Grains were sourced from "La Brasserie du Dauphiné". Temperatures considered were 200, 250, 300, 315 °C and residence times, 0, 15, 60 min. Experiments were performed in a 600 mL batch reactor with an heating rate of 15 °C/min. Resource to water mixture ratio was kept constant at 9:1. For each experiment, mass and carbon balances are verified.

Proximate and ultimate analysis of these resources were subcontracted at SOCOR. Results are given in the table below for comparison. Even if the elemental analyses look similar, the biochemical composition of those two resources are quite different except for their protein content.

Table 1. Feedstock characteristics

	Blackcurrant Pomace	**Spent brewery pomace**
Feedstock origin	Les vergers	La Brasserie du

		Boiron	Dauphiné
Total moisture. as received	wt%	52.5	72.5
Ash 550 °C, dry matter	wt%	3.7 ± 0.3	3.0 ± 0.2
Carbon , dry matter	wt%	48.7 ± 0.7	44.7 ± 0.3
Hydrogen, dry matter	wt%	6.5 ± 0.1	6.6 ± 0,1
Nitrogen, dry matter	wt%	2.8 ± 0.1	2.8 ± 0.1
Sulfur, dry matter	wt%	0.2 ± 0.1	0.2 ± 0.1
Cellulose, dry ash free	wt%	16.0	11.5
Hemicellulose, dry ash free	wt%	15.1	30.1
Lignin, dry ash free	wt%	16.5	3.3
Sugars, dry ash free	wt%	9.6	26.0
Proteins, dry ash free	wt%	18.4	19.9
Lipids, dry ash free	wt%	20.7	6.2

Biocrudes are complex mixtures containing an oily and a solid fraction. This solid fraction is in fact an insoluble fraction in a determined solvent. In this work, the biochar fraction X_{char} into the biocrudes is determined by the use of ethyl acetate as solvent. Yield of biocrude Y_{bc} is the weight of dry biocrude W_{bc} divided by the initial weight of dry matter entered into the reactor and yield of biochar is the weight of biochar divided by the initial weight of dry matter DM .

$$Y_{char} = (W_{bc} * X_{char}) / DM \qquad \text{Eq. 1}$$

The Gas yield is determined by calculation of the gas produced by using the initial pressure value Pi at the initial temperature Ti and the final pressure value Pf in the reactor at final temperature after cooling, with the ideal gas law. In addition, the quantity of CO2 dissolved in the aqueous phase in the final conditions W_{CO2d} is calculated with Henry's law.

$$Y_{gas} = ((V_R - V_L)/R * (P_f/T_f - P_i/T_i) + W_{CO2d})/DM \qquad \text{Eq. 2}$$

With V_R reactor volume, V_L volume of liquid in the reactor

Identification of molecules in the light fraction of biocrudes oil (T_{eb} <250 °C) and in the aqueous phase was done by Gas chromatography with a masse detector. Based on our previous work [3] and with the identification of the main intermediate species of this work a global conversion mechanism was defined see figure 1. The kinetic parameter of this mechanism were optimized by minimizing the differences with the experimental yields of gas, aqueous phase, bio-oil and bio-char for 24 experimental points. Each point was produced from 2 to 4 experiments.

Results

A reaction scheme was proposed after compositional analysis of the resources and the reaction products. Figure 1 presents the reaction scheme. Fitted parameters are reaction kinetics and stoichiometric coefficients (X1, X3, X4 and X6) for CO2 production. As we will be fitting the model on observed product yields, rather than working on absolute measures of compounds, the model also fits a distribution of the compounds between the biooil and aqueous phase (X2 for organic compounds, X7 for lignin decomposition products) and between biochar and biooil for Maillard products X5.

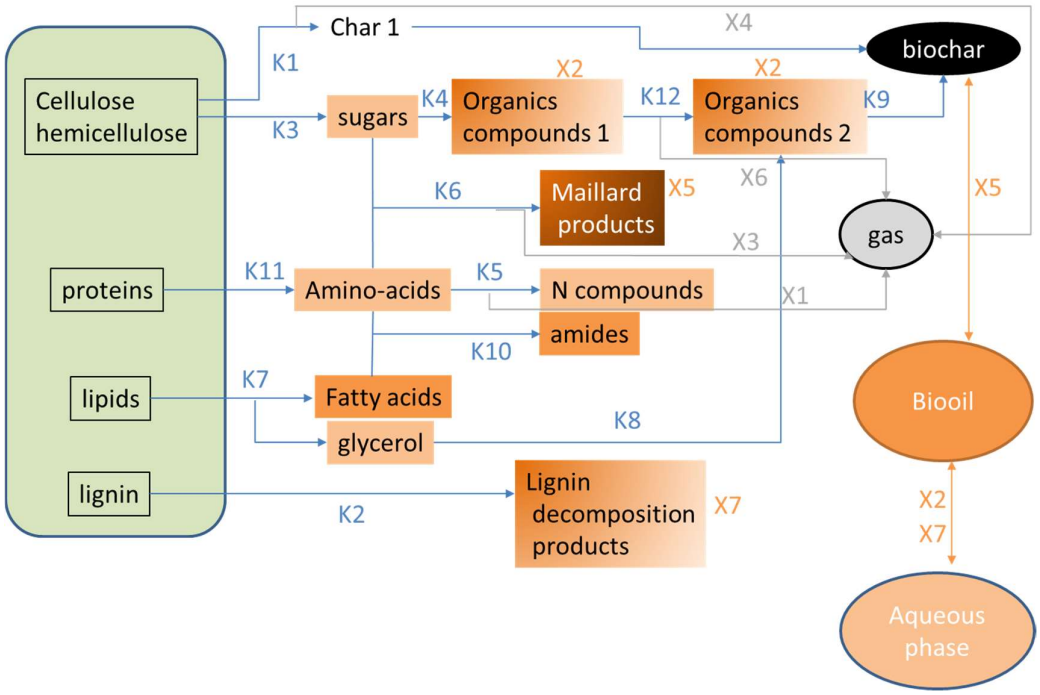

Figure 1 Global conversion mechanism for HTL of organic wastes

Figure 2 present a comparison of the experimental data and the results of the prediction calculated by the optimized model. The model starts with the biomass composition. Temperature is ramped up with a fixed rate until the final temperature is reached. The products are calculated following the evolution of the reaction compounds. The model was fitted to the combined data set containing all temperatures, reaction times and for two resources.

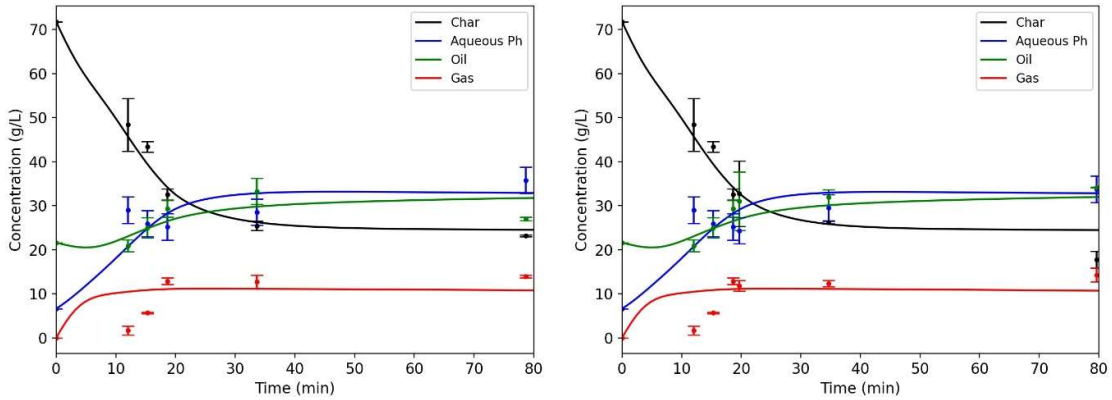

Figure 2 : HTL product yields for blackcurrant pomace at 300°C (left) and 315 °C (right)

The models shows interesting evolutions of the yields. Gas is produced relatively late in the conversion, the model tends to produce somewhat too fast.

The model has been integrated in a process simulator via Cape-Open interface. This allows us to evaluate process conditions and the effect of the recycling of process water in the process. Calculations results are presented below in table 2 for blackcurrant pomace and in table 3 for brewers' spent grains.

Table 2 : Results process simulation for blackcurrant pomace at 300 °C, 15 min

Mass Yields (%)	Experimental results	Simulation	Simulation with aqueous phase recycle
Gas	13 ± 2 %	11 ,8	15,3
Bio-oil	33 ± 2 %	28,1	39,9
Bio-char	24 ± 1 %	24,6	28,2

Table 3 : Results process simulation for brewers' spent grains at 315 °C, 15 min

Mass Yields (%)	Experimental results	Simulation	Simulation with aqueous phase recycle
Gas	15 ± 2 %	17,1	21,2
Bio-oil	24 ± 8 %	11,0	14,7
Bio-char	23 ± 6 %	36,4	40,6

Conclusions

The model is able to reproduce the evolution of the different product fraction with time except at the beginning between 0 and 20 min this is during the heat up time were the temperature is always changing leading to a non-stationery situation. This tool can be used for a process simulation in the prediction of product yields and. To obtain a more precise model, a work is ongoing in the laboratory with quantification of intermediate species in an objective of developing a comprehensive and predictive model of intermediate species or intermediate family of species.

References

1. Goudriaan, F. and D.G.R. Peferoen, *Liquid fuels from biomass via a hydrothermal process.* Chemical Engineering Science, 1990. **45**(8): p. 2729-2734.
2. Elliott, D.C. and G.F. Schiefelbein, *Liquid Hydrocarbon fuels from biomass*, in *Division of Fuel Chemistry Annual Meeting Preprints*. 1989, American Chemical Society. p. 1160-1166.
3. Deniel, M., et al., *Hydrothermal liquefaction of blackcurrant pomace and model molecules: understanding of reaction mechanisms.* Sustainable Energy & Fuels, 2017.