HYDROTHERMAL LIQUEFACTION OF SEVERAL FOOD RESIDUES

Maxime Déniel[a,b,*], Geert Haarlemmer[a], Julien Roussely[a], Anne Roubaud[a,†]
Elsa Weiss-Hortala[b], Jacques Fages[b]

[a] CEA, Grenoble, LITEN, DTBH, Biomass Technology Laboratory, 38054 Grenoble, France
[b] Université de Toulouse, Ecole des Mines d'Albi, CNRS, RAPSODEE research centre, 81013 ALBI, France
[*] Corresponding Author: Maxime.Deniel@cea.fr, Tel. 0033438784026, Fax 0033438785251
[†] Presenting Author : Anne.Roubaud@cea.fr, Tel. 0033438780454, Fax 0033438785251

ABSTRACT

Agricultural and food processing wastes are one of the most abundant resources of biomass worldwide. For instance in 2010, it was estimated that 89 Mt of food waste were generated in the EU-27. Unlike other traditional biomasses, such as wood, these wastes usually contain more than 50 wt. % water. In comparison with thermochemical processes such as incineration or pyrolysis, Hydrothermal Liquefaction (HTL) does not require the costly preliminary step of drying the biomass: water is a solvent and a reactant for this process. It is therefore possible to economically treat wet wastes. HTL typically generates 4 phases: an oily product known as 'bio-oil', an aqueous phase containing dissolved organics, a solid residue and a gaseous phase.

In this study, several agricultural products were tested, including fruit residues and potato starch. All of the feedstocks were subjected to a detailed chemical analysis. These residues were then exposed to subcritical water in a batch autoclave. Operating conditions were 280-350°C, 8.5-20 MPa, and a reaction time between 15 and 60 min. For each experiment, the aqueous, solid and oily fractions were analysed. This paper focuses on the carbon distribution in the different phases recovered, and the organic compounds contained in the aqueous phase, as regards to the operating conditions. Raw resources are mainly acidic (3 < pH < 5), and initial pH values were modified by addition of NaOH or Na_2CO_3.

The results show that increasing the initial pH of the feed has a significant influence on the fraction of organic carbon remaining in the aqueous phase: it increases from 10% at pH = 4, to 35% at pH = 12.5. The nature of the biomass is also important: for example, more organic carbon is transferred from grape to the aqueous phase, compared to starch. This paper mainly consists in exploratory runs: further studies should focus on model compounds, in order to unveil the mechanisms leading to the products. Especially, the knowledge on the dependency to acidity of the aqueous phase will allow us to optimize the liquefaction process, and the role of alkali catalysts would be clarified.

INTRODUCTION

Agricultural and food processing wastes are one of the most abundant resources of biomass worldwide, and are today mostly treated for disposal, for instance for fertilizing purposes. In 2010, it was estimated that 89 Mt of food waste were generated in the EU-27 [1]. Reducing the amount of biomass waste is a key parameter in a global waste management strategy, in relation with environmental policy obligations such as reducing the amount of greenhouse gases emissions, and increasing the share of chemicals and fuels produced from renewable resources, because of the upcoming shortage of fossil resources (e.g. crude oil).

In the past years, novel methods have emerged, such as anaerobic digestion for the production of biogas, fermentation of remaining sugars to produce alcohols, and thermochemical conversion routes (gasification, pyrolysis). Each conversion route is substrate-specific, because of the wide variety of chemical compositions (carbohydrates, proteins, lipids, ash) and physical aspects related to the nature of feedstocks.

Unlike other traditional biomasses, such as wood, food processing wastes usually contain more than 50 wt. % water, and up to 95 wt. % in the case of sludge and wastewaters. This feature makes them unattractive for further utilization, due to increased transport costs, costly drying prior to further processing, and also environmental considerations. For this reason, hydrothermal treatments have gained attention during the past years, as potential conversion routes for wet biomass waste.

In comparison with thermochemical processes such as incineration or pyrolysis, Hydrothermal Liquefaction (HTL) does not require the costly preliminary step of drying the biomass: water is a solvent, a reactant and a catalyst for this process. HTL uses the specific properties of subcritical water, which is water at medium temperatures and high pressures below its critical point (T_c = 374°C, P_c = 22.1 MPa). In these conditions, water loses its polarity, becoming similar to an organic solvent, and its ionic product K_w increases up to three orders of magnitude [2]. In addition, reaction rates of biomass in water are relatively high (even a few seconds), and high conversion can be achieved. It is therefore possible to economically treat wet organic wastes. HTL typically generates 4 phases: an oily product known as 'bio-oil', an aqueous phase containing dissolved organics, a solid residue and a CO_2-rich gaseous phase.

In this study, several agricultural products were tested, including black currant pomace, grape pomace, and potato starch. These residues were exposed to subcritical water in a batch autoclave. For each experiment, the aqueous, solid and oily fractions were analysed. This paper focuses on the carbon distribution in the different phases recovered, and the organic compounds contained in the aqueous phase, as regards to the operating conditions. Raw resources are mainly acidic (3 < pH < 5), and initial pH values were modified by addition of NaOH or Na_2CO_3. It has been previously demonstrated that pH conditions affect reaction mechanisms[3].

MATERIALS AND METHODS

Biomass residues were supplied by local producers, except for potato starch which was purchased from VWR ProLabo, and used as received. Pellets of Sodium Hydroxide NaOH were purchased from Merck and anhydrous Sodium Carbonate Na_2CO_3 was purchased from Sigma Aldrich, and used as received. For each experiment, distilled water was used. Table 1 gives the typical composition of biomass samples used in this study, and Table 2 gives the elemental composition of feedstocks, obtained from external analysis laboratories.

Table 1: Global composition of biomass
(all values are given in wt. % on a wet basis)

Biomass	Moisture content	Carbohydrates	Protein	Lipids	Ash content
Potato starch	19.6	80.4	-	-	Traces

Black currant pomace	54.8	35	8	0.4	1.7
Grape pomace	54.7	34	6.2	1.9	3.4

Table 2 : Elemental composition of feedstocks
(all values are given in wt. % on a dry basis)

Biomass	Carbon content	Hydrogen content	Nitrogen content	Oxygen content	Ash content
Potato starch	44.4	6.2	N.D.	49.3	Traces
Black currant pomace	52.8	6.97	2.61	33.8	3.8
Grape pomace	49.5	5.75	2.23	35	7.5

Hydrothermal liquefaction experiments were performed in a 0.6 L stainless steel (SS316) stirred batch reactor (Parr Instruments). Approximately 240 g of biomass slurry (sample, water, catalyst when used) were introduced in the reactor, with a dry matter to water ratio of 15 wt. %. Biomass was ground using a Fritsch Variable-Speed Rotor Mill Pulverisette 14 if required. Before each experiment, pH was measured using a Scientific Instruments IQ170 pH meter. The autoclave was then purged and pressurized to 1 MPa with nitrogen gas. The pressure inside the reactor was a function of the reaction temperature and the amount of water. The reactor was heated to the reaction temperature at a rate of 15-20°C/min. Once the reactor had reached the reaction temperature, it was held during a specified time. The combination of the heating and holding times is considered as the reaction time. After the holding time, the reactor was rapidly cooled by an air quench, and the gas phase was then analysed by a micro-chromatograph. Separation of bio-oil and aqueous phase was accomplished by a filtration on a Buchner filter.

Bio-oil was then extracted by ethyl acetate for further analysis by GC-MS (Perkin Elmer Clarus 500/Clarus 600S) equipped with DB-1701 capillary column 60 m × 0.25 mm, 0.25 μm film thickness and injector (split-splitless). The total carbon of the bio-oil phase and char were quantified by a total organic carbon analyser (Shimadzu SSM-5000A).

Gas phase was analysed by a micro-chromatograph (Varian Quad CP 4900) used in line for hydrothermal experiments. Permanent gases (O_2, H_2, CO and CH_4) were analysed by a molecular sieve column using argon as carrier gas. Light hydrocarbons (C_2H_4, C_2H_6, C_2H_2 and C_3H_8), CO_2 and sulphur species (H_2S and COS) were analysed on a Poraplot-U column using helium as carrier gas. Total carbon of the aqueous phase obtained by hydrothermal liquefaction was quantified by a total organic carbon analyser (Shimadzu TOC-L CSH/CSN).

RESULTS

Fruit residues – namely black currant and ground grape pomace – as well as potato starch were exposed to subcritical water, with temperatures between 280°C and 350°C, pressures of 8.5-20 MPa, and holding times between 15 and 60 min. Table 1 and Table 2 show that fruit residues share very similar global compositions, being predominantly composed of carbohydrates, with a fibre content of respectively 56 wt. % and 57 wt. % on a dry basis. Because of this high content in carbohydrates, it is expected that hydrothermal liquefaction of the feedstocks would give sugar degradation products, such as furans,

aldehydes, ketones and carboxylic acids [4-6]. Since these reactions are either acid or base catalyzed, a special attention should be given to the influence of pH on the results of hydrothermal liquefaction of the feedstocks. Thus, Figure 1 compares the residual amount of carbon in the aqueous phase as a function of the initial pH of the slurry and the nature of the feedstock. In order to adjust the pH of slurries, Sodium Carbonate Na_2CO_3 (weak base), and Sodium Hydroxide NaOH (strong base) were added to the mixture.
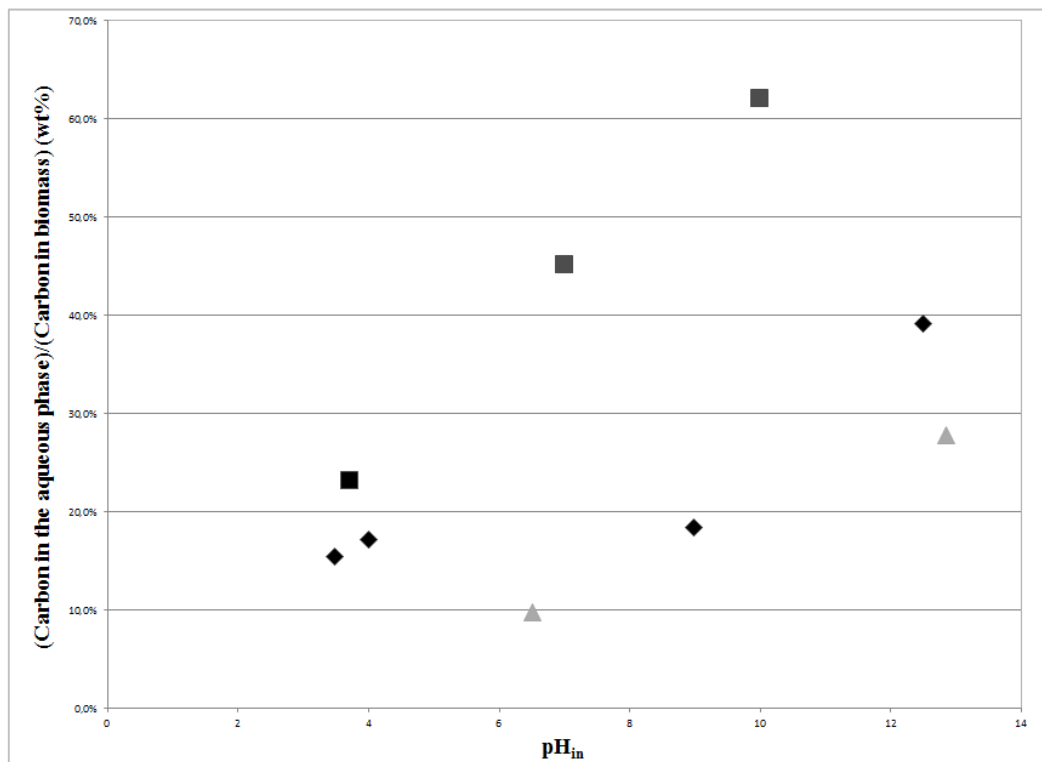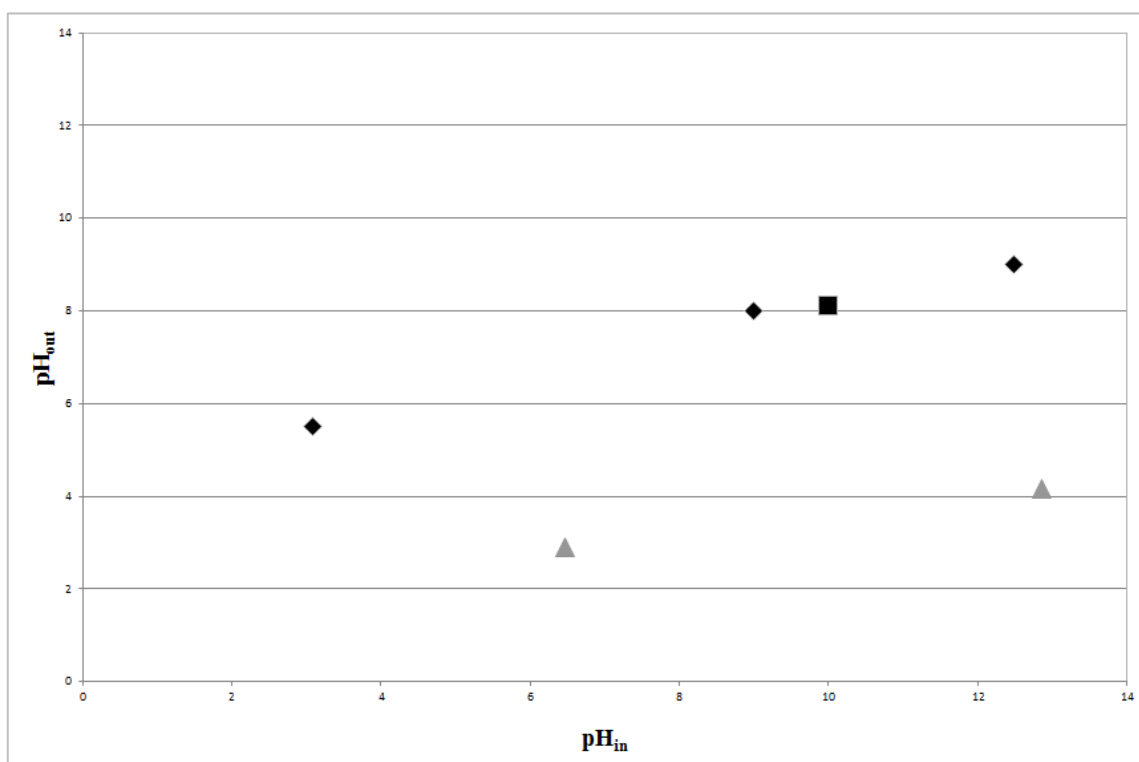

Figure 1 : Residual carbon (wt. %) in the aqueous phase as a function of initial pH
■ : Ground grape pomace (280°C, 60 min); ♦ : Raw black currant pomace (300°C, 60 min);
▲ : Potato starch (300°C, 30 min)

Firstly, the results show that increasing the initial pH of the feed has a great influence on the final organic carbon recovered in the aqueous phase: for instance, it increases from about 23% at pH = 3.7, to more than 60% at pH = 10 using ground grape pomace as feedstock. This dependency is slightly lower for the other feedstocks.

Despite similar chemical compositions, fruit residues show different behaviours. As shown in Figure 1, ground grape pomace is more readily hydrolysed in subcritical water than raw black currant pomace, in spite of the harsher conditions used in the case of black currant. This might be attributed to the effect of grinding, which ameliorates diffusion of chemical reactive species and heat transfer in the case of grape, compared to black currant. In fact, black currant – especially the seeds – is difficult to decompose, even in hydrothermal conditions at 250°C (results not shown). With a prior step of grinding, milder conditions can be operated to convert the feedstocks efficiently. As well as for black currant, harsher conditions for potato starch, compared to those for grape pomace, result in less carbon recovered in the aqueous phase. This could be due to the different nature of feedstocks.

Secondly, a similar trend was observed among the feedstocks with the variation of pH, namely an increase of the carbon transferred to the aqueous phase from the feedstock. This

means that more water-soluble compounds are formed when pH increases. This observation is consistent with results reported in the literature [3, 7-10]. In fact, an acidic pH will drive the reaction mechanism towards dehydration of sugars, forming mainly furanic compounds such as 5-HMF and furfural, which are found in the bio-oil. With an increase in pH, the reaction mechanism will shift to retro-aldol reactions, leading to the formation of short-chain polar compounds, soluble in water: aldehydes, ketones, and ultimately carboxylic acids such as formic, acetic and lactic acids. Figure 2 shows that in most cases pH decreased during the experiments, which illustrates the formation of acidic compounds, and/or the consumption of a significant amount of OH^- initially added in the media. For example, during basic hydrolysis, OH^- acts as the nucleophile [11]. In one case, with black currant, pH increased when starting from acidic values, indicating that other mechanisms such as dehydration and decarboxylation took place.

Figure 2 : pH after HTL of various feedstocks as a function of initial pH of the slurry
■ : Ground grape pomace (280°C); ◆ : Raw black currant pomace (300°C);
▲ : Potato starch (300°C)

CONCLUSION

Fruit residues – namely black currant and ground grape pomace – as well as potato starch were exposed to subcritical water in a batch autoclave. Operating conditions were 280-350°C, 8.5-20 MPa, and holding times between 15 and 60 min. The results show that increasing the initial pH of the feed has a clear influence on the fraction of organic carbon remaining in the aqueous phase: the higher the alkalinity, the more water-soluble compounds are produced. Especially, the decrease observed in final pH compared to initial pH indicates that acidic compounds were formed. Pre-treatment of feedstocks is also important, since the grinding of grape pomace allowed to operate at milder conditions, in comparison with black

currant pomace which has similar chemical composition. This paper mainly consists in exploratory runs. Further studies should focus on model compounds, in order to unveil the mechanisms leading to the products. Especially, the knowledge on the dependency to acidity of the aqueous phase will allow us to optimize the liquefaction process, and the role of alkali catalysts would be clarified.

ACKNOWLEDGEMENTS

REFERENCES

[1.]   Pavlovič, I., Ž. Knez, and M. Škerget, *Hydrothermal Reactions of Agricultural and Food Processing Wastes in Sub- and Supercritical Water: A Review of Fundamentals, Mechanisms, and State of Research*, Journal of Agricultural and Food Chemistry, 61, **2013**. p. 8003.

[2.]   Kruse, A. and E. Dinjus, *Hot compressed water as reaction medium and reactant: Properties and synthesis reactions*, The Journal of Supercritical Fluids, 39, **2007**. p. 362.

[3.]   Yin, S. and Z. Tan, *Hydrothermal liquefaction of cellulose to bio-oil under acidic, neutral and alkaline conditions*, Applied Energy, 92, **2012**. p. 234.

[4.]   Aida, T.M., K. Tajima, M. Watanabe, Y. Saito, K. Kuroda, T. Nonaka, H. Hattori, R.L. Smith Jr, and K. Arai, *Reactions of d-fructose in water at temperatures up to 400°C and pressures up to 100MPa*, The Journal of Supercritical Fluids, 42, **2007**. p. 110.

[5.]   Aida, T.M., N. Shiraishi, M. Kubo, M. Watanabe, and R.L. Smith Jr, *Reaction kinetics of d-xylose in sub- and supercritical water*, The Journal of Supercritical Fluids, 55, **2010**. p. 208.

[6.]   Aida, T.M., Y. Sato, M. Watanabe, K. Tajima, T. Nonaka, H. Hattori, and K. Arai, *Dehydration of d-glucose in high temperature water at pressures up to 80MPa*, The Journal of Supercritical Fluids, 40, **2007**. p. 381.

[7.]   Watanabe, M., Y. Aizawa, T. Iida, T.M. Aida, C. Levy, K. Sue, and H. Inomata, *Glucose reactions with acid and base catalysts in hot compressed water at 473K*, Carbohydrate Research, 340, **2005**. p. 1925.

[8.]   Watanabe, M., Y. Aizawa, T. Iida, R. Nishimura, and H. Inomata, *Catalytic glucose and fructose conversions with TiO2 and ZrO2 in water at 473K: Relationship between reactivity and acid–base property determined by TPD measurement*, Applied Catalysis A: General, 295, **2005**. p. 150.

[9.]   Antal Jr, M.J., W.S.L. Mok, and G.N. Richards, *Mechanism of formation of 5-(hydroxymethyl)-2-furaldehyde from d-fructose and sucrose*, Carbohydrate Research, 199, **1990**. p. 91.

[10.] Salak Asghari, F. and H. Yoshida, *Acid-Catalyzed Production of 5-Hydroxymethyl Furfural from d-Fructose in Subcritical Water*, Industrial & Engineering Chemistry Research, 45, **2006**. p. 2163.

[11.] Akiya, N. and P.E. Savage, *Roles of Water for Chemical Reactions in High-Temperature Water*, Chemical Reviews, 102, **2002**.