Monomeric Biomass Compounds Decomposition in Subcritical and Supercritical Water: Multi-technical Characterization of Intermediates and Products

Jérémie *Barbier* [a,*], *Nadège Charon* [a], *Nathalie Dupassieux* [a], *Anne Loppinet-Serani* [b,c], *François Cansell* [b,c]

[a] IFP, BP3, 69390 Vernaison, France

[b] Université de Bordeaux, UPR 9048, ENSCPB, 87 avenue du Dr. Albert Schweitzer, 33608 Pessac Cedex, France

[c] CNRS, Institut de Chimie de la Matière Condensée de Bordeaux, 33608 Pessac Cedex, France

*Corresponding author E-mail: jeremie.barbier@ifp.fr & Fax: +33 4 78 02 20 15

Renewable energy sources are currently receiving much attention since they can contribute to secure the energy supply and to reduce the emission of fossil CO_2. In this context, production of biofuels and chemicals from lignocellulosic biomass resources (forest and agricultural residues, herbaceous crops) is being investigated. The objective of this study is to compare the reactivity of monomeric glucidic and phenolic compounds in sub- and supercritical water. Experiments have been carried out at different conversion conditions, using a 500 ml batch reactor, during 0-60 min, at a pressure of 25 MPa and at temperatures of 300 and 400 °C. Glucose and vanillin have been chosen as suitable model compounds for lignocellulosic biomass. Products resulting from monomers conversions have been analysed by a high resolution mass spectrometry technique (FT-ICR/MS) as well as by gas chromatographic methods (GC-MS and GC-FID).

INTRODUCTION

Lignocellulosic biomass resources are composed of glucidic (cellulose and hemicellulose) and phenolic (lignin) biopolymers. Their structures and compositions are different from the ones of petroleum products [1]. Development of an efficient biofuel production process requires a further understanding of reaction pathways that occur during the transformation of lignocellulosic compounds. Due to its complex chemical composition, the reactivity of lignocellulosic biomass under a hydrothermal treatment is not completely elucidated even if it has been widely studied in literature [2-6].

Water near its critical point (Tc = 374 °C, Pc = 22.1 MPa) has got very interesting properties that are continuously adjustable with temperature and pressure. In the subcritical region, the ionic product is up to three orders of magnitude higher than at ambient conditions [7] and the relative dielectric constant is much higher than in the supercritical region [8]. As a reaction medium, water has acid-base catalytic effects and supports more ionic reaction. In supercritical region, the medium exhibits the properties of a non-polar solvent from a macroscopic point of view. Sub- and supercritical water can support ionic, polar non-ionic and free radical reactions; the relative rates of these different classes of reactions can be very sensitive to the reaction conditions. On the other hand, change of the reaction pathways from mainly ionic to mainly free radical reactions can be induced by a change of the water properties with increasing temperature [9-10].

The objective of this study is to investigate degradation pathways of lignocellulosic monomeric biomass compounds during their conversion in subcritical and supercritical water. To reach this goal, a characterization approach has been developed to analyze degradation products resulting from hydrothermal conversion of glucose and vanillin.

MATERIALS AND METHODS

Materials that were investigated in this work were D-glucose and vanillin purchased from Sigma-Aldrich. Hydrothermal conversions were performed in a 500 ml batch reactor as shown in Figure 1. Nitrogen was used to purge the reactor before each conversion. Experiments were carried out using a 2 $_{wt}$ % of glucose or vanillin aqueous solution which was introduced into the reactor at ambient conditions. Temperature was raised up to 300°C (28 °C/min) or 400°C (50 °C/min) and final pressure was about 25 MPa. Residence times varied from 30 minutes to 60 minutes, under a 1500 cycles/min stirring. Then, the reactor was cooled down to the room temperature by air stream.

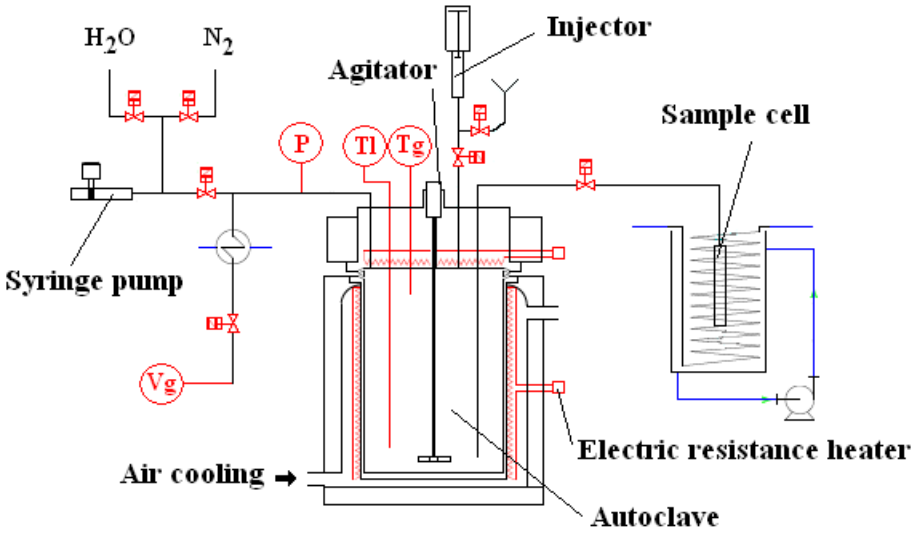

Figure 1: Batch reactor used for conversions in sub- and supercritical water

Products resulting from glucose or vanillin conversion were separated into different fractions. Gaseous products were collected and analyzed by gas chromatography (GC) coupling with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The solid and liquid products were separated by filtration under vacuum into a water soluble fraction (WS) and a water insoluble fraction (WI). WS fraction was analysed by different techniques: Total organic carbon (TOC), GC-MS (mass spectrometry), GC-FID and Electrospray positive mode ionization-Fourier transform ion cyclotron resonance mass spectrometry (ESI^+-FTICR/MS). WI fraction was dried during 12 hours at 105°C and elementary composition was determined.

RESULTS

Table 1 shows mass yields of gas, WS and dry WI fractions produced at different conversion conditions. Carbon balances (not shown) are in progress. According to Table 1, the quantity of gaseous products is significant for supercritical conditions. WI fractions are produced in significant amounts only for glucose conversions at 300°C.

Table 1: Gas, WS and dry WI fractions mass yields (mass of fraction / mass of starting material) resulting from glucose and vanillin conversions at 25 MPa

	Glucose				Vanillin			
	300°C		400°C		300°C		400°C	
	30 min	60 min	30 min	60 min	30 min	60 min	30 min	60 min
$_{wt.}$% gas	nd	0.1	0.3	0.3	nd	nd	0.2	0.4
$_{wt.}$%dry WI	0.3	0.3	nd	nd	nd	nd	nd	nd
$_{wt.}$% WS	96.2	95.2	94.3	94.4	98.8	97.7	95.0	92.4

nd: not detected

In this paper, we have chosen to show only analytical results of WS fractions, other results will be presented in a later communication. To focus on water soluble products resulting from glucose conversion, Figure 2 shows ESI^+-FTICR/MS spectra of glucose conversions carried out during 30 minutes residence time at 300°C and 400°C. The FT-ICR mass spectrometry is a very high resolution technique which enables mass determination with a very high accuracy [11]. Molecular weight range of compounds contained in WS fractions can be determined using FT-ICR/MS technique. According to the ESI^+-FTICR/MS spectrum of products obtained from glucose in subcritical water at 300°C, 25 MPa and 30 min residence time, mass-to-charge ratios (m/z) are measured up to 850 u. However, we can note that a more reduced molecular weight range (700 u maximum) is observed for supercritical water conversion at 400°C. Since m/z of glucose equals to 181 u, it means that condensation reactions take place during glucose conversion in subcritical and supercritical conditions.

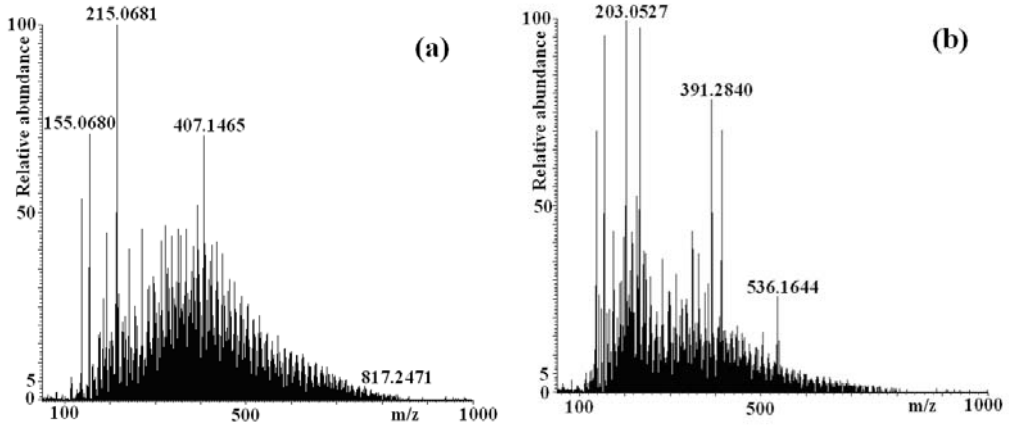

Figure 2: ESI^+-FTICR/MS spectrum of water solutes from glucose conversion at 25 MPa, 30 minutes, (a) 300°C and (b) 400 °C

Maximum mass-to-charge ratios determined by ESI+-FT-ICR/MS are indicated in Table 2 for WS fractions of glucose and vanillin products. A residence time increasing from 30 to 60 minutes does not induce any significant modification of the products molecular weight range for products obtained by glucose conversions.

Table 2: Least upper bounds of molecular weight range obtained by ESI^+-FTICR/MS of WS fractions under different temperatures and residence times of glucose and vanillin conversions at 25 MPa

	Glucose				Vanillin			
	300°C		400°C		300°C		400°C	
	30 min	60 min	30 min	60 min	30 min	60 min	30 min	60 min
(m/z) max	850 u	850 u	700 u	700 u	500 u	500 u	450 u	550 u

FT-ICR mass spectrometry provides very useful data about the mass molecular range WS fractions. Nevertheless, this method can be applied to characterize compounds whose m/z are higher than 100 u. Therefore, to analyse compounds having lower m/z, GC-MS and GC-FID coupling methods have been used respectively to identify and quantify the eluable compounds that are detected in WS fractions. Table 3 shows the composition of the main detected WS compounds (in % of area) obtained from glucose and vanillin conversions.

Table 3: Compositions of the main WS compounds (in % of area) determined by GC-FID

	Glucose				Vanillin			
Temperature (°C)	300		400		300		400	
Residence time (min)	30	60	30	60	30	60	30	60
carbonyls								
acetaldehyde	11.9	20.1	11.3	5.11	nd	nd	nd	nd
acetone	2.4	3.5	7.7	6.0	nd	nd	0.1	nd
2,3-butanedione	0.9	1.1	1.9	2.5	nd	nd	nd	nd
1-hydroxy-2-propanone	0.8	0.6	nd	0.3	nd	nd	nd	nd
2,3-pentanedione	0.4	0.3	0.9	0.8	nd	nd	nd	nd
2-cyclopentenone	1.4	4.1	5.4	9.6	nd	nd	nd	nd
cyclopentanone	nd	0.2	0.5	1.0	nd	nd	nd	nd
2-methyl-2-cyclopentenone	0.3	0.5	1.5	1.3	nd	nd	nd	nd
2,5-hexanedione	0.4	0.5	1.4	2.0	nd	nd	nd	nd
3-methyl-1,2-cyclopentanedione	1.2	1.1	1.0	0.6	nd	nd	nd	nd
2,3,4-trimethyl-2-cyclopentenone	nd	0.5	nd	0.3	nd	nd	nd	nd
carboxylic acids								
formic acid	0.9	0.5	1.4	1.2	nd	nd	nd	nd
acetic acid	1.6	1.6	2.8	4.3	nd	nd	0.1	nd
lactic acid	0.6	0.5	1.6	1.3	nd	nd	nd	nd
levulinic acid	10.0	9.8	6.0	4.3	nd	nd	nd	nd
furans								
furfural	10.9	3.0	12.4	9.8	nd	nd	nd	nd
5-methyl-2-furaldehyde	1.3	1.0	6.3	6.8	nd	nd	nd	nd
5-hydroxymethylfurfural	1.4	1.1	3.9	2.0	nd	nd	nd	nd
2-ethyl-5-methylfuran	nd	0.2	0.4	0.4	nd	nd	nd	nd
phenols								
phenol	0.2	0.3	nd	2.0	nd	nd	1.3	5.8
catechol	0.4	0.6	1.9	6.7	nd	0.3	14.0	31.8
hydroquinone	1.4	1.6	3.7	4.2	nd	nd	nd	nd
1,2,4-benzentriol	19.5	12.8	2.5	0.3	nd	nd	nd	nd
o-cresol	nd	nd	nd	1.5	nd	nd	1.2	5.1
2-methyl-1,4-benzendiol	nd	nd	1.2	1.8	nd	nd	nd	nd
4-hydroxybenzaldehyde	nd	nd	nd	nd	nd	nd	2.0	2.1
guaiacol	nd	nd	nd	nd	0.6	1.9	19.2	14.1
4-methylguaiacol	nd	nd	nd	nd	nd	nd	0.6	1.3
vanillin	nd	5.9	0.2	3.2	97.1	88.7	53.8	19.2
not identified	32.1	28.6	24.1	20.7	2.3	9.1	7.7	20.6

Glucose is completely converted, producing carbonyls, carboxylic acids, furans and phenols. In subcritical conditions, levulinic acid and 1,2,4-benzentriol are produced in higher amounts than in supercritical conditions. At 400°C, acetone, 2-cyclopentenone and acetic acid are detected in more important quantities. Furfural and 1,2,4-benzentriol proportions decrease when residence time goes up from 30 to 60 minutes, which could indicate that they are intermediate products into the degradation pathway of glucose. These observations are in agreement with conversion pathway proposed in literature [12]. According to Figure 4 (a), dehydration and condensation reactions are favoured in subcritical conditions whereas gasification and carbon backbone cleavages are favoured in supercritical conditions.

For the WS fractions produced from vanillin conversion, Figure 3 shows discrete ESI^+-FTICR/MS spectra, which are completely different when compared to the spectra of glucose products (Figure 2). We can notice that some compounds having higher m/z than vanillin (153 u) have been detected. Nevertheless, molecular weight ranges of vanillin products are narrow when compared to those of glucose products (Table 2).

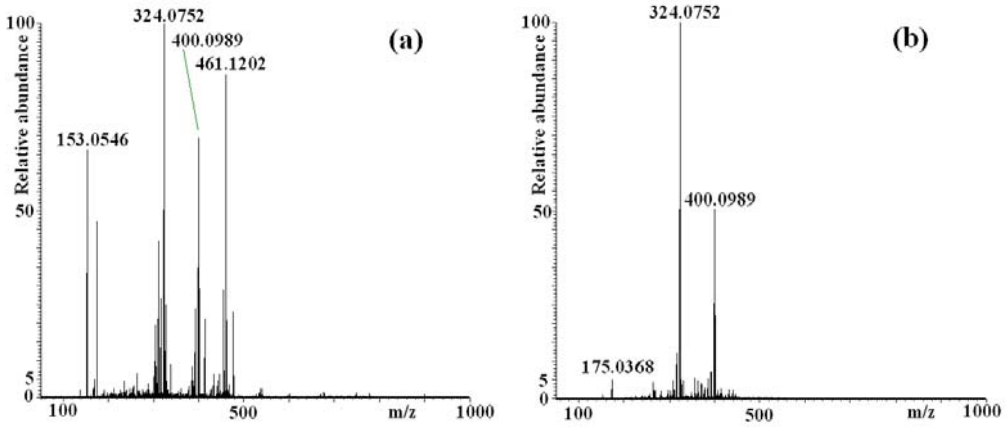

Figure 3: ESI^+-FTICR/MS spectrum of water solutes from vanillin conversion at 25 MPa, 30 minutes, (a) 300°C and (b) 400 °C

As shown in Table 3, vanillin is less reactive than glucose since it is not completely converted. In subcritical conditions, gas product is mainly CO (data not shown) and guaiacol is the main water soluble product. Thus, mainly decarbonylation reaction takes place at 300°C and for a residence time lower than 60 minutes. Moreover, in supercritical conditions, demethoxylation reactions produce phenol and catechol. The degradation pathway of vanillin that can be deduced from these results is shown in Figure 4 (b) and is in agreement with literature data about guaiacol [13] and vanillic acid [14].

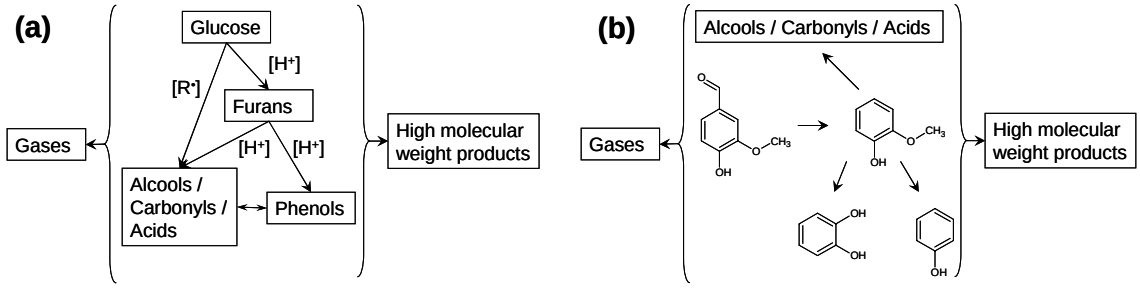

Figure 4: degradation pathway in sub- and supercritical water of (a) glucose [12] and (b) vanillin

CONCLUSION

Conversions of lignocellulosic materials occurring in sub- and supercritical water produce complex mixtures of products whose contents dependent on temperature, and more generally on the properties of the reactional medium. In this work, glucose and vanillin have been chosen as suitable model compounds to represent lignocellulosic biomass. In this work, a very high resolution mass spectrometry technique called FT-ICR/MS has been used to determine the mass molecular ranges of water soluble fractions of the product while gas chromatographic methods provided a molecular description of the chemical composition of those fractions. It has been deduced from the analytical results that glucose and vanillin products conversion come from decomposition and condensation reactions. The degradation pathways that are deduced from the analytical data are in agreement with literature. In the next step of this work, conversions will be carried out using a different way of introduction of starting material. The feed (i.e. aqueous solution of glucose, vanillin and mixture of both) will be directly injected into the hot compressed reactor using a piston injector and sampling will be performed using a sample cell during different residence time. In this case, pressure will be kept constant at 25 MPa through a syringe pump. This procedure is very interesting since starting materials are submitted to very short heating times and very short residence times can be operated. Then, conversion of polymeric lignocellulosic compounds (i.e. lignin, cellulose and biomass) will be studied in the next step of this work to define degradation pathways of lignocellulosic biomass. The multi-technical characterisation approach will be completed using liquid chromatography and spectroscopic techniques to characterize and quantify compounds that are not eluable in gas chromatography.

ACKNOWLEDGMENTS

The project is financially supported by the Enerbio fund of the Tuck foundation. Acknowledgements to IFP GC and MS laboratories teams for their technical support.

REFERENCES:

[1] DUPLAN, J.L. , DUPASSIEUX, N., QUIGNARD, A., CHARON, N., Biofuels by Biomass Pyrolysis Pathway, Gordon Research Conference on ORGANIC GEOCHEMISTRY , Plymouth **2006**
[2] SAKA, W., KONISHI, R., Progress in Thermochemical Biomass Conversion, **2001**, p. 1338
[3] TAKADA, D., EHARA, K., SAKA, S., Journal of Wood Science, Vol.50, **2004**, p. 253
[4] KARAGOZ, S., BHASKAR, T., MUTO, A., SAKATA, Y., Fuel, Vol.84, **2005**, p. 875
[5] YOSHIDA, K., KUSAKI, J., EHARA, K., SAKA, S., Applied Biochemistry and Biotechnology, Vol.123, **2005**, p. 795
[6] LOPPINET-SERANI, A., AYMONIER, C., CANSELL, F., ChemSusChem, Vol.1, **2008**, p. 486
[7] MARSHALL, W., L., FRANCK E., U., Journal of Physical and Chemical Reference Data, Vol.10, **1981**, p. 295
[8] FERNANDEZ, D., P., MULEV, Y., GOODWIN, A., R., H., Levelt Sengers, J., M., H., Journal of Physical and Chemical Reference Data, Vol.24, **1995**, p. 33
[9] AKIYA, N., SAVAGE, P., E., Chemical Reviews, Vol. 102, **2002**, p. 2725
[10] KRUSE, A., DINJUS, E., The Journal of Supercritical Fluids, Vol. 41, **2007**, p. 361
[11] MARSHALL, A., G., HENDRICKSON, C., L., JACKSON, G., S., Mass Spectrometry Reviews, Vol. 17, **1998**, p. 1
[12] KRUSE, A., GAWLIK, A., Industrial & Engineering Chemistry Research, Vol. 42, **2003**, p. 267
[13] LAWSON, J., R., KLEIN, M., T., Industrial & Engineering Chemistry Fundamentals, Vol. 24, **1985**, p. 203
[14] GONZALEZ, G., SALVADO, J., MONTANE, D., The Journal of Supercritical Fluids, Vol. 31, **2004**, p. 57