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PH Effect on Hydrothermolysis of the Carbohydrate Fraction of the Biomass

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Abstract - *We have used Glucose and Cellobiose as a model compounds to study the reactions occurring in the hydrothermolysis of the carbohydrate fraction of the biomass (Cellulose or Hemicellulose). The influence of the PH of the aqueous reactant was discussed.*

Résumé - *Nous avons employé le glucose et la cellobiose en tant que composes d'un modèle pour étudier les réactions se produisant dans l'hydrothermolysis d'une fraction d'hydrate de carbone de la biomasse (cellulose ou hémicellulose). L'influence du PH sur le réactif aqueux a été discutée.*

Key Words: Hydrothermolysis – Biomass – Carbohydrate - Agricultural wastes - Chemical analyses.

1. INTRODUCTION

The formation of fossil resources from biomass is a very slow process, and at present these resources are being depleted a 100000 times faster than they are being formed. The research on biomass energy might therefore be an attractive option for future energy supply [1, 2]. The biomass is the common expression for all green feedstock, than, the overage chemical composition based on dry weight for wood is : 40 - 50 % Cellulose, 20 - 30 % Hemicellulose and 20 - 30 % Lignin [3].

In the figure 1, we indicate the most important processes and techniques applied in the biomass conversion technology : Biological conversion, Gasification and Thermochemical liquefaction (Thermolysis, Pyrolysis and Hydrothermolysis).

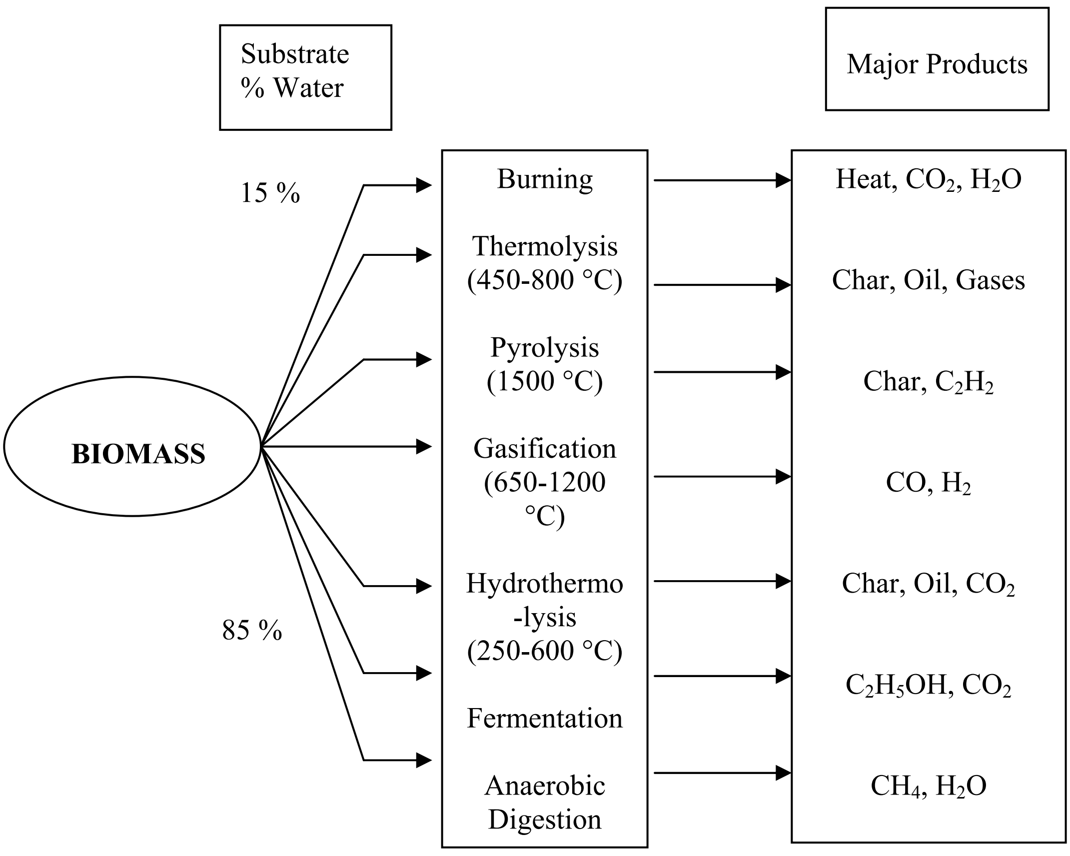


Fig. 1: Biomass conversion process

Lignocellulosic biomass, such as agricultural wastes or wood, can be liquefied using hydrothermal conversion techniques. In contrast to Pyrolysis, no drying of the biomass is required for hydrothermal conversion [4, 5].

The hydrothermolysis technique was required in water at high pressures (5 - 30 MPa) and relatively low temperature (250 - 500 °C). The oil produced by this process has low oxygen content when compared to pyrolytic techniques and this oil is easily separates from water layer.

2. RESULTS AND DISCUSION

A lot of research is directed to carbohydrates because of their ample Availability, easy purification and relatively low price [6, 7]. Thus, the transformations of carbohydrates under hydrothermal conditions has been the subject of numerous studies. Under neutral and acidic conditions, the products 5-hydroxymethyl-2-furaldehyde (HMF), 2-furaldehyde, laevulinic acid and some small aldehydes were formed in the hydrothermolysis of D-xylose, D-fructose, D-galactose, D-mannose and D-glucose [8 - 11].

We have used mono and di–sacharides : glucose 1 and cellobiose 2 (Fig. 2), as a model compounds to study the reactions occurring in the hydrothermolysis of the carbohydrate fraction of the biomass (cellulose or hemicellulose)

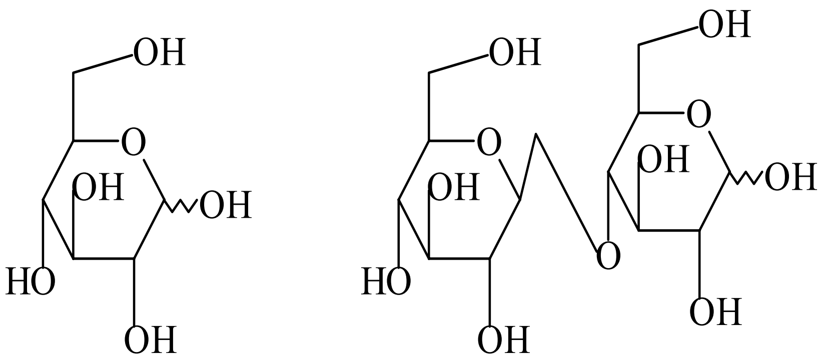
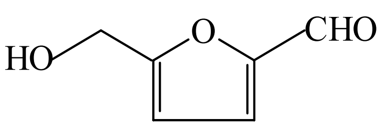


Fig. 2: Starting materials Glucose 1 and Cellobiose 2

The major products identified and quantified in the hydrothermolysis of D-glucose 1 and cellobiose 2 are laevulinic acid 6, Dihydroxyacetone 7, glycolic acid 8, acetic acid 9 and formic acid 10 (Fig. 3). The influence of the PH was considerably observed in the hydrothermolysis of glucose and cellobiose, thus, under alkaline conditions NaOH (0.01 M) the formation of products HMF 3, 2–furaldehyde 4 and Hydroxyhydroquinone 5, were considerably inhibited. Contrary to the formation of carbon dioxide (CO_2) and carbon monoxide (CO) was increased (Table 1).



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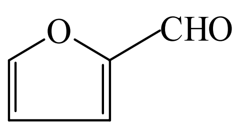

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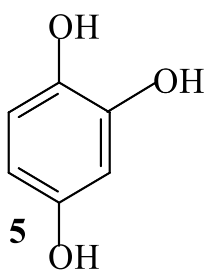

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$MeCO(CH_2)_2COOH$

6

$(HOCH_2)_2CO$

7

$HOCH_2COOH$

8

CH_3COOH

9

HCOOH

10

Fig. 3: Identified Compounds in hydrothermolysis of Glucose 1 and Cellobiose 2

Table 1: Influence of the basic PH on the formation of the product's hydrothermolysis

	Glucose 1		**Cellobiose 2**	
Conditions	**H_2O**	**NaOH**	**H_2O**	**NaOH**
Conversion (%)	98	100	97	100
Compounds Obtained (Yield %)	(%)	(%)	(%)	(%)
5 (hydroxymethyl)-2-furfural (HMF) **3**	8.6	-	10.2	-
2–furaldehyde **4**	3.5	-	7.2	-
Hydroxyhydroquinone **5**	3.8	-	2.0	-
Laevulinic acid **6**	10.3	14.0	16.5	28.4
Dihydroxyacetone **7**	25.0	31.2	21.3	26.8
Glycolic acid **8**	33.5	27.1	37.1	27.6
Acetic acid **9**	9.7	12.5	7.4	11.2
Formic acid **10**	12.0	15.3	14.6	19.4
Gases (H_2, CO, CO_2, CH_4)	19.4	25.0	17.3	26.8

3. EXPERIMENTAL

3.1 Reactions

Hydrothermolysis was performed in a continuous tube reactor (Inox, lengt 270 mm, i.d. 10 mm full - up with morsel of Quartz) designed and built in our laboratory as described previously [12].

The reactant aqueous solution (0.1 M glucose or cellobiose) was heated to 60 °C, and sparged with hélium during 30 mn to remove the oxygen. The aqueous solution was pumped with a peristaltic pump through the preheated reactor (350 °C, fitted with helium (8 l/h)). The hydrothermolysis products were collected in cold trap at - 50 °C (acétone / liquid air).

3.2 Analysis

The reaction mixtures were quantitatively analysed by HPLC (waters porasil 30 cm x 4,6 mm, silice 10µm, eluent hexane/EtOAc (85/15) at 0,5 ml/mn) coupled to differentiel Refractometer Bishoff R.I8110.

GC analyses were performed on OV 225 column using Girdel 300 with FID detection. CG - MS analyses were performed on CP - WAX 52 Capillary column (50 m x 0.25 mm) using Nermag R 10 (EI 70 eV) equipped with Delsi 700 Chromatograph.

Gas formed was analysed in a Propak Q , N or Molecular sieve column as described in [13]. Some samples of the aqueous reaction mixture were extracted with chloroform and EtOAc, afforded a fraction which was analysed by ^{1}H, ^{13}C NMR and IR spectrometer. NMR spectra were recorded with a Bruker AM 200 at 200 MHz for ^{1}H and 50,32 MHz for ^{13}C. IR spectra were recorded with Nicolet 20 SX apparatus.

4. CONCLUSION

The kind and yields of products formed in the hydrothermolysis of D-glucose and cellobiose were significantly influenced by the PH of the aqueous reactant. Small aldehydes and organic acids such as laevulinic, formic, acetic, and glycolic acids, were predominately formed under basic condition. The result of our work gives significant information which can be used for understanding the chemistry of hydrothermolysis of the principal constituent of the biomass : the carbohydrate

REFERENCES

[1] A. Blazej and M. Kosik, "*Phytomass. A raw Materials for Chemistry and Biotechnology*", Ellis Horwood, Chichester, 1993.
[2] G.C.A. Luijks, PhD Thesis, Delft University, The Netherlands, 1994.
[3] E. Sjostrom, "*Wood Chemistry - Fundamentals and Applications*", Academic Press, New York, 1981.
[4] A. Cheriti et A. Babadjamian, SIPE 4, Béchar, 1998.
[5] A. Cheriti et B. Draoui, Journées de Technologie, Ouargla, 1999.
[6] A. Cheriti et A. Kessat, Bull. Un. Phys., Vol. 90, 107, 1996.
[7] R.L. Whistler and M.L. Wolform, "*Methods in Carbohydrate Chemistry*", Vol. 2, Academic Press, New York, 1963.
[8] S. Friedman, H. Ginsberg, I. Wender and P.M. Yavorsky, '3rd Mineral Waste Utilisation Symposium, Chicago, Illinois, 1972.
[9] P.J. Oefner, A.H. Lanziner, G. Bonn and O. Bobleter, Monatsh. Chem., 123, 547, 1992.
[10] K.D. Baugh and P.L. McCarty, Biotechnol. Bioeng., 31, 50, 1988.
[11] M.J. Antal, W.S. Mok and G.N. Richards, Carbohydr. Res., 199, 91, 1990.
[12] J. Afxantidis, Thèse Doctorat, Université Aix - Marseille 3, France, 1993.
[13] N. Bouchry, Thèse Doctorat, Faculté des Sciences El Jadida, Maroc, 1995.