

Steam Treatment of Wood in Close System

B. FDILI ALAOUI,* A. ZERIOUH, and L. BELKBIR

Laboratory of Reactivity of Solid /Gas Systems

Department of Chemistry, Faculty of Science, Universite Mohammed V

AV. Ibn Battouta, B.P. 1014, Rabat, Morocco

The present work consists to determine the reactivity of argania wood after its steam treatment at the temperature T_T in autoclave. The thermogravimetric study in dynamic pyrolysis mode under T_T ($T_T = 153; 169; 200; 236$ and 250°C) and R ($R = 3; 6; 9$ and 12) indicates that the wood present the same type of losses before and after treatment with various intensities. Consequently the light organic materials the quantity of hemicellulose and lignin in this wood are modified by this treatment while the cellulose remains practically intact. Furthermore the observed modifications are due to the action of the saturating water pressure, and not to the applied temperature. The tratment with steam in closed system could be used to modify the composition of argan wood essentially for hemicellulose and lignin constituents.

INTRODUCTION

The wood, as much as biomass, is a complex substance, contains three major macromolecular compounds (hemicellulose, cellulose and lignin)¹. The thermal decomposition of wood produces more volatile matters by depolymerisation and deoxygenation. During these reactions, some condensations and repolymerisations of the intermediate products take place. In order to reduce these undesirable reactions, some methods were applied such as the use of hydrogen. Miller and Fellows² use the phenol like donor solvent of hydrogen in the thermochemical conversion of wood. Generally, during the course of this type of treatment and using different solvents, the solubility of wood is never complete. The literature^{1, 3-6} shows that the residual solid is little studied; it may be of great interest to determine the physical and chemical characteristics by using the thermal analysis techniques.

In this work, we used water as a reactional constituent because it does not provide hydrogen to the reaction and hydrolyses the polysaccharides of elevated mass molar. To the liquid state, the water acted like solvent and vehicle of the constituent of the reaction. It permits also to reduce the polymerisation reactions of some reactive intermediates in the solution⁷. As much as polar solvent, the water reacts with the polar organic constituent produced by the deterioration of wood³.

This study consists of a thermal treatment of argania wood in the closed system

under distilled water. The residual solid will be analyzed by thermogravimetry in order to determine the chemical transformations.

In order to carry out this study, we used a mini-autoclave in stainless steel to support steam pressures. We placed some sealed tubes of pyrex glass containing the reactional mixture (water/wood) (Fig. 1) in the autoclave. The whole experiment was carried out at given temperature T_T obtained by an electric oven. The reaction mixture contained 0.2 g of powder wood [granulometry ($0.125 < G < 0.2$ mm)] and a quantity of distilled water in mass connection R (water/wood) ($R = 3; 6; 9$ and 12). The sealed tubes, placed separately in the autoclave, were carried to different temperatures ($T_T = 153; 169; 200; 236$ and 250°C) for 30 min. After drying the residual solid at 64°C (Figure 2), samples were analyzed by thermogravimetry⁸. This technique is used often in order to determine the changes to phases of a solid/gas system and the kinetic parameters⁹⁻¹¹.

EXPERIMENTAL

In order to prepare the samples, the solid residues of a wood treated in the conditions of the liquefaction of wood in presence of distilled water, we achieved a mini autoclave in rustproof steel (Fig. 1).

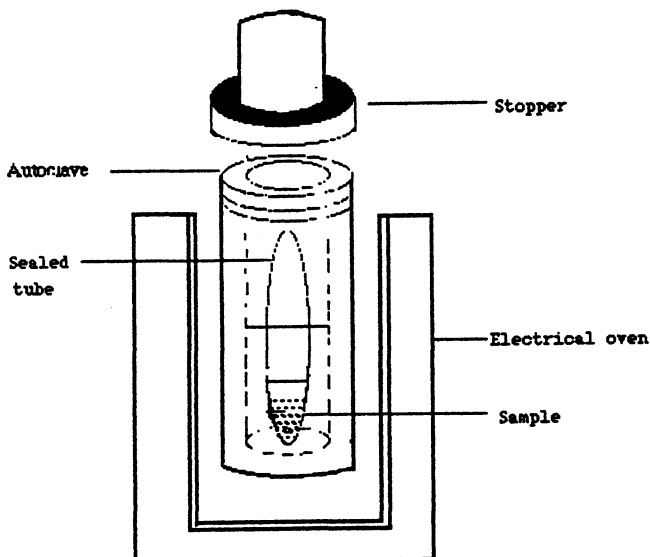


Fig. 1. Mini autoclave for treatment of wood under steam pressure.

This mini autoclave is capable of supporting some high temperatures and pressures achieved tanks to an electric oven and to the evaporation inside the water.

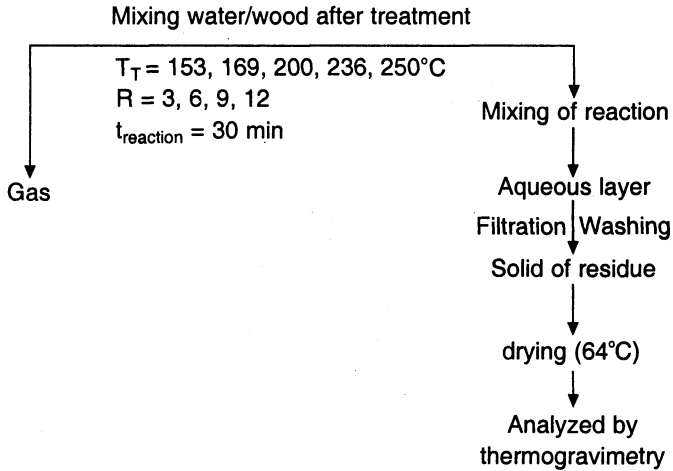


Fig. 2. Process used to obtain residual solid from the wood under steam pressure.

The treatment carries out on some samples of wood of ground argania wood ($0.125 < G < 0.2$ mm). A mass of 0.2 g of wood powder of it, mixed to a variable quantity of distilled water in a connection $R = \text{water/wood}$ ($R = 3; 6; 9$ and 12) is placed in a tube sealed in Pyrex glass. All the sealed tubes are then placed separately in the autoclave in order to be carried to different temperatures ($T_T = 153; 169; 200; 236$ and 250°C) for 30 min. During every treatment, the sealed tube, brought back to the ambient temperature, is opened and the solid residue will have separated from the liquid phase then rinsed to the distilled water. The solid residue is dried at 64°C for 24 h, will be analyzed by thermogravimetry. The diagram of separation of solid some products of reaction mixture is represented in Fig. 2.

RESULTS AND DISCUSSION

In order to determine the characteristics of residual mass of wood treated under high pressure of steam of water in the autoclave, we proceeded the thermogravimetric analysis. The survey of the pyrolysis, in microthermobalance, was achieved on a mass of the order of 5 mg, in dynamic regime to $\beta = 10^\circ\text{C min}^{-1}$ and under an atmosphere of nitrogen of $16 \text{ cm}^3 \text{ min}^{-1}$. The result is represented under shape of loss in weight with $\Delta m = m_0 - m(t)$; m_0 initial mass of the sample and $m(t)$ the mass to a given instant. The curves represent the thermograms of pyrolysis on a dry basis of the argania wood of residual treated to $T_T = 153; 169; 200$ and 250°C ($R = 12$) (Fig. 3) or to $T_T = 169^\circ\text{C}$ ($R = 3; 6; 9$ and 12) (Fig. 4).

According to the pace of these thermograms, one could say that the wood is appreciable to the temperature of treatment but not R . We then determine the evolution of the different constituent matters such as light volatiles and condensable volatile matters with the treatment of wood to T_T .

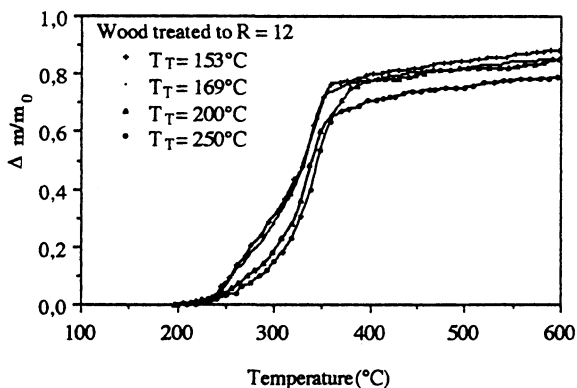


Fig. 3. Thermograms of pyrolysis of treated wood at $T_T = 153; 169; 200$ and 250°C and $R = 12$

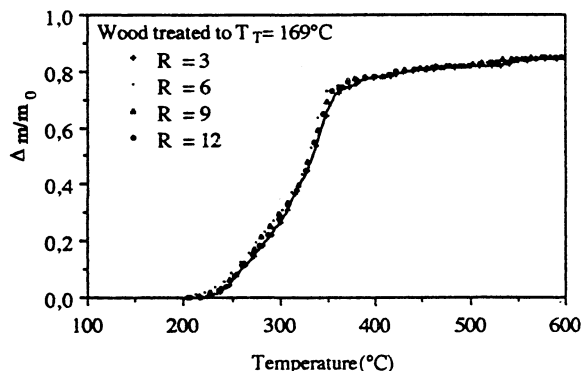


Fig. 4. Thermogram of pyrolysis of treated wood at $T_T = 169^\circ\text{C}$ and $R = 3; 6; 9$ and 12

Study of light volatile matters: Generally the wood decomposition between 50 and 200°C ¹²⁻¹⁵ give water and volatile light matters. In order to study this phenomenon in the solid residue of wood treated to T_T ($T_T = 153; 169; 200; 236$ and 250°C), we represented the mass loss pyrolysis of this material versus of T (Fig. 5).

This study indicates that the loss of the volatile light matters decreases progressively with treatment temperature T_T (Fig. 6).

Taking account of sealed tube volume and of water quantity in the reaction mixture and of temperature T_T , the pressure of steam produced inside is always equal to the saturating pressure. We conclude that the water acted on the constituent of wood by its saturating pressure of steam [$P_e(T_T)$]. In these conditions, the mass losses of treated wood could be interpreted in function of this new variable (Fig. 7).

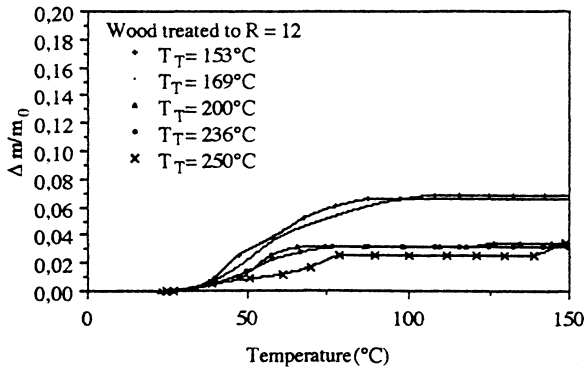


Fig. 5. Weight loss of the residual solid of the treated wood at $T_T = 153; 169; 200; 236$ and 250°C

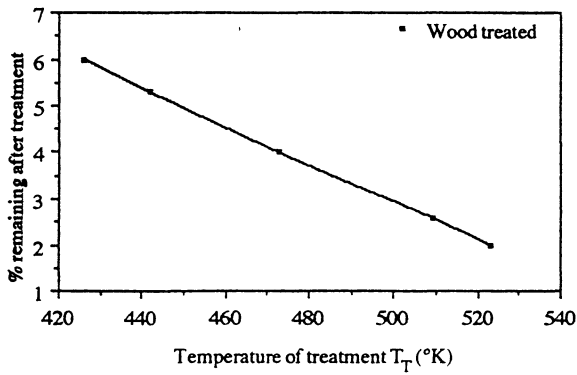


Fig. 6. Rate evolution of humidity and volatile light matters of residual solid of treated wood at the temperature T_T .

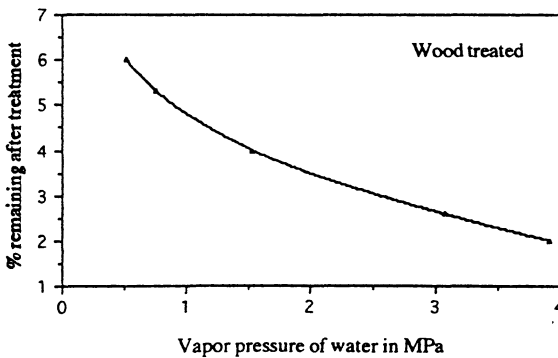


Fig. 7. Relation between weight losses on the volatile light matters of treated wood and the saturating pressure steam.

The thermodynamical relation between P_e and T can be represented as:

$$P_e(T) = e^{-\Delta G/RT} \quad \text{then} \quad \frac{\Delta m}{m_0} = e^{-\Delta G/RT}$$

with ΔG free energy of the reaction and $\Delta m/m_0 = -aT + b$ (Figure 6) or $T = (-\Delta m/m_0 + b)/a$.

Then

$$P_e(T) = \exp\left(\frac{-a\Delta G}{R\left(-\frac{\Delta m}{m_0} + b\right)}\right)$$

or

$$\log P_e(T) = \frac{-a\Delta G}{2.3R\left(-\frac{\Delta m}{m_0} + b\right)}$$

with

$$\Delta G = \Delta H - T\Delta S$$

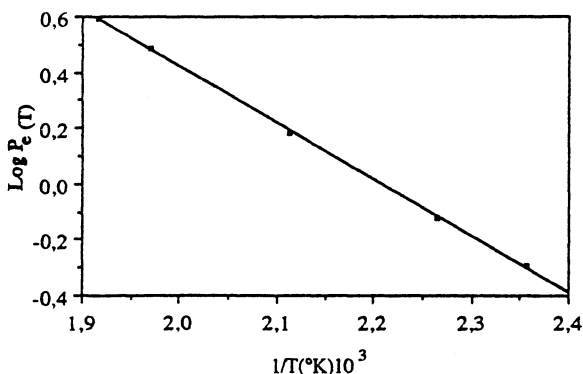


Fig. 8. Residual thermograms of the treated wood at $T_T = 153; 169; 200; 236$ and 250°C

The expression of $\log P_e(T)$ allows to determine ΔH and ΔS of the reaction between the steam and the wood in the mentioned conditions (Figure 8). The obtained straight line gives $\Delta H = 9.32$ kcal/mol and $\Delta S = 20.6$ cal/mol. These thermodynamic values differ from those of the water evaporation in the same conditions ($\Delta H = 13.7$ kcal/mol and $\Delta S = 39.3$ cal/mol). In the light of these results we can conclude that the volatile light matters are essentially formed by the organic matters.

Study of the condensable volatile matters: Since the wood contains three main constituents (hemicellulose, cellulose and lignin), we have then to determine their evolution. Knowing the chemical structures and reactivity of these polymeric constituents are different¹⁶⁻¹⁸, we can then study their evolution in the residual solid of treated wood vs. T_T .

A set of pyrolysis experiments, achieved on the treated wood at $T_T = 153; 200$ and 250°C , shows that the reactivity of the principal constituents is different (Figure 9) in spite of their association (wood).

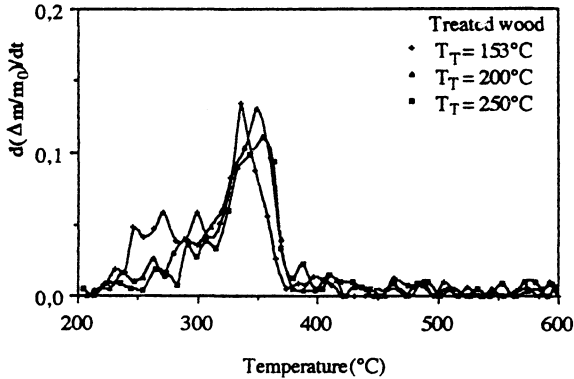


Fig. 9. Instantaneous rate of the residual solid pyrolysis at $T_T = 153, 200$ and 250°C , and $R = 9$

From the derivative weight loss curves vs. the temperature, we conclude that the thermal treatment to T_T concerns mainly the lignin and the hemicellulose decomposition but the cellulose remains intact. The quantity of these constituents (hemicellulose and lignin) decreases progressively when the temperature increases and influence the reactivity of cellulose. The residue appears progressively to take place in temperature intervals $325\text{--}375^\circ\text{C}$ as mentioned in the literature^{19, 20}.

According to the literature, the thermal deterioration of some hemicellulose produce to low temperature ($180\text{--}280^\circ\text{C}$) besides they are soluble in the bases and same in the water for some hemicellulose of foliate. They are easily hydrolysable by the acids. These chemical properties proceed of their amorphous structure who confers them a high reactivity in comparison with the one of the cellulose. This is characterized by thermal stability who is bound to the narrow association of its polymerized glycosidical chains by some hydrogen linkages. Therefore, the deterioration takes place in two stages which concern the decomposition of the amorphous cellulose ($T < 300^\circ\text{C}$) and the pure cellulose perfectly crystallized ($325\text{--}375^\circ\text{C}$). The thermal stability of pure cellulose is due to the position of the reactive groupings when they are located to the interior of crystallized phase. In this case, same solvents and the water can't penetrate in its structure (Fig. 9).

Conclusion

We conclude that the steam vapour treatment of the arganier wood in a closed system at different temperatures, modifies its composition, in volatile light matters, in hemicellulose and in lignin. On the other hand, the amorphous cellulose is affected whereas the crystallized cellulose remains intact. This technique could be used in order to isolate the cellulose from this species of wood.

REFERENCES

1. T. Ogo and S. Yokoyama, *J. Japan Petrol. Inst.*, **36**, 73 (1993).
2. I.J. Miller and S.K. Fellows, *Nature*, **289**, 398 (1982).
3. T. Ogi, S. Yokoyama and K. Koguchi, *J. Japan Petrol. Inst.*, **28**, 239 (1985).
4. T. Ogi, S. Yokoyama, T. Minowa and Y. Dote, *J. Japan Petrol. Inst.*, **33**, 383 (1990).
5. T. Ogi, S. Yokoyama, K. Koguchi and T. Minowa, *J. Japan Petrol. Inst.*, **32**, 21 (1989).
6. S. Yokoyama, T. Ogi, K. Koguchi, M. Murakami and A. Suzuki, *J. Japan Petrol. Inst.*, **29**, 262 (1986).
7. J. Reningovolo, thèse de 3ème cycle, Université de Nancy, 1 (1988).
8. A. Zeriouh and L. Belkbir, *Thermochim. Acta*, **258**, 243 (1995).
9. S.S. Alves and J.L. Figueiredo, *J. Anal. Appl. Pyrolysis*, **13**, 123 (1988).
10. R. Bilbao, A. Millera and J. Arauzo, *Thermochim. Acta*, **165**, 103 (1990).
11. E. Khamlich, Thèse de 3ème cycle, Université de Rabat (1994).
12. A. Zeriouh, M. Boumahaza and L. Belkbir, First International Thermal Energy Congress Proceedings, (2), p. 793 (1993).
13. A. Zeriouh and L. Belkbir, *Thermochim. Acta*, **258**, 244 (1995).
14. ————, *Thermochim. Acta*, **287**, 293 (1996).
15. ————, 26ème Congrès International des techniques de Microbalances, Marrakech (Maroc), 18 (April 1995).
16. F. Kifani-Sahban, L. Belkbir and A. Zoulalian, *Thermochim. Acta*, **284**, 341 (1996).
17. A. Zeriouh and L. Belkbir, 26ème Cong. Int. des Tech. de Microbalances, Marrakech (Maroc), 258 (April 1995).
18. F. Shafizadeh, *J. Anal. Appl. Pyrol.*, **3**, 283 (1982).
19. E.J. Soltes and T.J. Elder, Pyrolysis, Chapter 5, p. 63 (1982).
20. F. Shafizadeh and P.S. Chin, Proc. 172nd Nat. ACS Meet., Am. Chem. Soc., Washington, USA (1976).

(Received: 9 August 2000; Accepted: 1 November 2000)

AJC-2146