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Influence of Certain Metallic Cations on the Pyrolysis of the Arganian Tree

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The study carried out essentially by the thermogravimetric analysis in a dynamic pattern has allowed us to highlight some properties, particularly the thermic behaviour of the arganian tree wood with some metallic cations, which show a great influence over the rate of the pyrolysis reaction.

INTRODUCTION

To increase the pyrolysis reactivity of the wood of the arganian tree, we studied the thermic behaviour of the reaction in presence of a number of metallic cations, such as Fe, Co, Zn and Cu, associated with a single anionic grouping SO_4^{2-}. This study was already conducted by Akira Tomita *et al.*[1]. They studied the pyrolysis of coal in presence of the following cations: K, Ba, Ni and Fe and observed that the reaction is very much influenced in presence of such cations. The same scientists[2] studied the behaviour of nickel in steam gasification of coal and observed that this cation has an effect on the products from the reaction. Another technique was also explored by Takayoki and others[3] by impregnating two different types of coal with potassium in the form of KCl salt; the exploration showed that the presence of potassium had modified the reactivity of one of the two examined types of coal. The study was also carried out by other scientists, in particular the gasification of carbon with a mixture of carbon dioxide and carbon monoxide in presence of some cations (Na, K and Cs) as catalysts by Cerfontain *et al.*[4] who observed that the presence of these elements increases the chemisorption rate of CO_2 on carbon. Li Jian *et al.*[5], for their part, examined the same reaction in presence of sodium carbonate and found that the presence of sodium increases the specific area of coal. For our part, we studied the pyrolysis of the arganian wood, in presence of catalysts, *via* thermobalance analysis in a dynamic regime and under nitrogen atmosphere[6,7]. We used a thermobalance of Mac Bain and Bakr type[8,9].

EXPERIMENTAL

To associate the metallic cation and wood, we used the technique consisting of impregnating the wood with aqueous solutions having the same concentration in metal ion. The salts were dissolved in distilled water in proportions for obtaining saline solutions with the same concentration [M^{2+} (0.1 M)]. We then took a series of identical samples of sawdust having the same mass (0.2 g). They were placed successively in a system that allowed to shake them consistently at constant rotation speed. The saline solution was added drop by drop on each sample using a syringe during its 15 min shaking.The samples then were dried in an incubator at 50°C for 24 h before examination. Finally, the samples were pyrolysed in a dynamic regime under nitrogen atomosphere with a constant gas flow (15 cc/min) and 15°C/min heating speed.

RESULTS AND DISCUSSION

The results of the study show that the pyrolysis reaction of the arganian tree is very much influenced by the presence of transition metal cations as evidenced by Figs. 1–4. All the figures reflect the trend of progress degree α according to the temperature of two samples of wood of the arganian tree, the first of which was processed without cation and the second was processed in presence of a metallic cation used as a catalyst, with

$$\alpha = \frac{m_0 - m}{m_0 - m_f}$$

where m_0 = initial mass of the sample,

m = mass of the sample at temperature T,

m_f = mass of the sample at the end of the reaction.

Figure 1 shows that the pyrolysis reaction is influenced by the presence of the iron cation. On the one hand we observe, with a temperature between 200°C and 250°C, that iron has almost no influence on the reaction. Thus, we can say that it does not affect the decomposition of light materials and of hemicellulose, which decomposes within a temperature range from 200°C to 270°C. Above this temperature, the presence of iron activates the pyrolysis reaction and activation continues until the organic material is completely decomposed, that is, at a temperature near 370°C. We can say that first, iron affects the decomposition of cellulose and lignin which deteriorates after hemicellulose, and secondly, it activates the decomposition of heavy material or tar which deteriorate after organic materials, and this results in smaller quantity of coal produced (Table-1).

TABLE-1
THE PERCENTAGES OF ORGANIC MATERIALS AND COAL IN WOOD SAMPLE IMPREGNATED WITH METALLIC CATIONS

Sample	Organic materials (%)	Coal (%)
Without cation	83.3	16.7
Fe	84.1	15.9
Co	83.6	16.4
Zn	83.8	16.2
Cu	83.7	16.3

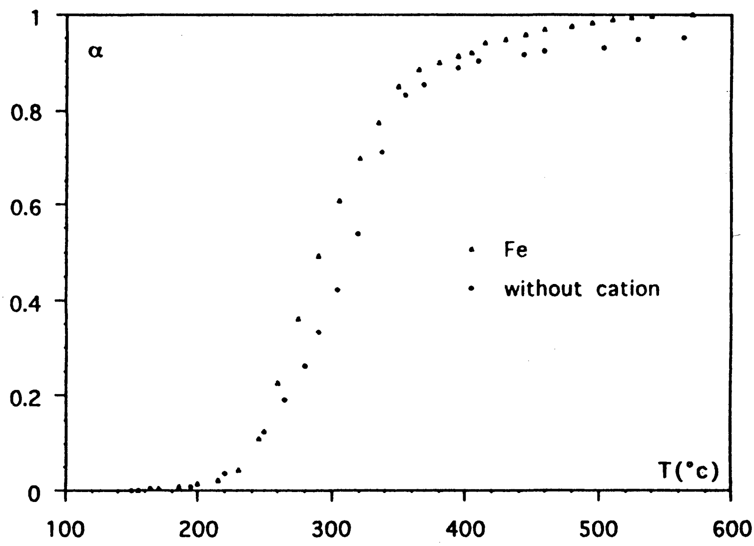

Fig. 1. Influence of iron on the pyrolysis of arganian tree wood

Figure 2 shows that the wood pyrolysis reaction is also influenced by the presence of cobalt even more than by iron. The curve shows a small deviation for temperatures ranging from 200°C to 250°C. So we can say that the presence of cobalt hardly causes the disappearance of light materials and hemicellulose. But from 250°C the reaction speed increases considerably. As an example, at 300°C temperature, we have a 0.35 rate for the sample without cation, compared to a 0.6 rate at the same temperature for the sample impregnated with cobalt.

Figure 3, the case of zinc, shows that this cation strongly affects the entire pyrolysis reaction, that is from disappearance of light materials until formation of coal. We also observed that this cation has a strong influence on the decomposition of the organic materials, *i.e.*, that of the three components of wood: hemicellulose, cellulose, lignin, a stronger influence than on the decomposition of light materials and tars.

Copper, as shown in Fig. 4, has a particular influence. On the one hand at temperatures ranging from 200°C to 270°C, it increases considerably the reacton speed, more than all other cations do (Fig. 5). But from 270°C we can observe a small deviation of the curve. So we can say that the copper cation activates the decomposition of light materials and hemicellulose and deactivates that of cellulose and lignin.

Conclusion

The study of the influence of transition metal cations on the pyrolysis reaction of the arganian tree wood showed that the reaction is very much affected by their presence in the following order: Cu > Zn > Co > Fe. But it should also be noted that each cation has a specific behaviour. Copper, in particular, has the special effect of activating significantly the volatilization of light materials and the decomposition of hemicellulose and deactivating that of cellulose and lignin.

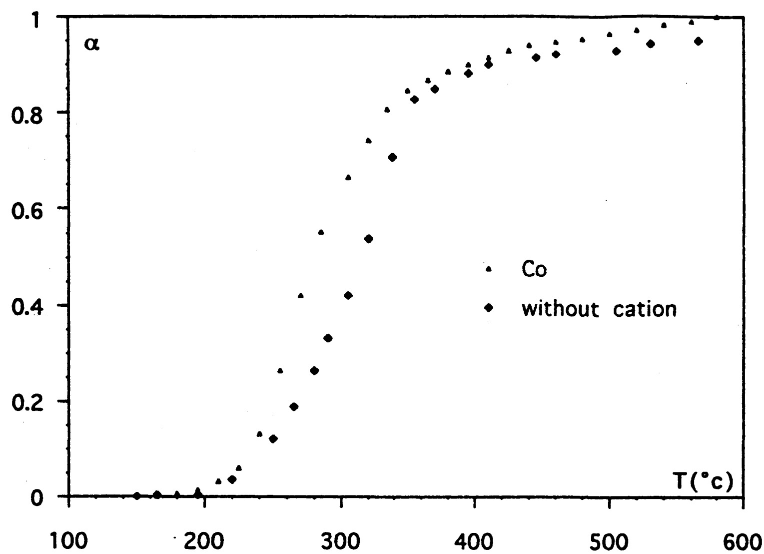

Fig. 2 Influence of cobalt on the pyrolysis of arganian tree wood

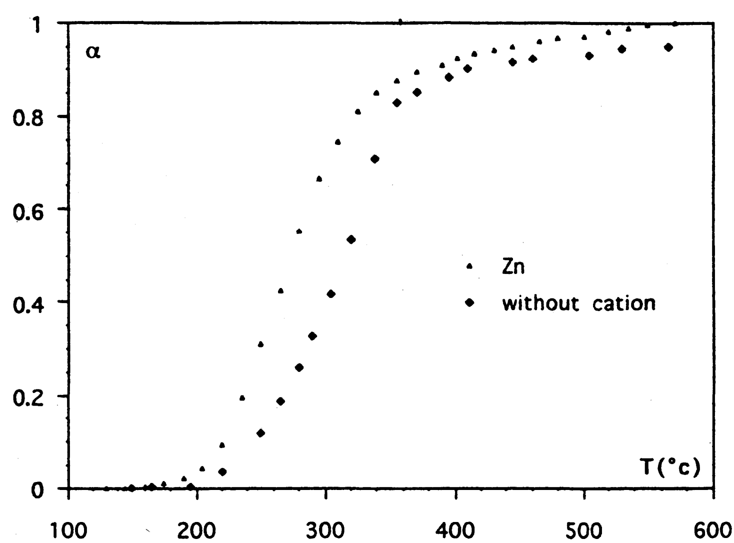

Fig. 3 Influence of zinc on the pyrolysis of arganian tree wood

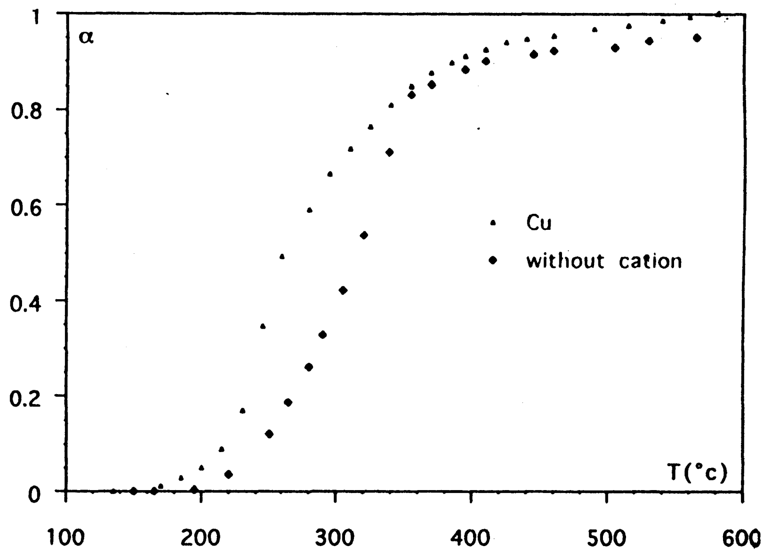

Fig. 4 Influence of copper on the pyrolysis of arganian tree wood

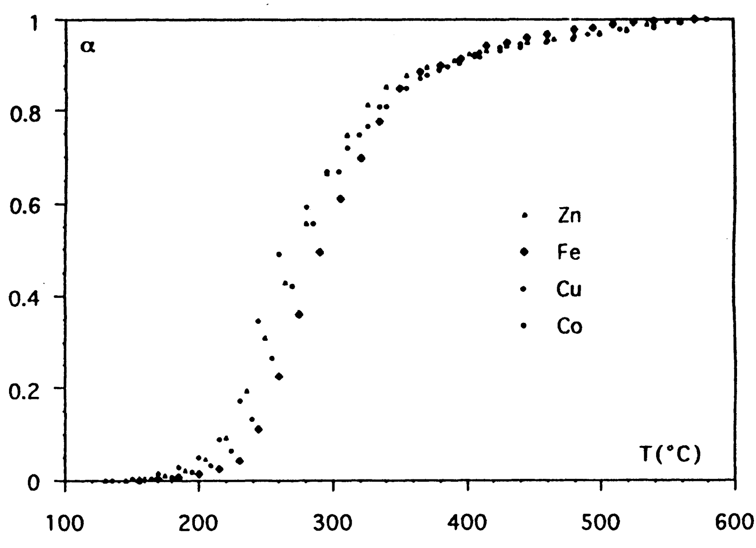

Fig. 5 Scheme representing the effect of four cations on the pyrolysis of arganian tree wood.

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