

KINETIC STUDIES ON THERMAL DEGRADATION OF NONWOOD PLANTS

*Mamdouh M. Nassar*¹

Department of Chemical Engineering, Technical University of Nova Scotia
P.O. Box 1000, Halifax, N.S., Canada B3J 2X4

(Received December 1983)

ABSTRACT

Thermal analysis of nonwood plants (bagasse, rice straw, and rice hulls) was carried by using differential thermal (DT) and thermogravimetric (TG) analysis under oxidizing and inert atmospheres. Degradation patterns were different, depending on the kind of material and on the pyrolytic atmosphere. Thermal curves of rice straw and hulls were very similar, but bagasse showed a different curve. Degradation of bagasse is similar to hardwood. The rate of thermal degradation of nonwood plants is faster than wood because of their porous structure. Kinetic studies were based on weight loss obtained from TG analysis. A dual mechanism concept, similar to wood, was found for nonwood plants. Two values of activation energy were obtained with a transition temperature at 335 C. Rice straw and hulls have low values of activation energy due to their porous structure and presence of high percentage of silica, while activation energies of bagasse are close to that of hardwood. The presence of inorganic impurities in the cellulosic material has an effect on the kinetics of thermal decomposition.

Keywords: Bagasse, rice straw, rice hulls, pyrolysis, combustion, TGA, DTA.

INTRODUCTION

Biomass products from nonwood plant may provide a means of an appropriate renewable energy source. They include bagasse, wheat straw, cereal straw, rice straw and hulls, bamboo, cotton stalks, peanut and coconut shells, wastes from fruit and vegetables, etc. Some of these have industrial utilization, such as rice hulls and bagasse in combustion to liberate energy. The nonwood plants are cellulosic material; their potential as an energy source is high (Beagle 1978; Govil 1960; Bhusha 1977; Naffziger 1960; Nassar 1979; Stout and Loudon 1977) (Table 1) either directly as fuel by combustion or to produce char or gaseous and liquid products. One advantage of nonwoody and woody material as a fuel is the low sulfur content in comparison with most fossil fuels.

An understanding of the thermal degradation characteristics of nonwood plants can help in developing and implementing methods to improve another source of energy; this is the first aim of the present work. The second aim is to understand the influence of impurities (mainly silica, which appeared as ash after combustion) on the kinetics of thermal degradation of the cellulosic material.

EXPERIMENTAL WORK

Air-dried Egyptian bagasse, rice straw, and rice hulls were chopped and screened. The fraction 18/20 mesh number was used for the thermal studies.

Thermograms were obtained using a CST Stona Premco Model 202 differential thermal analysis (DTA) and Model 1050 gravimetric thermal analysis (TGA) with

¹ Permanent address: Faculty of Engineering, Department of Chemical Engineering, Minia University, El-Minia, Egypt.

TABLE 1. *Energy content and chemical composition of some plant biomass.*

Plant	Plant residue	Moisture (%)	Chemical composition (2)				Ash	Silica in ash	Calorific value, kcal/kg
			Cellulose	Pentosans	Lignin				
Sugar cane	bagasse (Rydholm 1967)	10	33.6	29.0	18.5	2.3	—	4041 (Nassar 1979)	
Sugar cane	bagasse	50	—	—	—	—	—	2220 (Nassar 1979)	
Rice	straw (Rydholm 1967)	9	28.1	26.5	12.5	18.1	90	3350 (Nassar 1979)	
Rice	hulls (Beagle 1978)	9	28.0	26.1	12.6	19.0	90	3290 (Nassar 1979)	
Wheat	straw (Rydholm 1967)	10	42.0	24.6	22.0	1.6	3	4305 (Stout and Loudon 1977)	
Peanut	shell (Govil 1960)	10	36.6	19.4	33.4	4.6	15	4015 (Nassar 1979)	
Coconut	shell (Bhusha 1977)	13	35.0	29.0	28.0	1.3	—	4196 (Stout and Loudon 1977)	
Bamboo	Cane (Naffziger, Matuszowski, Clark and Wolf 1960)	10	34.8	28.5	23.0	2.3	0.14*	4106 (Stout and Loudon 1977)	
Birch	wood (Rydholm 1967)	12	39.4	21.4	21.0	0.4	2	3986 (Stout and Loudon 1977)	
Pine	wood (Rydholm 1967)	12	39.1	9.0	29.0	0.3	2	4416 (Stout and Loudon 1977)	

* Based on original material.

temperature programmed at 5 C/min heating rate, from room temperature to 800 C. Helium gas was used as an inert medium and air as an oxidizing medium during the thermal analysis; the flow rate was 0.025 ft²/h at atmospheric pressure. The amount of material used was 18 mg. The reference material was aluminum oxide.

The off gases, in separate experiments, at temperatures 100, 200, 300, 400, 500 and 600 C were analyzed for carbohydrate using a gas chromatograph, CARLE Model 211-253-A, Series SX.

DISCUSSION

Nonwood plants as cellulosic material have a chemical composition comparatively rich in carbohydrate and fairly low in lignin compared to wood, as shown in Table 1. However, nonwood plants resemble hardwood in chemical composition more than they do softwood. Most of the nonwood plants are characterized by a porous structure and high ash content, which is mainly silica, as in rice straw and hulls.

Thermal analysis of nonwood plants (rice straw, rice hulls, and bagasse) heated dynamically at a rate of 5 C/min reveals distinct differences between oxidation

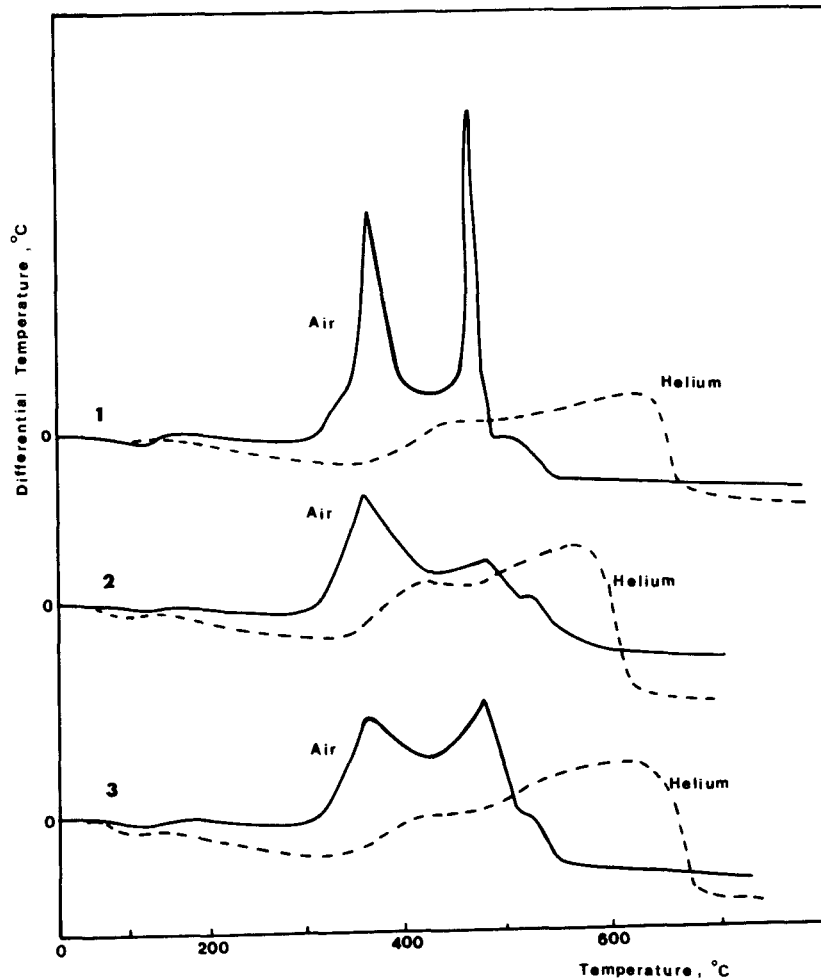


FIG. 1. DTA thermograms for nonwoody materials under oxidized and inert atmosphere.

and inert conditions as shown in Figs. 1–4. The first endothermic reaction occurred between room temperature and about 200 C, with a nadir at about 125 C. Above 200 C active pyrolysis takes place. In a helium atmosphere, a large exotherm starts at about 300 C and ends at about 600 C. In air, strong exothermic reaction begins at about 280 C and ends at about 520 C. This exotherm is interrupted by an endotherm, centered at about 420 C. In the combustion of cellulosic material (Tang 1967; Amyl 1961), the endotherm can be attributed to the formation and evaporation of volatile products. The exotherm is divided into two peaks; the first peak is due to the oxidation of these products, and the second peak represents the oxidation of charred residue. It is of interest to note that during the combustion of the three nonwood plants, the first exothermic peak is sharp at a temperature of 350 C. The second peak appeared at 460 C for bagasse and at a somewhat higher temperature (475 C) for both rice straw and rice hulls.

In general, thermal decomposition of nonwood plants in air appears to begin

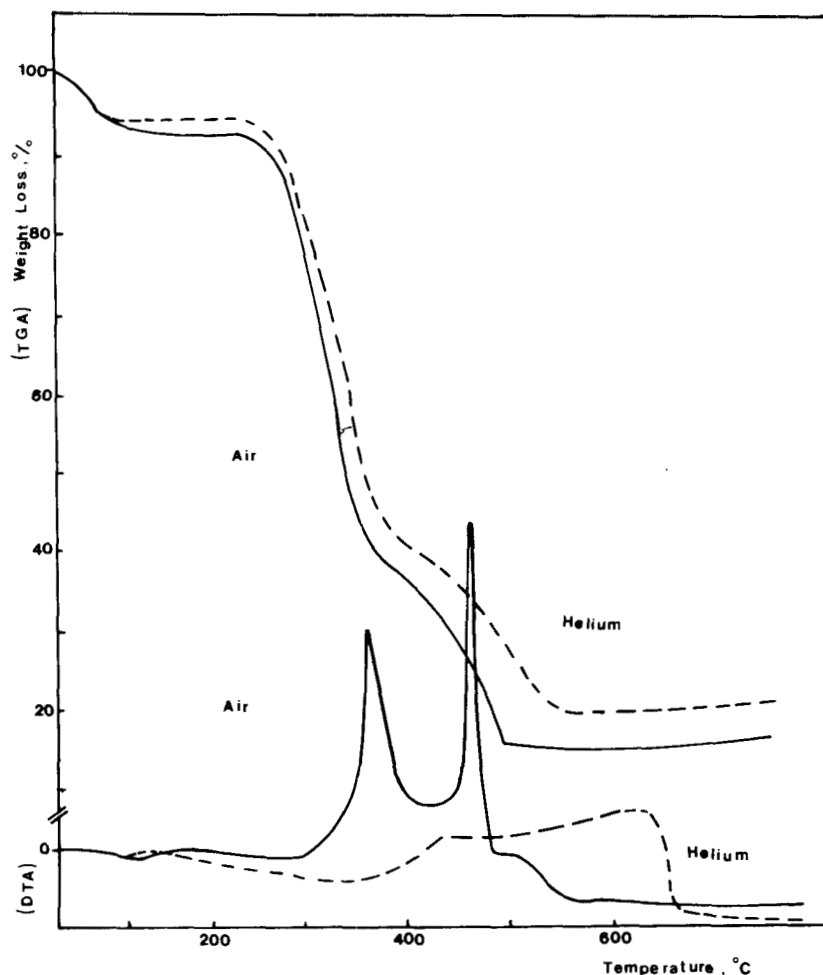


FIG. 2. DTA and TGA thermograms for bagasse under oxidized and inert atmosphere.

at lower temperatures than in inert gas. The pyrolysis reaction is not strongly exothermic, and it must be overpowered by oxidation before heat is evolved.

The rather shallow nature of the exothermic peak of the DTA curve for rice straw and rice hulls compared to that of bagasse may consequently reflect the effect of silica in the rice straw and hulls. Thermal decomposition of bagasse is similar to hardwood. Hardwood has two exothermic peaks at 330 and 450 C temperature range (Heinrich and Krischer 1962) which coincide with that of bagasse. This is due to the similarity in chemical composition (Table 1).

For more meaningful interpretation of the DTA data obtained on combustion and pyrolysis of nonwood plants, it is desirable to expand the comparison to include the TGA data. The TGA curves of pyrolysis and combustion are similar; therefore TGA pyrolysis curves will be considered in more detail.

At 100 to 200 C nonwood plants exhibited a small weight loss; the reaction took place endothermally by DTA. The TGA weight loss ranges between 6 to 7%

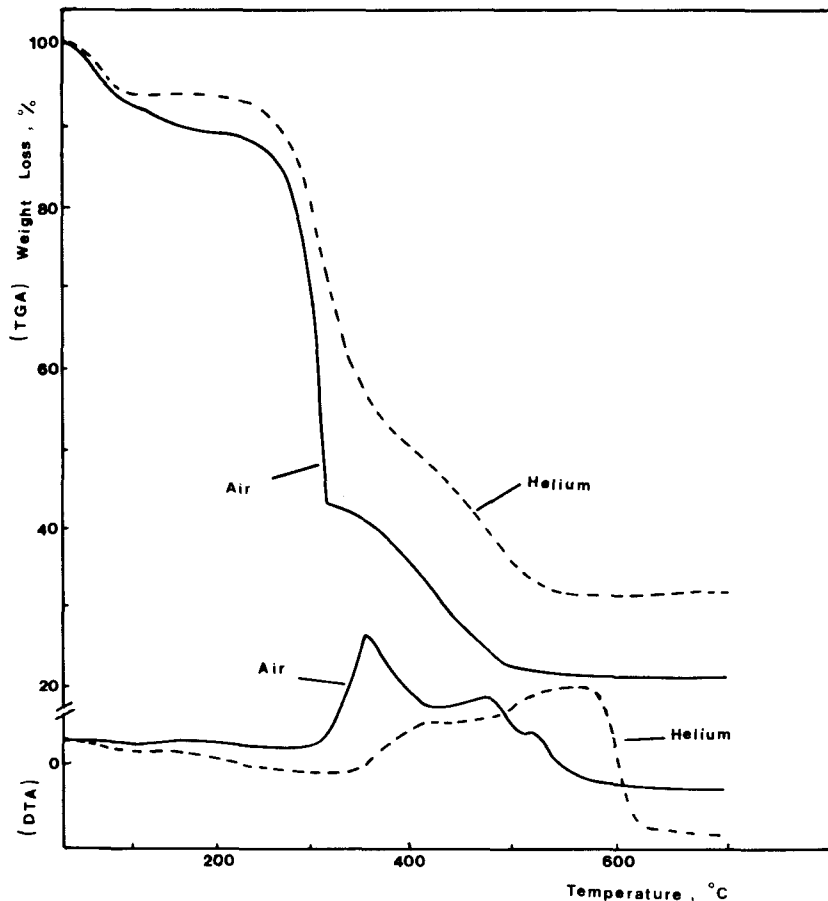


FIG. 3. DTA and TGA thermograms for rice straw under oxidized and inert atmosphere.

in inert atmosphere, as shown in Figs. 1–4. Gas analysis in an inert atmosphere showed traces of carbohydrates, 0.01 to 0.05% mole (Fig. 5); the loss in weight at this temperature range is probably due to moisture.

Combustion of volatiles takes place exothermally by DTA between 200 and 350 C in an oxidized atmosphere. The rate of weight loss by TGA reached its maximum at this temperature range; weight loss of rice hulls is about 40% and for rice straw and bagasse is about 50% (excluding the initial moisture). The weight loss for hardwood, at this temperature range, is also 50% (Horowitz and Metzger 1963); this could mean that the weight loss is due mainly to decomposition of cellulose. Analysis of the off gases in Fig. 5 showed that carbohydrates reached a peak at a temperature of 400 C, indicating the pyrolysis of cellulose. Near 450 C, the pyrolytic endotherm and the weight loss indicated that active pyrolysis with the evolution of flammable compounds was almost completed. Gas analysis confirms this observation. Carbohydrates in the pyrolyzed gas was diminished after 500 C, indicating the end of the thermal decomposition of the cellulosic materials.

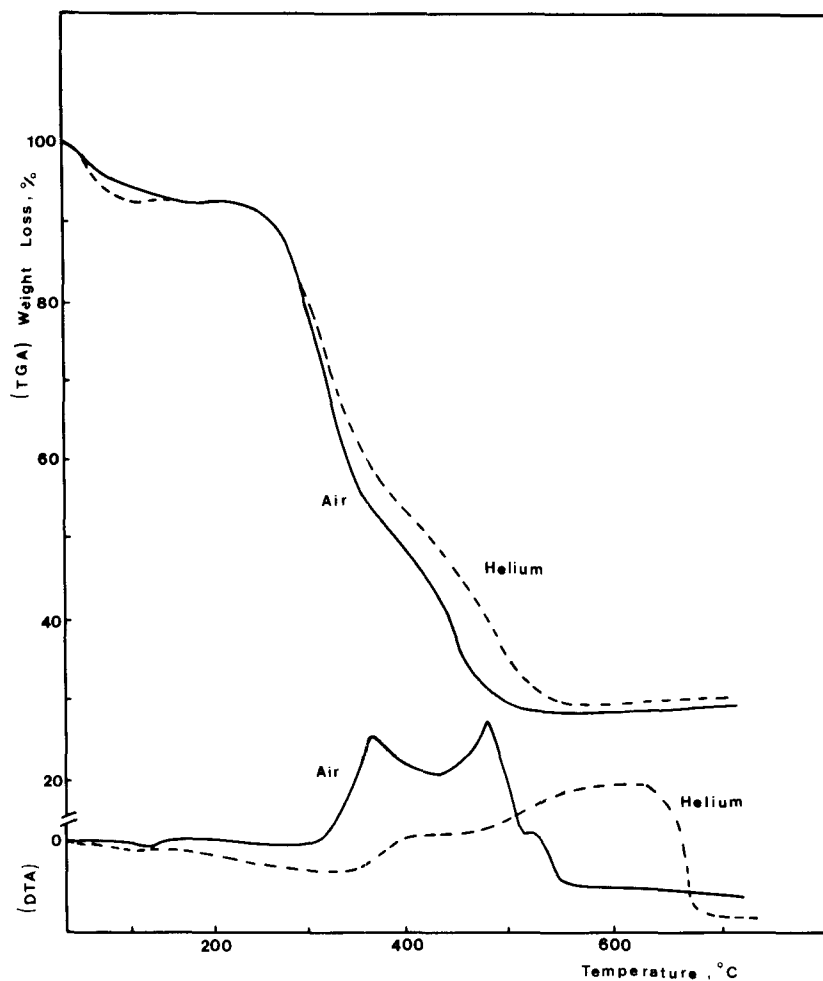


FIG. 4. DTA and TGA thermograms for rice hulls under oxidized and inert atmosphere.

During combustion, an exothermic reaction continued as a second peak in DTA because of the char being consumed by glowing at about 470 C. The TGA combustion curves showed 21% residue for rice straw, 28% residue for rice hulls, and 14% residue for bagasse. This compares to hardwood, forming 17% residue at 450 C (Heinrich and Krischer 1962), which is closer in residue to bagasse than rice straw and hulls. The higher percentage of residue in rice straw and hulls is due to the higher silica in the raw material (Rydholm 1967; Beagle 1978).

Kinetic studies were based on the weight loss data obtained in the TGA. The activation energy has been evaluated by applying Farmer's (1963) method of analysis. For pseudohomogeneous kinetics, the irreversible rate of conversion of the weight fraction of reactant may be expressed by the following equation (at a constant temperature):

$$dw/dt = KW^n \quad (1)$$

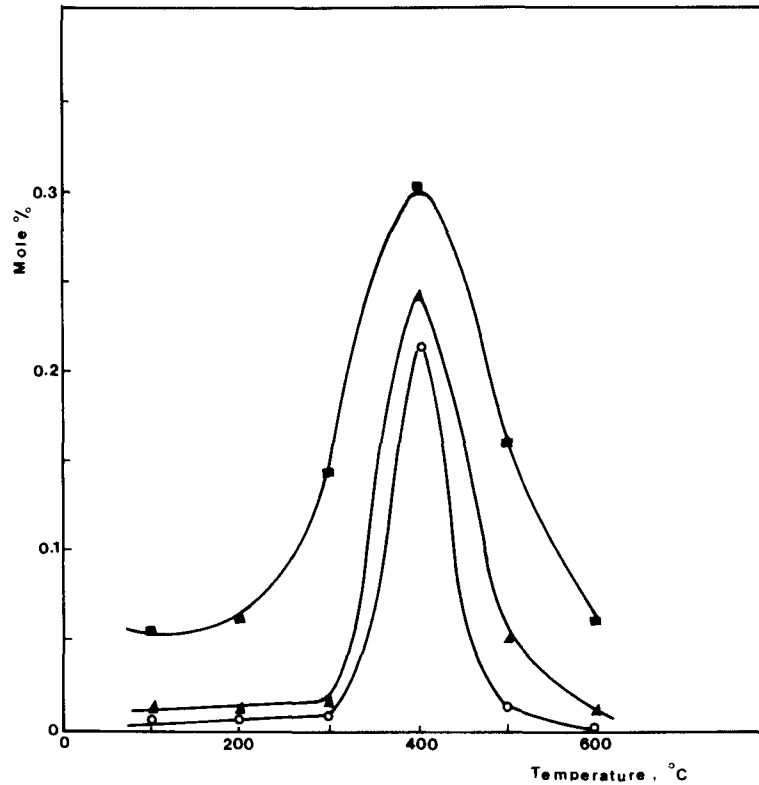


FIG. 5. Mole % of carbohydrates at different temperatures; bagasse (■), rice hulls (▲) and rice straw (○).

According to the work on wood (Tang 1967), pseudo first order reaction can be assumed. The temperature difference of K is generally expressed as the Arrhenius equation:

$$K = Ae^{-E/RT} \quad (2)$$

For calculating activation energy (combining Eqs. 1 and 2 and rearranging after taking the logarithm) Eq. 3 was used

$$\ln(-dw/dt) = \ln A - E/RT \quad (3)$$

Results of activation energy in Table 2 reveal that a two-step decomposition was found to occur in thermal decomposition of nonwood plants as that in wood (Akita 1959; Stamm 1956). On the basis of the activation energy data shown in Table 2, and according to the findings on wood, evidence is given of an expected alteration in kinetics on passing from slow decomposition below the exothermic region to fast decomposition above it.

The computed activation energies are nearly the same for rice straw and rice hulls (Table 2). This is because the energies required to activate the reactions, regardless of the structural changes, are the same. Activation energies of such material, which contain high silica, are low compared to bagasse and wood.

TABLE 2. Activation energy of some cellulosic materials under air and helium atmospheres.

Material	Air atm.			Helium atm.		
	TT* °C	Activation energy		TT °C	Activation energy	
		Below TT	Above TT		Below TT	Above TT
Rice hulls	335	19.4	18.4	350	15.7	14.4
Rice straw	325	19.2	16.3	350	16.0	13.7
Bagasse	360	33.4	18.3	350	28.2	16.5
Hardwood (Beech) (Sanderman and Augustin 1963)	—	—	—	285	25.0	15.0
Softwood (Pine) (Tang 1967)	—	—	—	325	23.0	54.0

* TT = transition temperature.

Activation energies of bagasse are in the same range to that of hardwood, probably due to the similarity in chemical composition. In general, activation energies of nonwood plants are lower than that of wood.

The lower values of the activation energy are due not only to the porous structure of the nonwood plants but also to the silica in plants. The presence of silica associated with cellulosic material is influencing the course of the thermal reaction and therefore is responsible for the large variation of activation energy. This finding supports the previous work (Tang 1967) that either impurities or addition of inorganic materials have an effect on the kinetic reaction of cellulosic material.

REFERENCES

- AKITA, K. 1959. Studies on the mechanism of ignition of wood. Rep. Fire Res. Inst. Japan 9(1-2): 99-106.
- AMYL, L. 1961. The physico-chemical bases of the combustion of cellulose and ligneous materials. Cah. du centre Tech, du Bois. No. 45.
- BEAGLE, E. C. 1978. Rice husk conversion to energy. FAO, Agricultural Service Bulletin. No. 31.
- BHUSHA, B. 1977. Agricultural residues and their utilization in some countries of South and South East Asia. FAO.
- FARMER, R. W. 1963. Air Force Aeronautical Systems. Division Rep. ASD-TDR-62-1043.
- GOVIL, R. S. 1960. Chemical pulp from groundnut shells. Tappi 43(6):215A-216A.
- HEINRICH, H. J., AND B. KAESCHE-KRISCHER. 1962. Spontaneous ignition of wood. Brennstoff-Chemi. 43:142-148.
- HOROWITZ, H. H., AND G. METZGER. 1963. A new analysis of thermogravimetric traces. Anal. Chem. 35:1464-1468.
- NAFFZIGER, T. R., R. S. MATUSZWSKI, T. F. CLARK, AND I. W. WOLF. 1960. Dissolving pulps from domestic timber bamboo, phyllostachys bambusoides, Tappi 43(6):591-596.
- NASSAR, M. M. 1979. Energy from Egyptian agricultural residues. Chem. Eng. Dep., Minia University, Egypt. Unpublished.
- RYDHOLM, S. V. 1967. Pulping process. Interscience publication, John Wiley & Sons, New York. Pp. 93.
- SANDERMANN, W., AND H. AUGUSTIN. 1963. Chemical investigations of thermal decomposition of Wood. Holz Roh-Werkst., 21:256-268.
- STAMM, A. J. 1956. Thermal degradation of wood and cellulose. Ind. Eng. Chem. 48:413-417.
- STOUT, B. A., AND T. L. LOUDON. 1977. Residue utilization. Management of agricultural and agro-industrial residue. FAO, Rome.
- TANG, W. K. 1967. Effect of inorganic salts on pyrolysis of wood. U.S. Forest Service Research Paper FPL 71.