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Pyrolysis of Cellulose, An Introduction to the Literature

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TABLE OF CONTENTS

LIST OF FIGURES

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Toshimi Hirata

Abstract

Topics related to cellulose pyrolysis are briefly surveyed under several headings. The principal aim is to give the reader some grasp of the issues involved and provide a guide to the relevant literature. The headings include: changes in cellulose fine structure with heating, chemical changes during pyrolytic weight loss, and kinetic modeling of pyrolysis. Principal emphasis is on the last area; it is concluded that no current kinetic model adequately predicts both the observed changes in degree of polymerization and the weight loss during heating.

1. INTRODUCTION

Pyrolysis of cellulose has been studied by many researchers in relation to fire-proofing of cellulosic fabrics and wood, of which cellulose is a principal component, in relation to charcoal production and in relation to gasification of biomass. Furthermore, many results on changes in physical properties, especially mechanical and visco-elastic properties, on production of useful materials, on gasification, and on thermal liquefaction have recently been reported in studies relating to the pyrolysis. There are inconsistencies among these results which have led to different interpretations and proposed models of the pyrolysis.

Approximately one half of wood consists of cellulose; the rest mainly consists of lignin (25 to 35 percent) and hemicelluloses (15 to 25 percent) with the exact content of each depending on the tree species. Cellulose is a simple linear polymer of repeating glucose units all identically linked together as shown in Figure 1. It rapidly decomposes to produce highly inflammable volatiles in a narrow temperature range around 300°C, as inferred from the ready combustibility of paper. On the other hand, lignin, an aromatic macromolecule whose elemental unit is phenyl propane, and hemicelluloses, whose main components are pentosans, are constructed with a variety of linkages. Lignin is generally the most stable wood component whereas hemicelluloses are comparable in stability to cellulose as shown by numerous thermogravimetric (TG) studies [1-10]. The pyrolysis of cellulose is thus a principal source of the flammable gases formed from gasifying wood.

The pyrolysis mechanism and kinetics of cellulose decomposition under pyrolytic conditions are complex and are not yet sufficiently known. The mechanistic and kinetic aspects have to be more satisfactorily clarified to allow exact predictions of combustibility and to aid in development of more effective fire-proofing of cellulosic and wood materials, as well as for other purposes such as the production of energy from biomass. An overview of the literature on pyrolysis should be useful in helping clear up some of the confusion and in obtaining clues as to the major difficulties in the clarification of the mechanism of cellulose pyrolysis. This survey is limited to anaerobic degradation conditions in order to exclude the additional complexities which oxygen introduces.

2. CHANGES IN FINE STRUCTURE WITH HEATING

Heating cellulose above 200°C first causes changes in the fine structure, in other words, in properties such as the crystalline fraction and crystallite form, length of the molecular chains and the accessibility. The accessibility is here defined as the proportion of hydroxyl groups available to a reagent; it depends on the fine structure, and is measured by the absorption rate, the reactivity, and so forth. Ordering seems to occur in the amorphous region before cleavage of the covalent bonds. This has been suggested as the cause of an increase in the crystallinity [1-4], a rise in the temperature of glass-transition [15], softening [16], a decrease in the accessibility [17], and changes in the mechanical properties [18-20].

Another type of change which causes an increase in the crystallinity, namely, chemical decomposition in the amorphous region, probably occurs later than the above rearrangement of chains. Since the products of pyrolysis of the amorphous region escape by volatilizing from the system, the percent crystallinity increases. The view that the thermal decomposition occurs first in the amorphous region has been supported by several experiments: the increase in crystallinity with heating as seen by x-ray scattering [12,13,21-23], by the interpretation that the leveling off of the degree of polymerization (DP) during heating is caused by decomposition of the amorphous region or weak linkages and that this result then indicates the length of the crystallite [12,13,24,27], by a decrease in the molecular accessibility measured by the reactivity with phenolic resin [28] and by other ways [22-29], such as moisture regain; finally, it is also supported by a proposed model for zeroth-order weight loss [30].

The main initial reaction of the pyrolysis in the amorphous region seems to be cleavage of glucosidic bonds and dehydration [22,24,31,32]; dehydration has been interpreted as leading to intermolecular cross linking [24,29,32). Following these reactions, levoglucosan (see Figure 2) as a sort of "monomer" appears to be produced in some amount from the less ordered region [33]. This conjecture is consistent with the results of Lipska and Parker [34,35], Lipska [36], and Lipska and Woodley [37], who have reported an initial rapid decrease in the number of glucose units in cellulose as determined by hydrolysis. Rapid shortening of the cellulose chains by cleavage of the glucosidic bonds at the initital stage of heating has been pointed to as the cause of the decrease in DP by many workers [12,13,17,24-28,33,38-55].

The idea that interchain cross-linking occurs (via dehydration) has been supported by several reports. These include the finding that water production by pyrolysis is associated with cross linking [56], that crosslinking is responsible for an increase in the mechanical strength with heating [28,39,57], that it causes an extraordinarily high apparent activation energy of 145 kcal/mole as determined from changes in the mechanical strength in the temperature range 115° to 175°C [58], and that cross-linking causes an increase in the dimensional stability [29,57]. Reported increases in the mechanical strength [18,20] and in the dimensional stability [12] which have otherwise been interpreted as being due to hydrogen bonding formed during heating, may be also interpreted as being due to interchain cross linking.

Most reported values of the leveling off DP obtained by heating roughly approximate those obtained by cellulose hydrolysis [59-70]. The length of the cellulose chains in a crystallite is considered to depend upon their arrangement in it. (There are several theories about this arrangement, i.e., those of folded chains [68-73] and spiral chains [74-77], in addition to the well-known fringed micellar model). The leveling-off values of DP found by hydrolysis, which differ depending on the source of the cellulose, agree with the size of the crystallite determined from x-ray measurements [68,78], electron microscopy [64], and from absorption [79]. Thus, it has been verified that the leveling-off of the DP found in hydrolysis is caused by the fine structure. The leveling-off of the DP found in pyrolysis, however, cannot be explained satisfactorily by the interpretation that it is based purely on the fine structure. For example, it is difficult to explain the large temperature dependency of the leveling-off DP [45,49-51,55] by this interpretation; also it is difficult to explain the actual values which can be about 10 times larger than the value of DP corresponding to a single crystallite length [17].

Only changes occurring before the main pyrolysis process, i.e., before the actual weight loss, have been discussed so far. Studies of changes in the fine structure during the main pyrolysis process are largely lacking in the literature. A gradual and almost linear decrease in DP with the progress of the main weight loss has been reported by Lipska [41], and by Lipska and Martin [42] who succeeded in measuring viscosity-average DP despite the presence of insoluble ingredients in their samples. This change in the DP was thought to be caused by the unzipping of cellulose chains whose number remained constant during the pyrolysis.

It has been contended that cellulose molecules pre-melt and lose their ordered structure at temperatures near 300°C [19]; the active weight loss process of cellulose in TG, with usual heating rates, begins beyond 300°C. On the other hand, Weinstein and Broido [80] have reported results showing that approximately one half of the initial crystallinity is retained after a 64 percent, heat-induced weight loss and that additives further increase the crystallinity in the residue. However, in a study by Inagaki and Katsuura [81], it was found that the crystalline structure disappeared in the presence of a reactive additive before the beginning of the rapid weight loss process. In any event, the changes in the fine structure at high temperatures or during the rapid weight loss process remain uncertain, because the fine structure present at high temperature, is not shown with certainty by measuring properties of the residue at room temperature, as has typically been done. Therefore, interpretation of the results of such studies will always be open to question.

3. CHEMICAL CHANGES DURING ACTIVE PYROLYSIS

The first significant chemical reactions in the crystalline region of cellulose definitely appear to be cleavage of glucosidic bonds followed by production of anhydro-glucoses (for the most part, levoglucosan); however, the presence of a primary product (unidentified) other than levoglucosan has been proposed by Broido et al. [82].

Levoglucosan is produced from the pyrolysis of cellulose; it constitutes the majority of the tar [14,22-24,31,33,44,83-98]. Its yield increases with the crystallinity [13,14,31-33,86], and decreases with impurities [92,96] and additives [31,45,82,83,87,88,91,93,94,98]. Furthermore, the idea that levoglucosan is a primary product of cellulose pyrolysis is supported not only by the large yield but also by the close similarity among the groups of identified degradation products from the pyrolysis of cellulose and from levoglucosan [42,99,100]. Levoglucosan has been assumed to function as the "monomer" in cellulose pyrolysis and various chemical mechanisms for its production have been proposed [31,83,84,93,98,101-110]. A mechanism based on a glucose intermediate in the production of levoglucosan was refuted by experimental evidence [31]. Depending on the position of the hydroxyl groups which attack the glucosidic bonds, levoglucosan may be formed via an intermediate of either 1,2-anhydro-[83,105,109] or 1,4-anhydro-glucose [109], or directly without an intermediate [31,46]. No decisive proof of the real course seems to have been presented yet [109].

In any case, the principal route of cellulose pyrolysis is assumed to be a process proceeding from cleavage of glucosidic bonds to production of levoglucosan; dehydration is considered to be a side reaction of lesser significance. However, this side reaction is important for the flame-retardation of cellulosic materials. One of the most effective means of flame-retardation is a greater production of water and a minimization of volatilized, inflammable levoglucosan in cellulose pyrolysis.

As stated above, the production of levoglucosan is very sensitive to additives and impurities. However, few results [101,111] have been reported regarding the chemical mechanism of action of any additive. Thus, the effects of additives on the production of levoglucosan are not well understood and require further study. Also, several chemical mechanisms have been proposed for the dehydration reaction [46,52,112-114].

Many degradation products have been identified by various analytical means, such as gas-liquid chromatography (GLC), mass spectrometry (MS), the combined methods of GLC and MS, IR and UV spectrometry, thin layer chromatography and nuclear magnetic resonance. The identified products of the secondary pyrolysis of cellulose, i.e. the main pyrolysis products of levoglucosan, may be classified into fixed gases such as hydrogen, carbon monoxide, carbon dioxide, methane, acetylene, ethylene, and propane, as well as semi-volatiles such as lower alcohols, water, ketones, aldehyde and carbonyl compounds, aliphatic acids, hydrocarbons, and furans. The yield of these products depends upon the atmosphere [25,88,90,115,116], and upon additives [4,45,48,82,83,88,93,95,100,104,117-124]. Additives generally tend to decrease the number of products [100].

Shafizadeh [93], and Shafizadeh and Lai [120] have presented chemical decomposition mechanisms for the production of many of the products via intermediates of 3-deoxy glucosan and its derivatives. The former compound (3-deoxy glucosan) was first identified by Kato and Komorita [125] as a product of levoglucosan pyrolysis. Furthermore, Shafizadeh et al. [126-129] have shown that many products of cellulose pyrolysis are produced from the pyrolysis of substances related to the intermediates. According to these authors, the course of levoglucosn pyrolysis is directed either to a process of condensation or of disproportionation depending on whether the reaction conditions are acidic, basic, or neutral.

The pyrolysis reactons beginning with the cleavage of a glucosidic bond of a cellulose chain are widely considered to be controlled by radical mechanisms. Many of the proposed radical mechanisms have been discussed extensively by Onishi and Sugisawa [108,109], and by Shafizadeh [107]. The existence of radicals has been confirmed in various degradation experiments by using electron spin resonance (ESR) analysis (93,120,130-132]. On the other hand, Byrne et al. [104] have proposed an ionic mechanism for the pyrolysis in which decomposition is caused by and develops with the formation of carbonium ion produced by heterolysis of the glucosidic bond. Shafizadeh et al. [132] have proposed heterolytic cleavage of a glucosidic bond in the pyrolysis of xylose on the basis of ESR measurements thus giving support to the interpretation by Byrne et al. Moreover, from measurements of radical concentrations by ESR analysis, Shafizadeh [93] has presented the interpretation that pyrolysis of cellulose is heterolytic in the temperature range below 280°C and homolytic in the higher temperature range in which the active weight loss occurs. Shafizadeh and Bradbury [54] have also presented a simple radical chain reaction mechanism which is composed of radical initiation, propagation, and formation of products.

In an inert atmosphere, the pyrolysis of cellulose yields a stable residual solid char plus liquid tars and gases. The char yield is found to increase with the addition of various chemicals and it has been reported to differ among types of cellulose [133]. It has been observed that cellulose can be converted to volatiles without char formation during pyrolysis in helium or in vacuo and this observation has lead to the interpretation that char is not a primary product of the pyrolysis [134].

The chemical mechanisms proposed concerning char formation may be divided into two types. The first type, due to Broido and Nelson [135,136], assumes the char derives directly from cellulose molecules by intermolecular dehydration; this is based on the "dehydrocellulose" concept of Kilzer and Broido [137]. Their proposal has been supported by the interpretation of thermal analysis curves [138,139] and agrees with the overall course of the pyrolysis as proposed by Lewin et al. [32]. The second type of mechanism is that the char is assumed to be formed not directly from the cellulose molecules, but rather by polymerization of levoglucosan or its derivatives; this has been proposed based on an increase in char formation from levoglucosan with the addition of chemicals [41,42,100,140,141], as is similarly observed for cellulose. This interpretation was based on results for pure levoglucosan pyrolysis and seems to be somewhat idealized; the actual reacton process of levoglucosan pyrolysis should be affected by the presence of cellulose which has been activated by heating, and by water and other products. The proponents of this mechanism seem to assume that levoglucosan produced from cellulose begins to pyrolyze only after the completion of conversion of cellulose molecules into levoglucosan.

4. PYROLYSIS REACTION KINETICS AND MODELS

An enormous amount of kinetic data has been presented for cellulose pyrolysis. The major part is derived from weight loss measurements. However, kinetic parameters of pyrolysis have been determined by other measurements such as changes in the mechanical properties [39,58], decrease in the DP [26,39,40,48-52,54,55,110], rates of gas release [54,142-144], changes in acid concentration [145], and changes in peak temperature of the differential thermal analysis curves [146,147]. For the most part, the kinetic parameters, including those for weight loss were determined with the assumption of a first-order reaction. Some authors [3,30,24-37,41,139,148-153] have reported results obeying a zeroth-order rate law over the major part or over a limited portion of the weight loss, depending on the heating conditions. Furthermore, the weight loss rate with heating has been fitted to expressions other than a first- or zeroth-order law [13,23,32,103,133,139,141,152-159]. Even if one limits his viewpoint to apparent values of Arrhenius parameters, the pyrolysis is found to consist of two or more stages [3,6,7,13,30,34-37,48,103,112,138, 139,142,148,149,151,152,154,155,158-161]. This suggests that the actual kinetic process of cellulose pyrolysis is complex.

In addition to the complexity of the pyrolytic chemical reactions, different calculating procedures [27,112,150,151,161-163] and experimental conditions, (namely, heating rates) [150,151,153,157,162,164], atmospheres [12,54,139,157,165,166], types of cellulose [13,23,32] and size of samples [156,163] have given a variety of different values for kinetic parameters.

Moreover, in general, additives appear to substantially decrease the apparent activation energy, to promote the onset and increase the rate of pyrolysis (except in the case of boric acid as reported by Rogers and Ohlemiller [153]), and to increase the char yield. The activation energy appears to decrease with an increase in the heating rate [150,151,157,164], with a decrease in the crystallinity [13,23,32], and it appears to be larger in an inert atmosphere than in an oxidizing atmosphere [139].

The atmosphere used in pyrolysis also affects heat transfer within a sample. Large temperature gradients in the solid may be due to a poorly conducting atmosphere [157] as well as to sample size [164]. Different local pyrolysis rates in a large solid sample as a result of temperature gradients have been observed with x-rays by Murty and Blackshear [164,167]. Thus, the rate of the pyrolysis can be ruled not only by chemical processes but also by physical factors, such as temperature gradients and migration of condensates. Maa and Bailie [156] have developed a mathematical model of the pyrolysis based on a shrinking, unreacted-core in which the pyrolysis is assumed to be determined in some regions by heat transfer control and in others by kinetic control.

Attempts have been made to express the overall weight loss during pyrolysis of cellulose more satisfactorily than with a simple power law, while still using a single set of values for activation energy and pre-exponential factor, by using rate laws for heterogeneous reactions [168]; the weight loss has been shown to obey random nucleation [133,152], phase boundary [139,141], or diffusion-controlled rate laws [153]. These results are sometimes useful for prediction of the amount and rate of evolution of fuel vapors from cellulose in fire conditions. However, they do not address the fact that a rate expression based on a single step Arrhenius rate law neglects the complex kinetic processes of the pyrolysis reactions as suggested above.

Few kinetic models based on true chemical reaction mechanisms have been presented to date. Most data on changes in DP during pyrolysis have been explained by using the following rate equation for isothermal random scission of a linear polymer

$$\frac{1}{p} - \frac{1}{p_o} = kt \tag{1}$$

where p is the number average DP at the time t, p_o the initial number average DP value, and k the rate constant of the random scission process. The observed changes in the DP appear to obey this equation only in the early stages, because of the leveling off of the DP. The majority of the experimentally determined activation energy values for this random scission fall into a range from 25 to 35 kcal/mole. As stated above, the leveling-off of the DP during pyrolysis cannot be satisfactorily explained by reference to the fine structure of cellulose.

A kinetic model based on a chain mechanism, which has been presented by Hirata et al., appears to reasonably explain the overall changes in the DP [49-51,55,110]. As shown in Figure 3, the mechanism consists of initiation of random scission of the chain, unzipping to produce levoglucosan, and termination by grafting between an activated chain fragment and a hydroxyl group of cellulose; this mechanism predicts the leveling off of the DP as a result of a stationary state between the initiation and termination reactions. The Arrhenius parameters for the three reactions have been given with the model [49, 110].

The weight loss process during pyrolysis has been explained by models with and without definite chemical reaction mechanisms. Chatterjee and Conrad [103] appear to be the first workers who interpreted the weight loss in terms of a definite chain mechanism and determined the Arrhenius parameters of the weight loss. According to their model, the weight loss reaction consists of initiation of random scission of the chains and unzipping which proceeds along an activated fragment, generated by the random scission, producing levoglucosan. In the early stages, the weight loss rate is controlled by both reactions and is predicted to be directly proportional to time. At later stages, it is assumed to be determined by the unzipping only and to obey a first-order reaction law. Furthermore, they have shown that a zeroth-order weight loss can be caused by establishment of a stationary state between both of the reactions in their model. Their model has been supported by early stage weight loss measurements by several authors [13,22,23,32, 149,154,160]. Despite this support, however, the model is in strong disagreement with observed changes in the DP. According to their model, the DP should decrease at a rate larger than that implied by Eq. [1], since the chains should be shortened by both random scission and unzipping. This prediction from the model goes against all of the reported results on the DP behavior.

Following the presentation of the Chatterjee and Conrad model [103], Parker and Lipska [30] proposed a model based on a zeroth-order reaction as a means to explain the zeroth-order weight loss rate observed over a relatively long portion of the heating time. In the model they have assumed that, during heating, scission of the chains first occurs at weak linkages, about every 500 units, until a constant number of active chains is produced; the active chains then undergo an unzipping reaction while the number of active chains stays constant. They propose that the weight loss due to pyrolysis essentially obeys a zeroth-order law and they have reported several results supporting their model [34-37]. However, their model cannot explain the many reported observations of first-order weight loss obtained without any accompanying stage of zeroth-order reaction. Furthermore, the assumed constant number of active molecules which was related to the fine structure, is inconsistent with the temperature dependent leveling off of DP during pyrolysis

Okamoto [169] has presented a review of the kinetics of cellulose pyrolysis. In his review, he has calculated Arrhenius parameters for random scission initiation, propagation producing levoglucosan, and termination, based on the assumption of a stationary state with a constant radical concentration produced by a chain mechanism. A definite chemical mechanism for the termination was not given in his radical chain scheme which was derived from a model for depolymerizaion of polymers by Boyd [170]. Despite this vagueness about the termination mechanism and a poor proof of the existence of a constant radical concentration, the general mechanism by Okamoto seems to have a good possibility of development into a viable explanation of the kinetics of cellulose pyrolysis.

Another model not based on a definite chemical reaction mechanism has been presented by Bradbury, Sakai, and Shafizadeh [171]. Their abstract and somewhat ambiguous model consists of initiation which produces "active" cellulose and two competing first-order reactions which yield from one path, volatiles, and from the other, char (plus gases) from the same active cellulose. They have obtained Arrhenius parameters for each reaction by applying weight loss data to the model. This model will be of more significance when a definite chemical mechanism is given to it.

At present, no single kinetic model for change in the DP or loss in the weight appears able to satisfactorily explain both types of behavior. These kinetic models have been constructed in the manner of those which succeed in explaining the pyrolysis of synthetic linear polymers. However it should be noted that at some point in the overall reaction, cellulose pyrolysis is different from that of synthetic polymers. Many synthetic polymers fuse before they decompose, while cellulose pyrolysis proceeds in the solid state. In the molten state the concentration of some activated centers such as free radicals, pertinent to calculating a bimolecular reaction rate such as for termination, can readily be obtained by assuming the sample volume is proportional to a monomer unit number. But, this assumption cannot be applied to cellulose pyrolysis, because the volume may not be directly proportional to the monomer unit number in the system. Furthermore, the concentration in the above sense may be meaningless due to the negligible mobility of activated centers in the solid state. Therefore, a realistic bimolecular termination mechanism must be independent of the mobility in the case of cellulose. Thus, a satisfactory explanation of both changes in the DP and in the weight, based on a realistic chemical mechanism for the solid state pyrolysis remains for the future. This model would provide a basis for exact predictions of various properties of cellulose pyrolysis.

5. SUMMARY AND CONCLUSIONS

The literature suggests that changes in cellulose during heating occur first in the amorphous region; ordering or rearrangement of the molecules increases the crystallinity, and cleavage of glucosidic bonds and dehydration occur as the first chemical changes. The former reaction leads to production of volatile levoglucosan and the latter causes cross-linking to increase the mechanical strength. These pyrolytic reactions increase the relative crystallinity. Following the amorphous region, the crystalline region decomposes also initially at a glucosidic bond and then produces a large amount of levoglucosan yielding active weight loss. In addition to volatiles (tar), fixed gases and char are simultaneously evolved from the pyrolysis. With additives or impurities or a decrease in the crystallinity, the yield of volatiles decreases and that of char increases.

The majority of the reported kinetic data have been obtained from weight loss and, to a lesser extent, from DP measurements. It is difficult to find satisfactory agreement among the data. Some indicate that pyrolysis proceeds in more than one step. These facts suggest that pyrolysis is a complex reaction sequence. Several kinetic models have been proposed in order to explain the overall behavior. However, no single kinetic model appears to succeed in a fully consistent explanation of all aspects of the pyrolysis behavior. Thus, there remains a need for a kinetic model, based on a realistic solid state chemical mechanism, capable of exact predictions of the pyrolysis behavior of cellulose.

6. References

[1] Browne, F. L. and W. K. Tang, Fire Res. Absts. Revs., 4, 76(1961)

[2] Eickner, H. W., For. Prods. J., 2, No. 4, 194(1962)

[3] Tang, W. K., U. S. Forest Service Res. Paper, FPL 71(1967)

[4] Satonaka, S., S. Kobayashi, and Y. Kawasima, Res. Bull. College Exp. Forests, Hokkaido Univ., 25, 235(1967)

[5] Kosik, M., L. Geratova, F. Rendos, und R. Domansky, Holzforsch. Holzverwert., 20, 15(1968)

[6] Beall, F. C., Wood Fiber, 1, 215(1969)

[7] Ramiah, M. V., J. Appl. Polymer Sci., 14, 1323(1970)

[8] Beall, F. C., Wood Sci., 5, 102(1972)

[9] Fang, P., G. D. McGinnis, and E. J. Parish, Wood Fiber, 7, 136(1975)

[10] Abe, F., Bull. Government Forest Exp. Station, No. 298, 187(1977)

[11] Lewin, M. and L. G. Roldan, J. Polymer Sci., C, No. 36, 213(1971)

[12] Broido, A., A. C. Javier-Son, A. C. Cuano, and E. M. Barrall, Jr., J. Appl. Polymer Sci., 17, 3627(1973)

[13] Basch, A. and M. Lewin, J. Polymer Sci., Polymer Chem. Ed., 11, 3071(1973)

[14] Cabradilla, K. E. and S. H. Zeronian, Modified Cellulosics, ed. by Rowell, R. M. and R. A. Young, Academic Press, pp. 321-340(1978)

[15] Sawabe, O., J. Japan Wood Res. Soc., 17, 51(1971)

[16] Sawabe, O., Res. Rept., Faculty of Agriculture, Iwate Univ., 10, 35(1970)

[17] Rusznak, I. and I. Tanczos, Polymer Symposia, No. 42, 1475(1973)

[18] Yano, S., H. Hatakeyama, and T. Hatakeyama, J. Appl. Polymer Sci., 20, 3221(1976)

[19] Zeronian, S. H. and E. Menefee, Appl. Polymer Symposium, No. 28-III, 869(1976)

[20] Zeronian, S. H. and M. S. Ellison, J. Appl. Polymer Sci., 24, 1497(1979)

[21] Shimazu, F. and C. Sterling, J. Food Sci., 31, 548(1966)

[22] Basch, A. and M. Lewin, J. Polymer Sci., Polymer Chem. Ed., 12, 2053(1974)

[23] Rordrig, H., A. Basch, and M. Lewin, ibid., 13, 1921(1975)

[24] Golova, O. P. and K. G. Kryilova, Dokl. Akad. Nauk SSSR, 116, 419(1975)

[25] Major, W. D., Tappi, 41, 530(1958)

[26] Philipp, B., J. Baudisch, and C. Ruscher, ibid., 52, 693(1969)

[27] Kosik, M., V. Luzakova, and B. Reiser, Cellulose Chem. Technol., 6, 589(1972)

[28] Chow, S. -Z. and H. N. Mukai, Wood Sci., 4, 202(1972)

[29] Back, E. L. and L. O. Klinga, Svensk Papperstid., 66, 745(1963)

[30] Parker, W. J. and A. E. Lipska, U. S. Navy Radiological Denfese Lab., San Francisco, Calif., Report USNRDL-TR-69 (1969)

[31] Golova, O. P., A. M. Pakhomov, E. A. Andrievskaya, and R. G. Kryilova, Dokl. Akad. Nauk SSSR, 115, 1122(1957)

[32] Lewin, M., A. Basch, and C. Roderig, Proc. International

Sym. Macromol., ed. by Mano, E. B., pp. 225-250(1974)

[33] Basch, A. and M. Lewin, J. Polymer Sci., Polymer Chem. Ed., 11, 3095(1973)

[34] Lipska, A. E. and W. J. Parker, U. S. Navy Radiological Defense Lab., San Francisco, Calif., Report USNRDL-TR-928(1965)

[35] Lipska, A. E. and W. J. Parker, J. Appl. Polymer Sci., 10, 1439(1966)

[36] Lipska, A. E., U. S. Navy Radiological Defense Lab., San Francisco, Calif., Report USNRDL-TR-67-89(1967)

[37] Lipska, A. E. and F. A. Wodley, J. Appl. Polymer Sci., 13, 851(1969)

[38] Millett, M. A. and V. E. Goedken, Tappi, 48, 367(1965)

[39] Millett, M. A., L. J. Western, and J. J. Booth, ibid., 50, No. 11, 74A(1967)

[40] Fung, D. P. C., ibid., 52, 319(1969)

[41] Lipska, A. E., Annual Rept. for Office of Civil Defense, DAHC20-70-C-0219, OCD Work Unit 2531C, Stanford Res. Inst., (1970)

[42] Lipska, A. E. and S. B. Martin, Final Rept. for Office of Civil Defense, DAHC20-70-C-0219, Stanford Res. Inst., (1971)

[43] Döhler, W., J. Baudisch, B. Philipp, and C. Ruscher, Cellulose Chem. Technol., 5, 215(1971)

[44] Basch, A., T. Wasserman, M. Lewin, and Y. Halpern, ibid., 5, 353(1971)

[45] Fung, D. P. C., Y. Tsuchiya, and K. Sumi, Wood Sci., 5, 38(1972)

[46] Philipp, B., J. Baudisch, and W. Stöhler, *Cellulose Chem. Technol.*, *6*, 379(1972)

[47] McCarter, R. J., *Text. Res. J.*, *42*, 709(1972)

[48] Nunomura, A., H. Ito, A. Kasai, and K. Komazawa, Rept. Hokkaido Forest Products Res. Inst., No. 54, 40(1972)

[49] Hirata, T., *Mokuzai Gakkaishi (J. Japan Wood Res. Soc.)*, *22*, 238(1976)

[50] Hirata, T., H. Okamoto, and K. Naito, ibid., *24*, 243(1978)

[51] Hirata, T. and K. Naito, ibid., *24*, 464(1978)

[52] Brown, W. P. and C. F. H. Tipper, *J. Appl. Polymer Sci.*, *22*, 1459(1978)

[53] Hebeish, A., A. T. El-Areff, E. A. El-Alfi, and M. H. El-Rafie, ibid., *23*, 453(1979)

[54] Shafizadeh, F. and A. G. Bradbury, ibid., *23*, 1431(1979)

[55] Hirata, T., *Mokuzai Gakkaishi*, *27*, 125(1981)

[56] McKay, G. D. M., *For. Prods. J.*, *18*, No. 5, 71(1968)

[57] Merritt, R. W. and A. A. White, *Ind. Eng. Chem.*, *35*, 297(1943)

[58] Millett, M. A. and C. C. Gerhards, *Wood Sci.*, *4*, 193 (1972)

[59] Jorgensen, L., *Acta Chemica Scandinavica*, *3*, 780(1947)

[60] Nickerson, R. F. and J. A. Habrle, *Ind. Eng. Chem.*, *39*, 1507(1947)

[61] Battista, O. A., ibid., *42*, 502(1950)

[62] Millett, M. A., E. W. Moore, and J. E. Saeman, ibid., *46*, 1493(1954)

[63] Battista, O. A., S. Coppick, J. A. Howsmon, F. F. Morehead, and W. A. Sission, ibid., *48*, 333(1956)

[64] Immergut, E. A. and B. G. Ranby, ibid., 48, 1183(1956)

[65] Sharples, A., Trans. Faraday Soc., 54, 913(1958)

[66] Nelson, M. L., J. Polymer Sci., 43, 351(1960)

[67] Daruwalla, E. H. and R. T. Shet, Text. Res. J., 32, 942(1962)

[68] Watanabe, S. and J. Hayashi, J. Polymer Sci., Polymer Chem. Ed., 12, 1065(1974)

[69] Chang, M. M. Y., ibid., 12, 1349(1974)

[70] Krassig, H., Appl. Polymer Symposium, No. 28, 77(1976)

[71] Manley, R. S. J., J. Polymer Sci., A-2, 9, 1025(1971)

[72] Chang, M., J. Polymer Sci., C, No. 36, 343(1971)

[73] Holt, C. and D. B. Sellen, J. Polymer Sci., Polymer Phys. Ed., 13, 1(1975)

[74] Ahmed, A. U. and W. H. Rapson, J. Polymer Sci., A-1, 9, 2297(1971)

[75] Viswanathan, A. and S. G. Shenouda, J. Appl. Polymer Sci., 15, 519(1971)

[76] Viswanathan, A. and S. G. Shenouda, ibid., 15, 2597(1971)

[77] French, A. D., ibid., 16, 1579(1972)

[78] Shenouda, S. G. and A. Viswanathan, ibid., 16, 395(1972)

[79] Stamm, A. J., Wood Sci. Technol., 11, 39(1977)

[80] Weinstein, M. and A. Broido, Combustion Sci. Technol., 1, 287(1970)

[81] Inagaki, N. and K. Katsuura, J. Chem. Soc. Japan, Ind. Chem. Section, 74, 982(1971)

[82] Broido, A., M. Evett, and C. C. Hodges, Carbohydrate Res., 44, 267(1975)

[83] Madorsky, S. L., V. E. Hart, and S. Straus, J. Res.

Natl. Bur. Stds., 56, 343(1956)

[84] Ivanov, I. V., O. P. Golova, and A. M. Pakhomov, Bull, Acad. Sci. USSR, Div. Chem. Sci., 1956, 1295

[85] Golova, O. P., A. M. Pakhomov, and I. I. Nikolaiva, ibid., 1957, 533

[86] Golova, O. P., A. M. Pakhomov, and E. A. Andrievskaya, Dokl. Akad. Nauk SSSR, 112, 430(1957)

[87] Schwenker, R. F., Jr. and E. Pacsu, Ind. Eng. Chem., 50, 91(1958)

[88] Holmes, F. H. and G. J. F. Shaw, J. Appl. Chem., 11, 210(1961)

[89] Sandermann, W. und H. Augustin, Holz Roh-Werkstoff, 21, 256(1963)

[90] Sandermann, W. und H. Augustin, ibid., 22, 377(1964)

[91] Tsuchiya, Y. and K. Sumi, J. Appl. Polymer Sci., 14, 2003(1970)

[92] Basch, A. and M. Lewin, J. Fire Flammability, 4, 92(1973)

[93] Shafizadeh, F., Appl. Polymer Symposium, No. 28, 153(1975)

[94] Franklin, W. and S. P. Rowland, Text. Res. J., 49, 170(1979)

[95] McCall, E. R., N. M. Morris, and R. J. Bernt, ibid., 49, 288(1979)

[96] Shafizadeh, F., R. H. Furneaux, T. G. Cochran, J. P. Scholl, and Y. Sakai, J. Appl. Polymer Sci., 23, 3525(1979)

[97] Franklin, W. E. and S. P. Rowland, ibid., 24, 1981(1979)

[98] Allan, G. G., B. B. Krieger, and D. W. Work, ibid., 25, 1839(1980)

[99] Glassner, S. and A. R. Pierce, III, Anal. Chem., 37,

525(1965)

[100] Wodley, F. A., U. S. Navy Radiological Defense Lab., San Francisco, Calif., Report USNRDL-TR-69 B(1969)

[101] Laible, R. C., Am. Dyestuff Reporter, 47, 173(1958)

[102] Tang, M. M. and R. Bacon, Carbon, 2, 211(1964)

[103] Chatterjee, P. K. and C. M. Conrad, Text. Res. J., 36, 487(1966)

[104] Byrne, G. A., D. Gardiner, and F. H. Holmes, J. Appl. Chem., 16, 81(1966)

[105] Kosik, M., F. Kozmal, V. Reiser, and R. Domansky, Holzforsch. Holzverwert., 20, 11(1968)

[106] Shafizadeh, F., Advances Carbohyd. Chem., 23, 419(1968)

[107] Duffy, J. V., J. Appl. Polymer Sci., 15, 715(1971)

[108] Onishi, A. and H. Sugisawa, New Food Ind.(Japanese), 18, 1(1976)

[109] Onishi, A. and H. Sugisawa, Chemical Region(Japanese), 30, 964(1976)

[110] Hirata, T., Bull. Forestry Forest Prods. Res. Inst., No. 304, 77(1979)

[111] Fung, D. P. C., Wood Sci., 9, 55(1976)

[112] Patel, K. S., K. C. Patel, and R. D. Patel, Makromol. Chem., 132,7(1970)

[113] Vigo, T. L., D. J. Daigle, and C. H. Mack, J. Appl. Polymer Sci., 15, 2051(1971)

[114] Hendrix, J. E., ibid., 16, 257(1972)

[115] Stamm, A. J., Ind. Eng. Chem., 48, 413(1956)

[116] Schwenker, R. F., Jr. and L. R. Beck, Jr., J. Polymer Sci., C, No. 2, 331(1963)

[117] Parks, W. G., J. G. Erhardt, Jr., and D. R. Roberts, *Am. Dyestuff Reporter*, *39*, 294(1950)

[118] Parks, W. G., M. Antoni, A. F. Petrarca, and A. R. Pitochelli, *Text. Res. J.*, *25*, 788(1955)

[119] Kosik, M. and R. Domansky, *Holzforsch. Holzverwert.*, *20*, 81(1972)

[120] Shafizadeh, F. and Y. Z. Lai, *J. Org. Chem.*, *37*, 278(1972)

[121] Garn, P. D. and C. L. Denson, *Text. Res. J.*, *47*, 485(1977)

[122] Garn, P. D. and C. L. Denson, ibid., *47*, 535(1977)

[123] Garn, P. D. and C. L. Denson, ibid., *47*, 591(1977)

[124] Barnes, D. P., R. P. Blankenhorn, and W. K. Murphey, *Wood Sci.*, *12*, 122(1979)

[125] Kato, K. and H. Komorita, *Agr. Biol. Chem.*, *32*, 715(1968)

[126] Shafizadeh, F. and Y. Z. Lai, *Carbohydrate Res.*, *40*, 263(1975)

[127] Shafizadeh, F. and Y. Z. Lai, ibid., *42*, 39(1975)

[128] Shafizadeh, F. and P. P. S. Chin, ibid., *46*, 149(1976)

[129] Shafizadeh, F., R. H. Furneaux, T. T. Stevenson, and T. G. Cochran, ibid., *61*, 519(1978)

[130] Arthur, J. C., Jr. and O. Hinojosa, *Text. Res. J.*, *36*, 385(1966)

[131] Arthur, J. C., Jr. and O. Hinojosa, *J. Polymer Sci.*, C, No. 36, 53(1971)

[132] Shafizadeh, F., G. D. McGinnis, R. J. Susott, and H. W. Tatton, *J. Org. Chem.*, *36*, 2813(1971)

[133] Dollimore, D. and B. Holt, *J. Polymer Sci.*, *Polymer Phys. Ed.*, *11*, 1703(1973)

[134] Lewellen, P. C., W. A. Peters, and J. B. Howard, *16th*

Symposium (International) on Combustion, Combustion Inst., Pittsburgh, Pa., 1471(1977)

[135] Broido, A. and M. A. Nelson, Western States Section of the Combustion Inst., Paper WSS/CI 74-32(1974)

[136] Broido, A. and M. A. Nelson, Combustion Flame, 24, 263(1975)

[137] Kilzer, F. J. and A. Broido, Pyrodynamics, 2, 151(1965)

[138] Arseneau, D. F., Can. J. Chem., 49, 632(1971)

[139] Fairbridge, C., R. A. Ross, and S. P. Sood, J. Appl. Polymer Sci., 22, 497(1978)

[140] Hendrix, J. E. and G. L. Drake, Jr. ibid., 16, 41(1972)

[141] Jain, R. K., S. Bhatnager, K. Lal, and H. L. Bhatnager, Ind. J. Chem., 19A, 1171(1980)

[142] Akita, K., Rept. Fire Res. Inst. Japan, 9, No. 1-2, (1959)

[143] Murphy, E. J., J. Polymer Sci., 59, 649(1962)

[144] Baker, R. R., J. Therm. Anal., 8, 163(1975)

[145] Kuman, W. G., For. Prods. J., 12, No. 6, 275(1962)

[146] Akita, K. and M. Kase, J. Polymer Sci., A-1, 5, 833(1967)

[147] Parks, E. J., Tappi, 54, 537(1971)

[148] Tang, W. K. and W. K. Neil, J. Polymer Sci., C, No. 6, 65(1964)

[149] Conrad, C. M. and P. Harbrink, Text. Res. J., 38, 366(1968)

[150] Hurduc, N., I. A. Schneider, and C. I. Simionescu, Cellulose Chem. Technol., 4, 195(1970)

[151] Simionescu, C. I., I. A. Schneider, and N. Hurduc, J, Polymer Sci., C, No. 37, 325(1972)

[152] Kala, C., I. S. Gur, and H. L. Bhatnager, J. Ind. Chem. Soc., 56, 890(1979)

[153] Roger, F. E. and T. J. Ohlemiller, Combustion Sci. Technol., 24, 129(1980)

[154] Chatterjee, P. K., J. Appl. Polymer Sci., 12, 1859(1968)

[155] Roberts, A. F., ibid., 14, 244(1970)

[156] Maa, P. S. and R. C. Bailie, Combustion Sci. Technol., 7, 257(1973)

[157] Antal, M. J., Jr., H. L. Friedman, and F. E. Roger, ibid., 21, 141(1980)

[158] Inagaki, N. and K. Katsuura, J. Chem. Soc. Japan, Ind. Chem. Section, 72, 2303(1969)

[159] Inagaki, N. and K. Katsuura, ibid., 73, 1433(1970)

[160] Hirata, T. and H. Abe, Mokuzai Gakkaishi, 19, 451(1973)

[161] Beal, F. C., W. Merrill, R. C. Baldwin, and J. -W. Wang, Wood Fiber, 8, 159(1976)

[162] Hurduc, N., C. I. Simionescu, and I. A. Schneider, Cellulose Chem. Technol., 4, 195(1970)

[163] Cardwell, R. D. and P. Luner, Tappi, 61, No. 8, 81(1978)

[164] Murty, K. A. and P. L. Blackshear, Jr., Pyrodynamics, 4, 285(1966)

[165] Kato, K. and N. Takahashi, Agr. Bio. Chem., 31, 519(1967)

[166] Fairbridge, C. and R. A. Ross, Wood Sci. Technol., 12, 169(1978)

[167] Murty, K. A. and P. L. Blackshear, Jr., Eleventh Symposium (International) on Combustion, The Combustion Inst., Pittsburgh, Pa., 517(1967)

[168] Roger, F. E. and T. J. Ohlemiller, J. Macromol. Sci.,

A15, 169(1981)

[169] Okamoto, H., Mokuzai Gakkaishi, 19, 353(1973)

[170] Boyd, R. H., "Thermal Stability of Polymers", Vol. 1, ed. by Conley, R., Dekker, New York, pp. 47-89(1970)

[171] Bradbury, A. W., Y. Sakai, and F. Shafizadeh, J. Appl. Polymer Sci., 23, 3271(1979)

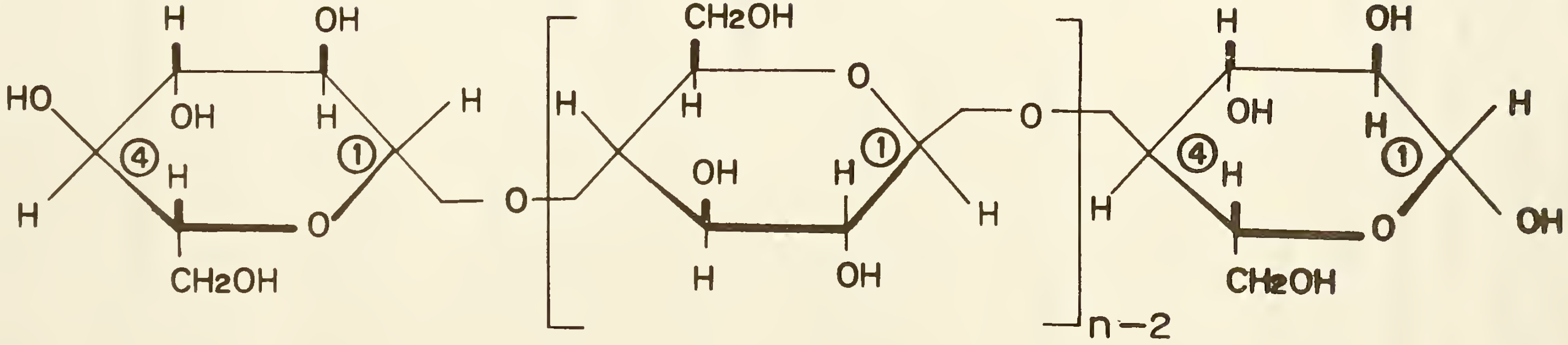

FIGURE 1 - CHEMICAL FORMULA OF CELLULOSE

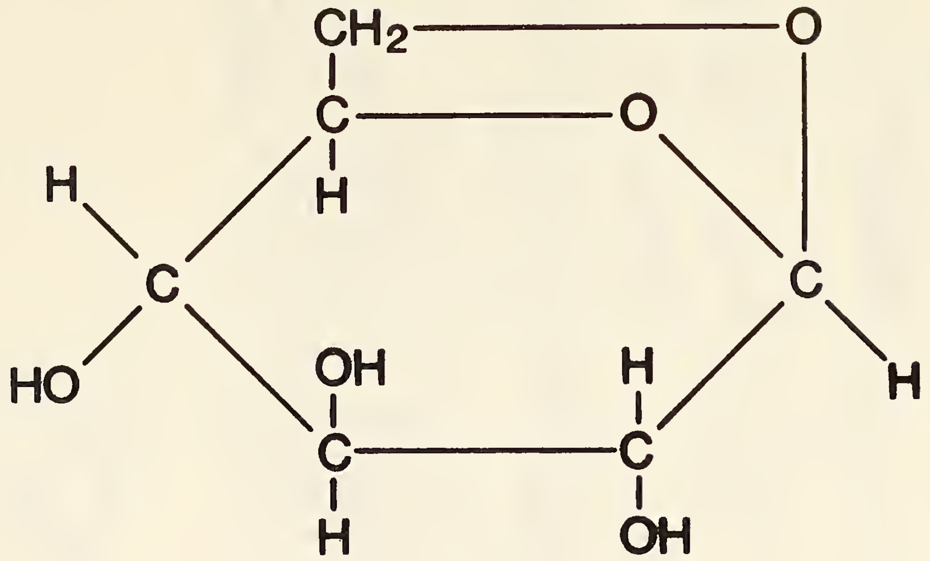

FIGURE 2 - 1-6 ANHYDRO-β-D GLUCOPYRANOSE (LEVOGLUCOSAN)

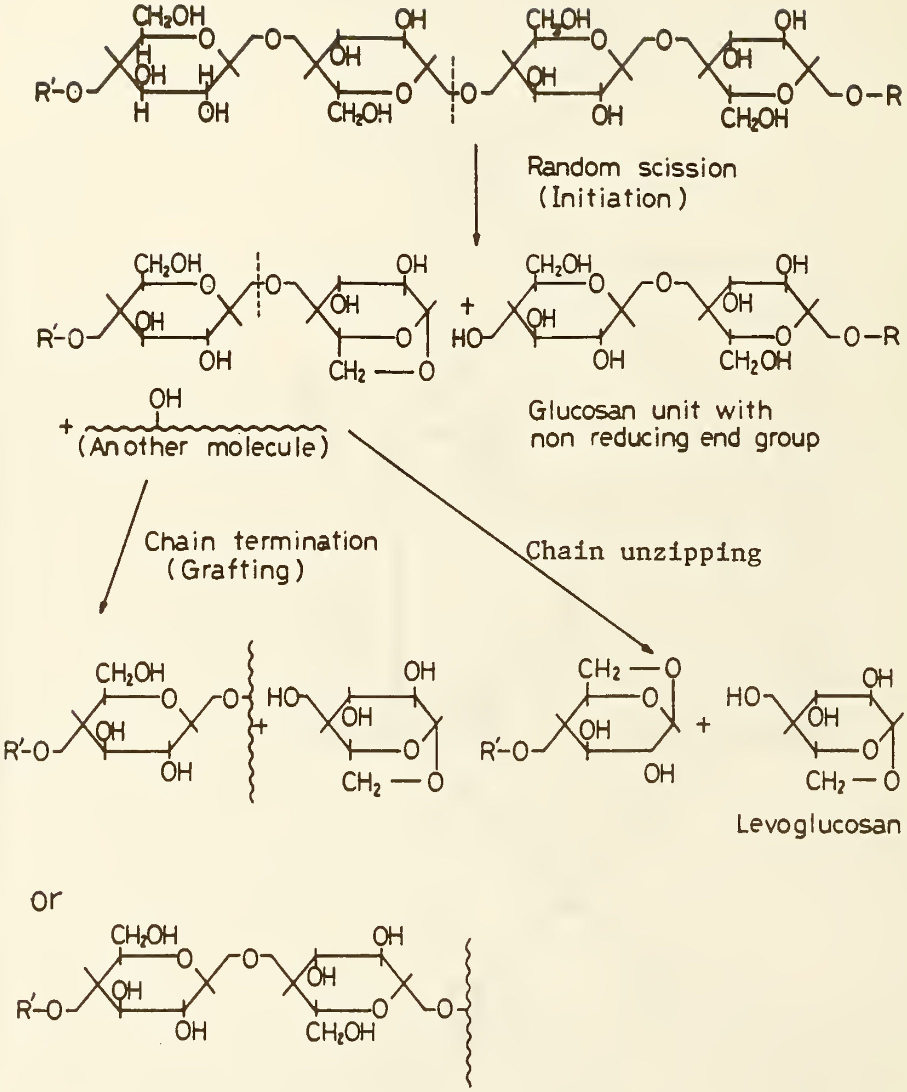

FIGURE 3 - CHAIN MECHANISM OF CELLULOSE PYROLYSIS
(REF. 49, 110)

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Topics related to cellulose pyrolysis are briefly surveyed under several headings. The principal aim is to give the reader some grasp of the issues involved and provide a guide to the relevant literature; 171 references are cited. The headings include: Changes in cellulose fine structure with heating; chemical changes during pyrolytic weight loss and kinetic modeling of pyrolysis. Principal emphasis is on the last area; it is concluded that no current model adequately predicts both the observed changes in degree of polymerization and the weight loss during heating.

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