PYROLYTIC BEHAVIOUR OF CELLULOSE IN A FLUIDIZED BED REACTOR

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The literature devoted to the competitive and sequential kinetics of cellulose pyrolysis is quite controversial, because of the ambiguous relationship established among cellulose molecules, levoglucosan and other products. A fast pyrolysis system composed of a feeding system, a fluidized bed reactor, carbon filter, vapour condensing system and gas storage is created to quantitatively investigate the yield of bio-oil, syngas and char from cellulose pyrolysis, at different temperatures (from 430 to 730 °C) and residence times (from 0.44 to 1.2 s). The products in the bio-oil are characterized by GC-MS, while the gas sample is analyzed by GC. The relationship between levoglucosan and the other main products (5-HMF, FF, HAA and HA) is estimated *versus* the possible routes for primary cracking of the cellulose molecules and the secondary reactions of fragments. CO formation is seen as enhanced at high temperature and residence time, while the yield of CO_2 is slightly changed. Further on, an improved kinetic scheme is proposed, to describe the pyrolysis steps of cellulose, showing that levoglucosan acts not only as a product of cellulose cracking, but also as a precursor for the formation of almost all the other products.

INTRODUCTION

Biomass energy is of growing attraction for alleviating the increasing global petroleum demand, due to its amazing characteristics as renewability, environment friendliness and wide distribution.[1] Thermo-chemical technologies, such as gasification and fast pyrolysis, are at present widely used for converting biomass to syngas, liquid fuel, char and chemicals.[2] The (cellulosic) biomass, including woody materials, agricultural, forestry and municipal wastes, is mainly composed of hemicellulose (10-25%), cellulose (55%) and lignin (10-30%). The analysis of the pyrolytic mechanism of the three individual components would give a better understanding of the thermo-chemical process of biomass, also facilitating the improvement of the kinetic models and the optimization of the reactor design.

The pyrolysis of cellulose is extensively discussed in the literature, due to the large content of cellulose in biomass.[3-18] The issues could be categorized into two groups: 1) the kinetic study of cellulose pyrolysis, and 2) the evolution of the products resulted from cellulose pyrolysis. In the first case, kinetic models of cellulose pyrolysis are proposed through the analysis of mass loss stages, presenting single reaction schemes,[19-20] one-, two- or three-step competitive reaction schemes[3,5,13,21,22] and multi-step consecutive reaction schemes.[9,16,23-25] Di Blasi[24] suggested that most of the kinetic models give a reasonable fit to the experimental data, yet t does not affect the evolution of the products.

The mechanism of volatile evolution from cellulose pyrolysis is comprehensively discussed in the second type of studies.[8,25-29] The yield and compositions of the volatiles is essentially affected by the feedstock, reactor, operating parameters and apparatus equipped for bio-oil or syngas.[30] Compared to the fixed

bed gasifier (plug-in furnace)[26,28,29] and to the updraft/downdraft draft gasifier,[8] cellulose pyrolysis in a fluidized bed reactor (a well-established thermal conversion technology) is less frequently reported in the literature. Moreover, most of the existing information[2] is devoted to the yield of the products and to the characterization of bio-oil or syngas, by different analytical methods (FTIR, GC, MS, NMR, HPLC), yet the possible chemical pathways for the formation of the main products is not thoroughly discussed.

For better understanding the pyrolytic behaviour of cellulose and for filling up the above-mentioned knowledge gap, the cellulose samples were tested in a fluidized bed reactor, at different temperatures and residence times. The yield of bio-oil, syngas and char is quantitatively determined by the experimental system, together with the GC-MS characterization of the products. The formation of the main products (Fig. 1), such as levoglucosan (LG), hydroxylacetaldehyde (HAA), hydroxylacetone (HA) and 5-hydroxymethylfurfural (5-HMF) is extensively discussed by speculative chemical pathways. Consequently, an improved kinetic scheme for cellulose pyrolysis is proposed for describing the decomposition routes, exhibiting its progressive characteristic on the involvement of the specified product.

EXPERIMENTAL
Materials

The sample tested in the experiments is a crystalline cellulose powder with an average diameter of 200 μm. According to the elemental analysis, the content of C, H, S, N and O is estimated as 44.97, 6.196, 0.096, 0.016 and 48.715%, respectively. The chemical structure of cellulose[31] is well-established as a linearly polymerized chain of glucopyranose linked by β-1, 4-glycosidic bonds (Fig. 1). The sample powder is dried in a furnace, at a temperature of 100 °C, for 2 h, prior to the experiment.
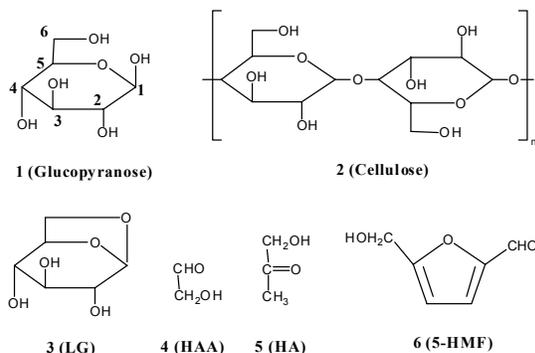
Fast pyrolysis system

The fast pyrolysis apparatus is composed of a feeding system, a gasification reactor, carbon filter, vapour-cooling system and gas storage (Fig. 2). The gasification reactor consists of a quartz tube (15 mm in diameter, 1200 mm length and 2 mm thickness) heated by a carborundum heater with a power of 8 kW, while the gap between them is of about 4 mm, for maintaining the temperature in the tube consistent with the heater. However, the heater temperature is not evenly distributed from the bottom to the top, and the difference decreases as the heating power increases (Fig. 3). The average value of the three points is estimated to be the required temperature of the experiment.

The feeding system and the carbon filter could be disassembled from the quartz tube reactor by conjunctions 1 and 2 (Fig. 2). The mass weight of the feedstock could be determined exactly, no pre-heating reaction occurring before the feeding system is connected to the reactor. After the experiment, the carbon filter is disassembled to obtain the yield of char residue by the difference of the carbon filter weight.

The bio-oil is collected by a two-step condensing system. The first condenser employs a mixture of water and ice to cool the hot volatiles, so that most of the high molecular weight compounds (heavy tars) are condensed and collected in the 'U' tube.

Figure 1: Chemical structures of glucopyranose, cellulose polymer and of the typical condensable products from cellulose pyrolysis
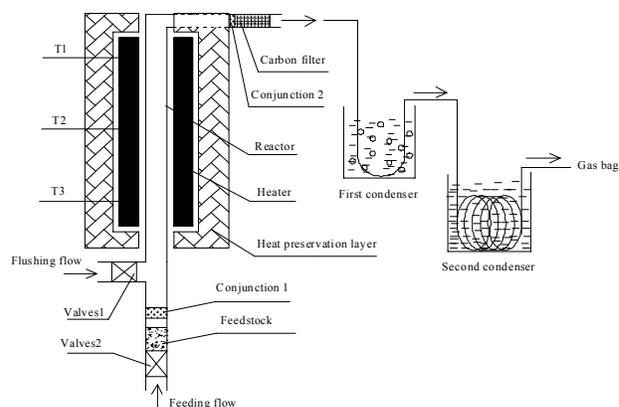
Figure 2: Fast pyrolysis system for cellulosic materials

The hot vapor is cooled to around 50 °C after the first condenser, after which it passes through the second condenser, where the light tars are coagulated by a mixture of dry ice and acetone (about -30 °C) and collected in a spiral circle tube.

Process

While the experimental temperature (average temperature) reaches the fixed value, the feeding system would be fixed to the reactor by the closed valve 2 (Fig. 2). The flushing flow is initially employed for about 1 min, to purge all oxygen out of the system, thus ensuring an inert atmosphere in the reactor tube. Further on, valve 1 is closed while valve 2 is opened to blow the feedstock up to the heated reactor by the feeding flow. The sample is quickly gasified in the reactor, and the updraft flow formed by the produced volatiles and the char residues passes through the carbon filter, where the char residue is separated. In a subsequent step, the stream of purified volatiles flows through the two-step condensing system, where the tars are condensed and collected, while the passed non-condensible volatiles together with the carrier gas (nitrogen) are collected by gas sample bags.

The yield of the char residue is estimated by the weight difference of the carbon filter before and after the experiment, while the yield of the tars is determined by the weight difference of the 'U' tube, spiral circle tube and connecting tubes. The yield of the gaseous products is calculated from the density and volume of the collected gaseous mixture. Density is assessed from the composition analysis of the mixture by GC (Voyager, Finnigan), while the volume is read from the integral flowmeter. The final yield of the gaseous products is found by eliminating the carrier gas (N_2) from the mixture. The estimated mass balance closure for the different experiments should be close to 1, errors below 5% being acceptable. Two runs are performed for each experiment, it being possible to repeat one of them if deviation exceeds the 5% limit.

To investigate the effect of temperature and residence time on the process, the cellulose samples were tested at temperatures from 420 to 730 °C and feeding flows from 200 to 600 L/h (corresponding to residence times of about 1.3 s to 0.44 s).

Characterization of products in bio-oil

As generally known,[9,28,29,32] the oxygenated compositions in bio-oil are very complicated, the GC-MS (Voyager from Finnigan Company) technique being employed to characterize the typical compounds of the bio-oil. The GC column should be applicable to the oxygenated and polar compounds containing hydroxyl, carbonyl and carboxyl groups. The GC-MS conditions are the following: capillary column: Wax-10 (30 m length, 0.25 mm in diameter), injector temperature: 250 °C, column temperature: 60 °C (5 min), 60→250 °C (heating rate of 10 K/min), 250 °C (25 min), carrier gas: helium, flow rate: 2 mL/min, ionization mode: electronic ionization, electronic bombardment energy: 70 eV, scanning time: 0.5 s, scanning range: 30-500 u. The yield and structure of the compounds could be determined by relevant software, by specific GC-MS graphs.

RESULTS AND DISCUSSION
Yield of gas, tar and char

The yields of the main products (gas, tar and char) from cellulose pyrolysis at different temperatures (from 430 to 730 °C) and feeding flows (from 200 to 600 L/h) are plotted in Figures 4 and 5. It is obvious that the gas yield increases at elevated temperature, while the char yield evidences an opposite trend (Fig. 4). When increasing temperature, the tar (bio-oil) yield is initially increased, reaching a maximum value of 72 wt% at a temperature of about 570 °C, after which it decreases. The influence of temperature on the yields of the products resulting from cellulose pyrolysis agrees with the results of Mohammed.[7] The temperature reported for the maximum production of bio-oil (60% without moisture) is of about 620 °C, when employing an electric heating reactor, in which temperature varies from 200 to 1000 °C. One should also observe that the char yield turns out to be minor (below 5 wt%), being maintained constant as temperature exceeds 550 °C (Fig. 4). Hence, the increased gas yield at a higher temperature stage may be possibly attributed to its competitive formation reaction over the tar formation reactions.[9,25,29,32,33]

The effect of the residence time (feeding flow) at a temperature of 530 °C is not visible for char production (always below 5%), as illustrated in Figure 5. However, quite noticeably, the yields of gas and tar are increased and decreased, respectively, with increasing the residence time (decreased feeding flow). It seems that the gas yield is enhanced by the longer residence time at the expense of the tar produced through secondary decomposition.[17,25,28,34] However, it is still ambiguous whether the gas and tar yields are controlled by a competitive,[35] sequential[36,37] or hybrid mechanism,[16] as the formation pathways are extremely different for the

complicated gas and liquid products. Extensive discussion on the mechanism should involve speculative chemical pathways for the primary cracking of cellulose and secondary decomposition of fragments.

Speculative chemical pathways for the products

Most of the studies available in the specialty literature are focused on the bio-oil from cellulose pyrolysis, due to its large yield as compared to other products (more than 70%). The yields of the main products in the bio-oil, influenced by temperature and residence time, are shown in Table 1. The speculative chemical pathways for primary cellulose pyrolysis and secondary decomposition of tars are systematically illustrated in Figures 6 and 7, respectively. Below, the formation of products (levoglucosan, 5-hydromethylfurfural, hydroxylacetone and hydroxylacetaldehyde) in the bio-oil will be extensively discussed, while the evolution of the gases will be elucidated briefly.
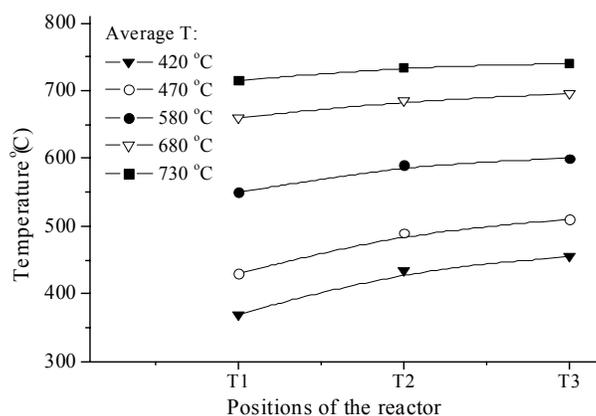
Figure 3: Temperature distribution in the reactor
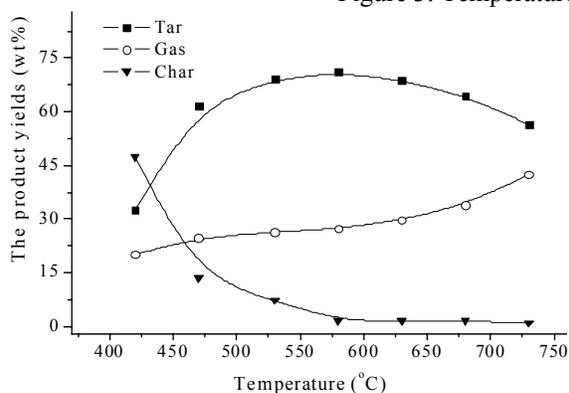
Figure 4: Yields of tar, gas and char upon cellulose gasification at different temperatures (feeding flow: 600 L/h)
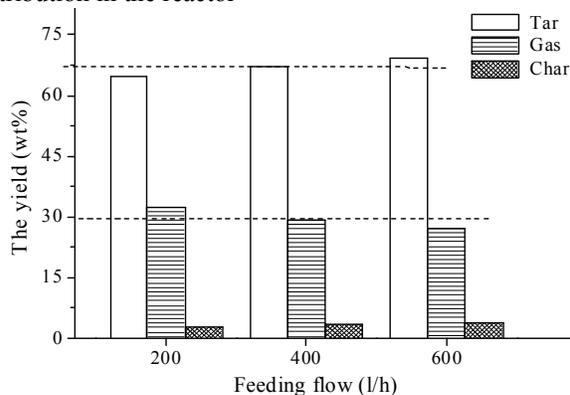
Figure 5: Yields of tar, gas and char upon cellulose gasification at different feeding flows (temperature: 530 °C)

Table 1

Yield of the typical condensable products upon cellulose pyrolysis, determined by GC/MS

RT (min)	Compounds		Molar fraction (%) (530°C, 600 l/h)	Molar fraction (%) (630 °C, 600 L/h)	Molar fraction (%) (530 °C, 200 L/h)
	Name (Abbreviation)	Formula			
2.19	Hexane	C_6H_{14}	0.16	1.58	0.33
2.89	Acetone	C_3H_6O	2.13	3.94	2.97
7.54	Pyruvaldehyde (PA)	C_3H_4O	0.17	0.35	1.16
10.43	Hydroxyacetone (HA)	$C_3H_6O_2$	2.22	4.69	3.43

13.61	Hydroxyacetaldehyde (HAA)	$C_2H_4O_2$	4.72	7.53	8.71
13.86	Furfural (FF)	$C_5H_4O_2$	0.75	0.97	0.92
17.05	2-Hydroxy-2-cyclopenten-1-one	$C_5H_6O_2$	0.55	0.88	0.92
22.28	2,3-Anhydro-D-mannose (2,3-AM)	$C_6H_8O_4$	0.44	0.92	1.09
23.37	Anhydro-D-mannose (AM)	$C_6H_{10}O_5$	2.32	1.61	3.01
24.32	5-Hydroxymethl-furfural (5-HMF)	$C_6H_6O_3$	1.62	3.54	1.64
41.26	Levoglucosan	$C_6H_{10}O_5$	62.22	51.07	53.11

Table 1 shows that levoglucosan (1,6 anhydro-β-D-glucopyranose) is the main component of bio-oil (representing more than 50% of the bio-oil mass), as confirmed by Piskorz,[9] according to whom the initial thermal decomposition of cellulose causes depolymerization of the cellulose polymer to form various anhydrosugar derivatives, the most prevalent being levoglucosan. Furthermore, Shafizadeh et al.[38] reported that the levoglucosan yield is affected both by the cellulose source and by the experimental conditions. The observation was made that the formation of levoglucosan is inhibited by an increased temperature, while that of almost all the other products is increased (Table 1), indicating a possibly competitive mechanism between levoglucosan and the other products (Fig. 6). A similar phenomenon is observed at long residence time (decreased feeding flow), which might involve a sequential mechanism between levoglucosan and the other products, which agrees with literature data.[9,10,17,25,28] Hence, levoglucosan, the major component in bio-oil, also acts as an intermediary for the formation of the other products in cellulose pyrolysis.

Levoglucosan formation from cellulose pyrolysis was explained by the cleavage of the 1,4-glycosidic linkage in the cellulose polymer, followed by intramolecular rearrangement of the monomer units.[28] The similar pathways (1) and (2) plotted in Figure 6 are proposed to express the possible formation of levoglucosan (LG). For pathway (1), the 1,4-glucosidic bond is presumably cleaved by the acetal reaction between C-1 and C-6, releasing the hydroxyl radical from C-6. Then, the free hydroxyl radical coalesces with the disrupted glucosidic bond on C-4 to form levoglucosan (1,6-anhydro-β-D-glucopyranose). Comparatively, the 1,4-glucosidic bond is possibly disrupted by the promotion of the H radical to form the hydroxyl group linked to C-4, after which the acetal reaction between C-1 and C-6 is favoured, releasing another H radical through pathway (2). It is suggested that the hydroxyl or hydrogen free radical might act as an initiator in the formation of levoglucosan.

The formation pathway for 5-HMF is not substantially discussed in the literature, while two of the chemical pathways are proposed in this work: the direct ring-opening and rearrangement reactions of cellulose unit molecules (pathway (4) in Fig. 6), and the secondary reaction of levoglucosan (pathway (8) in Fig. 7). Pathway (4) is initiated through cleavage of the ring glucosidic bond on the cellulose unit to form an aldehyde structure on C-1, followed by the formation of a double-bond on C-4 and C-5, through chain structure rearrangement. Another double-bond on C-2 and C-3 is formed through dehydration of the corresponding hydroxyl groups. Then, the acetal reaction of the hydroxyl groups on C-2 and C-5 is viewed as the essential step in 5-HFM formation. The secondary reactions of levoglucosan to produce 5-HMF (pathway (7) in Fig. 7) were proposed by Shafizadeh,[3] where the pyran-ring is initially cleaved to a hexose chain structure, followed by dehydration of the hydroxyl groups and a sequential acetal reaction on C-2 and C-5. Whatever the origin of the 5-HFM is, furfural (FF) is thought as being produced[25] from the secondary reaction of 5-HFM, along with the formation of formaldehyde through the dehydroxymethylation reaction of the side chain of the furan-ring. Another pathway proposed for the secondary reaction of 5-HMF by Shafizadeh[3] is the rearrangement reaction to form aryl compounds, such as benzene and

phenol, detectable in the bio-oil (yet not presented in Table 1).

The hydroxyacetaldehyde (HAA) is viewed as a major component of the oxygenated products in the bio-oil from cellulose pyrolysis. The well-established chemical pathway for the formation of HAA is presented as pathway (3) in Figure 6 and (6) in Figure 7. Piskorz[9] reported that the ring hemiacetal bond is very active under thermal conditions and also that the bond between C-2 and C-3 is longer than the other positions of the ring. Hence, HAA is easily produced on C-1 and C-2 by ring-opening, through the cleavage of the above two active bonds, a four-carbon fragment being also produced. Furthermore, HAA is also formed on C-5 and C-6 through pathway (7) from Figure 7. It is also suggested by Liao[25] that almost all carbons present on the ring could contribute to HAA formation. HAA decomposition at high temperature is assumed to comply with the chemical pathways (7) – Figure 7 – which produces CO and methanol through the decarbonylation reaction. Pathways (3) from Figure 6 and (6) from Figure 7 show that the possible routes to produce HA (hydroxyacetone) involve mainly cleavage of the four-carbon fragments, either from direct conversion of the cellulose polymer or from the secondary decomposition of levoglucosan. Possibly, HA is mainly produced from the direct conversion of cellulose molecules and partly from the secondary decomposition of levoglucosan, since a higher temperature improves the HA yield more substantially than a longer residence time (Table 1).

Several chemical pathways, involving both direct cracking of the cellulose molecules (Fig. 6) and secondary decomposition of tars (Fig. 7), could account for the formation of CO. Almost all C_{1-6} fragments containing an aldehyde structure, such as tetrose, HAA, HA and aldehyde, can produce CO by decarbonylation reactions. Hence, the carbon position of the produced CO is not specified on the pyran ring. Comparatively, CO_2, produced primarily by decarboxylation reactions, is specified[3] from positions C-1 and C-2. The ketene structure, as a precursor for the formation of the carboxyl group (pathway (5) → (10)), is favoured during a relatively low temperature stage of cellulose pyrolysis.[13,28] The formation of ketene during a high temperature stage is normally overwhelmed by other secondary reactions, producing aldehyde-type compounds. Thus, the CO_2 yield is slightly changed when increasing both temperature and residence time.

Improved kinetic scheme for cellulose pyrolysis

The extensive discussion on the chemical pathway for the main products, at different temperature and residence time values, is conducive to the proposal of an improved kinetic scheme to describe the pyrolysis process of cellulose (Fig. 8). Levoglucosan is viewed as competitive with the formation of Tar 1 (such as HAA, HA, GA and so on) and Tar 2 (such as furfural and 5-HMF) and of char. Meanwhile, levoglucosan also acts as a precursor for the formation of Tar 1 and Tar 2 through secondary decomposition, and of char formation through polymerization and cross-linking reaction. CO formation occurs mainly from the secondary reaction of the fragments (tars), while CO_2 is produced in the initial low-temperature stage through decarboxylation of the ketene structure. The kinetic scheme could assure an improvement of the kinetic model of cellulose pyrolysis, also providing a possible prediction on the formation of a specific product.
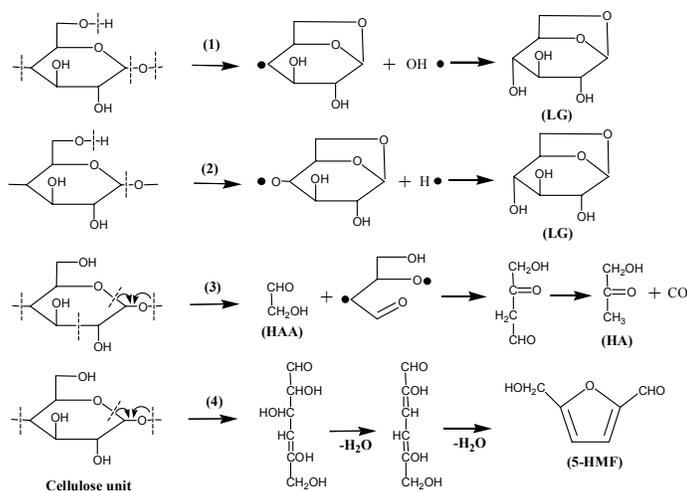
Figure 6: Speculative pathways for the primary pyrolytic reactions of cellulose
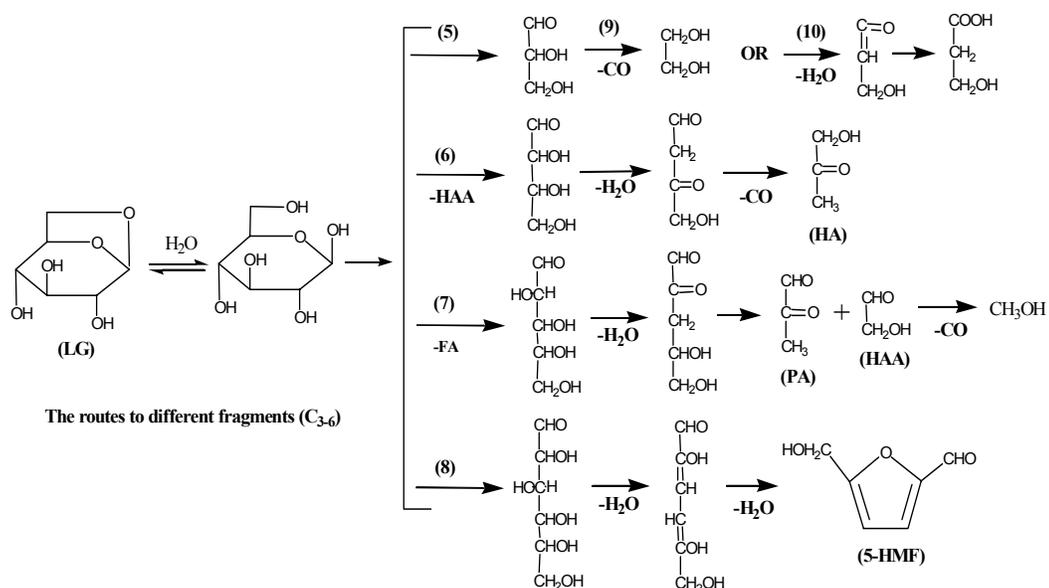
Figure 7: Main chemical routes for the secondary decomposition of levoglucosan
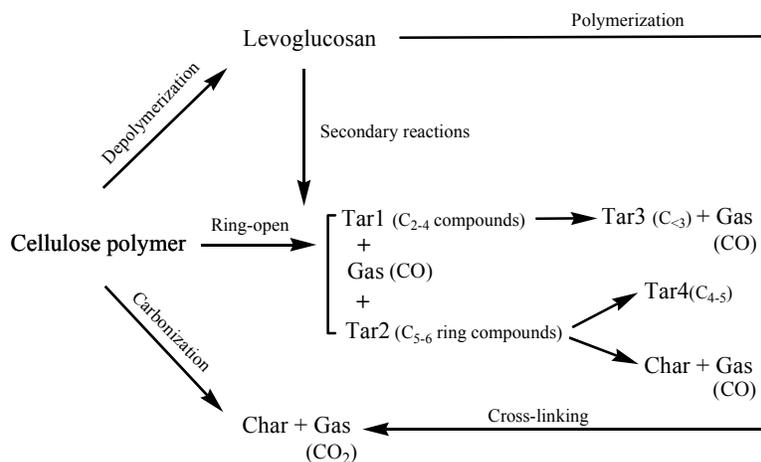
Figure 8: Proposed kinetic scheme for the fast pyrolysis of cellulose

CONCLUSIONS

In cellulose fast pyrolysis experiments, char yield decreases to minor values (less than 5 wt%), remaining stable as temperature exceeds 550 °C, whichever the residence time. The yield of the gaseous products is enhanced at elevated temperature and residence time values, while the bio-oil yield reaches its maximum value (75%) at 570 °C, after which it decreases. Possibly, the formation of gases is not only competitive with the formation of tars, but is also enhanced by the sequential secondary decomposition of tars.

Levoglucosan appears as the major product in bio-oil, being inhibited at elevated temperatures and residence times. Comparatively, almost all main products (5-HMF, FF, HAA and HA) are enhanced at elevated temperature and residence time. It is speculated that levoglucosan acts as not only a competitor with the other fragments in the primary cracking of cellulose, but also as a precursor for secondary decomposition.

Finally, the mechanism working among the cellulose, levoglucosan and other products is estimated by an improved kinetic scheme (Fig. 8), promoting the modification of the kinetic model of cellulose pyrolysis by specific product formation.

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