Comparison of the Pyrolysates of Glucose, Sucrose, Starch and Cellulose

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Summary: Glucose, sucrose, cellulose and starch were pyrolyzed at 300 °C. The liquid products were collected and analyzed using GC-MS. The product distribution on the basis of which the cracking mechanism and path of depolymerization was discussed to evolve a model.

Introduction

Glucose is the simple unit of the oligomeric sucrose and polymers like cellulose and starch. These compounds differ from each other in term of the number and or arrangement of the glucose units. The pyrolysis of these compounds may give products of similar nature. Its determination may help to sort out the path of the pyrolysis of polymeric products like cellulose and starch. It will also help to establish the conditions for the pyrolysis and utilize it as a useful tool for the synthesis of a variety of compounds.

Earlier workers attempted the pyrolysis of saccharides and polysaccharides to explain the emission of toxic products in cigarette smoke [1]. The conversions of cellulose, sucrose and D-glucose into polycyclic aromatic hydrocarbons (PAHs) at 300 to 600 °C also gave a useful clue to the mechanism of this process [2]. Laser pyrolysis of cellulose char also gives the formation of polycyclic aromatic hydrocarbons [3]. The pyrolysis of saccharides and polysaccharides can also be exploited for the analysis of these in various combinations [4]. High frequency pyrolysis of selected carbohydrates *e.g.* glucose, cellulose etc were also carried out by cutie point pyrolysis at 700 °C [5]. Thermal degradation of starch is carried out at 300 °C and volatile products were identified by GC [6].

In the present work attempts are made to investigate the effect of the number of the glucose basic units as well as its arrangement in the polymer on the nature of products and path of the reaction. The liquid products were selected for this task, which were analyzed using GC coupled with mass spectrometer.

Results and Discussions

Cellulose, starch, glucose and sucrose were pyrolyzed at 300 °C into liquid products [6] which appeared as reddish brown liquids. The products can be separated into oily and aqueous portions having the same characteristic smell.

The oil portion becomes indistinguishable from the aqueous by addition of alcohol or acetone. The liquid products of the cellulose starch, sucrose and glucose were analyzed using GC-MS. The components were identified by library matching and fragmentation pattern. The quantitative analysis was carried out by peak area and the composition of the pyrolysates is given in the following Table 1. Glucose is the simplest carbohydrate and gives furans, furanones and acids on pyrolysis. The pyrolysis process of glucose began with the dehydration and ring opening. This is a free radical type reaction, which is followed fragmentation. Among these fragments the five carbons fragment cyclize to form furan. The smaller fragments may interact to form derivatives of the furans or carboxylic acids and homocyclic compounds. These fragments may be acetyl, formyl or alkyl compounds. The presence of anhydro pyranose confirms the dehydration, while the formation of furans, furanones and hydroquinones suggests other than primary reactions.

The analysis on the pyrolysate of sucrose show that it also passes through complex reactions. Some of these are similar to those occurring in the pyrolysis of glucose. Therefore the furans, furanones and carboxylic acid formation are the common steps which led to the formation of 1-(2-

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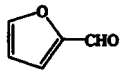
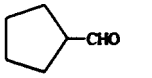
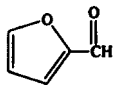
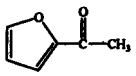
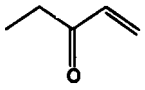
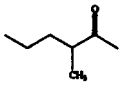
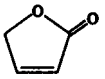
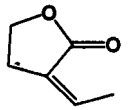
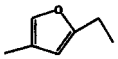
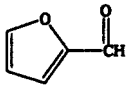
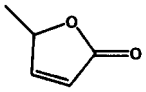
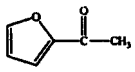
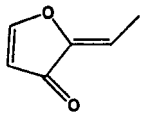
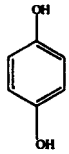
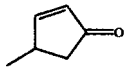
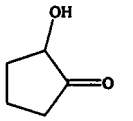
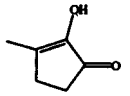
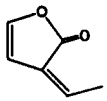
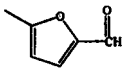
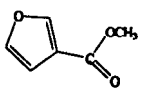
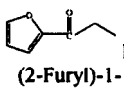
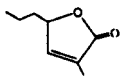
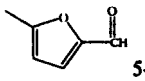
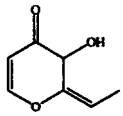
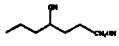
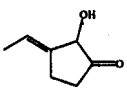
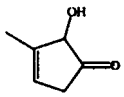
Table-1. Pyrolysates products of glucose, sucrose, starch and cellulose.

S. No	Glucose		Sucrose		Starch		Cellulose	
	Name of compound	Conc. %	Name of compound	Conc %	Name of compound	Conc. %	Name of compound	Conc. %
1	 2-Furaldehyde	29.748	 Ethenyl propyl ether	1.867	 Cyclopentane carbaldehyde	12.752	 2-Furaldehyde	9.906
2	 1-(2-Furyl)-1-ethanone	1.591	 Pent-1-en-3-one	7.105	 3-Methyl-2-hexanone	0.548	 2-(5*H*)-Furanone	1.640
3	 3-(*Z*)-Ethylidene]di-hydro-2-furanone	0.036	 2-Ethyl-4-methyl furan	9.701	 2-Furaldehyde	0.217	Unknown	0.683
4	 5-Methyl-2(5*H*)-furanone	0.329	 1-(2-Furyl)-1-ethanone	1.503	 2-Ethenyl furanone	0.090	Unknown	2.478
5	 Hydroquinone	2.369	 4-Methyl-2-cyclopenten-1-one	0.205	 2-Hydroxycyclopentane	0.501	Unknown	0.410
6	 2-Hydroxy-3-methyl cyclopent-2-en-1-one	0.415	 3-Ethenyl furanone	1.457	 5-Methyl furfural	5.602	Unknown	0.410
7	 Methyl-3-furoate	0.956	 1-(2-Furyl)-1-propanone	10.111	 3-Methyl-5-propyl-2-(5*H*)-furanone	0.474	 5-Methyl furfural	3.484
8	 2-Ethenyl-3-hydroxy-4*H*-pyran-4-one	0.697	 1,4-Heptandiol	0.491	 3-Ethenyl-2-hydroxy cyclopentanone	0.246	 2-Hydroxy-3-methyl-3-cyclopenten-1-one	0.455

9	1,4:3,6-Dianhydro-α-D-glucopyranose	0,727	4-Methyl-3, 5-dienecoctanal	0.141	4-Hexen-3-one	3.051	3-Methyl-1,2-cyclopentandione	2.550
10	5-(Hydroxymethyl)-2-furaldehyde	14.118	Methyl-3-furoate	1.421	2,5-Dimethyl-3-furanol	3.197	Unknown	0.5465
11	5-Methyl-1,2,3,4-cyclopentanetetrol	2.733	1-(2-Furyl)-1,2-butanediol	0.410	3-Hydroxy-2-methyl-4*H*-pyran-4-one	2.186	Unknown	0.455
12	Hexadecanoic acid	3.182	Unknown	0.273	3-Hydroxy-4*H*-pyran-4-one	0.414	Methyl-2-furoate	1.275
13	Unknown	19.675	Unknown	2.013	1,4:3,6-Dianhydro-α-D-glucopyranose	5.465	2-Octen-1-ol	1.275
14	Unknown	0.547	Hexadecanoic acid	2.097	5-(Hydroxymethyl)-2-furaldehyde	8.380	5-(Hydroxymethyl)-2-furaldehyde	18.034
15	Octadecanoic acid	0.820	Unknown	24.593	Unknown	0.765	2-Methyl-3,5-dihydroxy-4*H*-pyran-4-one	0.820
16			Octadecanoic acid	0.182	Unknown	7.970	1,4:3,6-Dianhydro-α-D-glucopyranose	25.500
17			Unknown	0.637	Unknown	1.822		
18					Hexadecanoic acid	1.321		
19					Octadecanoic acid	0.510		

furyl)-1-ethanone, ethenyl furanones, hexadecanoic acid and octadecanoic acid in the pyrolysates of glucose and sucrose.

The pyrolysis of starch and cellulose follow two common steps. The depolymerization and dehydration process. The dehydration process of the starch results in the formation of more stable anhydro sugars. This is due to the unique attachment of cellobiose or glucose units in starch. This is clear from the greater concentration of 1,4: 3,6-dianhydro-α-D-glucopyranose in the pyrolysate of starch as compared to that of cellulose. The pyrolysis of starch involves dehydration and depolymerization into smaller units including glucose to sucrose. The ring opening and fragmentation of these smaller units leads to the formation of furans, furanones, homocylics and carboxylic acids. The proof of this is the presence of 2-furaldehyde, furaldehyde acid, octadecanoic acid etc. in the pyrolysate of glucose and cellulose. The presence of three types of sugars e.g. 3-hydroxy-2-methyl-4*H*-pyran-4-one (maltol), 3-hydroxy-(4*H*)-pyran-4-one and 1,4: 3,6-dianhydro-α-D-glucopyranose in the pyrolysate of the starch is due to the high molecular weights and characteristic arrangement of the glucose units in starch.

In case of cellulose the glucose units which have 1,4 linkage, its pyrolysis gives different products than starch, but the mechanism is the same *i.e.* dehydration, depolymerization, fragmentation ring closure, oxidative addition and substitution. Thus the product distribution is similar to all the above mentioned. It also forms furans, furanones, aldehydes and ketones but not long chain acids [7].

Based on these observations it can be concluded that the pyrolysis of glucose that it under goes dehydration resulting in the formation of levoglucosan (1,6-anhydro-β-D-glucopyranose) which is a dehydrated sugar, then after a series of bond rearrangements, dehydration and by the lose of formaldehyde yield furfuraldehyde along with other products. Hydrolysis of glucose units proceeds through the formation of epoxide or an enol followed by internal rearrangement, dehydration, elimination of formaldehyde to yield furfuraldehyde and other products [8].

Since pyrolysis of these glucose polymer pass through an additional dehydration and oxidations in polymeric state and after depolymerization, this model is different from earlier finding [1], in which the pyrolysis of D-glucose, fructose and sucrose is distinguished from that of cellulose. Cellulose and starch differ from each other due to variation in the position of linkages of glucose units. This difference also found in the formation of pyrolysate products and their yields [9]. Cellulose is a linear polymer of β-D-glucopyranosyl units and its degradation occurs through dehydration, hydrolysis, oxidation, decarboxylation and transglucosylation. The primary reaction at high temperature is depolymerization through cleavage of the glycosidic linkage to produce glucose, which undergo dehydration to form levoglucosan (1,6-anhydro-β-D-glucopyranose) and oligosaccharides [10-12].

Experimental

The apparatus for the preparation of sample include a Pyrex vessel of 58 mm external diameter and 300 mm length connected with a condenser and receiving flask through a bent adaptor. It is kept in an externally heated furnace powered through a temperature controller equipped with thermocouple.

Fine cuttings of 25 g of paper which usually used in computer printing were taken in the glass vessel and kept in preheated furnace for one hour. The temperature of furnace was kept between 200-300 °C. The liquid product distilled and collected in a receiving flask.

The same apparatus was used for the pyrolysis of D-glucose, sucrose and starch. The distillates of all these compounds are brown liquids distinguishable into a dense oily film in the aqueous portion.

GC-MS Analysis

General profiles for liquid product of pyrolysis was obtained using EI-MS. Analysis of the liquid product was conducted on a mass spectrometer JMS 600 H Jeol and the product was separated into its components using Agilent 6890N gas chromatograph equipped with a fused capillary column (HP 0.5 L; 30 m i.d.; 0.32 mm, film thickness 0.25 μm) with polydimethylsiloxane as

the stationery phase. The carrier gas was helium at a flow rate of 1.8 ml/min.

The conditions for analysis were;Injection mode was split at split rate 35. The column was held at 50 °C for five minutes and then to 240 °C at the rate of 5 °C/ min. The injector temperature was 250 °C. While the amount of sample was 1 μl.

The identification of major components of the product was confirmed using total ion chromatogram analysis (TIC) as well as fragmentation pattern and library matching. However, the quantification was carried out by using the appropriate software of the system.

Conclusions

The pyrolysis of D-glucose, sucrose, starch and cellulose at lower temperature give liquid product of the similar physical characteristics. Their chemical composition is similar in having furans, furanones, anhydro sugars, aldehydes, ketones and acids with some variations despite of the presence of the compound of the same composition. The pyrolysis of this entire follow similar path. This gives similar product. All these were investigated from GC-MS analysis.

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