Journal of Chemical Technology and Metallurgy, 56, 4, 2021, 725-729

THE THERMAL ANALYSIS OF THE LINEAR CARBOHYDRATES CONSTRUCTED OF GLUCOSE RINGS

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Received 12 November 2019
Accepted 10 March 2020

ABSTRACT

This article presents the results of a thermal analysis of individual linear carbohydrates, the molecules of which consist of pyranose rings interconnected by the same type of α-glycosidic bonds. It is shown that, when heated, substances first lose adsorbed and crystalline hydrate water, some of them melt, and then decompose in two stages. The amount of weight loss with carbohydrates and the temperature of their individual stages depend on the number of pyranose rings in the saccharide molecules. With an increase in the average degree of polymerization of saccharides, their heat resistance generally increases. The temperature, thermal and gravitational effects of each stage, as well as the heat resistance of saccharides depend on the number of pyranose rings in the molecules of carbohydrates.

Keywords: IR-Fourier spectrum, carbohydrate, thermal analysis, α-1,4-glycosidic bond, pyranose ring.

INTRODUCTION

A carbohydrate is any representative of a large group of compounds that contain carbon, hydrogen, and oxygen, and which have the general formula $C_x(H_2O)_y$. Starches and sugars called carbohydrates are the main source of dietary energy [1 - 3]. Carbohydrates (monosaccharides, oligosaccharides, polysaccharides) are an important source of energy: they are produced by plants and enter the body of animals and humans with food, being one of the three main components of food. All carbohydrates are ultimately broken down in the body to simple glucose sugar, which then takes part in the metabolic processes with the release of energy [4 - 7]. Many of the carbohydrates subjected to a heat treatment in obtaining products or during the use of already produced on their base materials, for example, as a part of composites. At the same time, they undergo numerous changes and decompose. It is known that the composition of the products of thermal decomposition of the main types of carbohydrates is often extremely complex [8 - 10], and a large number of chemical reactions can occur which cause their appearance [11 - 14]. In this paper, an attempt was made to identify general patterns in the behavior when heating a number of similar saccharides, whose molecules are constructed from pyranose rings of glucose, interconnected by α-glycoside bridges of C-O-C. In this case, we did not focus on the details of the question concerning the nature and composition of the products of thermal decomposition of carbohydrates. The task of this study was to establish how the average degree of polymerization in linear saccharides affects the temperature thresholds of their transformations and the magnitude of thermal effects.

EXPERIMENTAL

Carbohydrates with a polymerization degree of 2 - 7, as well as glucose and high polymer amylose were tested (Table 1). Some commercial characteristics of the examined compounds are given in the table. For the study of the sugars a device combined thermal analysis STA 449 F3 Jupiter Netzsch company was used. Samples weighing

3 - 4 mg were heated in closed corundum crucibles with a volume of 85 µl. at a speed of 5 deg $\min^{-1}$ in dry nitrogen atmosphere. The device was pre-calibrated by temperature using the Netzsch method and standard samples.

RESULTS AND DISCUSSION

Thermal analysis indicates that glucose undergoes several endothermic transformations when heated to 500°C (Fig. 1(a)). During the first of these, starting above 144°C and reaching a maximum depth of about 154°C, the substance obviously melts, since the process occurs with heat absorption, but without weight change. According to literary data, for example, given in [8], glucose melting, in fact, takes place near 150°C - 160°C. Immediately after the first endo-effect weight substances begins to decrease. This occurs to a greater extent, the higher the temperature, but by 250°C the process slows down. As a result, a stage is formed on the TG curve, the end of which corresponds to a reduction in the weight of the sample by 23 %.

Heat absorption at this stage is manifested in the DSC (Differential Scanning Calorimetry) curve in the form of a not very intense, but rather wide thermal effect, completely coinciding in temperature with the step on the TG curve, which indicates the beginning of glucose destruction [1]. The results of the kinetic analysis, published in [4, 5], indicate that in the specified temperature range several consecutive and parallel reactions take place, whose contribution to the overall process depends on the temperature and heating rate.

According to [6, 7] on the course of the process also affect the composition of the atmosphere, the presence of impurities in substances and many other factors. According to [2], the products of glucose thermolysis are represented by several tens of compounds, and according to [3] their number reaches 130.

Due to the complexity and variability of the composition of volatile products of thermal degradation of glucose, as well as other carbohydrates, their analysis in this work was not performed. Weak decomposition of glucose is possible earlier, already close to the melting point, but with prolonged heating.

Further heating of the substance leads to the continuation of weight loss, which is manifested on the TG curve by an even greater step than the previous one: the total loss at this stage is approximately 55 %. However, on the DSC curve, this transformation is found in the

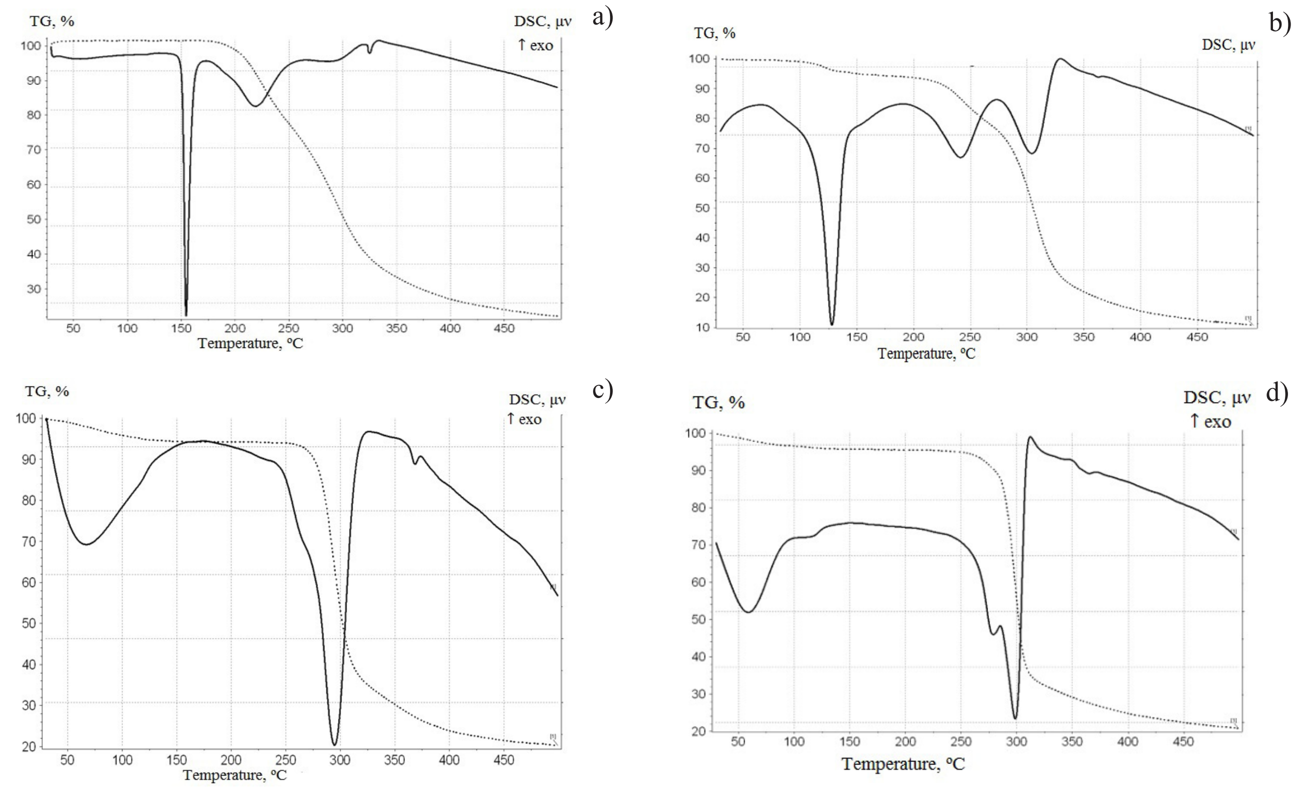

Fig. 1. DSC and TG curves for glucose (a), maltose (b), amylose (c) and amylopectin (d).

Table 1. Characteristics of carbohydrates.

No	Name of carbohydrate	Content of the main substance, %, additional characteristics	The ratio of the number of bonds $\alpha(1\rightarrow4)$ to the number of pyranose rings in a sugar molecule (conditional value R)	Manufacturing firm, serial number
1	Glucose	≥99.5% D-(+)-glucose BIOXTRA	0	Sigma No G8270
2	Maltose	≥98.0% D-(+)- maltose monohydrate	0.50	Sigma-Aldrich No M5885
3	Maltotriose	98.0%	0.67	Sigma-Aldrich No M8378, lot 017K0679
4	Maltotetraose	96.0%	0.75	Sigma-Aldrich No M8253, lot 109K1271
5	Maltopentaose	96.0%	0.80	Sigma-Aldrich No M8128, lot 040M1774
6	Maltohexaose	≥90.0%	0.83	Sigma-Aldrich No M9153,
7	Maltoheptaose	94.0%	0.86	Sigma-Aldrich No M7753, lot 079K0987
8	Amylose	98.0%	1.00	City Chemical LLC, lot 01M54
9	Amylopectin	≥95.0%	1.00	Sigma-Aldrich, 10118, lot 1422493

form of a very small thermal effect. The discrepancy between the thermal and gravitational manifestations can be explained by the superposition of several reactions, including the secondary ones. This refers to the reaction between the primary product glucose thermolysis occurring, for example, in the gas phase. As a result, with a significant decrease in the weight of the substance, the thermal effect of the process may be small.

The condensed phase remaining after removal of the main part of the volatile products from glucose consists mainly of carbon. However, judging by the fact that the TG curve does not reach the horizontal section even at the end of heat treatment (500°C), the resulting residue is not an individual substance, but rather a substance in which organic components are preserved in addition to carbon.

The second representative of the homologous series of linear carbohydrates, the disaccharide maltose, when heated should behave like glucose [1]. Indeed, this saccharide resembles glucose in its behavior, but at the same time it differs from it. As in the case of glucose, there are three endo-peaks on the DSC curve of maltose, but not two, like glucose, but three stages of weight loss (Fig. 1(b)).

The lowest temperature endo-effect on the DSC curve of maltose with a minimum of about 128°C is most intense. During it, water is released from the substance in an amount of about 4 %, which corresponds to the monohydrate composition of the starting saccharide. Since the anhydrous disaccharide melts at 107°C, at the temperature of the endothermic effect the substance passes into a liquid state.

The second endo-peak in the DSC maltose curve is shifted to higher temperatures compared to the same effect of glucose. On the TG line, it corresponds to a reduction in weight in the form of a distinct step, which indicates the beginning of destruction. It is likely that at this stage the same transformations occur in maltose as in glucose.

The third stage of transformations in the disaccharide is expressed on the DSC curve much stronger than that of glucose, although the weight loss on it is almost the same.

If a small heat absorption with significant decom-

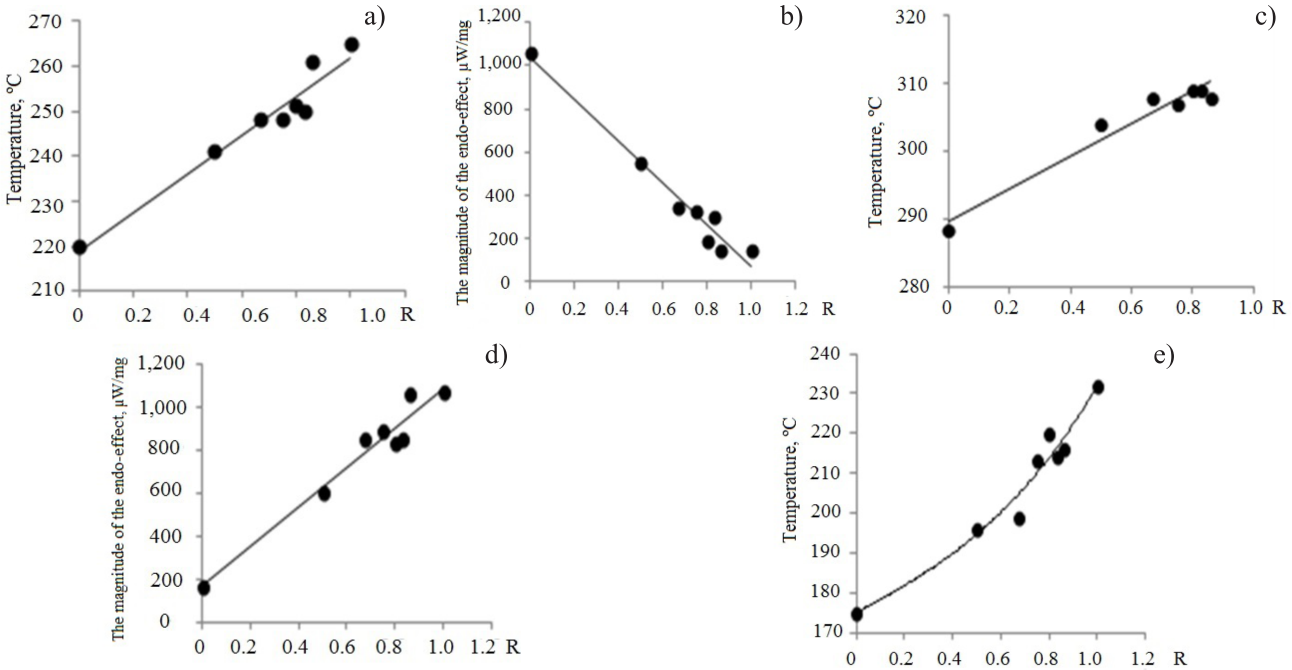

Fig. 2. The effect of the ratio of the number of α-glycosidic bonds to the number of pyranose rings in carbohydrate molecules (R) on the temperature of the minimum and the value of the second (a, b) and third endo effects (c, d, e).

position of glucose could be associated with the imposition of exothermic reactions between the thermolysis products of the saccharide on the main process, in the case of maltose, the situation is probably more natural: a significant reduction in weight corresponds to a significant heat absorption.

The rest of the studied oligosaccharides character of DSC and TG curves is almost the same as maltose, but there are quantitative differences. Thus, with an increase in the degree of polymerization of carbohydrates or with an increase in the ratio of the number of α-glycosidic bonds to the number of pyranose rings in the molecules of substances, the temperature of the second endo-effect increases, and its area decreases. In this case, the third thermal effect increases at a practically constant temperature (Fig. 2). As for the first stage of transformations, due to the presence of different amounts of adsorbed moisture in substances, the magnitude of the corresponding thermal effects in this work was not analyzed.

The most polymerized of saccharides with only α-glycosidic bonds, amylose, should form a natural continuation of a number of carbohydrates studied. Fig. 1(b) confirms that in general this is the case. In accordance with the tendencies shown in the Fig. 1(b), the second endo-effect on the DSC amylose curve is very close to the third one, almost fused with it, and greatly weakened, and the third one, on the contrary, is strengthened.

Since amylose is one of the two main components of natural starches, it was of interest to touch upon the issue of the thermal behavior of the second macro-component of starch, amylopectin. From the Fig. 1(d) it follows that this substance by its behavior when heated resembles amylose. Indeed, the first stage of transformations in it involves the loss of moisture, accompanied by a slight heat absorption. This is followed by two mutually overlapping stages of endo-thermic decomposition, which, however, are more distinguishable than in the case of amylose.

It should be noted that both the temperatures and the magnitudes of the endo-effects on the DSC curve of amylopectin go beyond the dependencies shown in the Fig. 2. And this is quite natural, since the structure of amylopectin is significantly different from linear saccharides.

CONCLUSIONS

Thus, individual linear carbohydrates built from glucose rings interconnected by α-glycosidic bonds, starting from glucose itself and ending with high-polymer amylose, undergo a certain transformation when heated in a nitrogen atmosphere. First, adsorbed and crystalline hydrated moisture is removed from the substances with the melting of some of the saccharides. Next, destruction begins in the form of a sequence of reactions, including those proceeding in parallel. And finally, deep transformations develop, as a result of which carbohydrates, having lost a significant part of their mass, form carbon substances with residues of organic matter. Amylopectin in its behavior under heating conditions resembles amylose, which it accompanies as a macro component in natural starches, although in general it falls out of the range of linear carbohydrates studied.

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