THERMAL DECOMPOSITION OF SOYBEAN HULL CELLULOSE: A KINETIC STUDY

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Abstract - Simultaneous DSC-TGA (SDT) technique was used to obtain thermal data from derivative TGA curves to investigate the kinetics of the decomposition process of cellulose extracted from soybean hull (CCS). A comparison with commercial microcrystalline cellulose (MCC) was made. The isoconversional Vyasovkin method was applied to DTG data and indicated that the kinetic degradation behavior of soybean hull cellulose is similar to that of commercial microcrystalline cellulose. In this work, it was evaluated the applicability of the software TA Instruments (TA Specialty Library Software Version 2.2), where kinetic parameters can be readily calculated through comparison to results obtained by Vyazovkin method calculations. The values of activation energy are comparable showing that both procedures are suitable for the determination of kinetic parameters.

Keywords: soybean hull cellulose, simultaneous DSC-TGA, kinetic methods, thermal decomposition.

Introduction

In the extracting process of soybean oil, the main by-products are the soybean meal (high fat protein and low fiber concentration) and soybean hulls (tissue coating the grain). As soybean hulls is 7-8% by weight of soybean, it can be estimated an annual production of 5 million tons in Brazil. This country is the second world largest producer of soybean with a planted area of 24.2 million hectares (EMPRAPA SOJA, 2013)[1]. The great importance about the knowledge of thermal properties of celluloses from plant residues is associated with wide applications such as generation of energy from biomass and the production of nanocellulose which can be a source of nanoparticles called whiskers. Several kinetic methods to evaluate thermal degradation of biomass and cellulose have been discussed in the literature [2-4]. Most of them considers the kinetic analyses based on multiple nonisothermal heating runs, performed by using methods such as those of Flynn-Wall-Osawa (FWO) [5,6] and Vyazovkin [7] presented in Table 1. These methods are isoconversional meaning that the activation energy is evaluated in each extent of conversion over the entire degradation process. The kinetic data can be obtained directly from TA Specialty Library Software Version 2.2 Built 2.2.0.1 which operates in accordance with the ASTM Standard E1641 "Decomposition Kinetics by TGA" [8]. This program utilizes data gathered by running a sample at various heating rate. The program analyzes results from TGA data files to calculate the heating rate at each conversion percentage, and then generates plots and tables of kinetic analysis results. This software is based in Flynn-Wall-Osawa (FWO) isoconversional method.

Table 1 - Kinetics methods based on nonisothermal runs (linear function: y = mx +c).

METHOD	Y	X	slope=m	Reference
Flynn-Wall- Osawa	$\log(\phi_i)$	$1/T_{\alpha,i}$	$-0.4567+E_\alpha/R$	5
Vyazovkin	$\ln(\phi_i/ T_\alpha^2)$	$1/T_\alpha$	$-E_\alpha/R$	7

$R=8.314 \times 10^{-3}$ kJ.K^{-1}.mol^{-1}; T_α: temperature at extent of conversion (α); ϕ: heating rate; E: activation energy

The activation energy of degradation (E) was obtained from the Flynn-Wall-Osawa method according to the terms listed in Table 1. Using this method, E for each conversion can be obtained from the slope of the plot of log(ϕ) versus 1000/T(K). Because isoconversional methods describe the kinetics of the process by using multiple single-step kinetic equations where each equation is associated with a certain extent of conversion, they permit that complex multi-step processes can be detected by a variation of E_α with α.

However there have been not many kinetics studies on volatilization taking into account cellulose from soybean hull and multiple isoconversional methods [9]. The aim of this work is to study the kinetics of degradation process of cellulose extracted from soybean hull and compare its behavior to that of commercial microcrystalline cellulose under inert environment using two nonisothermal kinetic methods. This study was performed using thermal analysis tools such as simultaneous DSC-TGA technique.

Experimental

Cellulose from soybean hull (CCS) was extracted from its source by means of an environmental-friendly multistep procedure involving alkaline treatment and a totally chlorine-free bleaching [10,11]. Microcrystalline cellulose (MCC) supplied by Quimsul (RS-Brazil) was used for comparison. TGA analyses using CCS and MCC celluloses were performed in a simultaneous DSC-TGA (so-called SDT) Q600 from TA Instruments under inert atmosphere of N_2 in a flow of 100 ml min^{-1}. The samples were submitted to a thermal procedure by which it was applied a ramp of 30 $^oC\ min^{-1}$ from room temperature to 150 ^oC and equilibrated at this temperature for 5 min to remove adsorbed water [9, 10]. After this isothermal condition, samples were cooled down to 35^oC and a second scan was performed at four different heating rate (5,10, 15, and 20 ^oC/min) up to 395^oC to obtain different mass loss curves parameters to study the degradation kinetics of celluloses.

Results and Discussion

Analyzing Fig. 1, it can be noticed that the decomposition process occurs in a single step for all cellulose samples and that increasing the heating rate (ϕ), the related curves shifted to higher temperatures, as expected. This can be more evident by observing the inset of DTG curves.

The peak of decomposition of MCC appeared around 300-400 ^oC and to CCS it appeared around 270-390 ^oC, but MCC peak temperature values were assigned at higher temperatures than the others. In addition it is known that crystallinity index χ_{MCC} is higher than that of χ_{CCS}[11], and this fact could be related to the position of the decomposition peak [12] temperatures obtained in this work by TGA as $T_{MCC} > T_{CCS}$. The celluloses which have higher crystallinity lead to higher thermal stability, in this sense the MCC thermal behavior showed a better thermal stability than CCS.

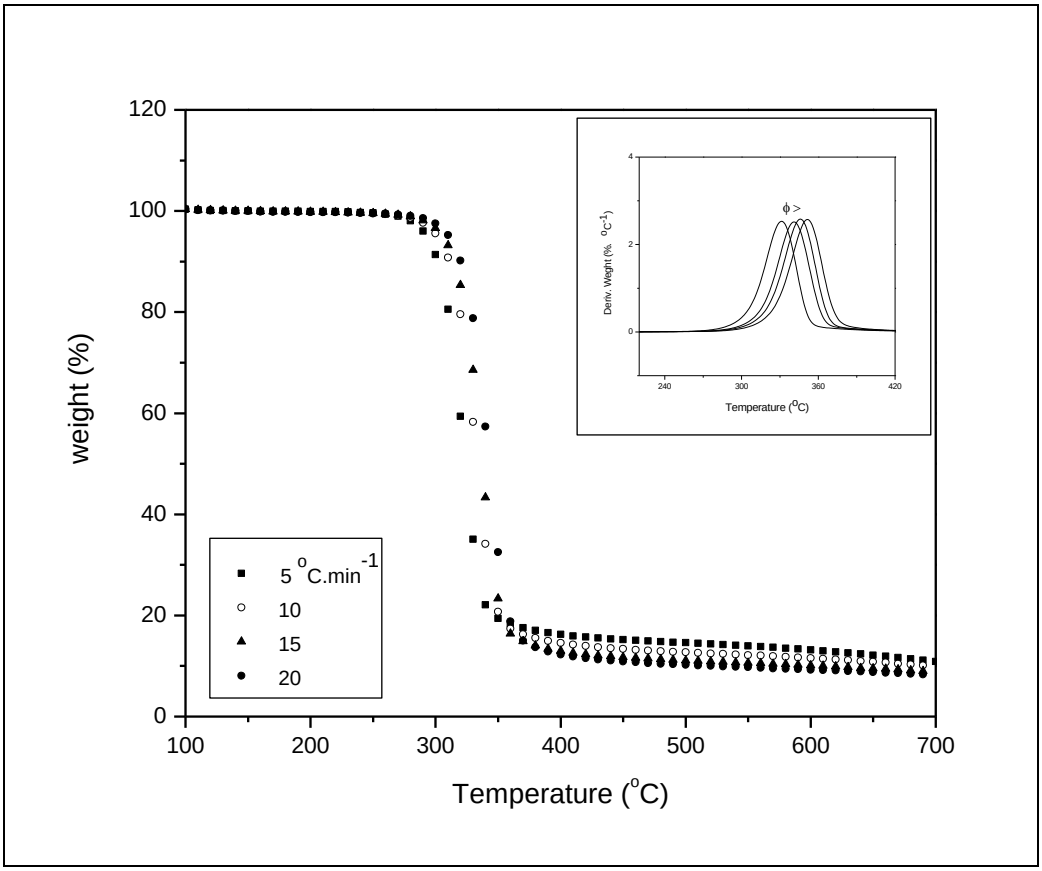

Figure 1 – Curves obtained by TGA analysis at different heating rate (5, 10, 15 and 20 ^oC/min) and an inset of DTG curves for soybean hull cellulose (CCS).

In this work the data were not integrated and it was made the calculation at the same conversion levels used in FWO and TA Software, as described on Table 1. Applying Vyazovkin method to DTG data on cellulose decomposition - where the process presented a single mass loss step - it is shown that at each extent of conversion (α) were examined celluloses (soybean hull and commercial microcrystalline) with different stability levels and degradation process characterized by different E (or E_α). It was verified that in all groups of plots the straight lines are almost parallel to each other as shown in Fig. 2 to CCS. This could indicate that E_α does not vary significantly with α and the process could be described by a single-step rate equation throughout the whole range of conversions and temperatures as well recommended by Vyazovkin et. al [13]. The same behaviour was observed to MCC (figure not shown).

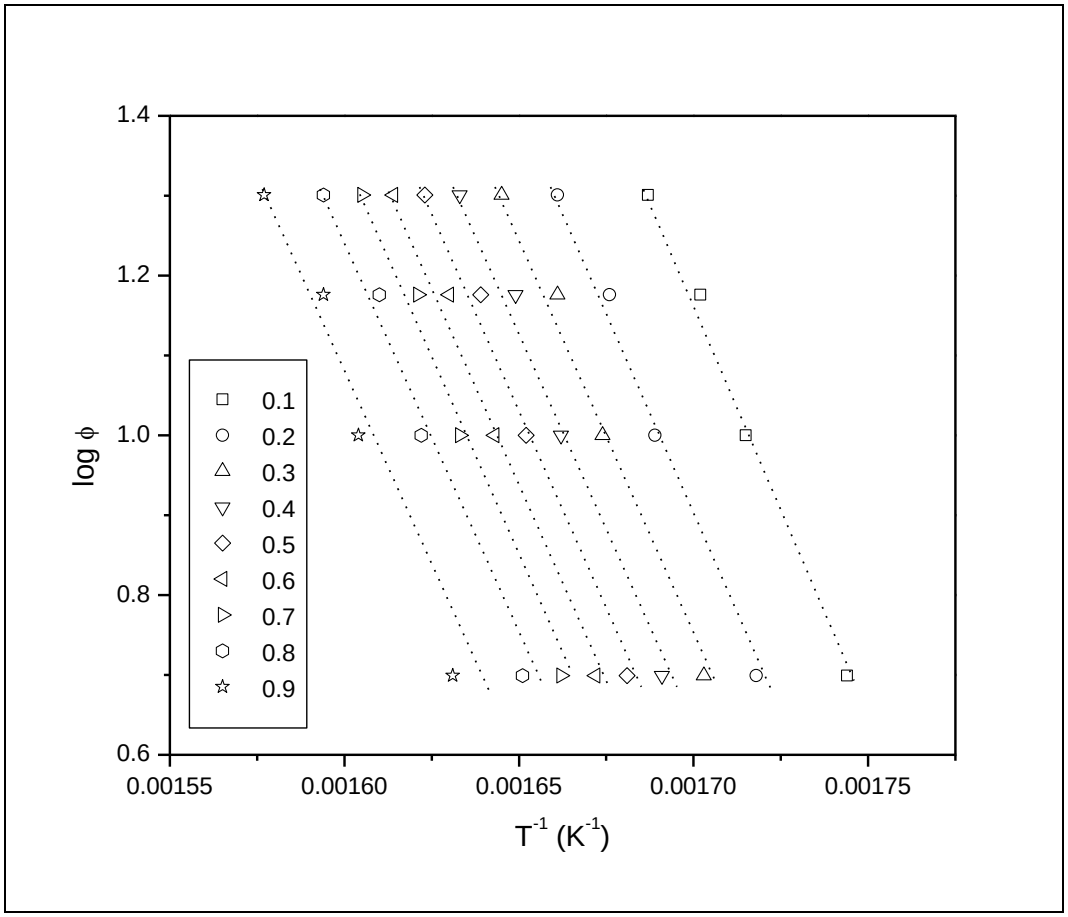

Figure 2 – Application of Vyazovkin kinetic method to soybean hull cellulose (CCS) at each extent of conversion (α: 0.1 to 0.9).

In Table 2 a comparison can be made between E^{TA} and E^{VYA} results. It can be noticed that E^{MCC} values are higher than E^{CCS} independently of the extent of conversion (α) or the kinetic methods applied. This tendency can be also related to the higher crystallinity of MCC [11, 12].

Taking into account that the E^{VYA} curves present higher values, it is possible to calculate a percentage of the difference for two calculations called ΔEa, which can be defined by equation $[\Delta Ea]\% = (E^{VYA} - Ea^{TA}/ E^{VYA})x100$ and they are listed on Table 2. These $[\Delta Ea]\%$ differences have been attributed to the smoothing effects preset generally in these softwares. The values calculated by TA Specialty Library Software can be acceptable since strong variations that can reach 20-30% when using isoconversional methods described in literature assumed that[9].

Table 2 - Activation energies calculated from isoconversional method of TA software (E^{TA}) and Vyazovkin method (E^{VYA}) determined at each extent of conversion (α).

α	CCS			MCC		
	*E^{VYA}	E^{TA}	[ΔE]%	E^{VYA}	E^{TA}	[ΔE]%
10	189.3	187.0	1.2	207.0	197.9	4.3
20	189.5	185.5	2.1	208.1	202.0	2.9
30	188.0	184.2	2.0	207.0	202.4	2.2
40	188.2	182.9	2.8	203.4	199.5	1.9
50	188.3	182.2	3.2	202.0	195.5	3.2
60	189.1	181.8	3.9	201.5	192.1	4.7
70	188.2	181.9	3.3	200.6	188.7	6.0
80	188.3	183.2	2.7	199.3	185.4	6.0
90	189.2	187.5	0.9	198.1	186.9	6.0

*E: kJ/mol

Conclusion

Techniques as simultaneous DSC-TGA improved the knowledge of thermal degradation concerning to the singular thermal events present in cellulose from soybean hull source under pyrolysis. The simultaneous DSC-TGA technique showed that DTG and DSC curves presented a unique process at higher temperature region which is significantly influenced by crystalline regions on thermal decomposition of celluloses. However, the activation energy values of MCC are higher than those of CCS; this is to be expected, once the crystallinity index of MCC is higher than that of CCS.

Kinetics studies on thermal decomposition process of soybean hull cellulose in comparison with a commercial microcrystalline showed that, considering the applicability of the TA Specialty Library Software Version 2.2, it was verified that it is suitable when compared to results obtained by other kinetic method. It can be concluded that an important potential relation between kinetics-thermal-crystallinity parameters was successfully established towards the understanding of cellulose decomposition process.

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