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Thermal Degradation Properties and Thermodynamics of Cellulosic Biomasses

Selülozik Biyokütlelerin Termal Bozunma Özellikleri ve Termodinamiği

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ABSTRACT

In this article, a compilation of articles examining the thermal and thermodynamic degradation of cellulose cores that occur naturally in nature and are produced as waste from foods consumed as food in daily life is presented. Thermal degradation behaviour and thermodynamic properties of cellulosic biomasses are investigated using thermogravimetric analysis (TGA) using different atmospheres. The aim of the studies was to understand the degradation properties and evaluate the energy parameters that are critical for bioenergy applications. Many different methods are used to evaluate the kinetic parameters without assuming a specific reaction mechanism. These methods are divided into two groups: model-fitting and model-free. Degradation of cellulosic substances can be single- or multi-step according to their content. A thermodynamic triplet can be calculated from these calculations. Activation energy values were determined as a function of the degree of conversion by revealing the different stages in the degradation process corresponding to the decomposition of hemicellulose, cellulose, and lignin. Thermodynamic parameters such as enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) were also calculated to evaluate the energetic feasibility and spontaneity of thermal reactions. The results show that cellulosic biomass exhibits a multistep degradation process with a significant change in activation energy across the conversion range. These findings provide valuable insights for the optimization of thermal conversion technologies such as pyrolysis and gasification and provide a basis for designing efficient biomass-to-energy systems.

Keywords: Biomass, Cellulose, Thermal Degradation

ÖZ

Bu makalede, doğada doğal olarak bulunan ve günlük yaşamda gıda olarak tüketilen gıdalardan atık olarak üretilen selüloz çekirdeklerinin termal ve termodinamik bozunmasını inceleyen makalelerden oluşan bir derleme sunulmaktadır. Selüloz biyokütlelerinin termal bozunma davranışı ve termodinamik özellikleri, farklı atmosferlerde termogravimetrik analiz (TGA) kullanılarak incelenmiştir. Çalışmaların amacı, bozunma özelliklerini anlamak ve biyoenerji uygulamaları için kritik olan enerji parametrelerini değerlendirmektir. Kinetik parametreleri değerlendirmek için belirli bir reaksiyon mekanizması varsaymadan birçok farklı yöntem kullanılmaktadır. Bu yöntemler, modele uygun ve modelsiz olmak üzere iki gruba ayrılır. Selüloz maddelerinin bozunması, içeriklerine göre tek veya çok adımlı olabilir. Bu hesaplamalardan termodinamik üçlü hesaplanabilir. Aktivasyon enerjisi değerleri, hemiselüloz, selüloz ve ligninin ayrışmasına karşılık gelen bozunma sürecindeki farklı aşamaları ortaya çıkararak dönüşüm derecesinin bir fonksiyonu olarak belirlenmiştir. Entalpi (ΔH), Gibbs serbest enerjisi (ΔG) ve entropi (ΔS) gibi termodinamik parametreler de termal reaksiyonların enerjik fizibilitesini ve kendiliğinden olabilmesini değerlendirmek için hesaplanmıştır. Sonuçlar, selülozik biyokütlenin, dönüşüm aralığı boyunca aktivasyon enerjisinde önemli bir değişimle çok aşamalı bir bozunma süreci sergilediğini göstermektedir. Bu bulgular, piroliz ve gazlaştırma gibi termal dönüşüm teknolojilerinin optimizasyonu için değerli bilgiler sağlamakta ve verimli biyokütle-enerji sistemleri tasarlamak için

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bir temel oluşturmaktadır.

Anahtar Kelimeler: Biyokütle, Selüloz, Termal Bozunma

Introduction

Due to the increasing world population and the increasing energy demand, all alternative energy sources are gaining importance. Biomass resources are abundant in the world, making them a sustainable, clean, and renewable alternative to fossil fuels (Qi, W. et al. 2020). There are many sources in nature for cellulose. Among the various biomass sources, cellulosic biomasses, including agricultural residues, forestry wastes, and other lignocellulosic materials, are particularly promising due to their abundance, low cost, and carbon-neutral nature. Understanding the thermal behavior of these materials is important for optimizing thermochemical conversion processes such as pyrolysis, combustion, and gasification. There are many studies on this subject in the literature. Biomass is a complex natural structure composed mainly of hemicellulose, cellulose, and lignin, as well as tannins, fatty acids, resins, and inorganic salts. Cellulose is the most important component in biomass due to its large proportion (Shen, D. K., & Gu, S. 2009). Cellulose is a polymer structure from the polysaccharide group. The fact that cellulosic substances are found in nature in various forms and as waste suggests that they can also be used as fuel.

The degradation of biomasses is generally given by the following equation: (Rahib, et al., 2020).

$$Biomass(solid) \rightarrow volitiles(gas) + char(solid) \qquad (1)$$

Understanding the thermal behavior of these materials is important for optimizing thermochemical conversion processes such as pyrolysis, combustion, and gasification. Thermogravimetric analysis (TGA) is a widely used technique to study the thermal degradation properties of biomass. It provides precise data on temperature and time-dependent mass loss and allows detailed investigation of decomposition mechanisms and material stability under controlled conditions. The complexity of the biomass structure, which is usually composed of hemicellulose, cellulose, and lignin, results in overlapping degradation zones that require advanced kinetic modeling.

In the thermal decomposition of celluloses, parameters such as heating rate, amount of substance, atmosphere, and shape are quite important. The basic classification of kinetic models is given in Table 1. There may be differences depending on the calculated thermodynamic ternary kinetic model. The most commonly used models in the literature are given in Table 2. Without making any assumptions about the reaction mechanism, the activation energy and exponential factor can be found using model-free iso-transformation methods as a function of temperature and transformation.

Table 1.
Classification of kinetic models

Model-fitting		Model-free (Isoconversional)	
Isothermal	**Non-isothermal**	**Isothermal**	**Non-isothermal**
Conventional	Differential Freeman-Carroll Coats-Redfern	Standart Friedman AIC	Kissinger Flynn-Wall and Ozawa Vyazovkin and AIC Kissinger-Akahira-Sonuse

Materials and Methods

Kinetic models

The conversion function (α), which relates to thermal decomposition, is determined using the following formula. It incorporates the initial mass (mo), the mass at a given time t (m), and the final remaining mass (mf):

$$\alpha = \frac{(m_o - m)}{(m_o - m_f)} \qquad (2)$$

The time-dependent behavior of the conversion value (α) can also be described through kinetic terms as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad (3)$$

In this expression, dα/dt represents the rate of conversion, while the function f(α) depends on the specific reaction mechanism involved. Here, f(α) denotes the solid-state reaction function, and its integral form is represented as g(α). Table 3 provides a summary of the most frequently observed reaction models for solid-state decomposition (Zhang, et al., 2021).

The rate constant k(T), which varies with temperature, is defined by the Arrhenius equation:

$$k(T) = A\, e^{-\frac{Ea}{RT}} \tag{4}$$

In this equation, A is the pre-exponential factor, Ea is the activation energy for the process at a given conversion level, R is the universal gas constant (8.314 $Jmol^{-1}K^{-1}$), and T is the absolute temperature in Kelvin.

Table 2.

The most common kinetic models and equations used to find the thermodynamic triplet

Type	Model	Equation	y-axis	x-axis	Slope	Ref.of Eq.
İsoconversional	KAS	$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AE_a}{Rg(\alpha)}\right) - \frac{E_a}{RT}$	$\ln\left(\frac{\beta}{T^2}\right)$	$\frac{1}{T}$	$\frac{E_a}{R}$	(Janković, & Manić, 2021)
İsoconversional	FWO	$\ln(\beta) = \ln\left(\frac{AE_a}{g(\alpha)R}\right) - 0.315 - 0.457(\frac{E_a}{RT})$	$\ln(\beta)$	$\frac{1}{T}$	$-0.457\frac{E_a}{R}$	(Lim, et al., 2016)
İsoconversional	Starink	$\ln\left(\frac{\beta}{T^{1,92}}\right) = C - 1.0008\frac{E_a}{RT}$	$\ln\left(\frac{\beta}{T^{1,92}}\right)$	$\frac{1}{T}$	$-1,0008\frac{E_a}{R}$	(Yan, et al., 2020)
İsoconversional	Tang	$\ln\left(\frac{\beta}{T^{1,894661}}\right) = C - 1.00145033\frac{E_a}{RT}$	$\ln\left(\frac{\beta}{T^{1,894661}}\right)$	$\frac{1}{T}$	$-1,000145033\frac{E}{F}$	(Yao, et al., 2020; Bottom, 2008)
Model-fitting	Coats-Redfen	$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a}\right) - \frac{E_a}{RT}$	$\ln\left(\frac{g(\alpha)}{T^2}\right)$	$\frac{1}{T}$	g(α)	(Bottom, 2008)
İsoconversional	Boswell	$ln\left(\frac{\beta}{T}\right) = C - \frac{E_a}{RT}$	$\ln\left(\frac{\beta}{T}\right)$	$\frac{1}{T}$	$-\frac{E_a}{R}$	(Kabakçı, et al., 2025)

By integrating equations (2) and (3), one can derive a relationship that allows the determination of the kinetic triplet—namely, the pre-exponential factor (A), activation energy (Ea), and the reaction model f(α):

$$\frac{d\alpha}{dt} = Ae^{\frac{Ea}{RT}} f(\alpha) \tag{5}$$

An important factor in thermal decomposition studies is the heating rate, symbolized by β, and it is given by the equation:

$$\beta = \frac{dT}{dt} \tag{6}$$

Thermodynamic parameters such as the pre-exponential factor (A) from the Arrhenius equation, along with enthalpy change (ΔH), Gibbs free energy (ΔG), and entropy change (ΔS), were also evaluated using the corresponding equations below.

$$A = \left[\beta . E\, exp\left(\frac{E}{RT}\right)\right] / (RT_m^2) \tag{7}$$

$$\Delta H = E - RT \tag{8}$$

$$\Delta G = E + RT_m\, ln[K_B Tm\, /\, hA) \tag{9}$$

$$\Delta S = \Delta H - \Delta G\, /\, Tm \tag{10}$$

Tm refers to the temperature at which the maximum rate of decomposition occurs. K_B is the Boltzmann constant, with a value of $1.381*10^{-23}$ $m^2kgs^{-2}K^{-1}$. h represents Planck's constant, with a value of $6.626*10^{-34}$ m^2kgs^{-1}. Table 3 summarizes the investigations of different cellulosic structures using TGA analysis.

In addition to the thermodynamic data calculated from TG data, the degradation mechanism of the substances can also be calculated. The most commonly used mechanisms for this purpose are given in Table 4.

Table 3.

Summary of thermogravimetric analysis (TGA) studies on different celluloses

Component	ΔH	ΔG	ΔS	Atmosphere	Kinetic Analysis Method	Ref.
Para grass	183.88	170.22	Variable	N_2	KAS, FWO	(Ahmad, et. al., 2017)
Sawdust	157.54	168.64	17.615	N_2	Starink, Friedman	(Sharma, et. al., 2019)
Smoked cigarette	98.67	122.63	-55.79	N_2	Friedman, FWO, KAS, Starink	(Alves, et. al., 2022)
Litchi	240.08	168.88	130.60	N_2	FWO, KAS, Tang, Starink	(Kumar, et. al., 2023)
Mango seed	109.89	16.13	-70.28	N_2	Friedman, FWO, KAS, Starink	(Alves, et. al., 2023)

Table 4.

Some of the kinetic models used in the solid-state kinetics

Mechanisms	Symbol	F(α)	G(α)
Reaction order models			
Chemical reaction (first order)	F1	(1-α)	-ln (1-α)
Chemical reaction (second order)	F2	(1-α)2	(1-α)-1-1
Chemical reaction (third order)	F3	(1-α)3	[(1-α)-2 -1]/2
Diffusion models			
One-dimensional diffusion	D1	0.5α	α2
Two-dimensional diffusion	D2	[-ln(1-α)]-1	α+(1-α)ln(1-α)
Three-dimensional diffusion (Ginstling Brounshtein equation)	D4	(3/2)/[1-α)1/3-1]	(1-2α/3)-(1-α)2/3
Three-dimensional diffusion (Zhuravlev equation)	D5	(3/2)(1+α)3/4[1+α)-1/3-1]-1	[(1-α)-1/3-1]2
Sigmoidal rate model			
Contracted geometry shape (disk symmetry)	R1	1	α
Contracted geometry shape (cylindrical symmetry)	R2	2(1-α)-1/2	1-(1-α)1/2
Contracted geometry shape (sphere symmetry)	R3	3(1-α)-1/3	1-(1-α)1/3
Nucleation and growth (n=2)	A2	2(1-α)[-ln(1-α)]1/2	[-ln(1-α)]1/2
Nucleation and growth (n=3)	A3	3(1-α)[-ln(1-α)]2/3	[-ln(1-α)]1/3
Nucleation and growth (n=4)	A4	4(1-α)[-ln(1-α)]3/4	[-ln(1-α)]1/4
Nucleation models			
Mample power law (n=2)	P2	2α1/2	α1/2
Mample power law (n=3)	P3	3α2/3	α1/3
Mample power law (n=4)	P4	4α3/4	α1/4

Thermal Behavior of Cellulosic Biomass

The samples used in the studies in the literature were first dried and then analyzed in thermal analysis devices. Models and calculations were made using the data obtained as a result of thermal analysis. These decays occur in single or multiple steps. Accordingly, the calculations were made either according to single steps or multiple times by taking this multiple decay into account. The thermogravimetric (TGA) and derivative thermogravimetric (DTG) curves of the cellulosic biomass samples revealed a **three-stage degradation pattern** typical of lignocellulosic materials:

Stage I (Moisture removal): Occurred below 120 °C, with minimal mass loss (~5%), attributed to the evaporation of physically bound water.

Stage II (Active pyrolysis): Occurred between 200 and 400°C, corresponding to the degradation of hemicellulose (200–300 °C) and cellulose (300–380 °C). This stage exhibited the **maximum weight loss** and the highest DTG peak.

Stage III (Lignin degradation and char formation): Extended up to 600–800 °C, characterized by slow, continuous weight loss and a broad DTG shoulder, indicative of lignin decomposition and residual char conversion.

An increase in heating rate shifted the decomposition temperatures to higher values, confirming the kinetic dependency of thermal degradation.

Conclusions

In summary, this article has investigated how thermogravimetric analysis (TGA) contributes to understanding the thermal behavior of cellulose and to assessing the effectiveness of different techniques to improve its thermal stability. The basic principles of TGA and its various models are summarized in articles examining the thermodynamic triplet and thermodynamic properties. These values vary depending on the cellulose content. Changing the cellulose, lignin, and hemicellulose ratios in cellulosic materials is highly influential. Both the material's composition and the experimental environment significantly alter these values, resulting in significantly different values obtained across models.

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