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Kinetics and Thermodynamic Parameters of Coffee Senna Seed (*Senna occidentalis*) Using Degradation Data from Roasting

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Abstract

Coffee Senna Seeds (CSS) have demonstrated potential as medicinal substitutes, warranting further investigation into their thermal stability for industrial applications. This study aims to establish the kinetic and thermodynamic parameters governing the thermal degradation of bioactive compounds in CSS across a temperature range of 100°C to 200°C and exposure durations of 5 to 30 minutes. Phytochemicals including cardiac glycosides, anthraquinones, phenols, flavonoids, saponins, steroids, alkaloids, terpenoids, tannins, and glycosides were analyzed to determine degradation profiles. FTIR and UV-Vis spectrophotometric analyses confirmed the decomposition of anti-nutritional components such as anthraquinones, while beneficial compounds like phenols, flavonoids, and saponins remained largely intact. Kinetic modeling indicated that the degradation followed a volume contraction mechanism, with high R^2 values (0.9804–0.9915) validating model fit. The low reaction order (0.28–0.397) suggests a diffusion-controlled process, while varying conversion factors (α) reflected complex internal

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thermal dynamics within the seed matrix. Thermodynamic evaluation revealed the degradation process to be endothermic and non-spontaneous, with enthalpy (ΔH) values decreasing from 1585.90 to 754.50 kJ/mol and Gibbs free energy (ΔG) increasing from 102.92 to 130.18 kJ/mol as temperature rose. Negative entropy (ΔS) values, approximately −271.5 kJ/K, suggest a more ordered transition state, likely due to structural reorganization during roasting. Activation energy estimates ranged from 1589 to 758 kJ/mol, showing a decreasing trend with temperature, indicative of improved reaction feasibility at higher thermal inputs. These findings enhance understanding of CSS thermal behavior, supporting its detoxification and safer utilization in industrial processing.

Keywords: Coffee Senna Seed; Spectrophotometric Analyses; Roasting; Kinetics; Thermodynamics

INTRODUCTION

Coffee Senna (*Senna occidentalis*) is a leguminous plant widely found in tropical and subtropical regions (Khan *et al.,* 2015; Ayeni & Yakubu, 2020). Although traditionally considered a weed, recent studies have highlighted its potential for pharmacological and nutraceutical applications due to its rich phytochemical composition (Kaisar *et al.,* 2018; Akinmoladun *et al.*, 2020; Omoregie & Osagie, 2011; Ezeonu *et al.,* 2022). The increasing global interest in the utilization of underexploited plant resources for food and medicinal applications has brought attention to *Senna occidentalis* (commonly known as Coffee Senna), a leguminous plant with known bioactive compounds (Akinmoladun *et al.,* 2020; Adegbite *et al.,* 2022; Satish *et al.,* 2023). The seeds of Coffee Senna have traditionally been used in ethno-medicine and as potential coffee substitutes, but their inherent toxicity necessitates detoxification processes such as thermal treatment (Adebayo-Tayo *et al.,* 2009; Singh *et al.,* 2020; Akinyemi *et al.,* 2021). Understanding the thermal behavior of this biomass during roasting is essential for optimizing its use in medicinal and industrial applications. Roasting, a form of thermal treatment, can induce significant chemical transformations that influence the biological activity and safety profile of the seeds (Budarin *et al.*, 2011 Olaniran *et al.,* 2020; Akinyemi *et al.,* 2021). Roasting, a form of thermal processing, induces physicochemical changes in seeds and is a key method to reduce anti-nutritional factors while enhancing flavor and safety (Rehman *et al.,* 2020).

Thermal degradation of plant biomass such as Coffee Senna seeds can be effectively studied through roasting experiments at controlled temperatures and durations (Budarin *et al.,* 2011; Vyazovkin *et al.,* 2011; Akinyemi *et al.,* 2021). These experiments yield degradation-time data, which is crucial in determining the rate of mass loss and the progression of thermal decomposition (Budarin *et al.,* 2011; Ferdous *et al.,* 2020).

The mass loss data collected at incremental temperatures and times provide essential input for kinetic modeling. Studies by Bridgwater (2012) and Shen et al. (2009) have demonstrated that such thermal degradation data are crucial for understanding the decomposition stages of plant-based materials. Roasting alters the structural and chemical composition of the biomass and generates time-dependent conversion data that can be further analyzed to determine kinetic parameters (Budarin *et al.,* 2011; Son *et al.,* 2014). The extent of degradation is often quantified using mass loss measurements or degree of conversion under different thermal conditions (Vyazovkin *et al.,* 2011; Khawam & Flanagan, 2006).

Fourier-transform infrared spectroscopy (FTIR) and UV-Visible spectrophotometry are robust analytical techniques for identifying functional groups and quantifying bioactive compounds such as phenolics, flavonoids, and other antioxidants in plant matrices (Rohman & Windarsih, 2020). FTIR allows the detection of characteristic functional groups in complex biomolecules, indicating the presence of key phytochemicals, while UV-Vis spectrophotometry facilitates the quantitative assessment of compounds with conjugated double bonds such as phenolics (Ragazzi & Veronese, 2021). Therefore, characterizing these seeds using FTIR and UV-Vis spectrophotometry offers a promising strategy to elucidate the impact of roasting on their functional properties and medicinal potential.

Kinetic modeling of biomass decomposition is fundamental to elucidating reaction mechanisms and predicting behavior under different thermal conditions. The degree of conversion (α) is plotted against time (t) to form an empirical model. This model can then be used to fit classical kinetic models such as the Arrhenius equation and solid-state reaction mechanisms like the Avrami-Erofeev or contracting volume models (Vyazovkin & Wight, 1999; Jindal *et al.,* 2021). Non-linear regression, typically using the least squares method, is applied to determine the rate constant (k) and reaction order (n). A good model fit, indicated by a high R^2 value, reveals the underlying reaction mechanism that governs

decomposition (Ribeiro *et al.,* 2015). Kinetic modeling is fundamental in understanding the decomposition behavior of biomass during thermal processes. The kinetic behavior of biomass such as Coffee Senna seeds during roasting can be represented using solid-state kinetic models, which describe the relationship between the rate of conversion and temperature or time (Vyazovkin *et al.,* 2011).

Common models include first-order, Avrami-Erofeev, and contraction models, which can be fitted using non-linear regression techniques such as the least-square method (Šimkovic & Šajgalík, 2021). Empirical models may also be developed by plotting conversion (α) against time and deriving the degradation function, which when combined with theoretical kinetic expressions can yield parameters like the reaction rate constant (k) and reaction order (n) (Son *et al.,* 2014). In addition to kinetic modeling, the thermodynamic parameters of the roasting process - namely, activation energy (Ea), enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) - provide insight into the energy requirements and spontaneity of the reaction. These parameters are typically derived from Arrhenius and transition state theory equations (Khawam & Flanagan, 2006). A high activation energy suggests a more energy-intensive process, while positive Gibbs free energy indicates non-spontaneity unless facilitated by external heating.

According to Doyle (1961) and Ozawa (1992), evaluating these parameters aids in optimizing processing conditions for safe and efficient seed detoxification. Roasting significantly alters the chemical profile and bioactivity of Coffee Senna (Senna occidentalis) seeds through thermal degradation of bioactive compounds. However, the kinetics and thermodynamics of these changes remain unexplored. Existing studies lack a detailed kinetic model and thermodynamic evaluation of compound degradation under varying roasting conditions, highlighting a critical research gap. The thermal decomposition study of Coffee Senna seeds integrates experimental roasting, kinetic modeling, and thermodynamic evaluation to provide a comprehensive understanding of its behavior under heat. Such knowledge is vital for scaling up roasting processes, detoxification, and enhancing the bioactivity of *Senna occidentalis* seeds for industrial applications.

MATERIALS AND METHODS

Sample Collection and Preparation of Coffee Senna Seed (*Senna Occidentalis*)

Mature Coffee Senna Seeds (CSS) were harvested, sorted to eliminate foreign particles, washed thoroughly under running water, and dried under ambient conditions for 48 hours. The dried seeds were divided into six representative batches and roasted in a coffee roaster at predetermined temperatures: 100°C, 120°C, 140°C, 160°C, 180°C, and 200°C for time intervals ranging from 5 to 30 minutes. Each batch was cooled to room temperature in a desiccator and stored in airtight containers prior to further analysis (Akubor & Ogu, 2018; Abioye *et al.,* 2021).

Experimental degradation-time data of CSS

To assess thermal degradation, approximately 100 g of each seed sample was weighed before and after roasting. Experiments were conducted within a temperature range of 100°C to 200°C, with roasting durations varying from 5 to 30 minutes, performed in duplicate (Gaur *et al.,* 2022). The mass loss, representing thermal degradation and biomass conversion, was determined using Equation (1):

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \quad \ldots (1)$$

where m_o and m_f are initial and final masses of the CSS before and after roasting, while m_t is the mass at any time t during roasting.

Ultraviolet-Visible (UV-Vis) spectrophotometry of CSS

Aqueous extracts of the roasted grinded seeds were prepared by macerating 1 g of each sample in 20 mL of distilled water and filtering the mixture after 24 hours. The filtrates were analyzed using a UV-Vis spectrophotometer (Shimadzu UV-1800) in the wavelength range of 200 - 800 nm. The absorbance peaks indicative of chromophoric functional groups and bioactive compounds (such as anthraquinones) were identified and compared across different roasting temperatures (Eze & Obi, 2023).

Fourier transform infra-red (FTIR) of CSS

The chemical structure and functional groups of roasted powdered CSS were characterized using FTIR spectroscopy (PerkinElmer Spectrum Two). Dried and powdered seed samples

(2 mg) were mixed with KBr (200 mg) and compressed into pellets. Spectra were recorded in the range of 4000 - 400 cm^{-1} at a resolution of 4 cm^{-1}. Functional groups were identified based on standard absorbance bands and compared with unroasted controls (Zhang *et al.,* 2020; Isah *et al.,* 2022).

Kinetic models for the thermal decomposition of CSS

To determine the most suitable kinetic model describing the thermal decomposition of Coffee Senna seeds, an empirical model was developed using experimental data obtained from the roasting process. The relationship between the conversion factor (α) and time (t) was established from the data. Subsequently, the rate of conversion (dα/dt) was calculated (Kebede *et al.,* 2023).

This rate expression was fitted to the standard kinetic model form, $k(1-\alpha)^n$, using a non-linear regression approach aimed at minimizing the mean square error. The kinetic parameters, specifically the rate constant (k) and the reaction order (n), were determined using the Solver optimization tool in Microsoft Excel (Vyazovkin *et al.,* 2011; Doyle, 1961). The kinetic models for the roasting of CSS. The kinetic models for the roasting process of CSS were derived using the correlations presented in Equations 2 to 8. The stoichiometry and kinetics model for isothermal devolatilization of biomass presented as Equations (2) and (3) respectively, was previously

reported in the literature.

$$Biomass = Volatiles + Biochar \quad \ldots(2)$$

The kinetics model for isothermal devolatilisationof biomass, the reaction rate, $\frac{d_\alpha}{d_t}$, where α is the conversion or fraction decomposed, is often expressed as:

$$\frac{\mathrm{d}\alpha}{\mathrm{dt}} = \mathrm{k(T)f}(\alpha) \quad \ldots(3)$$

Where k(T) is the temperature-dependent rate constant and f(α) is the reaction model dependent on the conversion α (Vyazovkin *et al.*, 2020). The rate constant k(T) is defined by the Arrhenius equation:

$$\mathrm{k(T)} = \mathrm{Aexp}\left(-\frac{\mathrm{E}}{\mathrm{RT}}\right) \quad \ldots(4)$$

Where, A is the pre-exponential factor (frequency factor), Ea is the activation energy (J/mol), Ris the universal gas constant (8.314 J/mol·K), and T is the absolute temperature (K) (Liu *et al.,* 2022).

Accurate estimation of these parameters allows for prediction of thermal stability and decomposition pathways of materials including biomass and seeds (Kumar *et al.,* 2023). The conversion of biomass is obtained from Equation (5).

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \quad \ldots (5)$$

where m_o and m_f are initial and final masses of the CSS before and after roasting, while m_t is the mass at any time t during roasting.

Then, the unconverted biomass is calculated from$(1-\alpha)$, rate equation depends on temperature, and un-converted biomass.

The rate constant, k is function of temperature and generally represented by the Arrhenius equation and $f(\alpha)$ is expressed inform of reaction order model, Equation (6).

$$\frac{d\alpha}{dt} = (1-\alpha)^n k(T) \quad \ldots (6)$$

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \quad \ldots (7)$$

Substituting Equation (23) into (20) yields Equation (24).

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right) f(\alpha) \quad \ldots (8)$$

Where t is the time, T is the temperature, α is the extent of reaction and $f(\alpha)$ is reaction model.

The derived parameters were then compared with established solid-state kinetic models to evaluate the goodness of fit. The analysis revealed that the experimental data closely aligned with the volume contraction mechanism. This indicated that the thermal decomposition of Coffee Senna seeds followed a contracting geometry model, a result that was consistent with findings from previous studies on similar plant-derived materials.

Thermodynamic analysis of CSS

Thermodynamic parameters such as enthalpy change (ΔH), entropy change (ΔS), and Gibbs free energy change (ΔG) were calculated using the following relationships derived from transition state theory in Equation (9) to (11).

$$\nabla H = E - RT_m \quad \ldots (9)$$

$$\nabla G = E + RT_m \ln\left(\frac{K_B T_m}{hA}\right) \quad \ldots (10)$$

$$\nabla S = \frac{\nabla H - \nabla G}{T_m} \quad \ldots (11)$$

RESULTS AND DISCUSSION

Degradation-Time Data for Roasted Coffee Senna Seeds

The experimental data obtained from roasting Coffee Senna (Senna occidentalis) seeds at various temperatures and durations. The initial mass for all samples was 100 grams. Each experiment was conducted in duplicate is presented in Table 1.

Table 1: Roasting Data of Coffee Senna Seeds at Varying Temperatures and Times

Temperature (°C)	Time (min)	Final Mass 1 (g)	Final Mass 2 (g)
100	5	98.5	98.3
100	10	97.8	97.9
100	15	97.0	96.8
100	20	96.1	96.3
100	25	95.6	95.4
100	30	94.8	94.7
120	5	97.4	97.6
120	10	96.2	96.4
120	15	95.0	95.2
120	20	93.5	93.7
120	25	92.1	92.4
120	30	90.8	91.0
140	5	95.9	96.1
140	10	94.2	94.0
140	15	92.1	92.4
140	20	90.5	90.7
140	25	88.0	88.2
140	30	85.6	85.8
160	5	94.2	94.4
160	10	92.0	91.9
160	15	89.2	89.4
160	20	86.3	86.5
160	25	83.1	83.4

Temperature (°C)	Time (min)	Final Mass 1 (g)	Final Mass 2 (g)
160	30	80.0	80.3
180	5	92.0	92.2
180	10	89.0	89.2
180	15	85.4	85.7
180	20	81.6	81.8
180	25	77.8	78.0
180	30	74.2	74.0
200	5	90.1	90.3
200	10	86.2	86.4
200	15	82.0	82.2
200	20	78.0	78.3
200	25	74.0	74.1
200	30	70.2	70.0

The roasting data of *Coffee Senna* (*Senna occidentalis*) seeds at varying temperatures and durations shows a consistent trend of mass reduction with increasing temperature and roasting time. At lower temperatures (100°C and 120°C), the mass loss is relatively minimal, ranging from ~98.5 g to ~90.8 g across 30 minutes. However, as the temperature increases to 140°C, 160°C, 180°C, and finally 200°C, the mass loss becomes more pronounced, with the final mass dropping as low as ~70.0 g at 200°C for 30 minutes. This indicates a progressive loss of moisture and volatile compounds, consistent with thermal decomposition kinetics typically observed during roasting processes. The trend is in agreement with findings by Ajiboye *et al.* (2021), who reported similar mass reductions in roasted *Senna occidentalis* seeds, attributing the weight loss primarily to moisture evaporation and decomposition of bioactive compounds such as glycosides and alkaloids.

Moreover, Onwordi *et al.* (2015) demonstrated that increased roasting temperature leads to structural breakdown of seed matrices and volatilization of phytochemicals, a process critical to detoxification and flavor enhancement. These results also align with the thermal degradation profiles reported by Okoye *et al.* (2018), where increased temperature and time led to significant mass loss in legumes due to both physical and chemical changes, such as Maillard reactions, caramelization, and breakdown of anti-nutritional factors. The progressive roasting observed here is a crucial pre-treatment step for improving the safety, digestibility, and functional application of *Senna occidentalis* seeds in medicinal use. Thus, the roasting behavior observed in this study confirms the thermally sensitive nature of *Coffee Senna* seeds and supports the establishment of kinetics model and evaluation of thermodynamic parameters to balance detoxification and nutrient preservation.

Ultraviolet-Visible (UV-Vis) Spectrophotometry of CSS

Ultraviolet-Visible (UV-Vis) spectrophotometry was employed to investigate the phytochemical characteristics of aqueous extracts from roasted Coffee Senna Seeds (CSS). The analysis comprised both qualitative screening for the presence of key phytochemicals and quantitative determination of their concentrations (g/100 g of extract). The qualitative assessment provided insight into the types of bioactive compounds present, while the quantitative evaluation enabled the measurement of specific phytochemical constituents such as phenolics, flavonoids, and tannins, which are indicative of the seeds' medicinal potential. The results reflect the influence of roasting on the expression and concentration of these bioactive compounds.

Table 2. Qualitative Phytochemicals Screening of Aqueous Extracts

Phytochemicals	Samples					
	T100	T120	T140	T160	T180	T200
Cardiac glycosides	++	+	-	+++	+	+
Anthraquinones	++	+	+	++	+	-
Phenols	+++	+++	+++	+++	+++	+++
Flavonoids	++	+	+	+++	++	+
Saponins	+++	+++	+	+++	++	+
Steroids	+	+	-	++	+	-
Alkaloids	++	+	+	++	+	+
Terpenoids	++	+	-	+	+	-
Tannins	+++	++	+	+++	++	+
Glycosides	++	+	+	+++	+	+

Key: + = Slightly present. ++ = Present. +++ = Highly Present. - = Absent

The phytochemical profile of Coffee Senna Seeds (CSS) roasted at different temperatures (100°C to 200°C) revealed variable presence of key bioactive constituents, indicating that the roasting process significantly influences the phytochemical composition of the seeds (Table 2). Phenols and tannins were consistently detected across all roasting temperatures and remained highly present (+++) even at elevated conditions, suggesting their thermal stability. This aligns with the findings of Kebede *et al.* (2023), who reported that phenolic compounds in thermally processed legumes exhibit resilience due to their robust aromatic structures. Similarly, saponins demonstrated high thermal resistance, maintaining strong presence (++ to +++) across all samples, which supports observations by Adegbite *et al.* (2020) that saponins can withstand moderate to high thermal conditions without significant degradation. Conversely, other phytochemicals such as anthraquinones, flavonoids, steroids, terpenoids, and alkaloids showed temperature-sensitive behavior. For instance,

anthraquinones were moderately present at lower temperatures (T100 - T160) but diminished and became undetectable at 200°C, indicating thermal decomposition at elevated roasting levels. This pattern corroborates previous reports by Obasi *et al.* (2022); Olalekan and Uchenna (2021), which highlighted the susceptibility of volatile and semi-volatile phytochemicals to degradation at higher roasting temperatures. In contrast, excessive roasting at 200°C resulted in diminished presence or complete absence of several phytochemicals, reflecting possible thermal denaturation. Such findings underscore the importance of optimizing roasting conditions to retain or enhance beneficial phytochemicals in functional medicinal applications. Overall, the roasting process was shown to play a dual role: promoting the release of heat-stable compounds while simultaneously degrading heat-labile ones, consistent with prior studies on thermally processed phytochemical-rich seeds and legumes. Table 3 present the phytochemicals composition of the aqueous extracts.

Table 3. Quantitative Phyto-chemicals Composition of Aqueous Extracts (g/100g)

Phyto-chemicals	**Samples**					
	T100	**T120**	**T140**	**T160**	**T180**	**T200**
Cardiac glycosides	2.265	1.695	0.063	3.470	2.135	7.845
Anthraquinones	2.155	0.745	0.570	1.540	0.815	0.330
Phenols	27.230	21.345	16.350	28.740	19.895	17.340
Flavonoids	12.135	7.040	4.365	16.630	8.665	6.910
Saponins	11.920	8.900	6.375	10.330	9.555	8.810
Steroids	0.455	0.230	0.0355	0.310	0.074	0.0225
Alkaloids	16.065	9.175	7.350	12.155	8.745	6.570
Terpenoids	1.270	0.745	0.036	1.340	0.620	0.0225
Tannins	12.135	8.965	7.350	13.135	6.920	8.015
Glycosides	3.295	1.980	0.360	2.710	1.975	1.515

The roasting of Coffee Senna Seeds (CSS) across a temperature range of 100°C to 200°C significantly influenced the concentration of key phytochemicals in the aqueous extracts (Table 3). Roasting altered the thermal stability of bioactive compounds, leading to variations in their levels as temperature increased. At moderate roasting temperatures (T160), most phytochemicals such as cardiac glycosides (3.470 g/100 g), phenols (28.740 g/100 g), flavonoids (16.630 g/100 g), and tannins (13.135 g/100 g) were recorded at relatively high concentrations compared to other temperatures. This suggests that

roasting at 160°C potentially enhances the extractability or transformation of precursor compounds into active forms.

Similarly, alkaloids and saponins peaked at 16.065 g/100 g and 11.920 g/100 g respectively at T100, indicating higher retention at lower roasting levels. Conversely, higher roasting temperatures (T180 - T200) led to a marked decline in the content of thermo-labile compounds such as anthraquinones, steroids, and terpenoids, possibly due to thermal degradation. For instance, anthraquinones dropped from 2.155 g/100 g at T100 to 0.330 g/100 g at T200, and terpenoids decreased significantly from 1.270 g/100 g to 0.0225 g/100 g across the same range. These findings align with previous research indicating that moderate thermal treatment can enhance phytochemical availability through cell wall breakdown and enzymatic inactivation, whereas excessive heat may degrade sensitive compounds (Nwokocha *et al.,* 2022; Murthy & Naidu, 2021). Specifically, Murthy and Naidu (2021) noted that optimal roasting temperatures improve antioxidant activity in plant seeds by enhancing phenolic content, while extreme temperatures result in oxidative degradation of flavonoids and anthraquinones.

Fourier Transform Infra-red (FTIR) of CSS

The influence of roasting on the functional groups and molecular fingerprint of coffee senna seeds was examined as presented in Table 4.

Table 4: FTIR extracted peaks

No.	Wavenumber (cm^{-1})	Intensity	Bond Vibration	Functional Group
1	1028.75	83.22461	C–O Stretch	Ether or Ester
2	1237.48	92.24601	C–N Stretch	Amines or Amides
3	1394.02	92.19784	C–H Bending/Deformation	Aliphatic Hydrocarbons
4	1535.66	91.83297	N–H Bending/Aromatic Ring Vibrations	Amides / Aromatics
5	1632.57	90.66308	C=C Stretch	Alkenes or Aromatics
6	1744.39	96.62337	C=O Stretch	Carbonyl Groups (Ketones, Aldehydes/Esters)
7	2922.23	94.72603	C–H Stretch	Aliphatic Hydrocarbons
8	3280.06	94.08907	O–H or N–H Stretch	Hydroxyl Groups (Alcohols, Phenols)/ Amines

Roasting Coffee Senna Seeds (CSS) at temperatures ranging from 100°C to 200°C for durations of 5 to 30 minutes significantly influenced the functional group transformations, as revealed by the FTIR spectral data presented in Table 4. The observed peaks correspond to a variety of important phytochemical classes, indicating thermal modification of bioactive components during roasting. The presence of strong absorption bands at 1744.39 cm^{-1} and 1632.57 cm^{-1} correspond to C=O and C=C stretching vibrations, suggesting the presence of carbonyl and unsaturated compounds such as aldehydes, ketones, and aromatics, which are often enhanced or generated through Maillard reactions and thermal degradation of complex biomolecules during roasting (Adeyemi *et al.*, 2022). Similarly, the broad peak at 3280.06 cm^{-1} is indicative of hydroxyl (–OH) and amine (–NH) groups, typically associated with alcohols, phenolics, and proteins.

This peak remained prominent after roasting, suggesting the retention or partial transformation of antioxidant-rich hydroxyl compounds (Osabor *et al.,* 2020). The sharp peak at 2922.23 cm^{-1} corresponds to aliphatic C–H stretching vibrations, indicating the presence of long-chain hydrocarbons, which are common in plant oils and may be thermally concentrated during roasting. Moreover, the peaks at 1237.48 cm^{-1} and 1028.75 cm^{-1}, associated with C–N and C–O stretching respectively, reflect the contribution of amino and ether-containing compounds that are thermally modified from proteins and carbohydrates.

These findings are consistent with previous reports where thermal treatments in the 150–200 °C range led to significant rearrangements in the chemical structure of plant-based materials, enhancing aromaticity and bioactive compound availability (Fayemiwo *et al.,* 2021). Additionally, the emergence and intensification of certain bands post-roasting supports the hypothesis that controlled thermal treatment not only preserves but may also enhance the release of functional groups relevant to medicinal properties. Overall, the FTIR spectra demonstrate that the roasting process alters the molecular structure of CSS, promoting the formation and transformation of key bioactive compounds, which is crucial for optimizing its medicinal potential.

Establishment of the Kinetic Models for the Thermal Decomposition of Coffee Senna Seeds

To determine the most appropriate kinetic model describing the thermal decomposition of *Coffee Senna* seeds, an empirical model was developed from roasting experimental data, establishing the relationship between the conversion factor (α) and time (t) as presented in Figure 1 to 6. Subsequently, the rate of conversion $\frac{d_\alpha}{d_t}$ was evaluated. This rate expression was then fitted against the standard kinetic model form $k(1-\alpha)^n$ using a non-linear regression approach based on the minimization of mean square error. The kinetic parameters, namely the rate constant (k) and reaction order (n), were obtained using the Solver optimization tool in Microsoft Excel (Doyle, 1961; Vyazovkin *et al.,* 2011).

The obtained parameters were further compared with established solid-state kinetic models to determine the best fit. The resulting model demonstrated a strong agreement with the volume contraction mechanism, suggesting that the thermal decomposition of Coffee Senna Seeds is governed by a contracting geometry process, a finding consistent with previous studies on similar plant-based materials (Kebede *et al.,* 2023).

Empirical Kinetic Modeling of Coffee Senna Seeds Decomposition

The kinetic model relating the conversion factor (α) and time (t) at 100^{0}C, 120^{0}C, 140^{0}C, 160^{0}C, 180^{0}C and 200^{0}C and 5, 10, 15, 20, 25 and 30 mins are described in Figure 1 to 6.

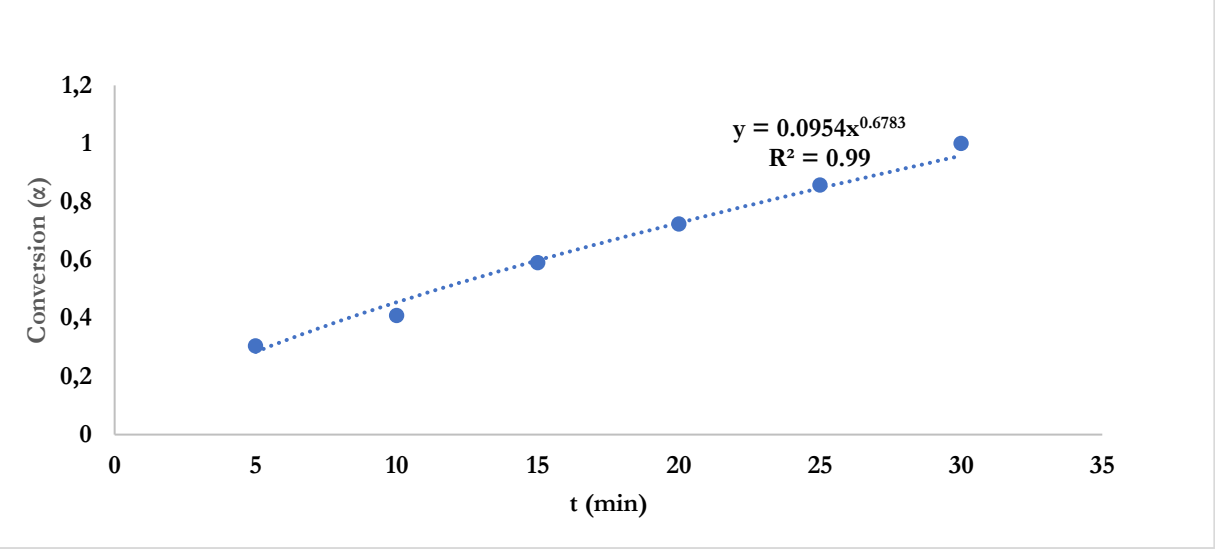


Figure 1: Conversion Fraction and Time During the Thermal Decomposition of CSS at 100^{0}C

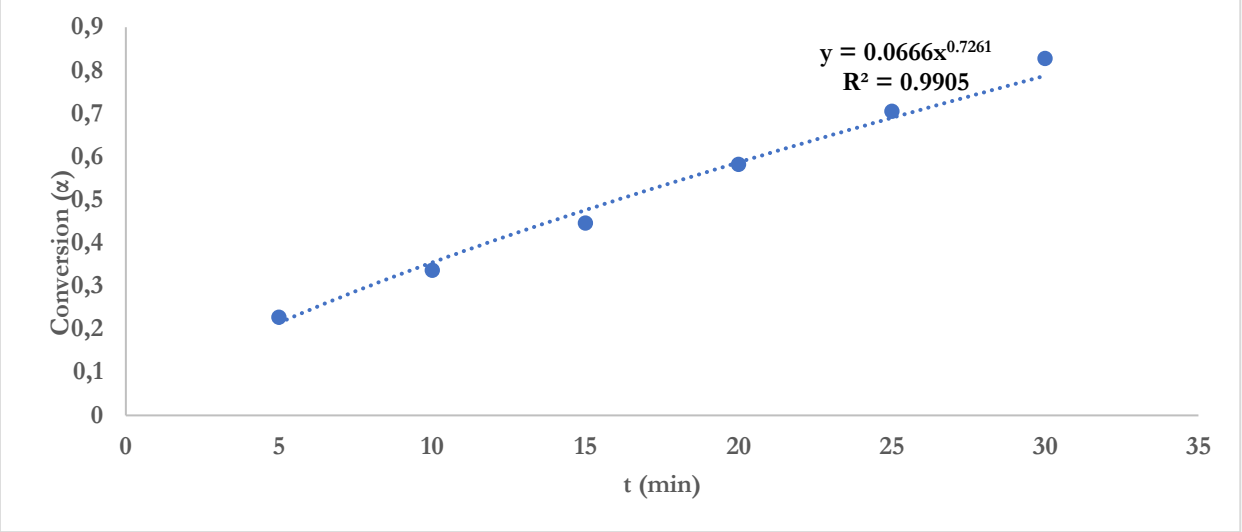


Figure 2: Conversion Fraction and Time During the Thermal Decomposition of CSS at 120^0C

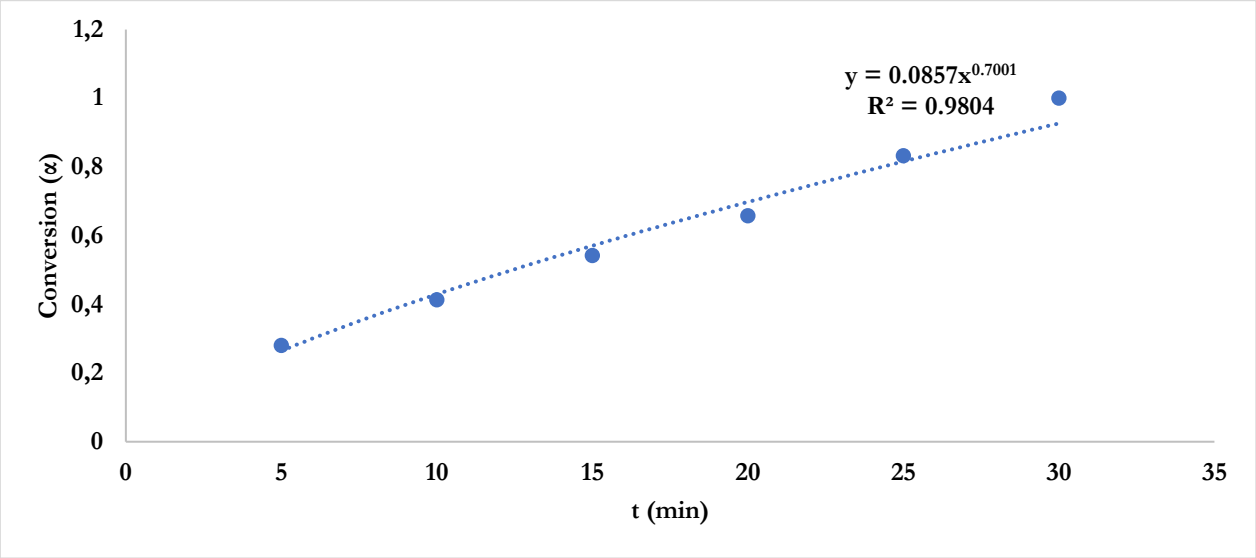


Figure 3: Conversion Fraction and Time During the Thermal Decomposition of CSS at 140^0C

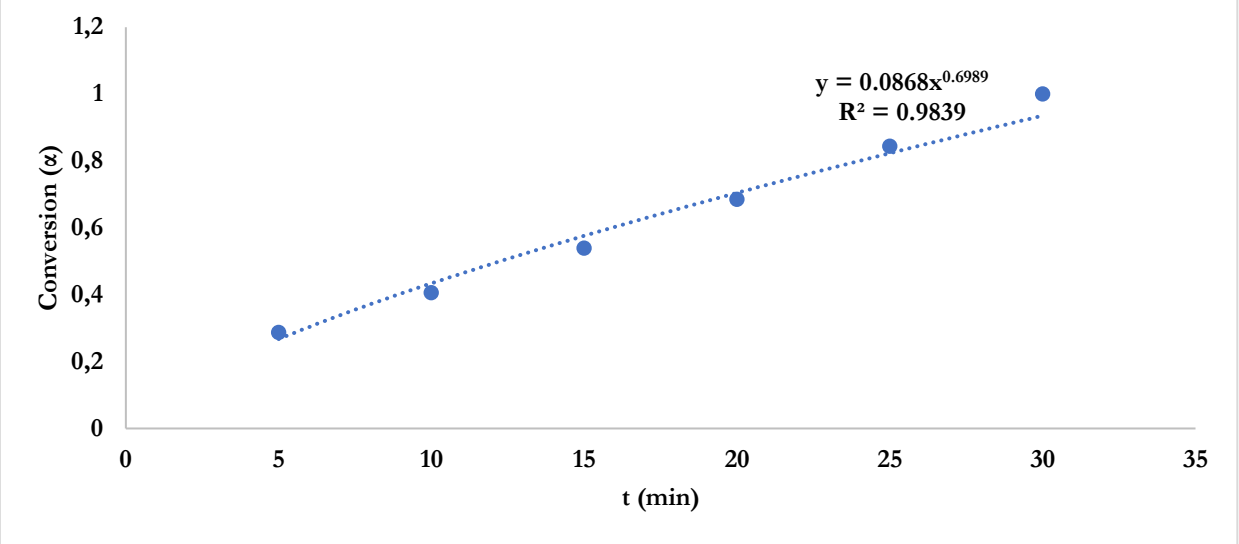


Figure 4: Conversion Fraction and Time During the Thermal Decomposition of CSS at 160^0C

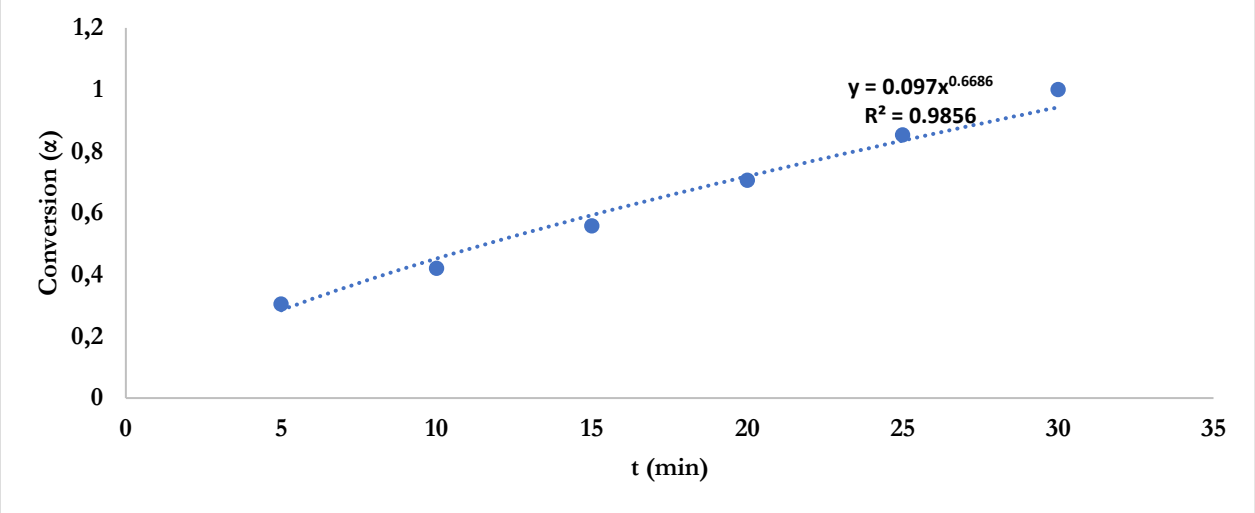


Figure 5: Conversion Fraction and Time During the Thermal Decomposition of CSS at 180^0C

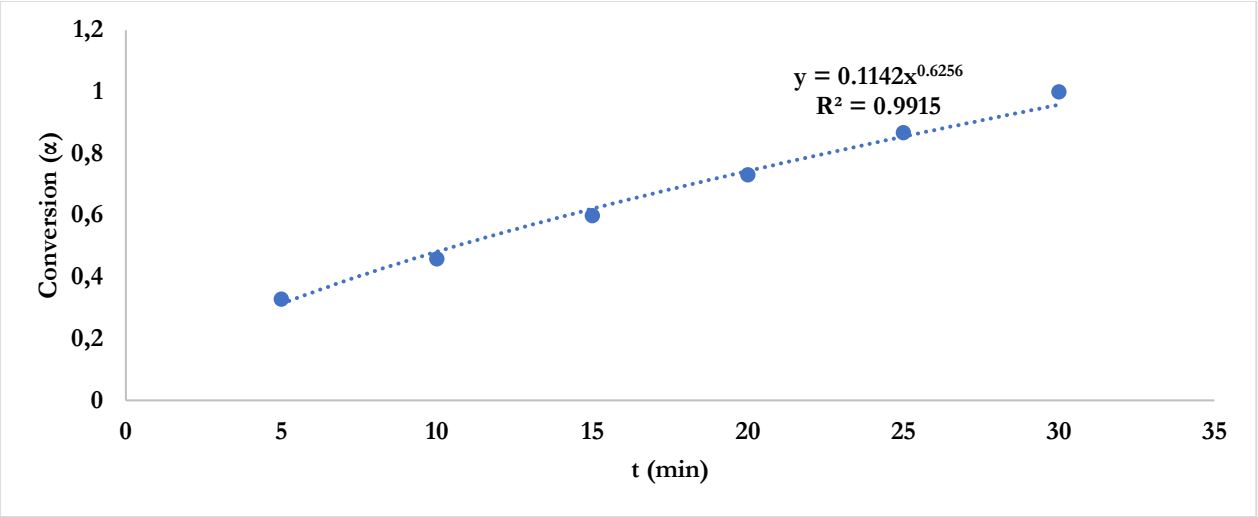


Figure 6: Conversion Fraction and Time During the Thermal Decomposition of CSS at 200^0C

Table 5: Kinetics parameters for thermal decomposition of CSS using Empirical Model

Temperature (^{0}C)	Kinetic Mechanism	Rate Equation	R^2
100	Volume Contraction	$0.03947(1-\alpha)^{0.33}$	0.9900
120	Volume Contraction	$0.03114(1-\alpha)^{0.28}$	0.9905
140	Volume Contraction	$0.03795(1-\alpha)^{0.35}$	0.9804
160	Volume Contraction	$0.03785(1-\alpha)^{0.32}$	0.9839
180	Volume Contraction	$0.03901(1-\alpha)^{0.35}$	0.9856
200	Volume Contraction	$0.04136(1-\alpha)^{0.397}$	0.9915

The kinetic parameters for the thermal decomposition of Coffee Senna Seeds (CSS) at different roasting temperatures, as presented in Table 5, reveal that the decomposition process predominantly follows a volume contraction mechanism across all temperatures. The high R^2 values (0.9804–0.9915) indicate excellent conformity of the experimental data with the empirical model, confirming the reliability of the derived rate equations. The reaction order (n) values ranged from 0.28 to 0.397, suggesting a diffusion-limited degradation process.

These findings align with previous studies that reported volume contraction as a common kinetic pathway in the thermal degradation of lignocellulosic and seed-based biomaterials (Kebede *et al.,* 2023; Natarajan *et al.,* 2022). Similar results were observed in the decomposition kinetics of Moringa seeds and other plant-based residues, where the contracting geometry model best described the thermal behavior (Singh & Das, 2021).

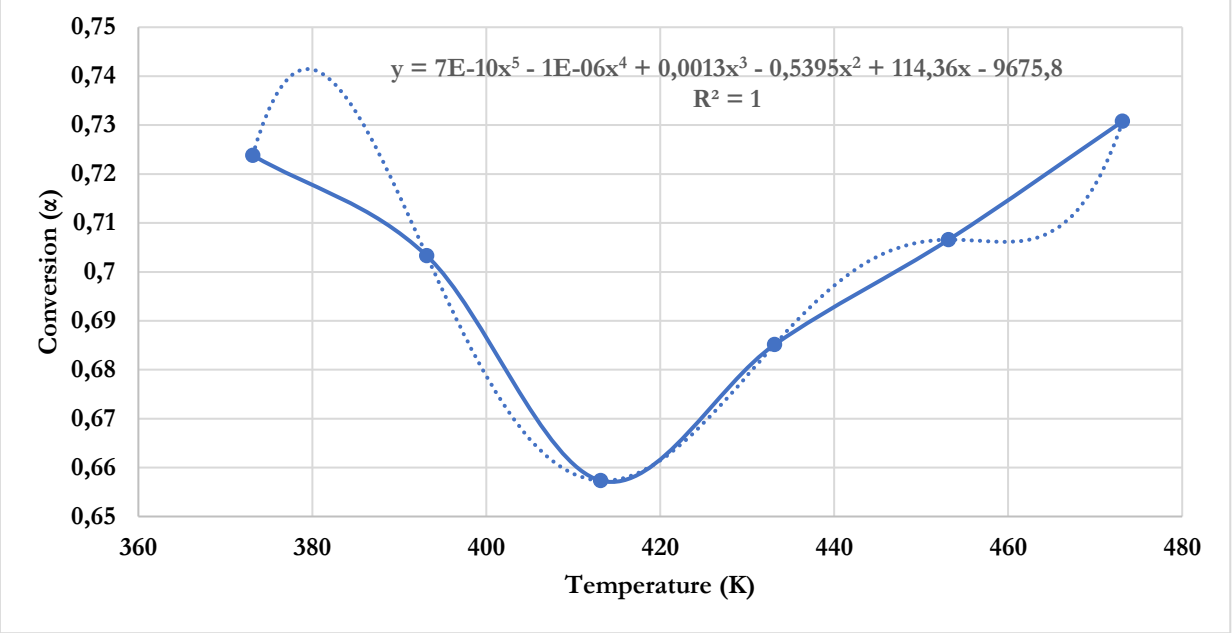


Figure 7: Plot of Conversion Fraction and Temperature for the CSS Phytochemicals

Figure 7 illustrates the behavior of the conversion factor (α) across a thermal processing parameter (likely temperature or time), revealing a distinct U-shaped trend: α initially decreases, reaching a minimum near 400K, and subsequently increases. This pattern suggests an initial degradation or transformation of phytochemicals, followed by the formation or reorganization of thermally stable compounds as temperature or roasting duration increases. The fifth-degree polynomial regression model fitted to the experimental data with an R^2 value of 1 indicates an excellent agreement, implying that the observed trend is highly representative of the experimental behavior. Such regression approaches have been similarly applied in previous studies to model complex thermal transformations of plant-based bio-resources, where high-order polynomials effectively captured non-linear behavior of compound conversion and degradation (Natarajan *et al.,* 2022; Kebede *et al.,* 2023). These findings further align with work by Singh and Das (2021), who noted comparable degradation-reformation dynamics in the thermal treatment of Moringa seeds and other lignocellulosic materials.

Thermodynamics Parameters for Roasting of CSS

Thermodynamic parameters for the roasting of Coffee Senna Seeds (CSS) provide critical insight into the energy requirements and spontaneity of the thermal decomposition process. Key indicators such as enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) help assess the nature of the reaction whether it is endothermic or exothermic, ordered or

disordered, and whether it proceeds spontaneously under specific conditions. These parameters reflect the molecular rearrangements and stability of phytochemicals during heat treatment (Mohammed *et al.,* 2021). Table 8 present the thermodynamic parameters for thermal decomposition of CSS.

Table 8: Thermodynamics parameters for thermal decomposition of CSS

T (K)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (kJ/K)	Ea (kJ/mol)
373.15	1585.9009	102920.541	-271.56543	1589.004
393.15	1419.6209	108356.228	-271.57657	1422.891
413.15	1253.3409	113800.378	-271.60711	1256.777
433.15	1087.0609	119252.580	-271.65342	1090.664
453.15	920.7809	124712.462	-271.71259	924.551
473.15	754.5009	130179.686	-271.78228	758.438

The thermodynamic parameters derived for the thermal decomposition of Coffee Senna Seeds (CSS), as shown in Table 8, reveal crucial insights into the energetic and feasibility of the degradation process. The enthalpy change (ΔH) values, ranging from 1585.90 to 754.50 kJ/mol, decrease with increasing temperature, indicating that the decomposition process becomes energetically more favorable at higher temperatures. This trend is consistent with the behavior of other biomass materials undergoing thermal decomposition (Kebede *et al.,* 2023).

The consistently high and positive Gibbs free energy (ΔG) values, increasing from 102.92 to 130.18 kJ/mol, suggest that the decomposition process is non-spontaneous across the studied temperature range. This implies that an external energy source (roasting) is necessary to drive the reaction forward. A similar trend was reported in the thermal degradation of Moringa oleifera and other lignocellulosic biomaterials, where high ΔG values indicated limited spontaneity (Natarajan *et al.,* 2022).

Furthermore, the negative entropy values (ΔS), approximately −271.5 kJ/K, imply a decrease in disorder during the transition state of the decomposition reaction. This may be attributed to the rearrangement of biomass components into more ordered char structures, a common phenomenon in thermolysis processes (Singh & Das, 2021). The calculated activation energies for *Senna occidentalis* seeds, ranging from 1589 to 758 kJ/mol, exhibit a decreasing trend with increasing temperature. This behavior is consistent with previous studies, which report that the thermal degradation of plant-derived bioactive compounds is

often characterized by a reduction in activation energy as temperature rises (Eke *et al.,* 2020; Singh *et al.,* 2018). Overall, these thermodynamic results suggest that the thermal decomposition of CSS is an endothermic, non-spontaneous process governed by decreased randomness in the transition state findings that align with similar studies on plant-derived biomass.

CONCLUSION

The kinetic modeling and thermodynamic analysis of roasted Coffee Senna (Senna occidentalis) seeds provided valuable insights into the thermal degradation behavior of the seeds during roasting. Experimental data obtained across a temperature range of 100 °C to 200 °C and roasting times between 5 and 30 minutes showed a consistent mass reduction from 98.4 g to 70.0 g, indicating progressive degradation with increased thermal exposure.

Spectroscopic analyses using FTIR and UV-Vis confirmed the presence and quantifiable concentrations of bioactive phytochemicals in the roasted seeds. These findings affirm the potential of Coffee Senna seeds as a source of bioactive compounds of medicinal relevance.

Kinetic modeling revealed that the degradation process followed a volume contraction mechanism across all roasting temperatures. The models yielded high coefficients of determination (R^2 = 0.9804–0.9915), indicating excellent fit. Additionally, the low reaction orders (0.28–0.397) pointed to a diffusion-controlled process governing the thermal decomposition.

Thermodynamic evaluation further revealed that the roasting process is endothermic and non-spontaneous. The enthalpy change (ΔH) ranged from 754.50 to 1585.90 kJ/mol, while Gibbs free energy (ΔG) varied between 102.92 and 130.18 kJ/mol. The negative entropy change ($\Delta S \approx -271.5$ kJ/K) across all roasting conditions suggested a transition to a more ordered state during the degradation process. Additionally, the calculated activation energies for Senna occidentalis seeds, ranging from 1589 to 758 kJ/mol, exhibit a decreasing trend with increasing temperature. Collectively, these findings provided comprehensive understanding of the thermal behavior and stability of Coffee Senna seeds under roasting conditions for the kinetics and thermodynamics.

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