Characterization and kinetic modeling for pyrolytic conversion of cotton stalks

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Abstract
Herein, cotton stalk biomass was initially characterized to understand its physico-chemical properties as a raw material for biochar production. Furthermore, thermal analysis was conducted using thermogravimetric analysis (TGA), and the results were further utilized to evaluate the cotton stalk’s kinetic behavior under thermal decomposition in an inert environment. Advanced kinetics and technology solutions (AKTS) software was for the first time employed to compute the kinetic parameters of cotton stalk pyrolysis, as well as provide kinetic predictions under isothermal conditions. Three methods were used to compute the activation energy ($E_a$) value, namely ASTM-E698, Flynn-Wall-Ozawa (FWO), and Friedman’s differential iso-conversional model. The results obtained using the ASTM-E698 method indicate an activation energy of 127.23 kJ·mol$^{-1}$. Furthermore, the FWO method presented an $E_a$ value ranging 35-250 kJ·mol$^{-1}$. The differential iso-conversional method is the most robust approach as it adequately represents the complex nature of lignocellulosic biomass decomposition, showing an $E_a$ range between 4 and 250 kJ·mol$^{-1}$. Based on the differential iso-conversional method, kinetic predictions under isothermal conditions were provided. The predictions offer valuable insight for industrial-scale biochar project developers in relation to production throughput optimization. Furthermore, the kinetic parameters obtained can be utilized in process modeling.

KEYWORDS
biochar, cotton stalk, iso-conversional method, kinetic modeling, pyrolysis
INTRODUCTION

Cotton stalk biomass, an abundant agricultural waste, is a promising feedstock for pyrolytic conversion to biochar, which has been recently highlighted as a reliable method that promotes atmospheric carbon removal.\(^1\)\(^{-}\)\(^3\) Cotton stalks are the residues remaining after cotton production, which are estimated to amount to 3.5-5 tons per ton of cotton crop.\(^2\) Global cotton production amounted to 25.8 million tons in 2018 and is expected to reach approximately 29.2 million tons by 2028.\(^5\) At recent production rates, global annual cotton stalk availability would be estimated between 90.3 and 129 million tons and is projected to grow accordingly. India, China, USA, Brazil, and Pakistan are the largest cotton producers, accounting for approximately 77% of global production in 2018.\(^5\) Thus far, cotton stalks have either been burnt in open fields, combusted for thermal energy production or used for light construction purposes. The utilization of cotton stalks to produce biochar would, therefore, add considerable value to the environment, through its carbon sequestration potential, as well as by enhancing food security and alleviating water stress in areas with limited access to irrigation water, if applied to soils. Furthermore, the utilization of such feedstock supports the concept of the circular economy.

An in-depth understanding of the characteristics of cotton stalks and the thermokinetic behavior under pyrolytic conditions is of great importance for the successful design and optimization of industrial biochar systems based on such feedstock. Kinetic analysis of biomass is mainly carried out to evaluate the kinetic triplet, activation energy ($E_a$), reaction rate, and pre-exponential factor ($k_o$). This information can then be used to predict reaction progress of a given feedstock under various thermal profiles and modes. Nonisothermal thermogravimetric analysis (TGA) is usually employed to determine the kinetic parameters under investigation. Various methods are utilized to analyze the data obtained through the TGA experiments, mainly model-fitting and model-free (also referred to as iso-conversional) methods.\(^6\)\(^{-}\)\(^7\) Model-fitting techniques are not recommended by the international confederation for thermal analysis and calorimetry (ICTAC) kinetics committee due to the uncertainty associated with kinetic parameter determination.\(^7\) The main model-free methods discussed in the literature include ASTM-E698, which is a model-free noniso-conversional approach, the Flynn-Wall and Ozawa (FWO), and Kissinger-Akahira-Sunrose (KAS), which are categorized as integral iso-conversional methods, and the Friedman method which is a differential iso-conversional method.\(^6\)\(^{-}\)\(^1\(^3\) The main issue related to the ASTM-E698 method is that a single activation energy value is calculated, not considering reaction progress in such a complex thermochemical process. It is more suitable for a single-step reaction. The FWO and KAS methods have been identified to lead to some systematic errors in computing activation energies, while the Friedman method, although potentially considered the most accurate approach, is identified to be sensitive to data noise, which in some cases may lead to a certain level of inaccuracy, as described by the ICTAC kinetics committee.\(^7\)\(^,\)\(^1\(^4\)\) Xia et al\(^1\(^5\)\) reported that advanced models must be developed to estimate product yield and composition as a function of biomass type/characteristics and process conditions. Utilizing catalysts such as zeolite in catalytic fast pyrolysis of lignocellulosic biomass is crucial, where properties of zeolites influence biomass pyrolysis routes.\(^1\(^6\)\(^,\)\(^1\(^7\)\) Ge et al\(^1\(^8\)\) also reported that agricultural waste provides environmental benefits as a sustainable feedstock, and they reported on the applications and new designs for microwave pyrolysis of agricultural wastes. Soft computing-based models, in addition to mathematical models, have been widely used to predict the kinetics of biomass pyrolysis. Aghbashlo et al\(^1\(^9\)\(^,\)\(^2\(^0\)\) recently used advanced soft computing methods to model biomass pyrolysis kinetics.

Several attempts to investigate the kinetic parameters of cotton stalks have been carried out. Mailto et al\(^2\(^1\)\) mainly used a linear model-fitting method using the Arrhenius equation and calculated an activation energy of 72.31 kJ·mol\(^{-1}\) based on a single heating rate of 10°C min\(^{-1}\). El-Sayed and Mostafa also used model-fitting methods using both, direct Arrhenius plotting and the Coats and Redfern model, calculating activation energies of 98.5-102 kJ·mol\(^{-1}\) and 72.5-127.8 kJ·mol\(^{-1}\), respectively. The range given represents two reaction zones. The analysis is also based on a single heating rate of 10°C min\(^{-1}\).\(^2\(^2\)\) Furthermore, Munir et al utilized the model-fitting approach and calculated an activation energy of 77 kJ·mol\(^{-1}\) using the Arrhenius equation. The analysis is based on a single stepwise heating rate of 10°C min\(^{-1}\) until 105°C followed by 20°C min\(^{-1}\) until 950°C.\(^2\(^3\)\) Tora et al.\(^2\(^4\)\) on the other hand, identified an activation energy for cotton stalks using the Coats and Redfern method to be 25 kJ·mol\(^{-1}\), which is
considerably low compared to the values obtained within the literature. Gupta et al investigated the activation energy of cotton stalks using both model-fitting and model-free techniques. The analysis is based on five heating rates (5, 10, 15, 20, and 30°C min⁻¹), resulting in activation energies of 97-124, 107-130, and 98.7-104 kJ mol⁻¹ based on KAS, FWO, and Coats and Redfern methods respectively.⁵⁻²⁶ Yao et al investigated the thermokinetic behavior of 10 biomass materials, which included cotton stalks, using various iso-conversional methods, FWO, Friedman and modified Coats and Redfern, and obtained average activation energies of 169.9, 165.3, 169.1 kJ mol⁻¹ respectively. The analysis is based on six different heating rates (2, 3.5, 5, 7.5, 10, and 15°C min⁻¹).²⁶ Chen and Liu examined cotton stalk kinetics by employing integral iso-conversional methods using five heating rates (15, 25, 35, 45, and 55°C min⁻¹). The average activation energy obtained was 145.39 kJ mol⁻¹ and 142.93 kJ mol⁻¹ using FWO and KAS methods, respectively.²⁷ It can be noted that many of the attempts to investigate cotton stalk kinetic behavior under pyrolytic conditions, thus far, have mainly been based on model-fitting methods, which carry a significant level of uncertainty. It is also worth noting that the standard Coats and Redfern model-fitting method has been empirically evaluated, presenting its unsuitability for determining kinetic parameters, especially for a process carrying complex reactions.²⁸ Furthermore, the investigations carried out using model-free methods have shown inconsistent results.

To the best of the authors’ knowledge, this study is the first attempt to study the kinetic behavior of cotton stalks under pyrolytic conditions using advanced kinetics and technology solutions (AKTS) software package. AKTS uses conventional thermoanalytical data, for example, obtained via TGA or differential scanning calorimetry (DSC), to carry out kinetic analysis using numerous model-free methods. In order to determine the kinetic parameters, TGA results are first transformed into a derivative thermogravimetric (DTG) signal and a baseline is constructed to further integrate the curve and compute the activation energy, rate of reaction and pre-exponential factor. AKTS provides various possibilities for advanced baseline construction, and this is perhaps the most critical step in kinetic data treatment. Moreover, the constructed baselines can be further optimized numerically. Based on the computed kinetic parameters, conversion progress predictions can be made for a wide range of temperature profiles. The results obtained through AKTS are highly robust and accurate due to the strict thermokinetic criteria employed by the software which defines an average correlation coefficient $R^2$ to be greater than 0.95. Furthermore, the plotting of high-resolution data over 10 000 data points promotes model robustness.⁸ This software has been successfully utilized in several investigations and is recommended by the ICTAC kinetics committee as a highly applicable tool for calculating kinetic parameters.⁸⁻¹¹,²⁹ Most importantly, the software can provide isothermal predictions, which is of great importance in analyzing kinetic behavior in continuous reactors operating under isothermal conditions, representing industrial-scale biochar production. This study aimed to characterize cotton stalk biomass, evaluate the kinetic triplet under pyrolytic conditions, and finally provide predictions on pyrolytic reaction progress of cotton stalks under various temperature profiles.

## 2 MATERIALS AND METHODS

### 2.1 Materials

The cotton stalks used in this study were sourced from southern Egypt, following crop harvest in 2019. The samples were dried naturally, and a hammer mill was used for size reduction to obtain a size of less than 1 mm.

### 2.2 Cotton stalk characterization

Cotton stalk composition was characterized using proximate and ultimate analyses, and a calculation of higher and lower heating values were carried out based on equation 1³⁰ and 2³¹

Higher heating value (HHV) = 0.3443C + 1.192H – 0.113O – 0.024N + 0.093S

(1)

Lower heating value (LHV) = HHV – 0.212H – 0.0245Moisture % – 0.008O

(2)

Furthermore, a Brunauer-Emmett-Teller (BET) analysis was conducted to investigate the surface area and pore size and volume. The chemical structure was evaluated using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and powder X-ray diffraction (XRD). Finally, Fourier transform infrared (FT-IR) was utilized to carry out a functional group analysis. Details of the characterization techniques are provided in the supplementary material.

### 2.3 Kinetic modeling

To determine the kinetic parameters of cotton stalks, a TGA was performed from 25 to 900°C using different heating rates of 0.5, 1, 2, 4, and 8°C min⁻¹ in an inert environment. Ultimately, the limitation of this study is dependent on the accurate reporting of thermoanalytical data in the form of TGA. The TGA instrument was calibrated for buoyancy effects to allow quantitative estimation of weight changes. Experiments were performed twice to ensure reproducibility and the standard error was found to be ±1°C.
Details of the TGA experiments are provided in the supplementary material. The data obtained through the TGA experiments were then used for kinetic modeling using the AKTS software to obtain the kinetic triplet ($E_a$, reaction rate, and $k_0$). The data is analyzed via AKTS using various methods such as ASTM-E698, FWO, and a highly robust differential iso-conversional model based on extensive TGA data using the slowest three heating rates. Based on the differential iso-conversional model, reaction progress predictions are made under isothermal mode. The following equations (3-5) represent the underlying methods utilized in the analysis.

1. ASTM-E698

\[
\frac{\beta \, da}{dt} = k_0 e^\left(\frac{-E_a}{RT}\right) (1 - a)
\]

2. Flynn-Wall and Ozawa

\[
\ln \beta = \ln \left(\frac{k_0 \cdot E_a}{R \cdot g(\alpha)}\right) - 5.331 - 1.052 \left(\frac{E_a}{RT}\right)
\]

3. Friedman/Differential Iso-Conversional

\[
\ln \beta \frac{da}{dT} = \ln[k_0 f(\alpha)] - \frac{E_a}{RT}
\]

### 3 | RESULTS AND DISCUSSION

#### 3.1 | Characterization results

Table 1 presents the physicochemical characteristics of the cotton stalk biomass used in this study and compares the results to the literature. The proximate analysis results show moisture content of 6.57%, volatile matter of 80.7%, fixed carbon 15.77%, and ash content of 3.53%. In general, the results are in line with those found in the literature, with volatile matter being in the upper range of those reported (74%-81.24%), fixed carbon within the lower range (14.28%-19.5%), while the ash content identified in this study is lower compared to the values reported, ranging 4.28%-6.5%.

Again, in terms of elemental analysis, the results (43.85 C%, 6.06 H%, 0.65 N%, 0.3 S%, and 45.61 O%) are similar to those obtained throughout the literature. Based on the elemental analysis HHV and LHV were calculated at 18.11 and 16.3 MJ·kg\(^{-1}\), respectively. The HHV value obtained in this study is found to be slightly higher than the values reported in the literature of 15.8-17.4 MJ·kg\(^{-1}\). The BET analysis results of the cotton stalks show a surface area of 2.28 m\(^2\)·g\(^{-1}\), pore volume of 0.000887 cm\(^3\)·g\(^{-1}\) and pore size of 12.6 Å, clearly indicating a nonporous structure.

Figure 1(A,B) presents the SEM images of the cotton stalk biomass under investigation. From the images, it can be noted that the morphological behavior is relatively bulky and nonporous. This supports the results obtained via BET analysis. Figure 1H and Table 1 present the surface composition of cotton stalks determined by the EDX analysis. It can be noted that the surface structure is mainly composed of carbon and oxygen at 53.2% and 39.3%, respectively.

Furthermore, a minor presence of calcium (5.7%) and sodium (1.7%) are detected. Figure 1C shows the combined elemental mapping image of cotton stalk biomass, while the specific elemental maps in Figure 1(D,F,G) show a uniform particle distribution within carbon, oxygen and sodium; furthermore, calcium shows a cluster particle formation, as presented in Figure 1E. XRD and FT-IR analyses are discussed in the supplementary materials with corresponding Figures S1A and B, respectively.

#### 3.2 | Kinetic modeling results

Nonisothermal TGA was carried out under the flow of nitrogen to represent pyrolytic conditions. The analysis was conducted at different heating rates of 0.5, 1, 2, 4, and 8°C min\(^{-1}\), while the experiment was repeated at 4°C min\(^{-1}\) to ensure reproducibility of the TGA data, as shown in Figure 2. The analysis is based on mass loss detection as a function of temperature and time as the reaction progresses. It can be clearly noted that the reaction follows three main stages of mass loss. Initially, the first stage can be noted between 80 and 150°C, resulting from dehydration. The second stage is mainly attributed to hemicellulose and cellulose decomposition, which occurred in the temperature range of 200-350°C. Most of the pyrolytic degradation took place in this region. The last stage is shown as a steep slope at temperatures higher than 350°C. Although lignin decomposition takes place throughout the entire temperature range, the mass loss taking place in the last stage is mainly attributed to lignin degradation. The results shown are in line with thermal decomposition profiles of typical lignocellulosic materials reported in the literature. The TGA results for the three slowest heating rates (0.5, 1, and 2°C min\(^{-1}\)) were then used in the AKTS software to compute the kinetic parameters using three methods, ASTM-E698, FWO, and Friedman’s differential iso-conversional model. Moreover, conversion predictions were provided under isothermal conditions. Figure S2 in the supplementary material presents the TGA results used in the kinetic analysis. Furthermore, Figure 3 presents the cotton stalk conversion progress as a function of temperature under three different heating rates (0.5, 1, and 2°C min\(^{-1}\)). The solid lines represent the actual results obtained via TGA, and the dashed lines represent those simulated by.
AKTS. It can be noted that the actual and simulated results are highly matching with an $R^2$ value of 0.98. It can also be noted that the reaction under the three heating rates is initiated at approximately 190°C. Furthermore, a shift in reaction temperature is observed as the heating rate is increased. The reason behind this shift has been explained by Osman et al., where a delay in decomposition may be attributed to a combined effect related to heat transfer and decomposition kinetics of the processed material. By increasing the heating rate, the time required for the cotton stalks to reach a specific temperature is shortened, which may cause limitations in mass and heat transfer and lead to a delay in decomposition until a higher reaction temperature is achieved. Moreover, the possibility of a temperature gradient occurring may lead to the occurrence of various devolatilization stages. Furthermore, this phenomenon can be attributed to the poor thermal conductivity of biomass, where a thermal lag can be realized across the whole cross-section of the biomass particle when heated. At very low heating rates, a uniform temperature profile can be observed throughout the whole cross-section; however, at higher heating rates, a temperature gradient across the inner layers and outer surface of the biomass particle can be realized, which can cause a delay in decomposition.

Figure 4 presents the reaction rate versus temperature for cotton stalk pyrolysis, providing both actual and simulated results, showing a high correlation with an $R^2$ value of 0.98. The maximum reaction rates identified were 0.00009, 0.000163, and 0.000311 $\text{s}^{-1}$, achieved at peak temperatures of 267, 278, and 292°C at heating rates of 0.5, 1, and 2°C min$^{-1}$, respectively. The reaction rate increased approximately 3.5 times by increasing the heating rate from 0.5 to 2°C min$^{-1}$.

Based on the ASTM-E698 method, a single value for activation energy was calculated at 127.23 kJ·mol$^{-1}$, as shown in Figure 5A. The thermal degradation of biomass is a complex process with multiple reactions taking place simultaneously. Osman et al. proposed a 10-step mechanism representing lignocellulosic biomass pyrolysis. The process comprises primary and secondary reactions, where separate reactions related to the decomposition of cellulose, hemicellulose, and lignin are taking place simultaneously. To effectively represent the complexity of biomass decomposition, a single activation value is not sufficient; therefore, the ASTM-E698 method is inadequate and may lead to inaccurate conversion.
FIGURE 1 SEM images of cotton stalks (A, B), elemental mapping (C-G) and EDX results (H)
predictions for cotton stalk pyrolysis. The same applies to any model-fitting approach that computes a single activation energy value. The integral iso-conversional method (FWO), on the other hand, would be more adequate, as it takes into account the kinetic behavior of the material processed as the conversion progresses. Figure 5B presents the activation energy for cotton stalk pyrolysis as a function of the reaction progress. The results indicate that high activation energy of ~250 kJ·mol\(^{-1}\) is observed as the reaction is initiated, and this value is reduced as the conversion progresses. \(E_a\) values of ~157, 135, 113, 44, and 35 kJ·mol\(^{-1}\) are identified at conversion rates of 20 (\(\alpha = 0.2\)), 40, 60, 80, and 100%, respectively. The results obtained are not in line with those reported in the literature. Gupta et al calculated the activation energy of cotton stalk pyrolysis in the range 107-130 kJ·mol\(^{-1}\) using the FWO method,\(^{25}\) while Chen et al reported 118.49-178.22 kJ·mol\(^{-1}\).\(^{27}\) Furthermore, Yao et al reported an average activation energy of 169.9 kJ·mol\(^{-1}\) using the FWO method.\(^{26}\) The reason behind such deviations may be due to the fact that the TGA experiments were carried out at very low heating rates (0.5, 1, and 2°C·min\(^{-1}\)) in this study as compared to those utilized by Gupta et al. (5, 10, 15, 20, and 30°C·min\(^{-1}\)), Chen et al. (15, 25, 35, 45, and 55°C·min\(^{-1}\)), as well as Yao et al. (2, 3.5, 5, 7.5, 10, and 15°C·min\(^{-1}\)), allowing for a larger dataset. Another explanation regarding the deviation in results can be related to the inherent characteristics of the cotton stalks used for analysis. This could be due to geographical differences, as well as differences in cultivation practices and actual species utilized. In relation to this study, the use of AKTS presents an opportunity for model construction optimization as well as facilitates the plotting of high-resolution data, covering 10 000 specific data points, which promotes model robustness and accuracy.\(^{8}\)

With the support of AKTS, Friedman’s differential iso-conversional model, a highly reliable method, was utilized in computing the kinetic parameters. Figure 6A presents the natural logarithm of the reaction rate (S\(^{-1}\)) versus inverse temperature (T\(^{-1}\)) and Figure 6B provides \(E_a\) and \(K_0\) as a function of the conversion rate (\(\alpha\)). The results indicate that a high activation energy of ~250 kJ·mol\(^{-1}\) is observed as the reaction is initiated. This value starts to decline as the conversion proceeds, reaching ~143 kJ·mol\(^{-1}\) at 20% conversion (\(\alpha = 0.2\)) and then ~127 kJ·mol\(^{-1}\) at 40% conversion (\(\alpha = 0.4\)). The activation energy then starts to increase, reaching ~133 kJ·mol\(^{-1}\) at 50% conversion and then sharply declines to ~55 kJ·mol\(^{-1}\).
at 60% conversion. Furthermore, a gradual decline is observed reaching a low of ~4 kJ·mol⁻¹ at 86% conversion, and then an increase is shown to reach ~40 kJ·mol⁻¹ toward the end of the reaction. The value obtained for the initial stage of the reaction (250 kJ·mol⁻¹) is in line with the results obtained using the FWO method in this study. Furthermore, a similar trend is observed in terms of declining activation energy during the initial conversion phase until 40%. The differential iso-conversional model results then start to deviate from those obtained through FWO, by showing a variation in activation energy of ~133, 55, 3.5, 40 as the reaction proceeded at conversion rates 50%, 60%, 86%, and 100%, respectively. The differential iso-conversional method, thus far, has shown dynamic results, which clearly considers the reaction complexity attributed to lignocellulosic biomass decomposition. Table 2 presents the kinetic results at various conversion rates using Friedman’s differential iso-conversional method as well as Flynn-Wall-Ozawa (FWO) integral iso-conversional approach. The results obtained in this study are compared to those reported in the literature.

Based on the results obtained using the differential iso-conversional method, isothermal predictions are constructed. Figure 7 provides cotton stalk kinetic predictions under isothermal pyrolytic conditions covering a temperature range between 300 and 800°C. The results indicate that at 800°C, the reaction reaches completion at approximately 150 minutes. Lower temperatures are not able to achieve 100% conversion within this timeframe. However, for biochar production, a 100% conversion may not be required to be achieved. Depending on the end product application, the required specifications can be met at a conversion rate that may range anywhere between 60% and 100%. Residence time in industrial-scale biochar systems is a critical aspect as it directly impacts production throughput and project profitability. Therefore, a short reaction time is desired, while achieving the required conversion rate. The kinetic predictions can provide further insight by providing more information on the state of conversion as a function of time under various isothermal temperatures, representing continuous biochar production in an industrial setting. For example, if an 80% conversion adequately meets product specifications, a reaction time of 18, 24, 35, 58, and 118 minutes is required at reaction temperatures of 800, 700, 600, 500, and 400°C, respectively. It may not be financially feasible to achieve an 80% conversion at 300°C as this would require ~349 minutes. Operating at a range between 500 and 800°C would provide good process efficiencies in terms of productivity; however, it is crucial to understand the impact of such temperature range on the biochar’s physicochemical properties. It is evident that a higher reaction temperature leads to a shorter residence time; thus, higher production throughput can be achieved. At a reaction temperature of 800°C, approximately three times the amount of biomass can be processed in a single hour as compared to a reaction.
The results based on the Friedman’s differential iso-conversational method showed a high degree of reliability as it adequately represents the complex nature of lignocellulosic biomass decomposition. Based on such results, kinetic predictions under isothermal conditions were provided. The predictions offer valuable insight for industrial-scale biochar project developers as production throughput optimization can be further investigated. Moreover, the kinetic parameters obtained can be utilized in process modeling. Further experimental work is required to validate the conversion predictions obtained in this study as well as further understand the impact of reaction temperature, residence time, and other potential production parameters, on product yield as well as biochar physicochemical properties, for process optimization. A balance between production yield and production throughput is required, as well as achieving product properties that meet specification requirements for the intended application.

Additionally, the differential iso-conversational method presented similar results to those obtained via FWO, however, showing more variation toward the second half of the reaction. However, the differential iso-conversational method adequately represents the complex nature of lignocellulosic biomass decomposition, showing an $E_a$ range between 4 and 250 kJ·mol$^{-1}$, depending on the state of conversion. Finally, from the thermal predictions outlined in the study, it can be concluded that there are diminishing returns from temperatures of 600°C and higher when considering the conversion of cotton stalk pyrolysis after 140 minutes. In the authors' opinion, a temperature of at least 550-600°C should be used to pyrolyze cotton stalks under isothermal heating.

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AUTHOR CONTRIBUTIONS
SF – Conceived the idea, collected the data, performed the analysis and wrote the paper; AO – supported with data analysis and reviewed the paper; CF – conducted AKTS analysis; AAM, AAF, AHF, JH, JD, HY, DR – reviewed the paper.
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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section.

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