

Kinetic and Thermodynamic Analysis of Pyrolysis of Coconut Wood Residue

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Physico-chemical properties, kinetics and thermodynamic analysis of biomass are important in designing an efficient pyrolysis process. The current study aims to investigate the physico-chemical behaviour, calorific value and kinetics of thermal decomposition of coconut wood (*Cocos nucifera*) at 10, 15, and 25 °C/min using the thermogravimetric analysis (TGA) technique in nitrogen atmospheres. Kinetic parameters were estimated using the Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (FWO), Starink, Tang, Friedman and Coats-Redfern (CR) methods. Average activation energy estimated from Kissinger-Akahira-Sunose (KAS), Starink, Tang and Coats-Redfern (CR) methods was ≈ 100 kJ/mol. The Flynn-Wall-Ozawa (FWO) method predicted a higher value of 104 kJ/mol and Friedman a lower value of 81 kJ/mol. Thermodynamic parameters like change in enthalpy, Gibbs free energy and entropy have also been evaluated.

Keywords: Coconut wood, Thermogravimetric analysis, Kinetic models, Activation energy, Thermodynamics.

INTRODUCTION

For the generation of energy using different agricultural resources and its utilization as liquid fuel, potential alternative technologies must be considered [1]. As a result, agricultural residues, which are useless and cause environmental problems, can become more valuable and environmentally friendly energy rich products. Belonging to the Arecaceae family, coconut tree (*Cocos nucifera*) is widely cultivated in Indonesia, Philippines, India and Sri Lanka. Coconut timber is now widely used as interior design and structural material. The residues from these industries can be utilized for the production of fuel [2].

For the correct energetic use of the residual biomass, the system must be designed accordingly. A thorough understanding of the process and its kinetic parameters and thermodynamic properties are essential for this. Literatures reported the thermo-degradation kinetics of various agricultural residues like municipal and agricultural wastes [3], Chinese silvergrass, corn stalks, rice husk and pine biomass [4], hullless barley straw [5], maize cob [6], sorghum straw [7], palm kernel shell [8], castor residue [9], skin, husk and shell of green coconut waste [10], coconut leaf [11], coconut shells [12], coconut fiber [13] and so on.

Thermogravimetric analysis (TGA) provides the kinetic parameters of the devolatilization process. Using TGA data, several researchers have developed various kinetic models such as Kissinger [14], Flynn-Wall-Ozawa method [8-10], Kissinger-Akahira-Sunose method [8,9], Starink method, Friedman method [10], distributed activation energy model (DAEM) [3,5], Coats-Redfern method [4,12,14] and Tang [14] are some of the methods adopted for the degradation mechanism. This study attempts to analyze the devolatilization kinetics and thermodynamic parameters like change in enthalpy (ΔH), change in Gibbs free energy (ΔG) and change in entropy (ΔS) of coconut wood residue through the thermogravimetric analysis.

EXPERIMENTAL

Coconut (*Cocos nucifera*) wood residues collected from wood mill near West hill, Kozhikode, India were sun-dried for around 4 days and was cut into pieces and milled to desired particle size (< 1 mm).

Characterization of biomass: The physico-chemical properties of biomass are very important to predict its bio-energy potential in the production of bio-oil and biochar. To analyze the moisture, volatiles, ash content and fixed carbon, a proximate analysis is carried out; whereas an ultimate analysis

is done to determine the composition of carbon, hydrogen, oxygen, nitrogen and sulphur based on ASTM standards. The ultimate analysis was carried out on a CHNSO elemental analyser (Elementar Vario EL III). The calorific value of the samples was determined using an oxygen bomb calorimeter (Parr, Model: 1341 Plain Jacket Calorimeter). The extractive content of biomass was determined using a Soxhlet apparatus in which ethanol was used as the solvent. The lignin content of the biomass was measured by Klason method. FTIR analysis (Perkin-Elmer UTAR Two) was carried out to determine the possible functional groups that may be present in the biomass.

Thermal analysis: Thermogravimetric analysis (TGA) was carried out with the Perkin-Elmer simultaneous thermal analyzer STA 6000 in an N₂ atmosphere with a purging rate of 19.8 mL/min over a temperature range of 30 to 600 °C with three different heating rates of 10, 15, 25 °C/min.

Kinetic modelling: Wood biomass consists of cellulose, hemicellulose, lignin and a small amount of inorganic substances, each of which has different structures and decomposes in different temperature ranges, so that an accurate prediction of a pyrolysis kinetic reaction is quite difficult. The following equation can be used to describe the kinetics of reactions in biomass:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

The conversion α is a normalized form of the decomposed biomass weight loss data and is defined as follows:

$$\alpha = \frac{m_i - m_\alpha}{m_i - m_f} \quad (2)$$

where m_i is the initial mass of the sample, m_α is the actual mass and m_f is the mass after pyrolysis.

Incorporating the Arrhenius equation for the temperature dependence of rate constant into eqn. 1 gives the basic expression (eqn. 3) of the analytical methods for calculating the kinetic parameters based on the TGA results.

$$\frac{d\alpha}{dt} = A.f(\alpha).e^{\frac{-E_a}{RT}} \quad (3)$$

The function $f(\alpha)$ and its derivative $f'(\alpha) = -1$ are used to describe the solid-state first order reaction, the mathematical function $f(\alpha)$ were restricted to the expression as shown below:

$$f(\alpha) = (1-\alpha)^n \quad (4)$$

where n denotes the order of the reactions. Substituting the expression (eqn. 4) into the equation (eqn. 3) yields the reaction rate expression in the form:

$$\frac{d\alpha}{dt} = A.(1-\alpha)^n .e^{\frac{-E_a}{RT}} \quad (5)$$

For non-isothermal TGA experiments at a linear heating rate, equation (eqn. 5) can be written as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} .(1-\alpha)^n .e^{\frac{-E_a}{RT}} \quad (6)$$

This equation represents the proportion of material consumption over time. The activation energy was obtained in this

study using non-isothermal TGA. The methods used to determine the kinetic parameters are known as non-isothermal, model free methods and they necessitate a series of experimental tests at various heating rates. In this study, iso-conversional model-free, non-isothermal methods like Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (FWO), Starink, Tang, Friedman, were applied for the estimation of kinetic parameters of pyrolysis process of coconut wood residue. To determine the reaction mechanism, the Coats-Redfern (CR) method was used as an individual heating rate model-fitting method.

Thermodynamic analysis: Considering that pyrolysis is an energy-intensive process, it is crucial to determine its thermodynamic characteristics. To understand the variations in enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) with conversion the following expressions were used [14]:

$$A = \frac{\beta E_a \exp\left(\frac{E_a}{RT_m}\right)}{RT_m^2} \quad (7)$$

$$\Delta H = E_a - RT \quad (8)$$

$$\Delta G = E_a + RT_m \ln\left(\frac{k_b T_m}{hA}\right) \quad (9)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \quad (10)$$

where k_b is the Boltzmann constant, h is the Planck's constant and T_m is the peak temperature from derivative thermogravimetric (DTG) curve.

RESULTS AND DISCUSSION

The physico-chemical properties of coconut wood residue is analyzed and presented in Table-1. Coconut wood has a high carbon content of 49.18% wt. and a hydrogen content of 6.13% wt. Because nitrogen and high levels of oxygen (~45% wt.) do not support combustion, their energy content is reduced [12]. The SO_x and NO_x emissions are negligible, indicating a cleaner fuel compared to fossil fuels. Compared to conventional fossil fuels like coal, which has a higher heating value of 30 MJ/kg and is similar to other coconut biomass, coconut wood has a higher heating value of 19.77 MJ/kg. It is reported that coconut shell has a HHV of 17 MJ/kg [12] and for skin, husk and shell of green coconut wastes 18.98, 18.15, 18.64 MJ/kg, respectively [10], HHV of leaflets, midrib and the whole leaf of coconut were 18.631 MJ/kg, 17.848 MJ/kg and 18.369 MJ/kg, respectively [11]. HHV indicates the potential of biomass as a fuel. As a result, it is critical to convert coconut wood waste into high-energy fuel *via* thermochemical processes like pyrolysis. The ultimate, proximate analysis and lignin content obtained in this study are also similar to the thermochemical studies of other coconut biomass [10-12].

FTIR studies: The FTIR spectroscopic analysis (Fig. 1) was conducted to determine the functional groups of the compounds contained in the organic matter of the coconut wood, which controls the thermal degradation behaviour. The bands

TABLE-1
PHYSICO-CHEMICAL ANALYSIS OF COCONUT WOOD RESIDUE

Ultimate analysis (wt.%)		Proximate analysis (wt.%)		HHV (MJ/kg)	LHV (MJ/kg)	Lignin content (wt.%)
C	49.18	Moisture content	8.8	19.77	18.43	29.9
H	6.13	Volatile matter	87.8			
N	0.32	Ash content	1.2			
S	ND	Fixed carbon*	2.2			
O*	44.37					

*By difference

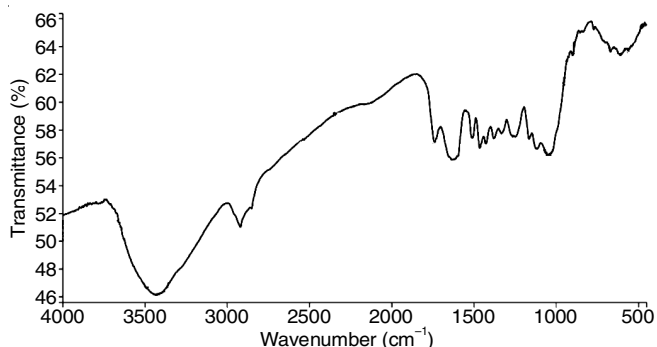


Fig. 1. FTIR spectrum of the coconut wood

and the corresponding functional groups [15] are presented in Table-2.

Thermal studies: Thermogravimetric (TG) profile for the thermal decomposition of coconut wood biomass is shown in Fig. 2a-b. The TG profile showed that only unbound moisture

is removed from the room temperature to 100 °C and bound moisture from 100 to 210 °C. The slope becomes steeper in the temperature range (210-400 °C), implying a faster rate of conversion and weight loss with rising temperature. The hemicellulose and cellulose in coconut wood residues degrade at these temperatures. In third temperature range (above 400 °C), the curves indicate a less steep change in conversion. This could be due to an increase in lignin degradation and heat interactions between degradation products.

Iso-conversional kinetic analysis: Using various iso-conversional models, the pre-exponential factor (A) and activation energy (E_a) were calculated from the thermogravimetric data. The values of E_a for the KAS, FWO, Starink, Friedman and Tang iso-conversional models were calculated from the slopes of the linear plots (Fig. 3a-f) using the relevant models at $\alpha = 0.1$ to 0.9. The highest activation energy value E_a obtained by studied several models are similar to other coconut biomass (Table-3). Literatures reported that the activation energy of

TABLE-2
FUNCTIONAL GROUPS PRESENT IN THE BIOMASS

Bands (cm ⁻¹)	Functional groups
3433	O-H stretching of water, phenolic and alcoholic groups
2922	Aliphatic CH, CH ₂ and CH ₃ elongation of the alkanes, asymmetric and symmetric stretching of methyl group
1626	Carbonyl group of C-C, amine N-H, alkyne C=C stretching, phenyl ring C-H group substitution
1509	Aromatic rings of lignin
1377	Aromatic methoxy groups
1332	C-H and aliphatic C-H ₂ in phenol
1254 to 1033	Cellulose and hemicellulose carbohydrates
1053	C-OH stretching vibrations
469 to 900	C-C stretching of aromatic ring

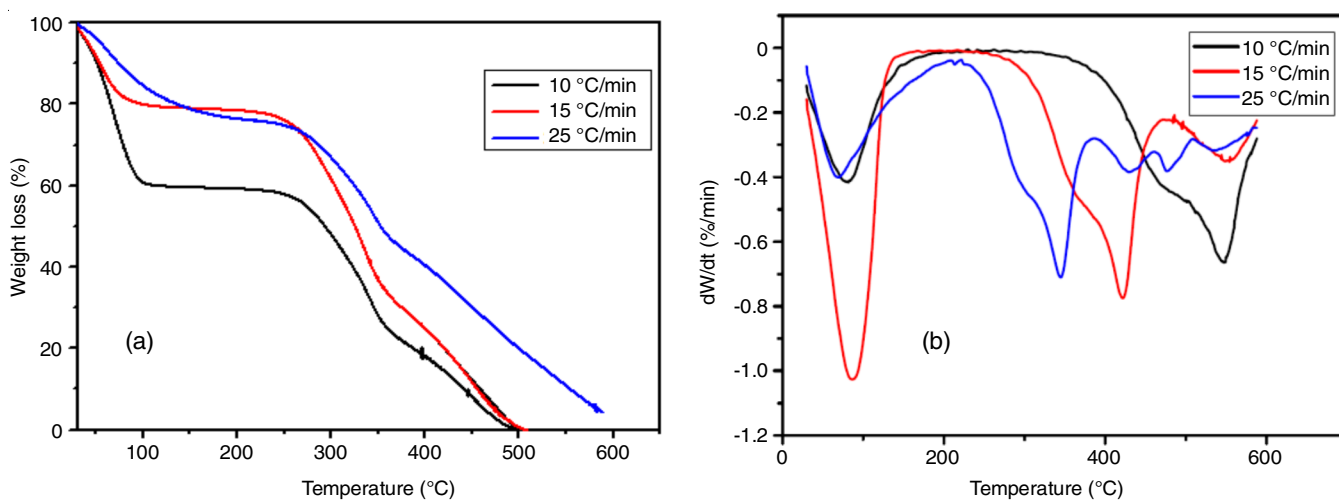


Fig. 2. (a) TG and (b) DTG profile for coconut wood

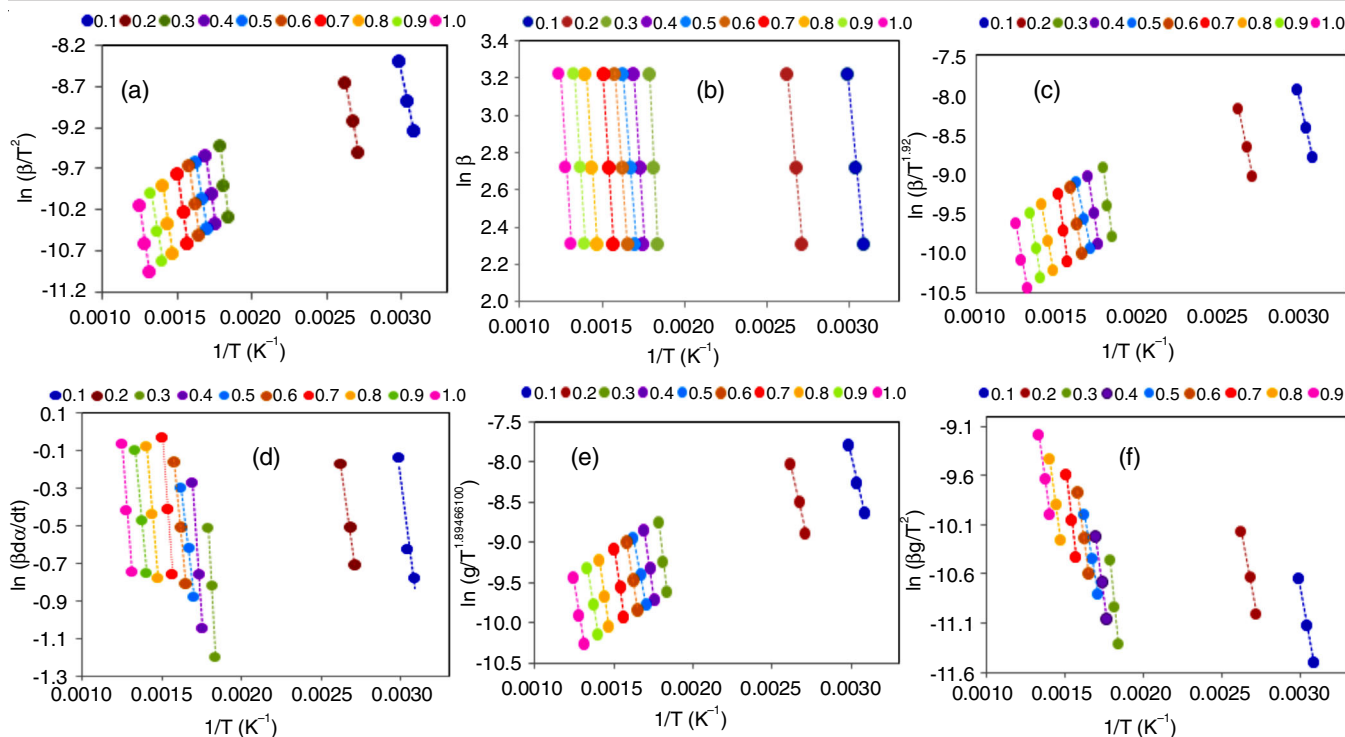


Fig. 3. (a) KAS method, (b) FWO method, (c) Starink method, (d) Friedman method, (e) Tang method, (f) Coats-Redfern method

TABLE-3
ACTIVATION ENERGY FROM EACH MODEL

α	KAS		FWO		Starink		Friedman		Tang		Coats-Redfern	
	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2
0.1	73.49	1.00	75.00	1.00	73.65	1.00	55.93	0.93	73.67	1.00	73.49	1.00
0.2	74.56	0.99	76.75	0.99	74.75	0.99	47.98	1.00	74.78	0.99	74.56	0.99
0.3	143.34	0.99	144.89	0.99	143.59	0.99	114.57	1.00	143.61	0.99	143.33	0.99
0.4	111.48	0.99	115.08	0.99	111.77	0.99	104.01	1.00	111.82	0.99	111.48	0.99
0.5	83.12	1.00	88.47	1.00	83.45	1.00	58.63	1.00	83.52	1.00	83.11	1.00
0.6	96.36	0.99	101.35	0.99	96.70	0.99	75.07	0.99	96.76	0.99	96.36	0.99
0.7	115.27	1.00	119.82	1.00	115.62	1.00	100.01	0.99	115.68	1.00	115.27	1.00
0.8	100.75	1.00	106.71	1.00	101.13	1.00	86.07	1.00	101.21	1.00	100.75	1.00
0.9	98.09	1.00	104.79	1.00	98.51	1.00	78.59	1.00	98.59	1.00	98.09	1.00
1	99.66	0.99	107.04	0.99	100.11	0.99	84.53	1.00	100.21	0.99	–	–
Average	99.61		103.99		99.93		80.54		99.99		99.61	

coconut shell was 122.780 kJ/mol [12]. The highest E_a value obtained by FWO and Friedman methods, respectively, was 158 kJ/mol and 183 kJ/mol for skin, 160 kJ/mol and 183 kJ/mol for husk and 188 kJ/mol and 214 kJ/mol for shell of coconut [10]. The activation energy varied between 184.0 and 236.1 kJ/mol for the FWO method, respectively for torrifed coconut fiber [16]. The variation of activation energy with conversion of biomass is shown in Fig. 4. The activation energy of a fuel is an important factor in calculating its reactivity. The reactivity of fuel is crucial in the thermal degradation processes [17].

In the conversion range of 0.2 to 0.3, activation energy (E_a) increases with conversion, which is primarily due to hemicellulose decomposition. After $\alpha = 0.3$, E_a decreases with increasing conversion until $\alpha = 0.5$. The decreasing trend of E_a is most likely due to pyrolysis of the cellulose crystal, as a result of decreasing decomposed activation energy with increasing

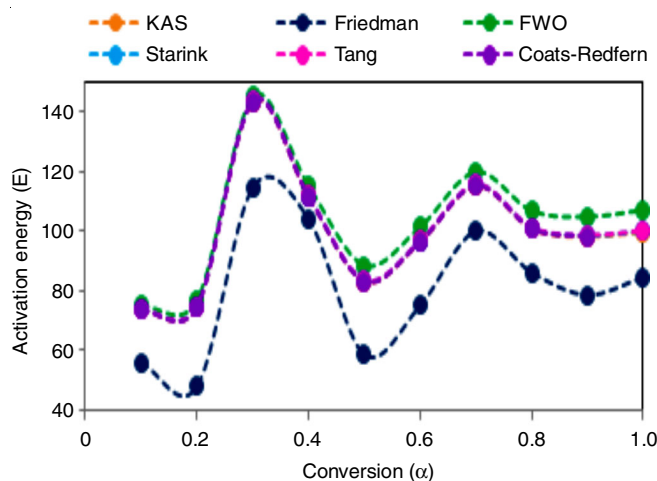


Fig. 4. Variation of activation energy with conversion

conversion. This is due to the fact that at lower conversions, heat is transferred throughout the sample *via* diffusion. The higher thermal stability of lignin, on the other hand, may be related to a difficulty in the heat transfer process due to the well-ordered cellulose regions [18]. The variation in activation energy with conversion suggests the presence of a multireaction mechanism during pyrolysis of coconut wood biomass [19].

Thermodynamic analysis: Thermodynamic parameters govern the pyrolysis cycle’s performance and heat measurement [14]. The sum of heat in a reaction is specified and the energy difference between raw feedstock and activated composite is easily quantifiable. The activation energy derived using KAS, FWO, Friedman, Starink, Tang and Coats-Redfern methods was used to estimate thermodynamic parameters (ΔH , ΔG and ΔS) for thermal breakdown of coconut wood residue. Eqns. 9-11, respectively, yielded ΔH , ΔG and ΔS , which are illustrated in Table-4. Enthalpy is a thermodynamic property that reflects a device’s overall thermal output. The minimum energy consumed by biomass during the pyrolysis process to produce various materials such as gas, oil or charcoal is referred to as enthalpy [9].

The positive value of ΔH suggest that the process is endothermic. The value of ΔH is very closer to the value of E_a for each conversion, implies that the product formation can be done by providing less additional energy. This is similar to the literatures reported [9,15,20]. As in the similar literatures [21], value of ΔH shows an increasing trend in the initial with a maximum 140.37 kJ/mol (FWO), at conversion 0.3 and decreased towards the end showing less energy requirements.

The thermodynamic parameter ΔG indicates how much bioenergy may be recoverable from pyrolysis. In other words, feedstocks for pyrolysis, which are more suited typically have greater ΔG values. The ΔG values obtained are in the range of

199 to 204 kJ/mol, which are comparable to the catole coconut pyrolysis reported in the range of 153.0 to 177.0 kJ/mol [20].

Also a low ΔS implies that the pyrolysis of coconut wood biomass tends towards thermodynamic equilibrium as a result of small physical and chemical changes. From the present analysis, ΔS values indicate that the system is highly reactive at the start and gradually achieves the chemical equilibrium as the reaction progresses. The $\Delta S < 0$ and $\Delta H > 0$ also indicate that the process will be spontaneous. Overall, thermodynamic parameters indicate that the process is endothermic, with decreasing reactivity with conversion. These results show similar trends to the available literature in the coconut biomass [21].

Conclusion

The results showed that the activation energy and physico-chemical properties of coconut biomass were in good agreement with the pyrolysis requirement. The activation energy of coconut biomass is lower than that of many other biomass feedstocks. Furthermore, the significant quantity of volatile components, as well as hemicellulose and cellulose, suggests that coconut biomass has biofuel potential. In the temperature range of 210 to 400 °C, significant biomass degradation was found. The average activation energies measured using various approaches were relatively similar (100 kJ/mol). The thermodynamic parameters showed that the reaction rate for the pyrolysis of coconut wood biomass was higher at a conversion of 0.3. The thermodynamic study reveals that the pyrolysis reactions of coconut wood biomass can be easily initiated.

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TABLE-4
THERMODYNAMIC DATA FROM EACH MODEL

α	KAS				FWO				Starink			
	A	ΔG	ΔH	ΔS	A	ΔG	ΔH	ΔS	A	ΔG	ΔH	ΔS
0.1	1.72×10 ⁴	203.93	70.80	-0.18	2.23×10 ⁴	203.80	72.30	-0.17	1.77×10 ⁴	203.91	70.96	-0.17
0.2	2.07×10 ⁴	203.84	71.50	-0.17	3.01×10 ⁴	203.65	73.68	-0.17	2.14×10 ⁴	203.82	71.69	-0.17
0.3	2.12×10 ⁹	199.71	138.82	-0.08	2.73×10 ⁹	199.64	140.37	-0.08	2.21×10 ⁹	199.70	139.07	-0.08
0.4	1.06×10 ⁷	201.30	106.75	-0.12	1.94×10 ⁷	201.09	110.35	-0.12	1.12×10 ⁷	201.28	107.04	-0.12
0.5	8.92×10 ⁴	203.15	78.24	-0.16	2.22×10 ⁵	202.76	83.60	-0.16	9.44×10 ⁴	203.13	78.58	-0.16
0.6	8.41×10 ⁵	202.22	91.33	-0.15	1.95×10 ⁶	201.90	96.31	-0.14	8.91×10 ⁵	202.19	91.66	-0.15
0.7	2.01×10 ⁷	201.08	109.96	-0.12	4.29×10 ⁷	200.84	114.51	-0.11	2.13×10 ⁷	201.06	110.31	-0.12
0.8	1.76×10 ⁶	201.94	95.10	-0.14	4.79×10 ⁶	201.57	101.07	-0.13	1.88×10 ⁶	201.91	95.49	-0.14
0.9	1.13×10 ⁶	202.10	92.15	-0.14	3.47×10 ⁶	201.69	98.85	-0.14	1.21×10 ⁶	202.08	92.57	-0.14
1	1.47×10 ⁶	202.00	93.35	-0.14	5.06×10 ⁶	201.55	100.72	-0.13	1.58×10 ⁶	201.98	93.79	-0.14
α	Friedman				Tang				Coats-Redfern			
	A	ΔG	ΔH	ΔS	A	ΔG	ΔH	ΔS	A	ΔG	ΔH	ΔS
0.1	8.12×10 ²	205.65	53.23	-0.20	1.77×10 ⁴	203.91	70.98	-0.17	1.72×10 ⁴	203.93	70.80	-0.18
0.2	1.98×10 ²	206.62	44.92	-0.21	2.15×10 ⁴	203.82	71.72	-0.17	2.07×10 ⁴	203.84	71.49	-0.17
0.3	1.78×10 ⁷	201.12	110.05	-0.12	2.22×10 ⁹	199.69	139.10	-0.08	2.12×10 ⁹	199.71	138.81	-0.08
0.4	3.05×10 ⁶	201.73	99.28	-0.13	1.13×10 ⁷	201.28	107.09	-0.12	1.06×10 ⁷	201.30	106.75	-0.12
0.5	1.31×10 ³	205.36	53.76	-0.20	9.56×10 ⁴	203.12	78.65	-0.16	8.92×10 ⁴	203.15	78.24	-0.16
0.6	2.26×10 ⁴	203.79	70.03	-0.18	9.00×10 ⁵	202.19	91.73	-0.15	8.41×10 ⁵	202.22	91.33	-0.15
0.7	1.55×10 ⁶	201.98	94.70	-0.14	2.15×10 ⁷	201.06	110.37	-0.12	2.01×10 ⁷	201.08	109.96	-0.12
0.8	1.47×10 ⁵	202.93	80.43	-0.16	1.90×10 ⁶	201.91	95.56	-0.14	1.76×10 ⁶	201.94	95.10	-0.14
0.9	4.12×10 ⁴	203.50	72.65	-0.17	1.22×10 ⁶	202.07	92.65	-0.14	1.13×10 ⁶	202.10	92.15	-0.14
1	1.14×10 ⁵	203.04	78.21	-0.16	1.61×10 ⁶	201.97	93.89	-0.14	–	–	–	–

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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