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Effect of hot water extraction on pyrolysis of tender coconut fruit biomass: kinetic and thermodynamic parameters

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Abstract

Effect of pre-treatment of tender coconut fruit bio-mass powder with hot water on physico-chemical properties and thermal degradation behavior were investigated. The physico-chemical parameters were evaluated using ASTM standard protocols. The thermal degradation behavior was studied at heating rates of 10, 15 and 20°C/min under inert (N₂) atmospheric conditions using TG/DTG techniques. The activation energies at each heating rate were determined using Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS), Starink, and Tang models. The pre-treatment with hot water improved the proximate and ultimate analyses parameters and calorific value. The higher heating values (HHV) for untreated and treated tender coconut fruit biomass were 18.57 and 21.26 kJ/kg, respectively. The values of activation energy (E_a) for the un-treated biomass powder were estimated to be 389.25, 397.81 and 398.77 and 397.97 kJ/mol for FWO, KAS, Tang, and Starink models, respectively and for the treated biomass these were 125.43, 118.61, 118.99 and 118.94 kJ/mol, respectively. On an average the E_a of the treated coconut biomass was nearly three times lower than that for the untreated biomass. The results indicated that pre-treatment with hot water improved the fuel characteristics and thermal degradation behavior of the tender coconut shell biomass. The water extract exhibited high COD and BOD values and might be used as the feed-stock for biogas generation.

Keywords Tender coconut biomass · Hot water extraction · TG & DTG analyses · Thermal degradation · Kinetic analysis · Thermodynamic parameters

1 Introduction

In view of the increasing environmental pollution and energy insecurity due to over exploitation of the finite fossil fuel reserves, various types of agricultural, domestic and industrial carbonaceous wastes, the globally available renewable materials, are being considered as the viable options for producing chemicals and energy. Several of these wastes are of little or no value as animal feed and will also not lead to the food-fuel conflict that may arise due to the use of cultivated biomasses or the ‘energy crops’. Waste biomasses produced

through the cultivation, processing, and use of oil bearing fruits and seeds like coconut (dry and green husk, shell, skin, and leaves), peanut or ground nut (plant stalk, nut skin, and nut shell), mustard (de-oiled cake and stalk), palm (de-oiled meal, husk, and shell) etc., have enormous potential as renewable feed-stock for obtaining energy and value added chemicals and have attracted the attention of researchers in recent years. The abundantly available coconut derived waste biomasses have very high energy potential [1–7].

The coconut (*Cocos nucifera* L.) is widely cultivated in as many as 92 countries of tropical and sub-tropical regions of Africa, Asia and Latin America over an area of 10 million hectares [8]. The total global coconut plantation area and production during 1994 to 2019 and production in top ten coconut producing countries are shown in Fig. 1. India, Indonesia and Philippines account for 75% of the total global coconut production. The coconut fruit is a drupe having an outer hard and thick layer comprising exocarp, mesocarp, endocarp, tegument and inner solid albumen (flesh or pulp), liquid albumen (coconut water) and embryo. Its solid and liquid albumen portions are edible.

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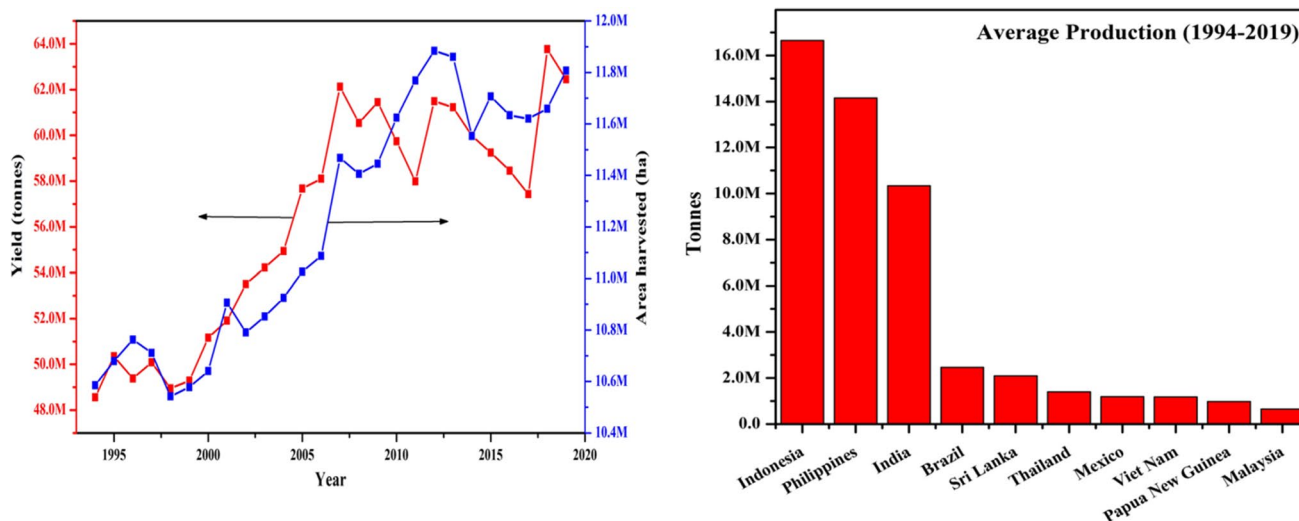


Fig. 1 World production of coconut during 1990 to 2019: (a) Plantation area and yield, (b) Top coconut producing countries of the world

Depending upon the geographical region and variant, the green coconut fruit normally weighs around 1 to 2 kg with liquid and solid albumen being about 33% of it [9]. The non-edible portion of green coconut has 33.2% cellulose, 29.1% hemicelluloses, and 25.4% lignin on dry weight basis [10]. The green tender coconut fruit (5 to 7 months old) is harvested for coconut water and flesh for consumption as such as beverage and food while the flesh of the ripe fruit is consumed either afresh or in the dried form in all coconut producing countries. After the edible components (coconut water and soft pulp) of the tender coconut fruits are devoured, the empty shells are thrown aside in most coconut-producing nations causing litter and environmental pollution. The open burning and improper disposal of the tender coconut shell debris lead to poor cleanliness, environmental damage, choked storm water drainage, and other related issues like mosquito breeding. Due to its typical composition and structure, the green coconut shell waste biomass can take up to 10 years to degrade in the environment. Due to high calorific value (HHV) (22 to 23 MJ/kg) dry husk, shell and skin are used as cheap fuel by poor people in most coconut producing countries [11–13].

The inner kernel (copra) obtained from the fully ripe coconut fruit is used for extracting coconut oil. The inner hard shell and the outer soft layer of dry husk and skin are produced as coconut waste. Use of coconut fibre and shell for making animal feed, door-mats, fibre boards, flexible-floor spreads, mattresses, ropes and other items and hard coconut shell for making eco-friendly cutlery etc. and activated carbon adsorbent has a long history. In the recent past attempts have also been made to produce briquettes, fuel additives for cleaner emissions, high surface area activated carbon (char) for dyes and metal sorption, thermal insulation, agglomerate blankets for soil protection, paper,

organic fertilizers, as in polymer foam mattresses, and in the cement–fibre composites using coconut husk and shell [10, 14]

The biochemical and thermal conversion of coconut derived waste biomasses into cleaner fuels and value added products have started receiving increasing attention in the recent past. Efforts have also been made to produce some value added chemicals and fuels such as formic and acetic acid from hydrothermal conversion of husk [15], bio-ethanol from coconut husk [10, 13] and green coconut hydro lysates [16], hydrogen through fermentation of coconut husk subjected to subcritical water and enzymatic hydrolysis [17] and treated with phosphoric acid [18], biodiesel through in situ transesterification of coconut waste [19]. The researchers have also shown renewed interest in the carbonization and pyrolysis of coconut wastes. Coconut shell has been used to prepare activated carbon with and without physico-chemical activation and used as high surface area adsorbent [20–24].

A summary of the recently published information on the pyrolysis and thermal degradation of coconut waste biomasses is given in Table 1. It is seen that the focus of these researches have been on improving the yields of gaseous and liquid products and producing activated char. Effects of heating rate, temperature, catalysts and presence of other degradable carbonaceous wastes have been studied using thermo-gravimetric analytical techniques, and fixed and fluidized bed pyrolyser. A few workers have also carried out kinetic and thermodynamic analyses of their thermo-gravimetric results using iso-conversional models and single-and multistep reaction models such as Coats-Redfern, multiple linear regression method, Flynn- Wall and Ozawa, Kissinger-Akahira-Sunose (KAS), Tang, Starink, Friedman, and Distributed Activation Energy Model (DAEM).

Table 1 Summary of the previous work using coconut biomass

References	Coconut biomass	Process details	Conclusion
[29]	Coconut shell	Captive sample technique; T=250-750°C; HR=13°C/min; Inert atmosphere	Volatile and char form through two parallel reaction; Active pyrolysis zone:360-700°C; For T>400°C, the devolatilization rate constant decreased with T; Deactivation model agreed well with experimental data
[30]	Coconut and Cashew nut shells	TG/DTG analysis; Mass<15mg; T=110-900°C; HR=5, 10, 20, 40, 50°C/min; Argon, 50mL/min	Pyrolysis profiles different than that for woody biomass; Profile exhibited two different peaks for hemicellulose and cellulose; At HR= 10 and 20°C/min, E _a varied from 130-174 and 180-216kJ/mol, for cashew and coconut shells, respectively
[22]	Coconut shell treated with H ₃ PO ₄ (Impregnation ratio-1, 1.5, and 2)	Carbonization; T=400, 450, 500°C; Time=10,20,30 min	Imp. Ratio= 1.345-2. Time=14.9-23.9 min, and T=394-416°C gave best results; RSM proved a good tool for getting optimized conditions
[31]	Carbonized coconut shell char	Carbonization; T=400, 600, 800, 1000°C; Time= 30, 60, 90, 120min; Activation at 900°C	High T carbonization gave high BET area, total volume, micro-pore volume and yield; Steam activation at proper carbonization T and time resulted in formation of high surface area activated carbon
[32]	Coconut shell, D _p = <0.15, 0.15-0.30, 0.30-0.60, 0.69-1.18, 1.18-1.80mm	Fixed-bed pyrolysis; Bed height=20,30cm;Dia=2.7cm; T=400-600°C; HR=20, 40, 60°C/min; Amount=15g	Highest liquid yield at 550°C; Yield varied from 22-31,38-44 and 30-33wt%, respectively for char liquid and gas; Effect of T and D _p was more pronounced than HR and residence time
[33]	Coconut shell	Pyrolysis; T = 400-800°C	Bio-oil and gas yields and acid content of bio-oil increased with increase in T; More acetic acid, phenols and nitrogenous compounds, less pentane and aldehyde; Suitable only for gasification; bio-oil composition changed with T; E _a =122.780kJ/mol
[34]	Coconut shell powder; D _p =0.1-1,4-8, 10-20mm	Pyrolysis; T=350,450,575,600°C; HR=2.5,5,10,15, 20°C/min	Maximum oil obtained at 575°C and 20°C/min an with 5 mm particles; Liquid products:50% water, rest aromatic phenolic acid, ketone, ether etc. compounds
[35]	Green tender coconut	Hollow elliptical briquette making machine and process including oxygen free heating chamber	Better fuel with superior characteristics, VM:17-20%, FC:65-73%, Ash:10.5%, Others:11-13%, CV:2800-3600kcal/kg than dried coconut pieces
[36]	Coconut shell; D _p = 1mm; Mass=15g	Pyrolysis reactor: steel tube(L= 14.5cm, Dj=3.7cm, D _o =4.1 cm); T=450- 600°C (step=25°C); HR=20°C/min	Maximum bio-oil yield of 49.5% at 575°C; Phenols and derivatives = 66.87%; Carbon range=C ₇ -C ₁₈ ; Emp. Formula= CH _{0.70} N _{0.06} O _{0.39} S _{0.14} CV of bio-char=23.68MJ/kg
[37]	Coconut shell	Pyrolysis; T=250-550°C	Pore size, total volume, and surface area increased with increase in T; Micro pore size 0.8-2.2nm, a good adsorbent for CO ₂ .

Table 1 (continued)

References	Coconut biomass	Process details	Conclusion
[38]	Coconut shell; $D_p=0.149$ mm	Pyrolysis; $T=40$ -995°C; HR = 10, 15, 20°C/min; N_2 , 20mL/min	Order-based and growth nucleation controlled; 4 parallel reactions; E_a increased in the order: water<hemicellulose<cellulose<lignin, nearly same for hemicellulose and cellulose (106.4 and 108.6 kJ/mol, respectively); Model-free methods are suitable for estimating E_a ; Hemi-cellulose and cellulose degrade 5-6 times faster than lignin; E_a for lignin ranged from 79.1-226.5kJ/mol.
[39]	Coconut copra and rice husk; $D_p=0.50$ mm	Catalytic pyrolysis, catalyst: Ni-Ce/Al ₂ O ₃ ; $T=30$ to 700°C; HR=10°C/min; $N_2=150$ mL/min	Under similar conditions coconut-rice husk ratio of 1:0.15 ratio gave the highest bio-oil yield; Catalyst was most effective in the middle phase of degradation and it reduced E_a from 79.28 to 53.10 kJ/mol
[40]	Coconut shell; $D_p=1.5, 3,$ and 4cm	Torrefaction; $T=250$ -350°C; Holding time =15, 30 and 45 min; Biomass particle size=1.5, 3 and 4cm	Optimum condition: $T=250$ °C, time =30min, size=1.5cm
[41]	Coconut husk	Pyrolysis; $T=400$ -1000°C	Increase in T caused decrease in char yield, VM, H and increase in ash, FC, C, aromaticity, pH, HHV, surface area and aromaticity; Char obtained in the range of 600-800°C good for metallurgical purposes and that obtained at 400-1000°C as soil conditioner, water treatment & carbon sequestration; Bio-char size: 212 microns; T and HR affected char characteristics.
[15]	Coconut husk	Hydrothermal conversion	Formic and acetic acid
[42]	Green coconut shell and orange peel	Pyrolysis $T=350$ °C; time =1hr	Characterization through proximate analysis, SEM, pH, bulk density, electrical conductivity, and particle size; Suitable for use as adsorbent & soil conditioner
[27]	Green coconut fibre	Catalytic thermal degradation, Co-ferrite catalyst	Full gasification, Activation energy= 82.29 kJ/mol, order of reaction = 0.122
[6]	Coconut husk + Fluidized bed reactor	Gasification; pulp and paper waste and Fluidized bed reactor	Metal constituents of waste water(Fe, Ni, Zn) improved gas yield; H_2 yield and HHV for gas from impregnated husk was 55.55vol %, and 5.24 MJ/Nm ³
[43]	Coconut husk, shell and skin	Thermo-gravimetric Heating rate= 5, 10, 20, 30°C/min	Kinetic analysis using Friedman and FOW models; HHV = 18.15, 18.64, 18.98 kJ/kg for husk shell and skin, respectively; Ash and moisture contents varied widely; Husk a better feedstock for pyrolysis
[44]	Coconut wastes	Carbonization	HHV of charred biomass was 42% higher than uncharred; Combustion of char caused less air pollution
[45]	Coconut shell	Modified pyrolyser: Dimensions: (2.4x1.2x1.2) m	Char yield increased from 23 to 28 %; Carbon content increased to 83.63%; Pore volume 0.7336 cc/g Surface area= 12.716 m ² /g
[28]	Coconut biomass	Pyrolysis; Fixed bed; $T=400$ -800°C; Heating rate=10°C/min Argon flow= 100mL/min	Char yield decreased from 33.6 to 28.6% on increasing T from 400 to 600°C Bio-oil a complex mixture with maximum yield at (48.7%) at 600°C;
[46]	Coconut husk(lignin immobilized)	Bio-adsorbent for metals	A good adsorbent for divalent ions of Cd, Cu, and Pb

Table 1 (continued)

References	Coconut biomass	Process details	Conclusion
[47]	Coconut shell	Fixed bed reactor, Micro-wave (MW) reactor; ore-shell catalyst: ZSM-5 on SiO ₂ /Al ₂ O ₃ , ZSM-5@SBA-15	Core shell catalyst increased bio-oil yield by 40% and hydrocarbon content by twice in both reactors; MW reactor controlled bio-oil composition; More phenols in fixed bed than MW reactor
[48]	Coconut fibre	Thermogravimetric analysis using four heating rates (5–20 °C/min) in nitrogen atmosphere.	The apparent activation energy (94.5–210.8 kJ/mol) was determined using five isoconversional methods and the global activation energy was found as 129.8 kJ/mol
[49]	Coconut shell	Pyrolysis; T=600, 800, 1000, 1150°C; Time=1hr	Increase in temperature caused significant change in VM, FC, Carbon content and functional groups; Electrical properties increased in char obtained at T from 600 to 1150°C
[50]	Catole coconut (<i>Syagrus cearensis</i>)	Thermogravimetric analysis; T=25 to 800°C HR=10, 20 and 30°C/min	Average activation energy estimated was in the range of 124.2–133.5 kJ/mol

The coconut and other ligno-cellulosic biomasses are a complex matrix of tiny fibres of cellulose interspersed in between chains of hemi-cellulose and lignin. The outermost layer is invariably rich in lignin that acts a strong barrier for the inner core of carbohydrates, hemicellulose and cellulose [25]. Hence efforts have also been made to improve the fuel value and degradability of lingo-cellulosic biomasses through pre-treatment [26]. The pre-treatment methods using mechanical disruption, micro-wave irradiation, steam explosion, hydrothermal treatment, extraction with hot water, and chemical treatment with acids and alkali or enzymes have been used to disrupt the ligno-cellulosic matrix and improve the availability of biomass components for bio-chemical and thermal conversion [27, 28]. Out of these, the extraction with hot water is the cheapest and simplest pre-treatment method.

From Table 1, it is seen that most of the available reported work on carbonization and pyrolysis of coconut biomass wastes are focussed on coconut shell and husk. In spite of the abundant availability of tender coconut shells as waste biomass in India and other coconut producing countries little reported information is available on its thermal degradation behaviour, though some efforts have been made for its torrefaction and briquetting. In the present work effect of pre-treatment with hot water on the thermo-physical properties and thermal degradation behaviour of green tender coconut biomass has been investigated for the first time.

2 Materials and method

2.1 Biomass collection and sample preparation

The tender coconut shells were collected from the vendors selling green tender coconut within the University campus for using coconut water as a beverage. About 2 kg of waste tender coconut shells were cut manually into small pieces using hand sickle and were washed with water and sun dried for about 48 hours under atmospheric conditions. The dry sample was further dried in a Tray Drier (NSW-148, New Delhi, India) maintained at the constant temperature of 60°C for 24 hours to remove the remaining surface moisture, if any. The dried biomass then was subjected to grinding in a Wiley Mill (Model no.2, Arthur H. Thomas Co, Philadelphia, USA). The coarse powder thus obtained was sieved using 18- mesh screen (1mm) to obtain uniform size powder. The undersize fraction of the sample was collected and stored in tightly sealed polythene bags for characterization and thermal degradation studies after further treatment.

2.2 Pre-treatment with hot water

Pre-treatment of biomass with hot water has been done some workers for a few seconds to several hours [51]. Besides removing the water soluble inorganic and organic constituents it leads to hemi-cellulose depolymerisation and lignin transformation and results in opening of the pores for accessibility of cellulose. Eco-friendly nature and low cost are its main advantages. Hence the coconut biomass powder was pre-treated with hot distilled water.

Approximately 5g of the biomass powder was mixed with distilled water in the ratio of 1:10 and then heated to boiling on a hot plate for about 2 hours. The resultant mixture was cooled and filtered. The filtrate was collected separately for further analysis. The biomass residue was washed 2–3 times with distilled water. The washed sample was then dried in an air oven (Universal Oven Model, NSW-143(OUA-2) at 60°C for 8h. The dried sample thus obtained was stored in an airtight polythene bag for further analysis. The schematic sequence of steps used for sample preparation is shown in Fig. 2.

The water extract (liquor) was collected and analysed for its COD, BOD and reducible sugar contents. The COD and BOD values of the water extract were determined using ASTM D-1252 and ASTM D-2339 [52] protocols and the reducing sugar content was determined using ASTM protocol for DNS method.

2.3 Physiochemical characterization

The ASTM protocols, E-871, E-872 and E1755 [52–54] were used for estimating moisture content (MC), volatile matter (VM) and ash content (AC) while the fixed carbon (FC) was calculated by difference (% FC = 100 - % (MC+VM+AC)). All these parameters were determined in triplicate on dry basis and the average values are reported. The ultimate analysis (C, H, N, and S contents) of the powder biomass was carried out using an elemental analyzer (Euro EA 3000, Elemental Analyzer, Lombardi a Milano, Italy). The oxygen content was calculated by the difference

(% O = 100 - % (C+H+N+S)). The higher heating value (MJ/kg) was estimated as per ASTM D240 protocol using a bomb calorimeter (RSB 3, Rajdhani Scientific Instruments Co. New Delhi, India). The energy density ratio and energy yield of the treated samples were calculated from the thermo-chemical data using following equations:

$$\text{Energy density ratio (EDR)} = \frac{HHV_{ULS}}{HHV_{TLS}} \quad (1)$$

$$\text{Energy yield (EY)} = SY \times EDR \quad (2)$$

where, HHV_{ULS} and HHV_{TLS} represent the higher heating values of untreated and treated green coconut husk. The ultimate analysis data were used to calculate the CHO index to explore the oxidation state of the carbon in biomass material as suggested by Mann et al [55]:

$$\text{CHO index} = \frac{2[O] - [H]}{[C]} \quad (3)$$

Fuel properties such as fuel ratio (FR), combustibility index (CI), and volatile ignitability (VI) of untreated and treated green coconut biomass samples were evaluated using following equations Conag et al. [56]:

$$\text{Fuel ratio (FR)} = \frac{FC}{VM} \quad (4)$$

$$\text{Combustibility index (CI, MJ/kg)} = \frac{HHV}{FR} \times (115 - Ash) \times \frac{1}{105} \quad (5)$$

$$\text{Volatile ignitability (VI, MJ/kg)} = \frac{[HHV - 0.338FC]}{[VM + MC]} \times 100 \quad (6)$$

2.4 The TGA/DTG analysis

The TG/DTG analyses of untreated and treated coconut biomass powder samples were carried out using a TGA/DTA analyzer (STA 8000 & 8500 Perkin Elmer Ltd;

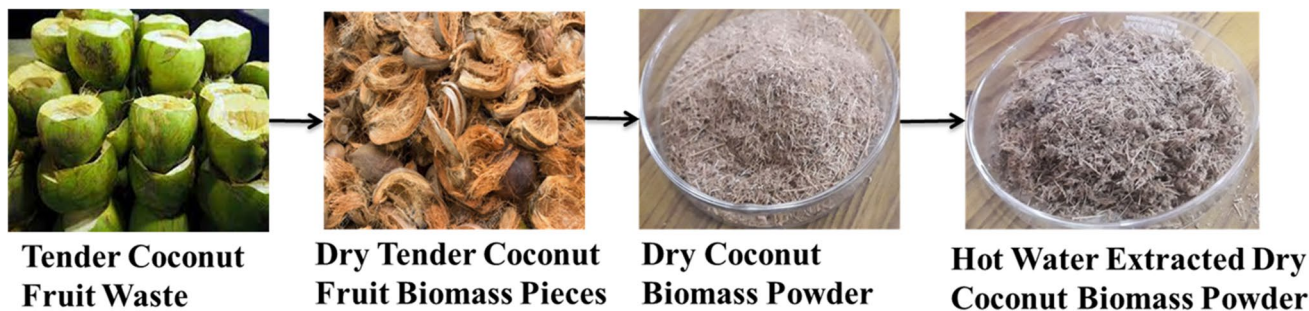
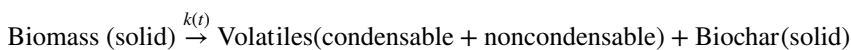


Fig. 2 The schematic sequence of steps used for sample preparation

having a precision of temperature: ± 0.1 K, DSC sensitivity: ± 0.1 mW and microbalance sensitivity: ± 0.1 μ g) in order to obtain the mass loss of biomass sample with respect to time/temperature throughout the pyrolysis process. About 5.5 ± 1.0 mg of biomass sample was taken in a TG/DTA crucible to carry out its thermal degradation from ambient temperature up to 1000°C at three different heating rates of 10, 20 and 30°C/min. All pyrolysis experiments were carried out in an inert atmosphere of N₂ gas flowing at the rate of 100 mL/min. The TGA data obtained were used for estimating the kinetic and thermodynamic parameters for treated and untreated biomass. The DTG data were obtained through the first order differentiation of the TGA data. Both the TGA and DTG curves for each sample were plotted by using Origin Pro software.

2.5 Kinetic analysis and thermodynamic parameters

The overall reaction that depicts the thermal conversion of biomass during pyrolysis is given by:



For this global reaction the rate of change in fractional conversion α , is expressed as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{7}$$

where $k(T)$ is the temperature dependent reaction rate constant and $f(\alpha)$ is a function of temperature. The fractional conversion is expressed in terms of initial mass m_0 , final mass residual mass m_f , and mass m_t at any time t is given by:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \tag{8}$$

The rate constant $k(T)$ is given by the Arrhenius equation as:

$$k(T) = A \exp\left(\frac{-E\alpha}{RT}\right) \tag{9}$$

Where A is the pre-exponential factor (s^{-1}), E_α is the energy of activation (kJ/mol), R is the universal gas constant (8.314 J/mol.K) and T is temperature (K).

Equations (7) and (8) give:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E\alpha}{RT}\right) f(\alpha) \tag{10}$$

The term β ($^\circ\text{C}/\text{min}$) known as the heating rate is defined as:

$$\beta = \frac{dT}{dt} = \frac{dT}{d\alpha} \cdot \frac{d\alpha}{dt} \tag{11}$$

Combining Equations (10) and Eq. (11) gives:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E\alpha}{RT}\right) f(\alpha) \tag{12}$$

Integrating Eq. (12) within the limits $\alpha = 0$ to α and $T = 0$ to T gives:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E\alpha}{RT}\right) dT \tag{13}$$

Equation (13) has been solved numerically using model-free and reaction fitting models based on appropriate approximations. The relations listed in Table 2 developed using model-free kinetic methods have been used to evaluate the values of A and E_α .

The values of E_α estimated using above methods have been used to evaluate pre-exponential factor (A), changes in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) at various conversions using following relations:

$$A = \beta E_\alpha \exp\left(\frac{E_\alpha}{RT_m}\right) / (RT_m^2) \tag{14}$$

$$\Delta H = E_\alpha - RT \tag{15}$$

$$\Delta G = E_\alpha + RT_m \ln\left(\frac{K_B T_m}{hA}\right) \tag{16}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \tag{17}$$

where, K_B is the Boltzmann constant (1.381×10^{-23} J/K), h is the Planck's constant (6.626×10^{-34} J-s) and T_m is DTG peak temperature (K).

2.6 Prediction of reaction mechanism: the z-master plot

The experimental and theoretical z-master plots for treated and untreated green coconut shell biomasses were prepared using Criado's method [61] to elucidate the prevailing reaction mechanism governing the pyrolysis process. These do not depend upon the values of energy of activation. The mathematical expressions for theoretical and experimental curves are written as:

Table 2 Iso-conversional kinetic models for calculation of activation energy

Reference	Equation	Comments	Advantages & disadvantages
Flynn Wall Ozawa (FWO) method [57]	$\log(\beta) = \log\left(\frac{AE_\alpha}{Rg(\alpha)}\right) - 2.315 - 0.457\frac{E_\alpha}{RT}$	Uses Doyel approximation, (Doyel, 1965), $P(x) = -2.315 + 0.457x$, Plot of $\log(\beta)$ vs. $(1/T)$ is linear and its slope gives E_α	A linear method; Utilizes over simplified mathematical approximation for temperature integral; Significant error is observed in E_α ; Assumes constant E_α from the beginning till the end of the reaction
Kissinger-Akahira-Sunose (KAS) method [58]	$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AE_\alpha}{Rg(\alpha)}\right) - \frac{E_\alpha}{RT}$	Uses mathematical assumption, $P(x) = x^2e^{-x}$ for $\alpha = 0.05$ to 0.95 , slope of plot between $\ln\left(\frac{\beta}{T^2}\right)$ vs. $1/T$ gives E_α	A linear method; Utilizes over simplified mathematical approximation for temperature integral; Significant error may be observed in E_α ; Assumes constant E_α from the beginning till the end of the reaction
Tang method [59]	$\ln\left(\frac{\beta}{T^{1.894661}}\right) = C_1 - 1.001450\frac{E_\alpha}{RT}$	For conversion (α) 0.05 – 0.95 the slope of plot between $\ln\left(\frac{\beta}{T^{1.894661}}\right)$ and $1/T$ gives value of E_α	A linear method; derived from KAS method and is more accurate
Starink method [60]	$\ln\left(\frac{\beta}{T^{1.92}}\right) = \text{Constant} - 1.0008\left(\frac{E_\alpha}{RT}\right)$	The slope of plot between $\ln\left(\frac{\beta}{T^{1.92}}\right)$ and $1/T$ gives the value of E_α at each conversion (α).	A linear relation; derived from KAS method and is more accurate

$$\frac{Z(\alpha)}{Z(0.5)} = \frac{f(\alpha) \times g(\alpha)}{f(0.5) \times g(0.5)} \quad (18)$$

$$\frac{Z(\alpha)}{Z(0.5)} = \left(\frac{T_\alpha}{T_{0.5}}\right)^2 \times \frac{(d\alpha/dT)_\alpha}{(d\alpha/dT)_{0.5}} \quad (19)$$

Here $f(\alpha)$ and $g(\alpha)$ are the values of functions at any given conversion, $f(0.5)$ and $g(0.5)$ are their values at 50% conversion ($\alpha = 0.5$), T_α and $T_{0.5}$ are the temperatures at $\alpha = \alpha$ and $\alpha = 0.5$, respectively. The theoretical Z-master curves for different reaction mechanisms were plotted using previously developed models (Supplementary information Table S1). The plausible reaction mechanism controlling the pyrolysis at different values of conversion (α) was inferred by comparing the theoretical and experimental plots.

3 Results and discussions

3.1 Physiochemical characteristics

The results of the proximate and ultimate analyses and calorific value together with the available published data on coconut biomass are given in Table 3. The moisture (MC), volatile matter (VM), ash (AC) and fixed carbon (FC) values for untreated green tender coconut biomass were found to be 5.8, 65.86, 3.34, and 25%, respectively and the corresponding values for the treated tender coconut shell biomass were 5.37, 77.84, 0.89, and 15.9%, respectively. The improved VM content and low ash content in the treated

tender coconut biomass indicated improvement in its fuel characteristics. The moisture content of less than 10% is generally considered as the acceptable limit for pyrolysis [62]. The higher VM/FC ratio and low ash content of the treated coconut biomass compared to the untreated biomass indicate higher energy availability, reduced slag formation and agglomeration. During combustion a fuel having the fuel ratio >2 can trigger ignition and flammability issues. The fuel ratios of untreated and treated tender coconut biomass were found to be 0.38 and 0.20, respectively. The ignitability index is also used to predict the performance of a biomass in a furnace or boiler. It was calculated to be 14.12 and 19.09 MJ/kg for the untreated and treated biomasses, respectively. When the ignitability index is less than 35, the fuel cannot be used effectively in the boiler. The combustibility index (CI) indicates the fire and combustion activity of a material. For the tender coconut biomass, it increased from 51.96 to 115.52 MJ/kg after pre-treatment with hot water indicating an improvement in the thermo-physical behavior of the treated tender coconut biomass.

A comparison of carbon, hydrogen, oxygen, nitrogen and sulfur contents of untreated and treated tender coconut biomass indicated an increase in carbon and decrease in hydrogen, oxygen, and nitrogen contents. This can be attributed to the removal of water soluble inorganic and organic constituents from the tender coconut biomass.

The CHO index can vary between -4 and $+4$. Higher CHO index values can be attributed to more oxidized compounds, while lower CHO index values are due to reduced molecules [55]. The CHO indices of the untreated and the treated green coconut biomass were found to be 0.41 and

Table 3 Physiochemical properties of untreated and treated tender coconut biomass

Characteristics parameter	Untreated tender coconut biomass (Present work)	Treated tender coconut biomass (Present work)	Coconut shell Tsamba et al. [30]	Coconut shell Wei et al.[47]	Coconut fibre Cristina et al. [48]
Proximate analysis					
Moisture	5.80	5.37	-	4.36	-
Volatile matter	65.86	77.84	74.9	72.91	79.61±2.09
Fixed carbon	25.0	15.9	24.4	18.75	2.90±0.36
Ash	3.34	0.89	0.7	3.98	17.50±2.43
VM/FC ratio	2.63	4.89	3.06	3.88	27.45
Ultimate analysis					
Carbon	41.23	46.21	53.9	47.43	46.54±0.21
Oxygen	52.74	46.96	39.44	37.2	43.13±0.01
Hydrogen	5.18	4.92	5.7	5.12	6.88±0.29
Nitrogen	0.85	1.91	0.1	0.48	0.36±0.02
Sulphur	0.00	0.00	0.02	-	0.19±0.07
Higher heating value (MJ/kg)	18.57	21.26	20.52	-	17.70±0.07
Energy density ratio (EDR)	-	1.14	-	-	-
Energy yield (EY, %)	-	95.75	-	-	-
Fuel properties					
Fuel ratio (FR)	0.38	0.20	0.33	0.28	0.04
Combustibility index (CI, MJ/kg)	51.96	115.52	67.68	-	410.89
Volatile ignitability (VI, MJ/kg)	14.12	19.09	-	-	-
H/C ratio	1.51	1.28	1.27	1.30	1.77
O/C ratio	0.96	0.76	0.55	0.59	0.69
CHO index	0.41	0.24	-0.17	-0.12	-0.39

0.24, respectively. The observed decrease can be attributed to the reduction in the oxygenated compounds from the biomass. The calorific value (HHV) for untreated green coconut tender biomass was found to be 18.57 MJ/kg where as for the treated coconut tender biomass it was found to be 21.26 MJ/kg. The higher HHV of the treated husk compared to that for untreated husk can be attributed to the increase in carbon content and reduction in oxygen content.

3.2 van Krevelen diagram

The van Krevelen diagram (H/C versus O/C plot) helps in determining the fuel efficiency of a carbonaceous fuel and helps in comparing biomasses with different types of coal. Figure 3 shows H/C versus O/C plots for different types of coal such as peat, lignite, bituminous and anthracite, coconut waste biomass and present work. Higher H/C ratio depicts higher energy content while the higher O/C suggests lower combustion efficiency [62]. The (H/C) and (O/C) ratios for the untreated biomass were found to 1.51 and 0.9, respectively and for the treated biomass these were found to be 1.28 and 0.76, respectively. Extraction with hot water has resulted in reduction in these ratios indicating a better fuel

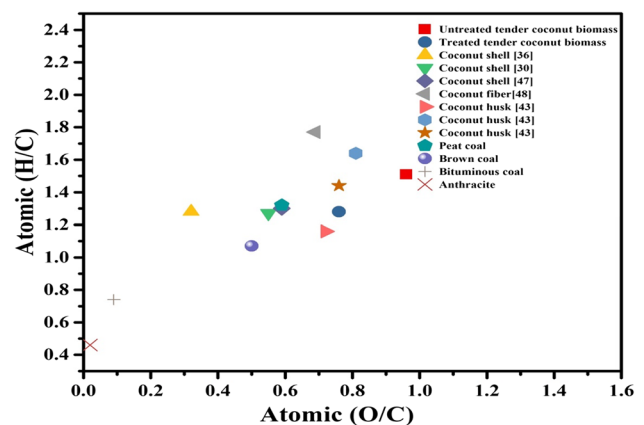


Fig. 3 van Krevelen plot of untreated and treated tender green coconut biomass with coal and other coconut biomasses

efficacy for pre-treated biomass. From Fig. 3, it is seen that treatment has brought green coconut closer to peat coal.

3.3 TGA/DTG analysis

Figure 4a and b show TG (residual biomass wt%)-temperature and DTG (residual biomass wt%/min)-temperature

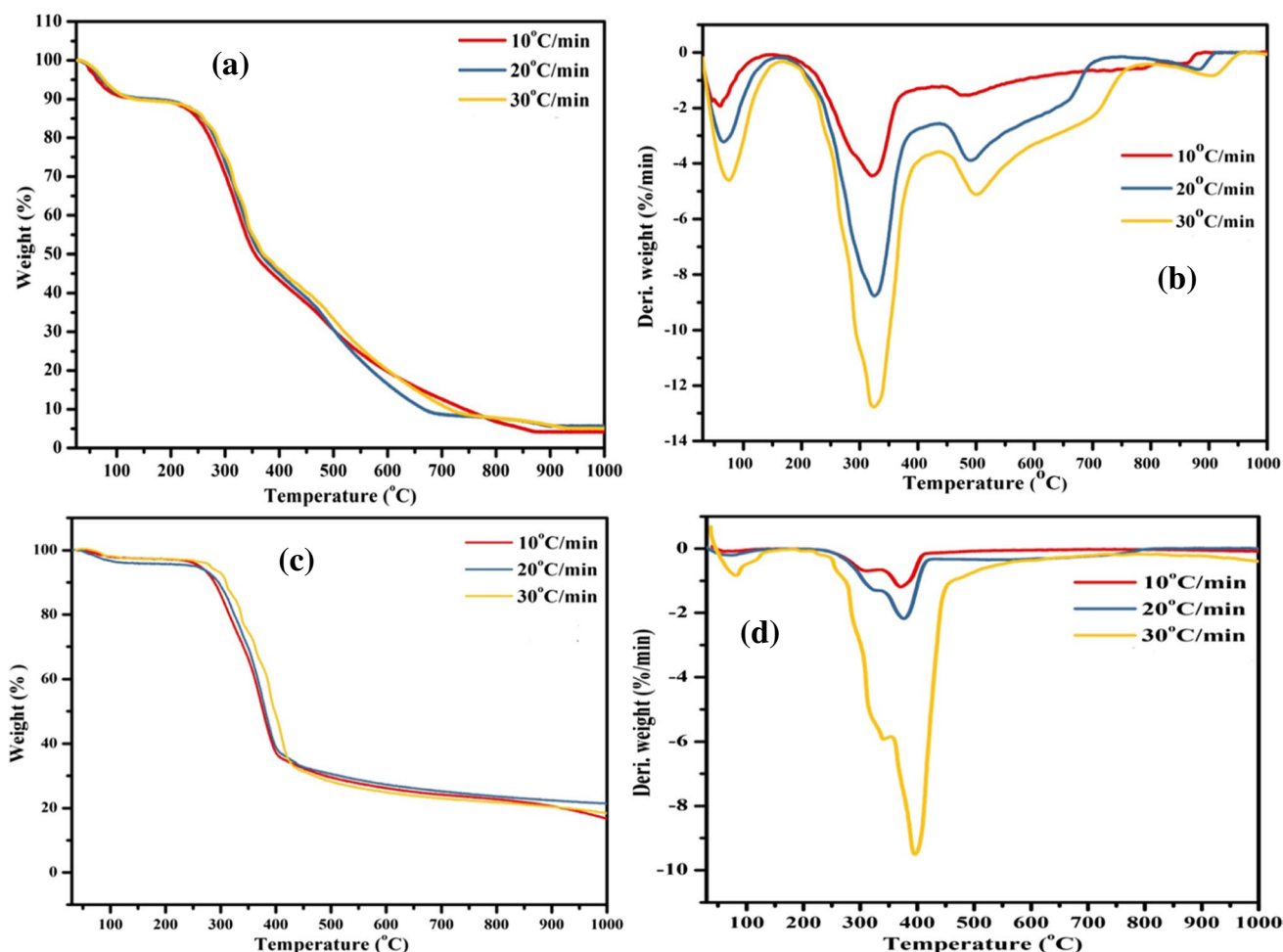


Fig. 4 TGA and DTG profiles for untreated and treated tender coconut biomass: **(a)** TG profile of untreated tender coconut biomass, **(b)** DTG profile of untreated tender coconut biomass, **(c)** TG profile of

treated tender coconut biomass, **(d)** DTG profile of treated tender coconut biomass

plots for un-treated tender coconut waste biomass and Fig. 4c and d show the corresponding plots for the hot water treated tender coconut biomass. Three major stages of pyrolysis are discernible from plots shown in Fig. 4a and 4c. In Stage I (<120–125°C) slow decrease in residual wt% is observed due to dehydration and removal of some easily volatile compounds. In Stage II (120–675°C) the reduction in residual wt% is much faster due to the degradation of hemi-cellulose, cellulose, higher molecular weight organic compounds and lignin with evolution of volatiles. In the initial part of this stage (120–400°C) most of the hemi-cellulose and cellulose together with other organic constituents and some lignin get degraded. In its latter part (400 to 675°C), the lignin and remaining hemi-celluloses and cellulose get degraded and the evolution of volatile matter gradually slows down causing reduction

in residual wt% change. In Stage III (>675°C) the rate of degradation becomes very slow and the residual wt% tends to a nearly constant value ($\approx 5\text{--}8\%$). The TG profiles for all three heating rates more or less overlap each other with slight deviation at higher temperatures. In case of the untreated tender coconut biomass, the TG profiles at all heating rates (Fig. 4a) exhibit a wavy nature and the three stages of pyrolysis are not as sharply delineated as in the case of treated green coconut biomass (Fig. 4c). This typical behavior can be attributed to the presence of organic compounds of varying molecular weight in the untreated biomass that degrades at different rates. The observed smoothing of the TG profile and clear delineation of the three stages of pyrolysis in case of treated biomass can be attributed to its relatively simpler chemical composition. The DTG-temperature profiles of untreated coconut

biomass at all heating rates as depicted in Fig. 4b exhibit four distinct peaks of varying height and peak area. The first peak lies between the ambient to 125°C, the second between 125 and 400°C, the third between 400 and 700°C and the fourth between 800 and 950°C. The last two peaks are relatively broader and may be attributed to the degradation of the residual lignin and some highly stable secondary organic compounds. The peak area and the peak temperature increase with increasing heating rate.

Figure 4d shows the DTG-temperature plots for the treated coconut biomass. It is seen that there are only two peaks- milder peaks in the temperature range of ambient to 125°C and sharper well defined peaks between 225 and 525°C. The third and fourth peaks observed in case of untreated biomass have either disappeared or flattened. The areas of the second set of peaks have reduced substantially compared to the untreated coconut biomass but the peak temperatures have shifted towards higher temperature range (250 to 450°C). Further the second set of peaks at all heating rates exhibit a shoulder prior to the main peak corresponding to the degradation of hemi-cellulose prior to cellulose. It is interesting to note that such shoulders are not clearly discernible in case of untreated coconut biomass. This can be attributed to the evolution of several other volatile organic compounds from the untreated biomass together with degradation of hemi-cellulose and cellulose. The observed changes in the TG and DTG profiles of the two coconut biomasses can be attributed to the extraction of soluble

inorganic and organic constituents (minerals, sugars, organic compounds, etc.) from the tender coconut biomass and to the disruption of the cellulose-hemicellulose-lignin matrix on treatment with hot water.

3.4 Effect of heating rate

The pyrolysis of treated and un-treated tender coconut biomass was carried out at three heating rates of 10, 20 and 30°C/min. The values of initial, final and peak temperatures and percent weight loss per degree C (%wt/°C) and total weight loss in the three stages of pyrolysis are listed in Table 4.

For un-treated biomass the peak temperatures are on an average 50 to 65°C lower and peak areas are larger than those for the treated biomass. This can be attributed to the evolution of volatile organic compounds together with the degradation of hemi-cellulose, cellulose and lignin. The treated biomass is almost devoid of such volatile compounds and the %weight reduction is primarily due to degradation of hemi-cellulose, cellulose and lignin. The observed residual weight for untreated tender coconut biomass (<10%) is nearly half of the residual weight (around 20 to 22%) for the treated biomass. In case of untreated biomass, the net amount of hemi-cellulose, cellulose and lignin is low resulting in low yield of char whereas in the case of treated biomass it is large and yield a higher amount of char.

Table 4 TG and DTG analysis parameters for untreated and treated tender coconut biomass

Samples	Untreated tender coconut biomass			Treated tender coconut biomass		
	Heating rates (°C/min)	10	20	30	10	20
Stage 1						
Initial temp. (°C)	26.81	27.00	26.76	40.16	27.16	37.00
Final temp. (°C)	200.08	200.14	200.12	200.19	200.03	200.46
Peak temp. (°C)	59.41	67.12	74.68	61.01	73.87	81.65
-DTG max (%/°C)	1.92	3.21	4.60	0.08	0.20	0.83
Weight loss (%)	10.77	10.48	10.90	2.72	4.23	2.71
Stage 2						
Initial temp. (°C)	201.12	201.04	201.28	201.02	201.16	201.15
Final temp. (°C)	700.00	700.25	700.33	700.14	700.05	700.01
Peak temp. (°C)	320.70	325.52	323.99	370.97	376.23	395.68
-DTG max (%/°C)	4.44	8.76	12.76	1.18	2.17	9.50
Weight loss (%)	76.59	80.92	78.08	72.97	88.29	74.25
Stage 3						
Initial temp. (°C)	701.03	701.24	701.37	701.04	701.03	701.01
Final temp. (°C)	999.89	999.89	999.73	999.86	999.77	999.55
Peak temp. (°C)	707.92	701.24	701.37	999.11	701.03	999.55
-DTG max (%/°C)	0.66	0.35	2.27	0.08	0.23	0.39
Weight loss (%)	8.40	2.70	6.03	7.58	4.36	4.57

3.5 Kinetic analysis and thermodynamic parameters

The thermal degradation results (TG temperature profiles Fig. 4a and c) of the untreated and treated tender coconut biomass were used to estimate the activation energies from room temperature up to 1000°C at the three heating rates of 10, 20 and 30°C/min. The multiple heating rate based iso-conversional models of FWO, KAS, Tang and Starink were used to evaluate the kinetic parameters- energy of activation E_α and pre-exponential factor A, in the fractional conversion (α) range of 0.1 to 0.9 using equations listed in Table 2 through regression analysis [63]. The calculated values of E_α and A are listed in Tables 5 through 8. The R^2 values have varied from 0.95 to 1.00 for the untreated biomass and from 0.996 to 0.999 for the treated biomass. The R^2 was found to be low at 0.8 and 0.9 due to the scattered data of TGA at the end of pyrolysis.

The variation of average values of E_α with conversion evaluated for four kinetic models are shown in Fig. 5a to 5d for treated and un-treated tender coconut biomasses. All plots show a similar pattern of variation with conversion. In case of untreated tender coconut biomass increase in conversion from 0.1 to 0.3, the values of E_α estimated using four models decreased from around 400 to 300kJ/mol. This may be attributed to the improved heat transfer by the evolved vapors. As the conversion increased from 0.3 to 0.5, the E_α values also increased to around 525kJ/mol. For $\alpha = 0.5$ to 0.7, the E_α again decreased but less steeply and then increased up to $\alpha = 0.8$ and then again decreased up to 0.9. This fluctuating behavior may be attributed to the frequently changing evolution rate of volatile compounds till the end of thermal degradation process and the corresponding variation in the heat and mass transfer rates. The fluctuation in the values of E_α with α is also observed in the case of the treated coconut biomass for all four kinetic models but the extent of variation is much milder and the trend is also slightly different due to lower rates of involved degradation reactions up to $\alpha = 0.2$, the E_α remains constant, between $\alpha = 0.2$ to 0.5, it fluctuates around a mean value of 150 to 200 kJ/mol and then decreases to a low value of around 25 kJ/mol up to $\alpha = 0.8$ and then increases to around 75kJ/mol. The smaller observed variation below $\alpha < 0.5$ can be attributed to less copious reactions due to the removal of easily degradable constituents by hot water. The steeper decrease between $\alpha = 0.5$ to 0.8 due to the higher rates of reactions involving large amount of reactive species formed during pyrolysis. The observed increase after $\alpha = 0.8$ may be due to increase in the char formation.

From Table 1, it is seen that the reported E_α values for coconut biomasses have varied from 79.1 to 226.5 kJ/mol for coconut shell [30, 33, 38], 124.4 to 133.5kJ/mol for Catole coconut [64], 94.5 to 210kJ/mol for coconut fiber [48], and around 229.87 to 232.17kJ/mol for coconut husk waste [65]. The estimated E_α values for the treated tender coconut biomass are nearly similar to the reported values for various coconut derived biomasses.

From Fig. 5 it can be seen that the values for the untreated tender coconut biomass are nearly three times larger. This large difference can be attributed to the evolution of large amount of covalently bonded and substituted aliphatic and aromatic molecules. Evolution of these molecules affects the inter- and intra-particle heat and mass transfer rates [66] and delay the devolatilization of biomass. Further, these molecules require high energy for disrupting their bonds to produce active species for further reaction. The resultant effect is the requirement of substantially high energy for thermal degradation in comparison to the treated tender coconut biomass that is devoid of such volatile molecules.

It was also noticed that each model gave different activation energy; this alteration may have arisen due to the adoption of different types of approximation during the mathematical solution of models. Nearly similar values of E_α obtained using KAS, Starink and Tang models indicate the consistency of these kinetic models and can be attributed to nearly similar mathematical approximations used for model development.

The pre-exponential factor (A) is a function of the peak temperature, activation energy and heating rate and is a measure of the frequency of collision between the reacting molecules. Lower values of the pre-exponential factor ($< 10^9 \text{ min}^{-1}$) indicate a higher surface reaction rate or the presence of highly branched compounds, the higher values of A ($> 10^9 \text{ min}^{-1}$), indicate the presence of linear compounds. A variety of parallel reactions occur during biomass pyrolysis and so A is also a key indicator that reflects the complexity of the surface structure of the biomass sample and reaction during the pyrolysis process. The values of A varied with heating rate for both treated and un-treated green coconut biomasses. For the untreated biomass its values were found to vary from 1.99×10^{26} to $1.06 \times 10^{45} \text{ min}^{-1}$ for FWO, 2.43×10^{26} – $3.08 \times 10^{46} \text{ min}^{-1}$ for KAS, 1.45×10^{27} to $2.96 \times 10^{46} \text{ min}^{-1}$ for Tang and 2.63×10^{26} – $3.1 \times 10^{46} \text{ min}^{-1}$ for Starink models. For the treated coconut biomass, the values of A were found to be 0.064967 to $8.34 \times 10^{15} \text{ min}^{-1}$ for FWO, 0.003823 to $4.57 \times 10^{15} \text{ min}^{-1}$ for KAS, 0.004529 to $4.6 \times 10^{15} \text{ min}^{-1}$ for Tang, and 0.004357 to $4.62 \times 10^{15} \text{ min}^{-1}$ for Starink models.

There is an order of magnitude difference between the A values for the untreated and treated green coconut biomasses

Table 5 Estimated kinetic factors and thermodynamic parameters using FWO for conversion (α) range 0.1 to 0.9 at different heating rates

Untreated tender coconut biomass		Treated tender coconut biomass											
Heating rate (°C/min)	Conv.	$E\alpha$ (kJ/mol)	A (min ⁻¹)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol.K)	R ²	$E\alpha$ (kJ/mol)	A (min ⁻¹)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (kJ/mol.K)	R ²
10	0.1	410.11	2.77E+34	405.49	167.03	401.55	0.992	123.71	64429184	119.00	188.89	-108.5	0.992
	0.2	351.76	1.75E+29	346.96	167.79	301.7	0.999	124.25	71575909	119.38	188.87	-107.9	0.988
	0.3	325.45	7.84E+26	320.48	168.17	256.48	0.974	198.46	1.19E+14	193.35	186.36	10.845	0.998
	0.4	415.33	8.06E+34	410.19	166.97	409.56	0.988	152.95	1.87E+10	147.76	187.76	-62.1	0.978
	0.5	529.16	1.06E+45	523.64	165.77	602.62	1	220.64	8.34E+15	215.29	185.79	45.797	0.996
	0.6	384.86	1.56E+32	378.8	167.34	356.07	0.959	151.57	1.43E+10	146.18	187.81	-64.63	0.978
	0.7	330.33	2.14E+27	323.82	168.10	262.22	0.977	71.07	1992.468	65.632	191.86	-196	0.658
	0.8	437.44	7.48E+36	430.34	166.71	443.92	0.971	22.02	0.064967	16.472	198.14	-282	0.274
	0.9	318.79	1.99E+26	311.06	168.27	379.27	0.994	64.20	498.9996	57.457	192.41	-95.56	0.981
	AVG.	389.25	1.18E+44	383.42	167.35	379.27		125.43	9.4E+14	120.06	189.76	-95.56	
20	SD	64.06	3.33E+44	64.26	0.78	100.45		60.77	2.61E+15	61.01	3.62	93.42	
	MD	52.23	2.09E+44	52.44	0.65	75.68		49.31	1.64E+15	49.41	2.91	69.36	
	S ²	4617.97	-	4645.88	0.68	11351.52		4155.13	-	4187.91	14.79	9818.48	
	0.1	410.11	1.39E+34	405.45	168.51	395.79	0.992	123.71	52571964	118.86	190.57	-110.4	0.992
	0.2	351.76	9.69E+28	346.91	169.27	296.73	0.999	124.25	58355759	119.23	190.54	-109.8	0.988
	0.3	325.45	4.54E+26	320.44	169.66	251.86	0.974	198.46	8.69E+13	193.26	188.02	8.0791	0.998
	0.4	415.33	4.03E+34	410.15	168.44	403.74	0.988	152.96	1.46E+10	147.62	189.42	-64.37	0.978
	0.5	529.16	4.39E+44	523.6	167.24	595.25	1	220.65	5.88E+15	215.2	187.44	42.742	0.996
	0.6	384.86	8.2E+31	378.75	168.82	350.66	0.959	151.57	1.12E+10	146.02	189.47	-66.91	0.978
	0.7	330.33	1.23E+27	323.75	169.58	257.51	0.977	71.08	1760.523	65.258	193.56	-197.6	0.658
30	0.8	437.44	3.61E+36	430.28	168.19	437.79	0.971	22.03	0.061824	15.472	199.89	-284	0.274
	0.9	318.79	1.17E+26	310.94	169.76	373.67	0.994	64.20	445.5161	56.862	194.11	-97.78	0.981
	AVG.	389.25	4.88E+43	383.36	168.83	373.67		125.43	6.63E+14	119.75	191.45	-97.78	
	SD	64.06	1.37E+44	64.27	0.78	99.65		60.77	1.84E+15	61.26	3.65	93.07	
	MD	52.23	8.67E+43	52.45	52.45	75.09		49.31	1.15E+15	49.57	2.93	69.03	
	S ²	4617.97	-	4647.65	0.68	11172.82		4155.13	-	4222.56	15.03	9745.92	
	0.1	410.11	1.73E+34	405.44	168.04	397.56	0.992	123.71	25452484	118.8	196.77	-116.6	0.992
	0.2	351.76	1.17E+29	346.89	168.8	298.23	0.999	124.26	28170626	119.17	196.74	-116	0.988
	0.3	325.45	5.4E+26	320.4	169.19	253.23	0.974	198.46	2.81E+13	193.2	194.14	-1.4	0.998
	0.4	415.34	5.02E+34	410.12	167.98	405.5	0.988	152.96	6.05E+09	147.57	195.59	-71.79	0.978
0.5	529.17	5.8E+44	523.58	166.77	597.52	1	220.65	1.69E+15	215.15	193.55	32.301	0.996	
0.6	384.86	1E+32	378.7	168.35	352.25	0.959	151.57	4.68E+09	145.97	195.64	-74.25	0.978	
0.7	330.33	1.46E+27	323.68	169.11	258.85	0.977	71.08	1131.766	65.359	199.85	-201.1	0.658	
0.8	437.44	4.54E+36	430.21	167.72	439.59	0.971	22.02	0.051763	16.075	206.37	-284.5	0.274	

Table 5 (continued)

Untreated tender coconut biomass		Treated tender coconut biomass											
Heating rate (°C/min)	Conv.	E _α (kJ/mol)	A (min ⁻¹)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol.K)	R ²	E _α (kJ/mol)	A (min ⁻¹)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (kJ/mol.K)	R ²
	0.9	318.79	1.38E+26	310.86	169.29	375.34	0.994	64.20	297.2001	56.647	200.41	-104.2	0.981
	AVG.	389.25	6.44E+43	383.32	168.36	375.34		125.43	1.91E+14	119.77	197.67	-104.2	
	SD	64.06	1.82E+44	64.28	0.78	99.91		60.77	5.30E+14	83.38	73.14	90.27	
	MD	52.23	1.14E+44	52.46	0.65	75.29		49.31	3.33E+14	49.51	3.02	67.01	
	S ²	4617.97	-	4649.23	0.68	11231.90		4155.13	-	4205.95	15.93	9167.30	

indicating the involvement of highly complex reactions taking place during the thermal-degradation of the untreated green coconut biomass than in case of the treated biomass. The energy of activation and pre-exponential factor both vary with conversion rate and also depend upon the structural integrity.

The values of E_α and A obtained using various iso-conversional models were used to calculate the Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) changes using equations (15), (16) and (17), respectively. The average values of ΔH for the untreated green coconut biomass were found to be 383.42kJ/mol for FWO, 391.97kJ/mol for KAS, 392.94kJ/mol for Tang and 392.14kJ/mol for Starink models and the corresponding values for the treated green coconut biomass were found to be 120.06 113.23, 113.62and 113.57 kJ/mol, respectively indicating the endothermic nature of reactions involved during the thermal degradation. The lower ΔH values for the treated green coconut biomass indicate lower energy requirement for its thermal degradation. The observed variation in ΔH with the extent of conversion can be attributed to the compositional and structural differences between the treated and untreated biomasses.

Difference between the values of activation energies E_α and ΔH reflects the feasibility of the reaction. Lower the difference, the more preferred would be the product formation. It is seen that the difference between E_α and ΔH is less than 1% for untreated and 3% for the treated tender coconut biomass, respectively.

The average values of ΔG for the untreated and treated green coconut biomasses estimated using FWO, KAS, Starink and Tang models were 167.35 and 189.76kJ/mol, 167.25 and 190.52kJ/mol 167.23 and 190.96kJ/mol, and 167.25 and 190.47kJ/mol, respectively. Nearly identical values of change in free energy change for Starink and Tang models are due to similar nature of the governing equations and underlying assumptions.

It is interesting to note that the Gibbs free energy increased after treatment due to the decrease in the pre-exponential factor of the treated biomass as it is a strong function of the pre-exponential factor. As discussed earlier the lower values of the pre-exponential factor indicate the higher rate of surface reaction. Therefore, the extractable available energy increased in the treated sample.

Moreover, the positive values of ΔG show that reaction is non-spontaneous in nature and energy has to be supplied for its completion. High value of ΔS shows that materials react faster and quickly produce products. The values of ΔS for untreated and treated coconut biomass for various models were found as 379.2 and -95.56J/mol.K for FWO, 395.46 and -106.20J/mol.K for KAS, 395.47 and -105.60J/mol.K for Tang and Starink models,

Table 6 Estimated kinetic factors and thermodynamic parameters using KAS for conversion (α) range 0.1 to 0.9 at different heating rates

Heating rate (°C/min)	Conv.	Untreated tender coconut biomass						Treated tender coconut biomass					
		E α (kJ/mol)	A (min ⁻¹)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol.K)	R ²	E α (kJ/mol)	A (min ⁻¹)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol.K)	R ²
10	0.1	422.26	3.34E+35	417.64	166.89	422.25	0.991	118.28	22347537	113.57	189.13	-117.3	0.991
	0.2	360.49	1.05E+30	355.69	167.67	316.61	0.999	118.51	23373609	113.64	189.12	-117.2	0.987
	0.3	332.40	3.27E+27	327.43	168.07	268.36	0.972	194.79	5.9E+13	189.68	186.46	4.9924	0.98
	0.4	426.64	8.19E+35	421.5	166.84	428.83	0.988	147.56	6.6E+09	142.37	187.95	-70.76	0.975
	0.5	545.66	3.08E+46	540.14	165.62	630.66	1	217.49	4.57E+15	212.14	185.87	40.787	0.996
	0.6	392.70	7.79E+32	386.64	167.24	369.44	0.956	145.71	4.62E+09	140.32	188.02	-74.05	0.975
	0.7	334.39	4.93E+27	327.88	168.04	269.16	0.975	62.26	336.8566	56.822	192.57	-210.8	0.58
	0.8	445.93	4.26E+37	438.83	166.62	458.38	0.969	10.71	0.003823	5.162	202	-305.6	0.092
	0.9	319.76	2.43E+26	312.03	168.26	395.46	0.993	52.15	42.71639	45.407	193.52	-106.2	0.971
	AVG.	397.81	3.43E+45	391.97	167.25	395.46		118.61	5.14E+14	113.23	190.52	-106.2	
	SD	67.83	9.67E+45	68.05	0.80	105.46		63.58	1.43E+15	63.83	4.71	98.43	
	MD	55.39	6.08E+45	55.60	0.67	79.61		51.36	9.01E+14	51.62	3.67	72.43	
	S ²	5176.92	-	5211.1	0.73	12513.7		4548.49		4583.9	24.98	10900.5	
20	0.1	422.26	1.65E+35	417.6	168.36	416.33	0.991	118.28	18385192	113.43	190.81	-119.2	0.991
	0.2	360.49	5.74E+29	355.64	169.15	311.51	0.999	118.51	19222647	113.49	190.8	-119.1	0.987
	0.3	332.40	1.87E+27	327.39	169.55	263.65	0.972	194.79	4.32E+13	189.59	188.12	2.2724	0.98
	0.4	426.64	4.02E+35	421.46	168.31	422.85	0.988	147.57	5.2E+09	142.23	189.62	-72.97	0.975
	0.5	545.66	1.25E+46	540.1	167.09	623.07	1	217.49	3.23E+15	212.05	187.52	37.771	0.996
	0.6	392.70	4.04E+32	386.59	168.72	363.92	0.956	145.71	3.64E+09	140.16	189.68	-76.26	0.975
	0.7	334.39	2.81E+27	327.81	169.52	264.4	0.975	62.26	301.6357	56.448	194.27	-212.2	0.58
	0.8	445.92	2.02E+37	438.77	168.09	452.13	0.969	10.71	0.003701	4.1622	203.78	-307.4	0.092
	0.9	319.76	1.42E+26	311.91	169.75	389.73	0.993	52.15	38.83947	44.812	195.23	-108.4	0.971
	AVG.	397.81	1.39E+45	391.92	168.73	389.73		118.61	3.64E+14	112.93	192.2	-108.4	
	SD	67.83	3.92E+45	68.07	0.81	104.63		63.58	1.01E+15	64.08	4.74	98.04	
	MD	55.39	2.46E+45	55.61	0.68	78.98		51.36	6.36E+14	51.85	3.70	72.08	
	S ²	5176.92	-	5213.0	0.74	12316.7		4548.49	-	4620.3	25.37	10813.6	
30	0.1	422.26	2.06E+35	417.59	167.89	418.15	0.991	118.28	9165293	113.37	197.02	-125.1	0.991
	0.2	360.48	6.94E+29	355.62	168.68	313.05	0.999	118.51	9570912	113.43	197.01	-125	0.987
	0.3	332.40	2.23E+27	327.35	169.08	265.05	0.972	194.79	1.43E+13	189.53	194.24	-7.042	0.98
	0.4	426.64	5.03E+35	421.43	167.84	424.67	0.988	147.56	2.21E+09	142.18	195.79	-80.15	0.975
	0.5	545.66	1.66E+46	540.08	166.62	625.41	1	217.49	9.44E+14	212	193.63	27.472	0.996
	0.6	392.70	4.97E+32	386.54	168.25	365.55	0.956	145.71	1.57E+09	140.11	195.86	-83.34	0.975
	0.7	334.39	3.36E+27	327.74	169.05	265.75	0.975	62.26	203.3323	56.549	200.59	-215.4	0.58
	0.8	445.92	2.56E+37	438.7	167.62	453.97	0.969	10.71	0.003294	4.7653	210.37	-307.4	0.092
	0.9	319.76	1.69E+26	311.83	169.27	391.45	0.993	52.15	27.64694	44.597	201.57	-114.5	0.971
	AVG.	397.81	1.84E+45	391.87	168.26	391.45		118.61	1.07E+14	112.95	198.45	-114.5	
	SD	67.83	5.21E+45	68.08	0.81	104.91		63.58	2.96E+14	63.96	4.89	95.14	
	MD	55.39	3.27E+45	55.62	0.67	79.2		51.36	1.86E+14	51.76	3.81	69.98	
	S ²	5176.92	-	5214.8	0.73	12382.1		4548.49	-	4603.1	26.90	10183.4	

respectively. The values of ΔS are both positive and negative (Tables 4, 5, 6, 7). The +ve ΔS values indicate that the system can easily form the activated complex while the -ve ΔS values suggest that randomness of the product formed is lower than that of its initial reactant (Table 8).

3.6 Effect of pre-treatment on reaction mechanism

The experimental z-master plots for the treated and untreated green tender coconut biomass are shown together in Fig. 6a and are separately compared with various theoretical curves

Table 7 Estimated kinetic factors and thermodynamic parameters using Tang for conversion (α) range 0.1 to 0.9 at different heating rates

Untreated tender coconut biomass										Treated tender coconut biomass									
Heating rate (°C/min)	Conv.	E α (kJ/mol)	A (min ⁻¹)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol.K)	R ²	E α (kJ/mol)	A (min ⁻¹)	ΔH (kJ/mol)	ΔG (kJ/mol.K)	ΔS (J/mol.K)	R ²						
10	0.1	422.14	3.26E+35	417.52	166.89	422.05	0.991	118.62	23880831	113.91	189.12	-116.80	0.992						
	0.2	360.48	1.05E+30	355.68	167.67	316.59	0.999	118.86	25025954	113.99	189.11	-116.60	0.987						
	0.3	332.45	3.3E+27	327.47	168.07	268.42	0.972	195.06	6.2E+13	189.94	186.45	5.4071	0.999						
	0.4	426.57	8.07E+35	421.43	166.84	428.71	0.988	147.91	7.07E+09	142.72	187.94	-70.20	0.975						
	0.5	545.46	2.96E+46	539.94	165.62	630.32	1	217.54	4.6E+15	212.18	185.87	40.851	0.997						
	0.6	392.78	7.92E+32	386.72	167.24	369.58	0.957	146.08	4.96E+09	140.69	188.00	-73.46	0.975						
	0.7	334.60	5.15E+27	328.09	168.03	269.52	0.975	62.76	372.0382	57.312	192.53	-209.90	0.584						
	0.8	446.03	4.34E+37	438.93	166.62	458.55	0.97	11.33	0.004529	5.772	201.70	-304.20	0.103						
	0.9	328.43	1.45E+27	320.7	168.13	395.47	0.993	52.82	49.03136	46.077	193.45	-105.60	0.971						
	AVG	398.77	3.29E+45	392.94	167.23	395.47		118.99	5.18E+14	113.62	190.46	-105.60							
20	SD	66.69	9.30E+45	66.89	0.78	105.32		63.42	1.44E+15	63.66	4.62	98.10							
	MD	54.47	5.84E+45	54.67	0.65	79.50		51.24	9.07E+14	51.48	3.62	72.23							
	S ²	5004.53	-	5034.67	0.69	12480.3		4525.01	-	4560.30	24.09	10827.0							
	0.1	422.14	1.61E+35	417.48	168.36	416.12	0.991	118.62	19636523	113.77	190.79	-118.60	0.992						
	0.2	360.48	5.73E+29	355.63	169.15	311.5	0.999	118.86	20570656	113.84	190.78	-118.50	0.989						
	0.3	332.44	1.89E+27	327.43	169.55	263.72	0.972	195.05	4.54E+13	189.85	188.11	2.68	0.999						
	0.4	426.57	3.96E+35	421.39	168.31	422.74	0.988	147.91	5.56E+09	142.58	189.6	-72.41	0.976						
	0.5	545.46	1.2E+46	539.90	167.09	622.73	1	217.53	3.26E+15	212.09	187.52	37.83	0.997						
	0.6	392.78	4.11E+32	386.67	168.72	364.06	0.957	146.08	3.91E+09	140.53	189.67	-75.67	0.976						
	0.7	334.60	2.93E+27	328.02	169.52	264.75	0.975	62.75	332.8919	56.938	194.23	-211.4	0.584						
30	0.8	446.03	2.07E+37	438.87	168.09	452.3	0.97	11.32	0.00438	4.7722	203.48	-306.00	0.103						
	0.9	328.43	8.34E+26	320.58	169.61	389.74	0.993	52.82	44.53614	45.482	195.16	-107.80	0.971						
	AVG	398.77	1.33E+45	392.89	168.71	389.74		118.99	3.67E+14	113.32	192.15	-107.8							
	SD	66.69	3.77E+45	66.90	0.79	104.49		66.69	1.02E+15	63.92	4.66	97.72							
	MD	54.47	3.77E+45	54.68	0.66	78.87		54.47	6.42E+14	51.72	3.64	71.88							
	S ²	5004.53	-	5036.48	0.70	12283.4		5004.53	-	4596.61	24.48	10743.5							
	0.1	422.14	2.01E+35	417.47	167.89	417.95	0.991	118.62	9771189	113.71	197.00	-124.50	0.992						
	0.2	360.48	6.93E+29	355.61	168.68	313.04	0.999	118.86	10222792	113.78	196.99	-124.40	0.989						
	0.3	332.45	2.26E+27	327.4	169.08	265.13	0.972	195.05	1.5E+13	189.79	194.24	-6.642	0.999						
	0.4	426.57	4.96E+35	421.36	167.84	424.55	0.988	147.91	2.36E+09	142.53	195.77	-79.60	0.975						
0.5	545.46	1.59E+46	539.88	166.62	625.07	1	217.54	9.51E+14	212.04	193.63	27.533	0.997							
0.6	392.78	5.05E+32	386.62	168.25	365.68	0.957	146.08	1.68E+09	140.48	195.84	-82.77	0.975							
0.7	334.60	3.5E+27	327.95	169.05	266.1	0.975	62.76	223.8106	57.039	200.54	-214.60	0.584							
0.8	446.03	2.61E+37	438.8	167.62	454.14	0.97	11.33	0.003885	5.3753	210.06	-306.00	0.10							

Table 7 (continued)

Untreated tender coconut biomass		Treated tender coconut biomass											
Heating rate (°C/min)	Conv.	E α (kJ/mol)	A (min ⁻¹)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol.K)	R ²	E α (kJ/mol)	A (min ⁻¹)	ΔH (kJ/mol)	ΔG (kJ/mol.K)	ΔS (J/mol.K)	R ²
	0.9	328.43	9.92E+26	320.5	169.14	391.46	0.993	52.82	31.58777	45.267	201.5	-113.90	0.971
	AVG	398.77	1.77E+45	392.84	168.24	391.46		118.99	1.07E+14	113.34	198.4	-113.9	
	SD	66.69	4.99E+45	66.91	0.79	104.76		66.69	2.98E+14	63.80	4.80	94.82	
	MD	54.47	3.14E+45	54.69	0.66	79.08		54.47	1.87E+14	51.62	3.75	69.78	
	S ²	5004.53	-	5038.00	0.70	12348.4		5004.53	-	4579.42	25.95	10114.8	

in Fig. 6b and c, respectively. From Fig. 6a, it is seen that for $\alpha < 0.5$, the plots for two biomasses differ only marginally indicating that the prevailing reaction mechanisms are similar, but above this ($\alpha > 0.5$) the plot for treated green tender coconut biomass follows a different path indicating change in the prevailing reaction mechanism. This can be attributed to the disruption of the ligno-cellulosic matrix caused by water hydrolysis. From Fig. 6b, it is seen that for conversion < 0.2 , the experimental curve for untreated biomass exactly overlaps the curve for boundary controlled reaction (contracting volume mechanism, curve R_3). As the reaction of thermal degradation progresses, the degradation process shifts towards the contracting area mechanism (curve R_2). For $\alpha = 0.2$ to 0.4 , the nature of reaction mechanism is not explicitly clear and for $\alpha = 0.4$ to 0.5 , the experimental curve exactly overlaps the curve for the contracting volume mechanism (curve R_2). For conversion up to 0.5 , the experimental curve for the treated biomass is closer to the theoretical curves R_2 and R_3 corresponding to the boundary reaction controlled mechanism. These changes are due to the transfer of heat from outer surface to the inner surface of particle which is controlled by the boundary controlled reaction process. For $\alpha = 0.5$ to 0.9 , the experimental z-master plots for untreated biomass does not follow any of the theoretical curve exactly, while that for the treated biomass it overlaps the curve for the boundary controlled reaction mechanism (contracting volume, curve R_3).

3.7 Characteristic of hot water extract

The pre-treatment of biomass affects the morphology and physico-chemical structure and thereby alters the intra-particle heat and mass transfer rates and hence the product yields. The chemical (acids, alkali); physical (crushing, grinding); thermal (drying, torrefaction, hot water extraction); and biological (enzymes, fungi) methods have been used for the pre-treatment of biomass [67–69]. The selection of method depends upon the type of conversion process to be used and the desired products. Pre-treatment with hot water is the most economical and simplest out of various methods and has been used in this work. As mentioned in Section 2.2 pre-treatment of tender coconut biomass powder was done by boiling with hot water for 120 minutes. The liquor was separated from the solid residue and was analyzed for its organic and sugar contents. The COD content of the extract was found to be 7200mg/L and its BOD content was 648 mg/L. The reducing sugar content was found to be 6.09g/L. From the discussion presented in earlier sections has already been inferred that the thermal degradability of treated biomass has improved. Sangian and Widjaja (2017) [70] reported that treatment of coconut husk with alkali (1% and

Table 8 Estimated kinetic factors and thermodynamic parameters using Starink for conversion (α) range 0.1 to 0.9 at different heating rates

Untreated tender coconut biomass								Treated tender coconut biomass					
Heating rate (°C/min)	Conv.	E α (kJ/mol)	A (min ⁻¹)	Δ H (kJ/mol)	Δ G (kJ/mol)	Δ S (J/ mol .K)	R ²	E α (kJ/ mol)	A (min ⁻¹)	Δ H (kJ/mol)	Δ G (kJ/mol)	Δ S (J/ mol.K)	R ²
10	0.1	422.31	3.37E+35	417.69	166.89	422.34	0.991	118.58	23695128	113.87	189.12	-116.80	0.991
	0.2	360.60	1.07E+30	355.8	167.67	316.8	0.999	118.82	24831363	113.95	189.11	-116.70	0.987
	0.3	332.55	3.38E+27	327.58	168.07	268.61	0.972	195.06	6.21E+13	189.95	186.45	5.42	0.999
	0.4	426.73	8.34E+35	421.59	166.83	428.98	0.988	147.88	7.03E+09	142.69	187.94	-70.25	0.975
	0.5	545.69	3.1E+46	540.17	165.62	630.71	1.000	217.55	4.62E+15	212.2	185.87	40.88	0.997
	0.6	392.89	8.1E+32	386.83	167.24	369.76	0.957	146.04	4.92E+09	140.65	188.00	-73.52	0.975
	0.7	334.67	5.22E+27	328.16	168.03	269.63	0.975	62.66	365.3132	57.222	192.54	-210.10	0.583
	0.8	446.16	4.46E+37	439.06	166.61	458.77	0.970	11.18	0.004357	5.632	201.77	-304.50	0.101
	0.9	320.14	2.63E+26	312.41	168.25	395.7	0.993	52.68	47.63955	45.937	193.46	-105.70	0.971
	AVG.	397.97	3.45E+45	392.14	167.25	395.7		118.94	5.2E+14	113.57	190.47	-105.7	
	SD	67.76	9.74E+45	67.98	0.80	105.39		63.47	1.44E+15	63.72	4.64	98.20	
	MD	55.33	6.12E+45	55.54	0.67	79.55		51.28	9.11E+14	51.53	3.63	72.29	
	S ²	5166.19	-	5200.19	0.72	12496.0		4532.53	-	4567.90	24.30	10849.0	
20	0.1	422.31	1.67E+35	417.65	168.36	416.41	0.991	118.58	19485003	113.73	190.80	-118.70	0.991
	0.2	360.60	5.87E+29	355.75	169.15	311.70	0.999	118.82	20411942	113.80	190.79	-118.60	0.987
	0.3	332.55	1.93E+27	327.54	169.55	263.90	0.972	195.06	4.55E+13	189.86	188.11	2.6997	0.999
	0.4	426.73	4.09E+35	421.55	168.31	423.01	0.988	147.88	5.53E+09	142.55	189.60	-72.46	0.975
	0.5	545.69	1.25E+46	540.13	167.08	623.12	1.000	217.55	3.26E+15	212.10	187.52	37.85	0.997
	0.6	392.89	4.2E+32	386.78	168.72	364.24	0.957	146.04	3.88E+09	140.49	189.67	-75.73	0.975
	0.7	334.67	2.98E+27	328.09	169.52	264.87	0.975	62.66	326.9191	56.848	194.24	-211.60	0.583
	0.8	446.16	2.12E+37	439.00	168.09	452.52	0.970	11.18	0.004215	4.6322	203.55	-306.30	0.101
	0.9	320.15	1.54E+26	312.29	169.74	389.97	0.993	52.68	43.2811	45.342	195.18	-107.80	0.971
	AVG.	397.97	1.39E+45	392.09	168.72	389.97		118.94	3.68E+14	113.26	192.16	-107.8	
	SD	67.76	3.92E+45	68.00	0.81	104.55		63.47	1.02E+15	63.97	4.68	97.81	
	MD	55.33	2.46E+45	55.55	0.68	78.92		51.28	6.42E+14	51.76	3.66	71.95	
	S ²	5166.19	-	5202.14	0.74	12299.2		4532.53	-	4603.99	24.69	10764.2	
30	0.1	422.31	2.08E+35	417.64	167.89	418.24	0.991	118.58	9697882	113.67	197.00	-124.6	0.991
	0.2	360.60	7.1E+29	355.73	168.68	313.24	0.999	118.82	10146104	113.74	196.99	-124.5	0.987
	0.3	332.55	2.3E+27	327.5	169.08	265.3	0.972	195.06	1.5E+13	189.80	194.24	-6.627	0.999
	0.4	426.73	5.12E+35	421.52	167.84	424.82	0.988	147.88	2.35E+09	142.50	195.78	-79.65	0.975
	0.5	545.69	1.67E+46	540.11	166.62	625.46	1.000	217.54	9.55E+14	212.06	193.63	27.564	0.997
	0.6	392.89	5.17E+32	386.73	168.25	365.87	0.957	146.04	1.67E+09	140.44	195.84	-82.83	0.975
	0.7	334.67	3.55E+27	328.02	169.05	266.22	0.975	62.66	219.9015	56.949	200.55	-214.7	0.583
	0.8	446.16	2.68E+37	438.93	167.62	454.36	0.970	11.18	0.003741	5.2353	210.13	-306.4	0.101
	0.9	320.15	1.83E+26	312.22	169.27	391.69	0.993	52.68	30.72078	45.127	201.51	-114	0.971
	AVG.	397.97	1.86E+45	392.04	168.25	391.69		118.94	1.08E+14	113.28	198.41	-114	
	SD	67.76	5.24E+45	68.01	0.81	104.83		63.47	2.99E+14	63.85	4.82	94.92	
	MD	55.33	3.29E+45	55.56	0.67	79.13		51.28	1.88E+14	51.67	3.77	69.85	
	S ²	5166.19	-	5203.70	0.73	12364.5		4532.53	-	4587.03	26.16	10137.7	

SD standard deviation, MD mean deviation, S² variance

4%) improved its enzymatic conversion to sugars by about 1.5 times. Nogueira et al (2019) [71] pre-treated green coconut with hot pressurized water (70°C, 150 bar) flowing at the rate of 1mL/min for 4hr. They reported that the liquor had a sugar content of 10g/L indicating the possibility of its use for fermentation.

The enzymatic hydrolysis of pre-treated green coconut shell improved substantially. Thus, the pre-treatment of green coconut biomass improves the biochemical and thermal degradability of tender coconut biomass. The extract liquor can be used for fermentation to produce biogas and ethanol.

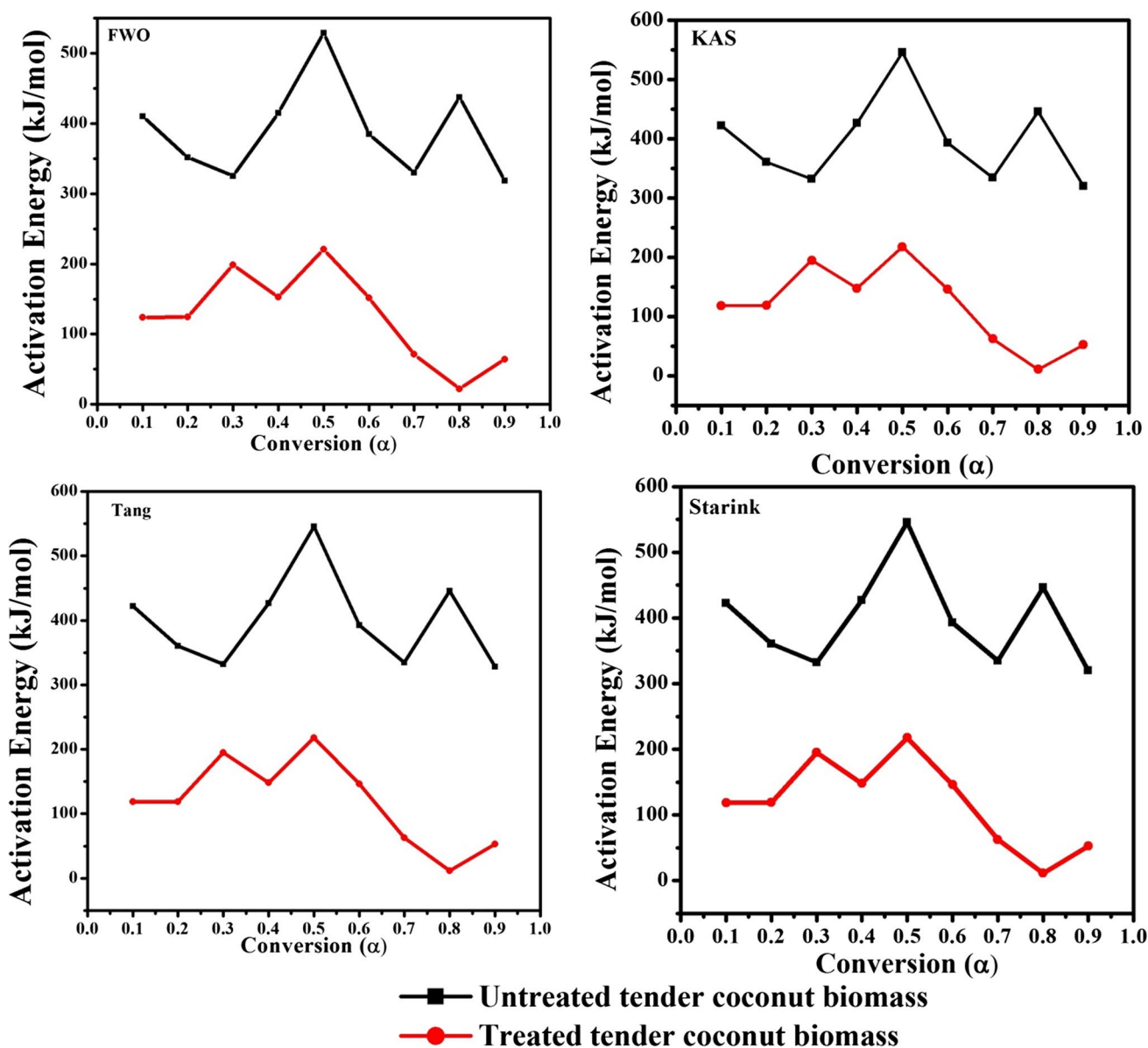


Fig. 5 Variation of activation energy with conversion for the untreated and treated green tender coconut biomass using FWO, KAS, Tang and Starink models

4 Conclusion

The pre-treatment with hot water altered the ligno-cellulosic matrix of the green tender coconut biomass hence its thermo-physical characteristics and thermal degradation behaviour. It caused reduction in FC and ash contents and increase in the VM content and HHV. The ash content decreased from 3.3 to 0.89% and the HHV increased from 18.5 to 21.26kJ/kg indicating appreciable improvement in the fuel characteristics. The thermal degradation-temperature profiles (TG & DTG versus temperature curves) also changed substantially indicating removal of easily volatile

organics and water soluble inorganic and organic compounds from the green tender coconut biomass responsible for the complex nature of the thermal degradation reactions resulting in smoothening of the degradation profile. The activation energies of the water treated tender coconut biomass calculated using various iso-conversional models were 3 to 4 times lower compared to those for the untreated biomass. It can be inferred that the pretreatment with hot water improved the quality of tender coconut shell biomass and making it more suitable as a renewable feedstock for obtaining energy and value added products. The water extract exhibited reasonably high COD (7200 mg/L),

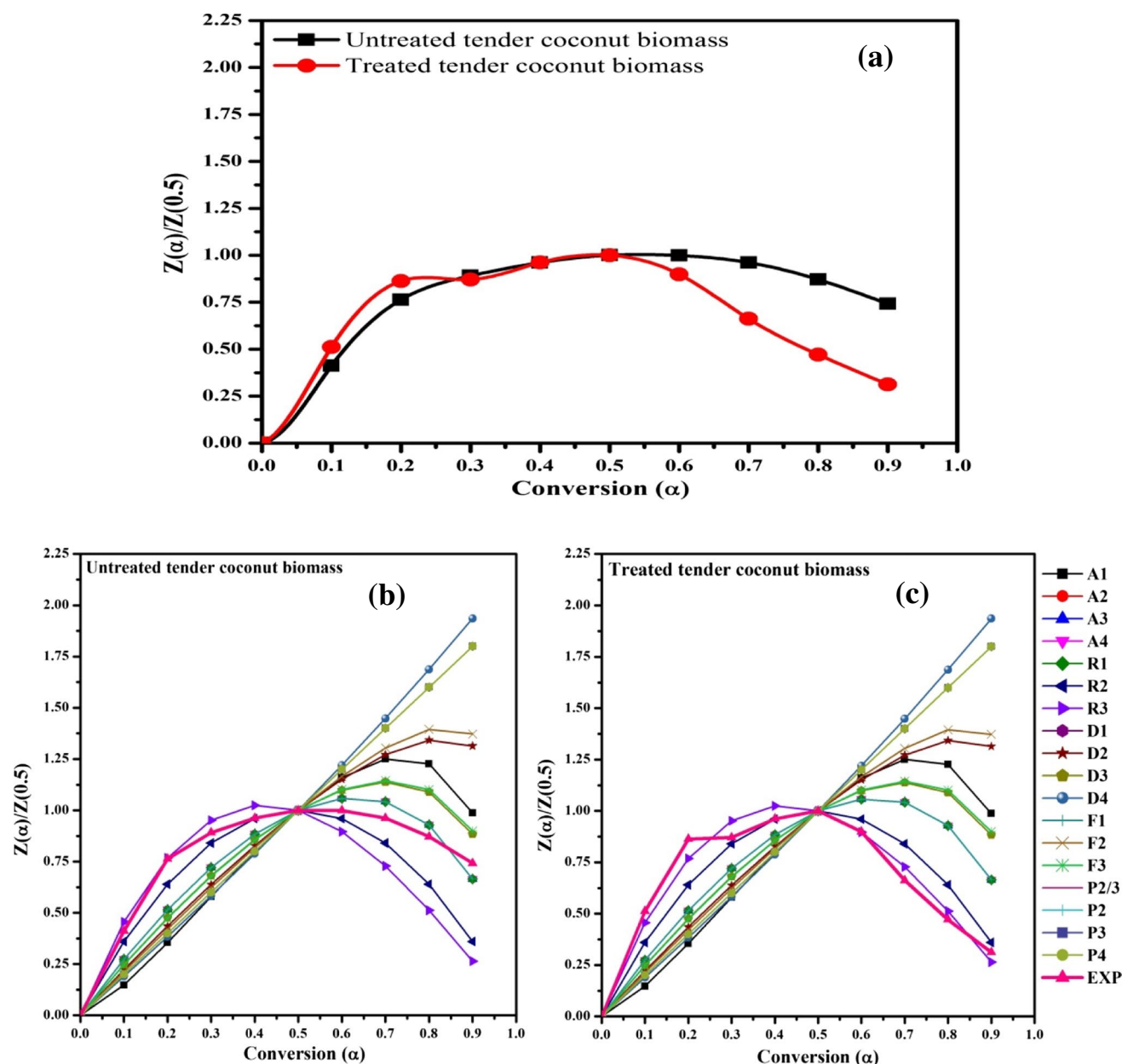


Fig. 6 Comparison of experimental and theoretical z-master plots (a) experimental z-master plots for treated and untreated tender coconut biomasses, (b) comparison of experimental and z-master plots for

untreated tender coconut biomass, (c) comparison of experimental and z-master plots for treated tender coconut biomass

BOD (648 mg/L) and reducing sugar (6.09g/L) contents indicating its suitability for obtaining other value added products like biogas and alcohol through fermentation.

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Author contribution Tanya Gupta and Mohit Kumar contributed equally to carry out literature search, conducted all experiments, analyzed the experimental data and prepared first draft of manuscript.

S. N. Upadhyay helped in planning the experiments, analysis of data and finalization of the manuscript and supervised the entire work.

P. K. Mishra and Amit K. Jaiswal helped in planning the experiments, analysis of data and finalization of the manuscript and supervised the entire work.

Data availability Not applicable

Declarations

Conflict of interest The authors declare no competing interests.

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