Application of weibull mixture model to illustrate wheat straw black liquor pyrolysis kinetics

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Abstract

Wheat straw soda black liquor is by-product of agricultural based paper industry. It is a promising resource of renewable energy. It is evaluated using thermogravimetric technique at different heating rates (e.g. 5, 10, 15 and 20 °C/min) in nitrogen atmosphere. From thermogravimetric analysis (TGA) graph it is found that there are three different mass loss processes, such as moisture or water molecule separating process, volatile material burning process and alkali salts reacting and fixed carbon burning process. TGA and Differential Thermogravimetric curves slightly move towards higher temperature side with increase in the heating rate. Weibull mixture model proposed allows for fitting an overall TGA curve of soda black liquor solid pyrolysis. The TGA curves of soda black liquor solids at different heating rates (5, 10, 15 and 20 °C/min.) have been analyzed and found the corresponding adjusted R-squared value greater than 0.99 in each case, thus the calculated TGA data by Weibull mixture model are in agreement with the actual experimental TGA data. Therefore, the TGA curve of soda black liquor solids pyrolysis can be understood as combination of three parallel reactions, where each single component represents one single reaction. Ozawa and Kissinger methods are used to find out the kinetic parameters such as activation energy and pre-exponential factor for the pyrolysis of soda black liquor solids. The activation energy of soda black liquor solids is almost equal in both methods. The experimental data and data driven models can help in smooth plant operations.

Keywords Wheat straw · Black liquor · Kinetics · Pyrolysis · Thermogravimetric

1 Introduction

The black liquor is the waste or by-product from the pulping of agricultural residues in the manufacture of pulp [1]. Various organic materials such as lignin, hemi-cellulose, carbohydrates and inorganics mainly NaOH are in the dissolved form in the black liquor, depending upon pH of the liquor [2]. The recovery of energy and chemicals from the SBL is important for the economic viability and environmental concern of the paper mills [3]. The black liquor generally with solids content above 60% is called heavy black liquor (HBL). The high solids content (usually at 75–78%) black liquor is sprayed into the lower part of the chemical recovery furnace, where it is burned in an

oxygen deficient environment [4]. The black liquor is pyrolyzed in three stages similar to other liquid and solid fuels. The three main stages are drying, devolatilization and char burning [5]. The process operational problems are there because of their available moisture content, higher silica content, lower fixed carbon, lower heating value, relatively higher viscosity and other challenging combustion properties. The bed combustion temperature control is very important parameter in the recovery furnace operation. It is essential to control the bed temperature of furnace to limit the emissions and bed material agglomeration. The agglomeration can be caused by ash containing high amounts of alkali (such as Na and K), other metals and phosphates, combining with silica and alumina to form

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low melting point eutectic mixtures and sintered. As a result, fluidization is obstructed and these large agglomerated particles become too heavy. The bed can solidify and prevent the combustion process, if left unchecked [6]. The disadvantage of the bed combustion process is that it will not operate if the bed contains salt whose fusion point is below the temperature necessary to oxidize the organic materials in the feed steam [7–9]. Thus, for preventing the agglomerate formation and sintering, the reaction temperature is kept around 700–750 °C. For this reason, the SBLS physicochemical and thermogravimetric analysis is very much necessary to operate and design chemical recovery furnace smoothly. Thermo-analytical technique is one of the popular techniques used to rapidly compare and investigate the thermal characteristics and kinetics during the pyrolysis of dry solid raw materials [10]. Various chemical reactions involved in the pyrolysis of black liquor, which cannot explain in detail. Normally, the two independent reaction models are used for biomass (black liquor solids) pyrolysis kinetics. It is based on the assumption that black liquor is composed from three different pseudo fractions. On the other hand, the separation problem associated with parallel reactions of two different pseudo fractions remain uncertain [11]. The present work is therefore carried out according to the following steps:

Delignification kinetics of wheat straw; proximate and ultimate analysis of black liquor solids; thermal analysis performed in inert atmosphere (nitrogen), followed by comparison of the TGA and DTG curves of the samples; analysis of the experimental data and overcoming the separation problem using Weibull mixture model for fitting the non-isothermal TGA curves. Extracting model equations from experimental data can help process planning designers make robust decisions in plant process optimization.

2 Experimental procedure

2.1 Pulping studies

The wheat straw pulping was carried out in a WEVERK electrically heated rotary digester of 0.02 m³ capacity. It was cooked under different cooking conditions, such as cooking time ranging from 20 to 150 min, maximum temperature ranging from 120 to 170 °C (shown in Table 1), 16 percent (w/w) cooking chemical (as NaOH) and bath ratio of 1:5. The purpose of this procedure was study of delignification rate of wheat straw pulping. After terminating the pulping at different temperatures, the pulp and spent liquor were analyzed according to standard procedures mentioned in CPPRI manual and TAPPI standards. The results are shown in Table 1.

2.2 Black liquor sample

The black liquor obtained from pulping of wheat straw at optimum conditions as maximum temperature 165 °C, cooking time 120 min, cooking chemicals 16% (w/w) and bath ratio 1:5 was dried in oven at 105 ± 1 °C. The oven dried sample was grinded in a high frequency ball mill and sieved. The sizes of the dried samples were 200–300 µm. The proximate analysis was carried out using ASTM E870-82. The ultimate analysis was conducted using an CHNS analyzer (Vario, Model: E III) for carbon, hydrogen, nitrogen and sulfur. The oxygen content was calculated by difference. The elemental analysis was performed by Atomic Absorption Spectra (AAS) (Perkin Elmer, Model: 800) after previously alkaline fusion in accordance with ASTM D368296. Results of the oven dried soda black liquor solids sample are summarized in Table 2.

Table 1 Analysis of pulp and black liquor during delignification of soda pulping of wheat straw at different temperatures

Parameters	Temperature (°C)	120	130	140	150	160	165	170	170
	Time (minutes) ^b	20	40	60	70	90	120	120	150
<i>Pulp analysis</i>									
Unbleached pulp yield (%), w/w		70.7	67.3	63.8	61.1	57.6	54.5	53.5	51.4
Klason lignin in pulp (%)		13.6	12.4	10.8	9.1	6.9	5	3.9	2.4
Kappa No. of pulp		69.4	58.1	48	40.1	31.9	25.6	23.1	19.6
Dissolved lignin ^a (%)		43.5	48	53.8	61	71.1	79.9	86.5	92.5
<i>Black liquor analysis</i>									
pH		12.2	12.1	12.1	12	11.9	11.7	11.6	11.3
Consumed alkali (%), w/w		68.7	70.3	72.6	75	79.2	85.8	87	96.1
RAA as NaOH, (%), w/w		12.1	10.7	9.6	9	7.4	4.5	4.5	2

^aExpressed on lignin present in raw material before pulping

^bCooking condition: Time from ambient to 100 ± 5 °C = 30 min, time from 100 ± 5 °C to maximum temperature

Table 2 Proximate and ultimate compositions of soda black liquor solids

Property	Quantity	Methods
<i>Proximate analysis</i>		
Moisture content (% w/w)	14.2	ASTM E870-82
Volatile (% w/w)	66.24	ASTM E870-82
Fixed carbon (% w/w)	14.40	ASTM E870-82
Ash (% w/w)	19.3	ASTM E870-82
<i>Ultimate analysis</i>		
Carbon (%)	40.2	ASTM D 3174
Hydrogen (%)	3.9	ASTM D 3174
Nitrogen (%)	1.2	ASTM D 3174
Oxygen (%)	36.78	By difference
Sulfur (%)	Nil	ASTM D368296
Chlorine (%)	3.15	ASTM D368296
Potassium (%)	4.54	ASTM D368296
Sodium (%)	9.86	ASTM D368296
Higher heating value (MJ/kg)	11.5	ASTM 5865

2.3 Experimental apparatus and procedures

A SII Seiko instrument Exstar 600 thermal analyzer (Model: TG/DTA6300, Tokyo, Japan) available at the Institute Instrumentation Centre (IIC) of Indian Institute of Technology Roorkee, India was used in the present investigation to continuously observe the mass loss in the SBLS in nitrogen gas atmosphere. The specifications of the thermogravimetric analyzer are given in Table 3. The thermogravimetric analyzer was logged to a personal computer for analysis and handling of experimental data.

The sample (12 mg approx.) was heated from ambient temperature to final pyrolysis temperature nearly 1000 °C. The heating rate was kept 5, 10, 15 and 20 °C per minute. The purge nitrogen gas flow was maintained around 200 ml per minute. A blank experiment was conducted to avoid the buoyancy effect. The experiments were repeated twice to

confirm the repeatability and authenticity of data. The data was analyzed to find out the mass loss and kinetic parameters such as apparent activation energy and pre exponential factor.

The data was analyzed to determine the TGA and DTG indices, mass loss and kinetic parameters such as activation energy and pre exponential factor. Using the prospective profiles, the influence of heating rate on the mass loss from the soda black liquor solids was studied.

2.4 Derivation of kinetic parameters from TGA curve

Thermogravimetric analysis (TGA) is an analysis technique for determining the thermal degradation of material with respect to time and temperature. It is also used for determining the final residue of material to analyze the thermal stability. Isothermal and non-isothermal data require different methods to calculate the kinetic parameter. In isothermal experiments, the samples are introduced in furnace at constant temperature and observing the degradation/decomposition of mass with time. In non-isothermal experiments, samples are heated from room temperature to higher temperature (up to 1200 °C) at constant heating rate (i.e., 5 °C/min., 10 °C/min., 15 °C/min. etc.). The weight loss of sample is observed with respect to temperature and time. Mass versus time or mass versus temperature curve is developed from experimental data [12].

Thermogravimetry analysis (TGA) and derivative thermogravimetry (DTG) curves of soda black liquor were plotted by the computer. The conversion ratio for kinetic modeling, α is defined as the mass ratio of the SBLS at time t to the initial SBLS, as shown below [13, 14],

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

Table 3 TGA specification

Item	Value
Make	SII Seiko instrument Exstar 600, Tokyo, Japan
Model	TG/DTA6300
Balance sensitivity	0.1 µg
Balance accuracy	Better than 0.02%
Sample mass range	Upto 1300 mg
Temperature range	Ambient to 1500 °C
Heating rates	0.1–200 °C
Cool down times	1000 °C to ambient temperature in less than 15 min under normal conditions
Sample type	liquid, powder, solids, films for fiber
Atmosphere	Dynamic or static including argon, helium, nitrogen, air, CO ₂ , O ₂ or other inert or reactive gases. The analysis carried out at reduces or normal pressure

Where, m_f , m_o are the final and initial masses of various proportion of soda black liquor solids, and, m_t is the mass of the soda black liquor solids at time t .

The kinetics on solid state reaction is known to be very complex. It can be estimated by two methods namely, differentiation and integration methods. The basic rate equation used in all kinetic studies is expressed as in Eq. (2),

$$\frac{d\alpha}{dt} = k \times f(\alpha)^n \quad (2)$$

Where, n , k and $f(\alpha)$ are the order of reaction, the rate constant and the temperature-independent function of conversion which depends on reaction mechanism, respectively. The rate constant k calculated by Arrhenius equation as follows,

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

Where, E , A , R and T are the activation energy (kJ/mole), the pre-exponential factor (1/min.), the universal gas constant (8.314 J/mol·K), and the gas temperature (T), respectively. The time- temperature relation was obtained as,

$$T = T_o + \beta t \quad (4)$$

Where, β ($^{\circ}\text{C}/\text{min}$) was the constant heating rate, and T_o the initial temperature. The kinetic value, obtained at the constant heating rate β , express as.

$$\alpha(T) = w_1 \exp\left[-\left(\frac{(T - T_o)}{\eta_1}\right)^{\beta_1}\right] + w_2 \exp\left[-\left(\frac{(T - T_o)}{\eta_2}\right)^{\beta_2}\right] + w_3 \exp\left[-\left(\frac{(T - T_o)}{\eta_3}\right)^{\beta_3}\right] + w_4 \quad (9)$$

$$\beta = dT/dt \quad (5)$$

Thus, the Eq. (4) may be written as,

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \times \exp\left(-\frac{E}{RT}\right) (1 - \alpha)^n \frac{d\alpha}{dT} = \frac{A}{\beta} \times \exp\left(-\frac{E}{RT}\right) (1 - \alpha)^n \quad (6)$$

Thus Eqs. 7 and 8 were obtained by the differential and integral transformation of Eq. (1).

$$\ln(\beta) = \ln \frac{AE}{Rg(\alpha)} - 5.331 - 1.052 \frac{E}{RT_p} \quad (7)$$

$$\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E}{RT_p} + \ln\left(\frac{AR}{E}\right) \quad (8)$$

Equations 7 and 8 provide the formulas for calculating the activation energy E and the pre-activation factor of

Ozawa and Kissinger respectively. The function $g(\alpha)$ is the integral form of the kinetic mechanism and T_p refers the temperature corresponding to the maximum mass loss peak. The function $g(\alpha)$ must not account for the activation energy of reaction, thus it is isolated in the linear coefficient. In Ozawa's method, the kinetic parameters such as activation energy and pre-exponential factor during the pyrolysis of soda black liquor solids (oven dry) were determined from the slope of and the intercept of the fitted plot of $1/T$ versus $\ln\beta$ [15]. Kissinger's method is an integral procedure, which is expressed in a graph of $1/T$ versus $\ln[\beta/T^2]$, which is obtained for each heating rate at constant conversion ratio [16].

2.5 Weibull mixture model

The Weibull mixture model proposes decomposition of the kinetic conversion curve into several Weibull distribution functions, assuming that decomposition kinetics of each component of the sample is represented by one or the sum of few functions [17]. The Weibull distribution function originally derived by Weibull is a probability density function, which differ in a scale and /or shape parameters. It was first applied to study the fatigue of materials. The three-mixed Weibull distribution is a probability mixture of three Weibull distributions, which differ in scale and/ or shape [18] [11].

To produce the asymptotic value at the end of TGA thermographs of black liquor pyrolysis, a constant (w_4) was added with $0 < w_1 < 1$, $0 < w_2 < 1$, $0 < w_3 < 1$, $\eta_1 > 0$, $\eta_2 > 0$, $\eta_3 > 0$, and $T \geq T_o$. In the Eq. (9), $\alpha(T)$ is the mass fraction at certain temperature (T) simulated through the Weibull 3-mixture model. w_1, w_2 and w_3 are the weight of first, second and third component of the Weibull 3-mixture model. η_1, η_2 and η_3 are the scale parameter of scale parameters of the Weibull distribution. β_1, β_2 and β_3 are the shape parameter or scale parameters of the Weibull distribution. From dimensional analysis, η_1, η_2 and η_3 are expressed as $^{\circ}\text{C}$ and β_1, β_2 and β_3 are dimensionless. T_o is the initial temperature of black liquor pyrolysis. When $T = T_o$, the $\alpha(T)$ function has to tend to 1. Therefore, the Eq. (9) written as,

$$w_1 + w_2 + w_3 + w_4 = 1 \quad (10)$$

2.6 Parameters estimation

For fitting the non-isothermal kinetic conversion data with Weibull mixture model, some estimation of the parameters in Eq. (9) is needed. To evaluate the parameters, the three parameters, reduced chi-square (χ^2), residual sum of square (RSS), and determination co-efficient (R^2) were used to evaluate the deviation between the predicted values and the experimental data for the dependent variable, and these can be used for comparing model representing the same dependent variable. The analysis of variance (ANOVA) of fitness parameters among the different models was performed at $p < 0.05$. The statistical values were calculated with equations,

$$\chi^2 = \sum_{i=1}^n \frac{(X_{i_{\text{exp}}} - X_{i_{\text{pred}}})^2}{X_{i_{\text{exp}}}} \quad (11)$$

$$RSS = \sum_{i=1}^n (X_{i_{\text{exp}}} - X_{i_{\text{pred}}})^2 \quad (12)$$

$$R^2 = 1 - \frac{\sum_{i=1}^n (X_{i_{\text{exp}}} - X_{i_{\text{pred}}})^2}{\sum_{i=1}^n (X_{i_{\text{exp}}} - \bar{X})^2} \quad (13)$$

$$R^2_{\text{adj}} = 1 - \frac{(1 - R^2)(n - 1)}{n - p} \quad (14)$$

where

$\bar{X}$ is the average value of experimental moisture ratio, $X_{i_{\text{pred}}}$ and $X_{i_{\text{exp}}}$ are predicted and experimental moisture ratios, respectively,

p is the number of constants, and n is the number of observations.

In this study, the nonlinear regression method was based on the Levenberg–Marquardt (LM) algorithm, which is most widely used algorithm in nonlinear least square fitting [19]. The Levenberg–Marquardt algorithm, starting with some initial parameter values, minimizes RSS by performing a series of iterations on the parameter values and computing RSS at each stage. The OriginPro 9 software (The OriginLab Corporation, USA) has been used for performing the optimization procedure.

3 Results and discussions

3.1 Delignification kinetics of wheat straw

The overall delignification and kinetics studies are useful in obtaining the information on rate of delignification and extent of chemical composition [20]. The pulping of wheat straw in alkaline medium is a complex process and involved numerous chemical reactions taking part simultaneously and these are influenced by both chemical and physical factors. It is well known that major proportion of cooking chemical (i.e. NaOH, Na_2S etc.) is consumed in the initial stage of pulping. It might be attributable to both carbohydrates degradation and lignin dissolution present in wheat straw. The kinetic studies may be helping in analysis the causes for chemical consumption the initial stage. The degradation reactions start at around 100 °C and completed at the temperature, where the delignification becomes the main reaction. The results of overall delignification and kinetics during pulping of wheat straw are shown in the Table 1. It is evident from the result that more than 70 percent of the alkali is consumed at around 120 °C, due to dissolution of carbohydrate and neutralization of various organic acids which present in the wheat straw and formed during the degradation of hemicelluloses. It is evident from the result that most of lignin is dissolved rapidly in the initial stage of the pulping [21]. From Klason lignin value in the pulp, it is notice that more than 50 percent of lignin dissolved before temperature 130 °C. The subsequent delignification is normally slower and it is primarily due to low concentration of available alkali. The Kappa number of resultant pulp show slow decrease in the later stage of pulping and finally acceptable Kappa number is obtained only when the cooking time was maintained for 90 min at 165 °C. This slow decrease might be due to slow auto condensation reactions taking places due to low alkali concentration in the final stage of pulping process.

3.2 Proximate and ultimate analysis

The physical and chemical composition of the black liquor solids are essential determining factors in the characteristics of pyrolysis or combustion. Black liquor solids can be analyzed by breaking it down into structural component called as proximate analysis and into chemical element called as ultimate analysis [22]. The proximate analysis helps to evaluate the percentage of volatile materials, fixed carbon and ash content in the black liquor. It is very essential to study the pyrolysis/combustion characteristics of black liquor solids. For example, ash content in black liquor solids can cause ignition and combustion problems. The

ash content having low melting point, it creates slagging and fouling problems. High volatility of the black liquor solids shows many advantages as combustion/pyrolysis feedstock. Furthermore, the high volatile and fixed carbon increase the heating value of black liquor solids. Ultimate analysis is an important factor, when studying the black liquor solids fuel characteristics. It helps to calculate the percentage of carbon (C), hydrogen (H) and oxygen (O) to estimate the heating value of black liquor. Further, it helps to estimate the percentage of nitrogen (N), sulphur (S) and chlorine (Cl) to study the environmental impact of black liquor [23, 24]. The proximate, ultimate and heating values of SBLS are shown in Table 2. The results show that the soda black liquor is an oxygen and carbon rich biomass containing trace amount of nitrogen and low hydrogen percentage. Wheat straw black liquor is a high ash containing material due to sodium hydroxide being cooking chemical, it has high fixed carbon, high volatile materials

and has a moderate heating value. These properties make black liquor a suitable material for comfortable combustion. It may be emphasized that the physico-chemical properties of soda black liquor vary from mill to mill due to the differing dose of cooking chemicals, type of raw materials and pulping techniques.

3.3 Thermal decomposition characteristics of soda black liquor solids

The Fig. 1a and b represent the thermogravimetric (TG) and differential thermogravimetric (DTG) graphs of the soda black liquor solids in the inert atmosphere at the heating rate (β) 20 °C per minute. The flow rate of purge nitrogen gas was at maintained 200 ml per minute. The soda black liquor contained mainly lignin, hemicelluloses and trace amount of cellulose. It is well known that the cellulosic raw material hemicelluloses

Fig. 1 a and b TG curves of wheat straw black liquor solids at 20 °C/min and c and d TG and DTG curve of wheat straw black liquor solids at different heating rates (5, 10, 15 and 20 °C/min)

Fig. 2 Overlay of experimental data and Weibull mixture model for different heating rates **a** 5 °C/min, **b** 10 °C/min, **c** 15 °C/min and **d** 20 °C/min

thermal decomposition starts at between 230 to 325 °C and the cellulose decomposition around 325 to 390 °C [25]. The macromolecules of lignin exhibit a wide range of temperature range of 250 to 540 °C. It can be seen from the Fig. 2b at a temperature lower than 140 °C, a small change of conversion in the soda black liquor solids sample was attributed to moisture vaporization, which was attached on the surface of the sample [26]. The mass loss of soda black liquor solids with increase in temperature is divided in three stages. In the first stage, the temperature range room temperature to 190 °C obtained from DTG graph was greatest devolatilization rate. During the devolatilization stage, the mass loss has been also attributed to breakdown of the organic materials like that oligosaccharides, smaller molecular weight organic acids, lignin etc. In the second stage, the mass loss in the temperature range from 190–540 °C is due to the decomposition of strong chemical bond of polysaccharides, organic acids and lignin. During the third stage, there is sharp peak of mass loss, generally the inorganic sodium salts and degradation of organic compounds in the soda black liquor at higher temperature. The amount of residuals remaining at around 700 °C

was about 52% from which it can be concluded that the organic materials make a relatively important contribution to the formation of char in pyrolysis of soda black liquor solids [27]. Higher temperatures can lead to devolatilization of part of the inorganic content of the black liquor. In the three stages, the fractional mass loss is about 10, 35 and 40% respectively. The residual of the degradation is ash and fixed carbon about 15%. It is revealed from the Fig. 1a of thermogravimetric (TG) curve that the total mass loss of soda black liquor solids is about 85%. Figure 1c and d are showing the graphs of thermogravimetric (TG) and differential thermogravimetric (DTG) at different heating rate from 5 °C/min to 20 °C/min in an inert atmosphere. It can be revealed, the thermogravimetric curve (Fig. 1c) and differential thermogravimetric curve (Fig. 1d) illustrate always higher degradation trend as the heating rate is increased. Table 4 represents the peak temperature (°C), maximum DTG peak (%/min) and residue at 1000 °C, (weight, %) from the thermogravimetric and differential thermogravimetric graphs. The onset and final temperature of the pyrolysis stage and the peak temperature increases slightly towards the higher temperature side

Table 4 Thermal degradation of wheat straw black liquor solids at different heating rates

Heating rate °C/min	Temperature range, (°C)	Peak tempera- ture, (°C)	Max.DTG peak, (%/min)	Residue at 1000 °C, (weight,%)
5	Ambient-190	241.2	1.01	12.72
	190–600	241.2	1.00	
	600–1000	854.9	2.01	
10	Ambient-190	149.7	1.39	14.84
	190–600	281.8	2.07	
	600–1000	898.4	4.34	
15	Ambient-190	149.7	1.7	15.77
	190–600	281.8	3.24	
	600–1000	898.4	6.48	
20	Ambient-190	145.4	2.5	16.98
	190–600	281.1	4.57	
	600–1000	909	8.25	

Table 5 Weibull mixture model parameters obtained from pyrolysis of wheat straw black liquor solids at different heating rates (5, 10, 15 and 20 °C/min.) with corresponding adjusted R^2 value

°C	w_1	η_1 (°C)	β_1	w_2	η_2 (°C)	β_2	w_3	η_3 (°C)	β_3	w_4	Red. χ^2	RSS	Adj. R^2
5	0.41676	852.0526	17.00665	−0.09919	183.4729	6.15694	0.54927	304.7918	2.16621	0.13745	2.49E-05	0.58118	0.99959
10	0.39858	865.2557	18.25778	−0.02403	88.68334	−6.80907	0.42087	357.8337	2.92529	0.1792	5.89E-05	0.68574	0.99899
15	0.36811	896.6556	21.49858	−0.21928	308.0519	−4.53258	0.27057	322.6552	1.33247	0.37589	3.65E-05	0.28323	0.99928
20	0.37737	903.0511	21.51674	−0.15506	307.5052	−5.99488	0.30809	369.604	1.85363	0.32054	4.33E-05	0.25246	0.99915

as heating rate increases. In addition, the peak area in the devolatilization stage increases as the heating rate is increased. The maximum mass loss rate and residue percentage of the soda black liquor solids (oven dry) increases with the increase in the heating rate as can be seen from the Table 4 and Fig. 1d. The soda black liquor solids pyrolysis reactions is incomplete and comparatively larger amount of residuals are left at 1000 °C as the heating rate increases. The heating rate has both negative and positive effect in the pyrolysis reaction. The rate of heating directly affects the temperature gradient and heat transfer between the outer layer of the sample and the furnace walls. The duration for complete pyrolysis of black liquor solids would be shorter with the increase in the heating rate. From the above discussion, it is revealed that the thermal degradation of soda black liquor solids can be classified into three steps such as drying upto 200 °C, pyrolysis within 200–550 °C and formation of sodium salts in between 700–1000 °C.

The Weibull mixture model proposed in this study have been successfully applied and analyzed for black liquor solids sample at different heating rates (5, 10, 15

Fig. 3 Curve of $\ln(\beta)$ verses $1/T$ by Ozawa method

and 20 °C/min.). Fig. (2) represent the overlays of experimental data and the Weibull mixture model prediction data for black liquor solids sample at different heating rates (5, 10, 15 and 20 °C/min.) [28]. Weibull mixture model parameters values obtained from black liquor solids sample pyrolysis at different heating rates with

Table 6 Parameter values in Ozawa formula

β (min ⁻¹)	T	$1/T \times 10^3$	$\ln \beta$
5	1131	0.884173	1.61
10	1146	0.8726	2.3
15	1160	0.862069	2.71
20	1167	0.856898	3

corresponding values of coefficient of determinants (R^2) are shown in the Table 5. The values of coefficient of determinants (R^2) are found higher than 0.999, thus the curves are good fit in the case of all heating rates. The separation into three single component function using Weibull 3-mixture model gives an approach to separate three parallel reactions involved in the black liquor solid pyrolysis process. Each parallel reaction corresponds to the decomposition of the each pseudo-fraction of black liquor solid [29].

3.4 Ozawa method

The effect of heating rate on the peak temperature of the DTG curves was followed in Eq. (15). The peak temperature and heating rates of Fig. 3 were summarized in Table 6, while the graph of $\ln \beta$ depending on $1/T_p$ was shown in Fig. 3. The graph of $\ln \beta$ versus $1/T_p$ represents a linear relation with the given value of the peak temperature in the DTG curves of different heating rates [30]. Fitting of the equation in Fig. 3 is expressed as,

$$y = -49.557 \times 10^3 x + 45.466 \quad (15)$$

Fig. 4 Curve of $\ln(\beta/T^2)$ versus $1/T$ by Kissinger method**Table 7** Parameter values in Kissinger formula

β (min ⁻¹)	T	$1/T \times 10^3$	$1/T^2 \times 10^6$	$\beta/T^2 \times 10^6$	$\ln(\beta/T^2 \times 10^6)$
5	1131	0.884173	0.78	3.91	-12.4523
10	1146	0.8726	0.76	7.61	-11.7855
15	1160	0.862069	0.74	11.1	-11.4043
20	1167	0.856898	0.73	14.7	-11.1287

The linear regression coefficient (R^2) is 0.99. The slope is 49.557×10^3 , from which the apparent activation energy (E) – 391.65 kJ mol⁻¹ is obtained; the intercept of the equation is 45.466, so the pre-exponential factor ($\ln A$) is 40.036 min⁻¹. Calculation of the Arrhenius equation parameters from the experimental data of $\ln(\beta)$ and $1/T$ are represented in Fig. 3.

3.5 Kissinger method

The Eq. (16) shows the effect of the heating rates on the peak temperature and Fig. 4 represents the graph between the peak temperature and heating rates [31]. The values of the peak temperature and the corresponding heating rates are summarized in the Table 7. The graph of $\ln(\beta/T^2)$ versus $1/T$ was plotted in Fig. 4. The equation obtained from Fig. 4 is expressed as,

$$y = -47.26 \times 10^3 x + 29.373 \quad (16)$$

The linear regression coefficient (R^2) is 0.99. Slope is -47.26×10^3 , from which the apparent activation energy (E) – 392.91 kJ mol⁻¹ is deduced; the intercept of fit equation was 29.373, so the pre-exponential factor ($\ln A$) was 23.94 min⁻¹. Calculation of the Arrhenius equation parameters from the experimental data of the temperature of the reaction peak of the curve of $\ln(\beta/T^2)$ and $1/T$ are represented in Fig. 4.

4 Conclusions

In the present study, the apparent activation energy values depend on conversion, showing that the pyrolysis of SBLS is not a single chemical process. It was found that pyrolysis process of SBLS takes places over three steps reaction. Finally, a statistical method has been develop to optimize the fitting of the kinetic conversion data for SBLS pyrolysis in nitrogen atmosphere, by using weighted sum of three cumulative weibull distribution with alternating shape parameter. The weibull mixture model provides a flexible model equation to solve the

rate limiting step of complex heterogeneous step. The weibull mixture model can fit very well the experimental kinetic conversion data of soda black liquor solids instead of solving complex system of equations. It is also very helpful to overcome the data noise problem, while analyzing thermal conversion of SBLS experimental data.

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Compliance with ethical standards

Conflict of interest On behalf of author, the corresponding author states that there is no conflict of interest.

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