

Study on kinetics, thermodynamics and co-pyrolysis studies of sugarcane bagasse and expanded polystyrene

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Abstract

The kinetic studies on co-pyrolysis of sugarcane bagasse, and expanded polystyrene (waste thermocol) was performed using a thermogravimetric analyzer to decipher the mechanism of co-pyrolysis at 5, 10, 15, and 20°C min⁻¹ and to estimate the kinetic triplet and thermodynamics of the co-pyrolysis process. The kinetic parameter values were estimated using Maples first order fitting process. The co-pyrolysis experiments was performed in a semi-batch reactor at 10°C min⁻¹ in an inert nitrogen atmosphere, from ambient temperatures upto 700°C. The outcome revealed that the optimum temperature and blending ratio was 550°C and 1:3 blending ratio of (sugarcane bagasse:thermocol waste) for the optimum bio-oil yield of 66.75 wt. %. The characterization of the co-pyrolysis bio-oil using FT-IR revealed the presence of more amount of aromatic compounds and hydrocarbons. The increase in aromatic compounds was mostly due to the addition of thermocol waste, which is an aromatic polymer.

1. Introduction

The increase in global warming and nearing the depletion of the fossil-based sources has shifted the dependency from non-renewable to renewable bio-energy sources. As biomass is considered as a carbonneutral alternative, it is an extensively accessible source for the satiation of energy demand. Therefore, the conversion of biomass using pyrolysis is considered a promising option, which involves certain steps of mass transfer, heat transfer, and some chemical reactions during its course (Dupont et al., 2009). Pyrolysis is a process for converting organics into energy-dense products that is both efficient and costeffective. In general, pyrolysis of biomass produces bio-oil, biochar, and non-condensable gases, among which bio-oil is considered as a drop-in-fuel because its combustion releases less amount of SO_x and NO_x (Banu et al., 2020). The bio-oil has some drawbacks such as high oxygen content (35-60 wt.%) which reduces calorific value, increases corrosion problems, leads to instability, and so on. As a result, certain upgradation procedures are used, such as co-pyrolysis of biomass with a hydrogen-rich precursor, which is a simple, cost-effective, and safe process for producing high-quality fuels (Uzoejinwa et al., 2018) (Abnisa et al., 2014). Plastic wastes are considered as one of the crucial hydrogen-rich sources and are generated from two sources i.e., industries and consumers. However, the plastic wastes generated from industrial sources are clean as compared to those generated by consumers. Plastics are, in general, of two types, i.e., thermoplastic and thermosetting, wherein thermoplastics constitute about 80% of plastic wastes and thermosetting plastics constitute 20% of plastic wastes. Moreover, thermoplastics are easily recycled, and they include polyethylene, polypropylene, polystyrene, etc. Moreover, the plastic wastes contain an abundance of hydrocarbons and possess a high calorific value and hence are considered as a crucial source of alternate fuels (Phanisankar et al., 2020) (Singh et al., 2019). The thermal pyrolysis and co-pyrolysis can be studied mathematically and validated by the use of kinetic models. Moreover, the information on the thermal degradation and kinetics of the precursor used in a process can help in the effective design of reactors and optimization of the process (Durange et al., 2013).. The biomass residues are a potent source of precursor for the biorefinery sector. Also, among the biomass residues, sugarcane bagasse residues are produced abundantly, and India is the second-largest producer of

sugarcane bagasse in the world. Besides bagasse, some residues produced are used in boiler plants of sugar mills, paper industries, production of value-added chemicals such as vanillin and syringaldehyde, cement production, production of ethanol, etc.(Roy & Dias, 2017), (Cardoen et al., 2015), (Varshney et al., 2019). Among the co-feeds, plastic wastes are one of the crucial waste generated primarily by consumers and are the major part of municipal waste and are termed plastic solid waste. Due to high cost of disposal and decreasing landfill space, plastic solid wastes are reclaimed and recycled using various procedures such as reuse, chemical and mechanical recycling, and energy recovery. Among the plastic solid wastes, thermocol waste is abundantly generated for it is used in our day to day activities in form of cups, trays, cartons, food containers, and protective packaging, etc. However, most of the generated thermocol wastes are subjected to landfilling, and energy recovery respectively by use of thermochemical conversion methods like combustion, pyrolysis, etc (Lopez et al., 2017) (Uttaravalli et al., 2020). Many researchers have explored the co-pyrolysis kinetics of biomass and polystyrene, including (epelioullar & Pütün, 2013), (zsin & Pütün, 2017), (Alam et al., 2020), (Ng et al., 2018), (Kositkanawuth et al., 2017), (zsin & Pütün, 2018), (H (Pradhan et al., 2020). However, kinetic, thermodynamic, and co-pyrolysis experiments combining sugarcane bagasse (SB) and thermocol waste (TW) have not been documented in the literature.

2. Materials And Methods

Shakthi Sugars in Dhenkanal, Odisha, provided sugarcane bagasse, while thermocol waste samples were gathered from the National Institute of Technology in Rourkela, Odisha. Prior to analysis, bagasse samples were sundried and oven-dried at 50°C for 24 hours, whereas TW samples were attrited with a shredder and then oven-dried at 130°C to minimise TW volume. Both feedstocks were maintained in a desiccator after oven drying. Figure. 1, and Figure. 2 depict pictures of bagasse and thermocol waste samples, respectively.

2.2 Methods of Characterization

The feedstocks, i.e., SB, and TW were analyzed for physicochemical composition study adhering to ASTM standards. The properties include proximate, ultimate analysis, Higher heating value, and elemental analysis respectively. The (1:1) ratio of SB:TW was subjected to thermogravimetric analysis at heating rates of 5, 10, 15, and 20°K min⁻¹ using a thermogravimetric analyzer (SDT Q 600) in an inert atmosphere of nitrogen. The chemical analysis of the liquid product obtained at optimum condition was performed for FTIR analysis using a spectrophotometer (Najo Mull) in an ATR mode within 400–4000 cm⁻¹. The GC-MS analysis of the co-pyrolysis bio-oil was conducted to determine the compounds present in the bio-oil using a GC analyzer (7890B, AGILENT). The GC analyzer was equipped with a DB5 MS detector, which determines the quantity of the compounds present in the form of area (%). The compounds were identified in terms of area (%) after comparing them with the NIST library.

2.3 Experimental setup and procedure

A stainless steel semi-batch reactor, an electrically heated furnace, a glass liebig condenser, and a measuring cylinder were used to conduct the co-pyrolysis experiments. The reactor had a length of 16.5 cm, an internal diameter of 4.7 cm, and an external diameter of 5 cm, and it had two openings: one for condensing gases and the other for allowing the inert gas to purge during pyrolysis. The furnace consisted of a K-type thermocouple for temperature measurement inside the furnace, and a PID controller to regulate the rate of heating. The furnace, condenser, and the nitrogen cylinder are all deployed in performing the co-pyrolysis experiments, and is portrayed in Fig. 3.

3. Kinetic Study

The thermal degradation of biomass, in general proceeds through a series of complex reactions due to the presence of many components present in the biomass which leads to the occurrence of series of parallel, and consecutive reactions respectively (Gouda & Kumar, 2019). However, the thermal degradation of any biomass is investigated after carrying out the thermogravimetric analysis of the biomass used. The reaction rate for the degradation of any biomass can be written as

$$\frac{\mathrm{dx}}{\mathrm{dt}} = \mathrm{kf}(\mathrm{x})^{\mathrm{n}} (1)$$

where 'x' stands for the fractional conversion of the precursor used and is written as, $x = \frac{w_{0-w_t}}{w_{0-w_f}}$, where ' w_0 ' is the initial weight of the sample, ' w_t ' denotes the degradation after a certain time elapsed i.e., 't', and ' w_t ' denotes weight loss after the final degradation of the material has occurred. Furthermore, 'k' is the rate constant, and 'n' stands for the order of the reaction. The arrhenius equation (1) can be written as

$$k = Aexp\left(-\frac{E}{RT}\right)(2)$$

where 'A' denotes the pre-exponential factor, 'E' stands for the activation energy, 'R' is the real gas constant, and 'T' is the absolute temperature. Now we introduce the term ' β ' wherein $\beta = \frac{dT}{dt}$ in the above equation, we get,

$$\frac{dx}{dt} \mathbb{I}\beta = \operatorname{Aexp}\left(-\frac{\mathbf{E}}{\mathbf{RT}}\right) \left(-\frac{\mathbf{E}}{\mathbf{RT}}\right) \left(-\frac{\mathbf{E}}{\mathbf{RT}}\right) \left(-\frac{\mathbf{E}}{\mathbf{RT}}\right)$$

Now, by integrating both the sides, we get,a

 $-ln \left(1-x\right) = \frac{{ART}^{2}}{\beta E {e}^{\frac{-E}{RT} dT}} - \frac{{E}{RT} \left(5\right)}{\theta E {e}^{\frac{-E}{RT} dT}} - \frac{{E}{RT} \left(5$

Equation $\left(5\right)$ in general, demonstrates a straight line having a negative slope. Now plotting the graph taking $\ln \left(-\left(1-x\right)\right)$ as ordinate vs $\left(1\right)$ as abscissa, we obtain a straight line with slope $m = \frac{E}{R}$. Now the activation energy can be written as

\frac{-E}{R}= -Slope \left(R\right) \left(6\right)

The graph reveals the Y-intercept can be written as $c = \ln\left(\frac{ART}^{2}}{\beta\right)$, however, the pre-exponential factor is equation is generated by the use of equation $\left(\frac{ART}^{2}\right)$,

 $A = \left(\frac{\text{E}_{RT}^{2}}\right) {e}^{c}\left(\frac{7\right)}$

3.1 Thermodynamics study

The thermodynamics study includes the change of parameters like Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) respectively. However, the aforementioned parameters are determined by the use of the theory of activated complex, which is expressed in the underneath equation as

 $A = \frac{\{e\}}{\{h\}}\left(x) = \frac{\{h\}}{\{h\}}\left(x) = \frac{\{h\}}$

Where '{e}_{\chi}' posses value of 2.7183 and is named as neper number; ' χ ' stands for transition factor and posses a value of unity for first-order kinetic equations; '{K}_{B}' is Boltzmann constant; '{T}_{P}' is the peak temperature obtained from the DTG curve, and 'h' is known as plancks constant. Now, the entropy associated during the formation of the activation complex can be written as

 $\Delta S = R \ln \frac{Ah}{e \cdot (K)_{B(T)_{P}}} \left(9 \right)$

The change in enthalpy \left(\varDelta \text{H}\right) can is determined by the use of the equation \left(10\right)given below

 $\label{eq:linear_p} $$\operatorname{T}_p \left(10\right)$$

The ' T_p ' value indicates the peak temperature which indicates the highest temperature at which the highest decomposition occurs. The change in gibbs free energy \left({\Delta }\text{G}\right), is calculated using the equation given below as equation\left(11\right)

 $\Delta G = \Delta H - T_p \Delta S \setminus (11 \setminus 1)$

The above three equations govern the calculation of values of ΔS , ΔS , ΔS , and ΔG respectively, which are the thermodynamic parameters.

4. Results And Discussion

4.2 Thermogravimetric analysis (TGA)

The thermogravimetric analysis and the differential thermogravimetry curves of SB: TW blend at 1:1 ratio at different heating rates of 5, 10, 15, and 20°C min⁻¹ are portrayed in Fig. 4 and Fig. 5 respectively. The results revealed that the initial weight loss occurred from room temperature upto 160°C resulting in some minor weight loss, indicating removal of moisture and some extractives. The active pyrolysis zone was found to take place between 190-510°C, wherein about 65-80% weight loss occurred indicating maximum volatilization in the zone. Furthermore, from 520-590°C, wherein, complete carbonization of the blends occur leaving behind the residue. However, the longer range of degradation is probably due to lignin component of SB. The degradation paradigm for the components present in the blend was the same irrespective of the rate of heating values, only the weight loss was more at higher heating rates. From the TGA study, we can comprehend that with excel in the rate of heating values, the rate of degradation becomes higher, wherein the increase in the rate of degradation may be attributed to a synergistic effect coming into action due to the interaction between SB, and TW. Furthermore, a marginal shift towards a higher temperature region was visible from the graphs. Pertinent results were reported by (Özsin & Pütün, 2018), wherein, the co-pyrolysis of lignocellulosic biomass and synthetic polymers was conducted. Moreover, it was witnessed that with excel in the rate of heating values, the amount of residue generated gets curtailed. The reason, however, could be attributed to more fast volatilization at higher heating rates. The DTG peaks, in general, give the idea of the maximum degradation temperature, during degradation. From our study for DTG, from Fig. 5, its visible that with excel in the rate of heating values the maximum peak for degradation also shifts marginally towards higher temperature zone from 410°C at 5°C min⁻¹ to 425°C at 20°C min⁻¹. However, the shift in peaks towards higher temperature regions could be attributed to resistance generated which thereby leads to an increase in mass loss rate at higher heating rates. (Pradhan et al., 2020). The radical study of TGA and DTG results demonstrate the shift in paradigm for different heating rates. Furthermore, by use of TGA and DTG results, we have estimated the kinetic, and thermodynamic parameters in the upcoming sections using the non-isothermal maples method and Gibbs free method respectively.

5. Kinetic And Thermodynamic Parameters Evaluation

The results of the method are portrayed in Fig. 6 with In \left(-\text{In}\left(1-x\right)\right) as ordinate vs \frac{1}{T} as abscissa in Fig. 6. The kinetics evaluation of the co-pyrolysis of SB and TW blend at 1:1 ratio is evaluated using the maples method at different heating rates of 5, 10, 15, and 20°C min⁻¹ to predict the values of the kinetic parameters at different heating rates. The kinetic parameters namely apparent activation energy, pre-exponential factor are determined by the use of arrhenius equation in its integral form. The results of the kinetic study are manifested in Table. 2, wherein the determined kinetic parameters are summed up for different heating rates and presented. According to Table. 2, the R² values increased with excel in the rate of heating values indicating the proximity of higher heating rates towards forming a straight line. Furthermore, the pre-exponential factor was found increasing with excel in the rate of heating values showing an utmost higher value may be attributed to the higher intensity of collision between the blends.

The thermodynamic study involves calculation of parameters namely ΔS , ΔH , and ΔG based on the peak temperature corresponding to maximum degradation from the DTG curves. The calculated thermodynamic parameters are displayed in Table. 2. The results showed negative values for ΔS for all the heating rates except for $20^{\circ}C$ min⁻¹. The lesser the ΔS values, the more developed is the complex formed albeit more ordered structure is formed. The ΔH provides an idea about exothermic or endothermic nature, along with signifying the formation of the activated complex. From our study the least ΔH value was found at $5^{\circ}C$ min⁻¹, which indicates ease for formation of activated complex as compared to other rates of heating values. The ΔG in general, gives the amount of energy consumed for the formation of the activated complex. From our study least ΔG value was found for $5^{\circ}C$ min⁻¹, which implies it's suitability in formation of activated complexs as compared to other rates of heating.

Table 2
Kinetic and thermodynamic parameters

SB: TW blend rates of heating (\(\(\mathbb{M}\)C/min)	T _{avg} (K)	R ² value	E _a (KJ mol ⁻¹)	A (min ⁻¹)	ΔS (J K.mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)
5	689.89	0.9548	80.18	1.76 × 10 ⁵	-157.85	74.507	182.352
10	681.00	0.9565	87.14	503203.08	-149.29	81.347	185.419
15	672.41	0.9542	96.94	2681326.66	-135.48	91.081	186.640
20	663.90	0.999	199.60	128847840518892.00	11.531	193.705	185.527
Average			115.96		-107.77	110.160	184.984

5. Co-pyrolysis Experiments

In the first set of experiments, we conducted co-pyrolysis at 1:1 blending ratio, and then by optimizing the temperature, we conducted co-pyrolysis of SB, and TW by varying the blending ratios of SB: TW at 1:0, 1:1, 1:2, 1:3, 3:1, and 0:1. The experimentation is performed to establish the optimum condition for the yield of co-pyrolysis bio-oil. The results of co-pyrolysis at 1:1 blending ratio of SB: PS is portrayed in Fig. 8. The study established an optimum co-pyrolysis bio-oil yield of 52.61 wt.% at 550°C, after which the bio-oil production indicated a decreasing trend. On the contrary, the biochar yield showed a consecutive decreasing trend and non-condensable gases showed reduced values upto 550°C, and thereafter they showed an increasing trend. However, the increase in gases was at the cost of a decrease in the bio-oil yield. Moreover, the reaction time decreased over the whole range of studies with increasing temperatures.

Based on the optimum temperature of 550°C obtained from the first set of experiments, co-pyrolysis experimentation by varying the blending ratio was conducted, and the results are manifested in Fig. 9. The results showed an optimum bio-oil yield of 66.75 wt.% at a 1:3 blending ratio of SB: PS and 10°C

min⁻¹. On the contrary, the biochar and non-condensable gases showed a decreasing trend in yield with the increase in TW content in the blends. Moreover, the reaction time showed an increasing trend with an increase in TW content in the blend. The increase in co-pyrolysis bio-oil yield with an excel in TW content is attributed to the synergistic effect coming into action.

6. Ftir Analysis Of The Co-pyrolysis Bio-oil

The FTIR spectrum of the co-pyrolysis bio-oil obtained at a 1:3 blending ratio of SB: TW is displayed in Fig. 10. The results presented the presence of several functional groups indicated by different transmittance peaks in the spectrum. There are several peaks observed at 3037 cm⁻¹, 1504 cm⁻¹, 905 cm⁻¹, and 692 cm⁻¹, demonstrating the presence of aromatic compounds. The abundance in aromatic compounds is due to the incorporation of TW in the blend with SB, which resulted in a synergistic effect between the precursors and thereby increased the aromatic compounds in the bio-oil. However, the upsurge in aromatic compounds in the co-pyrolysis bio-oil is reported by using polystyrene as a co-feed by (Abnisa et al., 2013), (Reshad et al., 2019).

7. Conclusion

The kinetic, thermodynamics, and the co-pyrolysis investigation of SB and TW revealed several key findings. The characterization of both the feedstocks revelaed presence of more volatile matter content, and least ash content in TW, as compared to SB. The TGA analysis of SB:TW blend at 1:1 ratio revealed that, with excel in heating rates, the degradation shifts towards higher temperature regions. The kinetic study showed that the apparent activation energy (E_a) increased along with pre-exponential factor (A), with increase in rate of heating values. The thermodynamics study showed that the Δ S, Δ H, and Δ G values increased with increase in rate of heating values. The kinetic and thermodynamic parameters study will help generate an idea on effective reactor design. The co-pyrolysis studies revealed 1:3 (SB: TW) as the optimum blend ratio and 66.75 wt.% as the optimum liquid product yield at 550°C. The characterization using FT-IR revealed the presence of several aromatic compounds.

Declarations

Ethics approval and consent to participate:

This article does not contain any investigations using human participants or animals explored by any of the authors.

Consent for publication:

Not applicable

Availability of data and materials:

All data generated or analyzed during study is involved in the current manuscript.

Competing interests:

The authors declare that there are no conflicts of interest.

Funding:

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Authors' contributions:

Sowhm Swain Mohapatra: Experimentation

Narayan Gouda: Methodology

Soumya Sanjeeb Mohapatra: Co-supervisor

Raghubansh Kumar Singh: Esteemed supervisor

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Figures

Figure 1
Sugarcane bagasse (SB)



Figure 2
Termocol Waste (TW)

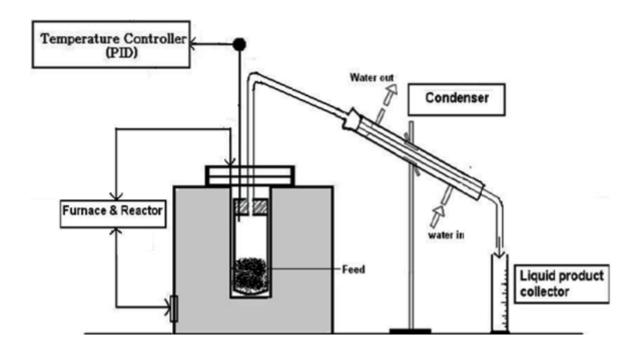


Figure 3

Schematic presentation of the co-pyrolysis experiment setup

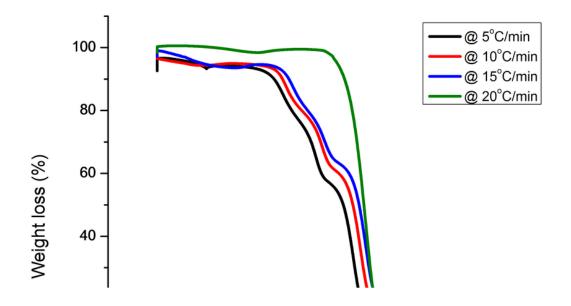


Figure 4

TGA analysis of SB: TW (1:1) blend at 5, 10, 15, and 20°C min⁻¹

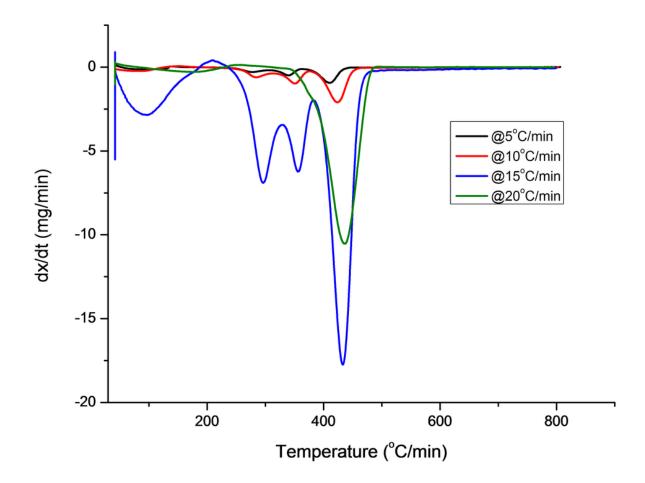


Figure 5

DTG curves of 1:1 co-pyrolysis blend of SB: TW blend at 5, 10, 15, and 20°C min⁻¹

Figure 6 Non-isothermal plots for kinetic study of SB:TW blend at different heating rates

Image not available with this version

Figure 7

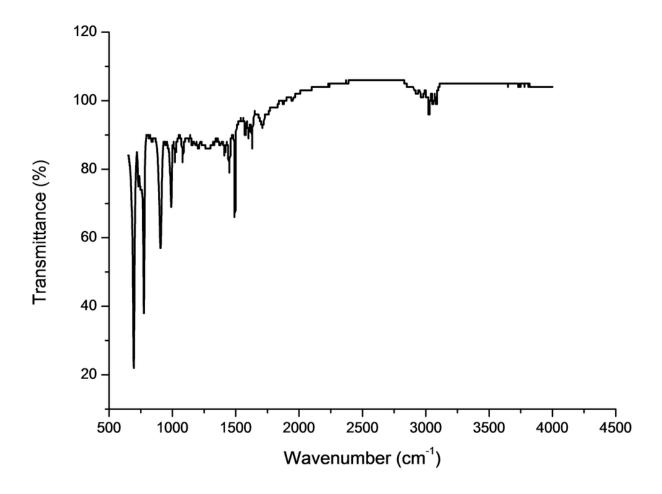
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Figure 8

Effect of temperature on yields of various products and reaction time during co-pyrolysis

Figure 9

Effect of blending ratio on yields of various products and reaction time during co-pyrolysis



FTIR spectrum of the co-pyrolysis bio-oil obtained at 1:3 blending ratio of SB: TW