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Co-gasification Study of blends of Municipal Solid Waste with Sugarcane Bagasse and Rice Husk using the Coats-Redfern method.

Zeeshan Hameed[a], Zakir Khan[a,*], Shahzad Khurram[a], Abrar Inayat[b], Naila Amin[a,c], Muhammad Aslam[d], Ian Watson[e]

[a]Biomass Conversion Research Group, Department of Chemical Engineering, COMSATS University Islamabad, Lahore Campus, Lahore Pakistan

[b]Department of Energy Engineering, School of Engineering, Robert Gordon University, Aberdeen, Scotland, United Kingdom.

[c]Department of Chemical Engineering, University of Gujrat, Gujrat, Pakistan

[d]Department Chemical Engineering, COMSATS University Islamabad, Lahore Campus, Lahore Pakistan

[e]Systems Power and Energy, School of Engineering, University of Glasgow, Glasgow, G12 8LL, UK

Abstract

Rapid development in the current economic situation has led to an increase in carbon emissions and to find sustainable solution to deal with this problem. Co-gasification of biomass with municipal solid waste is gaining significant importance to utilize the energy content of both raw materials judiciously and efficiently. This current work includes the study of physico-chemical characterization, thermal decomposition of MSW, sugarcane bagasse, rice husk, and their blends with 30:70, 50:50, and 70:30 ratios. Employing a thermogravimetric analyzer (TGA) under controlled conditions, the Coats-Redfern approach integrated sixteen reaction models to determine kinetic and thermodynamic parameters. This study intends to interpret the influence of mixtures on activation energy and synergy effect of mixing two different materials to check its market compatibility. The physicochemical properties of the feedstocks showed good agreement and suitability to be utilized for thermal conversion. Thermal degradation mainly appeared in the temperature range of 150-500°C for all 99.4% total weight loss for all parent samples as well as their blends. Linear regression coefficients (R^2) were in the range of 0.90-0.99 for all sixteen calculated models. The lower activation energies were obtained from the 50:50 blend for sugarcane bagasse and MSW while 70:30 for rice husk with MSW respectively which proved a great affinity to thermal degrading under a gasification environment.

Keywords: Gasification, Municipal Solid Waste, Sugarcane Bagasse, Rice Husk, TGA/DTA, Kinetics, Coats – Redfern Method

Abbreviations

TGA	Thermogravimetric analysis
MSW	Municipal solid waste
B	Sugarcane bagasse
RH	Rice husk
Eα	Activation energy
ΔH	Change in enthalpy
ΔG	Change in Gibbs free energy
ΔS	Change in entropy
Tp	Peak temperature
DTA	Differential thermal analysis

A	Fractional conversion
f(α)	Conversion function
HHV	High heating value
GHG	Greenhouse gas

1. Introduction

Biomass has an evident possibility to generate products of significant importance such as fuels, heat, energy, and platform chemicals, and obtaining these products via thermochemical conversion is receiving particular importance. Additionally, it is also possible to lessen environmental contamination brought on by the accumulation of garbage and burning of these sources [1]. Biomass is turning into one of the most significant inputs in energy applications as a clean, sustainable alternative to fossil fuels. Among all available varieties of biomass, agricultural leftovers are in the limelight because of multiple advantages such as ease of availability and abundance [2]. Pakistan has agricultural importance because 40% of its economic growth comes from agricultural fields, especially with the production of approximately 67.1 million tons of sugarcane, 25 million tons of wheat, and 10.8 million tons of rice [3]. The current economic stress can be greatly lowered by switching to alternative sources of energy. Another good point of using biomass is the substantial decline in GHG emissions, which is currently a top priority for Pakistan [4]. Municipal solid waste and agriculture biomass such as rice husk and sugarcane bagasse are some of the most attractive options. Compared to conventional fuels, they are cheaper, widely available, and have demonstrated their potential to be used as renewable energy[5].

Gasification, as a thermochemical conversion process, holds great appeal for the conversion of rice husk and sugarcane bagasse and is regarded as a highly attractive option compared to other available thermochemical conversion processes like combustion, hydrothermal liquefaction, and pyrolysis. This process enables the production of a diverse array of value-added products such as syngas, biochar, and petrol. Additionally, gasification offers the advantage of reducing biomass waste without causing harmful emissions. Additionally, gasification is a low energy-intensive operation and eco-friendly [6]. Gasification is the cracking of biomass under a partially oxygenated environment at restricted conditions to produce energy and biofuels. Despite being a complicated process, it can produce industrially significant chemicals and biofuels. It is an essential energy transporter and chemical source in various biorefineries [7]. Thermo-kinetic analysis is one of the most vital methods to deliver statistics and practical approaches to the complete gasification conversion for different feedstocks. To improve the process and make it work on a commercial scale, it presents the idea of the gasification reaction mechanism and parameters [8, 9]. To forecast kinetic and thermodynamic profiles including activation energy (ΔE), enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS), which entirely depends on thermodynamic analysis (TGA) [10]. There are two types of thermo-kinetic evaluation methods that are being used commonly, one is model free approach and other is model fitting approach. The key significance of model free approach, which is also called 'the Coats and Redfern model", is its ability to determine the activation energy and reaction mechanism without prior knowledge of the reaction kinetics. It provides a straightforward and model-independent way to extract kinetic parameters from TGA data throughout the temperature range even at a single heating rate. The Coats-Redfern approach does not make assumptions about the reaction pathway. It is particularly advantageous when dealing with complex reactions or situations where the reaction mechanism is not well understood.[11], [12]

Many researchers have worked on the thermochemical conversion of different biomass by using various conditions and kinetic models[11, 12]. Naqvi et al. [15] studied the thermal profile of sewage sludge and rice husk by using the Coats and Redfern model. Malika et al.[16] investigated the decomposition patterns of almond shells, nutshells, acorn shells, and acorn cups under oxidative atmosphere and kinetics by using kinetic models based on simple Arrhenius' law. But all these previous works have primarily focused on technological aspects, such as reactor design and operating conditions, without thoroughly investigating the fundamental thermochemical interactions between MSW and biomass. Furthermore, the diversity in waste composition and biomass types introduces complexities that necessitate a more differentiated exploration. Moreover, a complete model-fitting kinetic and thermodynamic analysis of MSW, sugarcane bagasse, rice husk, and their blends has never been presented using the Coats-Redfern approach, which certainly helps in the commercial scale-up of the process. These blending may also result in better gas yield, low carbon footprint, and increased feed-to-gas conversion. Such knowledge can give a vision into the ecologically sound and sustainable aspects of biomass and help in developing robust and efficient systems for their thermochemical conversion. Additionally, the integration of these two feedstocks in gasification is expected to address the limitations observed in individual gasification processes, leading to improved overall performance in terms of reduced activation energy.

The objective of this work is to study the decomposition performance of MSW blends with sugarcane bagasse and rice husk under gasification conditions by using a thermogravimetric analyzer (TGA) and to estimate the kinetic and thermodynamic profiles. To determine the kinetic and thermodynamic parameters, a total of 16 models based on the Coats-Redfern method were utilized. This research endeavors to explore the synergistic effects of co-gasifying MSW with biomass, aiming to contribute to the understanding of the thermochemical conversion processes involved. The obtained results were compared with those from similar studies reported in the existing literature, focusing on comparable biomass wastes.

2. Methodology

2.1 Sample Preparation and Characterization

Municipal solid waste (MSW) pellets were collected from a local vendor in Lahore mainly consisting of paper, yard trimming, wood, and agricultural waste.

Municipal solid waste (MSW) was collected from the Municipal Corporation Office, Lahore, which usually consists of paper, yard trimming, wood, and agricultural waste. Sugarcane bagasse and rice husk were collected from local sugar and rice industries in the vicinity of Lahore. The MSW and biomass (sugarcane bagasse and rice husk) were thoroughly mixed with different blending ratios of MSW-to-biomass. The prepared samples were subjected to conventional oven drying at 105°C for an entire day, ensuring that the moisture content reached the permissible limit. Through mortar and pestle, the size of the dried samples was demoted to a powdered form. A sieve shaker was used to strain the crushed sample into more fine powder at the size of 150-200μm. After completing this step, the sample was preserved in a desiccator to prevent direct contact with moisture and soil contamination. The characteristics of municipal solid waste, sugarcane bagasse, and rice husk were evaluated by proximate analysis and ultimate analysis to describe the percentage of moisture, ash, volatiles, fixed carbon, and elemental composition according to ASTM standard methods. To explore the synergistic effect of the co-gasification process of MSW with sugarcane bagasse and rice husk, different blends were prepared in the ratios of 1, 7:3, 5:5, 3:7, and 1 for MSW-to-biomass (wt.: wt.). Fourier-transform infrared spectroscopy (FTIR) profiles of raw materials and blends were assessed to check the synergistic effect of MSW with sugarcane bagasse SB and rice husk RH via PERKIN ELMER Spectrum

Two FT-IR Spectrometer. The resolution was kept at $4cm^{-1}$. The selected IR range was from 400 to $4000cm^{-1}$.

2.2 Co-gasification Investigation using TGA

Co-gasification behavior of municipal solid waste and its blends with sugarcane bagasse and rice husk were examined via PERKIN ELMER TGA 4000 thermogravimetric analyzer. Sample weights of 5–6mg were positioned in an alumina pan and heated up from ambient temperature to 1000°C at a constant heating rate of 10°C/min. Air (0.35L/min) was used as a gasifying agent to create a gasification environment.

3. Kinetic Analysis

Kinetic analysis of MSW and its blends with sugarcane bagasse and rice husk starts from Arrhenius' law, which can lead to the rate of reaction as:

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

Where T depicts absolute temperature (K), t represents time (s), α and f(α) are fractional conversion and functions relevant to the reaction mechanism respectively. The fractional conversion can be calculated by $\alpha=(x_i-x)/(x_i-x_f)$ in which x_i, x_f, and x are the mass of the sample at initial, final, and particular temperature points. Merging Arrhenius and the rate of reaction equations gives:

$$\frac{d\alpha}{dt} = Aexp\left(\frac{-E_\alpha}{RT}\right)f(\alpha) \tag{2}$$

Where f(α) can be defined as $f(\alpha)=(1-x)^n$ where n is the order of reaction, A portrays the pre-exponential factor and R depicts the gas constant with a value of 0.008314 kJ/mol K, After combining all equations, multiplying with 1/β (where $\beta=\frac{dt}{dT}$) and integrating, the new equation obtained as given below

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f\alpha} = \frac{A}{\beta}\int_0^T \exp\left(\frac{-E_\alpha}{RT}\right)dT = \frac{AE_\alpha}{\beta R}p(x) \tag{3}$$

It is challenging to integrate equation (3) analytically. For its solution, several models have been developed and put forth based on reaction mechanisms. Among these, the Coats and Redfern method's model-fitting approach is well known and frequently used to determine the pre-exponential factor (A) and activation energy (ΔE) and to forecast the behavior of various reaction processes. The Coats and Redfern model's primary equation is provided below.:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E_\alpha}\left[1 - \frac{2RT}{E_\alpha}\right] - \frac{E_\alpha}{RT} \quad (4)$$

The slope of a line representing the relationship between 1/T and $\ln(g)/T^2$ can be used to determine E_α. The intercept of this curve leads to A. A variety of proven models can be produced by g(α), depending on the response mechanisms. Table 1 lists and uses some of the functions relevant to the reaction mechanism used in this study [15, 16].

Table 1: Conversion function of several reaction mechanisms used in the Coats and Redfern Method

S. No.	Model Name	Symbol	g(α)
01.	Chemical reaction order 1	F1	$-\ln(1-\alpha)$
02.	Contracting cylinder	F2	$1-(1-\alpha)^{1/2}$
03.	Contracting sphere	F3	$1-(1-\alpha)^{1/3}$
04.	Parabolic law- one-way diffusion	R1	α^2
05.	Two-dimensional diffusion	R2	$(1-\alpha)-\ln(1-\alpha)+\alpha$
06.	Chemical reaction 3rd order	R3	$\frac{1}{2}[(1-\alpha)^{-2}-1])$
07.	Chemical Reaction 2nd order	R4	$2[(1-\alpha)^{-1/2}-1])$
08.	Avrami–Erofeev	A1	$[-\ln(1-\alpha)]^{3/4}$
09.	Avrami–Erofeev	A2	$[-\ln(1-\alpha)]^{1/2}$
10.	Avrami–Erofeev	A3	$[-\ln(1-\alpha)]^{1/3}$
11.	Avrami–Erofeev	A4	$[-\ln(1-\alpha)]^{1/4}$
12.	Power Law	P4	$\alpha^{1/4}$
13.	Power Law	P3	$\alpha^{1/3}$
14.	Power Law	P2	$\alpha^{1/2}$
15.	Diffusion control (Jander)	D3	$[1-(1-\alpha)^{1/3}]^2$
16.	Diffusion control (Crank)	D4	$(1-\frac{2}{3}\alpha)-(1-\alpha)^{2/3}$

4. Thermodynamic Analysis

Change in Enthalpy (ΔH), Gibbs free energy (ΔΔG), and entropy (S) are thermodynamic parameters that must be understood to understand the gasification process's behavior. These characteristics are evaluated using TGA and kinetic data from municipal solid waste and its blends with bagasse and rice husk, and their respective equations are given below.

$$\Delta H = E_\alpha - RT \tag{5}$$

$$\Delta G = E_\alpha + RT_p ln(K_B T/hA) \tag{6}$$

$$\Delta S = \frac{\Delta G - \Delta H}{T_p} \tag{7}$$

Where K_B is the Boltzmann constant with a value of 1.381×10^{-23} $m^2 kg/s^{-2}$ K^{-1} and h is Planck's constant with a value of 6.626×10^{-34} $m^2 kg/s$.

5. Synergetic Calculations

The synergistic effect in the co-gasification of rice husk and sugarcane bagasse blends with MSW was assessed at a certain temperature range used in TGA analysis with the help of the given equation.

$$\Delta W = W_{(exp.)} - W_{(cal.)} \tag{8}$$

Where $$W_{(cal.)} = x1W1 + x2W2. \tag{9}$$

In this equation, $x1$, and $x2$ represent the blended ratios of individual biomasses in the mixture, while $W1$, and $W2$, denote the weight losses of each component. Typically, the percentage variation between experimental values and theoretical values determines the synergistic effects, indicating either an increase or decrease in the observed values compared to the expected ones.

6. Results & Discussions

6.1 Physico-chemical characterization of MSW and Biomass wastes

Table 2 exhibits the values of the proximate and ultimate analysis of municipal solid waste, rice husk, and bagasse on a dry basis. The raw material qualities have a significant impact on the operating factors and gasifier efficiency. It can be seen that the MSW and sugarcane bagasse have a higher percentage of volatile matter (74.5 and 80.9 wt.% respectively) and a slightly lower fixed carbon content of (8.71 and 3.6 wt.%) as compared to rice husk, This shows that the feedstock is lignocellulosic, which allows it to produce a higher bio-oil output [19]. Results showed a lower ash content for all three samples as compared to other biomass e.g. garden waste pellets, coal, and algae [20]. Because of the reduced ash concentration, energy outputs are higher. It also minimizes slag formation and thus process maintenance expenses.

Table 2: Proximate and ultimate analysis, and HHV values of MSW, Bagasse, and Rice husk

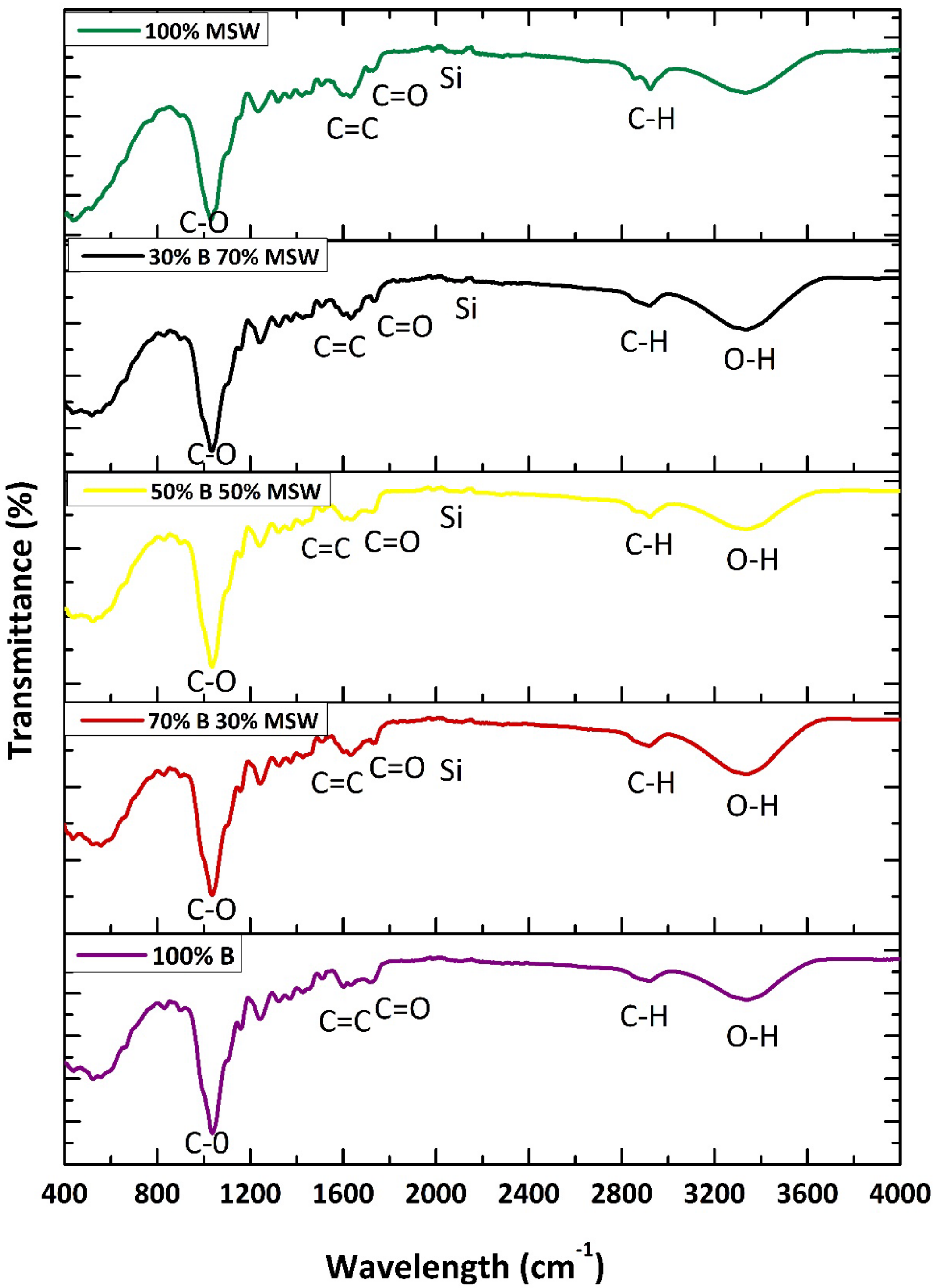
Sample	MSW	Sugarcane Bagasse (B)	Rice Husk (R)
		Ultimate Analysis (wt.%)	
Carbon (C)	42.04	43.3	47.7
Hydrogen (H)	5.95	6.11	6.7
Nitrogen (N)	0.65	0.22	0.4
Sulfur (S)	0.14	0.03	0.9
Oxygen (O)	51.2	50.3	44.3
HHV (MJ/kg)	22.4	16.4	14.7
		Proximate Analysis (wt.%)	
Moisture (M)	4.2	8.4	3.5
Volatile matter (VM)	74.5	80.9	25.4
Fixed Carbon (FC)	8.71	3.6	59.9
Ash (A)	12.6	7.9	11.2

Naqvi et al. explored the thermal behavior of multiple biomass sources, including rice husk and sugarcane bagasse, in the absence of oxygen and confirmed that these feedstocks are suitable for thermochemical conversion. The ultimate analysis results on a dry basis for MSW, sugarcane bagasse, and rice husk showed a prominent percentage of carbon and a lower percentage of hydrogen, sulfur, and nitrogen. The result obtained from previous studies [13, 14, 19] validates well the outcomes presented in this current analysis. For thermal degradation processes like gasification, the larger proportions of carbon and oxygen are advantages. It is environmentally safe because of the lower sulfur and nitrogen content [22]. The higher heating value (HHV) of sugarcane bagasse and rice husk is 16.4 and 14.7MJ/Kg, respectively. The range of HHV of agricultural biomass calculated by Garcia et al. was in the range of 11.872 to 18.893 MJ/Kg. These values indicate the potential of this biomass to be used as renewable fuel.

6.2 FTIR Analysis

Figure 1 represents FTIR curve of MSW, sugarcane bagasse, rice husk and their blends with 30, 50 and 70% ratios. The peaks around 3400-3200 cm^{-1} indicated the presence of O-H hydroxyl group in all the samples. The rice husk and sugarcane bagasse both come in the agricultural biomass category. There are no obvious differences of functional groups in both rice husk and sugarcane bagasse. The presence of peaks around 1730-1630 cm^{-1} (carbonyl C=O stretch) and 1240-1160 cm^{-1} (C-O-C stretch) give presence of cellulose and hemicellulose and the peaks in the region of 1500-1600 cm^{-1} (aromatic C=C stretching) and 830-760 cm^{-1} (aromatic C-H bending) give presence of lignin. Bands around 1100-1000 cm^{-1} (Si-O-Si stretching), 1460 cm^{-1} (CH_2 bending) and 720 cm^{-1} (CH_2 rocking) are indication of metal oxide, polyethylene, and polypropylene, which are main characteristics of MSW and the intensity becoming more visible when the amount of MSW increases in the blend. The identification of specific components was done by comparing the obtained spectrum with reference spectra from literature. [23], [24]

(a)



100% MSW
30% B 70% MSW
50% B 50% MSW
70% B 30% MSW
100% B
C-O
C=C
C=O
Si
C-H
O-H
Transmittance (%)
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Wavelength (cm^{-1})

(b)

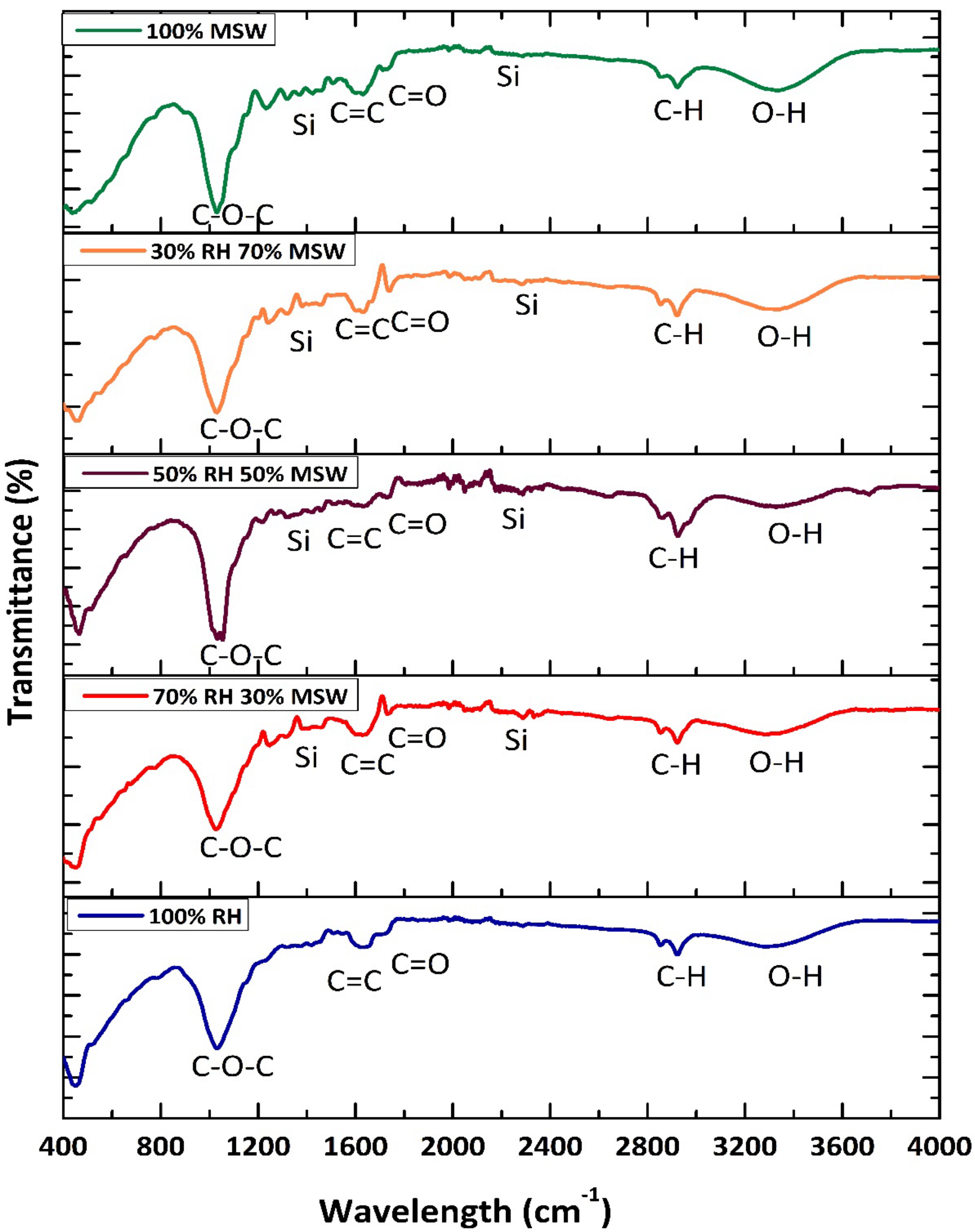
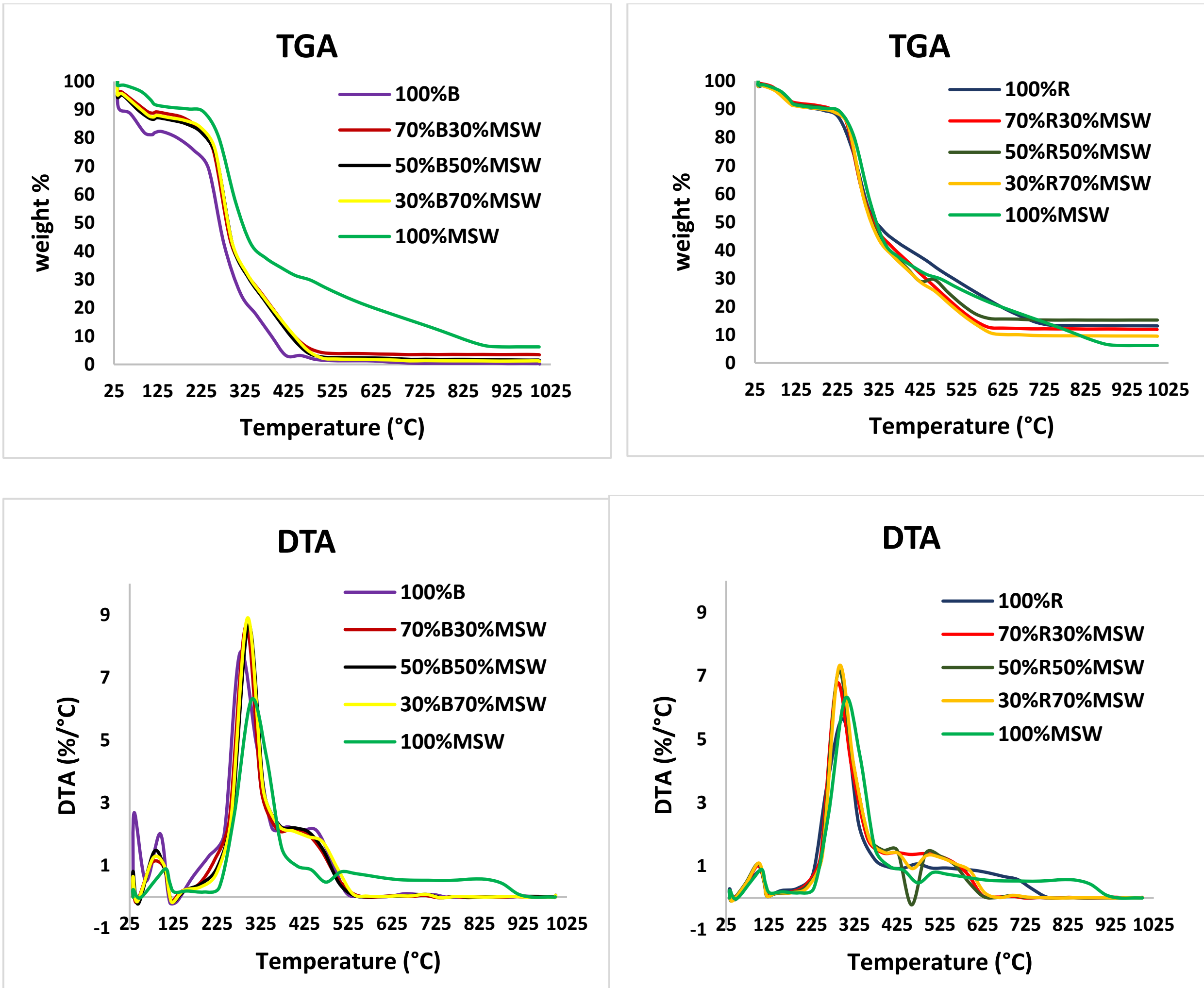


Figure 1: FTIR curves for (a) MSW and sugarcane bagasse (b) MSW and rice husk, and their blends

6.3. Thermogravimetric Analysis

TGA and DTA profiles taken under a gasification environment for MSW, sugarcane bagasse, rice husk, and their blends at a heating rate of 10°C/min are presented in Figure 2. The TGA curve is segregated into 3 main portions concerning degradation behavior over temperature. The 1st portion is from 25 to 150°C, which corresponds to the moisture loss and removal of light volatile matters. The 2nd portion is from 150 to 500°C named as the main degradation zone because the maximum compositional breakdown of MSW, bagasse, rice husk, and their blends occurs in this portion. This 2nd portion is further subdivided into two parts based on degradational substance nature. Subsection I is from 150 to 350°C for sugarcane bagasse and its blends and from 200 to 400°C for rice husk and its blends, this subsection involves degradation of organic and hemi cellulosic substances. Subsection II starts at 350 and ends at 550°C for sugarcane bagasse and its blends and from 400 to 550°C for rice husk and its blends which involves degradation of non-biodegradable organic and cellulosic substances. The 3rd portion is from 550°C and above, which explains the partial decomposition of lignin. TGA curves demonstrated that pure rice husk and sugarcane bagasse started to decompose before pure MSW. All the blends showed similar trends in the main decomposition zone. This is mostly because cellulose, hemicellulose, and lignin are present and are structured in the macro-molecular pattern with relatively weak bonds that degrade at lower temperatures.

DTA curves in Figure 2 provide details on the amount of heat gained or lost during the degrading process. Additionally, it specifies the peak temperature (T_P) at which the greatest mass loss occurs as well as the beginning and conclusion of the primary degradation. Initially, pure MSW, B, and RH decay show endothermal behavior committing maximum conversion at 50-150°C temperature range with 6 to 9% mass loss, respectively as compared to their blends. Different blends of MSW with sugarcane bagasse and rice husk give an endothermic reaction at maximum conversion temperature at 95°C with 5-7% mass loss due to moisture and low volatile components removal. As the temperature grows above 150°C, the decomposition behavior changes from endothermic to exothermic reactions. The peak temperature for 100%MSW, 100%B, and 100%RH, are 303.08, 276.80, and 300.16°C with maximum 77, 65, and 70% mass loss, respectively.



(a) **(b)**

Figure 2: TGA and DTA curves for (a) MSW and sugarcane bagasse (b) MSW and rice husk, and their blends

6.4 Kinetic Analysis

Several kinds of kinetic models with various kinetic mechanisms of gasification were employed based on information provided by TGA-DTA curves after exhibiting the gasification behavior of MSW, sugarcane bagasse, rice husk, and their blends in TGA. These results were replicated using developed mechanism functions g(α), as shown in Tables 3 and 4 for MSW with sugarcane bagasse and rice husk, respectively. Linear regression R^2 values ranging from 0.90 to 0.99 provide strong evidence regarding the accuracy and precision of the plot depicting the relationship between the model function g(α) and temperature. [21]. All the reaction models employed in the Coats-Redfern approach demonstrated highly fitting values in terms of linear regression. especially at the 2nd portion 350-550°C for both parent samples and their blends with MSW (R^2= 0.8-0.99). However, the quantities of linear regression R^2 in the temperature range 150-350°C deviated little from the standard range (0.8 – 0.99). The activation energy (E_α) refers to the minimum energy required for reactant bonds to undergo a transformation and form products. It acts as a threshold energy for the reaction to occur. The pre-exponential factor A is the quantity of molecules that must collide in one direction for the reaction to begin [13]. Eα is given by the slope derived from Arrhenius' rule, and the intercept aids in determining the value of A. It can be seen in Table 3 and Table 4 that a lower value of E_α was obtained for 50%B50%MSW and 70%RH30%MSW while an opposite trend can be observed for higher values in both samples. For sugarcane bagasse and rice husk blends with MSW, the value of E_α increased while decreasing the quantity of bagasse and rice husk. In both sample blends, E_α reduces from a high value to a low value as the temperature rises, depicting that the rate of reaction improves continuously and speeds up the gasification process, and mass loss occurs earlier. Diffusivity models give higher activation energy values for sugarcane bagasse and rice husk blends with MSW, and the power law gives lower activation energies for all blends. The pre-exponential factor A increased with temperature. The reaction will proceed depending on the value of A, which specifies the frequency of collisions between reactant molecules. The range 10^{10}–10^{12} indicates that cellulose is degrading, the value of A higher than 10^{14} indicates high energy demand due to high molecular collisions during the heat process, and the value of A 10^9 confirms the presence of just surface reaction.[21]. In the temperature range of 150 to 350°C, the values of pre-exponential factor A are in the range of 10^3 to 10^6 min^{-1}, and in the temperature range of 350 to 550°C, the range starts from 10^4 min^{-1} to 10^9 min^{-1} for blends of both biomass wastes with MSW.

The Coats-Redfern model can be used to predict the behavior of the reaction under different conditions. This predictive capability is valuable for optimizing process parameters and predicting the performance of materials under various thermal conditions. Understanding the underlying mechanisms is crucial for the design and optimization of processes in various fields, including materials science and chemistry. Comprehensively, the novelty in using the Coats-Redfern model lies in its versatility, interpretative power, predictive capability, insights into reaction mechanisms, and its utility for comparative studies, ultimately contributing to a more comprehensive understanding of thermal decomposition kinetics. It gives a predictable range of parameters with certain reaction mechanisms to develop the process at a commercial scale. [25], [26]

Table 3: Kinetic Parameters of Sugarcane Bagasse, MSW and its blends

Symbol	Sample	Temperature (150-350°C)			Temperature (350-550°C)		
		R^2	E_α kJ/mole	A min^{-1}	R^2	E_α kJ/mole	A min^{-1}
R1	70%B30%MSW	0.84	35.64877	5759.682	0.19	1.401075	482570.6
	50%B 50%MSW	0.81	33.25683	6326.368	0.27	2.48705	931223
	30%B70%MSW	0.9	47.98508	5056.216	0.32	2.90142	1029181
R2	70%B30%MSW	0.83	38.85382	5615.294	0.91	10.50723	127212.4
	50%B 50%MSW	0.81	36.53837	6059.445	0.37	4.599721	334636.4
	30%B70%MSW	0.9	52.52037	5034.298	0.69	7.541629	217231.2
R3	70%B30%MSW	0.75	33.27595	5161.645	0.96	222.9981	8.14E+12
	50%B 50%MSW	0.73	32.71226	5189.199	0.96	183.5731	8.08E+09
	30%B70%MSW	0.85	47.54693	5007.885	0.96	203.8676	1.86E+11
R4	70%B30%MSW	0.9	25.26209	6161.77	0.68	13.85611	14361
	50%B 50%MSW	0.77	22.18591	8483.525	0.97	63.37097	9501.772
	30%B70%MSW	0.74	21.19239	9440.401	0.95	49.4949	9519.983
F1	70%B30%MSW	0.89	19.88293	9922.147	0.04	0.831816	172254.8
	50%B 50%MSW	0.76	19.05735	13329.01	0.99	26.65718	11517.87
	30%B70%MSW	0.74	17.95741	15837.85	0.88	18.66576	17583.66
F2	70%B30%MSW	0.88	15.25785	39372.08	0.97	8.59917	2612044
	50%B 50%MSW	0.77	16.2281	41790.69	0.92	4.883477	312049.4
	30%B70%MSW	0.73	15.04169	53630.2	0.32	2.302978	492610.2
F3	70%B30%MSW	0.88	16.71945	39717.53	0.92	6.722368	2276573
	50%B 50%MSW	0.77	17.14014	47744.68	0.99	10.5804	152700.4
	30%B70%MSW	0.74	15.98034	61274.68	0.76	6.682211	296145.1
A1	70%B30%MSW	0.83	10.37421	41607.19	0.75	4.650519	484466.7
	50%B 50%MSW	0.68	10.04082	54563.01	0.99	13.92429	33818.68

	30%B70%MSW	0.63	9.187801	65596.96	0.76	8.360558	73587.2
A2	**70%B30%MSW**	0.73	5.605216	105207.7	0.91	6.565566	822104.7
	50%B 50%MSW	0.53	5.396119	129243.7	0.98	7.36504	97228.32
	30%B70%MSW	0.46	4.789862	148630.6	0.44	3.192493	190454.3
A4	**70%B30%MSW**	0.49	1.533767	456802.3	0.99	9.432233	1823419
	50%B 50%MSW	0.27	1.434664	484740.2	0.97	2.280863	587887.9
	30%B70%MSW	0.36	1.793995	527823.9	0.84	4.5441	865478
P4	**70%B30%MSW**	0.92	3.663897	811129.8	0.99	11.76764	3934983
	50%B 50%MSW	0.75	2.776128	704415.3	0.99	10.26114	2946796
	30%B70%MSW	0.79	3.173454	772581.5	0.99	11.05679	3374707
P2	**70%B30%MSW**	0.27	1.344956	323698.2	0.99	11.83498	3811356
	50%B 50%MSW	0.37	2.713191	268814.1	0.98	8.595013	2272043
	30%B70%MSW	0.23	2.030861	314279.3	0.98	9.832136	2806338
D3	**70%B30%MSW**	0.92	42.11207	5591.818	0.075	1.145503	1277562
	50%B 50%MSW	0.83	42.54523	5986.339	0.99	33.08806	14879.77
	30%B70%MSW	0.81	40.33787	6663.868	0.86	22.96826	40476.99
D4	**70%B30%MSW**	0.92	38.12967	6738.017	0.9	6.403942	5772680
	50%B 50%MSW	0.84	40.07597	6966.676	0.97	17.14763	143957
	30%B70%MSW	0.81	37.79628	8364.047	0.66	9.951027	474596.4

Table 4: Kinetic Parameters of Rice Husk, MSW, and its blends

Symbol	**Sample**	**Temperature (200-400°C)**			**Temperature (400-550°C)**		
		R^2	**E_α kJ/mole**	**A min^{-1}**	**R^2**	**E_α kJ/mole**	**A min^{-1}**
R1	**70%RH30%MSW**	0.88	50.82	6.05 E+03	0.05	0.69	7.08 E+05
	50%RH 50%MSW	0.88	52.03	6.04 E+03	0.09	1.16	9.13 E+05
	30%RH70%MSW	0.88	50.89	6.05 E+03	0.07	0.73	8.82 E+05
R2	**70%RH30%MSW**	0.9	55.75	6.03 E+03	0.9	8.82	2.49 E+05
	50%RH 50%MSW	0.9	57.74	6.02 E+03	0.72	7.44	2.96 E+05
	30%RH70%MSW	0.9	56.13	6.03 E+03	0.88	7.70	2.99 E+05

R3	**70%RH30%MSW**	0.95	51.85	6.00 E+03	0.9	187.45	7.75 E+08
	50%RH 50%MSW	0.96	59.54	6.00 E+03	0.94	243.17	3.45 E+12
	30%RH70%MSW	0.95	54.45	6.00 E+03	0.92	207.55	8.17 E+09
R4	**70%RH30%MSW**	0.91	33.66	6.40 E+03	0.91	52.43	1.10 E+04
	50%RH 50%MSW	0.93	37.28	6.18 E+03	0.95	66.53	1.10 E+04
	30%RH70%MSW	0.92	35.03	6.33 E+03	0.93	57.28	1.10 E+04
F1	**70%RH30%MSW**	0.9	29.08	7.37 E+03	0.93	21.19	2.02 E+04
	50%RH 50%MSW	0.91	31.22	6.80 E+03	0.95	25.66	1.56 E+04
	30%RH70%MSW	0.9	29.67	7.22 E+03	0.95	22.63	1.91 E+04
F2	**70%RH30%MSW**	0.86	24.65	1.43 E+04	0.73	2.63	6.02 E+05
	50%RH 50%MSW	0.87	25.91	1.20 E+04	0.48	2.60	5.95 E+05
	30%RH70%MSW	0.86	24.90	1.39 E+04	0.71	2.28	6.50 E+05
F3	**70%RH30%MSW**	0.87	26.07	1.47 E+04	0.92	7.50	3.60 E+05
	50%RH 50%MSW	0.88	27.60	1.19 E+04	0.88	8.45	3.09 E+05
	30%RH70%MSW	0.87	26.43	1.41 E+04	0.94	7.57	3.70 E+05
A1	**70%RH30%MSW**	0.85	16.27	2.25 E+04	0.87	9.77	8.41 E+04
	50%RH 50%MSW	0.87	17.69	1.75 E+04	0.92	12.63	5.80 E+04
	30%RH70%MSW	0.85	16.76	2.09 E+04	0.91	10.71	7.78 E+04
A2	**70%RH30%MSW**	0.79	9.85	6.32 E+04	0.69	4.04	2.17 E+05
	50%RH 50%MSW	0.81	10.90	4.99 E+04	0.85	6.10	1.61 E+05
	30%RH70%MSW	0.78	10.11	6.02 E+04	0.78	4.57	2.10 E+05
A3	**70%RH30%MSW**	0.49	3.43	2.05 E+05	0.51	1.69	5.94 E+05
	50%RH 50%MSW	0.57	4.12	1.73 E+05	0.05	0.43	4.91 E+05
	30%RH70%MSW	0.5	3.58	1.99 E+05	0.49	1.47	5.90 E+05
P4	**70%RH30%MSW**	0.34	1.86	6.28 E+05	0.99	11.38	3.66 E+06
	50%RH 50%MSW	0.31	1.74	6.05 E+05	0.99	11.92	3.95 E+06
	30%RH70%MSW	0.34	1.91	6.36 E+05	0.99	11.90	3.95 E+06
P2	**70%RH30%MSW**	0.58	5.67	1.69 E+05	0.98	9.66	2.89 E+06
	50%RH 50%MSW	0.59	5.94	1.56 E+05	0.98	10.39	3.21 E+06
	30%RH70%MSW	0.56	5.63	1.70 E+05	0.99	10.30	3.19 E+06
D3	**70%RH30%MSW**	0.91	61.52	6.03 E+03	0.97	28.10	3.74 E+04

	50%RH 50%MSW	0.92	64.62	6.01 E+03	0.96	30.37	2.92 E+04
	30%RH70%MSW	0.91	62.32	6.03 E+03	0.98	28.64	3.73 E+04
D4	**70%RH30%MSW**	0.9	57.66	6.08 E+03	0.96	14.50	3.63 E+05
	50%RH 50%MSW	0.91	60.01	6.05 E+03	0.9	14.02	3.80 E+05
	30%RH70%MSW	0.9	58.17	6.08 E+03	0.98	13.83	4.17 E+05

6.5 Thermodynamic Analysis

The peak temperature at which maximal degradation occurs, along with the kinetic characteristics, serve as the basis for evaluating thermodynamic parameters, which can be done using DTA data. Tables 5 and 6 show that values in the first temperature zone vary in enthalpy and Gibbs free energy more than values in the second temperature zone. It can be seen in Tables 5 and 6 that a lower value of ΔH was obtained for 50%B50%MSW and 70%RH30%MSW while an opposite trend can be observed for higher values in both samples. For sugarcane bagasse and rice husk blends with MSW, the value of ΔH increased while decreasing the quantity of bagasse and rice husk. In both sample blends, the value of ΔH declines from a high value to a low value as temperature rises, and mass loss occurs earlier. MSW, Sugarcane bagasse, rice husk, and their blends exhibit the positive value of ΔH in all selected reaction mechanism models in the entire main decomposition zone. Positive ΔH specifies the exothermic nature of the reaction. ΔG represents the system's energy buildup as a result of reactant degradation [27]. For all models of the aforementioned reaction mechanisms, the change in entropy in both temperature zones is negative. Negative entropy values, in which degrees of freedom are lost as a result of the development of an active complex, may be caused through the association mechanism [28]. Diffusivity models give higher change in enthalpy energy values and change in Gibbs free energy for sugarcane bagasse and rice husk blends with MSW, and power law gives lower values of change in enthalpies and Gibbs free energy for all parent samples and their blends.

Table 5: Thermodynamic Parameters of Sugarcane bagasse, MSW and its blends

Symbol	Sample	Temperature (150-350°C)			Temperature (350-550°C)		
		ΔH kJ/mole	ΔG kJ/mole	ΔS KJ/mole	ΔH KJ/mole	ΔG KJ/mole	ΔS KJ/mole
R1	**70%B30%MSW**	33.57	85.56	-0.18	-2.55	61.55	-0.15
	50%B 50%MSW	31.18	83.96	-0.18	-1.46	61.10	-0.14
	30%B70%MSW	45.91	98.79	-0.18	-1.05	60.79	-0.14
R2	**70%B30%MSW**	36.78	88.82	-0.18	6.56	75.42	-0.16
	50%B 50%MSW	34.46	87.34	-0.18	0.65	66.92	-0.15
	30%B70%MSW	50.44	103.34	-0.18	3.59	71.04	-0.16
R3	**70%B30%MSW**	31.20	83.45	-0.18	219.05	223.69	-0.01
	50%B 50%MSW	30.63	83.90	-0.18	179.62	209.33	-0.07
	30%B70%MSW	45.47	98.38	-0.18	199.92	218.18	-0.04
R4	**70%B30%MSW**	20.11	71.16	-0.18	59.42	137.56	-0.18
	50%B 50%MSW	19.11	70.90	-0.17	45.55	124.71	-0.18
	30%B70%MSW	29.62	82.32	-0.18	52.55	131.26	-0.18
F1	**70%B30%MSW**	16.98	66.93	-0.17	22.71	100.16	-0.18
	50%B 50%MSW	15.88	66.39	-0.17	14.72	91.66	-0.18
	30%B70%MSW	25.17	77.45	-0.18	18.61	95.94	-0.18
F2	**70%B30%MSW**	14.15	61.34	-0.16	0.93	66.59	-0.15
	50%B 50%MSW	12.96	60.46	-0.16	-1.65	63.22	-0.15
	30%B70%MSW	21.15	71.65	-0.17	-1.26	63.41	-0.15
F3	**70%B30%MSW**	15.06	61.93	-0.16	6.63	74.84	-0.16
	50%B 50%MSW	13.90	61.07	-0.16	2.73	69.44	-0.15
	30%B70%MSW	22.44	72.83	-0.17	3.90	70.82	-0.15
A1	**70%B30%MSW**	7.96	54.51	-0.16	9.98	83.57	-0.17
	50%B 50%MSW	7.11	54.11	-0.16	4.41	76.17	-0.16
	30%B70%MSW	13.19	62.54	-0.17	7.02	79.58	-0.17
A2	**70%B30%MSW**	3.32	47.77	-0.15	3.42	73.24	-0.16
	50%B 50%MSW	2.71	47.69	-0.15	-0.76	67.55	-0.16

	30%B70%MSW	7.18	54.01	-0.16	1.21	70.15	-0.16
A4	**70%B30%MSW**	-0.64	40.61	-0.14	-1.67	61.73	-0.15
	50%B 50%MSW	-0.28	41.57	-0.14	0.59	63.42	-0.14
	30%B70%MSW	-1.81	40.77	-0.14	-0.41	62.61	-0.15
P4	**70%B30%MSW**	0.70	41.05	-0.14	6.31	63.95	-0.13
	50%B 50%MSW	1.09	42.01	-0.14	7.11	65.00	-0.13
	30%B70%MSW	-0.44	40.93	-0.14	6.83	64.55	-0.13
P2	**70%B30%MSW**	0.63	43.32	-0.15	4.65	63.21	-0.14
	50%B 50%MSW	-0.05	43.08	-0.15	5.88	64.45	-0.13
	30%B70%MSW	3.38	47.91	-0.15	5.36	63.88	-0.14
D3	**70%B30%MSW**	40.47	92.36	-0.18	29.14	105.67	-0.18
	50%B 50%MSW	38.26	90.91	-0.18	19.02	92.94	-0.17
	30%B70%MSW	55.69	108.58	-0.18	23.99	99.36	-0.17
D4	**70%B30%MSW**	38.00	89.52	-0.18	13.20	81.62	-0.16
	50%B 50%MSW	35.72	87.81	-0.18	6.00	71.00	-0.15
	30%B70%MSW	52.18	105.04	-0.18	9.55	76.08	-0.15

Table 6: Thermodynamic Parameters of Rice husk, MSW, and its blends

Symbol	**Sample**	**Temperature (200-400°C)**			**Temperature (400-550°C)**		
		ΔH kJ/mole	**ΔG kJ/mole**	**ΔS KJ/mole**	**ΔH KJ/mole**	**ΔG KJ/mole**	**ΔS KJ/mole**
R1	**70%RH30%MSW**	48.33	99.67	-0.18	-3.89	68.29	-0.15
	50%RH50%MSW	49.54	101.41	-0.18	-3.41	68.01	-0.15
	30%RH70%MSW	48.40	100.64	-0.18	-3.84	68.01	-0.15
R2	**70%RH30%MSW**	53.26	104.61	-0.18	4.25	80.69	-0.16
	50%RH50%MSW	55.25	107.13	-0.18	2.87	78.89	-0.15
	30%RH70%MSW	53.63	105.89	-0.18	3.12	79.42	-0.15
R3	**70%RH30%MSW**	49.36	100.72	-0.18	182.87	226.55	-0.09
	50%RH50%MSW	57.04	108.92	-0.18	238.60	248.08	-0.02
	30%RH70%MSW	51.96	104.22	-0.18	202.98	237.31	-0.07

R4	**70%RH30%MSW**	31.17	82.38	-0.18	47.85	136.98	-0.18
	50%RH50%MSW	34.78	86.60	-0.18	61.96	151.45	-0.18
	30%RH70%MSW	32.54	84.68	-0.18	52.71	142.57	-0.18
F1	**70%RH30%MSW**	26.59	77.47	-0.18	16.61	103.27	-0.18
	50%RH50%MSW	28.73	80.31	-0.18	21.09	109.14	-0.18
	30%RH70%MSW	27.18	79.00	-0.18	18.06	105.66	-0.18
F2	**70%RH30%MSW**	22.15	71.47	-0.17	-1.94	70.90	-0.15
	50%RH50%MSW	23.41	73.65	-0.18	-1.97	71.20	-0.15
	30%RH70%MSW	22.41	72.66	-0.17	-2.30	70.81	-0.15
F3	**70%RH30%MSW**	23.58	72.82	-0.17	2.92	77.85	-0.15
	50%RH50%MSW	25.11	75.36	-0.18	3.88	79.73	-0.15
	30%RH70%MSW	23.94	74.15	-0.17	3.00	78.42	-0.15
A1	**70%RH30%MSW**	13.78	62.04	-0.17	5.19	86.05	-0.17
	50%RH50%MSW	15.20	64.53	-0.17	8.06	90.76	-0.17
	30%RH70%MSW	14.27	63.54	-0.17	6.13	87.96	-0.17
A2	**70%RH30%MSW**	7.36	53.18	-0.16	-0.53	76.46	-0.16
	50%RH50%MSW	8.41	55.26	-0.16	1.53	80.04	-0.16
	30%RH70%MSW	7.61	54.35	-0.16	-0.01	77.75	-0.16
A3	**70%RH30%MSW**	0.93	43.99	-0.15	-2.89	70.01	-0.15
	50%RH50%MSW	1.62	45.51	-0.15	-4.14	69.82	-0.15
	30%RH70%MSW	1.08	44.96	-0.15	-3.11	70.40	-0.15
P4	**70%RH30%MSW**	-0.64	39.78	-0.14	6.81	72.30	-0.13
	50%RH50%MSW	-0.76	40.15	-0.14	7.35	72.78	-0.13
	30%RH70%MSW	-0.58	40.50	-0.14	7.33	73.02	-0.13
P2	**70%RH30%MSW**	3.18	46.69	-0.15	5.08	71.53	-0.14
	50%RH50%MSW	3.45	47.59	-0.15	5.81	72.10	-0.13
	30%RH70%MSW	3.14	47.38	-0.15	5.73	72.31	-0.13
D3	**70%RH30%MSW**	59.03	110.38	-0.18	23.53	107.68	-0.17
	50%RH50%MSW	62.12	114.00	-0.18	25.79	111.29	-0.17
	30%RH70%MSW	59.82	112.08	-0.18	24.06	108.91	-0.17
D4	**70%RH30%MSW**	55.17	106.50	-0.18	9.93	84.83	-0.15

50%RH50%MSW	57.52	109.39	-0.18	9.45	84.45	-0.15
30%RH70%MSW	55.68	107.91	-0.18	9.26	84.19	-0.15

6.6 Synergistic effects during co-gasification

A comparison between the experimental and calculated weight losses reveals the extent of synergistic effects 70%RH30%MSW, 50%RH50%MSW, 30%RH70%MSW, and 70%B30%MSW. 50%B50%MSW and 30%B70%MSW biomass blends during co-gasification as shown in figure 3. This interaction was particularly pronounced within a specified temperature range, as detailed in Table 7. Notably, temperature ranges of 400–800 °C and 400–750 °C exhibited positive synergy in 70%RH30%MSW, 30%RH70%MSW, and 50%RH50% MSW blends respectively during the co-gasification process. Strong negative synergy was observed during the initial volatile removal phase below 350°C and gas formation above 800 °C, while positive synergy prevailed in the main conversion zone.

The sugarcane bagasse blends with MSW blends show a more positive trend towards positive synergy as compared to rice husk and MSW blends throughout the process. The temperature range temperature range of 250-300 °C only exhibited negative synergy in 70%B30%MSW and 50%RH50%MSW blends. Other than all ranges show a positive effect on all the available ranges till 1000 °C. The blend of 30%B70% MSW shows a positive synergetic effect throughout the conversion process. The introduction of sugarcane bagasse into MSW shifted the positive synergy to the wider temperature range, suggesting that bagasse and MSW are reacting as a unified component in contrast to the RH and MSW blend.

Table 7. Synergy analysis for RH, B, and MSW blends during co-gasification.

Blends	Temperature °C	Interactions	Synergetic Effects
70%RH30%MSW	30-400	Experimental value higher than calculated.	Negative
	400-800	**Experimental value lower than calculated.**	**Positive**
	900-1000	Experimental value higher than calculated.	Negative

50%RH50%MSW	30-350	Experimental value higher than calculated.	Negative
	350-700	**Experimental value lower than calculated**.	**Positive**
	700-1000	Experimental value higher than calculated	Negative
30%RH70%MSW	30-200	Overlapped	Neutral
	200-400	Experimental value higher than calculated.	Negative
	400-800	**Experimental value lower than calculated**	**Positive**
	800-1000	. Experimental value higher than calculated	Negative
70%B30%MSW	30-250	Experimental value higher than calculated.	Negative
	250-850	**Experimental value lower than calculated**.	**Positive**
	850-1000	Experimental value higher than calculated	Negative
50%B50%MSW	**30-250**	**Experimental value lower than calculated.**	**Positive**
	250-300	Experimental value higher than calculated.	Negative
	300-1000	**Experimental value lower than calculated**	**Positive**
30%B70%MSW	**30-1000**	**Experimental value lower than calculated.**	**Positive**

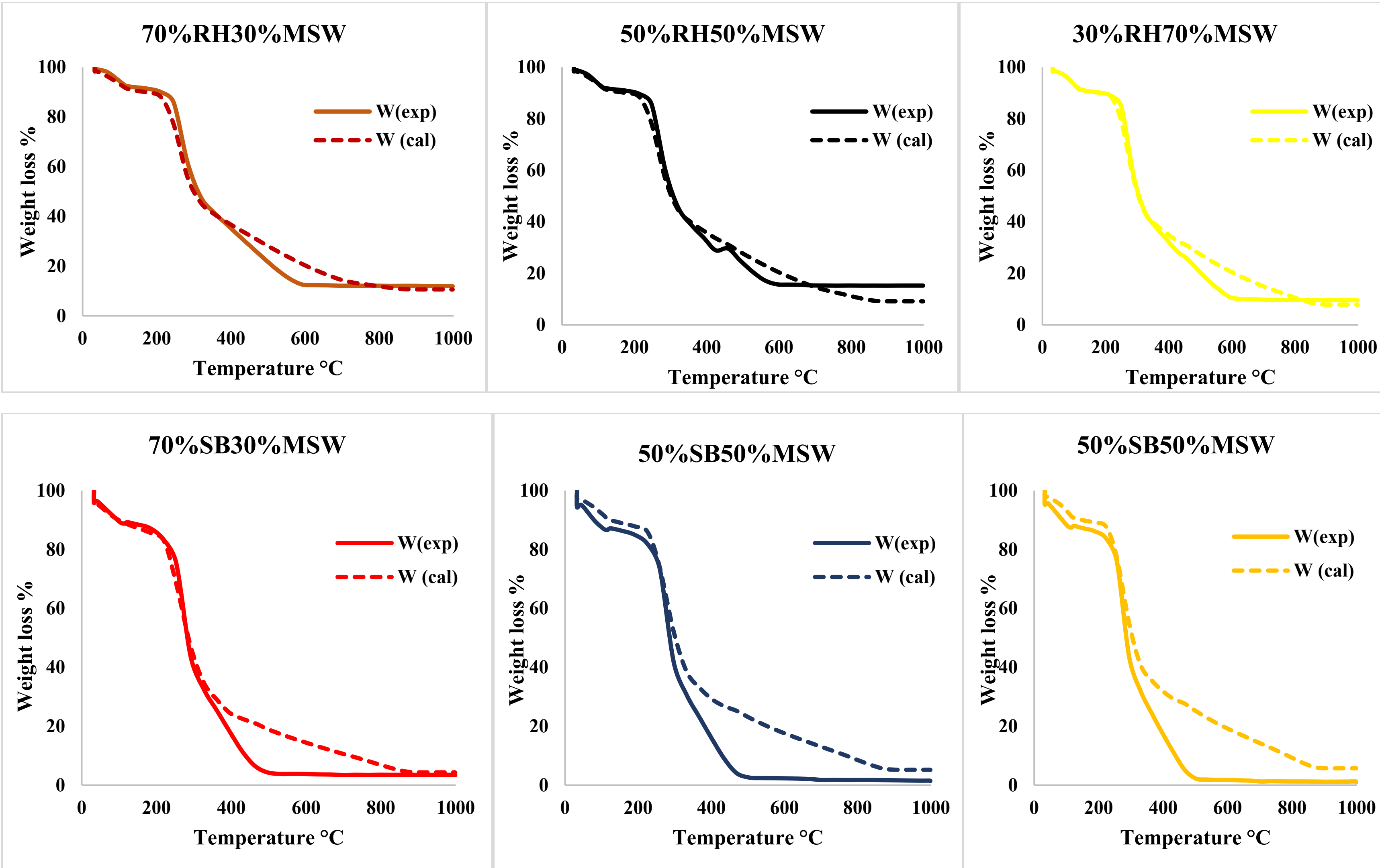


Figure 3: Experimental and calculated weight loss curves for RH and B blends with MSW in different ratio

7. Comparison with Previous Literature

Table 8 displays the values of kinetic and thermodynamic parameters of MSW and agriculture biomass along with data from the literature. Edreis et al.[29] studied the kinetic parameters of sugarcane bagasse with petroleum coke and the results showed that the boundary-controlled reaction model (R^2) depicts the minimum values of $E\alpha$ for all the blends. Maham et al.[22] explored the kinetic profile of rice husk and coal blends to investigate mechanistic behavior and explored that adding more percentage of rice husk into coal proved to be advantageous in decreasing values of activation energy and enthalpy which is in good agreement with the current study. According to Yanhui et al.[30], the addition of MSW with agriculture biomass in an equal ratio gives average optimal activation energy whose value was 191.37 kJ/mole which was much higher than our current studies. Mohapatra et al.[31] studied the thermodynamic profile of sugarcane bagasse and expanded plastic waste and identified that 3:1 was the optimal ratio with enthalpy in the range of 74-193kJ/mole and the Gibbs free energy was from 100-186kJ/mole. The current study shows that if the MSW material is used along with sugarcane bagasse and rice husk it gives much lower activation energies and changes in enthalpy, especially for the initial temperature ranges in all reaction mechanisms.

Table 8: Comparative study of Kinetic and thermodynamic parameters with literature using Coats – Redfern method.

Biomass	Heating rate °C/min	Kinetic Parameters KJ/mole	Thermodynamic Parameters KJ/mole	Ref.
Sugarcane Bagasse/coke blends	20	E_α: 33-171	-	[29]
Municipal solid waste	10, 20, 40	E_α:109.89–119.86, 99.64–109.09	-	[32]
Municipal solid waste	10	E_α: 22-69	-	[33]
Coal/Rice husk	20	E_α: 5-99	ΔH: -3-95 ΔG: 445-535	[22]
Sugarcane Bagasse/Municipal Solid waste	5, 10, 15, 20	E_α:1.08-42.54, 1.14-183	ΔH: -0.2-37.99, -0.75-179	Current study
Rice husk/Municipal Solid waste	5, 10, 15, 20	E_α:1.73-64.61, 0.14-187.4	ΔH: -0.63-59.02, -3.88-189	Current study

8. Conclusion

In this work, the gasification of MSW, sugarcane bagasse, rice husk, and their blends have been investigated through TGA, using Coats – Redfern models for kinetic and thermodynamic analysis. MSW (Municipal Solid Waste), sugarcane bagasse, and rice husk offer several advantages as eco-friendly fuels, having high volatility. The peak temperatures and weight loss patterns observed in these samples indicate that their structures are highly susceptible to thermal degradation. 50% Bagasse 50% MSW 70% Rice Husk 30% MSW show higher reactivity and lower activation energy than all other contemporary biomass. This research might be useful for planning and modeling a thermochemical conversion system based on a mixture of MSW and biomass wastes at the commercial level.

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