Chapter 6

Energy and exergy analysis for the torrefaction and pyrolysis of raw and torrefied biomass

6.1 Overview

This chapter focuses on the energy perspective involved in the pre-treatment of biomass through torrefaction and followed with their pyrolysis. In order to have a better understanding and discussion, the Chapter 6 includes the comparative study between the pyrolysis of raw and torrefied biomass on energy-exergy analysis basis. The Chapter 6 also includes the theoretical analysis for the possibility of tapping or recuperating energy from by-products obtained during torrefaction or pyrolysis process in order to increase its overall efficiency and thus meeting or decreasing the energy required by the furnace.

6.2 Materials and Methods

6.2.1 Material Selection

The biomass feed for the torrefaction purpose have been pigeon pea stalk and eucalyptus, while for the pyrolysis purpose both raw and torrefied biomass (feed at the optimum torrefaction condition as obtained in the Chapter 3) have been used. The procedure involved in the preparation of raw and torrefied biomass have already been discussed in the Chapter 3.

6.2.2 Experimental procedure

Based on the statistical analysis of both torrefaction and pyrolysis as discussed in the Chapter 3 and Chapter 5, respectively, it has been found that temperature in both the processes has the maximum influence on the qualitative and quantitative analysis of the desired products. Hence, for better comparison and to maintain the uniformity between both the biomass for their energy and exergy analysis of torrefaction and pyrolysis only temperature has been varied while maintaining other parameters to a constant value which lies at their respective moderate range. The torrefaction of both the biomass have been performed at 200, 250 and 300 °C while maintaining the residence time at 30 min and heating rate at 15 °C/min. On the other side for the pyrolysis of raw and torrefied biomass the operating conditions have been kept at 350, 450 and 550 °C while maintaining the residence time at 15 min, heating rate at 40 °C and nitrogen sweeping rate at 70 ml/min.

6.2.3 Energy analysis

In present chapter all energy and exergy calculations have been represented in kJ per kg of biomass feed (raw/torrefied biomass). In order to compute the energy recovery, energy streams in and out of the torrefaction or pyrolysis system have been mentioned in the control volume as illustrated in Fig. 6.1. The energy inputs that have been considered in the present study have been the energy of raw or torrefied biomass and the electrical energy input to the furnace. The system boundary have been defined at ambient condition (T_o and P_o) as given in Fig. 6.1 and other small energy inputs (like chiller and MFC) and outputs

(physical energy of solid and liquid) have been neglected in the present study. Energy recovery in products (%) can be defined as in Eq. (6.1):

$$\textbf{Energy recovery in products (\%)} = \frac{\textbf{Useful energy output}}{\textbf{Energy input}} \times \textbf{100} \qquad (6.1)$$

Energy input has been the summation of energy from raw or torrefied biomass and electricity, and energy output has been from torrefied-biomass/bio-char, torrefaction-liquid/bio-oil and torgas/pyrolytic gas product obtained after torrefaction process.
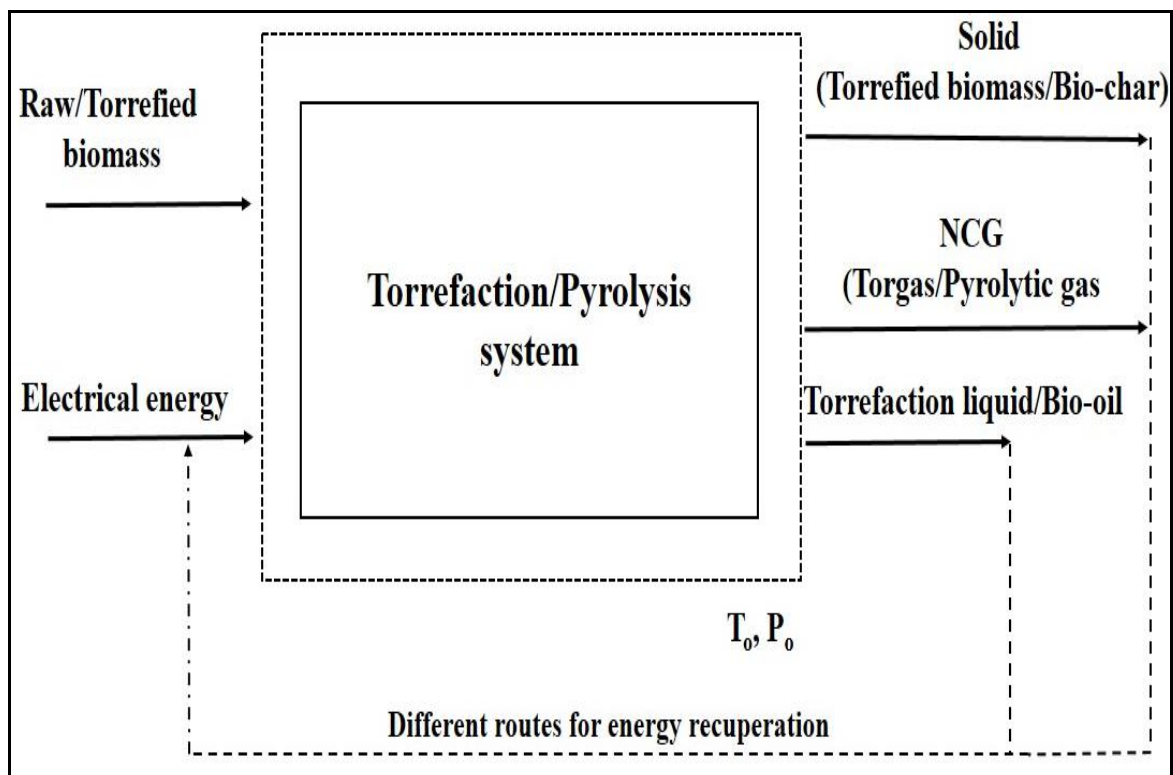

Fig. 6.1 Energy and exergy flows for both torrefaction and pyrolysis system.

6.2.3.1 Energy of NCG (torgas/pyrolytic gas)

Table. 6.1 Standard specific enthalpy, entropy, HHV and standard chemical exergy of NCG (Liu et al., 2014; Wang et al., 2016)

	H_2	CO	CO_2	CH_4
S_0, (kJ/kmol-K)	130.6	197.5	213.7	186.1
h_0, (kJ/kmol)	8468	8669	9364	-
HHV, (kJ/kmol)	285840	282990	-	890360
ex^{std}, (kJ/kmol)	236100	275100	19870	831650

Total energy (En_{Total}) carried away by NCG has been the sum of all kinds of energy values (Wang et al., 2016; Zhang et al., 2011) and has been given by Eq. (6.2):

$$En_{Total} = En_{PHY} + En_{CHE} + En_{KE} + En_{PE} \tag{6.2}$$

The kinetic and potential energy of the non-condensable gases have been small enough and may be neglected. Hence, the total energy equation simplifies as Eq. (6.3):

$$En_{Total} = En_{PHY} + En_{CHE} \tag{6.3}$$

Where physical and chemical energy of NCG can be calculated using Eq. (6.4) and (6.5), respectively.

$$En_{PHY}^{NCG} = \sum n_i h_i \tag{6.4}$$

$$En_{CHE}^{NCG} = \sum n_i HHV_i \tag{6.5}$$

Under standard condition the specific enthalpy (h_o) and HHV of the individual gas components have been given in Table 6.1 (Liu et al., 2014; Wang et al., 2016).

6.2.3.2 Energy of solid product (torrefied biomass/bio-char)

As discussed in Section 6.2.4, the kinetic energy and potential energy during torrefaction or pyrolysis process may be neglected. Further the physical energy of the solid can be neglected in comparison to its chemical energy and hence the total energy (En_{Total}) of solid product has been due to the chemical energy (Boateng et al., 2012; Wang et al., 2016) and has been given by Eq. (6.6) and the chemical energy can be calculated by using Eq. (6.7):

$$En_{Total} = En_{CHE} \tag{6.6}$$

$$En_{CHE}^{Solid} = M_{solid} \times HHV_{Soild} \tag{6.7}$$

6.2.3.3 Energy of liquid product (torrefaction liquid/bio-oil)

Similarly as mentioned in Sections 6.2.4 and 6.2.5, the physical energy of the liquid has been negligible in comparison to its chemical energy and hence the total energy (En_{Total}) has been due to the chemical energy and the same has been given in Eq. (6.6). The chemical energy of the liquid product obtained during torrefaction or pyrolysis can be calculated by Eq. (6.8):

$$En_{CHE}^{liquid} = M_{liquid} \times HHV_{liquid} \tag{6.8}$$

6.2.3.4 Energy of raw biomass

The kinetic, potential and physical energy of the raw biomass has been negligible in comparison to its chemical energy and hence, the total energy (En_{Total}) has been due to its chemical energy and the same has been given in Eq. (6.6). The chemical energy of biomass can be calculated by using Eq. (6.9):

$$En_{CHE}^{raw\,biomass} = M_{raw\,biomass} \times HHV_{raw\,biomass} \tag{6.9}$$

6.2.4 Exergy calculation

Exergy of a substance may be defined as the maximum theoretical work available when it achieves equilibrium with the environment. Due to the presence of some unavoidable irreversibility, the exergy does not follow conservation law (Wang et al., 2016). However, after considering some assumptions such as torrefaction and pyrolysis occurs within a control volume, input exergy is from raw or torrefied biomass and electric heat, while output exergy consists of solid, liquid and gas product obtained during torrefaction or pyrolysis, and the internal exergy loss (irreversibility) has been from the lost part. Hence, on the basis of these assumptions the exergy balance equation can be given as in Eq. (6.10):

$$Ex_{raw\,biomass} + Ex_{electricity} = Ex_{solid} + Ex_{liquid} + Ex_{NCG} + Ex_{irreversibility} \tag{6.10}$$

$Ex_{electricity}$ has been the total exergy value of electrical power consumption of the furnace (considered work) and has been equivalent to electrical energy (Boateng et al., 2012; Moran, 2008). $Ex_{irreversibility}$ denotes the exergy loss during torrefaction or pyrolysis process.

6.2.3.2   Exergy of NCG (torgas/pyrolytic gas)

Total exergy (Ex_{Total}) of the NCG has been the summation of all the exergy values associated with it at the given condition and can calculated as given in Eq. (6.11):

$$Ex_{Total} = Ex_{PHY} + Ex_{CHE} + Ex_{KE} + Ex_{PE} \tag{6.11}$$

Where Ex_{KE} and Ex_{PE} is the kinetic and potential exergy of the non-condensable gases and can be neglected. Hence, the total exergy (Ex_{Total}) can be expressed as in Eq. (6.12):

$$Ex_{Total} = Ex_{PHY} + Ex_{CHE} \tag{6.12}$$

The physical exergy of NCG can be calculated by using the Eq. (6.13):

$$Ex_{PHY}^{NCG} = n_i[(h - h_0) - T_0(s - s_0)] \tag{6.13}$$

The C_p for the NCG components can be calculated using the empirical formula as given Eq. (6.14):

$$C_p = a + bT + cT^2 + dT^3 \tag{6.14}$$

Where a, b, c and d have been the constant coefficients (independent of temperature) and Table 6.2 presents the values of these coefficients for the individual gases (Peters et al., 2014).

Table. 6.2 Value of the coefficients for the constant pressure specific heat of NCG (Peters et al., 2014)

Gas	a	$b*10^2$	$C*10^5$	$d*10^9$	Temperature range, (^oC)
H_2	29.11	-0.192	0.4	-0.87	0-1500
CO	28.16	0.168	0.533	-2.222	0-1500
CO_2	22.26	5.981	-3.501	7.469	0-1500
CH_4	19.89	5.024	1.269	-11.01	0-1500

Ex_{CHE} of the NCG (Wolff, 1997) can be calculated by using the Eq. (6.15):

$$Ex_{CHE}^{NCG} = \sum n_i \left(ex_i^{std} + RT_0 \ln \gamma_i Y_i\right) \tag{6.15}$$

Where ex_i has been the specific chemical exergy of individual gases at standard condition and its values has been represented in Table 6.1. Also, γ_i has been the activity coefficient of the individual gases (considered unity for ideal mixture) and Y_i has been the mole fraction of the individual gases.

6.2.4.2   **Exergy of solid product (torrefied biomass/bio-char)**

Total exergy of solid and liquid products can be calculated by using Eq. (6.12). However, the physical exergy of the solid and liquid products may be neglected as compared to their chemical exergy, so the total exergy can finally be expressed as in Eq. (6.16):

$$Ex_{Total} = Ex_{CHE} \tag{6.16}$$

Chemical exergy has been generally calculated by establishing the chemical reactions involved between the given chemicals and elements present in the environment. This gives the maximum theoretical work that could be obtained from the reaction (Moran, 2008). However, in case of raw or torrefied biomass, bio-char, and bio-oil associated with pyrolysis or torrefaction process, exergy has been not very well defined. Hence, in the present study use of various statistical methods and regression equations have been done which have been defined especially for organic fuels and compounds (Szargut et al., 1987). Chemical exergy of solid product may be calculated by using Eq. (6.17):

$$Ex_{CHE}^{solid} = \beta_{solid} M_{solid} LHV_{solid} \tag{6.17}$$

Where β_{solid} has been the correlation factor (Boateng et al., 2012) and LHV_{solid} has been the lower heating value in kJ/kg of torrefied biomass or bio-char (Demirbas, 2007) and can be calculated using Eq. (6.18) and (6.19), respectively.

$$\beta_{solid} = 1.0437 + 0.1896\frac{H}{C} + 0.0617\frac{O}{C} + 0.0428\frac{N}{C} \tag{6.18}$$

$$LHV_{solid} = HHV_{solid} - 2535\,(9H + W) \tag{6.19}$$

Where H has been hydrogen, C as carbon, O as oxygen, N as nitrogen content of the torrefied biomass and bio-char in wt.% and W has been the moisture content of torrefied biomass or bio-char in wt.%.

6.2.4.3 Exergy of liquid product (torrefaction liquid/bio-oil)

As mentioned in Section 6.2.4.2 similarly the physical exergy of the liquid can be neglected, so the total exergy of liquid product can be given by Eq. (6.16) and the chemical exergy can be calculated by using Eq. (6.20):

$$Ex_{CHE}^{liquid} = \beta_{liquid} M_{liquid} LHV_{liquid} \tag{6.20}$$

Where β_{liquid} has been the correlation factor for the liquid product (Boateng et al., 2012) and LHV_{liquid} has been the lower heating value in kJ/kg for liquid product (torrefaction liquid or bio-oil) produced during torrefaction or pyrolysis process and can be expressed as in Eq. (6.21) and (6.22), respectively.

$$\beta_{liquid} = 1.0401 + 0.1728\frac{H}{C} + 0.0432\frac{O}{C} + 0.2169\frac{S}{C}\left(1 - 2.0628\frac{H}{C}\right) \tag{6.21}$$

$$LHV_{liquid} = HHV_{liquid} - M_w \times h_f \tag{6.22}$$

Where M_w has been the mass of moisture content (wt.%) in the liquid product and has been determined by using Karl Fischer titrimetric method with h_f being the latent heat of vaporization (2260 kJ/kg).

6.2.4.4 Exergy of raw biomass

The physical exergy of the biomass can be neglected, so the total exergy has been due to its chemical exergy and can be given by Eq. (6.23):

$$Ex_{CHE}^{raw\,biomass} = \beta_{raw\,biomass} M_{raw\,biomass} LHV_{raw\,biomass} \tag{6.23}$$

Where $\beta_{raw\,biomass}$ has been the correlation factor for raw biomass (Boateng et al., 2012) and $LHV_{raw\,biomass}$ has been the lower heating value of raw biomass and has been given by Eq. (6.24) and (6.25), respectively.

$$\beta_{raw\,biomass} = \frac{1.0412 + 0.216\frac{H}{C} - 0.2499\frac{O}{C}\left[1 + 0.7884\frac{H}{C}\right] + 0.0450\frac{N}{C}}{1 - 0.3035\frac{O}{C}} \tag{6.24}$$

$$LHV_{rawbiomass} = HHV_{raw\,biomass} - 2535(9H + W) \tag{6.25}$$

Where $HHV_{raw\,biomass}$ has been the higher heating value of raw biomass in kJ/kg, H has

been the hydrogen content and W has been the moisture content in wt.%.

Exergy efficiencies (Ψ) associated with torrefaction or pyrolysis products (solid, liquid and

NCG) have been calculated using Eq. (6.26):

$$\Psi_{product}(\%) = \frac{Ex_{product}}{Ex_{raw\,or\,torrefied\,biomass} + Ex_{electricity}} \tag{6.26}$$

Irreversibility ($\Psi_{irreversibility}$) has been calculated using Eq. (6.27):

$$\Psi_{irreversibility} = 100 - (\Psi_{solid} + \Psi_{liquid} + \Psi_{NCG}) \tag{6.27}$$

Where Ψ_{solid}, Ψ_{liquid} and Ψ_{NCG} are exergy efficiency associated with solid, liquid and NCG,

respectively.

6.3 Energy and exergy analysis for the torrefaction of pigeon pea stalk and eucalyptus

6.3.1 Influence of torrefaction temperature on energy and exergy value of NCG and liquid product

Figs. 6.2 and 6.3 represent the variation of chemical and physical energy with temperature,

respectively, for the individual components of torgas (NCG). The lines joined in these

figures have not been for the mathematical trend but guides to the eye. It may be

observed from Fig. 6.2 that the chemical energy of individual components increases rapidly

(CO_2 has zero chemical energy) with increase in torrefaction temperature. The results

suggested that CO has been the main contributor of chemical energy and exergy in torgas

evolved during the torrefaction of biomass followed by CH_4 and H_2. However the trend changes for the physical energy and exergy with $CO_2 > CO > H_2 > CH_4$, this has been due to the fact that CO_2 has the highest concentration in torgas as explained in Section 4.14 of the Chapter 4. Even though the concentration of CO_2 decreases with increase in temperature, its physical energy and exergy increases due to increase in value of enthalpy.
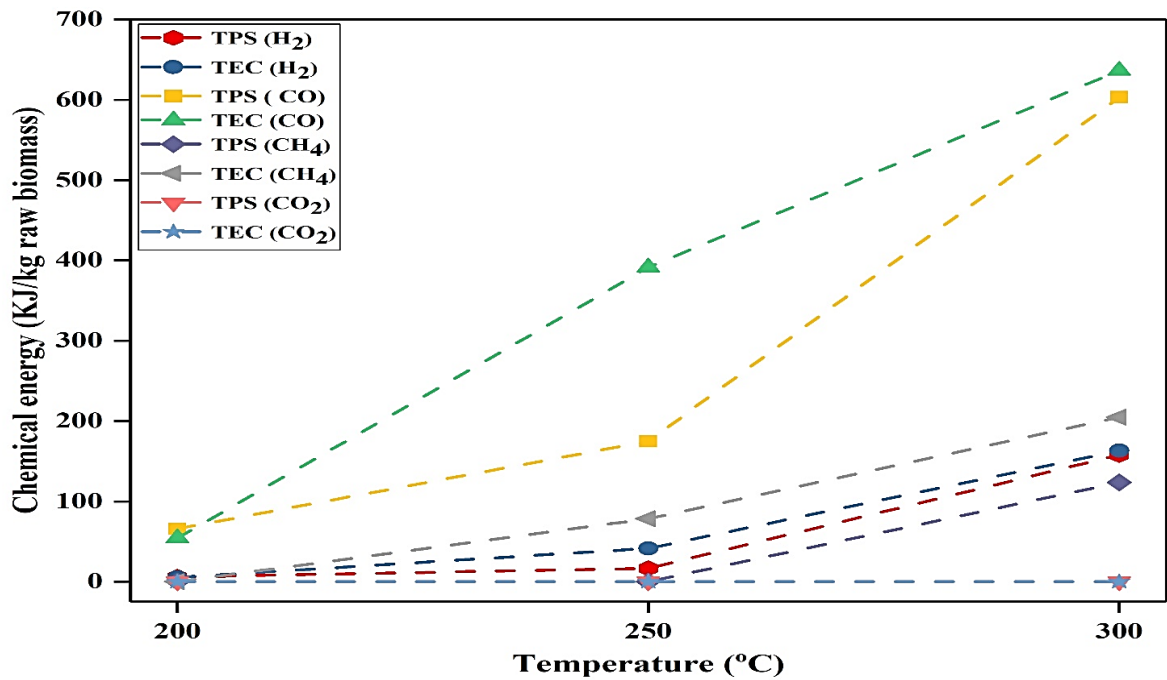

Fig. 6.2 Variation in chemical energy of torgas (NCG) components with temperature.

During torrefaction as the operating range of temperature (200-300° C) remains on the lower side as compared to pyrolysis and gasification, the physical energy and exergy for both biomass have been very low as compared to their chemical energy and exergy. The total chemical energy and exergy of torgas for TPS-300 have been 884.6 and 887.5 kJ/kg raw biomass, respectively, as compared to their physical energy (121.5 kJ/kg raw biomass) and exergy (19.3 kJ/kg raw biomass). Similar results have been observed for eucalyptus

where for TEC-300 the total chemical energy (1004.4 kJ/kg raw biomass) and the total

chemical exergy (995.6 kJ/kg raw biomass) of torgas has been much higher as compared to

their total physical energy (121.5 kJ/kg raw biomass) and total physical exergy (19.4 kJ/kg
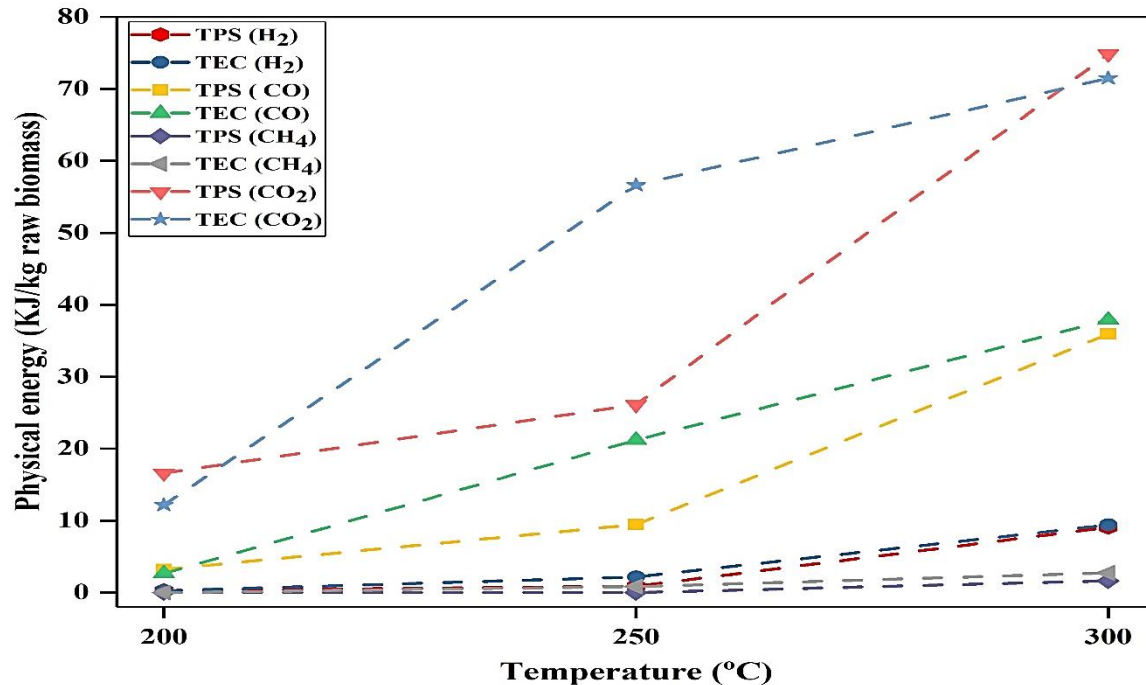
raw biomass), respectively.

Fig. 6.3 Variation in physical energy of torgas (NCG) components with temperature.

It can be observed from Fig. 6.4 and Table 6.3 that both woody biomass (eucalyptus) and

agricultural residue (pigeon pea stalk) showed similar trend towards the variation of

torrefaction temperature for total energy and exergy of torgas. The total energy and exergy

have been increased substantially with the increase in temperature. Total energy for TPS-

300 and TEC-300 increased from 92.1 to 1006.1 kJ/kg raw biomass and 74.9 to 1125.9

kJ/kg raw biomass, respectively as compared to TPS-200 and TEC-200. Also, it is worth

mentioning that total exergy of torgas have been less as compared to total energy, which remains in compliance with exergy definition.

Table. 6.3 Total energy and exergy of raw biomass and torrefaction products

| Sample	Raw/Torrefied biomass (solid)		Torrefaction liquid		Torgas (NCG)	
	Energy (kJ/kg raw biomass)	Exergy (kJ/kg raw biomass)	Energy (kJ/kg raw biomass)	Exergy (kJ/kg raw biomass)	Energy (kJ/kg raw biomass)	Exergy (kJ/kg raw biomass)
RPS	16670	17139.9	-	-	-	-
REC	17800	18573.1	-	-	-	-
TPS-200	15763.4	16133.2	498.3	566.9	92.1	89.2
TEC-200	16311.4	16992.9	877.0	987.1	74.9	72.0
TPS-250	13252.3	13661.7	2734.1	2961.4	227.9	212.3
TEC-250	13398.4	14054.9	1905.1	2092.4	592.2	476.7
TPS-300	9583.0	9929.1	4195.5	4513.1	1006.1	906.8
TEC-300	10802.3	11324.2	3897.6	4230.9	1125.9	1015.4
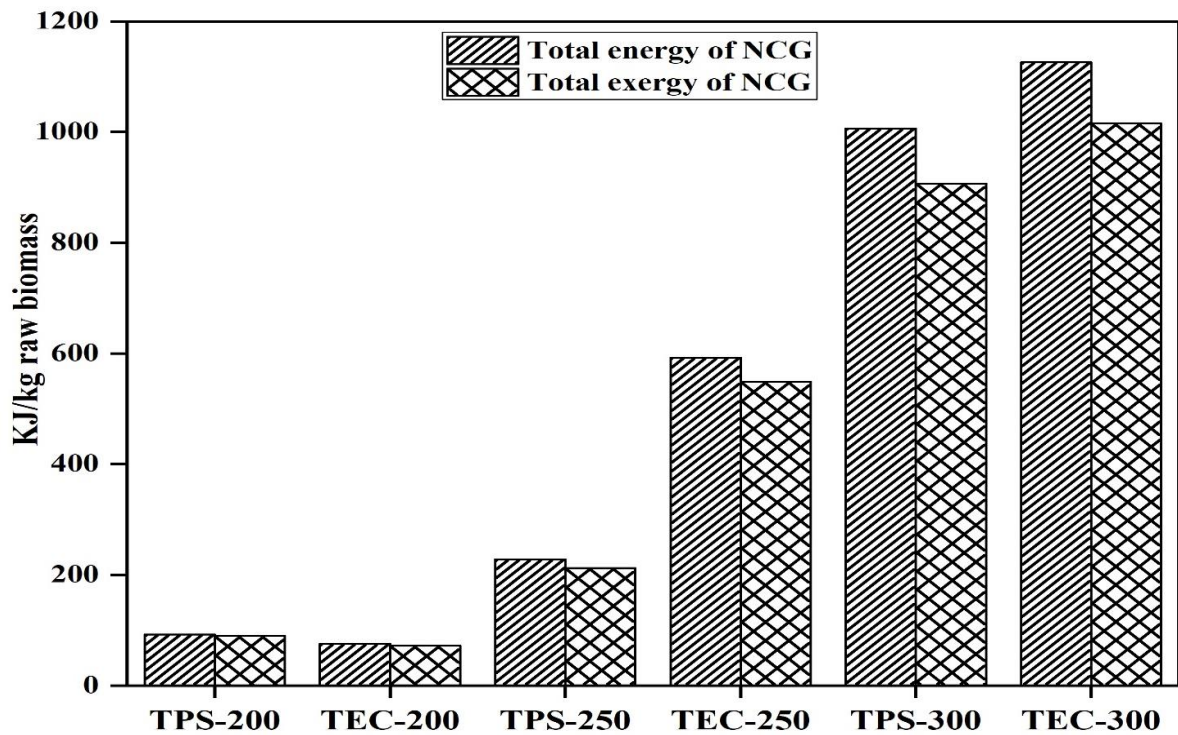
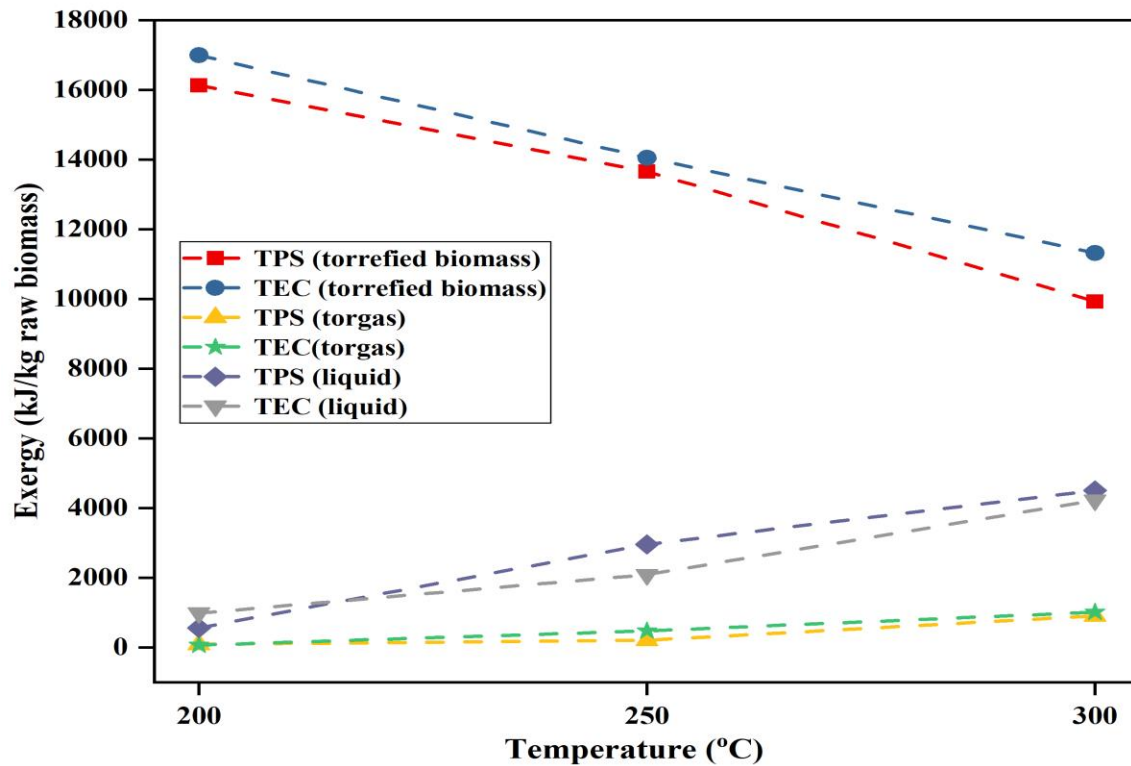**Fig. 6.4** Total energy and exergy variation of torgas with temperature.

Fig. 6.5 Influence of temperature on total exergy of torrefaction products.

It can be illustrated from Fig. 6.5 and Table 6.3 that both energy and exergy of liquid product from torrefaction increased significantly with increase in temperature. The value of β associated with exergy calculation of liquid product has been depicted in Table 6.4 (supplementary material). The value of β for liquid product obtained during torrefaction of agricultural residue and woody biomass decreased with increase in temperature due to increase in carbon content and decrease in oxygen content of liquid product with increase in temperature. Total energy of liquid product for TPS-300 and TEC-300 have been increased by 742 % and 344 % respectively as compared to TPS-200 and TEC-200. This increase has been due to appreciable increase in the yield of liquid product and increase in HHV for severe torrefaction (300 ℃) condition as compared to mild (200 ℃) torrefaction

condition. Similar trends have been observed for exergy value of the liquid product and has been in the range of 566.9 to 4513.1 kJ/kg raw biomass. The total energy and exergy value of liquid product have been much higher compared to the values of NCG suggesting that liquid obtained during torrefaction process can be used for energy recuperation to increase the overall efficiency of the torrefaction unit.

Table 6.4 The value of β associated with exergy calculation

Sample	β for liquid	β for torrefied biomass
RPS	-	1.14
REC	-	1.13
TPS-200	1.15	1.12
TEC-200	1.15	1.12
TPS-250	1.13	1.11
TEC-250	1.13	1.11
TPS-300	1.12	1.10
TEC-300	1.12	1.10

6.3.2 Influence of torrefaction temperature on energy and exergy value of torrefied biomass

Fig. 6.5 represents the variation of total exergy with torrefaction temperature for torrefied biomass (solid), liquids and torgas obtained during the process. It has been quite clear that with increase in temperature the total exergy of both torrefied biomass decreases. This has been due to decrease in the solid yield for torrefaction have been higher as compared to its increase in HHV, thus a proper balance between the two have to be maintained. Table 6.4 also represents the value of β associated with the exergy calculation of raw biomass and their subsequent solid product obtained during the torrefaction process.

Table 5 represents the total energy and exergy of torrefied biomass, liquid and torgas at different torrefaction temperature. Total energy of torrefied biomass for TPS-250 and TEC-250 have been 13252.3 and 13398.4 kJ/kg raw biomass, respectively. Similar results were obtained by Granados et al. (Granados et al., 2014) for solid product of palm oil fiber (10884 kJ), sugarcane bagasse (14190 kJ), rice husk (12644 kJ) and sawdust (15195 kJ) at 250 $^{\circ}$C and 30 minutes residence time. Total exergy of solid product for TPS-250 (13661.7 kJ/kg raw biomass) and TEC-250 (14054.9 kJ/kg raw biomass) have been also in accordance with the results of Granados et al. (Granados et al., 2014) where the palm oil fiber, sugarcane bagasse, rice husk and saw dust yielded 12806, 15069, 12066 and 16381 kJ/kg raw biomass. There has been 39.2 % and 33.8 % drop in the total energy of solid product for pigeon pea stalk and eucalyptus, respectively, when the temperature increased from 200 to 300 $^{\circ}$C. Yan et al. (Yan et al., 2010) based on their study for the torrefaction of loblolly pine, concluded that operating temperature in the range of 220-260 $^{\circ}$C would be beneficial for achieving a balance between the energy perspective and the enhancement of solid fuel properties. Similarly, other studies were carried out by Cardona et al. (Cardona et al., 2019) for three different biomass, Iroba et al. (Iroba et al., 2017) for municipal wastes and Nam et al. (Nam and Capareda, 2015) for rice straw and cotton stalk, where the recommended severity of torrefaction were either mild (200-230 $^{\circ}$C) or moderate conditions (230-270 $^{\circ}$C) depending upon energy-exergy analysis and desired physicochemical properties. Hence, it can be recommended that for the biomass obtained from different sources, the severe torrefaction (270-300 $^{\circ}$C) will be non-beneficial as the

major portion of energy from raw biomass would be carried away by the byproducts (liquid and torgas).

6.3.3 Influence of torrefaction temperature on total exergy at inlet, at outlet and its irreversibility
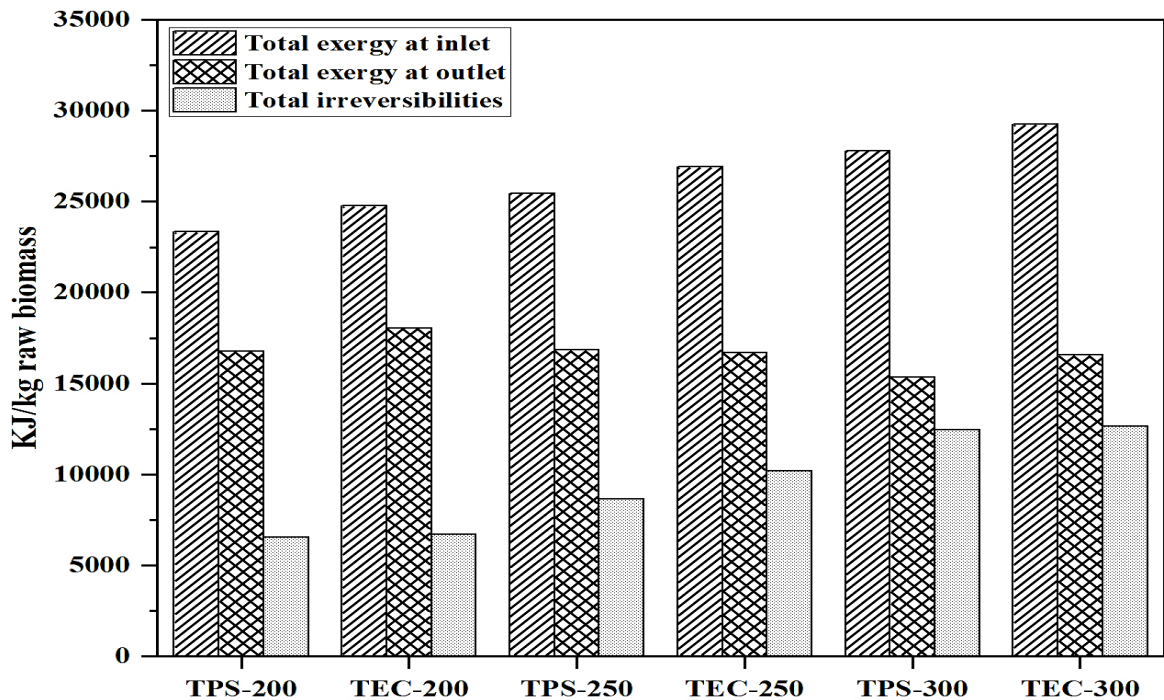

Fig. 6.6 Influence of temperature on total irreversibilities, total exergy in and out during torrefaction process.

The variation of total exergy at inlet and outlet with torrefaction temperature have been represented in Fig. 6.6. In Fig. 6.6 the total exergy input increases with increase in temperature due to increased input electric exergy given to the furnace. The total exergy at outlet for TPS-250 (16835.4 kJ/kg raw biomass) increased marginally as compared to TPS-200 (16789.2 kJ/kg raw biomass). However once the torrefaction moves from moderate to severe torrefaction the exergy at outlet decreases appreciably due to losses occurring due to

high amount of volatile release. Fig. 6.6 also represents the variation of total irreversibility (exergy lost) with torrefaction temperature. The irreversibility increases by 90.2 and 88.5 % for TPS-300 and TEC-300, respectively as compared to their 200 °C condition. This clearly suggest that severe torrefaction is not desirable irrespective of biomass until the lost exergy can be recycled or utilized for biomass preheating. Similar losses were also experienced by other researchers during the torrefaction and the pyrolysis of biomass (Boateng et al., 2012; Granados et al., 2014; Peters et al., 2014; Wang et al., 2016).

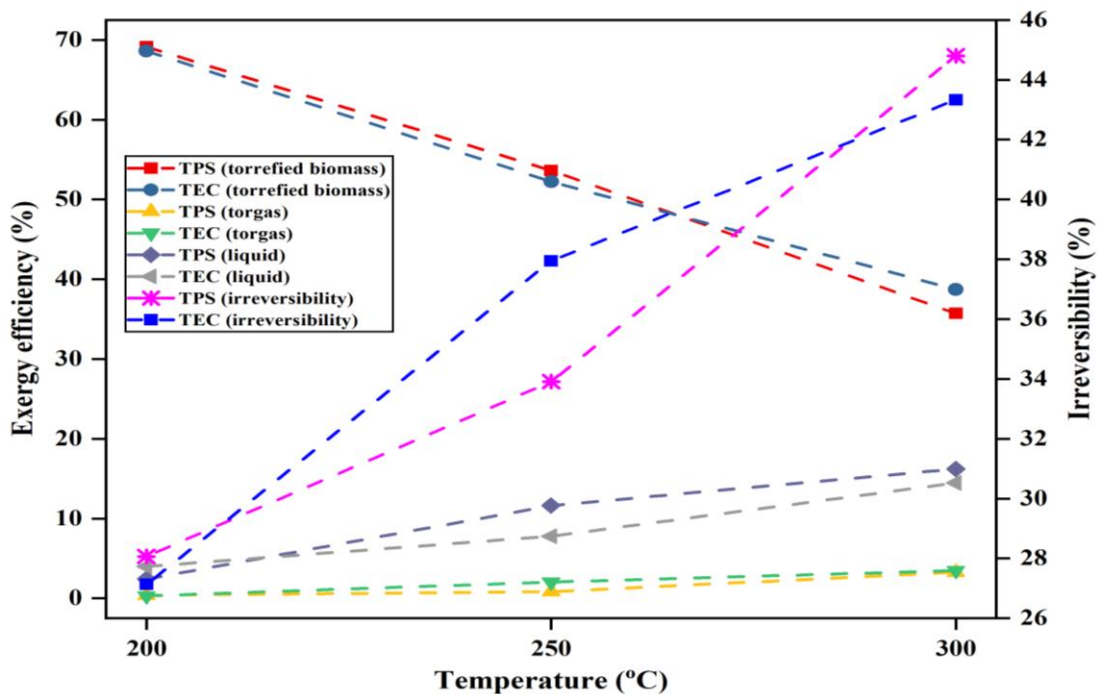## 6.3.4 Influence of torrefaction temperature on exergy and irreversibility efficiency

Fig. 6.7 Effect of temperature on exergy efficiency and irreversibility of torrefaction products.

The variation of exergy or exergy efficiency of torrefied biomass, liquid and NCG have been represented in Fig. 6.7. A clear trend can be observed that exergy efficiency for both liquid and torgas increases marginally with increase in temperature due to increase in total exergy input. However for the same condition there has been sharp decrease in exergy efficiency of solid due its decreased yield and increased input exergy. Exergy efficiency of solid product for TPS-200, TEC-200, TPS-250 and TEC-250 have been 69.1, 68.6, 53.6 and 52.2 %, respectively clearly suggesting that up to 250 $^{\circ}$C the torrefaction process can be employed with some changes to achieve higher efficiencies. Fig. 6.7 also represents the variation of irreversibility efficiency with torrefaction temperature. The irreversibility efficiency for both types of biomass have been in the range of 27 to 38 % when the temperature is in the range of 200 to 250 $^{\circ}$C. These irreversibilities can be reduced by employing some changes like reducing heat loss from furnace (improving insulation), better reactor design and recirculation of energy associated with byproducts (liquid and torgas) to decrease the required energy input.

6.3.5 Energy recovery for torrefaction

Table 6.5 reports the variation of energy recovery for the torrefaction products with temperature. It can be observed that under respective entrees the energy recovery in torrefied biomass decreases, while in liquid and torgas increases with increase in torrefaction temperature. The entrees under "No recycle" illustrate the condition when no energy from the byproducts (liquid and torgas) have been recuperated in order to potentially reduce the energy input. Under this condition the energy recovery in solid for TPS-250, TEC-250, TPS-300 and TEC-300 have been 53.0, 51.9, 35.1 and 37.9 %,

respectively. Under "Torgas recycled" the entrees represent the energy recovery under the condition when the energy from torgas can be potentially recycled to reduce the amount of energy input. This condition did not predict any appreciable increase in energy recovery to main product (torrefied biomass). However, when observed under the entrees "Liquid recycled" and "Liquid +torgas recycled" the energy recovery in solid product (torrefied biomass) increases appreciably. Under "Liquid recycled" the energy recovery in solid have been 59.5 and 55.3 % for TPS-250 and TEC-250, respectively. Under "Liquid +torgas recycled" the increase in energy recovery for TPS-250 and TEC-250 have been 60.1 and 56.7%, respectively. Energy recycle from byproducts in order to increase the energy recovery in solid products remains less than 50% for the severe (300 ºC) torrefaction condition.

Table. 6.5 Energy recovery in products of biomass torrefaction

Sample	Energy recovery (%)											
	No recycle			Torgas recycled			Liquid recycled			Liquid +torgas recycled		
	Solid	Liquid	NCG	Solid	Liquid	NCG	Solid	Liquid	NCG	Solid	Liquid	NCG
TPS-200	68.9	2.2	0.4	69.2	2.2	-	70.5	-	0.4	70.8	-	-
TPS-250	53.0	10.9	0.9	53.5	11.0	-	59.5	-	1.0	60.1	-	-
TPS-300	35.1	15.3	3.7	36.4	15.9	-	41.4	-	4.3	43.3	-	-
TEC-200	68.0	3.7	0.3	68.2	3.7	-	70.5	-	0.3	70.8	-	-
TEC-250	51.3	7.3	2.3	52.5	7.5	-	55.3	-	2.4	56.7	-	-
TEC-300	37.9	13.7	4.0	39.5	14.3	-	44.0	-	4.6	46.1	-	-

In the present study, the energy-exergy analysis showed the possibility of recovering the energy from byproducts and this could decrease energy requirement in the pre-treatment

process. Also, torrefaction operates in a lower temperature range (200-300 ℃) and there are many industries such as sugar, leather, fertilizer and power plants, for which waste heat can be utilized to meet the energy requirement for pre-treatment process. There were case studies by Sermyagina et al. (Sermyagina et al., 2016) and Starfelt et al. (Starfelt et al., 2015) on the possible integration of torrefaction with combined heat and power (CHP) plants, and results pinpointed that this integration could be profitable, and this multigenerational smart system can run fully on renewable energy resources without compromising on production of electricity or heat.

6.4 Energy and exergy analysis for the pyrolysis of raw and torrefied biomass (pigeon pea stalk and eucalyptus)

6.4.1 Influence of pyrolysis temperature on the energy and exergy value of pyrolytic gas and bio-char

The variation of chemical and physical energy (similar trend for exergy values have been observed) for the components (CO, CO_2, H_2 and CH_4) of pyrolytic gas with varying pyrolysis temperature have been presented in Figs. 6.8-6.9 and Figs. 6.10-6.11, respectively. On analyzing Fig. 6.8 and 6.9 it can be observed that the chemical energy or exergy of each components (except for CO_2 which does not have any chemical energy or exergy) for all the cases increases with increase in pyrolysis temperature. The maximum chemical energy for the pyrolytic gas has been provided by CO in all the cases of pyrolysis such as for PRPS-550, PTPS-550, PREC-550 and PTEC-550, CO has 1570.54, 1483.63, 1314.30 and 1640.57 kJ/kg biomass while CH_4 stands at second position with 858.28, 1352.10, 862.10 and 1261.11 kJ/kg biomass, respectively. However, on further analyzing

Fig. 6.8 and 6.9 it can be observed that the most prominent effect in the improvement of chemical energy or exergy for the pyrolytic gas after using torrefied biomass feedstock as compared to raw biomass feedstock has been provided by CH_4. There has been 76.60, 69.80, 57.53 and 46.28 % increase the chemical energy of CH_4 for PTPS-450, PTEC-450, PTPS-550 and PTEC-550 as compared to PRPS-450, PREC-450, PRPS-550 and PREC-550, respectively. Based on these results and also, as discussed in Sections 5.8.1 and 5.8.6 of the Chapter 5 it can be asserted that even though the concentration of CO in the pyrolytic gas increases for the pyrolysis of both the torrefied biomass but due to a nominal change in yield of pyrolytic gas there has been not much effect on the chemical energy or exergy provided by CO. On the other side there has been appreciable increase in the chemical energy or exergy of CH_4 for the pyrolysis of torrefied biomass in both the cases mainly due to very significant increase in the concentration of CH_4 on the expense of decrease in the concentration of CO_2 as already discussed in Section 5.8.6 of the Chapter 5. In Figs. 6.10 and 6.11, on analyzing these figures it can be observed that the physical energy or exergy of all the components increases with increase in temperature and this increase has been due to the increase in value of enthalpy of gases with increase in temperature (Singh et al., 2020). However, no clear trend has been observed for the contribution of physical energy or exergy by individual components during the pyrolysis of raw or torrefied biomass, as the physical energy or exergy depends heavily on the concentration of gases. Also, on comparing Figs. 6.10 and 6.11 with Figs 6.8 and 6.9, it can asserted that the total physical energy of the pyrolytic gas has been only 10-15 % of total chemical energy of pyrolytic gas in all the observed cases.
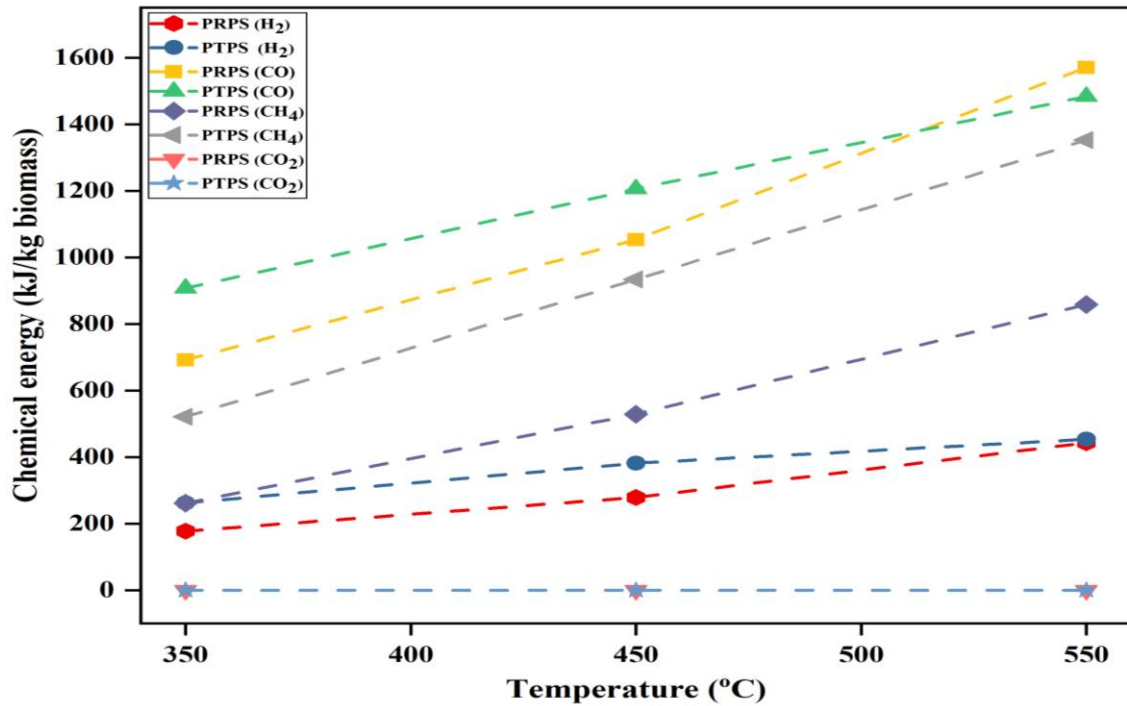
Fig. 6.8 Chemical energy of the components for the pyrolytic gas during the pyrolysis of raw and torrefied pigeon pea stalk.
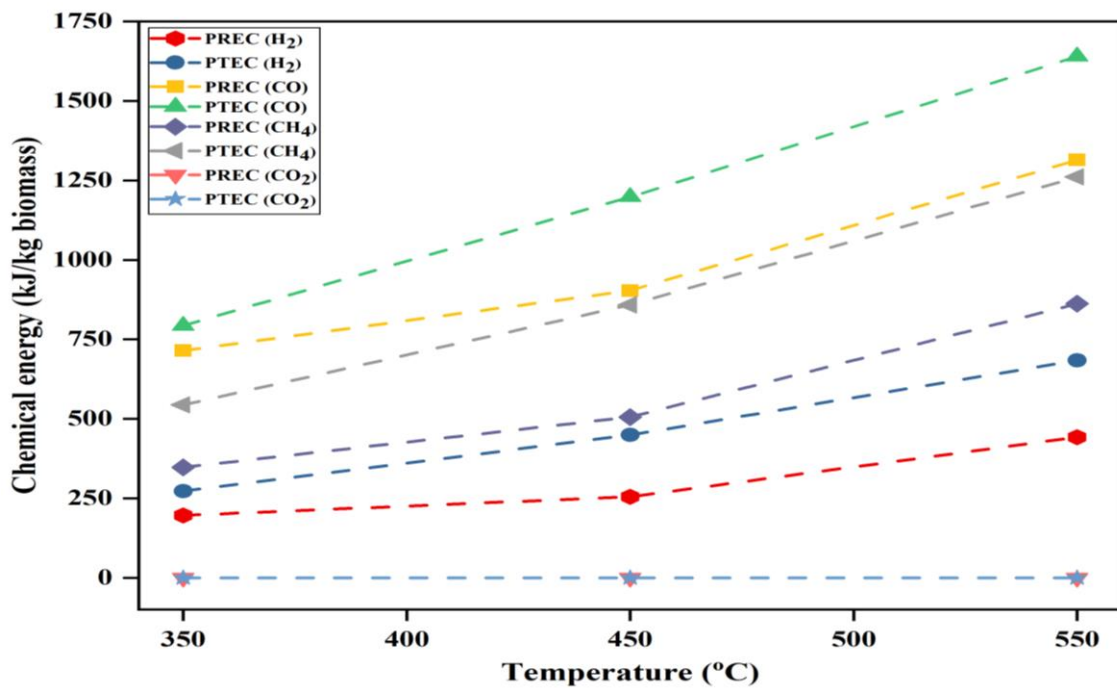

Fig. 6.9 Chemical energy of the components for the pyrolytic gas during the pyrolysis of raw and torrefied eucalyptus.
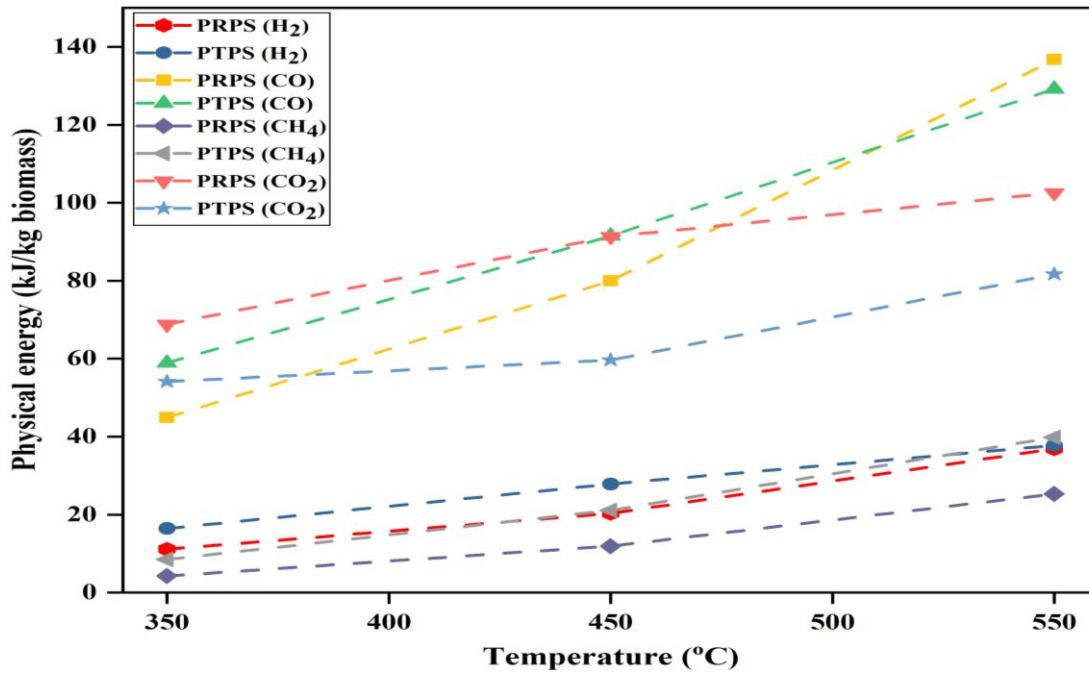
Fig. 6.10 Physical energy of the components for the pyrolytic gas during the pyrolysis of raw and torrefied pigeon pea stalk.
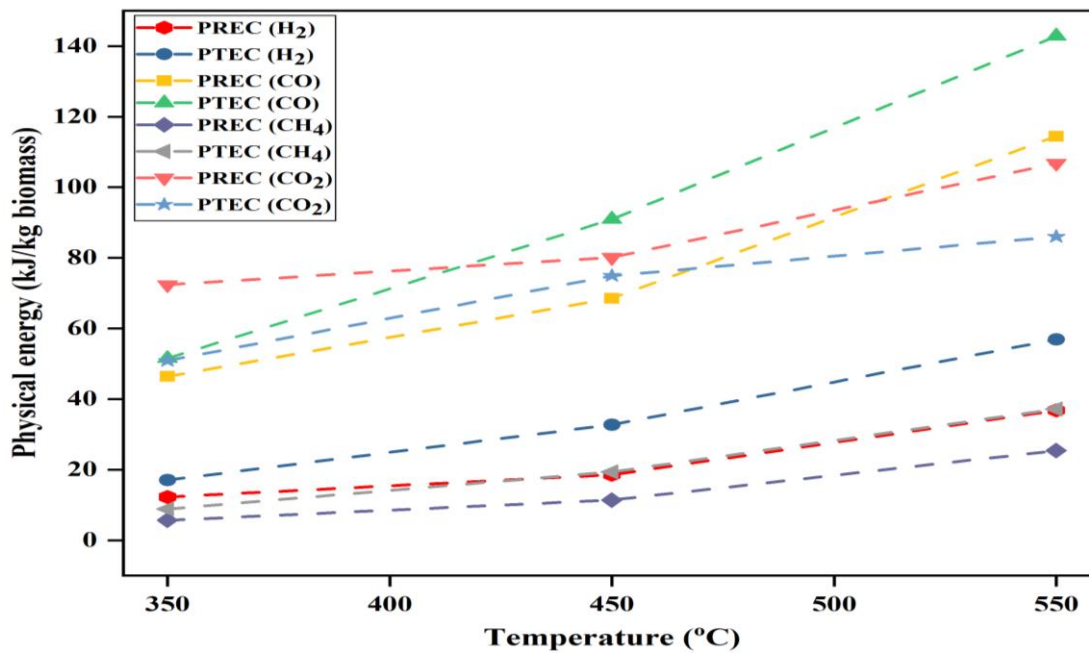

Fig. 6.11 Physical energy of the components for the pyrolytic gas during the pyrolysis of raw and torrefied eucalyptus.

Table. 6.6 Total energy and exergy of raw biomass, torrefied biomass and their pyrolysis products

Sample	Raw/Torrefied biomass/bio-char		Bio-oil		Pyrolytic gas (NCG)	
	Energy (kJ/kg biomass)	Exergy (kJ/kg biomass)	Energy (kJ/kg biomass)	Exergy (kJ/kg biomass)	Energy (kJ/kg biomass)	Exergy (kJ/kg biomass)
RPS	16670	17139.9	-	-	-	-
REC	17800	18573.1	-	-	-	-
TPSO	20890	21555.61	-	-	-	-
TECO	21340	22324.62	-	-	-	-
PRPS-350	9524.16	9859.66	6058.42	6558.38	1259.26	1130.00
PRPS-450	7953.07	8209.14	8064.67	8777.55	2064.27	1839.24
PRPS-550	6053.38	6231.30	9266.78	10079.48	3173.42	2814.58
PREC-350	9653.62	9977.73	6043.96	6567.13	1395.12	1251.78
PREC-450	8578.67	8879.19	8767.44	9524.87	1842.39	1640.75
PREC-550	6167.41	6366.23	10044.16	10896.98	2901.98	2567.23
PTPS-350	15028.60	15542.50	4337.34	4761.35	1828.27	1637.65
PTPS-450	13519.46	14034.45	7282.19	7961.96	2721.01	2425.72
PTPS-550	13226.90	13692.65	7033.79	7670.41	3577.40	3184.85
PTEC-350	15943.73	16534.75	4696.59	5154.89	1738.81	1553.95
PTEC-450	12799.91	13278.26	8062.95	8782.83	2723.91	2416.85
PTEC-550	12398.21	12828.60	7617.79	8265.45	3908.60	3450.29

Table 6.6 represents the total energy and exergy values of the pyrolysis products. There have been increase of 31.89 and 47.30 % increase in the total exergy value of PTPS-450 and PTEC-450 as compared to PRPS-450 and PREC-450, which confirm that there has been a significant improvement in the quality of pyrolytic gas obtained from the pyrolysis of torrefied biomass and comes in compliance with the discussions held in Chapter 5. Table

6.6 also represents the effect of pyrolysis temperature on the total energy and exergy values of the bio-char obtained from raw or torrefied biomass. There has been a significant increase in the energy or exergy values of bio-char obtained from the pyrolysis of torrefied biomass as compared to their raw biomass. On analysing Table 6.6 the energy value of bio-char for PTPS-450 and PTEC-450 have been 66.99 and 49.20 % higher as compared to PRPS-450 and PREC-450, respectively. This high energy or exergy value have been due to better solid fuel properties (HHV, carbon and oxygen content) of the torrefied biomass as compared to raw biomass when used as a feed for pyrolysis which produced a much higher quality of bio-char as discussed in Section 5.8.5 of the Chapter 5. Other very important aspect which increased the energy or exergy value of bio-char from the pyrolysis of torrefied biomass have been the high bio-char yield as compared to that of raw biomass pyrolysis as discussed in Section 5.8.1 of the Chapter 5.

6.4.2 Influence of pyrolysis temperature on energy and exergy value of bio-oil

Fig. 6.12 and Table. 6.6 represents the total energy or exergy values for the pyrolysis product and their variation with pyrolysis temperature. On analysing these figure and table it can be asserted that the energy or exergy values for the bio-oil from the pyrolysis of torrefied biomass decreased as compared to its raw biomass pyrolysis. Initially for the lower temperature pyrolysis the difference between the energy or exergy values of bio-oil from the pyrolysis of raw and torrefied biomass has been higher such as between PREC-350 and PTEC-350 the difference has been 1347.37 kJ/kg biomass. However, this difference got reduced significantly to 704.52 kJ/kg biomass for PREC-450 and PTEC-450,

which has been also close to the recommended optimum operating condition as obtained in
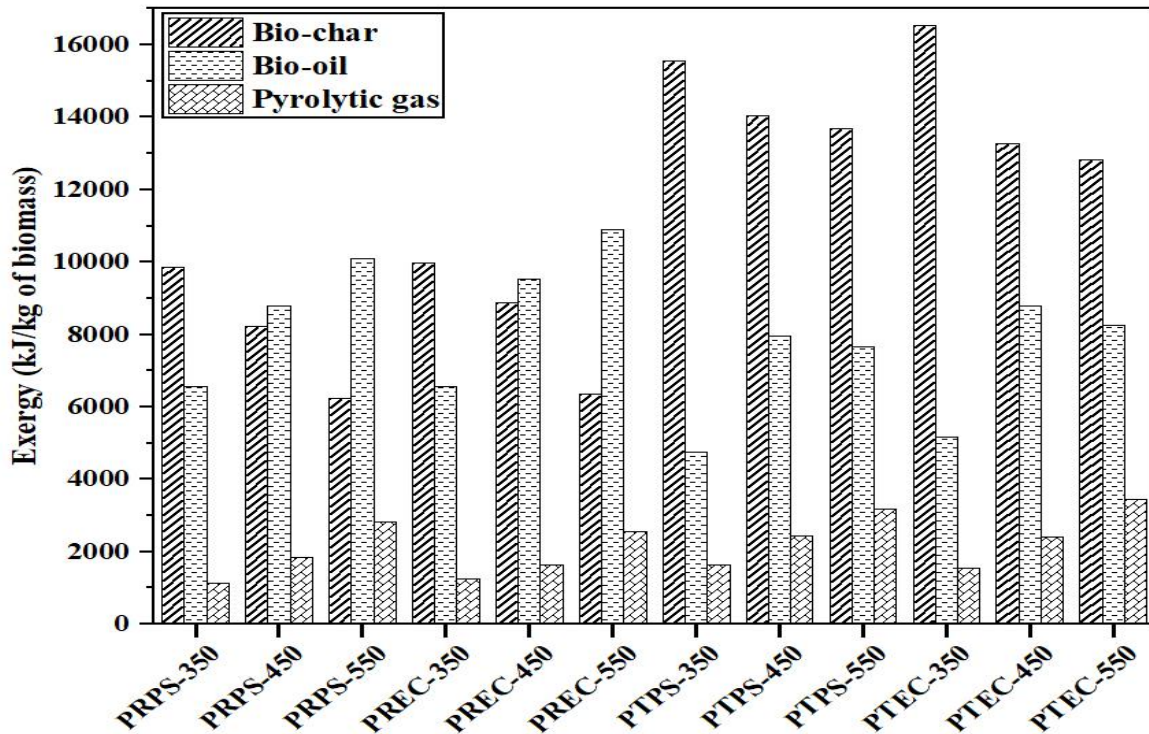
the Chapter 5.

Fig. 6.12 Effect of pyrolysis temperature on the exergy of its products.

It has been also worth mentioning that even though on considering the total energy or

exergy recovered in bio-oil from the pyrolysis of torrefied biomass might be not appealing

but considering the on the basis of qualitative analysis such as HHV, oxygen and water

content as discussed in the Chapter 5 the process with some further modifications can be

utilized to generate high quality bio-oil. Also, many researchers like Cheng et al. (Cheng et

al., 2018), Kim et al. (Kim et al., 2019), Hansen et al. (Hansen et al., 2020) and Louwes et

al. (Louwes et al., 2017) have clearly mentioned that the cost of upgradation contributes

maximum to the total cost of producing transportation fuel from bio-oil obtained from the

pyrolysis of raw biomass due to its high oxygen and water content. On the other side the bio-oil from the pyrolysis of torrefied biomass contains much less amount of oxygen and water which could drastically reduce the overall cost of producing transportation fuel through pyrolysis of biomass.

6.4.3 Influence of pyrolysis temperature on total exergy at inlet, at outlet and its irreversibility

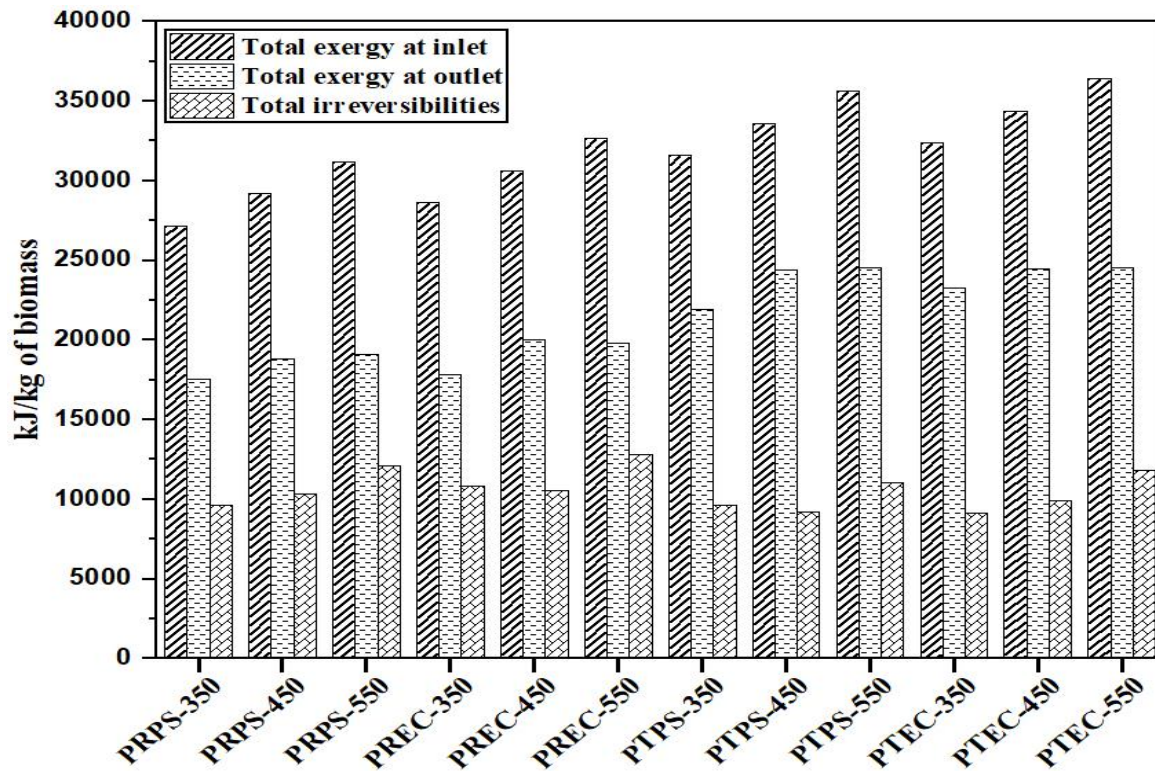**Fig. 6.13** Impact of pyrolysis temperature on total exergy in and out along with total irreversibilities of the pyrolysis system.

The influence of torrefaction and pyrolysis temperature on the total irreversibilities (exergy destruction) along with total exergy in and out can be observed in Fig. 6.13. There has been a continuous increase in the exergy in for the increase in pyrolysis temperature mainly due

to the increase in energy requirement for the furnace in the form of electrical energy. Similar when the pyrolysis temperature increase the exergy out also increased, however, when the pyrolysis temperature changes from 450 to 550 °C no appreciable change in the value of exergy out has been observed which suggests that high temperature pyrolysis might not be recommended especially for the pyrolysis of torrefied biomass. On analysing Fig. 6.13 it can be observed that there has been a significant decrease in the value of irreversibilities for the pyrolysis of torrefied biomass mainly due to the fact that lean energy volatiles has been already removed during the pre-treatment of biomass through torrefaction which otherwise would have carried away much of the energy with it without being tapped for some useful work.

6.4.4 Energy recovery for pyrolysis

The variation of energy recovery in the pyrolysis products with varying pyrolysis temperature for raw and torrefied pigeon pea stalk and eucalyptus can be observed from Table 6.7. The entrees under "No recycle" stands for the situation where no energy from either of the byproducts (bio-char and pyrolytic gas) have been tapped back or recycled for reducing the energy required as input. On analysis this condition it can be observed that for PRPS-450 and PREC-450 the energy recovered in bio-oil have been 28.07 and 29.37 %, respectively, while for PTPS-450 and PTEC-450 have been 22.10 and 24.16 % respectively. These results clearly suggests that for the pyrolysis of raw biomass the energy recovered in bio-oil has been higher as compared to the pyrolysis of torrefied biomass and this difference has been mainly due to decreased bio-oil yield during the pyrolysis of torrefied biomass. However, under "bio-char recycled" condition, the energy recovered in

bio-oil yield increases significantly to 37.48 and 39.17 % for PTPS-450 and PTEC-450 and becomes comparable to PRPS-450 (38.82 %) and PREC-450 (41.20 %). These results clearly suggest that after the tapping or recycling the energy from by-products will increase the efficiency of the pyrolysis of torrefied biomass and at the same time providing a much higher grade bio-oil which would be helpful in cutting down the cost of upgradation to produce transportation fuel.

Table. 6.7 Energy recovery in the pyrolysis products form raw and torrefied biomass

	Energy recovery (%)											
Sample	**No recycle**			**Pyrolytic gas recycled**			**Bio-char recycled**			**Bio-char +pyrolytic gas recycled**		
	Bio-char	**Bio-oil**	**Pyrolytic gas**	**Bio-char**	**Bio-oil**	**Pyrolytic gas**	**Bio-char**	**Bio-oil**	**Pyrolytic gas**	**Bio-char**	**Bio-oil**	**Pyrolytic gas**
PRPS-350	35.66	22.68	4.71	37.42	23.80	-	-	35.25	7.33	-	38.04	-
PRPS-450	27.68	28.07	7.19	29.83	30.24	-	-	38.82	9.94	-	43.10	-
PRPS-550	19.69	30.15	10.32	21.96	33.62	-	-	37.54	12.85	-	43.07	-
PTPS-350	48.59	14.02	5.91	51.64	14.90	-	-	27.28	11.50	-	30.82	-
PTPS-450	41.03	22.10	8.26	44.72	24.09	-	-	37.48	14.00	-	43.58	-
PTPS-550	37.83	20.12	10.23	42.15	22.41	-	-	32.36	16.46	-	38.74	-
PREC-350	34.68	21.71	5.01	36.50	22.85	-	-	33.23	7.67	-	35.99	-
PREC-450	28.73	29.36	6.17	30.62	31.29	-	-	41.20	8.66	-	45.10	-
PREC-550	19.35	31.52	9.11	21.29	34.67	-	-	39.08	11.29	-	44.05	-
PTEC-350	50.81	14.97	5.54	53.79	15.84	-	-	30.43	11.26	-	34.29	-
PTEC-450	38.32	24.16	8.16	41.73	26.31	-	-	39.17	13.22	-	45.14	-
PTEC-550	35.01	21.51	11.04	39.36	24.18	-	-	33.10	16.99	-	39.88	-

6.5 Summary

Energy and exergy value of torrefied biomass decreased while for torgas and torrefaction liquid increased with increase in temperature. Energy and exergy value of torrefied biomass have been highest followed by liquid and then torgas. CO has been the main contributor in the total energy and exergy of NCG. Exergy efficiency of solid product has been in the range of 52 to 54% under moderate torrefaction. Irreversibility increased with increase in temperature. Recuperation of energy from byproducts (liquid and NCG) could increase the energy recovery in solid by 8 to 9 %.

During the energy and exergy analysis for the pyrolysis of torrefied biomass there was a significant increase in the chemical energy of CH_4 which confirmed the enhancement of pyrolytic gas on using torrefied biomass as a feed. Similarly the energy or exergy value of bio-char from torrefied biomass also witnessed a sharp increase in its value. However, on analyzing the energy-exergy value of bio-oil there was a decrease in its value for the torrefied biomass as compared to raw biomass feed but considering the yield of bio-oil the quality of bio-oil increased significantly in terms of HHV.