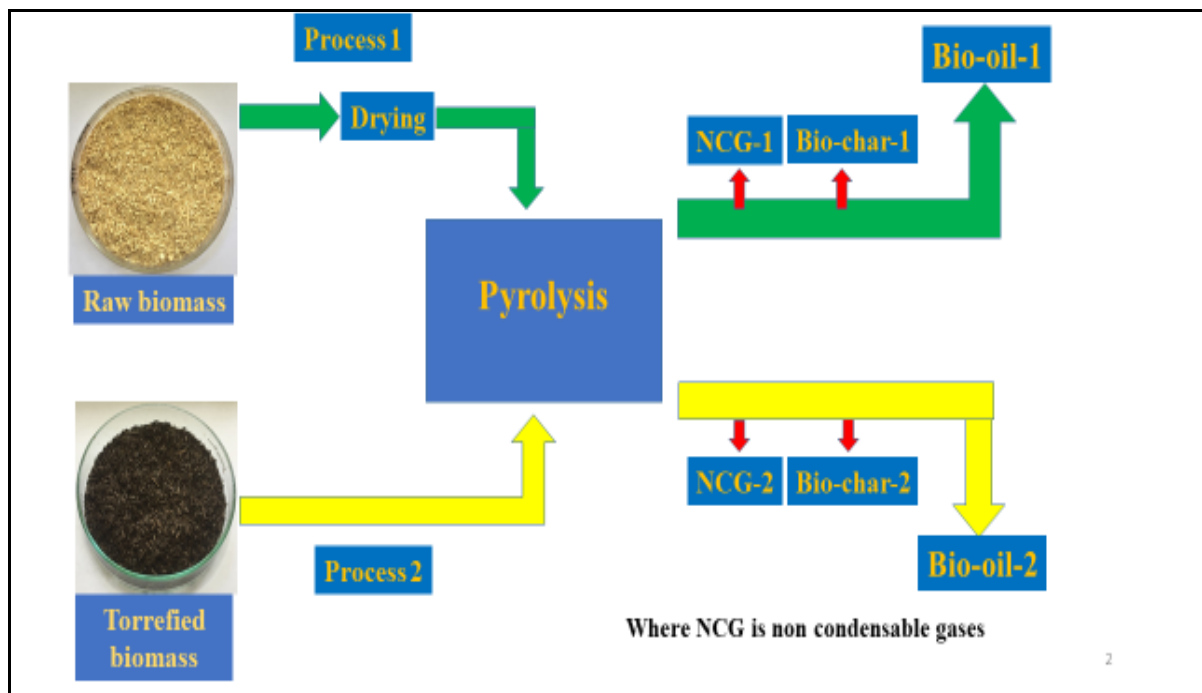


Chapter 5

Pyrolysis: Optimization and characterization

5.1 Overview



This Chapter represents the effect of torrefaction on the quantitative and qualitative analysis of pyrolysis products (bio-oil, bio-char and pyrolytic gas). The Chapter 5 includes the optimization for the pyrolysis of torrefied biomass (pigeon pea stalk and eucalyptus) with the objective to maximize the bio-oil yield (BY). This chapter also includes the comparative study between the pyrolysis products obtained from raw and torrefied biomass.

5.2 Materials and Methods

5.2.1 Material Selection

The biomass feed selected for the pyrolysis purpose are the torrefied pigeon pea stalk and the torrefied eucalyptus obtained at the optimum torrefaction conditions. The detailed experimental procedure for torrefaction process and its optimization have already been discussed in the Chapter 3. Further for the purpose of comparative study between pyrolysis of raw and torrefied biomass, pyrolysis of raw pigeon pea stalk and raw eucalyptus have also been performed at few operating conditions.

5.2.2 Experimental design and statistical analysis

Four influential operating parameters during pyrolysis (temperature, residence time, heating rate, and nitrogen sweeping rate) have been used in the present study. Central composite design (CCD) in RSM has been employed to determine the optimum conditions, quadratic effects, main effects and interaction effects of the pyrolysis operating parameters on the bio-oil yield (BY). In CCD option central face-centered ($\alpha = 1$) has been chosen. There have been 28 experiments performed, which includes 16 factorial points, 4 center points and 8 axial points. The coded levels of 350, 450, and 550 °C temperature, and 0, 15, and 30 minutes residence time, and 20, 40, and 60 °C/min, and 40, 70, and 100 ml/min nitrogen sweeping rate have been marked with -1, 0, and +1, respectively. In order to fit a second-order polynomial to the experimental data, a non-linear regression method has been employed. The predictive polynomial quadratic equation in general form is given by Eq. 5.1:

$$Y = \beta_0 + \sum_{j=1}^k \beta_j X_j + \sum_{j=1}^k \beta_{jj} X_j^2 + \sum_{i < j} \beta_{ij} X_i X_j \quad (5.1)$$

Where Y is the response (bio-oil yield), β_0 is the intercept coefficient, β_i , β_{ij} and β_{jij} are the interaction coefficient of the linear, second-order and quadratic terms, k is the number of independent parameters ($k=4$ in this study), X_j are the independent variables (temperature, residence time, heating rate, and nitrogen sweeping rate).

5.2.3 Experimental procedure

The detailed description for the experimental set-up has already been discussed in the Chapter 3. In each experiment, the fixed bed reactor has been fed with a 6-8 g sample supported with ceramic wool. For the pyrolysis of torrefied biomass, set of experiments performed at different operating conditions have been mentioned in Table 1 and 2. Procedures related to the collection of liquid part (bio-oil in pyrolysis), solid residue (bio-char in pyrolysis), and non-condensable gases remains same as discussed in the Chapter 3.

5.2.4 Characterization methods

The information related to the equipment details and their operating procedure for various characterization methods such as proximate analysis, elemental analysis, HHV, FTIR, gas chromatography (GC-TCD) and GC/MS have already been discussed in the Chapter 4. The viscosity of bio-oil obtained from the pyrolysis of raw and torrefied biomass have been measured using a digital viscometer (Brookfield, model number- LVDV-II+Pro).

5.3 CCD and statistical analysis

The design and the statistical analysis of pyrolysis of torrefied pigeon pea stalk and eucalyptus have been carried out using State Ease Design Expert. Tables 5.1 and 5.2 provides the experimental matrix along with their corresponding predicted and actual values (experimental values) for the bio-oil yield (BY). During pyrolysis each set of

experiment has been repeated twice and reported values have been their average values with same being used for the further analysis. However, for the centre point of the experimental matrix these have been repeated thrice and these points serve the purpose of evaluating experimental error and also helps in determining the reproducibility of the estimated and actual output. Hence, the centre points are mostly performed in high numbers which helps in establishing a model which predicts results with better accuracy and high reproducibility (Tripathi et al., 2020).

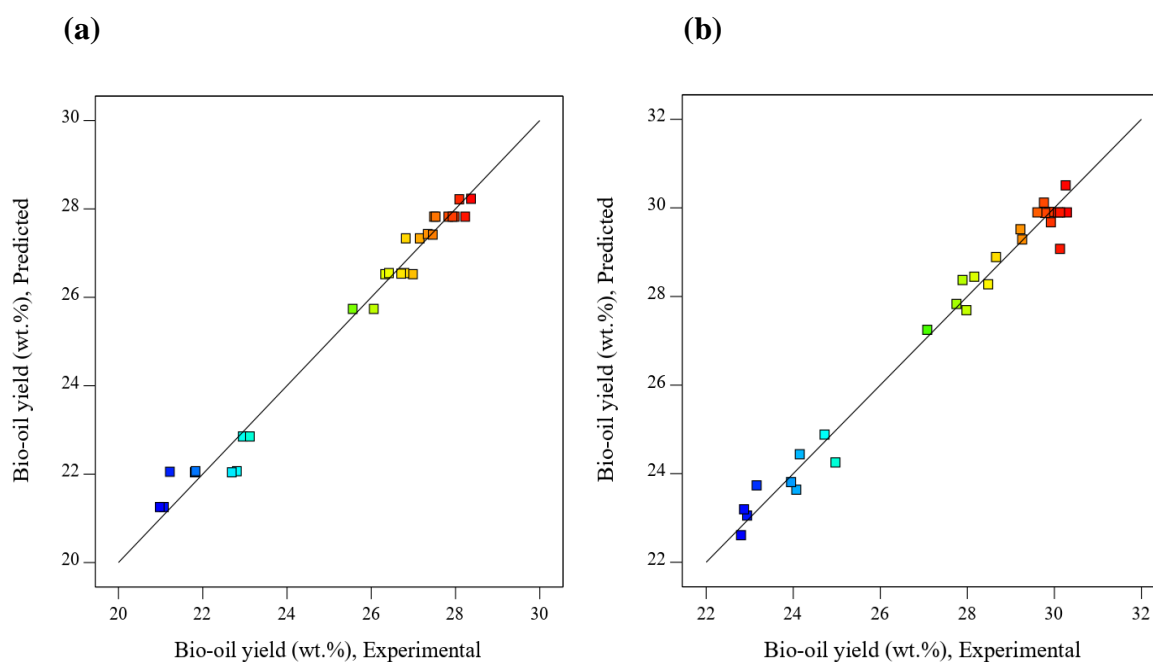


Fig. 5.1 Comparison of experimental and predicted values of the responses for bio-oil yield of (a) torrefied pigeon pea stalk and (b) torrefied eucalyptus

Figs. 5.1 (a) and (b) presents the comparison plot for actual verses predicted values obtained for the response (bio-oil yield) of pyrolysis of torrefied biomass at different sets of experimental conditions. On observing Figs. 5.1 (a) and (b) it has been quite clear that most of the experimental and predicted values of bio-oil yield have been very close to each

other. This implies that the proposed quadratic model in its reduced form successfully predicts the bio-oil yield within the limits of operating parameters.

Table 5.1 Experimental matrix with responses for the pyrolysis of torrefied pigeon pea stalk

Run	X ₁	X ₂	X ₃	X ₄	Energy yield (wt.%)		
	Temperature (°C)	Residence time (min)	Heating rate (°C/min)	Nitrogen sweeping rate (ml/min)	Experimental value	Predicted value	Residual
1	450	30	40	70	27.34	27.43	-0.0917
2	550	0	20	100	26.99	26.52	0.4656
3	350	0	20	40	21.81	22.04	-0.2322
4	350	0	20	100	22.69	22.04	0.6478
5	350	30	20	40	21.08	21.26	-0.1756
6	450	15	40	70	27.53	27.83	-0.2950
7	350	30	60	40	22.81	22.07	0.7433
8	350	0	60	40	22.95	22.85	0.0967
9	450	15	40	70	27.83	27.83	0.0050
10	450	15	40	40	27.49	27.83	-0.3350
11	550	0	20	40	26.33	26.52	-0.1944
12	550	30	20	40	25.56	25.74	-0.1778
13	350	30	20	100	20.98	21.26	-0.2756
14	550	0	60	40	26.82	27.34	-0.5156
15	350	15	40	70	21.22	22.05	-0.8344
16	450	15	60	70	28.37	28.23	0.1394
17	450	15	40	70	28.23	27.83	0.4050
18	450	0	40	70	28.09	28.22	-0.1283
19	450	15	40	100	27.98	27.83	0.1550
20	350	0	60	100	23.12	22.85	0.2667
21	550	15	40	70	26.71	26.54	0.1733
22	550	30	20	100	26.06	25.74	0.3222
23	550	0	60	100	27.15	27.34	-0.1856
24	550	30	60	40	26.42	26.55	-0.1289
25	350	30	60	100	21.83	22.07	-0.2367
26	450	15	40	70	27.93	27.83	0.1050
27	450	15	20	70	27.46	27.42	0.0406
28	550	30	60	100	26.79	26.55	0.2411

Table 5.2 Experimental matrix with responses for the pyrolysis of torrefied eucalyptus

Run	X ₁	X ₂	X ₃	X ₄	Energy yield (wt.%)		
	Temperature (°C)	Residence time (min)	Heating rate (°C/min)	Nitrogen sweeping rate (ml/min)	Experimental value	Predicted value	Residual
1	350	0	60	100	24.97	24.25	0.7153
2	550	0	20	40	27.98	27.69	0.2887
3	350	30	20	40	22.80	22.61	0.1876
4	450	0	40	70	29.76	30.12	-0.3597
5	450	30	40	70	29.92	29.68	0.2437
6	450	15	40	70	30.13	29.90	0.2320
7	350	0	20	100	24.07	23.64	0.4302
8	450	15	40	70	30.29	29.90	0.3920
9	450	15	60	70	30.26	30.51	-0.2486
10	550	0	20	100	28.48	28.28	0.2047
11	450	15	20	70	29.26	29.29	-0.0274
12	550	30	20	40	27.08	27.25	-0.1680
13	550	30	20	100	27.75	27.83	-0.0820
14	450	15	40	70	29.61	29.90	-0.2880
15	350	30	60	100	23.95	23.81	0.1387
16	550	0	60	40	29.22	29.52	-0.2987
17	350	0	20	40	22.94	23.06	-0.1158
18	550	30	60	40	30.13	29.08	1.05
19	350	30	60	40	24.15	24.44	-0.2898
20	450	15	40	70	30.08	29.90	0.1820
21	450	15	40	40	29.88	29.91	-0.0291
22	550	0	60	100	28.66	28.89	-0.2302
23	550	30	60	100	28.16	28.45	-0.2869
24	350	30	20	100	22.87	23.20	-0.3265
25	450	15	40	100	29.79	29.89	-0.0969
26	350	0	60	40	24.72	24.88	-0.1631
27	550	15	40	70	27.89	28.37	-0.4822
28	350	15	40	70	23.16	23.74	-0.5767

5.4 ANOVA analysis

ANOVA analysis for the experimental data of bio-oil yield obtained during the pyrolysis of torrefied pigeon pea stalk and eucalyptus have been carried out and summarized in Table 5.3 and 5.4. ANOVA helps in understanding the efficiency, reproducibility and reliability of the proposed quadratic models in their reduced form.

Table. 5.3 ANOVA of reduced quadratic model for pyrolysis of torrefied pigeon pea stalk

Source	Sum of squares	DF	Mean square	F-value	p-value
Bio-oil yield (wt.%)					
Model	176.23	4	44.06	316.18	< 0.0001
X ₁	90.41	1	90.41	648.80	< 0.0001
X ₂	2.78	1	2.78	19.99	0.0002
X ₃	2.96	1	2.96	21.25	0.0001
X ₁ ²	80.08	1	80.08	574.70	< 0.0001
Residual	3.20	23	0.1393	-	-
Lack of fit	2.95	20	0.1477	1.77	0.3550
Pure error	0.2500	3	0.0833	-	-
Standard deviation=0.37, mean=25.56, co-efficient of variation(%)=1.46, R ² =0.98, R ² _{Adj} =0.98, R ² _{Pred} = 0.97, Adeq precision= 44.22					

Table. 5.4 ANOVA of reduced quadratic model for pyrolysis of torrefied eucalyptus

Source	Sum of squares	DF	Mean square	F-value	p-value
Bio-oil yield (wt.%)					
Model	200.73	6	33.46	193.60	< 0.0001
X ₁	96.70	1	96.70	559.58	< 0.0001
X ₂	0.8845	1	0.8845	5.12	0.0344
X ₃	6.71	1	6.71	38.83	< 0.0001
X ₄	0.0022	1	0.0022	0.0129	0.9108
X ₃ X ₄	1.47	1	1.47	8.51	0.0082
X ₁ ²	94.97	1	94.97	549.58	< 0.0001
Residual	3.63	21	0.1728	-	-
Lack of fit	3.37	18	0.1874	2.19	0.2839
Pure error	0.2565	3	0.0855	-	-
Standard deviation=0.42, mean=27.43, co-efficient of variation(%)=1.52, R ² =0.98, R ² _{Adj} =0.98, R ² _{Pred} = 0.96, Adeq precision= 37.99					

The F-value and p-value have been used to establish the significance, acceptance and validity of the reduced quadratic models using regression techniques. F-value gives the comparison for the mean square values of the proposed regression model and the mean

square values of residual (value of residual given in Table 5.1 and 5.2). The high F-value indicates good reliability and reproducibility while its low value gives poor reliability and reproducibility for the proposed regression model. On the other hand when p-value is on lower side it implies high significance to the model and high p-value gives insignificance to the model (Mubarak et al., 2011).

In the present work the F-value of the proposed reduced quadratic models for the bio-oil yield during the pyrolysis of torrefied pigeon pea stalk and eucalyptus have been 316.2 and 193.6, respectively. These F-values can be considered high enough implying that the proposed quadratic models in their reduced form have been reliable with high reproducibility. Also, the corresponding p-value for both the models have been less than 0.001 indicative towards the high significance of the models and the probability of F-value being high due to noise could be only 0.01%. The terms whose p-value have been less than 0.05 can be considered as significant terms (Singh, R.K. et al., 2020a; Singh, R.K. et al., 2020b) and the same can be observed from Table 5.3 and 5.4 where only significant terms have been listed for the development of reduced quadratic models. In the proposed models the significant terms for the pyrolysis of torrefied pigeon pea stalk have been X_1 , X_2 , X_3 and X_1^2 , whereas for the pyrolysis of torrefied eucalyptus it has been X_1 , X_2 , X_3 , X_4 , X_3X_4 and X_1^2 . The number of significant terms during the pyrolysis of torrefied eucalyptus being different to that of torrefied pigeon pea stalk clearly suggest that bio-oil yield depends not only on the operating parameters but also on the pre-treatment of biomass leading to changes such as substantial decrease in the thermal stability of the lignin for the eucalyptus as discussed in the Chapter 4. However, it can also be inferred that temperature, residence

time and heating rate will always play an important role in the bio-oil yield with nitrogen sweeping rate being either significant or insignificant depending upon the biomass selection.

Now the extent of influence of significant terms on the response (bio-oil yield) could be analysed by comparing their corresponding F-value where large value have higher influence. On this basis it can be inferred that the sequence of influence of significant terms on bio-oil yield have been $X_1 > X_1^2 > X_3 > X_2$ and $X_1 > X_1^2 > X_3 > X_3X_4 > X_2 > X_4$ for pyrolysis of torrefied pigeon pea stalk and eucalyptus, respectively. Another very important parameter during the development of regression model is the analysis of LOF which indicates whether the proposed model can be trusted or not. If for the LOF its F-value is small and p-value is >0.05 then the proposed mathematical model can be considered as accurate and reliable with LOF being insignificant (Arvindekar and Laddha, 2016; Bezerra et al., 2008; Ghelich et al., 2019). In the present analysis, the F-value of LOF have been 1.77 and 2.19 for pyrolysis of torrefied pigeon pea stalk and eucalyptus, respectively, with p-value being more than 0.05. Hence, on the basis of small F-value for LOF in combination with insignificant LOF the proposed quadratic models in its reduced forms holds good and have been well fitted (Hemmat Esfe et al., 2020; Pinto et al., 2020).

Pyrolysis of torrefied pigeon pea stalk:

$$BY = 27.83 + 2.24X_1 - 0.39X_2 + 0.41X_3 - 3.53X_1^2 \quad (5.2)$$

Pyrolysis of torrefied eucalyptus:

$$BY = 29.90 + 2.32X_1 - 0.22X_2 + 0.61X_3 - 0.01X_4 - 0.30X_3X_4 - 3.84X_1^2 \quad (5.3)$$

In the present study only significant terms have been used for establishing the effective mathematical models which can predict the bio-oil yield accurately and have higher

reproducibility within the stated range of operation. The developed quadratic models in its reduced form obtained after carrying out regression analysis of experimental data to predict the bio-oil yield for the pyrolysis of torrefied pigeon pea stalk and eucalyptus have been presented by Eqs. 5.2 and 5.3, respectively. In Eqs. 5.2 and 5.3 single terms such as X_1 and X_2 provides the information about the influence of individual operating parameters on response (bio-oil yield). Similarly, two factor terms such as X_1^2 , X_2^2 , X_3X_4 and X_1X_2 provide the combined effect of the factors on the bio-oil yield. Also, in Eqs. 5.2 and 5.3 few terms will support the response and hence will help in achieving higher bio-oil yield while others will inhibit the response and try to reduce the bio-oil yield. The synergistic and antagonistic effect of factor terms can be made by observing positive and negative sign prior to these terms, respectively. Based on these it can be inferred that X_1 and X_3 have synergistic effect on bio-oil yield while X_2 , X_4 , X_3X_4 and X_1^2 have antagonistic effect.

5.5 Influence of operating parameters on bio-oil yield

In pyrolysis temperature as an operating parameter provides with the necessary energy in the form of heat required in the decomposition of various types of bonds present in biomass (Angin, 2013; Ly et al., 2015). Many researchers have mentioned that generally on increasing the temperature positive influence or synergistic effect on the bio-oil yield has been observed however, when the temperature was increased above certain limit negative or antagonistic effect was observed (Garg et al., 2016; Islam et al., 2010; Varma and Mondal, 2017). This happens mainly due to favourable conditions for secondary cracking at higher temperature for the volatiles releasing during pyrolysis and resulting into higher yield of non-condensable gases (also known as pyrolytic gas during pyrolysis) (Isahak et

al., 2012). On observing Table 5.1 and 5.2 it can be inferred that when temperature has been increased from 450 to 550 °C the bio-oil yield decreases. This can also be confirmed by analysing Eq. 5.2 and 5.3 where sign prior to two factor term (X_1^2) associated with temperature has been negative while single factor term (X_1) has opposite sign (+). Similar trend was observed by Jung et al. (Jung et al., 2008) where bio-oil yield during the pyrolysis of bamboo sawdust decreased from 72 to 61 wt.% when the temperature increased from 405 to 510 °C. Zheng et al. (Zheng, 2007; Zheng et al., 2006) also observed that during the pyrolysis of rice husk the bio-oil yield above particular temperature (540 °C) got significantly reduced while same thing happened for cotton stalk at 530 °C.

Another important operating parameter during the decomposition of biomass is residence time (X_2) which represents the duration for which the biomass has been sustained at a specific temperature. This is a very important aspect especially in a fixed bed batch operations such as in the present study where biomass should be exposed sufficiently for achieving desired results. However, longer residence time can lead to secondary reactions such as gasification, carbonization and thermal cracking for the volatiles released during pyrolysis which results in to lower bio-oil yield (Bartoli et al., 2016; Guedes et al., 2018; Tsai et al., 2007). In the present study on analysing Table 5.1 and 5.2, Eq. 5.2 and 5.3, we can clearly inferred that increasing residence time has antagonistic effect on the bio-oil yield. Similar results was also observed by Tsai et al. (Tsai et al., 2007) where bio-oil yield during the pyrolysis of rice husk in a fixed bed had yield decreased after increasing the

residence time above 2 min and hence they concluded that very short residence time was beneficial in achieving high bio-oil yield at a particular temperature.

Heating rate also substantially influences the quality and quantity of the bio-oil during pyrolysis. Heating rate (X_3) during the pyrolysis of both the torrefied biomass has the positive influence on the bio-oil yield as observed in Table 5.1 and 5.2, Eq. 5.2 and 5.3. The increase in heating rate reduced the chances of secondary cracking of the released pyrolysis volatiles and thus increased the bio-oil yield (Ben Hassen-Trabelsi et al., 2014). Ates et al. (Ateş et al., 2004) and Onay et al. (Onay and Mete Koçkar, 2004) also observed increase in bio-oil yield when the heating rate was increased in a fixed bed reactor. However, some researchers also mentioned that increase in heating rate may decrease the bio-oil yield and this depends greatly on other factors such as biomass composition and operating temperature (Razuan et al., 2010; Şensöz and Angın, 2008).

As discussed earlier secondary reaction of volatiles released during pyrolysis decreases the bio-oil yield and in this regard nitrogen sweeping rate (X_4) also plays an important role. In pyrolysis the purging of volatiles, nitrogen is the most commonly used gas due to its various benefits such as readily available, economical and being inert even at high temperature range. However, in the present study significant influence of nitrogen sweeping rate on bio-oil yield has been observed only in the case of pyrolysis of torrefied eucalyptus suggesting that source of biomass and its composition also plays an important role. Several studies have shown contradicting results on the effect of varying nitrogen sweeping rate on bio-oil yield. Asadullah et al. (Asadullah et al., 2013) reported increase of 14% in the bio-oil yield when nitrogen sweeping rate increased from 1000 to 2000 ml/min

on the other side Garg et al. (Garg et al., 2016) reported continuous decrease in bio-oil yield from 44 to 30 wt.% when nitrogen sweeping rate increased from 100 to 400 cm³/min. Also researchers like Huang et al. (Huang et al., 2014) and Heo et al. (Heo et al., 2010) reported nominal effect of varying nitrogen sweeping rate on bio-yield.

5.6 Optimization and 3-D plots

Table. 5.5 Constraints provided during process optimization

Constraints name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Temperature	is in range	350	550	1	1	3
Residence time	is in range	0	30	1	1	3
Heating rate	is in range	20	60	1	1	3
Nitrogen sweeping rate	is in range	40	100	1	1	3
Pigeon pea stalk						
Bio-oil yield (wt.%)	maximize	20.98	28.37	1	1	5
Eucalyptus						
Bio-oil yield (wt.%)	maximize	22.8	30.29	1	1	5

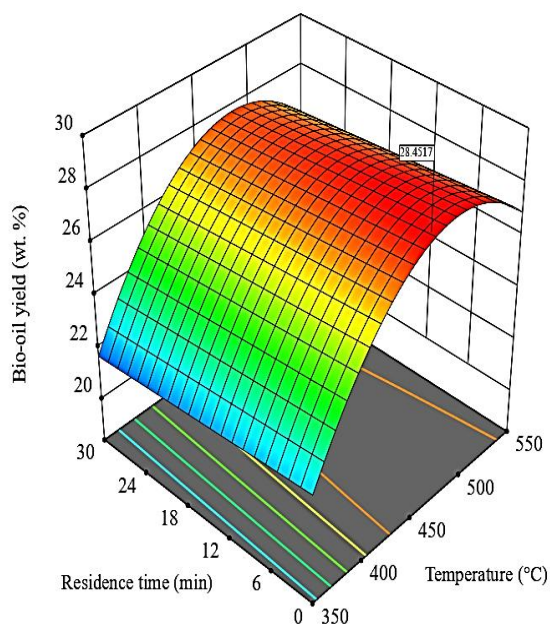
In order to produce bio-oil efficiently through pyrolysis of torrefied biomass it becomes necessary to optimize the operating parameters. To optimize the operating parameters for the maximum bio-oil yield during the pyrolysis of torrefied pigeon pea stalk and eucalyptus, the operating parameters for both the cases have been kept as “in range” with equal weightage. Table 5.5 presents the constraints given in Design of Expert software while optimizing pyrolysis for both the biomass. In the present study during pyrolysis as only single response (bio-oil yield) has been maximized the number of solutions with adequate desirability value have been close to hundred for each cases. However, the solution which offered with maximum value of desirability has been selected for both the biomass. The optimum operating parameters for maximum bio-oil yield during pyrolysis of

torrefied pigeon pea stalk and eucalyptus have been 461.25 °C, 0.75 min, 42.25 °C/min, 73.40 ml/min and 442.06 °C, 0.29 min, 55.42 °C/min, 41.97 ml/min, respectively, and the same has been presented in Table 5.6. As discussed in Section 5.4 and 5.5, that the temperature has the most prominent influence on bio-oil yield as compared to other operating parameters. In the present study for both the torrefied biomass the optimum operating temperature (442.06 and 461.25 °C) which yields maximum bio-oil has been much less as compared to various raw biomass which yielded maximum bio-oil yield between 500-650 °C as mentioned by researchers such as Gupta et al. (Gupta and Mondal, 2019), Mohammed et al. (Mohammed et al., 2017a; Mohammed et al., 2017b) and Abas et al. (Abas et al., 2018). Based on these observations it can be inferred that torrefaction reduces the required energy for obtaining maximum bio-oil yield by decreasing the optimum operating temperature and the same can also be supported by kinetic parameter estimation for pyrolysis where total activation energy decreased significantly for optimum torrefaction condition as discussed in the Section 4.12 of the Chapter 4.

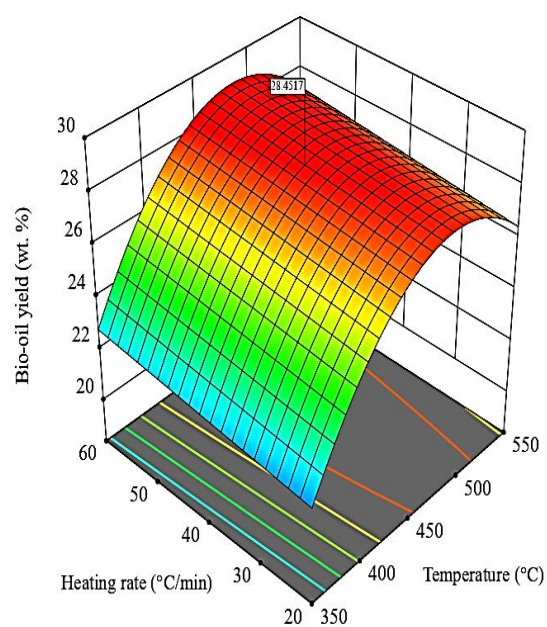
Table 5.6 Optimum operating conditions with predicted and experimental values

	Temperature (°C)	Residence time (min)	Heating rate (°C/min)	Nitrogen sweeping rate (ml/min)	Bio-oil yield (wt.%)	Desirability
Pigeon pea stalk						
Predicted	461.25	0.75	42.25	73.40	28.45	1
Experimental	461	1	42.3	73	29.53±42	-
Deviation (%)					3.80	-
Eucalyptus						
Predicted	442.06	0.29	55.42	41.97	30.59	1
Experimental	442	0	55.4	42	31.87±62	-
Deviation (%)					4.18	-

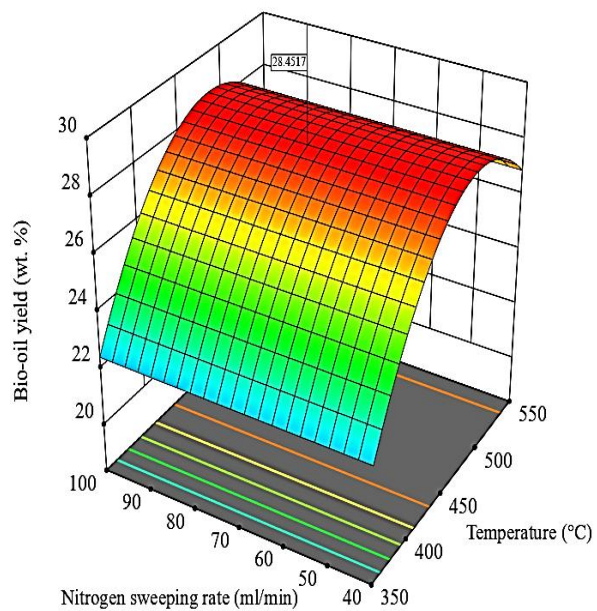
(a)



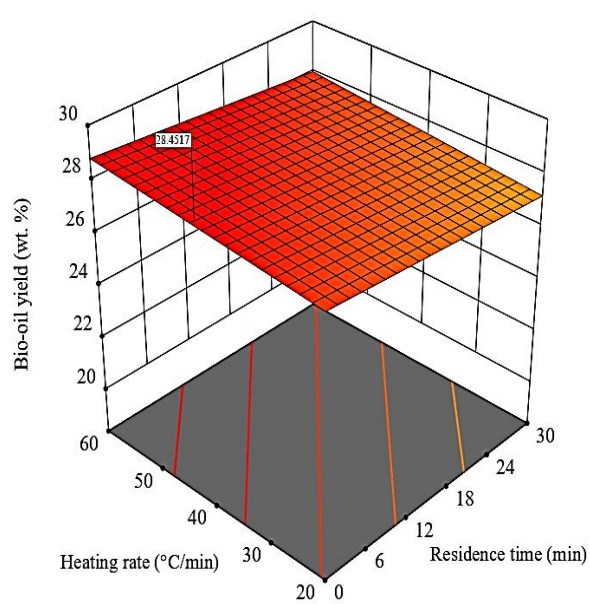
(b)



(c)



(d)



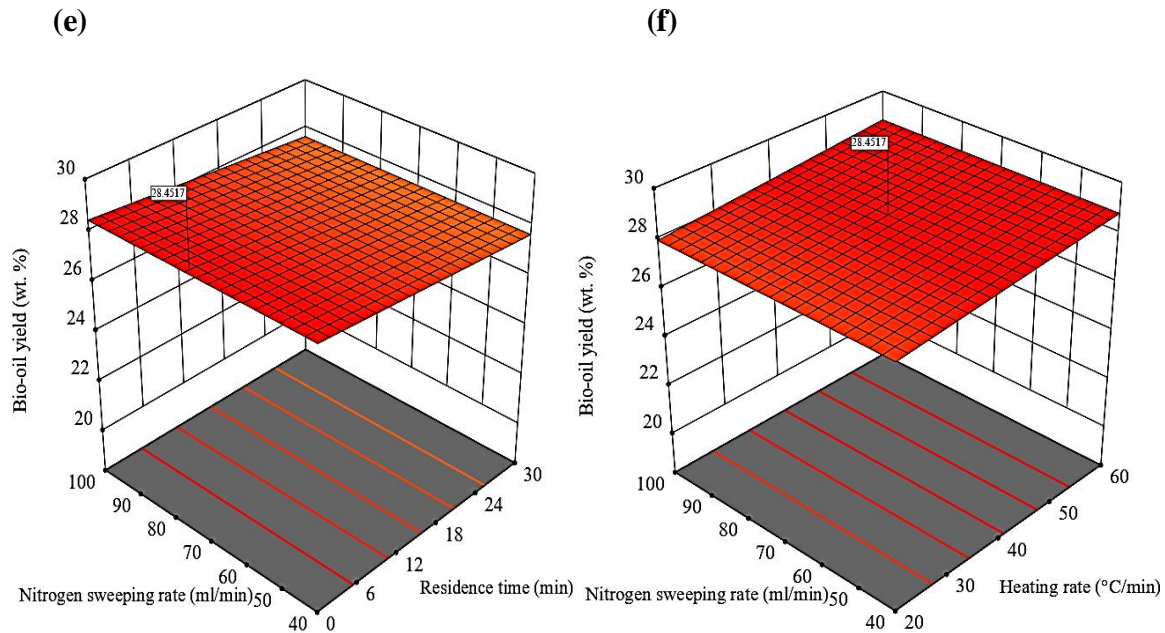
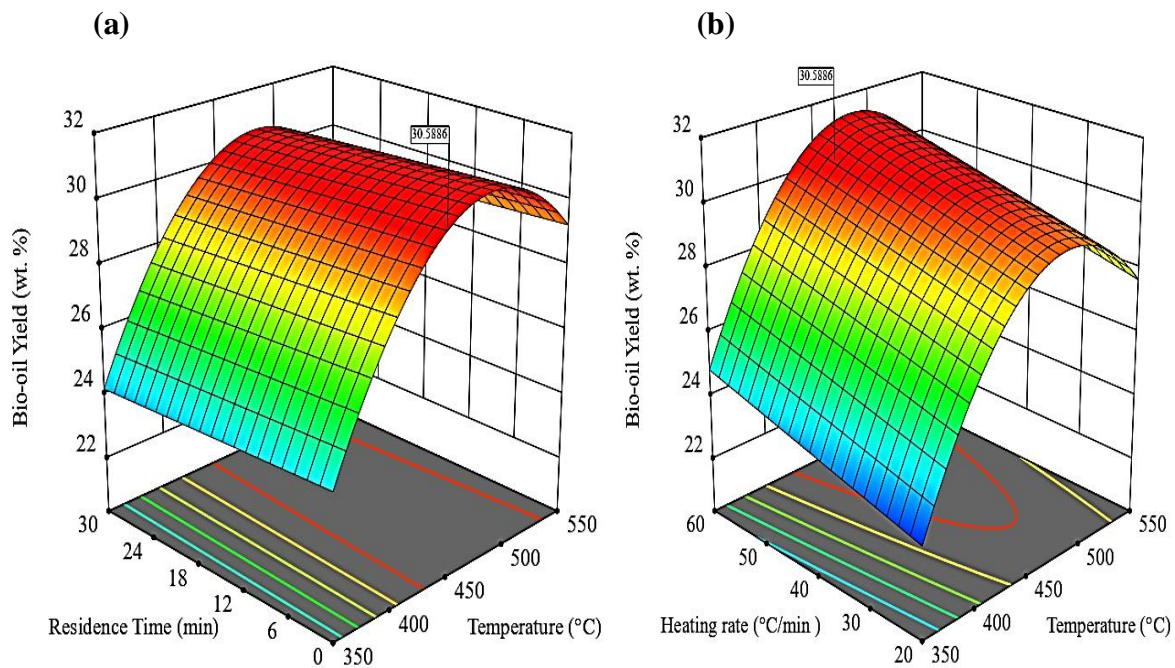


Fig. 5.2 3-D plots for the combined effect of (a) temperature and residence time, (b) temperature and heating rate, (c) temperature and nitrogen sweeping rate, (d) residence time and heating rate, (e) residence time and nitrogen sweeping rate, and (f) heating rate and nitrogen sweeping rate, on bio-oil yield of torrefied pigeon pea stalk



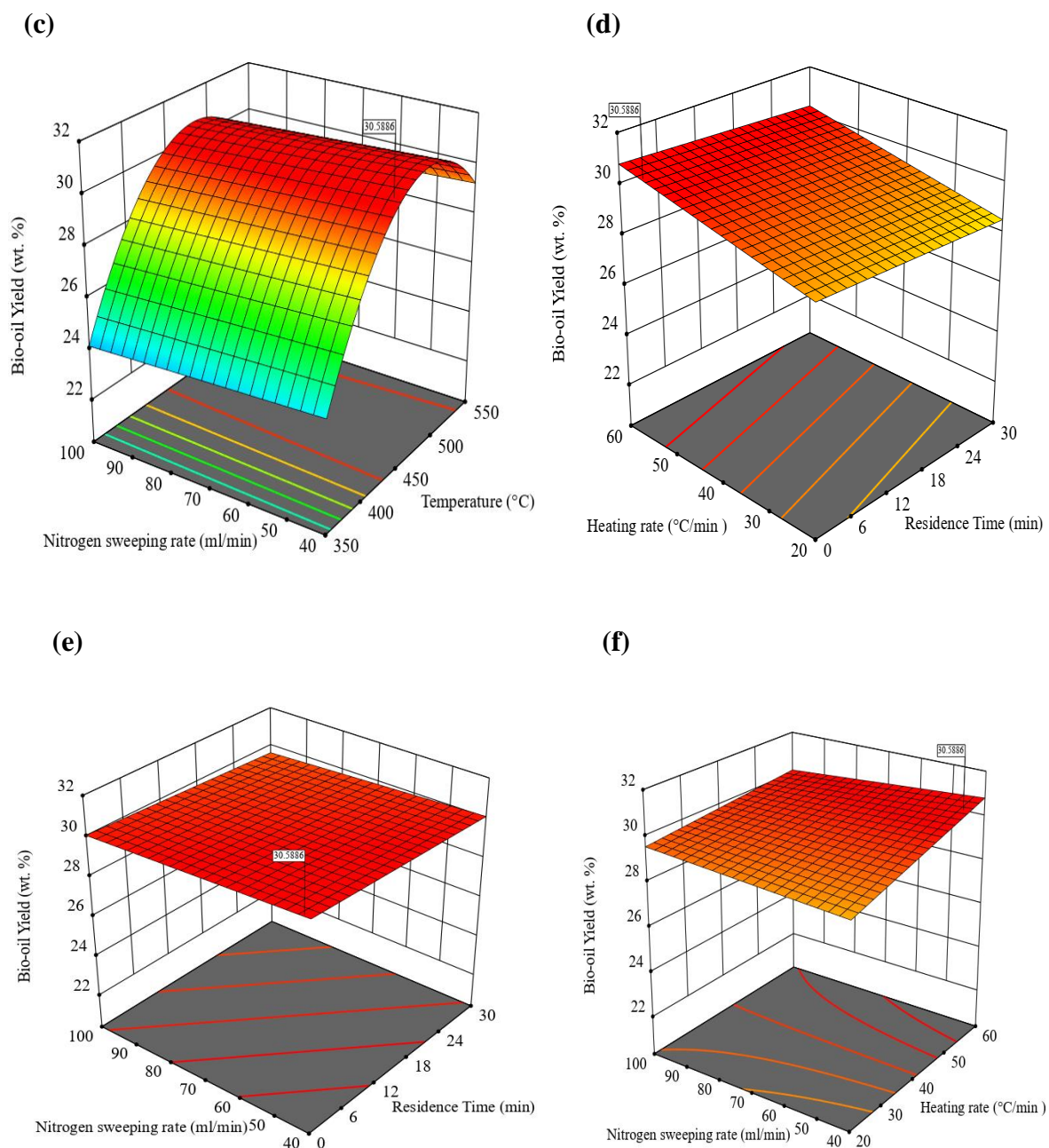


Fig. 5.3 3-D plots for the combined effect of (a) temperature and residence time, (b) temperature and heating rate, (c) temperature and nitrogen sweeping rate, (d) residence time and heating rate, (e) residence time and nitrogen sweeping rate, and (f) heating rate and nitrogen sweeping rate, on bio-oil yield of torrefied eucalyptus

3D plots have been used to study the individual and the combine effect of operating parameters on the response. To present the variation of all four operating parameters in a single 3-D plot has not been possible, hence a single plot represents the effect of variation of two parameters on the response while other two parameters have been kept at a constant value obtained after process optimization. Figs. 5.2 (a)-(f) and 5.3 (a)-(f) have been the 3-D plots which represents the individual and interactive effect of operating parameters (temperature, residence time, heating rate and nitrogen sweeping rate) on bio-oil yield for the pyrolysis of torrefied pigeon pea stalk and eucalyptus, respectively.

Figs. 5.2 (a) and 5.3 (a) have been plot between temperature and residence time verses bio-oil yield while keeping heating rate and nitrogen sweeping rate at a constant value. The constant value of heating rate and nitrogen sweeping rate for Fig. 5.2 (a) has been 42.25 °C/min and 73.40 ml/min, while for Fig. 5.3 (a) it has been 55.42 °C/min and 41.97 ml/min, respectively. On analysing these two plots one can observe that the individual impact of residence time has been much less as compared to that of temperature while the combined effect seems to be mainly depending on temperature value which has been similar to the findings of ANOVA analysis where X_1X_2 for both the cases have been insignificant. Also, in Figs. 5.2 (a) and 5.3 (a) it can be observed that to obtain maximum bio-oil yield the recommended region of operation would be at moderate temperature range (430-470 °C) with low value of residence time as after increasing the temperature above range the bio-oil yield gets decrease. The 3-D plots between temperature and heating rate verses bio-oil yield have been represented by Figs. 5.2 (b) and 5.3 (b) with other two parameters (residence time and nitrogen sweeping rate) kept constant for both the pyrolysis

of torrefied pigeon pea stalk (0.75 min and 73.40 ml/min) and eucalyptus (0.29 min and 41.97 ml/min). In these two plots on analysing the individual effects, it can be observed that temperature has more prominent influence on bio-oil yield as compared to heating rate and for their combined effect no significant influence can be observed. Similarly, on observing Figs. 5.2 (c) and 5.3 (c) again the temperature has more influence on bio-oil yield with no significant combined effect being observed.

Figs. 5.2 (d) and 5.3 (d) represents the 3-D plots between residence time and heating rate verses bio-oil yield while the values of both temperature (461.25 and 442.06 °C for the pyrolysis of torrefied pigeon pea stalk and eucalyptus, respectively) and nitrogen sweeping rate have been kept constant. On analysing these two plots for individual effect it can be inferred that heating rate has positive effect while nitrogen has negative effect where magnitude of effect being more for heating rate. Hence, based on these observations the recommended range of operation for heating rate would be between moderate to high (40-60 °C). In Figs. 5.2 (e) and 5.3 (e) which have been the 3-D plots for residence time and nitrogen sweeping rate verses bio-oil yield it can be observed that residence time has more individual influence on bio-oil yield as compared to nitrogen sweeping rate while the combined effect on bio-oil yield has been very nominal. Similarly in Figs. 5.2 (f) and 5.3 (f) the heating rate has more impact on bio-oil yield as compared to nitrogen sweeping rate. The interactive influence of heating rate with nitrogen sweeping rate has been nominal in Fig. 5.2 (f), however, some interactive influence can be observed in Fig. 5.3 (f). Based on these observations the recommended range of operation for nitrogen sweeping rate would be between mild to moderate region (40-80 ml/min).

5.7 Experimental validation for optimized process parameters

To validate the optimized process parameters as obtained in Table 5.6, experiments at optimum condition for their respective biomass have been performed thrice and average values have been quoted in the present study. The actual bio-oil yield (29.53 ± 42 and 31.87 ± 62 wt.%) at the optimized condition for both the biomass have good agreement with the predicted values (28.45 and 30.59 wt.%). It can be notice that actual bio-oil yield deviated by 3.80 and 4.18 % from their respective predicted values for the pyrolysis of torrefied pigeon pea stalk and eucalyptus, respectively. Similar deviations were also reported by other researchers while performing RSM based optimization process (Baruah et al., 2018; Singh, S. et al., 2020; Tripathi et al., 2020). These deviations can be attributed to the fact that there have been some practical limitations associated with the experimental set-up such as keeping exact values of operating parameters as predicted by the software for the optimized condition while performing experiments. These limitations led to a condition such as the software predicted the optimized condition for the pyrolysis of torrefied pigeon pea stalk at 461.25 °C, 0.75 min, 42.25 °C/min, and 73.40 ml/min however, the experiments have been performed at 461 °C, 1 min, 42.3 °C/min and 73 ml/min.

5.8 Product distribution and their characterization

In order to understand the effect of torrefaction on the quantitative and qualitative aspects of products obtained after pyrolysis, these products have been compared with the ones obtained from the pyrolysis of raw biomass performed at the same operating conditions. Also, the impact of severity of pyrolysis conditions have been analysed by comparing the

products obtained at the least severe (PTPS-350-0-20-40, PTEC-350-20-0-40, PRPS-350-0-20-40 and PREC-350-0-20-40) and the most severe (PTPS-550-30-60-100, PTEC-550-30-60-100, PRPS-550-30-60-100 and PREC-550-30-60-100) conditions of pyrolysis for both raw and torrefied biomass of pigeon pea stalk and eucalyptus.

5.8.1 Product distribution for the pyrolysis of raw and torrefied biomass

Fig. 5.4 represents the effect of torrefaction on the product distribution for the pyrolysis of pigeon pea stalk and eucalyptus, and have been compared with their respective raw biomass pyrolysis. On analysing Fig. 5.4 it can be observed that for the pyrolysis of torrefied biomass decrease substantially for both pigeon pea stalk and eucalyptus. The bio-oil yield for PTPSO and PTECO has been 29.53 and 31.87 wt.%, respectively, while for PRPSO and PRECO it has been 44.69 and 46.13 wt.%, respectively, and have been performed at the same optimum condition of pyrolysis for their respective torrefied biomass. This reduction in bio-oil yield has been due to release of lean energy components such as H₂O, CO₂, acetic acid, CO and other substances during the torrefaction of raw biomass especially from dehydration and hemicellulose decomposition (Boateng and Mullen, 2013; Chen, Y. et al., 2016). Louwes et al. (Louwes et al., 2017) also observed similar results for three different biomass feedstocks where the bio-oil yield decreased significantly for the pyrolysis of torrefied biomass and was in range of 25-36 wt.%, while for their respective raw biomass it was in the range of 42-45 wt.%.

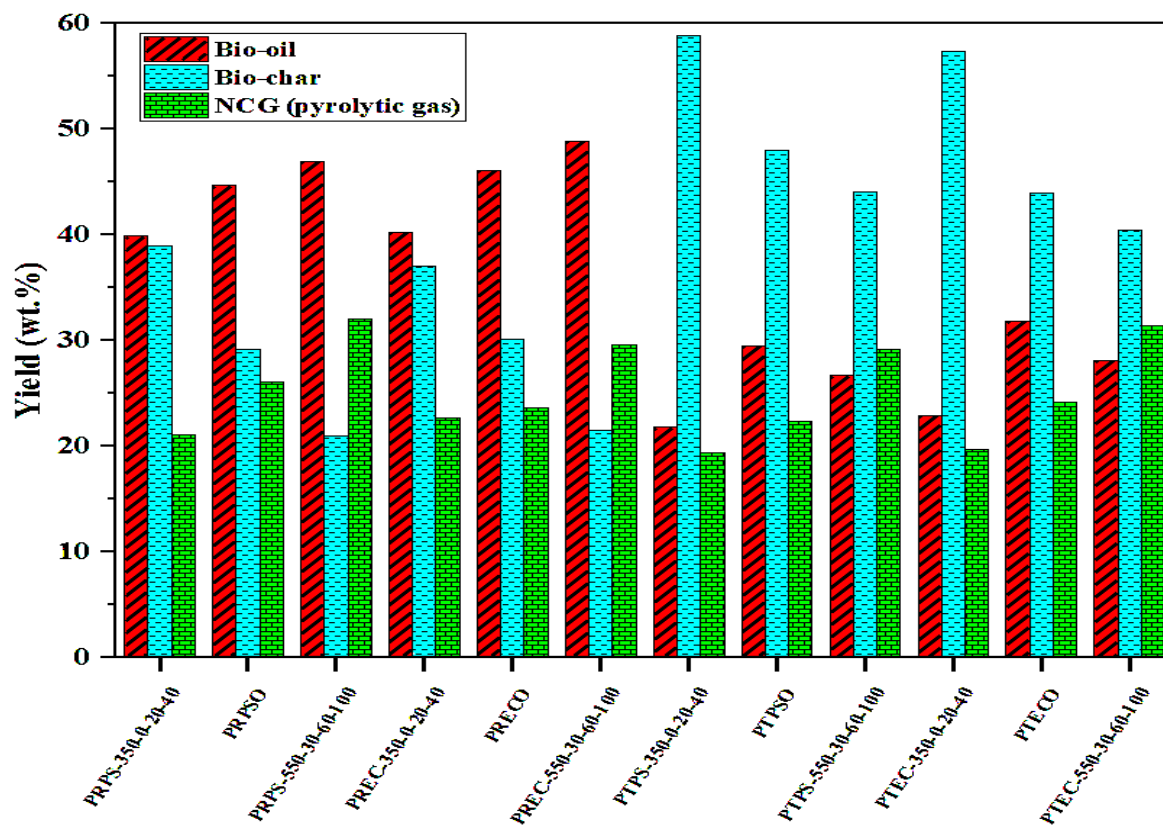


Fig. 5.4 Product distribution for the pyrolysis of raw and torrefied biomass.

In the present study, there has been a significant increase in the bio-char yield for the pyrolysis of torrefied biomass. Bio-char yield has been increased from 29.19 to 48.05 wt.% and 30.18 to 43.96 wt.% for PTPSO and PTECO, respectively, as compared to PRPSO and PRECO. This increase in bio-char yield has been due to carbonization of biomass when they underwent through pre-treatment process of torrefaction (Chen, Y. et al., 2016). Also, torrefied biomass have been relatively high in the lignin composition as compared to their respective raw biomass which has been already discussed in the Section 4.7 of the Chapter 4. This high concentration of lignin leads to increase in char formation as lignin is much

more recalcitrant during pyrolysis as compared to hemicellulose and cellulose (S and P, 2019; Vijayaraghavan, 2019).

On analyzing Fig. 5.4 no clear trend can be observed regarding the effect of torrefaction on the yield of NCG (pyrolytic gas). The yield of pyrolytic gas has been decreased for all the cases of torrefied pigeon pea stalk as compared to its raw biomass such as for PTPSO and PTPS-550-30-60-100, the yield has been 22.42 and 29.17 wt.%, respectively, as compared to PRPSO (26.12 wt.%) and PRPS-550-30-60-100 (32.05 wt.%). On the other side, the pyrolytic gas yield marginally increases for PTECO (24.17 wt.%) and PTEC-550-30-60-100 (31.4 wt.%) as compared to PRECO (23.69 wt.%) and PREC-550-30-60-100 (29.59 wt.%). The higher bio-oil yield and pyrolytic gas yield for the pyrolysis of torrefied eucalyptus as compared to the pyrolysis of torrefied pigeon pea stalk can be attributed to the substantial decrease in the thermal stability of lignin present in eucalyptus after it underwent through torrefaction process. Majority of the studies on the pyrolysis of torrefied biomass reported decreases in the yield of pyrolytic gas (Chen, D. et al., 2016; Gogoi et al., 2017; Louwes et al., 2017) while few had observed marginal increase in their pyrolytic gas yield (Chen, Y. et al., 2016; Zheng et al., 2013).

5.8.2 Effect of torrefaction on the physicochemical properties of bio-oil

The qualitative differences between the bio-oils obtained from raw and torrefied biomass have been presented in Table 5.7. On analyzing Table 5.7 significant improvement in terms of HHV, elemental analysis, water and organic content can be observed for the bio-oil obtained from the pyrolysis of torrefied as compared to bio-oil obtained from their corresponding raw biomass, however, in terms of viscosity the quality of bio-oil decreases.

Table 5.7 Properties of bio-oil obtained from raw and torrefied biomass (pigeon pea stalk and eucalyptus)

Samples	HHV (MJ/kg)	Elemental analysis (wt.%)				Water content (wt.%)	Organic Content* (wt.%)	Viscosity (cSt) (25 °C)
		C	H	N	O*			
PRPS-350-0-20-40	14.18	44.6	7.3	0.7	47.4	43.1	56.9	3.5
PRPSO	18.56	46.4	7.4	0.8	45.4	34.7	65.3	3.8
PRPS-550-30-60-100	20.05	48.3	7.3	0.9	43.5	30.2	69.8	3.9
PREC-350-0-20-40	14.74	44.3	7.2	0.9	47.6	41.4	58.6	4.3
PRECO	19.43	47.8	7.3	0.8	44.1	33.6	66.4	4.6
PREC-550-30-60-100	20.94	49.8	7.2	0.8	42.2	29.2	70.8	4.9
PTPS-350-0-20-40	18.73	48.4	7.6	0.9	43.1	28.5	71.5	4.1
PTPSO	24.89	51.4	7.5	0.8	40.3	23.2	76.8	4.4
PTPS-550-30-60-100	25.93	53.1	7.5	0.9	38.5	21.3	78.7	4.9
PTEC-350-0-20-40	19.51	48.1	7.3	0.8	43.8	26.7	73.3	4.8
PTECO	25.64	53.6	7.1	0.7	38.6	22.1	77.9	5.1
PTEC-550-30-60-100	26.57	55.4	7.2	0.6	36.8	20.1	79.9	5.4

*Calculated by difference.

The HHV for PTPSO and PTECO increases from 18.56 (PRPSO) to 24.89 MJ/kg and 19.43 (PRECO) to 25.64 MJ/kg, respectively. Meng et al (Meng et al., 2012) also witnessed a significant increase in the HHV of bio-oil which increased from 20 to 26.3 MJ/kg for the pyrolysis of torrefied loblolly pine and Singh et al. (Singh, S. et al., 2020) also witnessed impressive increase from 24.73 to 30.55 MJ/kg for its bio-oil obtained from the pyrolysis of torrefied *Acacia Nilotica* as compared to its raw biomass. This increase in HHV has been found because the torrefied biomass used as a feed stock for the pyrolysis purpose contains less amount of lean energy volatiles which have been removed during the torrefaction process and hence, the bio-oil obtained from its pyrolysis contains less amount

of water and oxygen with higher carbon content which have been evident on the analysis of Table. 5.7. Several researchers such as Guedes et al. (Guedes et al., 2018), Dai et al. (Dai et al., 2019) and Putun et al. (Pütün et al., 2008) had also mentioned in their respective studies that the HHV of a bio-oil depends heavily on its oxygen and water content.

In the present study, oxygen content decreased by 11.23 and 12.47 % while carbon content increased by 10.77 and 12.13 % for PTPSO and PTECO, respectively, as compared to their respective raw biomass pyrolysis at the same operating conditions. Gogoi et al. (Gogoi et al., 2017) also reported 11.59 % increase in its carbon content while 13.12 % decrease in its oxygen content for the bio-oil obtained from the pyrolysis of torrefied Arecanut Husk as compared its raw biomass and similar results were reported by other researchers for the bio-oil obtained from the pyrolysis of torrefied biomass (Louwes et al., 2017; Meng et al., 2012; Singh, S. et al., 2020).

On analyzing Table 5.7 a further noticeable difference can be observed for water and organic content where for both the biomass the bio-oil from their torrefied samples have witness sizeable decrease in its water content followed with significant increase in its organic content as compared to their respective bio-oil obtained from the pyrolysis of raw biomass. The water content for RTPSO and PTECO has been decreased by 33.14 and 34.23 %, respectively, as compared to PRPSO and PRECO along with organic content increasing in the same proportionate. Zheng et al. (Zheng et al., 2013) also witnessed a huge drop in its water content with maximum drop being up to 40 % for the bio-oil from the pyrolysis of torrefied corncobs.

Table 5.7 also represents the effect of torrefaction on the viscosity of bio-oil obtained from pyrolysis and substantial increase in the viscosity has been observed for all the cases of bio-oil obtained from either torrefied pigeon pea stalk or eucalyptus. There have been 15.79 and 10.87 % increase in the viscosity of bio-oil for PTPSO and PTECO, respectively, as compared to their respective raw biomass. The viscosity of bio-oil from torrefied biomass increases due to decrease in its water content and increase in its organic content (Louwes et al., 2017; Singh, S. et al., 2020), It may also be noted that during the torrefaction a huge portion of light components get removed which subsequently does not come into the bio-oil after the pyrolysis of torrefied biomass. This increase in viscosity can lead to improper atomization and may require pre-heating, however, the bio-oil obtained after pyrolysis generally undergoes through some further upgradation where other drawbacks including this can be addressed effectively. Also, the viscosity of bio-oil obtained either from raw or torrefied biomass have the value greater than conventional fuels such as diesel and ethanol, hence, will require upgradation anyways before being used as a transportation fuel (Meng et al., 2015; Sallevet et al., 2014).

Table. 5.7 also represents the effect of pyrolysis severity on the properties of bio-oil for both raw and torrefied biomass. It can be observed that when the severity of pyrolysis increases the values of HHV and carbon content increase while the values of oxygen and water content decrease for the bio-oil obtained from either raw or torrefied biomass such as the HHV value for PRPS-550-30-60-100, PREC-550-30-60-100, PTPS-550-30-60-100, and PTEC-550-30-60-100 increases from 14.18, 20.94, 18.73 and 19.51 MJ/kg to 20.05, 20.94, 25.93 and 26.57 MJ/kg, respectively, when the severity increased from 350 °C, 0

min, 20 °C/min and 40 ml/min to 550 °C, 30 min, 60 °C/min and 100 ml/min. Ly et al. (Ly et al., 2016) and Ates et al. (Ateş and Işıkdağ, 2008) also observed increase in HHV and carbon content while the oxygen and water content decreased with an increase in severity of pyrolysis.

5.8.3 Effect of torrefaction on the FTIR analysis of bio-oil

In the present study, FTIR analysis for all the samples have been performed using thin KBR pellets. Figs. 5.5 and 5.6 represent the effect of torrefaction on the FTIR analysis of bio-oil and have been compared with their respective raw biomass pyrolysis (PRPSO and PRECO). Table 5.8 presents the position of significant peaks which have been collected together with their corresponding identification groups. On analyzing Figs. 5.5 and 5.6 the maximum intensity peak for the functional groups O-H present in polymer compounds (3410 and 3431 cm^{-1}) and C-H aliphatic symmetrical (2940 and 2942 cm^{-1}) have been observed for PRPSO and PRECO which confirms that the bio-oil obtained from raw biomass contains these functional groups in significant amount. In Table 5.8 and Fig. 5.5 and 5.6 in the range of wavenumber between 1730 to 1020 cm^{-1} , the presence of ester, carbonyl, phenolic, primary alcohol and alkanes have been observed for all the cases. (Yu et al., 2019).

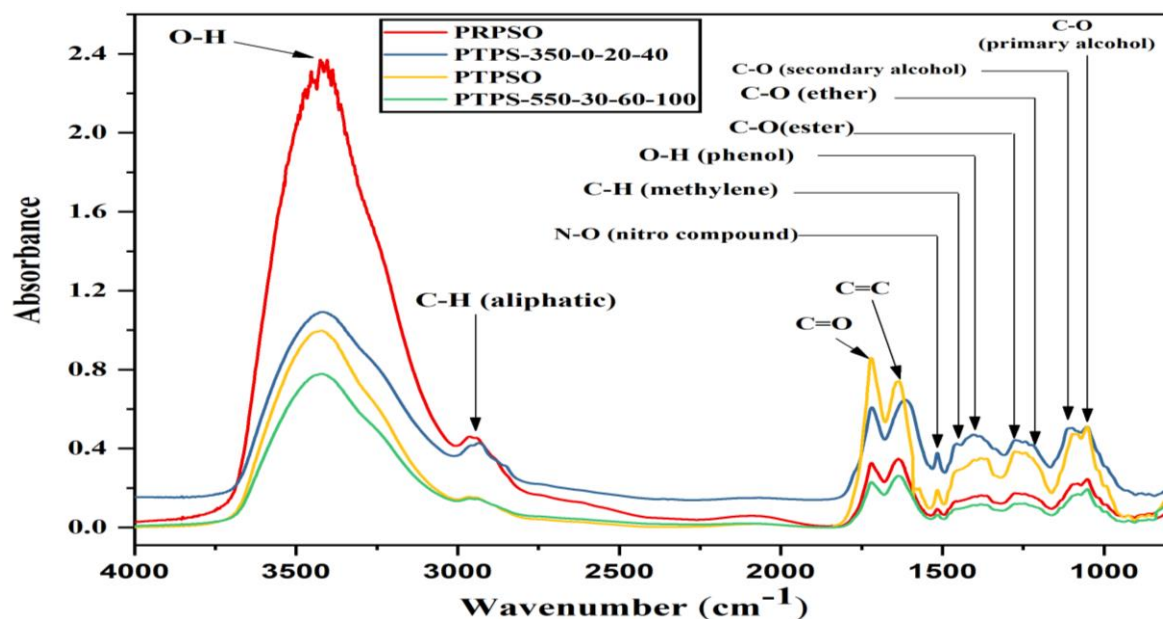


Fig. 5.5 Effect of torrefaction on the FTIR spectra of the bio-oil from pigeon pea stalk.

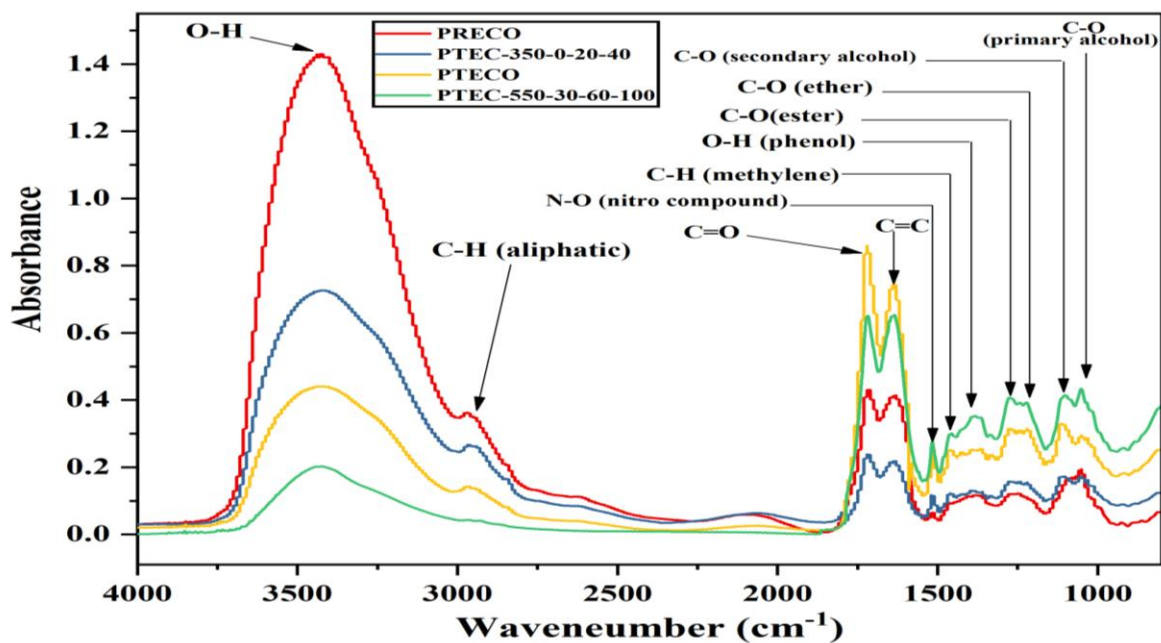


Fig. 5.6 Effect of torrefaction on the FTIR spectra of the bio-oil from eucalyptus.

Table 5.8. Position vibration, in cm^{-1} , of the most representative peaks found during infrared analysis for bio-oil.

FUNCTIONAL GROUP	Pigeon pea stalk				Eucalyptus			
	PRPSO	PTPS-350-0-20-40	PTPSO	PTPS-550-30-60-100	PRECO	PTEC-350-0-20-40	PTECO	PTEC-550-30-60-100
O-H in polymer compounds	3410	3414	3423	3426	3431	3420	3429	3425
C-H aliphatic symmetrical	2940	2929	2936	2944	2942	2943	2946	2942
C=O stretching Aldehyde, Ester	1721	1718	1722	1728	1720	1723	1718	1725
C=C stretching alkene	1633	1640	1638	1642	1631	1635	1639	1636
N-O nitro compound	1514	1518	1520	1515	1518	1516	1522	1513
C-H bending alkane	1453	1458	1459	1454	1461	1458	1463	1457
O-H bending in alcohol and phenol	1401	1389	1391	1379	1380	1383	1388	1400
C-O stretching Alkyl Aryl ether, vinyl ether, ester, primary alcohol, secondary alcohol, tertiary alcohol	1280, 1220, 1097, 1038	1278, 1218, 1103, 1042	1288, 1220, 1093, 1037	1279, 1216, 1101, 1039	1284, 1224, 1099, 1037	1286, 1223, 1108, 1029	1284, 1218, 1095, 1027	1283, 1217, 1094, 1033

The FTIR spectra for bio-oil shows a sharp peak for O-H ($3410\text{-}3431\text{ cm}^{-1}$) especially for PRPSO and PRECO which has been diminished for the bio-oil samples of torrefied biomass such as PTPSO and PTECO. The presence of O-H peak in the range of $3410\text{-}3440\text{ cm}^{-1}$ confirms the presence of water, phenol and alcohol in bio-oil, however this reduction in the intensity of peak has been mostly due to decrease in water content from bio-oil which has been already discussed in Section 5.8.2. Also, the presence of O-H peak in $1370\text{-}1410\text{ cm}^{-1}$ has been mainly due to the presence of phenol whose intensity in bio-oil has been increased for the torrefied biomass as compared to their respective raw biomass, phenol derivatives have been formed due to de-polymerization of lignin present in biomass

and this process has been facilitated by the thermochemical pre-treatment (torrefaction) of biomass which reduced the thermal stability of lignin as discussed in Section 4.12 of the Chapter 4 (Amutio et al., 2015). The other constituents in reference to O-H group detection observed in FTIR spectra may have been due to presence of other aromatic and aliphatic alcohols which also suggests that presence of these compounds have been less in the bio-oil obtained from raw biomass however, the intensities of these groups have been increased for the bio-oil obtained from torrefied biomass (Wan Sulaiman and Lee, 2012) (Ertas and Hakkı Alma, 2010).

The C-H intensity peak between 2920 to 2950 cm^{-1} indicates its stretching vibrations while presence of its intensity between 1450 to 1470 cm^{-1} corresponds to the deforming range which indicates the presence of alkane (Wan Sulaiman and Lee, 2012). In the range of 1710 to 1730 cm^{-1} a sharp intensity has been attributed to C=O stretching vibrations that indicates the presence of various organic functional groups like ketones, quinones and aldehydes in bio-oil. There has been a significant increase in the intensity of C=O stretching vibration for the bio-oil obtained from torrefied biomass with maximum intensity being observed for TPSO and TECO. This increase in intensity suggests that the presence of ketones in the bio-oil increases for both the torrefied biomass.

C=C stretching vibrations peaks in the range of 1630-1645 cm^{-1} confirms the presence of alkene group in bio-oil whose intensity has been also increased for the bio-oil from torrefied biomass as compared to raw biomass. The different intensity peaks for C-O (ether), alcohol (primary and secondary) and C-O (ester) in the range of 1020-1280 cm^{-1} indicates the presence of their corresponding groups in bio-oil (Ertas and Hakkı Alma,

2010). On analyzing Figs. 5.5 and 5.6 it can be observed that for the bio-oil from torrefied biomass the intensity of various derivatives such as ketones, phenols, alkenes, aromatic and aldehydes have increased. In the present study, the bio-oil obtained from the torrefied biomass (pigeon pea stalk and eucalyptus) both have shown different trends for the increase in the severity of pyrolysis on the variation of intensity for various functional groups present in the range of 1600-1000 cm^{-1} . Similar trend were observed by other researchers such as Chen et al. (Chen et al., 2019), Musellim et al. (Müsellim et al., 2018) and Trabelsi et al. (Ben Hassen-Trabelsi et al., 2014) where the intensity of various functional groups present in the bio-oil showed no clear trend towards the increase in the severity of operating conditions during the pyrolysis of biomass.

5.8.4 Effect of torrefaction on the GC-MS analysis of bio-oil

In order to determine the main organic components present in bio-oil, GC-MS analysis has been performed. The relative yield for various derivatives of compound groups present in the bio-oil obtained at the optimum condition of pyrolysis for both the torrefied biomass (PTPSO and PTECO) have been compared with the bio-oil of their respective raw biomass at the same optimum condition (PRPSO and PRECO). Fig. 5.7 presents the comparison between the bio-oils obtained from raw and torrefied biomass on the basis of their relative yield for various compound derivatives. In the present study for better representation and analysis the various compounds present in the bio-oil have been grouped into nine different compound derivatives of acids, alcohols, aldehydes, furans, ester, benzene + toluene, ketones, phenol and pyrazole.

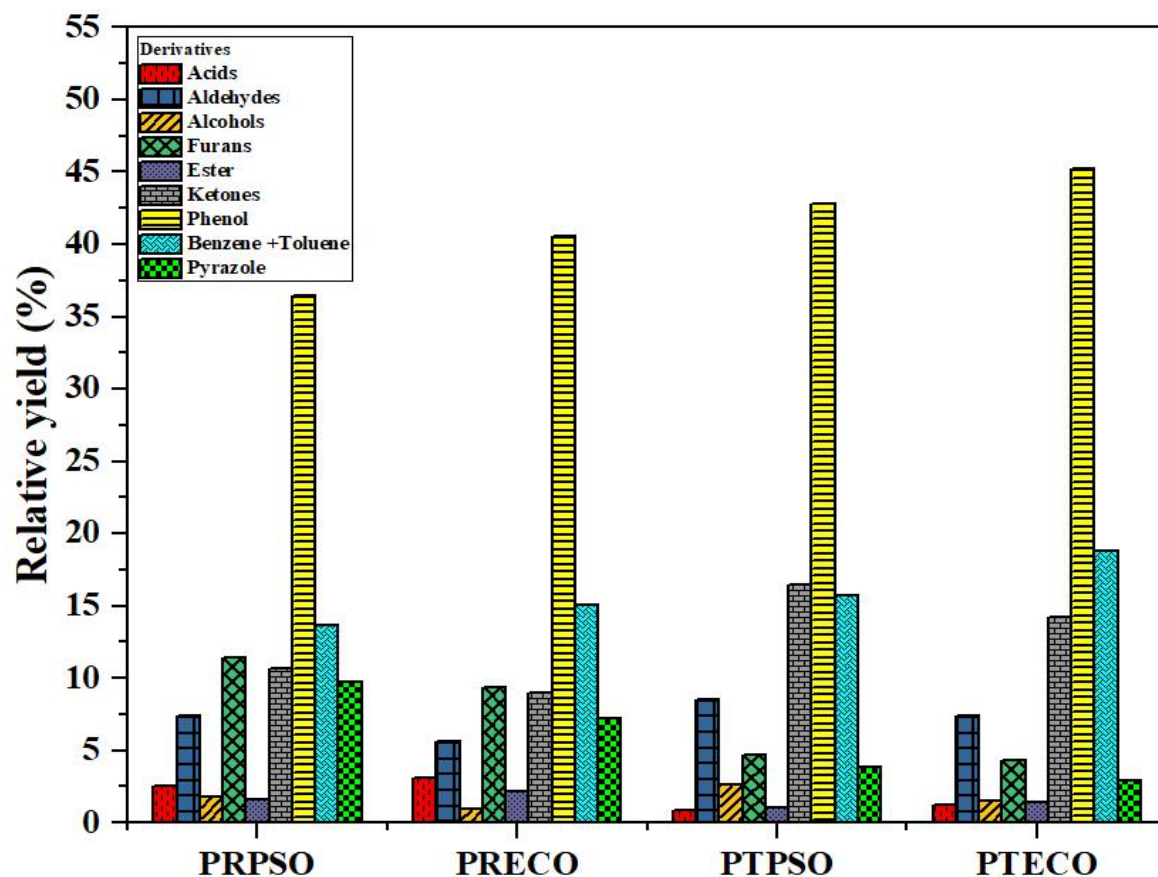


Fig. 5.7 Effect of torrefaction on the Relative yield (%) of various compound derivatives of present in the bio-oil.

The bio-oil from the pyrolysis of raw or torrefied biomass have the presence of phenol derivatives in the highest amount as compared to other compound derivatives. The presence of phenol derivatives have been increased from 36.42 to 42.83 % and 40.52 to 45.19 % for PTPSO and PTECO, respectively, as compared to their raw biomass (PRPSO and PRECO). The presence of other derivatives from aromatic compounds such as Toluene and benzene have also been increased from 13.71 to 15.71 % and 15.09 to 18.84 % for PTPSO and PTECO, respectively, which confirms the improved quality of bio-oil from torrefied biomass for the production of drop in fuel. There were many researchers who had

supported that the increased presence of benzene and toluene derivatives in the bio-oil improved its quality as a transportation fuel (Hilten et al., 2013; Singh, R.K. et al., 2020b). The increase in the presence of phenol, benzene and toluene derivatives for torrefied biomass have been due to depolymerisation of lignin present in the biomass (Heidari et al., 2014; Hilten et al., 2013) and it comes with the agreement of decrease in the thermal stability of lignin which has been observed during the torrefaction of eucalyptus and pigeon pea stalk as discussed in Section 4.12 of the Chapter 4. Chen et al. (Chen et al., 2017) also reported increase in the presence of phenol derivatives with significant decrease in acid derivatives for the bio-oil obtained from torrefied biomass.

The furan derivatives have been present in sufficient amount for PRPSO (11.38 %) and PRECO (9.40 %) as observed in Fig. 5.7 and which have been produced due to the dehydration reaction of anhydro-sugars (Wang et al., 2017a; Wang et al., 2017b). However, the presence of furan derivatives have been decreased significantly for the bio-oil obtained from torrefied biomass as observed in Fig. 5.7 for PTPSO (4.71 %) and PTECO (4.29 %). This decrease in furan derivatives have been due to the removal of furan compounds during the pre-treatment of raw biomass which has been already confirmed during the GC-MS analysis of liquid product obtained during the torrefaction of pigeon pea stalk and eucalyptus as discussed in Section 4.13 of the Chapter 4. Also, there has been a remarkable decrease of 67.19 and 61.22 % in the presence of acids in the bio-oil for PTPSO and PTECO, respectively. Zheng et al. (Zheng et al., 2013) also reported decreased presence of furan and acids in the bio-oil from torrefied corncob as compared to its raw biomass and concluded that this happened due to biomass pre-treatment through

torrefaction which restrains the formation of furan and acids at the cost of reduced bio-oil yield. Similarly, Chen et al. (Chen et al., 2018) also reported reduced content of furan and acids for the bio-oil from torrefied rubber wood husk and also contained less oxygen with more uniform properties.

The presence of ketone derivatives have been increased significantly for the bio-oil obtained from torrefied biomass (PTPSO=16.45 and PTECO=14.21 %) as compared to that of raw biomass (PRPSO=10.69 and PRECO=9.03 %). This can also be confirmed from the FTIR analysis (Figs. 5.5 and 5.6) where the intensity of C=O stretching increased substantially for PTPSO and PTECO which corresponds to the presence of ketone and aldehyde groups. Perez et al. (Arteaga-Pérez et al., 2017) stated that the presence of acids reduced while that for furan increased due to the removal of hemicellulose during torrefaction which reduced the selectivity for carboxylic acid while increased for ketones as a result of elimination of methoxy and acetoxy groups from xylose units which were present in hemicellulose. This facilitation of ketone derivatives formation during the pyrolysis of torrefied biomass has been due to ketonization and rearrangement reaction between furans and carboxylic acids. The GC-MS analysis has also revealed the presence of pyrazoles in bio-oil which have been formed due to the decomposition of proteins (amino acid) (Harman-Ware et al., 2013) or intramolecular cyclization of nitrogenous compounds present in biomass (Campanella et al., 2012).

5.8.5 Effect of torrefaction on the properties of bio-char

Table 5.9 represents the properties of bio-char obtained from the pyrolysis of raw and torrefied biomass. In Table 5.9 on analysis the data for the proximate analysis of bio-char it

can be observed that the ash content for PTPSO and PTECO have been increased from 6.17 to 8.19 wt.% and 3.51 to 4.63 wt.%, respectively, which has been due to the presence of high ash content in the torrefied biomass (TPSO=2.98 and TECO=1.18 wt.%) as compared to raw biomass (RPS=1.58 and REC=0.61 wt.%) when the former has been used as a feed for the pyrolysis purpose. The volatile matter of the bio-char obtained from the pyrolysis of torrefied biomass (PTPSO=21.06 and PTECO=21.68 wt.%) has been very less as compared to that of raw biomass (PRPSO=31.31 and PRECO=63.07 wt.%), as during the pre-treatment of raw biomass through torrefaction a good amount of volatile matter has been already removed via devolatilization reaction. Similarly, the fixed carbon of bio-char from the pyrolysis of torrefied biomass (PTPSO=70.75 and PTECO=33.42 wt.%) has been much higher as compared to raw biomass pyrolysis (PRPSO=62.52 and PRECO=63.07 wt.%) mainly due to previous devolatilization and carbonization of raw biomass through torrefaction. Dai et al. (Dai et al., 2019) in its review article for the pyrolysis of torrefied biomass had observed that due to the two stage devolatilization (first during torrefaction and second during pyrolysis) of biomass during the production of bio-char through the pyrolysis of torrefied biomass resulted into higher fixed carbon and ash content with lesser volatile and moisture content.

Table 5.9 also represents the effect of torrefaction on the elemental analysis and HHV of bio-char. The bio-char from the pyrolysis of torrefied biomass has higher carbon content (PTPSO=71.4, PTECO=74.5, PRPSO=63.8 and PRECO=66.9 wt.%) and better HHV (PTPSO=28.36, PTECO=29.79, PRPSO=26.02 and PRECO=27.06 MJ/kg) along with much lesser oxygen content (PTPSO=23.1, PTECO=19.6, PRPSO=29.3 and PRECO=26.9

wt.%) as compared to the bio-char obtained from the pyrolysis of raw biomass. The influence of change in the severity of pyrolysis on the properties of bio-char can be observed from Table 5.9. There has been a similar trend followed by the bio-char obtained either from the raw or torrefied biomass for the change in severity of pyrolysis on their HHV, proximate and elemental analysis.

Table 5.9 HHV, elemental and proximate analysis of bio-char from the pyrolysis of raw and torrefied biomass (pigeon pea stalk and eucalyptus)

Samples	Proximate analysis, dry basis (wt.%)			Elemental analysis (wt.%)				HHV (MJ/kg)
	ASH	VM	FC*	C	H	N	O*	
PRPS-350-0-20-40	4.23	39.76	56.01	57.4	6.4	0.8	35.4	24.78
PRPSO	6.17	31.31	62.52	63.8	6.1	0.8	29.3	26.02
PRPS-550-30-60-100	7.28	27.19	65.53	65.8	5.8	0.9	27.5	27.13
PTPS-350-0-20-40	6.31	26.22	67.47	69.1	4.8	1.2	24.9	26.14
PTPSO	8.19	21.06	70.75	71.4	4.2	1.3	23.1	28.36
PTPS-550-30-60-100	9.43	16.88	73.69	75.3	3.9	1.4	19.4	29.84
PREC-350-0-20-40	2.94	41.73	55.33	62.4	5.7	0.7	31.2	25.21
PRECO	3.51	33.42	63.07	66.9	5.3	0.9	26.9	27.06
PREC-550-30-60-100	4.17	27.81	68.02	69.3	5.2	0.8	24.7	28.17
PTEC-350-0-20-40	3.82	28.94	67.24	71.4	4.4	1.3	22.9	27.45
PTECO	4.63	21.68	73.69	74.5	4.1	1.8	19.6	29.79
PTEC-550-30-60-100	5.09	18.52	76.39	78.2	4.1	1.6	16.1	30.73

*Calculated by difference.

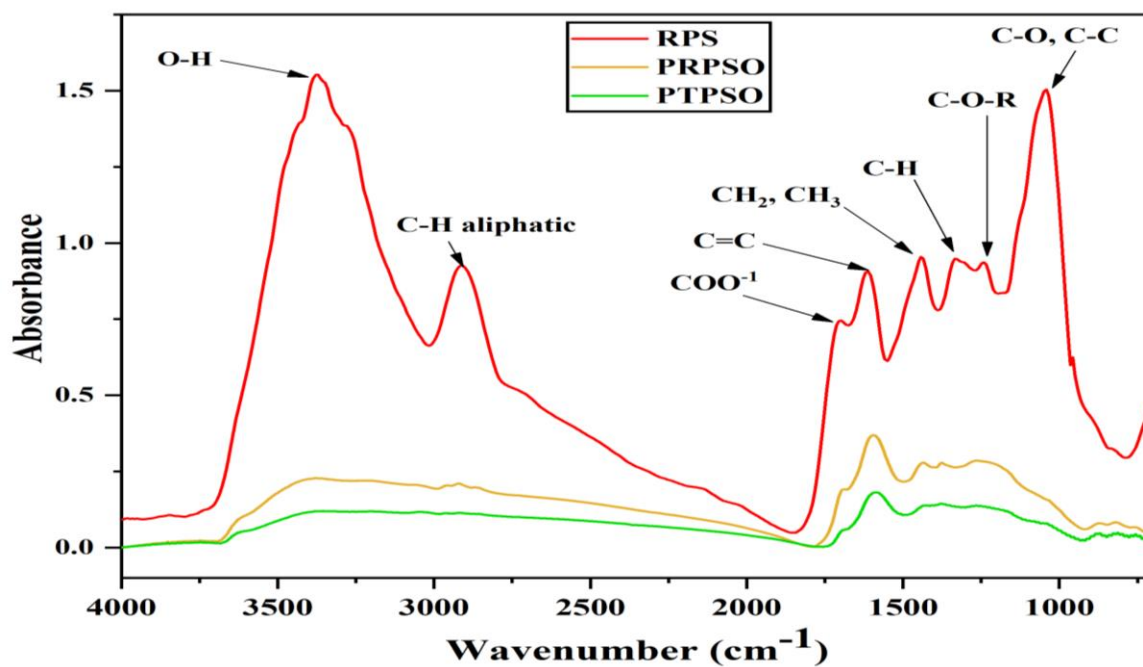


Fig. 5.8 FTIR spectra of bio-char from the pyrolysis of raw and torrefied pigeon pea stalk.

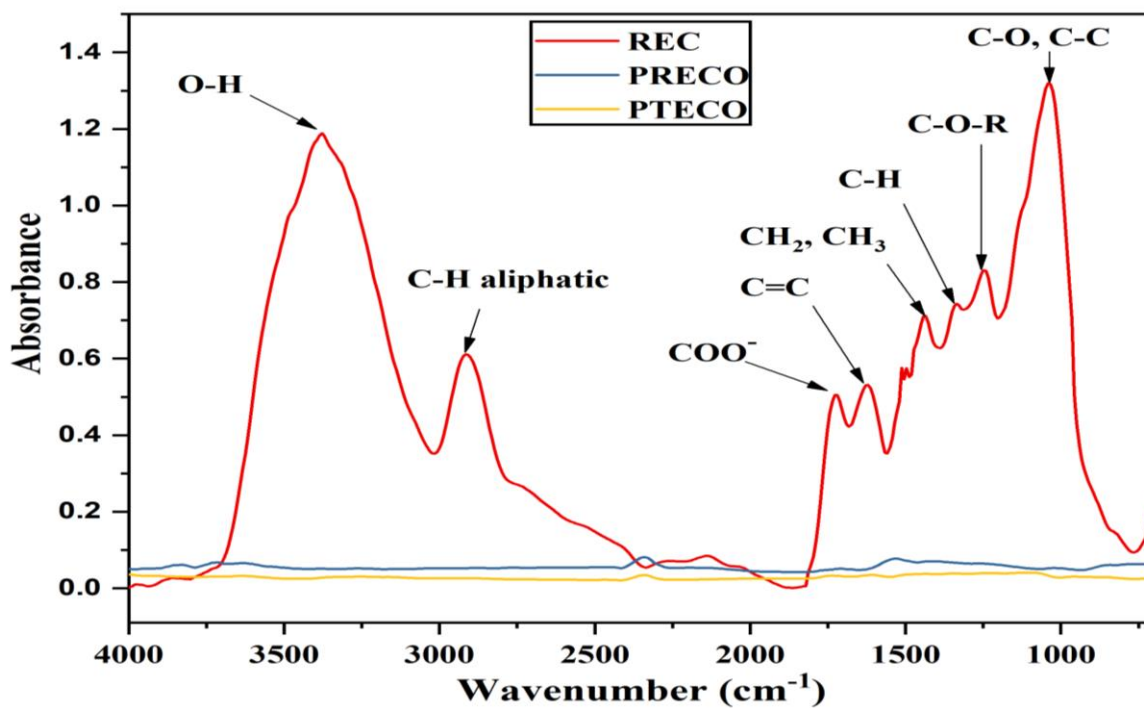


Fig. 5.9 FTIR spectra of bio-char from the pyrolysis of raw and torrefied eucalyptus.

Figs. 5.8 and 5.9 shows the comparison of FTIR spectra of bio-chars obtained from the pyrolysis of raw and their respective torrefied biomass performed at the optimum conditions. Also, for the better analysis and to show the decomposition of various functional groups the FTIR spectra of bio-chars (PTPSO, PTECO, PRPSO and PRECO) have been compared with the FTIR spectra of their respective raw biomass (RPS and REC). In Fig. 5.8 and 5.9 the FTIR spectra for the bio-chars of all four cases show substantial decrease in the intensity for all the functional groups as compared to RPS and REC. This indicates that after pyrolysis the intermolecular bonds like in O-H groups break in good amount left with very less amount of oxygenated groups.

Based on observations like high bio-char yield, improved HHV, less volatile and oxygen content with high carbon content, the bio-char obtained from the pyrolysis of torrefied biomass can be an excellent option as a solid fuel which can be used for combustion purpose.

5.8.6 Effect of torrefaction on NCG (pyrolytic gas)

Fig. 5.10 represents the gas composition (nitrogen free basis) in the volume fraction percentage for hydrogen (H₂), carbon monoxide (CO), methane (CH₄), and carbon dioxide (CO₂). The concentration of CO₂ and CO in all the cases have been on the higher side such as for PRPSO (38.45 and 43.28 %), PRECO (37.32 and 43.07 %), PTSO (24.74 and 48.31 %) and PTECO (26.02 and 45.93 %). This high concentration of CO₂ and CO have been due to the fragmentation and the subsequent transformation of unstable carbonyl groups and carboxyl present in biomass (Collard and Blin, 2014).

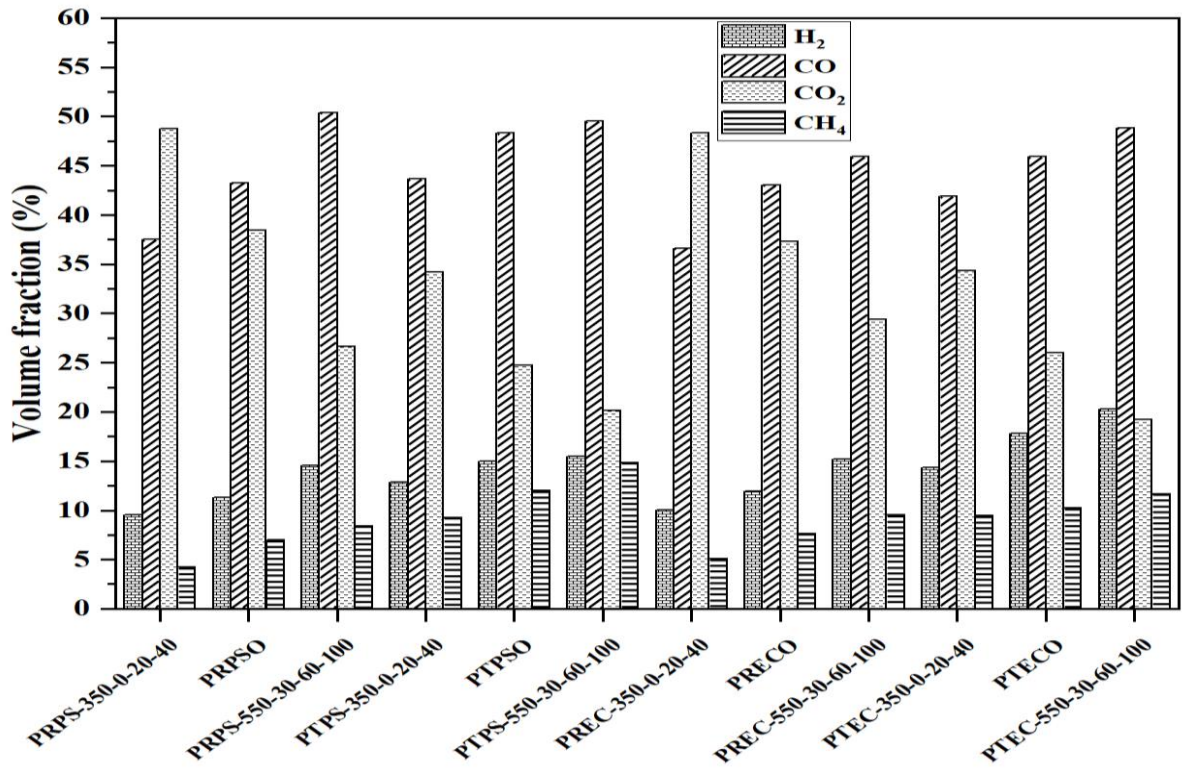


Fig. 5.10 Comparison of pyrolytic gas (NCG) evolving from the pyrolysis of raw and torrefied biomass.

However, on comparing the composition of pyrolytic gas from raw and torrefied biomass, it can be clearly observed that the concentration of CO₂ from the torrefied biomass has been decreased and that of CO has been increased as compared to their respective raw biomass. The formation of CO is due to decarbonylation reaction while CO₂ depends up on decarboxylation reaction and based on this it can be asserted that during pyrolysis the torrefied biomass facilitates decarbonylation while raw biomass favors decarboxylation. The decreased concentration of CO₂ in the pyrolytic gas obtained from torrefied biomass can also be attributed to the substantial decrease in its hemicellulose content as compared to untreated raw biomass (Konsomboon et al., 2019). In the present study, the concentration of CH₄ and H₂ in the pyrolytic gas have been on the higher side for both the

torrefied biomass as compared to their raw biomass. The concentration of CH₄ for PTPSO and PTECO increased from 6.69 to 11.99 % and 7.65 to 10.24 % while H₂ increased from 11.31 to 15.01 % and 11.96 to 17.81 %, respectively, as compared to PRPSO and PRECO. This increase in the concentration of H₂ and CH₄ can be attributed to the substantial increase in lignin concentration and its decreased thermal stability in the torrefied biomass (Singh, S. et al., 2020). Also, the significant number of alkyl branches present in lignin along with the demethoxylation reaction happening on the benzene ring present in lignin contributes to the increase in the synthesis of CH₄ and H₂ (Shen et al., 2010). The thermal decomposition of cellulose also contributes to the formation of CH₄ (Yang et al., 2007).

5.9 Summary

As a closure, this chapter demonstrated that the temperature had the most significant influence on the bio-oil yield as compared to other operating parameters. Also, for both the torrefied biomass the optimum pyrolysis temperature (442.06 and 461.25 °C) which yielded maximum bio-oil were close to each other suggesting that we can establish a generalised operating condition for the pyrolysis of torrefied biomass. GC-MS analysis revealed that the bio-oil from torrefied biomass contained less acid with increased concentration of phenol, benzene and toluene derivatives which indicates the improved quality of crude bio-oil. These results have confirmed that even though there have been only a marginal change in the pyrolytic gas yield from torrefied biomass as compared to raw biomass but the on the qualitative basis there was a significant improvement which can be utilized as a high grade pyrolytic gas for the production of energy.