Torrefied biomass fuels as a renewable alternative to coal in co-firing for power generation

Farooq Sher[1,*], Aqsa Yaqoob[1,2], Farrukh Saeed[1], Shengfu Zhang[3,4], Zaib Jahan[5], Jiří Jaromír Klemeš[6]

[1]*School of Mechanical, Aerospace and Automotive Engineering, Faculty of Engineering, Environmental and Computing, Coventry University, Coventry CV1 5FB, UK*

[2]*Department of Chemistry, University of Agriculture, Faisalabad 38000, Pakistan*

[3]*College of Materials Science and Engineering, Chongqing University, Chongqing 400044, PR China*

[4]*Chongqing Key Laboratory of Vanadium-Titanium Metallurgy and Advanced Materials, Chongqing University, Chongqing 400044, PR China*

[5]*School of Chemical and Materials Engineering, National University of Sciences and Technology, Islamabad 44000, Pakistan*

[6]*Sustainable Process Integration Laboratory - SPIL, NETME Centre, Faculty of Mechanical Engineering, Brno University of Technology - VUT Brno, Technická 2896/2, 61669 Brno, Czech Republic.*

[*] Corresponding authors:
E-mail address: Farooq.Sher@coventry.ac.uk (F.Sher), zhangsf@cqu.edu.cn (S. Zhang)
Tel.: +44 (0) 24 7765 7754

Abstract

This study aims to check whether the torrefaction of biomass as alternative renewable energy fuel to coal during co-firing. It was evaluated that either torrefaction improves biomass grindability to such an extent that it can be used in the coal mills with coal in co-firing without capital intensive modification. Torrefaction of beechwood was performed on a batch scale reactor at three different temperatures (200, 250 and 300 °C) at 30 min of residence time. The chemical structural changes in torrefied biomass were investigated with binding energies and FTIR (Fourier transform infrared) analysis. Monocombustion and co-combustion tests were performed to examine the combustion behaviour regarding flue gas emissions (CO, NOx and SO_2) at 0.5, 1.5 and 2.5 m distance from the burner opening along with fly ash analysis. The FTIR and binding energies showed that lignin hardly affected during light torrefaction while hemicellulosic material was significantly depleted. The Hardgrove grindability index (HGI) was calculated with three methods (DIN51742, IFK and ISO) that make this study novel. The medium temperature torrefied biomass (MTTB) yields HGI value in the range of 32–37 that was comparable with HGI of El Cerrejon coal (36–41). A slight change in temperature enabled the torrefied beech wood to be co-milled with coal without capital intensive modification and improved the grindability. Comparing the combustion behaviour of single fuels, low temperature torrefied biomass (LTTB) produces less amount of NOx (426 mg/m^3), CO (0.002 mg/m^3) and SO_2 (2 mg/m^3) as compared MTTB and raw beech wood. In case of co-combustion, it is found that blending of the coal with raw biomass does not show a stable behaviour rather premixing of 50% of coal with 50% of torrefied biomasses (MTTB and LTTB) gives most stable behaviour and reduces NO_x almost 30% and SO_x up to almost 50% compared to coal. The fly ash contents analysis proved that K_2O content is much decreased in case of co-firing of coal and torrefied fuels that may be ash related issues during combustion of raw biomass.

Keywords: Renewable energy; CO_2 emissions; Torrefaction; Biomass; Hardgrove grindability index; Co-combustion; Emission profile and Power plant.

1 Introduction

One of the current demands of the global energy network is to mitigate its dependence on fossil fuels and to attain a sustainable environment scenario [1]. Among the developed renewable energy resources (solar, wind, geothermal and biomass) bioenergy is considered the largest and promising renewable energy in the world as well as close to CO_2-neutral fuel [2]. It directly contributes to preserving the equilibrium of ecosystems by reducing the greenhouse effect [3] and environmental pollution [4]. Moreover, biomass has been widely used for getting heat, power, chemical raw materials and electricity either by using thermochemical conversion (gasification, direct combustion and pyrolysis) or through biological routes (fermentation and anaerobic digestion) [5, 6].

Although the wide application of biomass, there are some drawbacks of raw biomass including high moisture content, hygroscopic behaviour, relatively low energy density, less grindability, larger volume, difficulty in handling, storage and transportation [7]. However, the efficiency of biomass utilisation can be improved by dewatering, drying, torrefaction, densification [8], size reduction with pulverisation as well as pelletisation [9]. Among the latest developments and conventional pre-treatments of biomass, special attention was paid to the torrefaction because of large-scale implementation of biomass into bioenergy. Torrefaction is a thermal pre-treatment that involves heating the biomass at a moderate temperature between 200 and 300 ^{o}C under an inert atmosphere [10]. The torrefaction includes a reduction in moisture content markedly to <3% and increment in energy density, heating value and carbon content of the biomass by 15–20 wt% [4, 11]. Easier storage, delivery, ignitability, milling power and reactivity of the fuel is improved to a great extent [12]. Additionally, the black torrefied biomass turns into uniform and brittle solid form having coal-like properties so that the energy is saved for milling. The cellulose and hemicelluloses content decreases in torrefaction, and biomass becomes concentrated and easy to grind [13].

Torrefaction has been performed by fluidised bed combustor, fixed bed reactor, as well as rotary kiln [1]. All previous studies outlined different processing condition such as temperature, type of reactor [14], biomass and residence time for torrefaction [5]. Valix et al. [15] examined the dry torrefaction of sugar cane bagasse in an inert atmosphere and chemical torrefaction with H_2SO_4 pre-treatment within a temperature range of 160–300 °C. All the issues regarding biomass feeding, handling and processing were demonstrated by using chemical torrefaction. Likewise, Rodrigues et al. [16, 17] focused their study on chemical torrefaction of sixteen woody biomasses from poplar short rotation coppice to Portuguese round wood species at 265 ºC for 105 min in the presence of nitrogen. Bach et al. [18] studied a combined process of torrefaction, CO_2 capture and gasification to improve the biomass gasification and quality of product gas.

According to Budde et al. [4], the torrefaction of rice straw exhibited excellent fuel properties at 275 °C while cotton stalk at 250 °C. Yilgin et al. [19] performed the torrefaction of beechwood sawdust at the light (220 °C), mild (260 °C) and severe (300 °C) temperature and concluded that mild temperature was the best optimum temperature to get higher calorific values. Jian et al. [20] explored the pyrolysis of dry torrefaction as well as wet torrefaction of beech wood and wheat straw. The wheat straw showed a significant chemical change in comparison to beech wood. Gucho et al. [21] investigated the torrefaction of miscanthus and beech wood by using 240–300 °C temperature and residence time of 15–150 min. Their results concluded that beech wood showed significant improved grinding behaviour after torrefaction at 280 °C for 15 min, which is almost similar to the low type of coal. Besides that, torrefaction of different biomasses such as empty fruit bunch [7, 22], stem wood, bark and stump of Norway spruce [23] palm kernel shell [7], beechwood, pine, miscanthus, deciduous wood, coniferous [24], wheat straw [20], eucalyptus [25] and vine prunings [26] exhibited high heating values and energy density that were found suitable for bioenergy application.

Kopczynski et al. [8] investigated the co-combustion of raw fuels of willow, furniture waste wood, olive oil and torrefied biomass regarding emission profile and ash behaviour. It suggested that SO_2 emission significantly decreased by using torrefied biomass as a substitute for raw biomass. Similar findings were found by Xue et al. for co-combustion of coal with Avocado and torrefied biomass. [27]. Mun et al. [28] explored the significant benefits of co-combustion of coal and torrefied biomass on boiler efficiency that was similar to reference coal. Rentizelas et al. [29] noticed positive outcomes of co-combustion of torrefied biomass with coal regarding reduction in global warming and human toxicity. Co-combustion of various biomass material with coal have attracted the attention of researchers to lessen the CO_2, SOx and NOx emissions because of low fuel nitrogen and CO_2-neutral biomass [30]. However, there is limited biomass that can be co-combusted with coal because of higher moisture content and poor grinding ability of biomass. The higher percentage of moisture in biomass has a direct effect of meeting the thermal loads in steam generating units [31].

An attempt has been made to fill the gap in knowledge regarding co-combustion of coal with torrefied biomass at different temperatures to examine the effect of torrefaction temperatures during co-combustion, and ash behaviour. In addition, the Hardgrove Grindability Index (HGI) has long been used by the coal and utility industries as a determinant of power consumption in grinding and pulveriser capacity. There is a lack of research on HGI investigation of biomasses, and this gap is covered by determining the HGI values with three different methods to compare the milling properties, particle size distribution and flue gas analysis during combustion and ash behaviour. This study has focused on the preparation of the torrefied biomass via torrefaction process. The structural changes were studied by FTIR analysis as well as binding energies. The main aim of the current study is to check whether torrefaction improves fuel's grindability to such an extent that it can be used in the coal mills with the coal in co-firing without capital intensive modification. It is also examined either co-combustion of torrefied biomass with coal has improved the combustion behaviour regarding flue gas emissions. The flue gas emissions were studied at 0.5, 1.5 and 2.5 m distances from burner opening that were rarely reported by the published studies.

2 Material and methods

2.1 Fuel samples

The raw beechwood (BW) biomass was used in the torrefaction experiments, and EI Cerrejon coal (EC) was used as a standard reference for comparing different fuel properties as well as for coal/biomass co-combustion. For combustion experiments, the particle size of raw and torrefied biomass was ≤ 250 µm to ensure complete combustion.

2.2 Fuel analysis

Proximate analysis of the fuels used in the present was carried out according to DIN51718, 51719, 51720 method and ultimate analysis was made according to DIN ISO 10694 [9, 32]. The heating values (HHV) of all fuel samples were investigated using a calorimetric pump of IKA C4000 [33]. The elemental and proximate analyses, along with calorific values for these fuels are represented in Table 1.

2.3 Torrefaction experiments

A bench-scale reactor was used for torrefaction of beech wood, as shown in Fig. 1. Almost 50 g of the raw material sample was torrefied at three different temperatures (200, 250 and 300 ºC) under an inert atmosphere of N_2 for 30 min of residence time [20]. Consequently, 50 g of the raw material sample was placed inside the rod in each batch and heated at desired torrefaction temperature under an inert atmosphere of N_2 for 30 min while heating at a rate of 50 °C/min. A small flow of nitrogen was maintained from one side to remove all oxygen traces and to avoid explosion while the flow of exhaust gasses and the liquid was collected from the opposite direction. After 30 min, the apparatus was switched off, and the torrefied solid product was collected, weighed, and elemental analysis was performed that is reported in Table 1.

2.4 FTIR (Fourier transform infrared)

The Fourier transform-infrared (FT-IR) spectra were recorded using Perkin Elmer FT-IR version 10.4.3 spectrometer in the range of 4,000-450 cm^{-1}.

2.4 Combustion test

Experiments for combustion of biomass and coal were performed in a combustion facility of 20 kW_{th} entrained flow combustion reactor (EFCR) that is shown in Fig. 2. The combustion reactor consists of an electrically heated ceramic tube having a diameter of 0.2 m and a length of 2.5 m. A constant wall temperature up to 1,300 ^{o}C was maintained by electrically heating around the reaction region, and all analyses were performed at this temperature The proper amount of various fuels (EI Cerrejon coal and torrefied beech wood) are injected into the reactor using fuel feeder at a rate of 0.5 g min^{-1} with the help of carrier air mixture by using a central tube of a circular jet. The feeding unit temperature was 20 ^{o}C. The outer concentric cylinders of burner were used for injection of combustion air streams that are categorised into primary air and secondary air stream. The axial analysis of flue gas concentration was done by a vertically movable probe that collected the flue gas and transported to standard flue gas analysers for analysing.

2.5 Standard flue gas analysis

Table 2 tabulated the standard measurement for used equipment and the calibration gasses employed for the calibration of the analysers. Experiments related to combustion and co-combustion of EI Cerrejon coal, beechwood and torrefied beech wood were performed using the atmospheric drop tube furnace BTS-VR. The general input parameters for various combustion settings are given in Table 3. All the standard gaseous concentrations such as O_2, NO_x, CO and SO_2 were expressed on a dry basis. The flue gas was quenched immediately by maintaining the oil-cooled probe temperature to 180 ^{o}C. The flue gas was collected from the end region of the heated reaction tube at 2.5, 1.5, and 0.5 m distance from the burner opening [34]. After each experiment, ash is collected from the bottom of the oil-cooled probe and further investigated for ash behaviour analysis. For each experiment of different fuels, ash collecting filter was changed to avoid any contamination [16].

2.6 Grindability test

The grindability behaviour of beech wood and torrefied biomass samples were determined by Hardgrove grindability index (HGI). The HGI values of all fuels were calculated in accordance with DIN 51742 Calibration, IFK Calibration and Indian Standard IS-4435-1979 Calibration [35]. Grindability experiment was carried out in Hardgrove laboratory grinder in accordance with ASTM D409 standard. Firstly, the torrefied fuel sample was milled to about the size of below 4.75 mm and screened between the sieves of 0.6 to 1.18 mm. Then, 50 g of the sample was removed and poured on grinding track of HGI equipment. The grinder was stopped after 60 rotations, and the ground sample was screened for 10 min between sieves of 0.75 and 0.6 mm. The grain particles were removed from the bottom, and screening was performed twice again for 10 min. After completion, the undersize and oversize samples were weight with 0.01 g accuracy.

The particle size distribution having D10, D50 and D90 were analysed. For a sieve analysis, the ground sample of 50 g was sieved for 10 min with increasing mesh sizes 32, 50, 63, 75, 90, 160, 200 and 353 µm. The fabric used for sieve analysis was standardised DIN ISO 3310. After each sieving, the weight of the sample on each sieve was measured and noted as a percentage of the original mass sample. The milling properties of torrefied biomass and coal were also compared using HGI. The ash fusibility temperatures were determined in accordance with CEN/TS 15404 method to investigate the ash melting behaviour of biomasses at 550 to 1,500 ^{o}C with a rate of 10 ^{o}C /min. The ash fusibility temperatures, including shrinking temperature (ST), start of sintering temperature (SbT) hemisphere temperature (HT) and low temperature (FT) were determined within the given range [36].

3 Results and discussion

3.1 Effect of temperature on torrefaction

The effect of temperature on torrefaction was investigated by a series of experiments. Beechwood biomass was torrefied for the same residence time that was 30 min at three different temperatures (200, 250 and 300 ^{o}C). After torrefaction, the elemental analysis of all three samples was performed, as shown in Fig. 3. The results showed, when torrefaction temperature was increased from 200 to 300 ^{o}C, there was an increment in nitrogen content of torrefied beechwood from 0.09 to 0.33% and carbon contents were increased from 48.55 to 73.78%. This may be explained by the decrease in mass yield with increment in temperature from 200 to 300 ^{o}C because of the devolatilisation of carbon, hydrogen and oxygen of hemicellulose during torrefaction. The sample becomes more densified due to weight loss during torrefaction.

A significant weight reduction and mass loss of H and O of the sample was observed due to the evaporation of moisture and hemicellulose. The hydrogen contents decreased evidently from 5.98 to 2.62% as temperature increased from 200 to 300 ^oC due to the release of volatiles and hydrocarbon at high temperature. While overall, no significant changes were observed in nitrogen and Sulphur contents [20]. Similar findings have been reported by Pawlak-Kruczek et al. [14] that the carbon amount of torrefied Leucaena is enhanced while the oxygen amount is reduced by increasing torrefaction temperature. The light torrefaction at 200 ^oC was influenced by the hemicellulose component of the biomass sample, while cellulose and lignin components were little affected [37]. In contrast, the lignocellulosic materials were significantly depleted in severe torrefaction at 300 ^oC.

That was why two-material named as low torrefied temperature biomass (LTTB) that was obtained at 200 ^oC and medium torrefied temperature biomass (MTTB) that was obtained at 250 ^oC were further used in combustion and co-combustion settings. For instance, it is reported above that increasing temperature resulted in decreased mass yield and increased densification of torrefied biomass and resulted in a solid with increased carbon content, decreased oxygen content and decreased volatiles. It is highlighted the weight losses of biomass materials in a light torrefaction environment (200 ^oC), medium torrefaction (250 ^oC) and a severe torrefaction one (300 ^oC). It is also pointed out that severe torrefaction has a drastic impact on the depletion of lignin and cellulosic material that have little effect in case of light and medium torrefaction.

3.2 Effect of binding energies on structural degradation

Biomass mainly composed of lignin, hemicellulose and cellulose components. The torrefaction process and performance of a lignocellulosic material depend strongly on the thermal degradation of these constituents. The binding energies are given in Table 4 clearly describe the degradation behaviour of these constituents. Firstly, the biomass constituents possess no nitrogen. Only available nitrogen in the biomass is primarily bound to proteins which are defragmented from peptides [20]. The wood chips are connected with melamine resins in which much amount of nitrogen is present. As C-N bound possess low binding energy (285 kJ/mol) in comparison to N-H bound (389 kJ/mol) which is rather stable, so it defragmented easily during torrefaction or pyrolysis. The half of nitrogen atom in heterorings is easily released at a medium temperature (250 ^{o}C) while another half of aliphatic nitrogen atom as amine is released at low temperature (200 ^{o}C) as NH form.

That is why nitrogen content was increased on torrefaction. The overall proportion of the nitrogen in the torrefaction of biomass is 2–4% high so that large NH is formed. It was also analysed by Wang et al. [23] that the mass loss increased evidently with increasing the torrefaction temperature to 275 °C, which is due to the degradation of hemicelluloses [16]. Secondly, C-C bound in aromatic rings of lignin possesses high binding energy (519 kJ/mol) in comparison to aliphatic C-C bound (348 kJ/mol) in hemicellulose and cellulose. Hence, their binding energies showed that lignin is thermally stable in chemical nature during torrefaction and not decomposed easily while hemicellulose and cellulose can be easily degraded at the light (200 °C) and medium torrefaction (250 °C).

3.3 Effect of torrefaction on energy properties of fuels

The proximate analysis of raw biomass and torrefied fuels is shown in **Table 1**. The results indicate a clear difference in fixed carbon (FC), ash content and volatile matter (VM) contents of raw and torrefied biomass (LTTB and MTTB) in comparison with coal. The similarities of LTTB with raw biomass suggested that only slight degradation or defragmentation occurred at low torrefaction temperature. The thermal decomposition of biomass constituents was directly affecting the moisture content. With increasing temperature from 200 to 250 ^{o}C, the moisture content of raw biomass was decreased from 5.41 to 2.38%. This reduction in moisture content is because of less availability of water bonding sites because of thermal degradation.

The dehydration process was involved in releasing the moisture, and the volatile content was decreased significantly from 82% to 71% whereas increment in FC from 16% to 27% on torrefaction at 200 to 250 ^{o}C was observed. The positive variation in FC has improved the bioenergy properties of torrefied beech wood that exhibited low VM. In accordance with the above results, torrefied beech wood has the ability to burn slowly in comparison to raw biomass. The values of FC and VM were in agreement with the range of values obtained by Ndibe et al. [34] that investigated the torrefaction characteristics of torrefied spruce. In addition, the ash content was found elementary characteristics that have a direct influence on the bioenergy properties of biomass. It has been reported that higher AC enhanced the handling and maintenance cost of combustor along with a reduction in heating values. In this study, the AC value for MTTB was found 1.15% that is a little less than the AC of raw biomass (1.16%).

In comparison to El Cerrejon that has 14% of AC, the MTTB has much least ash content that is suggesting it more suitable biomass for combustion. The AC values are closely related to the literature within the range of 0.7 to 6.0% reported by Yelverton et al. [38] that performed the torrefaction of four woody biomass. Similar findings were reported in the published analysis of torrefied logging residue as well as waste wood [39]. The ultimate analysis that is given in Table

1 indicates that Content of carbon in the solid product had increased at the medium temperature of torrefaction whereas the hydrogen and oxygen content was decreased, resulting in increased the heating value of torrefied biomass. MTTB has shown the highest heating value that was 21,698 kJ/kg in comparison to raw biomass and LTTB that was comparable to El-Cerrejon having 28,134 kJ/kg heating value [40].

3.4 FTIR analysis

The effect of torrefaction on the chemical structure of beechwood was investigated by performing FTIR analysis. The IR spectra of raw and torrefied beechwood (MTTB and LTTB) are given in Fig. 4. The interpretation of the IR band for raw and torrefied beechwood was made by a literature review [41]. The peaks indicate the functional group evolution of the corresponding sample and their absorbance intensity indicate the transformation, degradation and chemical reactions of polymer components (lignin, hemicellulose, cellulose) of beechwood during torrefaction [20]. Their spectra had similar peaks, but the absorbance intensity of the peaks was different. The broadband in the region of 3,300-3,400 cm^{-1} and 2,880-2,923 cm^{-1} is indicated the stretching vibration of -OH and -CH for all samples. Their intensity of peaks is reduced with increasing torrefaction temperature from 200 to 250 °C because of demethoxylation, dissociation of the side chain and dehydration reaction during torrefaction [42].

The C=O peaks observed at 1,720 cm^{-1} is associated with carboxylic acid, aldehyde and ketone that are formed after decomposition of cellulose and hemicellulose. The peaks in the region of 1,450-1,610 cm^{-1} were due to C-H deformation of cellulose component, methoxy stretching vibration of lignin as well as a ketonic component of hemicellulose. The intensity of these peaks is reduced significantly in case of LTTB and MTTB, showing the thermal degradation of holocellulose and lignin component. The peaks in the region of 1,160-1,270 cm^{-1} are associated with C-O stretching vibration of the aromatic component of lignin as well as C-OH and C-O-C stretching vibration of hemicellulose and cellulose. The sharp peak at 1,025 cm^{-1} is observed due to C-O, C-C-O and C=C stretching vibrations of biomass constituents [43]. The absorbance intensity is stable at 200 ^{o}C torrefaction and then disappeared with increasing torrefaction temperature up to 250 ^{o}C. Lignin is thermally stable in comparison to cellulose and hemicellulose component and the C− O−C peak at 1,160 cm^{-1} of lignin is retained in case of LTTB and MTTB without any changes in absorbance intensity.

3.5 Hardgrove grindability index of fuels

HGI was determined from calibration line relating to the mean value of calculated mass passing through a >74 µm sieve, to the certified HGI values of the Standard test coals. The HGI values provide information for determining grinding power consumption and pulverised capacities [44]. Coal HGI ranges from 40–80 or even 90, higher the HGI, easier to grind. A change from 47 to 50 in HGI is very negligible. The HGI has an inverse relation to grinding power and power consumption [35]. Three standard methods (DIN 51742, IFK, and Indian Standard IS-4435-1979) were used to determine HGI values of raw biomass, torrefied biomass and coal. It is noticed from the HGI values of different fuels that determining HGI by different methods yield different results due to the difference in grindability characteristics of biomass.

Comparing HGI values of raw biomass with torrefied biomass and coal (Fig. 5), it can be clearly seen that raw biomass has lower HGI values in the range of 20–27 that means it is relatively tougher to grind and needs more grinding power consumption and less mill power capacity. Therefore, raw biomass is difficult to mill because of having a tenacious component like fibres.

The torrefied biomasses (LTTB and MTTB) needs less grinding power in the consumption and have more mill capacity due to higher HGI value ranging from 23 to 37. The results of HGI test show that torrefied biomass has HGI ranging between a minimum of 23 and a maximum of 32 value of HGI by DIN calibration whereas IFK calibration showed a minimum HGI of 24 and maximum HGI of 33. Similarly, IS calibration giving a minimum HGI of 28 and a maximum HGI of 37. This trend confirms that as the fuel becomes softer, the HGI value is higher and needs less power for grinding. By comparing MTTB and LTTB, it can be said that MTTB has high HGI values as compared to LTTB in all calibration methods. This could be due to increasing temperature, and the sample becomes more densified because of the removal of carbon, hydrogen and oxygen contents as a result of hemicelluloses devolatilisation.

They were a significant mass loss and an overall reduction in weight of the sample due to the evaporation of moisture and hemicellulose. Because of less mass, low power would be required for grinding. Now comparing torrefied biomasses with coal, results show that HGI values of MTTB are only 3–4 less than HGI values of the referenced coal that was in the range of 37–41. Therefore, coal requires less power consumption with higher HGI to produce a product of the same fineness. Mun et al. [28] study was also used ASTM-D-409 method for HGI determination and find closest HGI values for blended torrefied biomass that was 46.9. It was suggested that torrefied biomass had highest grindiability among all blends of coal with raw palm kernel shell, wood pellets, walnut shell and empty fruit bunch.

In the current study, the HGI test of raw and torrefied beechwood with three different methods made this study novel from all other published methods. Hence, it can be concluded that medium temperature torrefied beech wood biomass may be used with coal in co-firing in the same installation equipment without any significant modifications or changes in the installation and grinding. Ohliger et al. [45] analysed that raw beech wood which had poor grindability and moderate HGI value. The HGI results reported that grinding ability and milling capacity was improved significantly on torrefaction but less than Rhenish lignite. Similarly, Zhang et al. [1] observed the torrefaction of poplar sawdust and analysed the grinding behaviour by a particle distribution method.

In general, coal mills break up coal by a brittle fracture mechanism, and most biomass has poor grinding properties. Consequently, some larger and coarse biomass particles cannot be milled properly, and this can lead to the limit of co-firing possibility. That is the reason why beech wood does not exhibit good grinding properties with lower HGI values and less carbon content in comparison to coal. But on torrefaction biomass can be easily milled and involved in the superior breaking of the fibrous chain (lignin, cellulose and hemicellulose) during grinding. It has been reported that HGI value becomes higher with the growth of carbon content [46]. This carbon content is increased on torrefaction and increasing the temperature. Apart from it, power consumption might be increased with increasing co-firing biomass ratio.

3.6 Effect of milling and particle size distribution

The particle size distribution (PSD) is the relative amounts of particles retained, sorted according to size. PSD is also termed as grain size distribution. Sieve analysis was performed to find out the percentage of different particle sizes retained within the fuel and to determine the distribution of finer as well as the coarser, particles [21]. The particle distribution having less than 75 µm particle diameter were 70% while 99.5% particle distribution was found for >300 µm particle diameter that is the suitable particle size range for torrefied biomass [47]. Biomass particles greater than 300 µm were not burned completely in the given residence time and can be obtained as unburned carbon. All fuel samples were milled to a particle size of less than 250 µm to enable complete burnout by using biomass crusher. The particle size distributions that are given in Fig. 6 shows that only 1.99% of the raw biomass passes through the 50 µm sieve and it improves the passage of biomass up to 7.3% that further increases up to 22.16% as the temperature of the torrefied biomass increases from low to medium (200–250 °C). In all cases, there is an improvement in the grindability characteristics of the torrefied biomass as the percentage of fines increases for the samples subjected to the torrefaction process [45].

Gil et al. [33] reported that torrefied chestnut woodchips showed good grindability behaviour at 280 °C and 22 min of residence time, which increased the amount of finer particles. Similarly, comparing the grindability characteristic of MTTB and LTTB at different sizes of sieve, it can clearly be noted from Fig. 6 that only 20.04% of the sample of LTTB pass through the 75 µm sieve while in case of MTTB it is 33.92%. In addition, the sieve of 200 µm passes only 67.45% of LLTB that enhanced up to 80.25% in case of MTTB. Compared with coal, it can be seen that 97.65% of MTTB particles show passage through 353 µm sieve, which was 99.82% in the case of El Cerrejon with the same sieve size. It can be concluded that the particle distribution of MTTB is closest to coal and higher than LTTB.

The results of particle size distribution suggested that grindability characteristics are improved to a great extent if the raw biomass is pre-treated like torrefaction. It can also be observed that particle size decreases significantly with the rise in torrefying temperature. Reduction of large particles is obtained with increment in torrefaction temperature that produces a major fraction of fine particles in the range of 200 µm < d < 353 µm. All trends are in good agreement with the study of Wang et al. [23] that reported the distribution of the particles of spruce bark having diameter <0.063 mm were increased with increment in temperature from 225 to 300 ^{o}C.

The cumulative particle distribution data at 10, 50 and 90% was used to determine the particle diameter of d10, d50 and d90. The summary of sieve analysis presented in Table 5 is the particle diameter of the samples that determines whether a particle passes through the sieve opening. It is observed from this sieve analysis that particle dimensions are greatly reduced on torrefaction and produce more fine particles. The raw biomass has a higher particle size diameter almost 70 µm that reduced their size up to 58 µm in low torrefaction while further reduction is observed at medium temperature torrefaction by 10% cumulative distribution (d_{10}). The particle size of MTTB (32 µm) was found that is comparable with coal particle size (38 µm) for combustion test. The particle distribution d90 showed that a suitable range of particle diameter for combustion is less than 300 µm. It can be concluded that the decrease in particle size is mainly due to the reduction of the particle length. In overall, torrefied biomass produced relatively narrower or uniform particle size ranges as compared to untreated biomass [34].

3.6 Combustion reactivity

Combustion reactivity was studied by measuring the oxygen consumption concentrations from furnace entry-level to furnace exit level (2.5 m distance from burner). The combustion of different fuels (100% of Beechwood, EI Cerrejon, LTTB and MTTB) and co-combustion of 50% EI Cerrejon with raw biomass (beech wood) and torrefied biomass (LTTB and MTTB) were performed to evaluate the consumption of oxygen and emission of CO, NOx and SO_2. Fig. 7 (a) indicates the oxygen concentrations based on the measurement's distances from the entrance level of the burner to 0.5, 1.5 and 2.5 m distance for all combustion settings.

The slowest oxygen consumption was found for beech wood combustion and co-combustion of beech wood and EI Cerrejon. The fastest oxygen consumption was observed for single coal combustion and cases involving torrefied beech wood either MTTB or LTTB (both combustion and co-combustion) [28]. The combustion of EI Cerrejon appears fastest in comparison to the combustion of MTTB or LTTB and co-combustion (50% EC+MTTB/LTTB) processes. The reason is that the introduction of torrefied biomass increased the combustion reactivity and less time is required for its combustion while raw biomass is usually contained larger particle size that burns out slowly and required more time for complete combustion [34].

3.7 Emissions profiles of CO, NOx and SO_2

Fig. 7 (b-d) presents the emission results during the combustion of 100% El Cerrejon and beech wood on a thermal basis while co-combustion of El Cerrejon with beech wood and torrefied biomass.

3.8.1 CO emissions

During the flue gas analysis, the average highest concentration of CO appears during combustion of LTTB that was 3,048 ppm as given in Fig. 7 (a). It is noted that the highest CO release was found at 0.5 m distance from burner. It indicates that raw biomass needs area to be burned completely, which provide complete combustion at 2.5 m distance from burner. The CO emission profile shows a significant reduction in moving from 0.5 to 2.5 m distance from the burner. It can be further noted that in case of co-combustion of 50% EI Cerrejon and 50% beechwood, the amount of CO is increasing as the oil probe moves from 1.5 m distance to 2.5 m distance which is also an unusual behaviour because of raw biomass. CO content is considered the first indicator for examining the combustion behaviour for the various fuel settings [34].

The CO emission was significantly less in the case of EI Cerrejon combustion that was 404 ppm. CO release was 2,238 ppm comparing to the beechwood combustion, while in comparison to torrefied biomass (LTTB and MTTB) CO content was much increased. The lowest CO emission for EI Cerrejon was due to the presence of a finer and homogeneous particle in coal as compared to the coarse particle in raw biomass. Similarly, comparing the MTTB and LTTB, the less CO release was found during MTTB combustion, which was 1,054 ppm while 3,048 ppm CO release was observed in LTTB combustion. This less emission in case of MTTB due to medium temperature torrefied biomass MTTB that improves the homogeneity of biomass as well as finer particle distribution.

The co-combustion of 50% EC and 50% beech wood release only 130 ppm of CO that decreased to 37 ppm until the distance becomes 1.5 m form burner while its concentration is increasing up to 179 ppm at 2.5 m distance which is an unstable behaviour due to raw biomass. The co-combustion of 50% EI Cerrejon with 50% MTTB or 50% LTTB release 2,373 ppm and 913 ppm CO. These co-combustions release greater CO as compared to coal because of introducing torrefied biomass that may still possess coarse particles [48]. Comparing the CO emission findings in this study with other published results such as Kopczynski et al. [8] reported >70 ppm volumetric fraction of CO, Lasek et al. [37] recorded up to 2,300 ppm while Varol et al. [49] reported >160 ppm of CO.

3.8.2 NOx emission

NOx emission is occurred due to the presence of fuel nitrogen during combustion and co-combustion. The overall NOx emission is depending on different factors, including temperature, residence time, volatiles amount and burner configurations [34]. Fig. 7 (c) indicates that the high amount of NOx was observed for EI Cerrejon combustion that was 730 ppm at 2.5 m distance from burner because of the already bound high amount of fuel nitrogen. Beechwood produces remarkably less amount of NOx as compared to coal. Overall combustion behaviour of beech wood is not stable, but mostly the combustion of El Cerrejon is stable. For torrefied beech wood (MTTB and LTTB), the NOx emissions were 269 ppm and 251 ppm respectively that representing only a little fraction of NOx emission comparatively to EI Cerrejon (730 ppm). The increment of NOx in MTTB was due to devolatilisation of O, H and C content during torrefaction at high temperature and maybe because of a large amount of production of NH bound as it is more stable compared to C-N in heterorings. Eddings et al. [48] analysed the reduction in NOx in raw pinewood combustion that is enhanced on torrefaction at high temperature. [33].

The NOx released during co-combustion of coal and beechwood increases till distance from the burner becomes 1.5 m, and from there it starts decreasing up to 450 ppm till 2.5 m distance from the burner. Comparing to the only El Cerrejon combustion, NOx amount was 450 ppm instead of 730 ppm that is almost half while comparing to Beechwood combustion NOx amount was 252 ppm and here in case of co-combustion NOx was 450 ppm which is almost double. Additionally, co-firing of 50% EI Cerrejon with 50% MTTB or 50% LTTB yields 555 ppm and 533 ppm NOx respectively. Comparing to EI Cerrejon, NOx contents is reduced during co-combustion of coal with torrefied biomass while in comparison to beech wood, NOx contents are enhanced. Therefore, higher volatile yield and low nitrogen amount for torrefied beech wood compared to coal resulted in lower emissions. Furthermore, Thanapal et al. reported the 12% reduction of NOx emission for torrefied mesquite in comparison to coal while in the present study, the reduction of NOx is up to 30%.

3.8.3 SO_2 emissions

Fig. 7 (d) also indicates the SO_2 emissions during all combustion and co-combustion settings. The highest concentration of SO_2 was released by EI Cerrejon combustion that was 593 ppm at 0.5 m distance from burner. This highest emission was due to the already bound high amount of fuel sulphur. The SO_2 emission was significantly decreased comparing with beechwood combustion, from 593 to 13.47 ppm. These SO_2 emissions were further decreased substantialy in the case of torrefied biomass and produce negligible SO_2 that was 1.98 ppm for MTTB and 1.07 ppm for LTTB. The SO_2 reduction was observed because the amount of fuel sulphur, as well as combustible sulphur, was decreased due to torrefaction [37]. Co-firing of EI Cerrejon with raw biomass and torrefied biomass (LTTB and MTTB) produces remarkably less amount of SO_2 as compared to coal. The co-combustion of 50% coal and raw biomass releases 78–266 ppm SO_2 while the release of SO_2 was 329 ppm and 269 ppm during co-firing of 50% EI Cerrejon with 50% MTTB and 50% LTTB.

The SO_2 concentration was reduced to half in case of co-combustion of torrefied fuels and coal in comparison to EI Cerrejon due to presence of less sulphur content in torrefied biomass as input [50]. Torrefied beechwood already has a negligible amount of fuel Sulphur that was in the range of 0.017-0.018% from fuel analysis given in Table 1. SO_2 has been significantly reduced in the case of MTTB and LTTB combustion. In case of co-combustion, the reduction was not only due to the replacement of 100% of coal input with 50% torrefied beech wood and 50% EI Cerrejon but was also due to sulphur capturing in ash. Lasek et al. [37] reported the SO_2 emission of 2 ppm for torrefied willow and 1,184 ppm for polish hard coal that is a positive agreement with our study where SO_2 emission was 1.98 ppm for MTTB, 1.07 for LTTB and 593 ppm for El Cerrejon and significant SO_2 reduction was observed in the current study.

3.8.4 Comparison of flue gas emissions at the furnace exit

To compare the flue gas emissions CO, NOx and SO_2 of different combustion and co-combustion settings, corrected to 6% O_2 in the flue gas, the data is shown in Fig. 8. It can be shown from the comparison of emissions of different fuels from the Fig. 8 that El Cerrejon produces almost double NOx and SO_2 as compared to raw biomass as well as torrefied biomass (LTTB and MTTB). In the case of monocombustion of all fuels, the El Cerrejon produces the 1,231 mg/m^3 of NOx, 1265 mg/m^3 of SO_2 and 17.5 mg/m^3 of CO. In contrast, the LTTB releases the 426 mg/m^3 of NOx, 2 mg/m^3 of SO_2 negligible amount of CO. This significant emission reduction was due to light torrefaction of biomass at low temperature 200 ^oC. But the co-combustion of the coal with raw biomass and torrefied biomass (LTTB and MTTB) reduces the NOx almost 30% and SO_2 release to about a half of coal emission [34]. Under the current scenario of environmental pollution [51, 52], there is a need to develop renewable fuels [53, 54] and sustainable energy technologies [55, 56] to reduce CO_2 emissions [30, 57] and control global warming [58]. Consequently, torrefied biomass is an excellent renewable fuel that could be used as an alternative to coal for co-firing in power plants.

4 Fly ash analysis

Ash is the inorganic incombustible part of the fuel, which is left after complete combustion, containing the bulk of mineral fraction of original biomass. During the process of combustion, the ash from the flue gas in the oil probe was collected and was analysed for multiphase carbon to determine the degree of fuel conversion during tests. The multiphase carbon analysis of all the fly ash samples is presented in Fig. 9 that was taken under different configurations showed complete combustion of the fuels in all the settings. Achieving complete combustion was a prerequisite for a good comparison of the flue gas emissions in the different configurations. Elemental analysis of the ashes of different fuels shows that total organic carbon (TOC) in El Cerrejon is higher than the total organic carbon in raw biomass and torrefied biomasses (MTTB and LTTB). It may be explained because biomass is considered as a near CO_2-neutral fuel and contains almost negligible CO_2 emission as compared to coal; however, NOx contributions to the GHG footprint should also be watched [59].

That is why the world is now focusing on replacing the coal with biomass to reduce CO_2 emission. Results also show that the MTTB which was prepared at 250 ^{o}C contains 0.4% of TOC while LTTB, which was prepared at 200 ^{o}C, contains only 0.1% of TOC. From these results, it can be concluded that by increasing the torrefaction temperature, total organic carbon content increases from 0.1 to 0.4%. It may be explained because the mass becomes more densified at high temperatures torrefaction with increment in fineness of fuel particle and more ash is collected at a lower portion of the combustion chamber due to higher weight loss [29]. The increment in TOC was reported because of 1.15% of ash content was found for MTTB while 1.12% of AC for LTTB form fuel analysis as given in Table 1. The co-combustion of coal and torrefied biomasses (LTTB and MTTB) improves the TOC content from 0.75 to 1.05% because of introducing torrefied biomass. But this content is decreased up to 0.1% in the case of co-combustion of 50% coal and 50% raw beechwood because biomass has a negligible amount of carbon.

3.8 Ash melting behaviour

Ash melting behaviour of biomasses and coal employed to determine the ash fusibility temperatures (IDT, ST, HT and FT) [36]. It can be seen from Table 6 in all possible configurations of combustion and co-combustion the IDT was increased after low and medium torrefaction of raw biomass as well as for all combinations of coal and torrefied fuels (50% El Cerrejon + 50% MTTB/LTTB). All mixtures of fuels after torrefaction showed IDT greater than 830 ℃. Vassilev et al. [60] proposed a wide range of IDT (670–1565 ℃) for 87 varieties of biomasses and coal. The ash melting behaviour is closely related to ash contents that contain various oxides including MgO, Na_2O, CaO, K_2O, Fe_2O_3, Al_2O_3, SiO_2 and little amount of TiO_2 as shown in Fig. 10. Niu, Tan [61] suggested that IDT is increased due to the presence of a large amount of CaO, Fe_2O_3, MgO and Al_2O_3 while IDT is decreased with increment of K_2O in ash composition.

In this study, IDT value decreases in following order: El Cerrejon (1240 ℃)> El Cerrejon + MTTB (980 ^{0}C) > El Cerrejon + LTTB (950 ℃) >El Cerrejon+ Beechwood (920 ℃) >MTTB (840 ℃) >LTTB (980 ℃)> Beechwood (790 ℃). It is concluded that all this IDT trend depends on the flue gas emission and mineral composition in ash. To get more information about ash melting, the hemisphere temperature is considered more informative characteristics of ash fusion temperature. The range of ashes of hemisphere temperatures for all fuels is almost 1,200–1,450 ^{o}C that can be categorised into moderate HT in accordance with Vassilev et al. [62] study. This temperature is decreased on the co-combustion of coal and torrefied fuels. It may be explained due to significant reduction up to 3% in K_2O content on co-combustion. The potassium content is much problematic during combustion of single fuels, but on co-combustion, it decreases.

Therefore, IDT temperatures are higher in the case of co-combustion of El Cerrejon and torrefied biomasses while the other melting temperature characteristics including ST, HT and FT are not presented a similar trend. These temperatures are reduced during co-combustion of coal and torrefied biomasses (LTTB and MTTB) as compared to mono-combustion. The reduction in all these temperatures in is because of torrefied biomass substitution and the particle size dimension. The obtained ranges of these melting temperatures are larger than 1,250 ℃. These ranges are considered as suitable values for the combustion in fluidised bed combustor. It is observed that slagging, corrosion and fouling is increased by introducing raw biomass into coal.

The sodium and potassium contents in biomass have a direct effect on the agglomerate formation during co-combustion. Agglomeration, as well as slagging, is enhanced due to the formation of eutectics that have melting points lower than their individual components [63]. The oxide in fly ash that is displayed in Fig. 10 indicate that the SiO_2 is most predominant oxide in all used fuels. CaO, as well as K_2O oxides, are additionally considered next predominant oxides that is greater in raw and torrefied biomass as compared to El Cerrejon combustion and all co-combustion configurations. Eddings, McAvoy [48] also observed the fly ash analysis of pinewood and torrefied types that proved that K_2O is decreased significantly on torrefaction of pine wood. Torrefied biomass contains 12–13% K_2O that reduced up to 3.8% during co-combustion of fuels while El Cerrejon was just 1.32%. Because biomass has more alkaline earth metals compared to coal that may cause slagging and fouling. The K_2O content in less amount is also responsible for the increment of IDT temperature that can be seen in El Cerrejon and prevents from slagging [64].

The CaO content is rich in raw biomass, almost 38% while its content is decreased in the case of torrefied biomass and co-combustion with torrefied biomass. The torrefaction reduced the fusion temperatures, especially softening temperatures in comparison to raw biomass that has high CaO content which makes it does not melt or hardly melt at physical operating temperatures. The MgO content in ashes of biomass and torrefied biomass combustion is high in the range of 3–5% that is significantly decreased during the separate coal combustion. Different ash component and minerals affect the ash fusibility temperatures in ash melting behaviours. The Na_2O content also has a direct effect in reduction of ash fusion temperatures in biomass and especially in those ash samples that have a larger amount of CaO. These characteristics temperatures and ash contents provide the first indication of the quality of ash for combustion in fluidised bed combustor [36].

5 Conclusions

Torrefaction of beech wood was performed using batch scale reactor at three different temperatures (200, 250 and 300 ^{o}C) and 30 min of residence time. The chemical structural changes on torrefaction were investigated by FTIR analysis as well as binding energies. The HGI values with three different methods like DIN51742, IFK and ISO Standard have shown that MTTB yields HGI value as 32.75 and LTTB yields HGI value as 23.78. The difference HGI values of coal and MTTB is almost 3–4, so by a minor change in torrefaction temperature biomass may be co-milled with coal in already existing pulverisers without any significant loss of mill capacity. During combustion of single fuels, the LTTB produces less amount of NOx (426 mg/m^3), CO (0.002 mg/m^3) and SO_2 (2 mg/m^3) as compared to MTTB. The torrefying the biomass at high temperatures increases Nitrogen content, so it is recommended that biomass should not be torrefied at high temperatures. In the case of co-combustion, it is found that premixing of coal with torrefied biomass gives the most stable behaviour and reduces the NOx almost 30% and SOx up to 50%

compared to coal. The ash melting behaviour showed that initial deformation temperature of co-combustion of torrefied fuels with coal was higher in comparison to raw biomass and coal. The fly ash contents analysis proved that K_2O content is much decreased in case of co-firing of coal and torrefied fuels that may be problematics issues during combustion of raw biomass. However, a further specific examination regarding slagging, fouling, as well as agglomeration, is required. Future study may include the usage of co-combustion of coal and torrefied beech wood for large scale implementation of bioenergy.

Acknowledgement

This research is supported by the project "Sustainable Process Integration Laboratory – SPIL", project No. CZ.02.1.01/0.0/0.0/15_003/0000456 funded by EU "CZ Operational Programme Research, Development and Education", Priority 1: Strengthening capacity for quality research. The authors are also thankful to the Higher Education Commission of Pakistan for financial support.

References

[1] Zhang Y, Song K. Thermal and chemical characteristics of torrefied biomass derived from a generated volatile atmosphere. Energy. 2018;165:235-45.

[2] Sher F, Iqbal SZ, Liu H, Imran M, Snape CE. Thermal and kinetic analysis of diverse biomass fuels under different reaction environment: A way forward to renewable energy sources. Energy Conversion and Management. 2020;203:1-12.

[3] Fan YV, Klemeš JJ, Ko CH. Bioenergy carbon emissions footprint considering the biogenic carbon and secondary effects. International Journal of Energy Research. 2020.

[4] Budde PK, Megha R, Patel R, Pandey J. Investigating effects of temperature on fuel properties of torrefied biomass for bio-energy systems. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 2019;41(9):1140-8.

[5] Garcia DP, Caraschi JC, Ventorim G, Vieira FHA, de Paula Protásio T. Comparative energy properties of torrefied pellets in relation to pine and elephant grass pellets. Bioresources. 2018;13(2):2898-906.

[6] Razzaq L, Farooq M, Mujtaba M, Sher F, Farhan M, Hassan MT, et al. Modeling Viscosity and Density of Ethanol-Diesel-Biodiesel Ternary Blends for Sustainable Environment. Sustainability. 2020;12(12):5186.

[7] Harun NHHM, Wahid FRAA, Saleh S, Samad NAFA. Effect of torrefaction on palm oil waste chemical properties and kinetic parameter estimation. Chemical Engineering Transactions. 2017;56:1195-200.

[8] Kopczyński M, Lasek JA, Iluk A, Zuwała J. The co-combustion of hard coal with raw and torrefied biomasses (willow (Salix viminalis), olive oil residue and waste wood from furniture manufacturing). Energy. 2017;140:1316-25.

[9] Sher F, Pans MA, Afilaka DT, Sun C, Liu H. Experimental investigation of woody and non-woody biomass combustion in a bubbling fluidised bed combustor focusing on gaseous emissions and temperature profiles. Energy. 2017;141:2069-80.

[10] Melkior T, Barthomeuf C, Bardet M. Inputs of solid-state NMR to evaluate and compare thermal reactivity of pine and beech woods under torrefaction conditions and modified atmosphere. Fuel. 2017;187:250-60.

[11] Klinger J, Bar-Ziv E, Shonnard D. Predicting properties of torrefied biomass by intrinsic kinetics. Energy & Fuels. 2015;29(1):171-6.

[12] Dudyński M, van Dyk JC, Kwiatkowski K, Sosnowska M. Biomass gasification: Influence of torrefaction on syngas production and tar formation. Fuel processing technology. 2015;131:203-12.

[13] Spîrchez C, Lunguleasa A, Antonaru C. Experiments and modeling of the torrefaction of white wood fuel pellets. BioResources. 2017;12(4):8595-611.

[14] Pawlak-Kruczek H, Krochmalny K, Mościcki K, Zgóra J, Czerep M, Ostrycharczyk M, et al. Torrefaction of various types of biomass in laboratory scale, batch-wise isothermal rotary reactor and pilot scale, continuous multi-stage tape reactor. Inżynieria i Ochrona Środowiska. 2017;20.

[15] Valix M, Katyal S, Cheung W. Chemical torrefaction as an alternative to established thermal technology for stabilisation of sugar cane bagasse as fuel. Environmental technology. 2017;38(13-14):1638-43.

[16] Rodrigues A, Nunes L, Godina R, Matias J. Correlation between Chemical Alterations and Energetic Properties in Torrefied Biomass. Conference Correlation between Chemical Alterations and Energetic Properties in Torrefied Biomass. IEEE, p. 1-5.

[17] Rodrigues A, Loureiro L, Nunes L. Torrefaction of woody biomasses from poplar SRC and Portuguese roundwood: Properties of torrefied products. Biomass and Bioenergy. 2018;108:55-65.

[18] Bach Q-V, Gye H-R, Song D, Lee C-J. High quality product gas from biomass steam gasification combined with torrefaction and carbon dioxide capture processes. International Journal of Hydrogen Energy. 2019;44(28):14387-94.

[19] Yılgın M, Duranay N, Pehlivan D. Torrefaction and combustion behaviour of beech wood pellets. Journal of Thermal Analysis and Calorimetry. 2019;138(1):819-26.

[20] Jian J, Lu Z, Yao S, Li X, Song W. Comparative Study on Pyrolysis of Wet and Dry Torrefied Beech Wood and Wheat Straw. Energy & fuels. 2019;33(4):3267-74.

[21] Gucho EM, Shahzad K, Bramer EA, Akhtar NA, Brem G. Experimental study on dry torrefaction of beech wood and miscanthus. Energies. 2015;8(5):3903-23.

[22] Uemura Y, Sellappah V, Trinh T, Komiyama M, Hassan S, Tanoue K. Improvement of energy density and energy yield of oil palm biomass by torrefaction in combustion gas. Conference Improvement of energy density and energy yield of oil palm biomass by torrefaction in combustion gas, vol. 458. IOP Publishing, p. 012061.

[23] Wang L, Barta-Rajnai E, Skreiberg Ø, Khalil R, Czégény Z, Jakab E, et al. Impact of torrefaction on woody biomass properties. Energy Procedia. 2017;105:1149-54.

[24] Becker A, Scherer V. A comparison of the torrefaction behavior of wood, miscanthus and palm kernel shells: Measurements on single particles with geometries of technical relevance. Fuel. 2018;224:507-20.

[25] Singh RK, Sarkar A, Chakraborty JP. Effect of torrefaction on the physicochemical properties of eucalyptus derived biofuels: estimation of kinetic parameters and optimizing torrefaction using response surface methodology (RSM). Energy. 2020:1-37.

[26] Margaritis N, Grammelis P, Karampinis E, Kanaveli I-P. Impact of Torrefaction on Vine Pruning’s Fuel Characteristics. Journal of Energy Engineering. 2020;146(3):040200061-9.

[27] Xue J, Chellappa T, Ceylan S, Goldfarb JL. Enhancing biomass+ coal Co-firing scenarios via biomass torrefaction and carbonization: Case study of avocado pit biomass and Illinois No. 6 coal. Renewable energy. 2018;122:152-62.

[28] Mun T-Y, Tumsa TZ, Lee U, Yang W. Performance evaluation of co-firing various kinds of biomass with low rank coals in a 500 MWe coal-fired power plant. Energy. 2016;115:954-62.

[29] Rentizelas AA, Li J. Techno-economic and carbon emissions analysis of biomass torrefaction downstream in international bioenergy supply chains for co-firing. Energy. 2016;114:129-42.

[30] Čuček L, Klemeš JJ, Varbanov PS, Kravanja Z. Significance of environmental footprints for evaluating sustainability and security of development. Clean Technologies and Environmental Policy. 2015;17(8):2125-41.

[31] Thanapal SS, Annamalai K, Ansley RJ, Ranjan D. Co-firing carbon dioxide-torrefied woody biomass with coal on emission characteristics. Biomass Conversion and Biorefinery. 2016;6(1):91-104.

[32] Sher F, Iqbal SZ, Liu H, Imran M, Snape CE. Thermal and kinetic analysis of diverse biomass fuels under different reaction environment: A way forward to renewable energy sources. Energy Conversion and Management. 2020;203:112266.

[33] Gil M, García R, Pevida C, Rubiera F. Grindability and combustion behavior of coal and torrefied biomass blends. Bioresource technology. 2015;191:205-12.

[34] Ndibe C, Grathwohl S, Paneru M, Maier J, Scheffknecht G. Emissions reduction and deposits characteristics during cofiring of high shares of torrefied biomass in a 500 kW pulverized coal furnace. Fuel. 2015;156:177-89.
[35] Manouchehrinejad M, van Giesen I, Mani S. Grindability of torrefied wood chips and wood pellets. Fuel processing technology. 2018;182:45-55.
[36] Wang Y, Xiang Y, Wang D, Dong C, Yang Y, Xiao X, et al. Effect of sodium oxides in ash composition on ash fusibility. Energy & Fuels. 2016;30(2):1437-44.
[37] Lasek JA, Kopczyński M, Janusz M, Iluk A, Zuwała J. Combustion properties of torrefied biomass obtained from flue gas-enhanced reactor. Energy. 2017;119:362-8.
[38] Yelverton TL, Brashear AT, Nash DG, Brown JE, Singer CF, Kariher PH, et al. Characterization of emissions from a pilot-scale combustor operating on coal blended with woody biomass. Fuel. 2020;264:1-10.
[39] Ohm T-I, Chae J-S, Kim J-K, Oh S-C. Study on the characteristics of biomass for co-combustion in coal power plant. Journal of Material Cycles and Waste Management. 2015;17(2):249-57.
[40] Stelte W, Nielsen NPK, Hansen HO, Dahl J, Shang L, Sanadi AR. Reprint of: Pelletizing properties of torrefied wheat straw. Biomass and bioenergy. 2013;53:105-12.
[41] Wilk M, Magdziarz A, Kalemba I. Characterisation of renewable fuels' torrefaction process with different instrumental techniques. Energy. 2015;87:259-69.
[42] Granados D, Ruiz R, Vega L, Chejne F. Study of reactivity reduction in sugarcane bagasse as consequence of a torrefaction process. Energy. 2017;139:818-27.
[43] Zheng A, Jiang L, Zhao Z, Huang Z, Zhao K, Wei G, et al. Impact of torrefaction on the chemical structure and catalytic fast pyrolysis behavior of hemicellulose, lignin, and cellulose. Energy & Fuels. 2015;29(12):8027-34.
[44] Deniz V. Evaluation of Grindability Behaviors of Four Different Solid Fuels Blending by Using the Hardgrove Mill. Inżynieria Mineralna. 2019;21.
[45] Ohliger A, Förster M, Kneer R. Torrefaction of beechwood: A parametric study including heat of reaction and grindability. Fuel. 2013;104:607-13.
[46] Junga R, Pospolita J, Niemiec P. Combustion and grindability characteristics of palm kernel shells torrefied in a pilot-scale installation. Renewable Energy. 2020;147:1239-50.
[47] Beery TB. Impacts of torrefaction and ash reduction on the catalytic fast pyrolysis of energy crops: University of Georgia, 2016.
[48] Eddings EG, McAvoy D, Coates RL. Co-firing of pulverized coal with Pinion Pine/Juniper wood in raw, torrefied and pyrolyzed forms. Fuel Processing Technology. 2017;161:273-82.
[49] Varol M, Atimtay AT, Olgun H, Atakül H. Emission characteristics of co-combustion of a low calorie and high sulfur–lignite coal and woodchips in a circulating fluidized bed combustor: Part 1. Effect of excess air ratio. Fuel. 2014;117:792-800.
[50] Rokni E, Ren X, Panahi A, Levendis YA. Emissions of SO2, NOx, CO2, and HCl from Co-firing of coals with raw and torrefied biomass fuels. Fuel. 2018;211:363-74.
[51] Hassan MHA, Sher F, Zarren G, Suleiman N, Tahir AA, Snape CE. Kinetic and thermodynamic evaluation of effective combined promoters for CO2 hydrate formation. Journal of Natural Gas Science and Engineering. 2020;78:103313.
[52] Zhang Y, Ran Z, Jin B, Zhang Y, Zhou C, Sher F. Simulation of Particle Mixing and Separation in Multi-Component Fluidized Bed Using Eulerian-Eulerian Method: A Review. International Journal of Chemical Reactor Engineering. 2019;17(11).

[53] Hai IU, Sher F, Zarren G, Liu HJJoCP. Experimental investigation of tar arresting techniques and their evaluation for product syngas cleaning from bubbling fluidized bed gasifier. 2019;240:118239.

[54] Al-Shara NK, Sher F, Yaqoob A, Chen GZ. Electrochemical investigation of novel reference electrode Ni/Ni (OH) $_2$ in comparison with silver and platinum inert quasi-reference electrodes for electrolysis in eutectic molten hydroxide. International Journal of Hydrogen Energy. 2019.

[55] Sher F, Pans MA, Sun C, Snape C, Liu H. Oxy-fuel combustion study of biomass fuels in a 20 kWth fluidized bed combustor. Fuel. 2018;215:778-86.

[56] Al-Shara NK, Sher F, Iqbal SZ, Sajid Z, Chen GZ. Electrochemical study of different membrane materials for the fabrication of stable, reproducible and reusable reference electrode. Journal of Energy Chemistry. 2020;49:33-41.

[57] Sehar S, Sher F, Zhang S, Khalid U, Sulejmanović J, Lima EC. Thermodynamic and kinetic study of synthesised graphene oxide-CuO nanocomposites: A way forward to fuel additive and photocatalytic potentials. Journal of Molecular Liquids. 2020:113494.

[58] Hai IU, Sher F, Yaqoob A, Liu HJF. Assessment of biomass energy potential for SRC willow woodchips in a pilot scale bubbling fluidized bed gasifier. 2019;258:116143.

[59] Nemet A, Klemes JJ, Kravanja Z. GHG emissions reduction by improving efficiency of utilities' transport and use and cross-sectorial energy integration. Chemical Engineering Transactions. 2018;63:19-24.

[60] Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the composition and application of biomass ash. Part 1. Phase–mineral and chemical composition and classification. Fuel. 2013;105:40-76.

[61] Niu Y, Tan H, Hui Se. Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures. Progress in Energy and Combustion Science. 2016;52:1-61.

[62] Vassilev SV, Vassileva CG, Vassilev VS. Advantages and disadvantages of composition and properties of biomass in comparison with coal: An overview. Fuel. 2015;158:330-50.

[63] Zhou C, Rosén C, Engvall K. Biomass oxygen/steam gasification in a pressurized bubbling fluidized bed: Agglomeration behavior. Applied Energy. 2016;172:230-50.

[64] Zeng T, Pollex A, Weller N, Lenz V, Nelles M. Blended biomass pellets as fuel for small scale combustion appliances: Effect of blending on slag formation in the bottom ash and pre-evaluation options. Fuel. 2018;212:108-16.

List of Tables

Table 1. Ultimate, proximate analysis and calorific values of coal and other biomass fuels.

Fuels	**Ultimate analysis**[a]					**Proximate analysis**[c]				**GCV**	**NCV**
	C (%)	H (%)	N (%)	O[b] (%)	S (%)	M[d] (%)	VM (%)	FC (%)	Ash[d] (%)	kJ/kg	kJ/kg
Beachwood	46.8	6.40	<0.3	42.5	0.021	5.41	82	16.84	1.16	19429	17374
El Cerrejon	78.5	5.98	1.57	13.48	0.47	2.25	31	55	14	28134	27205
LTTB	49.9	6.32	<0.3	40.1	0.017	3.00	77.88	21	1.12	21058	19690
MTTB	53.3	6.18	<0.3	36.7	0.018	2.38	71.85	27	1.15	21698	20352

M: moisture, VM: volatile matter, FC: fixed carbon, GCV: gross calorific value, NCV: net calorific value, LTTB: low torrefied temperature biomass, MTTB medium torrefied temperature biomass

a. On a dry basis except as denoted in the table.
b. Calculated by the difference.
c. On a dry basis except for moisture which is on an as-received basis.
d. As the received basis.

Table 2. Equipments and techniques for standard flue gas analysis.

Gas component	Manufacturer technique	Manufacturer	Calibration gas
O_2	Paramagnetism	Rosemount	3 vol% in N_2
CO	NDIR	Rosemount	200 ppm in N_2
NO_x	Chemiluminescence	ECO Physics	800 ppm in N_2
SO_2	Infrared	Siemens	700 ppm in N_2

Table 3. Input BTS-VR parameters for the different combustion settings.

Parameter	Values at STP
Wall Temperature (°C)	1,300
Air ratio	1.15
Transport air (m^3/h)	1.50
Primary air (m^3/h)	2.08
Secondary air (m^3/h)	3.12
Total burner air flow rate (m^3/h)	6.70
Residence time (Minutes)	0.70

Table 4. Thermal kinetics and binding energies of various bonds in biomass.

Bonds	**Binding energy (kJ/mol)**	**Bonds**	**Binding energy (kJ/mol)**
C=C	615	**C-H (methane)**	415
C-C (aromatic)	519	**N-H**	389
C-H (-CH_3)	507	**C-O**	364
O-H	465	**C-C**	348
C-H (-CH_2-)	444	**C-O**	331
N=N	419	**C-N**	285

Table 5. Summary of fuels' sieve analysis.

Diameter	**Beechwood**	**El Cerrejon**	**LTTB**	**MTTB**
D_{10} (µm)	70	38	58	32
D_{50} (µm)	188	50	150	120
D_{90} (µm)	300	87	300	250

Table 6. Ash fusion temperatures for different combustion and co-combustion settings.

Tempertures (ºC)	**Beech wood**	**El Cerrejon**	**LTTB**	**MTTB**	**EC+ Beech wood**	**EC+ LTTB**	**EC+ MTTB**
Initial deformation (IDT)	790	1,240	830	840	920	950	980
Softening (ST)	1,440	1,260	1,310	1,350	1,310	1,220	1,240
Hemisphere (HT)	1,420	1,270	1,390	-	1,320	1,220	1,240
Fluid (FT)	-	1,290	1,400	1,370	1,320	1,220	1,240

List of Figures

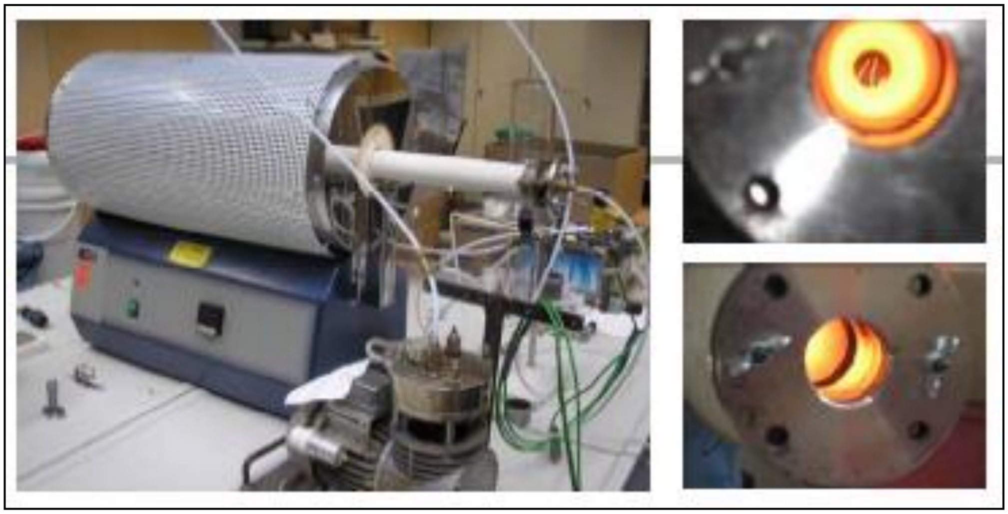

Fig. 1. Horizontal tube furnace setup for batch torrefaction experiments.

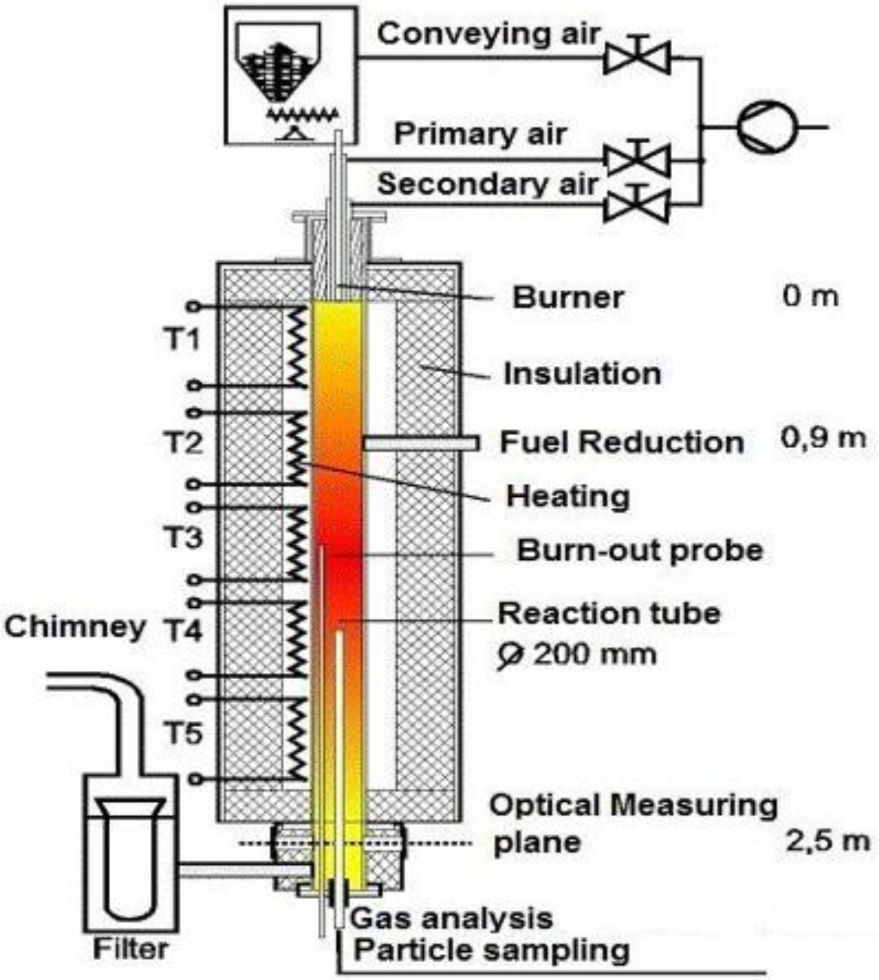

Fig. 2. Atmospheric entrained flow combustion reactor setup.

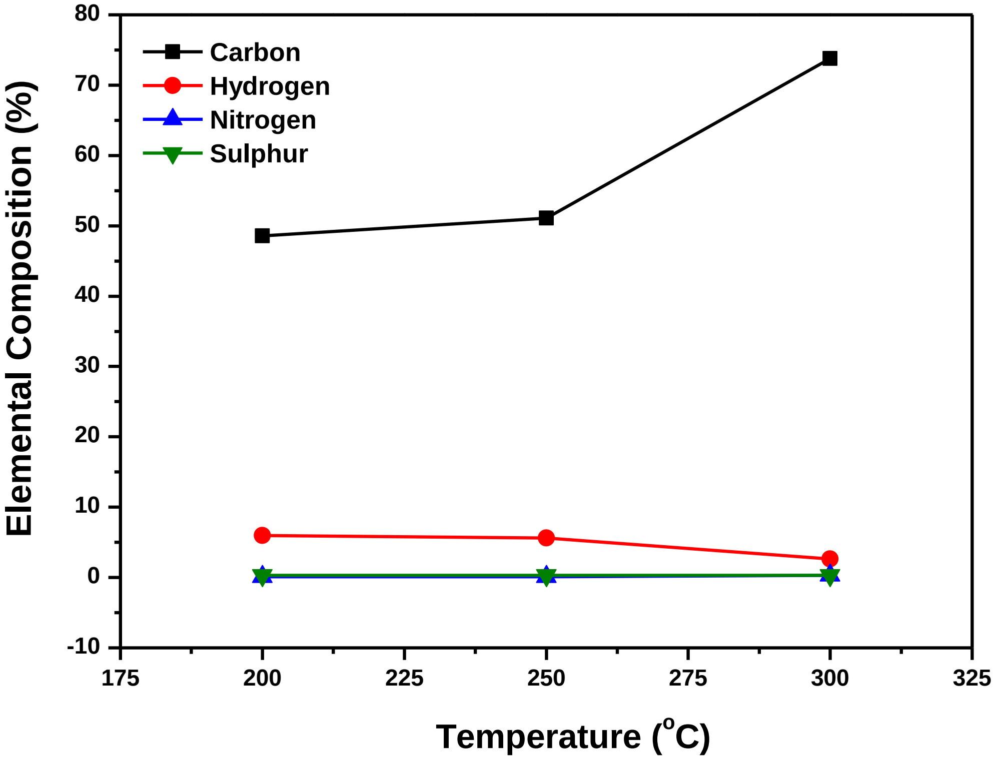

Fig. 3. Elemental analysis of beechwood at different torrefaction temperatures.

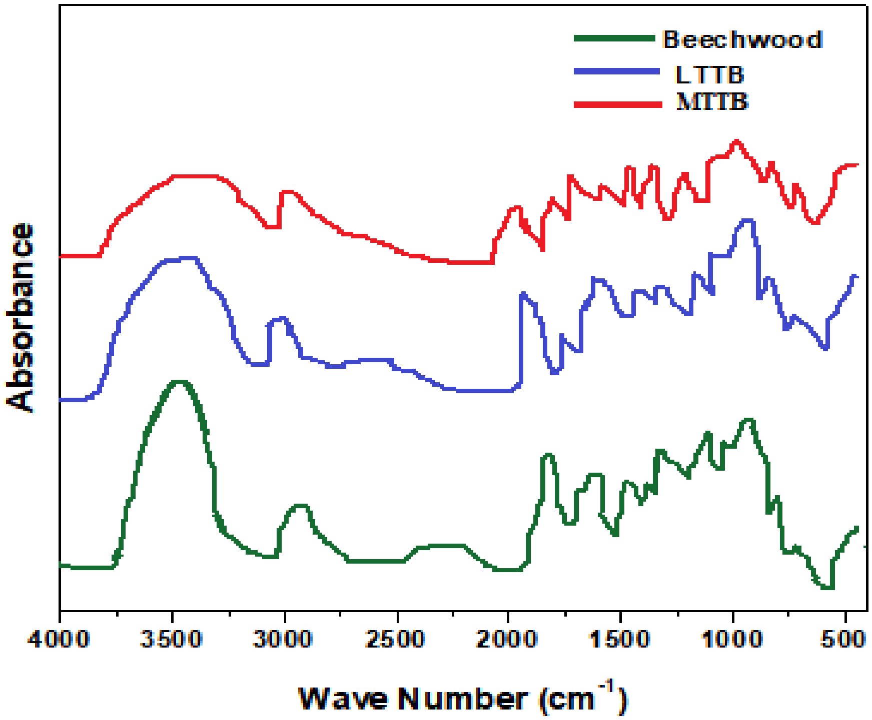

Fig. 4. FTIR spectra of raw and torrefied beechwood (LTTB and MTTB)

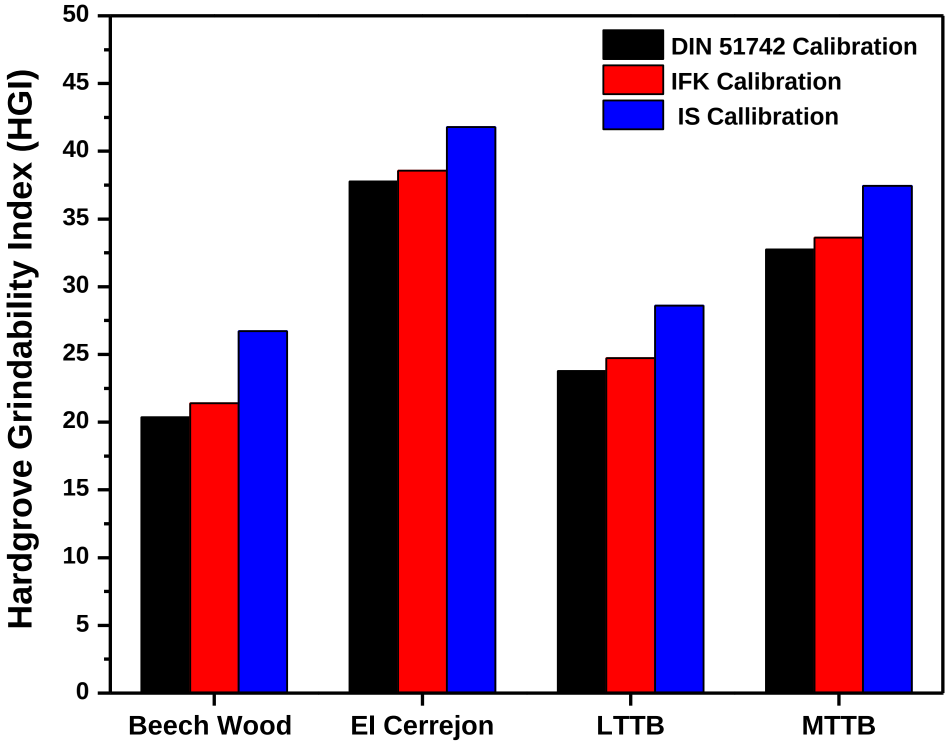

Fig. 5. Comparison of HGI values of different fuels found by DIN 51742, IFK, and IS calibration methods.

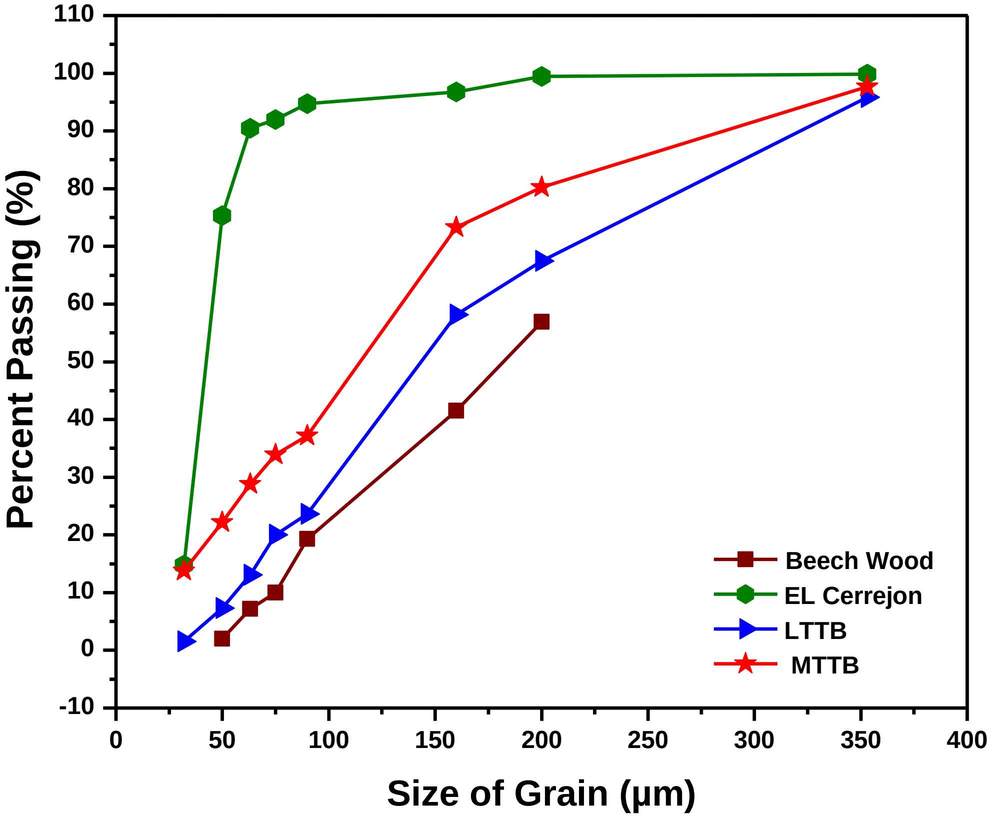

Fig. 6. The particle size distribution of coal, raw biomass and torrefied biomasses (LTTB and MTTB) after grinding.

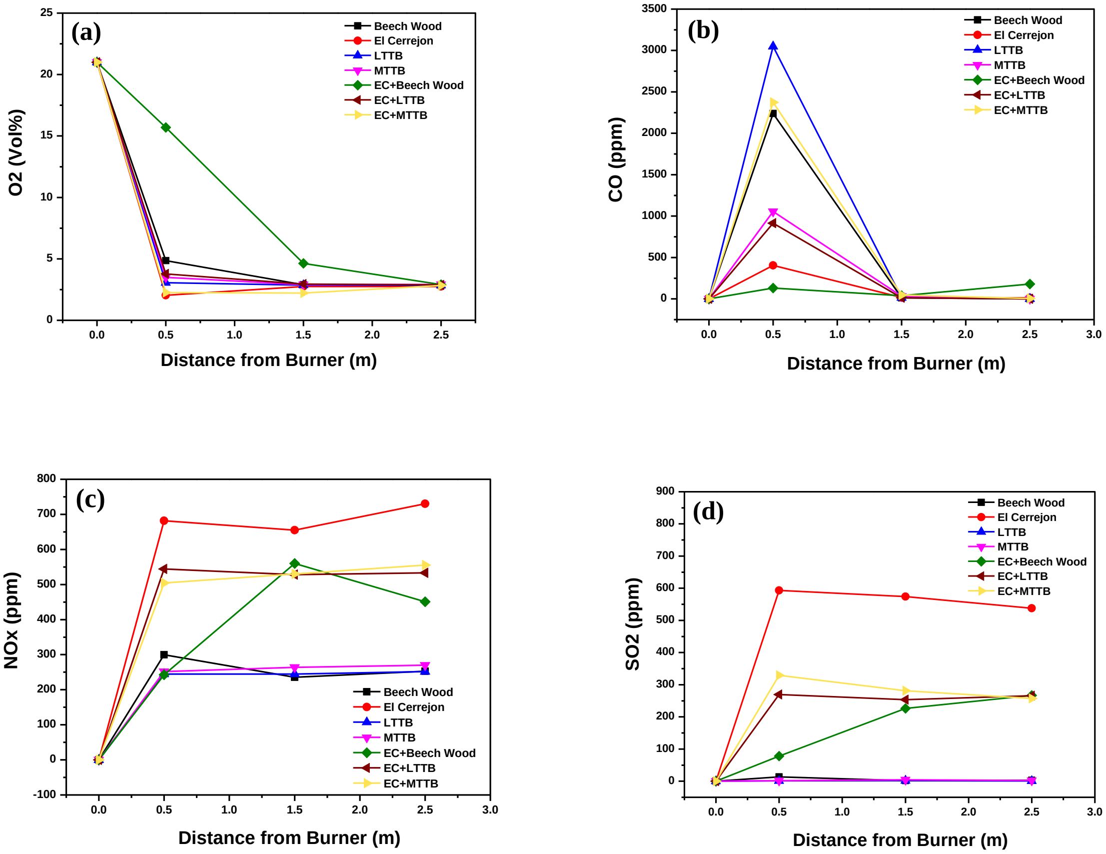

Fig. 7. Flue gas emission profiles at various distances from the burner during combustion and co-combustion of raw biomass, coal and torrefied biomasses (LTTB and MTTB); (a) O_2, (b) CO, (c) NO_X and (d) SO_2.

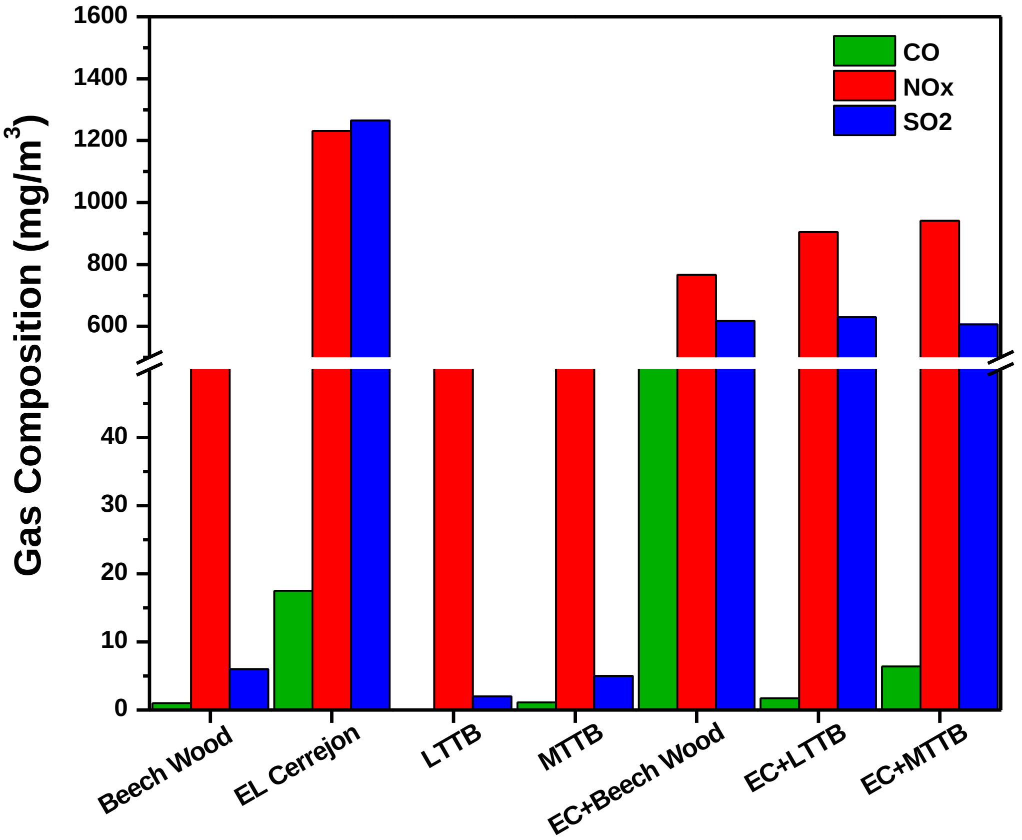

Fig. 8. CO, NO_X and SO_2 concentrations at the furnace outlet of the flue gas for the various combustion settings, corrected at 6% O_2 in the flue gas.

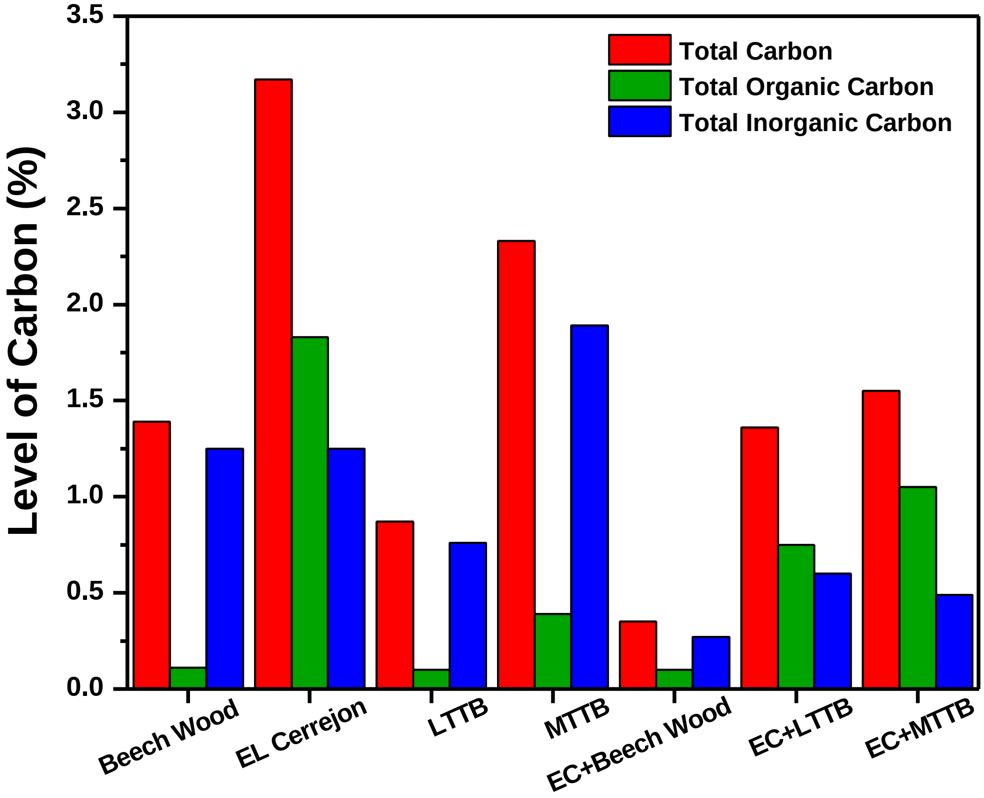

Fig. 9. Multiphase carbon analysis of fly ash taken from furnace exit.

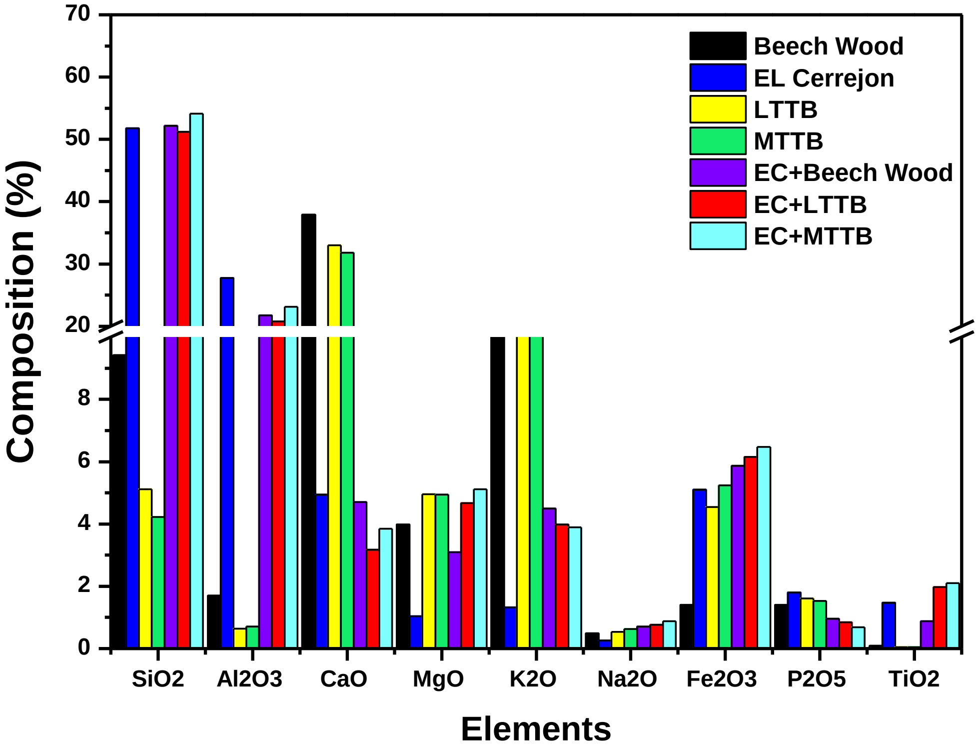

Fig. 10. Fly ash composition of different fuels in terms of elemental oxide.