Research article

Microwave-assisted co-pyrolysis of high ash Indian coal and rice husk: Product characterization and evidence of interactions

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ABSTRACT

In this study, microwave-assisted co-pyrolysis of high ash Indian coal and rice husk is investigated to evaluate the yield and quality of the pyrolysis oil, and to understand the interactions during co-pyrolysis. Microwave co-pyrolysis experiments were conducted in a bench scale unit, and the effects of various parameters such as microwave power (420 W and 560 W), coal:rice husk ratio, and feed:susceptor (graphite) ratio on product yields and oil composition were thoroughly evaluated. Oil yield was not significantly affected by microwave power and feed:susceptor ratio for a particular coal:rice husk ratio. The oil yields were 11 ± 2 wt%, 15 ± 2 wt%, 18 ± 2 wt%, 21 ± 2 wt% and 26 ± 2 wt% for 100:0, 75:25, 50:50, 25:75 and 0:100 wt./wt. coal:rice husk, respectively, at both microwave powers, and followed an additive effect with increase in rice husk amount in the mixtures. Pyrolysis oil contained monoaromatic hydrocarbons, naphthalene derivatives, aliphatic hydrocarbons and phenolic derivatives. The interactions between coal and rice husk pyrolysis intermediates were evidenced in the form of enhanced yields of polyaromatic hydrocarbons with a concomitant reduction in yield of methoxy phenols. Pyrolysis oil from coal had highest heating value (36–38 MJ kg^{-1}) due to the presence of aliphatic hydrocarbons, while that from rice husk had the lowest heating value (28–30 MJ kg^{-1}) due to high oxygenate content. The heating values of co-pyrolysis oils were in the range of 30–36 MJ kg^{-1}. Hydrogen constituted a major fraction in the pyrolysis gases, and the addition of rice husk to coal promoted the evolution of CO.

1. Introduction

With the share of over 60% in the commercial energy sector, coal has become India's energy security. The relative abundance of coal in India compared to other fossil fuels makes it a natural choice as the primary source of fuel. The reserves-to-production ratio of coal, at the current rate of production, is around 230 years as against 15 and 23 years, respectively, for indigenous crude oil and natural gas [1]. India has got 192 billion tons of coal reserves, but the majority are of high ash variety [2]. High mineral content is the major constraint for its utilization in process industries at commercial scale. Removal of ash to a permissible level is not economical through beneficiation [2]. Presently, majority of the high ash Indian coals are used in electricity generation, and in other industries such as cement, smelting-reduction processes of steel making, chemical, paper, etc. However, due to high mineral content, which is associated with the coal matrix, current coal-based technologies are less efficient, environment-unfriendly and involve high pretreatment costs. Owing to the emission of huge amounts of fly ash, environmental legislation is against the use of high ash coals. In order to improve the utilization of high ash Indian coal, and to

increase the carbon and energy density, co-pyrolysis, co-gasification and co-combustion with lignocellulosic biomass and agro residues have been developed, as biomass is renewable and CO$_2$ neutral [3].

Coal is a complex heterogeneous material consisting of a number of distinct organic (maceral) and inorganic (mineral) compounds [4]. Although regained interest in the production of transportation fuels from coal is a positive sign, it is not sufficient, as liquefaction of coal yields relatively low liquid compared to biomass liquefaction. The conversion of coal/biomass to liquid hydrocarbon fuels offers great hope in commercialization than other alternatives, as it not only reduces the carbon footprint in the environment but also facilitates the utilization of locally available low-rank coals [5]. Among co-processing techniques, co-pyrolysis of coal with biomass is a promising route. Pyrolysis is considered not only as a technique to produce oil, char and gases, but it is also a fundamental step in combustion and gasification [6]. Further, co-processing of coal and lignocellulosic agro residues can provide a solution for the utilization of biomass on a commercial scale.

Conventional heating involves heat transfer in the form of conduction, convection and radiation, while in microwave heating electromagnetic energy is converted to thermal energy from the core of the

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sample to its surface. Due to its uniform, volumetric, rapid, selective and efficient heating mechanism, microwave heating reduces the processing time and enables the selective production of chemicals [7]. Energy efficiency is a great advantage of microwave heating. The typical energy efficiency of industrial magnetrons is about 80% at 100 kW output power, while domestic microwave magnetrons exhibit 65–70% efficiency at an output power of around 1 kW [8]. Suitable use of susceptor in the pyrolysis process can convert maximum fraction of microwave energy into heat energy. Importantly, the generation of microplasma facilitates the faster escape of volatiles thereby restricting the secondary cracking and enhancing the oil yield.

Many studies are available on conventional co-pyrolysis of coal with biomass [9–17]. In some of the studies, mild synergy was observed in product yields and composition, while many studies observed no significant synergy in the vapor phase products. Synergistic effect of co-conversion of coal and biomass is expected to increase the total volatiles (tars and light gases) yield and reduce the char yield. Haykiri-Acma and Yaman [18] studied the interaction between woody biomass and different ranks of coals during co-pyrolysis using a thermogravimetric analyzer (TGA). They observed no synergy when bituminous coal was used, while the char yield increased and decreased when peat and lignite were mixed, respectively, with biomass. Vuthaluru [15] conducted co-pyrolysis of a sub-bituminous coal with waste wood and wheat straw using TGA, and concluded that there is no synergy between coal and biomass. Collot et al. [10] conducted pyrolysis experiments with Daw mill coal (bituminous) and wood in a fixed bed reactor at 850 °C and 1000 °C at a heating rate of 10 °C min^{-1} and different pressures from 1 bar to 25 bar, and observed no synergy in product yields or composition. Similarly, Moghtaderi et al. [12] conducted co-pyrolysis of high-volatile bituminous coal and Radiata pine sawdust and found no synergy. Idris et al. [19] co-pyrolyzed Malaysian sub-bituminous coal with empty fruit bunches, kernel shell, mesocarp fibers of palm tree in a TGA, and observed no synergy. In contrast, Jones et al. [11] conducted devolatilization studies of blends of bituminous and lignite coals with a variety of biomasses such as pinewood, cellulose and lignin. Experiments were conducted in an analytical pyrolyzer (Py) coupled with gas chromatograph/mass spectrometry (GC/MS), TGA and static batch pyrolysis reactors at different heating rates. Py-GC/MS and TGA results displayed additive behavior, while synergy was observed in the batch pyrolysis reactor. Oney et al. [20] conducted co-pyrolysis experiments in TGA and fixed bed reactor with lignite and safflower seed blends, and observed synergy in the fixed bed reactor, especially when the proportion of coal was < 33% in the mixture. Park et al. [21] co-pyrolyzed sub-bituminous coal and sawdust in TGA and fixed bed reactor, and observed that the yield of char was lower than expected. The above results are quite contrasting, and it is evident that the synergy or interactions also depend on the reactor type, heating rate, and the nature of coal or biomass.

The effectiveness of microwave heating is determined by the absorbing capability of the microwaves by the feedstock material. This is characterized by dielectric loss tangent (tan δ), which is defined as the ratio of dielectric loss factor to dielectric constant. More the tan δ value, better is the microwave absorbing capability of the material. Typically, coal and biomass exhibit low tan δ. The loss tangent for coal is reported to be in the range of 0.02–0.1 [22], while that for biomass is < 0.05 [23]. For carbonaceous materials like biomass char, activated carbon and carbon black, tan δ values are 0.134, 1.63 and 0.83, respectively [24]. The microwave absorption capability and its conversion to heat energy by the material also depends on other factors such as moisture content, volatile matter, fixed carbon and ash composition. In order to enhance the heating rate of the process and to achieve fast pyrolysis conditions in microwave heating, susceptors have to be used.

Microwave-assisted pyrolysis of individual biomasses and coals are available in the literature. Biomasses such as maize stalk [25], peanut shell [25], rice straw [26], Douglas fir [27], wheat straw [28], corn stover [29], pine wood sawdust [22], *P. juliflora* [30], oil palm biomass [31], rice husk [32], and coals such as Creswell coal, Gedling coal [33], Indonesian coal [24,34], high volatile bituminous coal [35], Black Thunder coal [8] and Indian coal [24] have been tested in microwave reactors.

To the best of our knowledge, there are no studies available on microwave-assisted co-pyrolysis of coal and biomass, especially high ash Indian coals and rice husk. Rice husk is abundant in rice growing countries such as India, China and Brunei. Rice husk is generated on site as a by-product in the milling factory. Rice husk is used as a value added raw material for different purposes, and also for bioethanol production [36]. Rice husk ash is rich in silica (87–97%) [37]. The objectives of the study are many fold. Firstly, the yields of oil, gas and char from microwave-assisted co-pyrolysis of high ash Indian coal and rice husk are assessed for different blend ratios of the feedstocks at different feed:susceptor ratios, and at two different microwave powers. Secondly, the detailed composition analysis of bio-oil and pyrolysis gases under the above conditions is performed. Thirdly, the interactions of coal with biomass, and between their intermediates during co-pyrolysis are understood in terms of the variations in predicted and experimental yields of various functional groups in the pyrolysis oil.

2. Experimental section

2.1. Materials and methods

High ash Indian coal was procured from Thermax Ltd., India. Rice husk was procured from a rice mill in Chennai. Both feedstocks were crushed, ground and sieved to fine fractions (< 0.5 mm size). Graphite (60/80 mesh, 180–250 μm) was procured from S.D. Fine Chem Pvt. Ltd., India, and used as the susceptor. Rice husk was mixed with high ash Indian coal at 75:25, 50:50, 25:75 (wt./wt.) using laboratory blending equipment. TGA was performed in a SDT-Q600 (TA instruments) using N$_2$ gas at 100 mL min^{-1}. The sample was heated from ambient to 800 °C at 10 °C min^{-1} to identify the decomposition regimes of coal, rice husk and their blends. Proximate analysis was performed in an automatic multiple sample TGA (TGA – 2000 A, Navas Instruments) by taking 1.0 g of sample according to ASTM E1131-08 method. Elemental analysis was performed in CHN analyzer (Thermo Flash 2000) by taking 2–3 mg of samples. Sulfur analysis was performed according to ASTM D4239-14e2 method. Higher heating values (HHV) of feedstocks and char were determined using a bomb calorimeter (IKA 2000) by taking c.a. 0.3 g sample. Ash analysis was performed according to ASTM D-3682:2011 method.

2.2. Microwave reactor

A domestic multimode on–off microwave oven (Whirlpool- MW 20 BS) that delivers microwaves at different powers (70–700 W) was used for pyrolysis experiments. Owing to the low dielectric loss tangent of coal and biomass (tan δ = 0.02–0.1) [24,30], low microwave powers (< 400 W) were not used. In a recent study on microwave pyrolysis of tire powder by Song et al. [38], medium microwave power of 450 W yielded high oil, while low (270 W) and high (720 W) microwave powers led to high yields of char and gases, respectively. In another study, low microwave powers are shown to produce high amount of char for Indonesian lignite coal [34]. Therefore, in this study the experiments were conducted at medium microwave powers of 420 W and 560 W to evaluate the oil yield. In order to recover the vapors, a 40 mm diameter hole was drilled on top of the microwave oven, and a borosilicate adaptor was inserted and attached to the quartz round bottom flask containing the feedstock. The exit of the adaptor was connected to a two-stage condensation system. The schematic of the experimental set-up is available in Fig. S1 (in Supplementary data). A modified thermocouple was also inserted into the reaction vessel through the adaptor to measure the reaction temperature during the off-time of the magnetron. The quartz round bottom flask was insulated with glass

Table 1
Characterization of high ash Indian coal and rice husk.

	Proximate analysis[a] (wt%)			Ultimate analysis[b] (wt%)					HHV[c] (MJ kg^{-1})
	VM[d]	FC[e]	Ash	C	H	N	S	O[f]	
High ash Indian coal	27.9	36.6	35.5	72.3	5.6	1.8	1.2	19.1	17.4
Rice husk	60.2	16.3	23.5	45.1	6.4	0.4	n.d.	48.1	13.1

[a] Dry basis.
[b] Dry ash free basis.
[c] High heating value.
[d] Volatile matter.
[e] Fixed carbon.
[f] By difference.

wool and Teflon® to restrict the heat losses due to conduction in the oven cavity. The condenser was connected to a glass collection flask, which was maintained at a temperature of 10 °C by continuous circulation of cold water. Utmost care was taken by wrapping Teflon® tapes at the top, bottom and around the adaptor to avoid microwave leakage from the oven cavity. To avoid leakage in the reactor and downstream condensation unit, and to avoid contamination of the products, all the joints in the system were sealed with Teflon®. Further details of the experimental set-up are available in our earlier studies [24,30].

The schematic of the modified chromel-alumel thermocouple used to measure the temperature of the reactants during the magnetron off-time is shown in Fig. S1 (in Supplementary data). The chromel-alumel thermocouple wires were separated from each other, and by electric arcing, a hot junction was made. The wires were then insulated using four successive layers of alumina beads, aluminum foil, quartz tube and aluminum foil. This four-layer sheathing ensured that the temperature sensor was unaffected by microwave interferences, and the temperature measured was that of the reaction mixture. The accuracy of the thermocouple was ± 2 °C. More details about the thermocouple set-up are available elsewhere [24,30].

2.3. Experimental details

Experiments were carried out by taking 40 g of the feed and required amount of susceptor in the quartz flask. The snapshots of coal, rice husk and their mixtures are shown in Fig. S2 (in Supplementary data). Owing to proper and homogeneous mixing of the feed and susceptor in a laboratory blending device, there was no formation of hotspots within the reaction vessel. This was confirmed by placing the thermocouple at different locations inside the quartz flask to ensure similar temperature was monitored. The entire system, including reactor and downstream condensation units, was purged with N_2 at a flow rate of 100 mL min^{-1} for 10 min before starting every experiment to maintain inert atmosphere. The thermocouple tip was placed in the reaction mixture. Pyrolysis was conducted upto a final temperature of 800 °C, and the reaction mixture was held at this temperature for typically 10 min in order to achieve complete evolution of gases. In a typical experiment, the evolution of condensable volatiles occurred until 650 °C, while at higher temperatures, only non-condensable gas evolution occurred, which typifies the secondary decomposition of char to light gases. At the end of every experiment, the mass of oil and char were measured gravimetrically, and the gas yield was calculated by mass balance. The mass of graphite susceptor was subtracted from that of the solid residue, as it was shown earlier that graphite does not significantly lose mass under microwave pyrolysis conditions [24]. The experiments were repeated three times non-consecutively, and the uncertainties in product yields are reported. Typically, the standard deviation in product yields with respect to the average values was within 5%, while that in functional group yields in oil was 5–8%.

2.4. Product analysis

The composition of oil was analyzed semi-quantitatively using a GC/MS (Agilent 7890-5975C). A DB-5MS (5%-phenyl-methylpolysiloxane, 30 m length × 0.25 mm i.d. × 0.25 μm film thickness) column was used to separate the volatiles. High purity (5.5 grade) helium was used as the carrier gas at a flow rate of 0.8 mL min^{-1}. Column oven was programmed as follows: isothermal at 45 °C for 2 min, heated to 300 °C at a rate of 5 °C min^{-1}, and finally maintained at 300 °C for 2 min. Injector, MS ion source and detector temperatures were set at 275 °C, 320 °C and 150 °C, respectively. The electron ionization voltage was 70 eV, and the mass range scanned was from 35 to 350 Da. Owing to the waxy nature of the coal oils, dichloromethane was used as the diluent at a dilution ratio of 25:1 (vol./vol.). The organic fraction of the oil was separated from the aqueous fraction by solvent extraction using dichloromethane. The mass spectra of the unknown organic compounds were compared with NIST mass spectral database. All the identified compounds had a match factor > 85%. The oil composition was evaluated by normalizing the peak area% with respect to the absolute yield of the oil fraction.

An online gas analyzer (Bhoomi Analyzers, India) was used to record the composition of non-condensable gases (CO, CO_2, H_2 and CH_4), while they were produced during pyrolysis. It contains a non-dispersive infrared sensor to detect CO, CO_2 and CH_4, and an electrochemical sensor for the detection of H_2. The typical response time of the analyzer was 1–2 s. The surface morphology of the solid residue was analyzed using a scanning electron microscope (SEM, Hitachi S4800).

3. Results and discussions

3.1. Characterization of feedstock

Table 1 depicts the proximate and elemental composition of high ash Indian coal and rice husk. As expected, coal and rice husk contain high amount of ash, i.e. 35.5 wt% and 23.5 wt% on dry basis, respectively. From the proximate analysis, it can be seen that volatile matter in coal is very low (27.9 wt%) compared to that in rice husk (60.2 wt%). From elemental analysis, it is clear that coal contains high amount of carbon (72.3 wt%), while rice husk contains high amount of oxygen (48.1 wt%) on dry ash free basis. The HHVs of coal and biomass are low, which is due to the high ash content. Although coal contains high ash than rice husk, due to its high carbon and low oxygen content, its HHV is higher than that of rice husk. Table 2 depicts the elemental composition of ash from coal and rice husk. Both feedstocks are rich in SiO_2 (62.5% in coal and 94.6% in rice husk). Coal ash contains alumina (Al_2O_3), oxides of alkali earth metals and Fe_2O_3 in significant quantities, while rice husk contains Fe_2O_3, alkali earth metals and P_2O_5 in significant quantities. Other heavy metals such as Cu, Mn, Zn are in ppm levels in the ash. The repeatability of the characterization data reported in Tables 1 and 2 was very good with < 2% standard deviation.

Table 2
Ash composition of high ash Indian coal and rice husk.

Composition	SiO$_2$ (%)	P$_2$O$_5$ (%)	Fe$_2$O$_3$ (%)	Al$_2$O$_3$ (%)	TiO$_2$ (%)	S (%)	Na$_2$O, K$_2$O, CaO (%)	Cr (ppm)	Cu (ppm)	Mn (ppm)	Zn (ppm)
High ash Indian coal	62.5	1.24	10.34	14.38	1.42	1.84	3.82	21.8	38.8	156.9	250.3
Rice husk	94.6	1.15	2.61	0.011	0.012	0.011	1.2	–	15.9	237.1	157.4
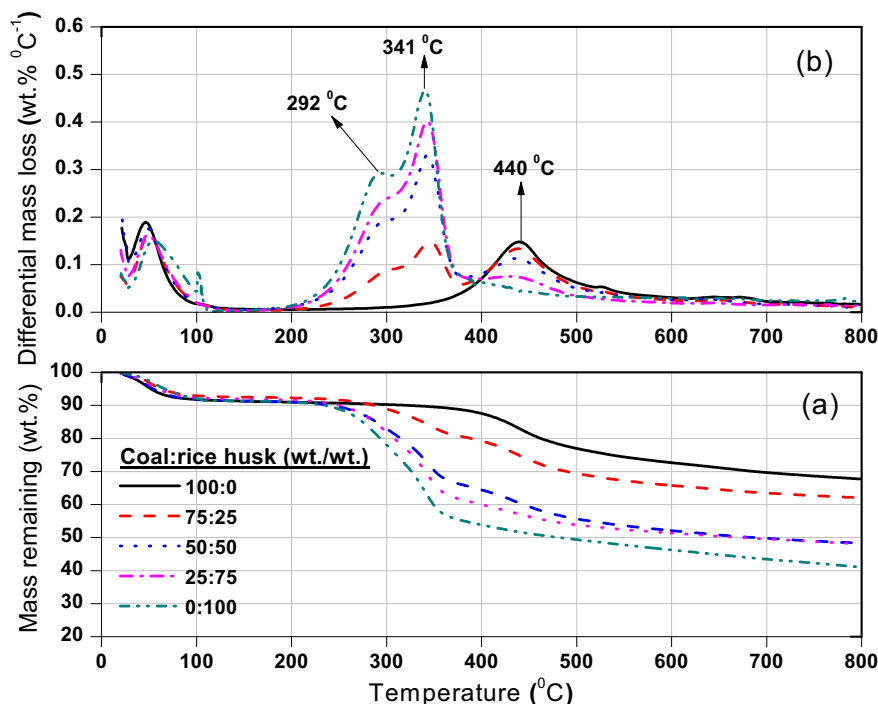
Fig. 1. (a) TG mass loss, and (b) differential mass loss profiles of individual components and blends at a heating rate of 10 °C min^{-1}

3.2. Conventional pyrolysis in TGA

In order to assess the typical decomposition temperature regimes of pure feedstocks and their mixtures, TGA was performed. Fig. 1 depicts the mass loss and differential mass loss profiles of pyrolysis of the individual components and the mixtures. High ash Indian coal exhibits single step decomposition in the range of 400–800 °C in agreement with the literature [39], while rice husk decomposes in the range of 230–600 °C with multiple decomposition peaks. This is due to complex decomposition pattern of hemicellulose, cellulose and lignin in biomass. The first degradation step (230–300 °C) can be attributed to hemicellulose and initial stage of cellulose decomposition, whereas the second degradation step (300–370 °C) is attributed to the final stage of cellulose decomposition [40]. Lignin decomposition occurs in a wide temperature range (250–700 °C) [27]. Residual mass at the end of 800 °C, increased with increasing coal content in the blends. This trend is due to the low volatile matter and high fixed carbon and ash content in coal compared to rice husk. The C─O─C bonds present in lignin possess a lower bond dissociation energy (380–420 kJ mol^{-1}) compared to C═C bonds present in the polyaromatic network of coal (c.a. 1000 kJ mol^{-1}). This results in early decomposition of biomass compared to coal, and increased char yield with increased coal content in the feedstock [22].

Differential mass loss profiles of the blends show that there is no significant interaction between coal and rice husk in terms of the shift in peaks to higher or lower temperatures. This is also substantiated by the significantly different decomposition ranges of these two feedstocks. Table 3 depicts the thermal events and maximum decomposition temperatures for different blend ratios. The maximum decomposition temperatures are similar for respective thermal events. Maximum

Table 3
Observed thermal events and decomposition temperatures during co-pyrolysis of coal and rice husk.

Coal:rice husk (wt./wt.)	Thermal event 1 (°C)	Thermal event 2 (°C)	Thermal event 3 (°C)
100:0	–	–	439.6
75:25	293.5	345.6	438.1
50:50	295.2	342.6	437.5
25:75	295.2	342.5	432.4
0:100	292	340.3	–

decomposition temperature for hemicellulose, cellulose and lignified matter in coal occurred at 293.5 ± 2 °C, 342.5 ± 2 °C and 433–439 °C, respectively. The deviations in thermal events reported in Table 3 are within 0.5–1 °C. The mixing ratio of rice husk to coal does not influence the thermal events 1 and 2, which correspond to biomass decomposition. The slight decrease in decomposition temperature of coal to lower values, i.e. 439.6 to 432.4 °C indicates that the formation of biochar might influence the decomposition of coal during co-pyrolysis. The maximum mass loss observed for pure rice husk and coal are 60 wt% and 35 wt%, respectively. Although no obvious interaction between the components is observed from the TGA, microwave heating is expected to improve the interactions between the pyrolysis intermediates due to the generation of tiny microplasma throughout the reaction mixture, which results in localized fast pyrolysis conditions.

3.3. Effect of microwave power and graphite ratio

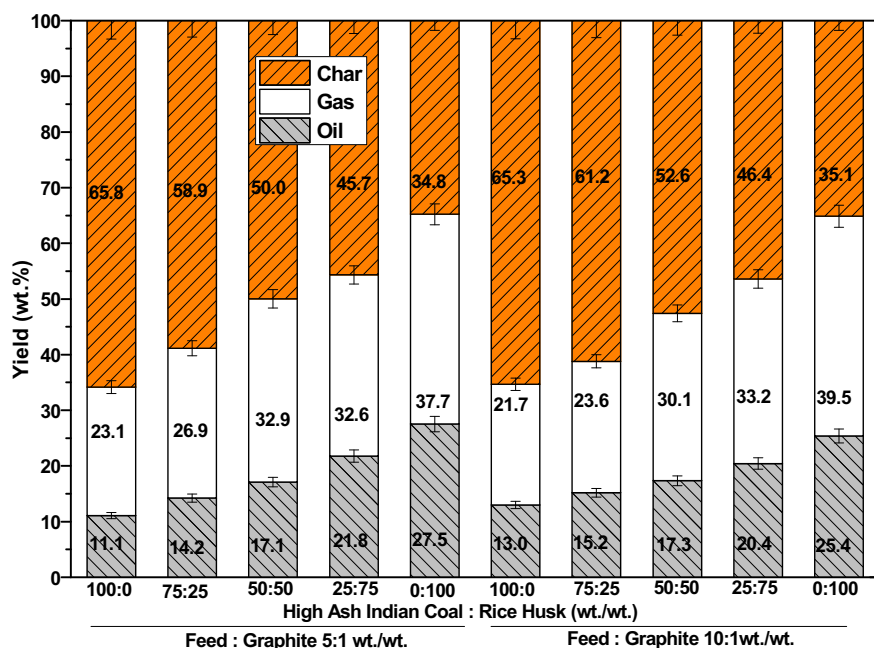Initial experiments were conducted with 40 g of individual coal and

Fig. 2. Yields of oil, gas and char obtained from different coal:rice husk blends at different susceptor ratios, and at 560 W microwave power.
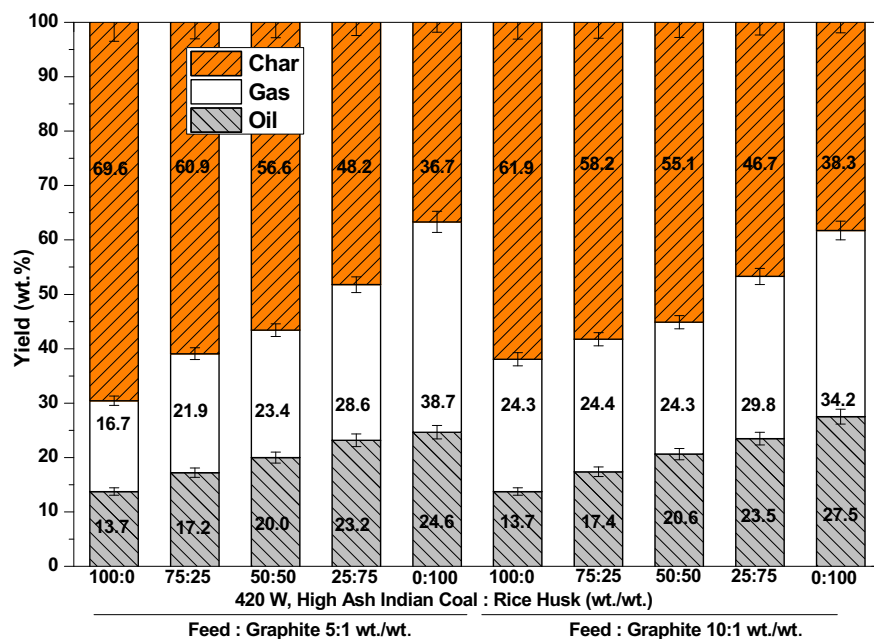

Fig. 3. Yields of oil, gas and char obtained from different coal:rice husk blends at different susceptor ratios, and at 420 W microwave power.

rice husk at 560 W without susceptor. The temperature achieved after 10 min of microwave irradiation was < 150 °C for both coal and rice husk, which indicates the poor absorbing capability of microwaves by these feedstocks. Pure graphite took 7 min to reach the final pyrolysis temperature of 800 °C. The temperature profiles of individual coal, rice husk and graphite are shown in Fig. S3 (in Supplementary data). Therefore, all further experiments were performed with graphite as susceptor. Figs. 2 and 3 depict the yields of oil, gas and char from individual coal, rice husk and different blends of coal and rice husk at different feed:graphite ratios at 560 W and 420 W, respectively. At higher microwave power (560 W), the oil yield is slightly lower compared to that at low microwave power (420 W) for both feed:graphite ratios (5:1 and 10:1 wt./wt.) for all blends. The yields of oil obtained at feed:graphite ratio of 5:1 and 10:1 wt./wt. are similar and the deviation

is within ± 2% at both 560 W and 420 W. The trends in oil yield for different blends when compared for 560 W and 420 W microwave power at feed:graphite ratio of 5:1 (wt./wt.) are given by: 11.1 wt % < 13.7 wt% (100:0), 14.2 wt% < 17.2 wt% (75:25), 17.1 wt % < 20.0 wt% (50:50), 21.8 wt% < 23.2 wt% (25:75), 27.5 wt % > 24.6 wt% (0:100). Similar results were also observed when feed:graphite ratio was 10:1 wt./wt. From the above results it is evident that at high microwave powers (560 W), yield of oil is relatively low as compared to low microwave powers (420 W) for all blend ratios. The gas yields also follow similar trends as oil yields for the mixtures at different microwave powers and feed:susceptor ratios. Interestingly, at 420 W power and 10:1 wt./wt. of feed:graphite, the gas yield is high with low yield of char as compared to 5:1 wt./wt. of feed:graphite. This can be explained, atleast partly, by using the specific microwave power
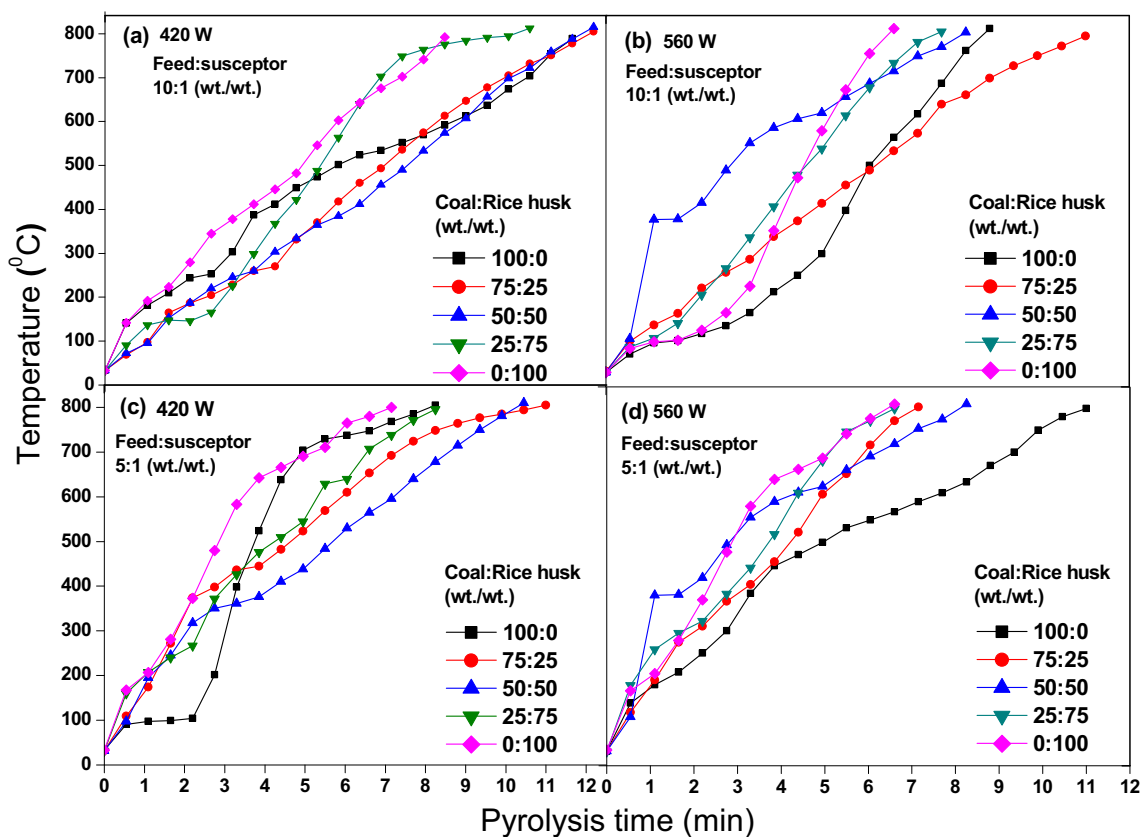
Fig. 4. Reaction temperature profiles during microwave co-pyrolysis of high ash Indian coal and rice husk mixtures at different feed to susceptor ratios and microwave powers.
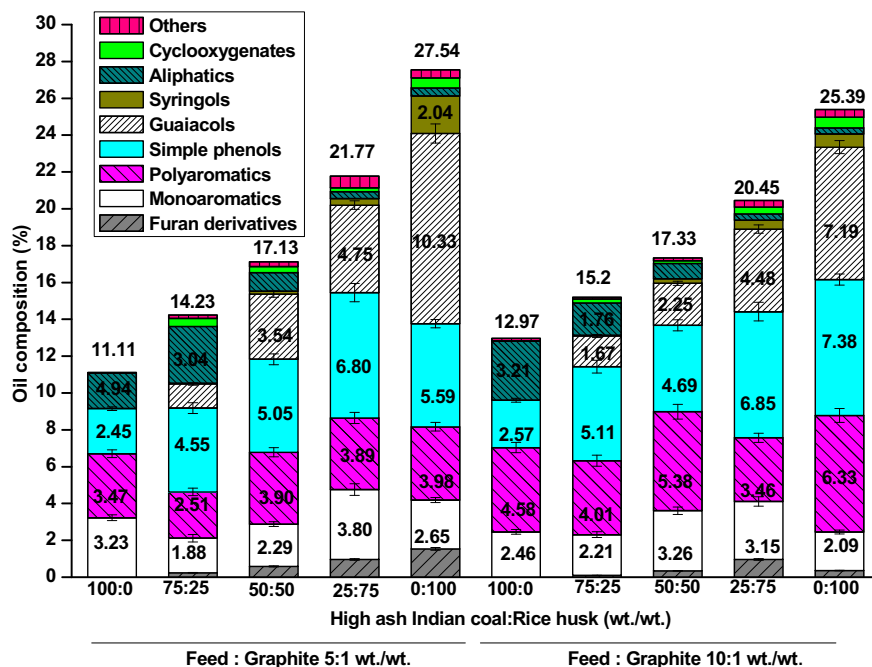

Fig. 5. Composition of oil at different mass ratios of coal to rice husk, and feed to susceptor ratios at 560 W microwave power.

consumed by the susceptor to heat up the feedstock. The specific microwave power consumed by the susceptor, defined as the ratio of microwave power to the mass of susceptor, is $105\,W\,g^{-1}$ for 10:1 wt./wt. of feed:susceptor, while it is $52.5\,W\,g^{-1}$ for 5:1 wt./wt. of feed:susceptor. This shows that when less amount of graphite susceptor is

used, more energy is consumed by the susceptor, which leads to self-heating of the susceptor, besides its microwave suscepting capability. This can lead to excessive localized cracking of the feedstock to generate more gases as compared to char.

Fig. 4 depicts the reaction temperature profiles for pyrolysis of high

ash Indian coal, rice husk and their blends at different conditions. Owing to the longer duration of microwave delivery by the magnetron at 560 W compared to 420 W, heating rate is slightly more at 560 W. Due to the high amount of susceptor, the average heating rates are similar at feed:graphite ratio of 5:1 wt./wt. It is important to note that the sample heating rate is influenced by microwave power, feed:susceptor ratio and the composition of coal:rice husk. Moreover, the char formed during the pyrolysis process also affects the dielectric loss tangent of the entire mixture, which in turn affects the heating rate. It can be observed that, for 420 W microwave power, time required to reach the final temperature (800 °C) is slightly longer (8–12 min) at feed:graphite ratio of 10:1 wt./wt. than at feed:graphite of 5:1 wt./wt. (7–10 min), which is clearly due to the low amount of graphite present in the former case. At 560 W, this effect is not observed as the supplied microwave energy per unit mass of sample plays a dominating effect as compared to the susceptor quantity. The average heating rates for all the samples are in the range of 65–110 °C min^{-1} and 72–120 °C min^{-1} for 420 W and 560 W microwave power, respectively.

Tables S1–S20 (in Supplementary data) depict the detailed list of organics present in the oil fraction from various experiments shown in Figs. 2 and 3. The organic compounds were classified into eight major categories, viz. furan derivatives, simple phenols, monomethoxy phenols (guaiacols), dimethoxy phenols (syringols), monoaromatic hydrocarbons, polyaromatic hydrocarbons, aliphatic hydrocarbons, cyclooxygenates and other compounds. Figs. 5 and 6 depict the oil composition based on the above classification of functional groups in oil. It is well known that coal oil does not contain furan compounds as furan compounds are usually produced from the decomposition of hemicellulose and cellulose in biomass [30]. Aromatic hydrocarbons were the major compounds in the pyrolysis oil from coal whereas simple phenols and methoxy phenols (syringols and guaiacols) were the major compounds in the pyrolysis oil from rice husk. Simple phenolic compounds (like phenol, cresol, catechol, alkyl phenols) mainly originate from the lignified matter present in the coal, while guaiacol, syringol and their derivatives like methyl guaiacol, vinyl guaiacol, vanillin, vanillic acid and alkyl syringols mainly originate from the decomposition of lignin present in the rice husk. The aliphatic hydrocarbons from coal pyrolysis are composed of a number of alkanes and alkenes in the carbon number range of C8–C26. The observed compounds in coal oil are in line with

the literature [24]. At 560 W microwave power, the total aromatic hydrocarbons in the pyrolysis oil follow the trend: only coal (100:0): 6.7% (5:1) ≈ 7.0% (10:1); 75:25 mixture: 4.4% (5:1) < 6.8% (10:1); 50:50 mixture: 6.2% (5:1) < 8.6% (10:1); 25:75 mixture: 7.7% (5:1) > 6.6% (10:1), and rice husk (0:100): 6.6% (5:1) < 8.4% (10:1). The variation of oil composition is mainly due to different heating rates obtained at different susceptor quantities. This shows that there is a significant contribution of graphite and microwave heating mechanism in altering the oil composition.

3.4. Effect of feedstock composition

Figs. 2 and 3 depict the product yields obtained at different blend ratios of coal and rice husk. The mixture composition had a compelling influence on the distribution of char, oil and gases. With increase in rice husk fraction in the feedstock, the yields of oil and gas increased, while that of char decreased owing to the high volatile content in rice husk [41,42]. The structure of coal comprises of highly cross-linked aromatics bonded together by stronger C═C bonds with bond dissociation energy > 1000 kJ mol^{-1} [43]. These are difficult to be ruptured during pyrolysis, while the crystalline and amorphous structures of biomass components can be relatively easily cleaved. The bond dissociation energy of the weak ether bonds (C−O−C) present abundantly in the lignin fraction of biomass is rather low (380–420 kJ mol^{-1}) [15]. Additionally, rice husk undergoes higher mass loss than coal as indicated in Fig. 1. Moreover, it can be seen that the TG curve for every rice husk:coal blend lies in between the TG curves of the individual components viz. coal and rice husk. High thermal reactivity and high volatile content of rice husk can facilitate the conversion of coal [44,45]. The degree of synergy depends on many factors. Usually, synergy is more pronounced when the biomass content is more in the mixture. This is expected to result in better availability of hydrogen via C−H bond dissociation for hydrogen donation to coal and coal pyrolysis intermediates [21,46–48]. However, the synergy may not be linearly dependent on the amount of biomass in the mixture. Some researchers reported that since thermal conductivity and packing density of biomass is lower than that of coal, increase in biomass amount in blend decreases the heating rate of the blends, which ultimately results in longer residence time of the volatiles [21]. Therefore, OH and H
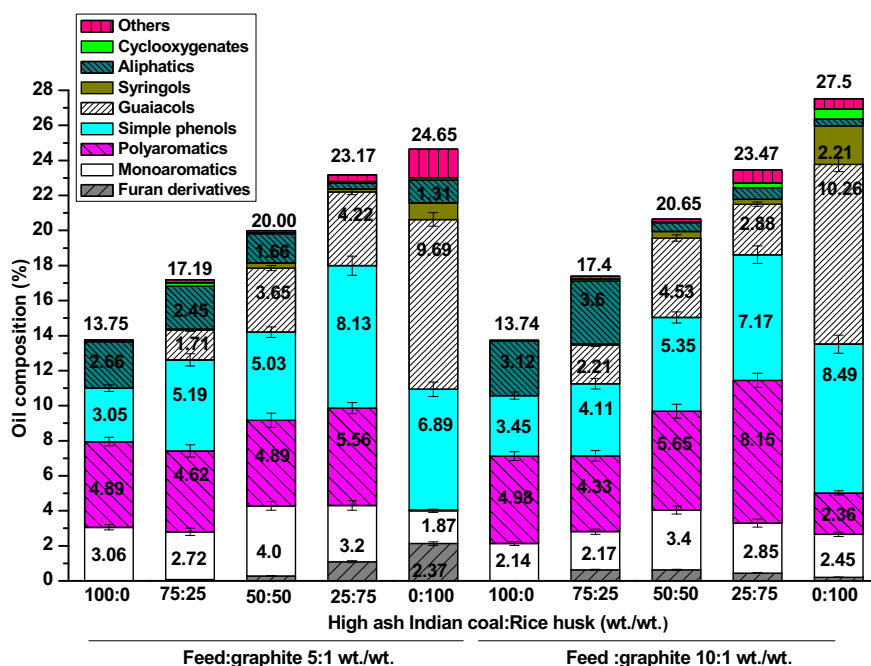

Fig. 6. Composition of oil at different mass ratios coal:rice husk ratio, and feed to susceptor ratios at 420 W microwave power.

radicals are released more slowly from biomass which enhances the cracking of coal tar [45]. Other researchers reported the inhibitive effect during the interaction between solid phases as biochar formed during pyrolysis of biomass gets accumulated on the surface of coal, and blocks the pores of coal molecule through which volatiles generated by coal pyrolysis are generally driven out [49–51]. However, in this study neither synergistic nor inhibition effects were observed in the product yields, as the product yields from the mixtures followed the additive rule.

To evaluate the interactions between biomass and coal during co-pyrolysis the experimental composition of pyrolysates was compared with the theoretical/calculated values. Theoretical values were calculated using a linear relationship as shown in Eq. (1).

$$Y_{mix} = xY_{coal} + (1-x)Y_{ricehusk}. \tag{1}$$

where Y_{mix} is the theoretical/calculated yield of a particular product or organic functional group from the mixture pyrolysis, Y_{coal} and $Y_{ricehusk}$ are the yields of a particular functional group from individual pyrolysis of coal and biomass, respectively, and x is the mass fraction of coal in the mixture. The percentage increase or decrease in the experimental values with respect to the theoretical values is called as synergetic/inhibition effect. The comparison between actual and theoretical yields of oil, gas and char is shown in the parity chart in Fig. 7. It is evident that the yields of various products are coinciding with the 45^0 line, which indicates that there is no significant interaction between coal and rice husk. Similar additive effect was also reported for pyrolysis of coal-biomass mixtures by Vuthaluru [15], Pan et al. [14] and Kastanaki et al. [52].

Fig. 8 depicts the parity chart for oil composition. The plot is drawn for three different coal:rice husk blends, viz. 75:25, 50:50 and 25:75
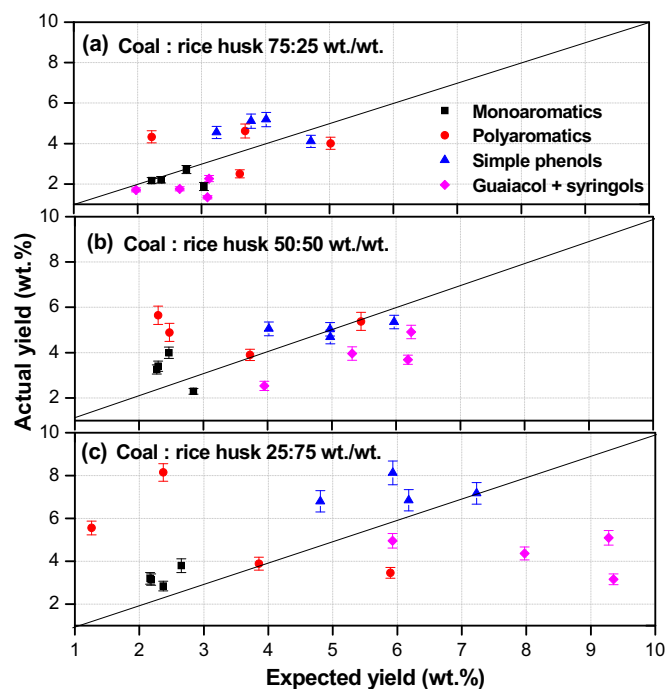

Fig. 8. Parity charts depicting the composition of functional groups at different experimental conditions for coal:rice husk compositions of (a) 75:25, (b) 50:50, (c) 25:75 (wt./wt.).
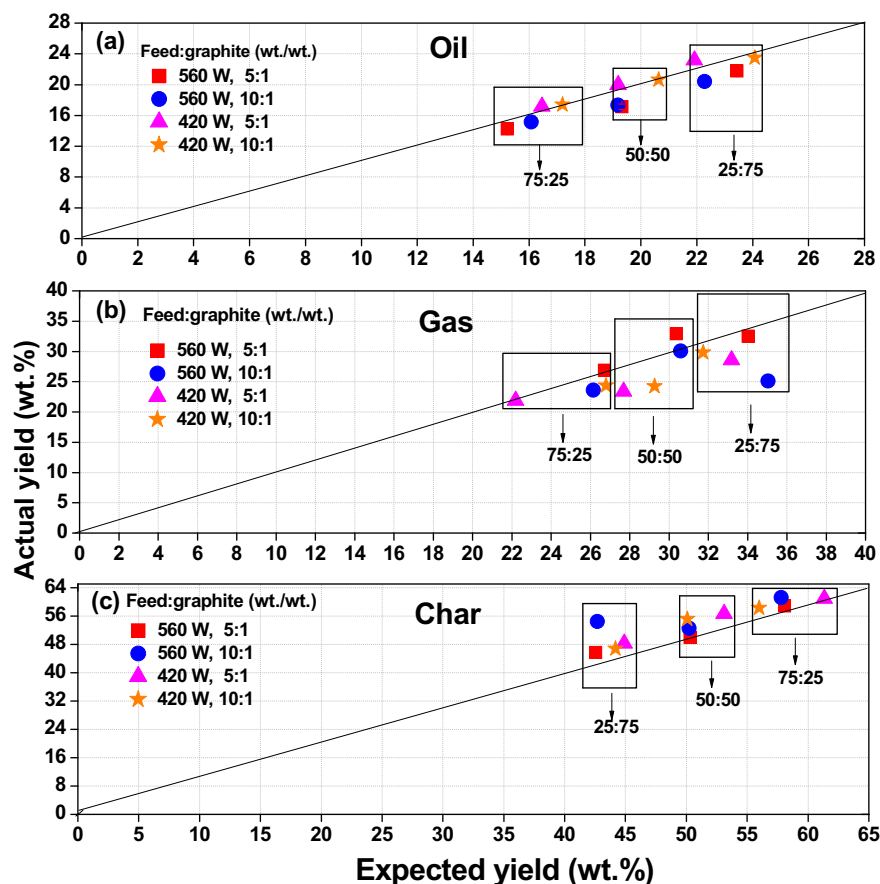

Fig. 7. Parity charts depicting the (a) oil, (b) gas and (c) char yields at different experimental conditions. Coal:rice husk composition (wt./wt.) is shown for different product fractions.
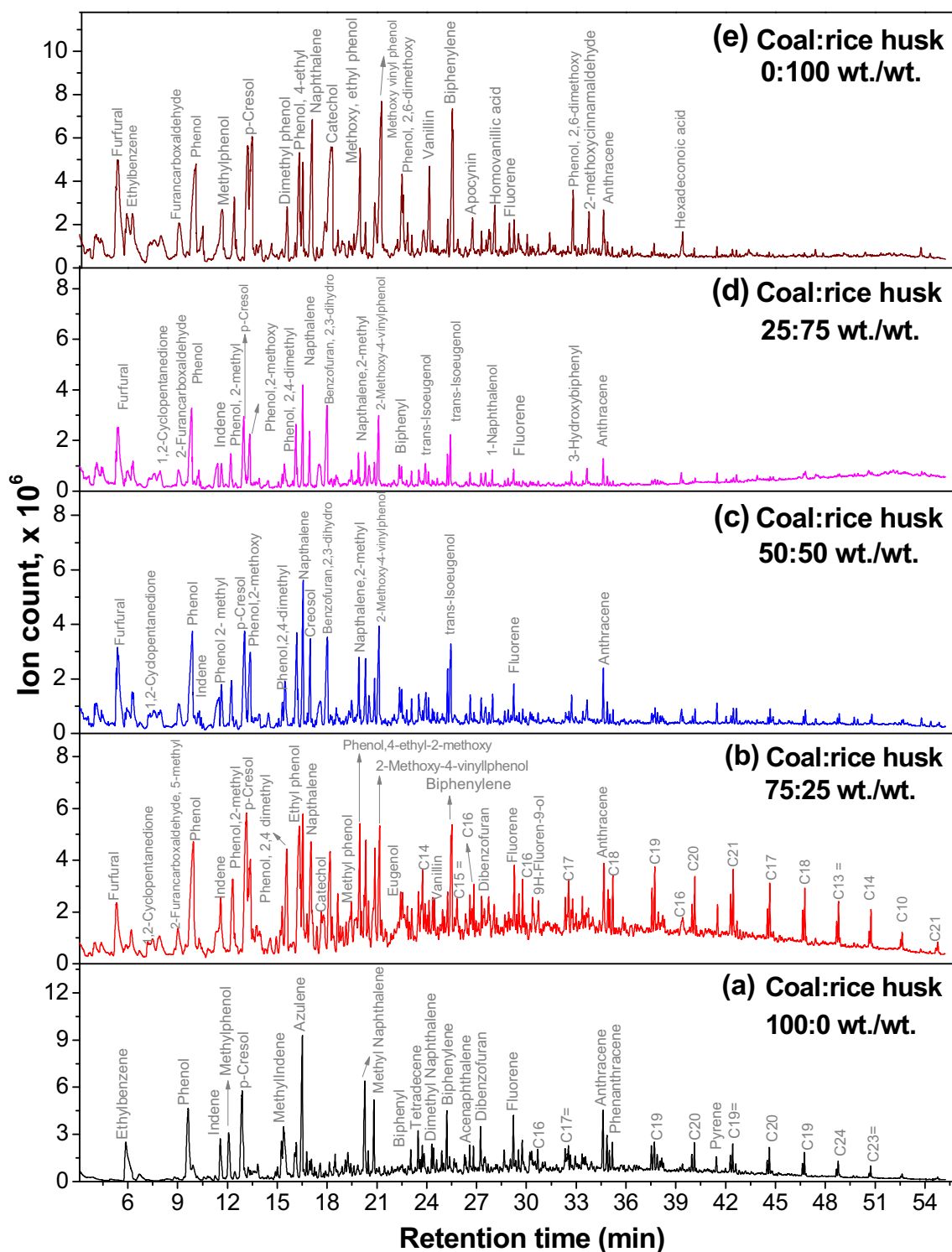
Fig. 9. GC/MS total ion chromatograms of oil fraction obtained under different conditions from coal, rick husk and their blends. (a) only coal (b) 75:25 (wt./wt. coal:rice husk), (c) 50:50 wt./wt., (d) 25:75 wt./wt., and (e) only rice husk. Feed to susceptor ratio was 5:1 wt./wt. and microwave power was 560 W. CX and CX = correspond to linear alkanes and linear alkenes with X carbon atoms, respectively.

wt./wt. The plot represents the variations in four major organic categories, viz. monoaromatics, polyaromatics, simple phenols and methoxy phenols (guaiacols + syringols). It is evident that synergetic effect, observed in the form of deviation from the diagonal, is more pronounced when the content of rice husk is more in the mixture, i.e. for coal:rice husk ratio of 25:75 wt./wt. The interactions are not significant with coal:rice husk ratios of 75:25 wt./wt., although significant

variations in the yields of polyaromatics and methoxy phenols begin to appear at 50:50 wt./wt. composition. Interestingly, the yields of monoaromatics and simple phenols are not significantly influenced by the feed composition, while the yields of polyaromatics and methoxy phenols exhibit large deviations. Moreover, the deviation is pronounced for simple phenols for rice husk-rich mixture, which substantiates the demethoxylation of methoxy phenols to form simple phenols during co-
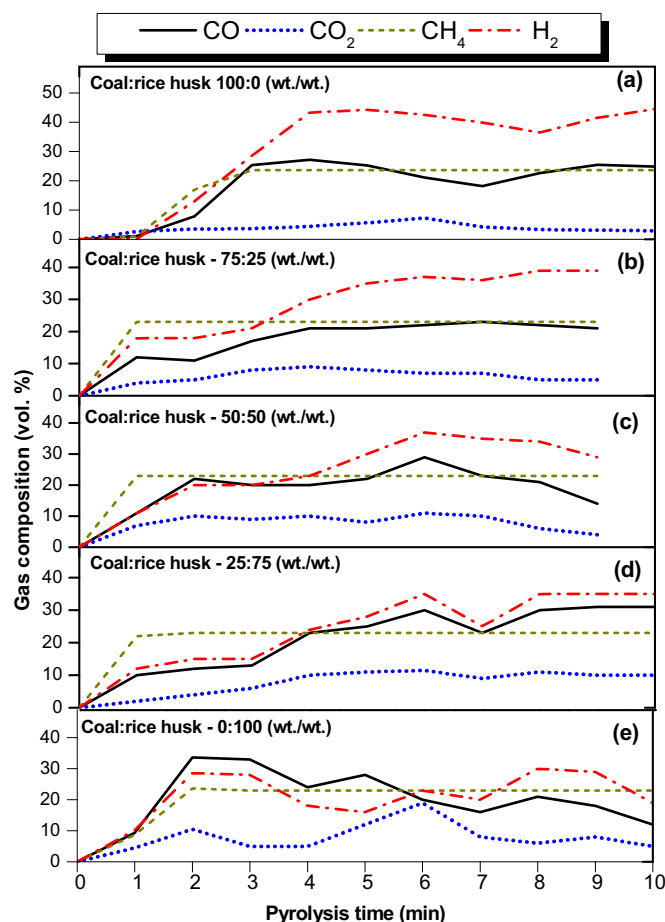
Fig. 10. Time evolution of non-condensable gases during microwave pyrolysis of coal, rice husk and their blends. (a) Only coal (100:0 wt./wt.), (b) coal:rice husk (75:25 wt./wt.), (c) coal:rice husk (50:50 wt./wt.), (d) coal:rice husk (25:75 wt./wt.), and (e) only rice husk (0:100 wt./wt.) at feed to susceptor ratio of 5:1 at 420 W.

pyrolysis with coal. Fig. 8(c) depicts the increase in the yield of polyaromatics and simple phenols, and decrease in the yield of methoxy phenols. This can be atleast partly attributed to the interaction of lignin fraction with coal during co-pyrolysis. This also justifies why the interactions are obvious with increasing rice husk content in the mixture. The decomposition regime of lignin overlaps partly with that of coal, especially at higher temperatures (400–700 °C). At this temperature zone, the decomposition of cellulose and hemicellulose is nearly complete. Co-pyrolysis enhances the transfer of radical hydrogen from coal to biomass-derived intermediates, which otherwise would be liberated as H_2 gas if coal were pyrolyzed alone [40]. Fig. 9(a–e) depicts the GC/MS total ion chromatograms (TICs) of the organics in oil from pyrolysis of individual coal, rice husk and their mixtures. It is evident that the composition of oil is significantly different with the addition of rice husk. Oil from coal-rich mixtures is rich in C10–C21 linear chain alkanes, alkenes and polyaromatics, while that from rice husk rich mixtures are rich in simple phenols, methoxy phenols and polyaromatics. Composition of co-pyrolysis oil is influenced by the early formation of biochar from rice husk, which primarily affects the localized heating rate of the entire feedstock owing to its microwave absorbing tendency. As a result, the dielectric constant of the suscepting medium can be thought to vary during the reaction. This affects the release of volatiles from coal at higher pyrolysis temperatures. Furthermore, the volatiles generated from coal can undergo bimolecular reactions with the biomass char thereby leading to changes in volatile product composition.

HHVs of pyrolysis oil from coal, rice husk and their mixtures

obtained under different conditions on dry basis were calculated by using the following empirical correlation:

$$HHV(MJ\,kg^{-1}) = 0.3491[\%C] + 1.1783[\%H] + 0.1005[\%S] - 0.1034[\%O]$$
$$- 0.0151[\%N] \qquad (2)$$

where %C, %H, %N, %S and %O were evaluated using the composition of organic compounds from GC/MS analysis of oils. Although the HHVs calculated using above formula are estimates, they do provide good information on the range of HHVs of oils from different feedstocks. The estimated HHVs of pyrolysis oils from various feedstocks can be ranked as follows: only coal (36–38 MJ kg^{-1}) > 75:25 coal:rice husk (34–36 MJ kg^{-1}) > 50:50 coal:rice husk (32–34 MJ kg^{-1}) > 25:75 coal:rice husk (30–32 MJ kg^{-1}) > only rice husk (28–30 MJ kg^{-1}). The difference in the HHVs can be attributed to presence of long chain aliphatic hydrocarbons and aromatics in the coal oil, as compared to high amount of phenols, guaiacols, syringols and furans in rice husk oil.

3.5. Analysis of gas and char

Fig. 10 depicts the time evolution of non-condensable gases during microwave co-pyrolysis monitored using online gas analyzer. The data was collected at 420 W microwave power, and feed:graphite mass ratio of 5:1 wt./wt. for all blends. The main constituents of the gaseous fraction are CO_2, CO, CH_4 and H_2. The experimental results show that the composition of the gases from the blends are significantly influenced by the coal:rice husk composition. Owing to the localized generation of microplasma spots in the reactor, evolution of non-condensable gases begin in the very first minute of pyrolysis when the bulk reaction temperature is 150 °C. This is characteristic of microwave-assisted pyrolysis [24]. In pure coal pyrolysis, H_2 (40 vol%) is the major gas and CO_2 (10 vol%) is the minor gas. However, in pure rice husk pyrolysis all the gases are significant, viz., CO (30 vol%), H_2 (25 vol%), CH_4 (23 vol%) and CO_2 (15 vol%). These general observations are in agreement with the literature on microwave pyrolysis of coal and biomass [24,53,54]. It can be observed that H_2 is the major gas component from co-pyrolysis of blends, especially when the fraction of coal is high in the mixture, i.e. 50:50 and 75:25 wt./wt. of coal:rice husk. Microwave co-pyrolysis is similar to fast pyrolysis due to the generation of localized tiny microplasma in the reaction mixture, which lead to the release of more H_2 in the pyrolysates. Formation and availability of hydrogen radical, which reacts with aromatic rings of coal and biomass is responsible for synergy in co-pyrolysis.

It is worthwhile to note that the evolution of methane occurs quite early during co-pyrolysis. Within a minute it reaches c.a. 20 vol% in co-pyrolysis, while its evolution is delayed upto 2–3 min in individual pyrolysis of coal and biomass. Moreover, the production of CO increases with increase in rice husk content in the mixtures, with H_2:CO ratio of 1–2. Lignin decomposition in biomass is characterized by a number of elementary reactions like demethylation, demethoxylation, and decarbonylation that involve the elimination of methyl, methoxy and CO groups from the structure. Low H_2:CO ratio in the co-pyrolysis gases and the early evolution of CH_4 indicate the facilitation of deoxygenation of rice husk through the transfer of hydrogen species from coal pyrolysis. This occurs by the recombination of methyl radicals from lignin with hydrogen free radicals from coal. This is supported by the low yield of methoxy phenols in the pyrolysates, and high yield of polyaromatic hydrocarbons than the expected values. The deoxygenated lignin fragments can further undergo C−H cleavage and condensation reactions with aromatic units from both coal and biomass to form polyaromatic hydrocarbons with concomitant elimination of hydrogen from the molecule. Higher production of H_2 with low CO_2 formation is a characteristic of microwave pyrolysis [24]. This is in sharp contrast to conventional pyrolysis, where (CO + CO_2) constitutes 75–90 vol% and H_2 constitutes only 5–10 vol% [53,55]. This is attributed to the generation of microplasma, whose energy is high enough to

Table 4
HHVs of chars (in MJ kg^{-1}) obtained at different pyrolysis conditions.

Coal:rice husk (wt./wt.)	Feed:graphite – 5:1 (wt./wt.)					Feed:graphite – 10:1 (wt./wt.)				
	100:0	75:25	50:50	25:75	0:100	100:0	75:25	50:50	25:75	0:100
560 W	16.8	14.5	12.0	12.9	12.6	15.4	13.2	12.0	12	12.1
420 W	15.3	14.6	13.9	14.5	12.6	15.3	14.5	14.2	12.9	12.5

cleave the C−H bonds present abundantly in biomass. From the gas composition, we can also conclude that the product gas has the potential to be used as syngas for the production of chemicals like methanol, which require high stoichiometric H$_2$/CO ratio.

The solid residue, char, produced from microwave pyrolysis experiments was characterized for its HHV and surface morphology. Graphite was separated from the char to the maximum possible extent by sieving as the crystalline graphite particles were in the form of fine powder, while the char from rice husk and coal were in the form of agglomerated flakes. Table 4 depicts the HHVs of char obtained at different pyrolysis conditions. Coal char possessed high HHV (15.5–16 MJ kg^{-1}), while the HHV of rice husk char was poor ($\approx$ 12 MJ kg^{-1}). The HHVs of co-pyrolysis chars were in between that of coal char and rice husk char, and significantly lower than that of coal and rice husk feedstocks. The low HHVs of chars are due to high ash and low volatile content in them. Proximate analysis of chars obtained from coal and rice husk pyrolysis revealed that the volatile matter, fixed carbon and ash content in coal char was 12.2 wt%, 43.2 wt% and 44.6 wt%, respectively, while these were 14.6 wt%, 35.1 wt% and 50.3 wt%, respectively, in rice husk char. This shows that compared to the feedstocks, the ash content in the chars is enhanced with a concomitant reduction in volatile matter content. Moreover, as shown in Table 2, both rice husk and coal ash are rich in silica (SiO$_2$). This substantiates the low HHV of the pyrolysis chars. Surface morphology of pyrolysis chars are shown in Fig. S4 (in Supplementary data). Significant differences were observed in the surface morphology of chars from coal-rich mixtures and rice husk-rich mixtures. Coal-rich mixture chars are highly flaky and porous, while rice husk-rich chars are fibrous, porous and layered in appearance.

3.6. Interaction between coal and rice husk

Rice husk is mainly composed of cellulose, hemicellulose, lignin, and minerals. It is reported that H and OH radicals released from biomass during pyrolysis can promote the reactions with aromatic rings of coal [11]. Moreover, the minerals present in biomass, especially potassium and magnesium, are known to act as catalysts to promote the synergy in product yields [10]. Cellulose and hemicellulose are mainly responsible for the volatiles in biomass pyrolysis, which can produce hydrogen by secondary reactions, whereas lignin hampers the release of volatile compounds from the coal by blocking the pores. Wei et al. [56] studied co-pyrolysis of coal with two different biomasses, viz. legume straw and pine sawdust, in a free fall reactor, and showed that the synergy was more with legume straw owing to its high cellulose, hemicellulose and ash content. Pyrolysis of lignin generates phenoxy radical and other reactive radicals such as *o*-hydroxyphenoxy, and *p*-hydroxyphenoxy radicals, which are effective in cleaving the methylene bridges to depolymerize coal. However, the lignin-derived intermediates are short-lived when compared to the time required for complete coal depolymerization [57,58]. In this study, the observed synergy in terms of increased polyaromatic hydrocarbons and decreased methoxy phenol production in co-pyrolysis oil is expected to be due to the interaction between lignin and coal, and not because of cellulose and hemicellulose with coal. From earlier studies, it is clear that low rank coals easily promote synergy with biomass, and interactions between low rank coal and biomass are more significant than

those between high rank coals and biomass [18,59]. The structural similarity between low rank coal and biomass is also expected to be a reason for this observation. It is known that, as the coal rank decreases, the pyrolytic decomposition occurs at lower temperatures due to the presence of more unmatured lignified matter, which coincides with lignin decomposition pattern in biomass [60]. Importantly, hydrogen accepting ability of low rank coal is also better than high rank coal [61]. During pyrolysis of coal, the crosslinked structure of coal is disturbed, and this results in the release of hydrogen from methylene carbon, which leads to hydrogen deficient system. Based on the results of this study, it is obvious that the hydrogen can be involved in hydrogen abstraction reactions with lignin intermediates from biomass. For example, the recombination of methyl radical from lignin with hydrogen radical can lead to methane formation. Furthermore, the aromatic units of lignin and coal can undergo bimolecular condensation reactions to form polyaromatic hydrocarbons. The major polyaromatic hydrocarbons in the oil such as naphthalene, alkyl-substituted naphthalene, and hydrogenated naphthalene derivatives support this claim.

4. Conclusions

The primary goal of this study was to evaluate the oil production from high ash Indian coal and rice husk, and understand the interactions between the feedstocks and their pyrolysates in microwave assisted pyrolysis process. The results demonstrate that microwave power and feed-to-susceptor ratio do not significantly affect the oil yields for similar coal:biomass mixture compositions, as the differences were within 2–3 wt%. Addition of rice husk to coal enhanced the oil yield, with experimental oil yields from the mixtures matching the theoretical values calculated using the additivity principle. While this observation suggests that there is no synergy in co-pyrolysis in terms of oil yields, the oil composition was non-additive in nature. The addition of rice husk to coal led to the formation of phenols and methoxy phenols. Phenolics, primarily phenol, cresols, ethyl phenol, methoxy phenols and dimethoxy phenols, were the major compounds in the co-pyrolysis oil. Interaction effect on oil composition was more pronounced in rice husk-rich mixtures. The yield of methoxy phenols reduced significantly with a concomitant increase in polyaromatic hydrocarbons and simple phenols. The early evolution of CH$_4$ and H$_2$:CO ratios of 1–2 in the gas fraction also supported the plausible interaction between biomass and coal via hydrogen radicals generated during microwave heating. HHVs for co-pyrolysis oils were in the range of 30–36 MJ kg^{-1}, which shows that mild upgradation of these can potentially replace the conventional fuels. The HHV of residual char was low (12–16 MJ kg^{-1}) due to the high ash content of both the feedstocks. This study shows that microwave co-pyrolysis is a promising technique to obtain high quantity and high quality oil from waste coal and biomass residues. Further studies are required to develop a scalable and continuous mode microwave pyrolysis unit to process different feedstocks and obtain valuable liquid fuels.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuproc.2018.04.018.

References

[1] https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy/coal/coal-reserves.html , Accessed date: 10 April 2017.

[2] S.S. Boparai, Coal Sector in India - Some Policy Issues, Coal Prep India, International Conference & Exhibition on Coal Beneficiation & Allied Subject, New Delhi, India, March 9–11, 2000.

[3] J. Wang, Q. Yan, J. Zhao, Z. Wang, J. Huang, S. Gao, S. Song, Y. Fang, Fast co-pyrolysis of coal and biomass in a fluidized bed, J. Therm. Anal. Calorim. 118 (2014) 1663–1673.

[4] S. Jayanti, V. Saravanan, S. Sivaji, Assessment of retrofitting possibility of an Indian pulverized coal boiler for operation with Indian coals in oxy-coal combustion mode with CO₂ sequestration, J. Power Energy 226 (2012) 1003–1013.

[5] B.C. Folkedahl, A.C. Synder, J.R. Strege, S.J. Bjorgaard, Process development and demonstration of coal and biomass indirect liquefaction to synthetic iso-paraffinic kerosene, Fuel Process. Technol. 92 (2011) 1939–1945.

[6] Y. Guan, Y. Ma, K. Zhang, H. Chen, G. Xu, W. Liu, Y. Yang, Co-pyrolysis behaviours of energy grass and lignite, Energy Convers. Manag. 93 (2015) 132–140.

[7] A.A. Shra'ah, R. Helleur, Microwave pyrolysis of cellulose at low temperature, J. Anal. Appl. Pyrolysis 105 (2014) 91–99.

[8] S. Singh, V.B. Neculaes, V. Lissianski, G. Rizeq, S.B. Bulumulla, R. Subia, J. Manke, Microwave assisted coal conversion, Fuel 140 (2015) 495–501.

[9] M.J. Blesa, J.L. Miranda, R. Moliner, M.T. Izquierdo, J.M. Palacios, Low-tempera-ture co-pyrolysis of a low-rank coal and biomass to prepare smokeless fuel bri-quettes, J. Anal. Appl. Pyrolysis 70 (2003) 665–677.

[10] A.G. Collot, Y. Zhuo, D.R. Dugwell, R. Kandiyoti, Co-pyrolysis and co-gasification of coal and biomass in bench-scale fixed-bed and fluidised bed reactors, Fuel 78 (1999) 667–679.

[11] J.M. Jones, M. Kubacki, K. Kubica, A.B. Ross, A. Williams, Devolatilization char-acteristics of coal and biomass blends, J. Anal. Appl. Pyrolysis 74 (2005) 502–511.

[12] B. Moghtaderi, C. Meesri, T.F. Wall, Pyrolytic characteristics of blended coal and woody biomass, Fuel 83 (2004) 745–750.

[13] K. Nikkah, N.N. Bakhshi, D.G. MacDonald, Co-pyrolysis of various biomass mate-rials and coals in a quartz semi-batch reactor, in: D.L. Klass (Ed.), Energy from Biomass and Waste XVI, Institute of Gas Technology, Chicago, 1993, pp. 857–902.

[14] Y.G. Pan, E. Velo, L. Puigjaner, Pyrolysis of blends of biomass with poor coals, Fuel 75 (1996) 412–418.

[15] H.B. Vuthaluru, Thermal behaviour of coal/biomass blends during co-pyrolysis, Fuel Process. Technol. 85 (2004) 141–155.

[16] N.T. Weiland, N.C. Means, B.D. Morreale, Product distributions from isothermal co-pyrolysis of coal and biomass, Fuel 94 (2012) 563–570.

[17] L. Zhang, S. Xu, W. Zhao, S. Liu, Co-pyrolysis of biomass and coal in a free fall reactor, Fuel 86 (2007) 353–359.

[18] H. Haykiri-Acma, S. Yaman, Interaction between biomass and different rank coals during co-pyrolysis, Renew. Energy 35 (2010) 288–292.

[19] S.S. Idris, N.A. Rahman, K. Ismail, A.B. Alias, Z.A. Rashid, M.J. Aris, Investigation on thermochemical behaviour of low rank Malaysian coal, oil palm biomass and their blends during pyrolysis via thermogravimetric analysis (TGA), Bioresour. Technol. 101 (2010) 4584–4592.

[20] O. Onay, E. Bayram, O.M. Kockar, Copyrolysis of Seyitömer lignite and safflower seed: influence of the blending ratio and pyrolysis temperature on product yields and oil characterization, Energy Fuel 21 (2007) 3049–3056.

[21] D.K. Park, S.D. Kim, S.H. Lee, J.G. Lee, Co-pyrolysis characteristics of sawdust and coal blend in TGA and a fixed bed reactor, Bioresour. Technol. 101 (2010) 6151–6156.

[22] S. Marland, A. Merchant, N. Rowson, Dielectric properties of coal, Fuel 80 (2001) 1839–1849.

[23] D.V. Suriapparao, R. Vinu, Resource recovery from synthetic polymers via micro-wave pyrolysis using different susceptors, J. Anal. Appl. Pyrolysis 113 (2015) 701–712.

[24] B.R. Reddy, R. Vinu, Microwave assisted pyrolysis of Indian and Indonesian coals and product characterization, Fuel Process. Technol. 154 (2016) 96–103.

[25] X.H. Wang, H.P. Chen, K. Luo, J.G. Shao, H.P. Yang, The influence of microwave drying on biomass pyrolysis, Energy Fuel 22 (2008) 67–74.

[26] Y.F. Huang, W.H. Kuan, S.L. Lo, C.F. Lin, Total recovery of resources and energy from rice straw using microwave-induced pyrolysis, Bioresour. Technol. 99 (2008) 8252–8258.

[27] Q. Bu, H.W. Le, S.J. Ren, L. Wang, J. Holladay, Q. Zhang, J. Tang, R. Ruan, Phenol and phenolics from lignocellulosic biomass by catalytic microwave pyrolysis, Bioresour. Technol. 102 (2011) 7004–7007.

[28] V.L. Budarin, J.H. Clark, B.A. Lanigan, P. Shuttleworth, S.W. Breeden, A.J. Wilson, D.J. Macquarrie, K. Milkowski, J. Jones, T. Bridgeman, A. Ross, The preparation of high-grade bio-oils through the controlled, low temperature microwave activation of wheat straw, Bioresour. Technol. 100 (2009) 6064–6068.

[29] H.W. Lei, S.J. Ren, J. Julson, The effects of reaction temperature and time and particle size of corn Stover on microwave pyrolysis, Energy Fuel 23 (2009) 3254–3261.

[30] D.V. Suriapparao, N. Pradeep, R. Vinu, Bio-oil production from *Prosopis juliflora* via microwave pyrolysis, Energy Fuel 29 (2015) 2571–2581.

[31] A.A. Salema, F.N. Ani, Microwave induced pyrolysis of oil palm biomass, Bioresour. Technol. 102 (2011) 3388–3395.

[32] S. Zhang, Q. Dong, L. Zhang, Y. Xiong, Quality syngas production from microwave pyrolysis of rice husk with char-supported metallic catalysts, Bioresour. Technol. 191 (2015) 17–23.

[33] T.N. Bailey, J.G. Lawson, P. Monsef-Mirzai, The use of microwave heating in the acetylation of coals, Fuel 69 (1990) 25–28.

[34] N. Wang, J. Yu, A. Tahmasebi, Y. Han, J. Lucas, T. Wall, Y. Jiang, Experimental study on microwave pyrolysis of an Indonesian low-rank coal, Energy Fuel 28 (2014) 254–263.

[35] L.L. Gasner, A.O. Denloye, T.M. Regan, Microwave and conventional pyrolysis of a bituminous coal, Chem. Eng. Commun. 48 (1986) 349–354.

[36] Y. Sudiyani, Muryanto, The Potential of Biomass Waste Feedstock for Bioethanol Production, Proceeding of International Conference on Sustainable Energy Engineering and Application, Yogyakarta, Indonesia, 2012.

[37] M. Sarangi, S. Bhattacharyya, R.C. Behera, Effect of temperature on morphology and phase transformations of nanocrystalline silica obtained from rice husk, Phase Transit. 82 (2009) 377–386.

[38] Z. Song, Y. Tang, J. Sun, X. Zhao, W. Wang, Y. Mao, C. Ma, Effect of power level on the microwave pyrolysis of tire powder, Energy 127 (2017) 571–580.

[39] C.A. Ulloa, A.L. Gordon, X.A. Garcia, Thermogravimetric study of interactions in the pyrolysis of blends of coal with radiata pine sawdust, Fuel Process. Technol. 90 (2009) 583–590.

[40] K.G. Mansaray, A.E. Ghaly, Thermal degradation of rice husks in nitrogen atmo-sphere, Bioresour. Technol. 65 (1998) 13–20.

[41] C. Quan, S. Xu, Y. An, X. Liu, Co-pyrolysis of biomass and coal blend by TG and in a free fall reactor, J. Therm. Anal. Calorim. 117 (2014) 817–823.

[42] M. Guo, J.C. Bi, Characteristics and application of co-pyrolysis of coal/biomass blends with solid heat carrier, Fuel Process. Technol. 138 (2015) 743–749.

[43] A.O. Aboyade, M. Carrier, E.L. Meyer, H. Knoetze, J.F. Gorgens, Slow and pres-surized co-pyrolysis of coal and agricultural residues, Energy Convers. Manag. 65 (2013) 198–207.

[44] Z. Wu, S. Wang, J. Zhao, L. Chen, H. Meng, Synergistic effect on thermal behaviour during co-pyrolysis of lignocellulosic biomass model compounds blend with bitu-minous coal, Bioresour. Technol. 169 (2014) 220–228.

[45] T. Sonobe, N. Worasuwannarak, S. Pipatmanomai, Synergies in co-pyrolysis of Thai lignite and corncob, Fuel Process. Technol. 89 (2008) 1371–1378.

[46] O. Onay, E. Bayram, O.M. Kocukar, Copyrolysis of seyitomer-lignite and safflower seed: influence of the blending ratio and pyrolysis temperature on product yields and oil characterization, Energy Fuel 21 (2007) 3049–3056.

[47] L. Zhang, S. Xu, W. Zhao, S. Liu, Co-pyrolysis of biomass and coal in a free fall reactor, Fuel 86 (2007) 353–359.

[48] S. Li, X. Chen, A. Liu, L. Wang, G. Yu, Co-pyrolysis characteristic of biomass and bituminous coal, Bioresour. Technol. 179 (2015) 414–420.

[49] C. Chen, X. Ma, Y. He, Co-pyrolysis characteristics of microalgae *Chlorella vulgaris* and coal through TGA, Bioresour. Technol. 117 (2012) 264–273.

[50] W.P. Yan, Y.Y. Chen, Experimental study on co-pyrolysis characteristics of lignite mixed with biomass mixture, J. Power Eng. 26 (2006) 865–893.

[51] H. Darmstadt, M. Garcia-Perez, A. Chaala, N.Z. Cao, C. Roy, Co-pyrolysis under vacuum of sugar cane bagasse and petroleum residue: properties of the char and activated char products, Carbon 39 (2001) 815–825.

[52] E. Kastanaki, D. Vamvuka, P. Grammelis, E. Kakaras, Thermogravimetric studies of the behaviour of lignite-biomass blends during devolatilization, Fuel Process. Technol. 77 (2002) 159–166.

[53] K. Jayaraman, I. Gokalp, Thermogravimetric and evolved gas analyses of high ash Indian and Turkish coal pyrolysis and gasification, J. Therm. Anal. Calorim. 121 (2015) 919–927.

[54] D.V. Suriapparao, R. Vinu, Bio-oil production via catalytic microwave pyrolysis of model municipal solid waste component mixtures, RSC Adv. 5 (2015) 57619–57631.

[55] L. Bosong, L. Wei, Z. Qi, W. Tiejun, M. Longlong, Pyrolysis and catalytic upgrading of pine wood in a combination of auger reactor and fixed bed, Fuel 129 (2014) 61–67.

[56] L.G. Wei, L. Zhang, P. Xu, Synergetic effects on tar components from co-pyrolysis of biomass and coal in a free fall reactor, J. Fuel Chem. Technol. 40 (2012) 519–525.

[57] J.W. Kim, S.B. Lalvani, C.B. Muchmore, B.A. Akash, Coliquefaction of coal and black liquor to environmentally acceptable liquid fuels, Energy Sources 21 (1999) 839–847.

[58] R.W. Coughlin, F. Davoudzadeh, Coliquefaction of lignin and bituminous coal, Fuel 65 (1986) 95–106.

[59] H. Haykiri-Acma, S. Yaman, Synergy in devolatilization characteristics of lignite and hazelnut shell during co-pyrolysis, Fuel 86 (2007) 373–380.

[60] E. Kastanaki, D. Vamvuka, A comparative reactivity and kinetic study on the combustion of coal-biomass char blends, Fuel 85 (2006) 1186–1193.

[61] K. Kidena, S. Murata, M. Nomura, Studies on the chemical structural change during carbonization process, Energy Fuel 10 (1996) 672–678.