



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 ($36\text{--}38$ MJ kg⁻¹) due to the presence of aliphatic hydrocarbons, while that from rice husk had the lowest heating value ($28\text{--}30$ MJ kg⁻¹) due to high oxygenate content. The heating values of co-pyrolysis oils were in the range of $30\text{--}36$ 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 CO₂ 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 ($\tan \delta$), which is defined as the ratio of dielectric loss factor to dielectric constant. More the $\tan \delta$ value, better is the microwave absorbing capability of the material. Typically, coal and biomass exhibit low $\tan \delta$. 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, $\tan \delta$ 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 N₂ 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 ($\tan \delta = 0.02\text{--}0.1$) [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

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