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Thermal decomposition study and pyrolysis kinetics of coal and agricultural residues under non-isothermal conditions

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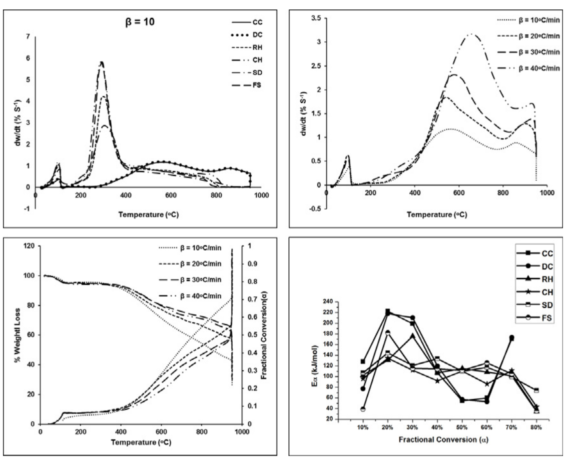
GRAPHICAL ABSTRACT



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ABSTRACT

In this work thermal decomposition along with pyrolysis kinetics of two coals namely Chamalang Coal (CC) and Dukki Coal (DC) and four agricultural residues i.e. Rice Husk (RH), Corn Husk (CH), Sunflower Disc (SD) and Falsa Stick (FS) were investigated under non-isothermal conditions. Four different parameters were used to evaluate the reactivity of fuels. These were peak temperature, average rate of weight loss, maximum rate of weight loss and pyrolysis factor. All these parameters were evaluated at four heating rates 10, 20, 30 and 40 °C/min. The average rates of weight loss were found higher in devolatilization region compared with char formation region of degradation. It was found from reactivity analysis that the fuels could be ranked in following order of reactivity CH > FS > RH > SD > DC > CC. It was observed that increasing heating rate shifted the reaction zone to higher temperature and increased the peak temperatures, rate of average and maximum weight loss that increased the reactivity and pyrolysis factor. Coals showed low reactivities and high activation energies compared to agricultural residues. The activation energy has been estimated using Friedman differential isoconversional model and it was found that the activation energy varied with fractional conversion. The estimated average values of activation energy (kJ/mol) for CC, DC, RH, CH, SD, and FS were found to be 134.54, 129.81, 109.43, 98.24, 113.25, and 103.64 respectively.

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1. Introduction

According to an assessment of World Bank, the population of world has increased by over 1.5 billion in the last 20 years [1]. Across the globe, 1.2 billion people are living without access to commercial energy, which is lesser than the previous estimate as of 2013 [1]. There is still need of more energy to provide electricity to deprived people.

Fossil fuels are still the most dominant among the fuels and have provided about 85% of world energy in 2015 [2]. Their share in energy production in next 20 years is not expected to reduce very much. It is estimated that share of fossil fuels in 2035 would be around three quarters of total energy supplies [2]. Apart from the abundant availability of fossil fuels across the globe, the fuel mix to provide the energy demands is continuously shifting from fossil fuels to renewables due to growing awareness of environmental protection rules and regulations. The contribution of renewable resources in providing energy is increasing gradually. Renewable energy has fastest growth rate and its share in primary energy is expected to increase from 3% in 2015 to 10% in 2035 [2].

The utilization of biomass for energy production can reduce dependence on fossil fuels [3,4]. Biomass is considered more sustainable fuel due to its very low carbon foot print and abundant availability at cheaper prices [4–6].

Pakistan is an agricultural country with large annual production of agricultural waste materials that can be used for energy production [7–11]. Currently, many crop residues are burnt in fields to clear land for new crop [12–14]. This on-field combustion should be discouraged due to high particle-matter-emission into the atmosphere that ultimately affects atmospheric air quality and public health [15]. It is difficult for the existing coal fired power plants to meet ever tightening environmental emission regulations. A partial substitution of agricultural residues with coal can be a retrofit solution for reducing environmental pollution. Moreover, pure biomass based energy recovery systems could be a CO_2 neutral solution. Prior to design these systems, a thermal decomposition and kinetic study results can aid for optimum reactor design.

Thermal analysis or thermogravimetry is a technique to look inside the thermal decomposition of coal and biomass materials. It is extensively used by researchers like [3,16–23]. The solid fuels show very different behaviour during thermal decomposition, and simple models that have been used for studying kinetics of homogeneous reactions cannot be used reliably for solid fuels. The kinetic models for thermal decomposition of coal and biomass can be broadly classified into two groups, model-fitting and model-free or isoconversional models [19,25–27]. Both of them can be used under isothermal and non-isothermal conditions [25]. A very good comparison of the applicability of model-fitting and model-free methods has been presented by Vyazovkin and Burnham [25,27]. Isoconversional methods are considered more accurate and reliable compared to model-fitting methods [24–30]. The main reason for this is that isoconversional models do not assume a reaction mechanism for data fitting which is a compulsory step in model-fitting methods. Model-fitting methods can force fit any reaction mechanism to any data at the cost of drastic variation in kinetic parameters [25]. Furthermore, thermal decomposition consists of more than one steps with different activation energies. Model-fitting methods however, extract a single value of activation energy for the whole decomposition process that represents apparent activation energy. The value of activation energy thus obtained is an average value and cannot reflect all decomposition steps. However, isoconversional models take into account this issue and estimate value of activation energy as a function of fractional conversion (α) that varies with the decomposition process till the complete decomposition. The isoconversional models have been used successfully for estimation of kinetic parameters of agricultural residues and other biomass fuels [31–36].

In this work, thermal decomposition and pyrolysis kinetics for two types of coal and four types of agricultural waste material have been investigated using Friedman differential isoconversional model with four heating rates (10, 20, 30 and 40 °C/min).

2. Materials and methods

Coal samples were taken from Chamalang and Dukki coal reserves located in province Baluchistan of Pakistan. Rice husk (RH), corn husk (CH), sunflower disc (SD) and falsa sticks (FS) (botanical names: Oryza sativa husk, Zea mays husk, Helianthus disc and Grewia asiatica respectively), were collected from local villages of Pakistan.

The GCV was determined using Parr 6200 calorimeter while the carbon-sulphur analysis was performed using Leco SC-144DR analyser. The GCV, proximate and carbon-sulphur analysis are presented in Table 1. True density was measured by using helium pycnometer PYC-100A. The results of particle density measurement are presented in Table 2. The chemical analysis of biomass materials is presented in Table 3. All experiments were performed three times to get consistent results.

All samples were ground to fine size and particle size distribution was studied using Microtrac Bluewave analyser. The results of PSD in the form of various measures of particle size are presented in Table 4. d[3,2] is Sauter mean diameter which is volume to surface mean diameter. d[4,3] is DeBroukere mean diameter which is mean diameter over volume. d[10], d[50] and d[90] are percentiles showing that 10, 50 and 90 percent of material lies below this diameter value.

Thermogravimetric analyses were performed in Leco TGA 701. Very fine particles size (< 75 µm) was used in TGA to get better insight of decomposition process. Flow rate of carrier gas (N_2) was fixed at 3.5 lpm for all experimental runs. Four heating rates (10, 20, 30, 40 °C/min) were used for all samples of coal and biomass.

3. Kinetic modelling

Rate of solid fuel's reactions is given as:

$$\frac{d\alpha}{dt} = f(T) \times f(\alpha) \tag{1}$$

where

$$f(T) = Ae^{-\frac{E}{RT}} \tag{2}$$

α is called fractional conversion, given as:

Table 1
Proximate Analysis, Carbon-Sulfur Analysis and GCV of Materials.

Sample	Proximate Analysis					Carbon-Sulfur Analysis(%)		GCV (MJ/kg)
	MC (%)	VM (%)	FC (%)	Ash (%)	VM/FC	C	S	
CC	1.99	37.67	40.07	20.27	0.94	75.64	4.10	24.74
DC	5.65	45.03	37.32	12.00	1.21	75.21	4.65	25.47
RH	7.94	56.19	11.75	24.13	4.78	34.35	0.28	17.57
CH	2.00	71.33	9.00	17.67	7.93	30.57	0.25	14.86
SD	4.00	50.00	19.51	26.59	2.56	29.99	0.29	10.76
FS	4.50	74.63	13.40	7.39	5.57	33.93	0.16	15.86