The effect of char properties on gasification reactivity

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ABSTRACT

In this study, CO_2 gasification of raw and acid-washed chars obtained from various types of lignocellulosic biomasses (woody and agricultural waste biomasses) was studied under isothermal conditions (850 °C) using thermal gravimetric analysis. The effect of surface area and alkali/earth alkali metals on the reactivity of the chars was investigated. The different kinetic models were used to fit with the reactivity data by using least square method. The gasification of chars with higher surface area was found to be faster than that of chars having lower surface area. The acid treatment decreased the overall gasification rate for each raw chars. However, although the AI (alkali index) values of chars obtained from agricultural biomasses had equal or higher than that of woody biomass chars, their initial rates were considerably lower. It was concluded that indigenous alkali metals of chars have a remarkable influence of gasification reactivity but an adequate surface area should be provided to react with CO_2.

1. Introduction

As known, biomass is the most important energy source in many developing countries. It also has an important role in industrialized countries to meet the Kyoto protocol requirements and to reduce their dependency on crude oil. Biomass can be converted to energy by thermo-chemical and biochemical processes. Pyrolysis is one of the thermochemical processes to obtain liquid (bio-oil) product which is used as an energy source and as a feedstock for chemical production. Biochar is a by-product from pyrolysis of biomass. It can be used as fuel, alone or mixed with other fuels, as a cheap adsorbent for wastewater treatment, and as soil amendment. As an alternative, fuel gases for gas engines and gas turbines and syngas or hydrogen can be produced from pyrolysis char by gasification process. In fact, gasification of biomass consists of two stages: 1) pyrolysis and 2) conversion of the residual char [1].

1) Biomass → volatiles + char
   $$C + CO_2 \rightarrow 2CO$$
2) Char $C + H_2O \rightarrow CO + H_2$
   $$2C + 3/2O_2 \rightarrow CO + CO_2.$$

In comparison to direct biomass gasification, biochar gasification has some advantages, such as lack of tar production [2] and high reactivity due to the pore structure. Overall, gasification of char as a separate process gives the opportunity for utilization of pyrolysis volatiles as fuel or chemical feedstock. The steam and/or O_2 and CO_2 can be used as gasification agent. In the case of CO_2, the main product is CO ($C + CO_2 \rightarrow CO$,

Boudouard reaction), which can be used in many processes besides its direct use in thermal energy production.

In an industrial gasifier, gasification of biomass consisted of a complex thermochemical processes including drying, pyrolysis and char gasification. Among these processes the char gasification is the rate-limiting step determining the residence time [3] that determines the residence time required. Because of this, kinetic data relating to char gasification is needed for the proper design and operation of gasifier.

There have been numbers of theorical or mathematical models, which can explain behaviors of carbon conversion against time or rate variation. The kinetics of the CO_2 gasification of biomass chars, which were studied by several researchers using various kinetic models, was summarized by Gomez-Bareaet al. [4]. Ollero et al. studied the CO_2 gasification kinetics of olive residue using the Langmuir Hinshelwood model [3]. Gupta et al. studied reaction rates of woodchips char gasification with using the random pore model [5]. Among these models, random pore model has often shown satisfactory agreement between theory and experiment, which considers the effects of pore growth and coalescence during reaction.

Although the model has received great successes in modeling gasification reactions of coal chars [5–7], it sometimes fails to describe the reactivity profiles of biomass chars, in which the reactivity increases with increasing conversion or exists a maximum in high conversion range. Two parameters were added in the random pore model to take inorganic element contents into account by Struis et al. Modified random pore model has been recently used to investigate reactivity of biomass chars with fitting the experimental data [8–10].

There have been numerous studies on the gasification of biomass chars. Previous researches have shown that gasification reactivity of

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chars depends many factors, such as pyrolysis temperature and heating rate [11,12], inorganic constituents [1,13,14], and pyrolysis pressure [12,15,16].

The kinetics for the carbon dioxide gasification of chars produced from lignocellulosic biomass has been reviewed by Di Blasi [17]. Min et al. [11] investigated the effect of pyrolysis temperature on the char reactivity and they observed a decrease in char-gasification reactivity with the pyrolysis temperature increase. They concluded that char's porous structure plays an important role in its gasification reactivity and high pyrolysis temperature leads to formation of more small cavities which causes difficulty for CO_2 to enter and product to release. Kumar and Gupta [18,19] investigated the influence of wood species and pyrolysis conditions, such as temperature, heating rate and soaking time, on the gasification of woody biomass chars by carbon dioxide. It was found that in comparison to eucalyptus wood chars, the Acacia wood chars exhibited higher reactivity due to its low lignin content. Similarly, the chars obtained from woody biomasses at high heating rates exhibited higher gasification reactivity than that of the char prepared at low heating rates [15,20,21]. Besides pyrolysis conditions, inorganic constituents have very important role in gasification due to the catalytic effect on char reactivity. In a previous study related to the CO_2 and steam gasification of char obtained from grapefruit skin, raw char showed relatively high reactivity than acid-washed char due to the presence of potassium [13]. Zhang et al. [10], who studied gasification reactivity of chars derived from a wide range of plant origins, concluded that the maximum rate at high conversion range was mainly attributed to the catalytic effect of K. On the other hand, Huang et al. [22] observed that gasification reactivity of fir char was improved through the addition of metal catalysts, in the order K > Na > Ca > Fe > Mg. Another study [23], about the combustion kinetics of corncob char and partially demineralized corncob char, reported that although demineralized char had a higher surface area than undemineralized char, it showed a much lower reactivity. This result shows that, water- or acid soluble minerals have a higher effect on char reactivity than the surface area. Based on an analysis of the literature review on lignocellulosic chars, Di Blasi concluded that the nature of the lignocellulosic biomass has no significant effect on the char reactivity and the differences among various samples can be attributed essentially to the amount and composition of ashes [17].

Interestingly, Khalil et al. [24], who studied the gasification kinetics of pine and birch charcoals, concluded that decomposition kinetics of both charcoals revealed considerable similarities, even though there were differences between the feedstock, ash composition, and pore structure of the two chars. On the other hand, Ikenaga et al. [25] investigated the CO_2 gasification behavior of various chars prepared from biomass, mostly garden trees. They concluded that the number of active sites in gasification was increased by mineral matter (especially K) and the disintegration of the char structure.

Although the effect of catalysts in biomass char gasification has been studied in laboratory and bench-scale reactors to some extent, however, fewer studies can be found in the literature concerning the influence of not only mineral content, but also other char properties on their reactivity. In this study, the chars obtained from different kinds of lignocellulosic biomass materials were gasified at 850 °C with CO_2 to investigate the effect of char properties on gasification yields. The used biomasses represent the most important forestry and agricultural products in Turkey and other part of the world. To deduce the effect of the inorganic constituents and biomass type, all biomass chars were prepared and gasified under identical conditions.

2. Materials and methods

2.1. Materials

Biochars were produced from different kinds of lignocellulosic biomass by carbonizing in a fixed-bed reactor using a stainless steel reactor (L, 210 mm; ø, 60 mm) at 500 °C for 1 h with a slow heating rate (8–10 °C/min) under nitrogen atmosphere. The used lignocellulosic biomasses were pine cone, pine bark, pine dust called as woody biomass, grape seed and safflower seed cake as agricultural industry biomass. The demineralized char was prepared by treating of the char with HCl solution (10 wt.%) at 100 °C for 2 h. After HCl treatment, the chars were washed with distilled water until no chlorine ions could be detected and then was dried at 100 °C for 24 h.

The chars obtained from pine cone, pine bark, pine dust, grape seed and safflower seed cake and their acid treated forms were named as PC and WPC; PB and WPB; PD and WPD; GS and WGS; SS and WSS, respectively. All biomass chars were sieved to 0.1 mm in size for gasification. In order to eliminate the limitations of the reaction by heat or mass transfer inside the particles, the chars with small size (<0.1 mm) were used in gasification experiments. Some properties of biomasses and chars are given in Tables 1 and 2 respectively.

2.2. Gasification

The CO_2 gasification of char was carried out in a thermo balance (Shimadzu TG-30) described in detail elsewhere [26]. In a typical run, the char (12–14 mg) was heated to 110 °C with a heating rate of 10 °C/min under 500 mL/min flow of pure nitrogen and kept for 30 min to remove the adsorbed water vapor and then the reactor temperature was increased.

When the temperature reached at 850 °C, the N_2 flow was switched to CO_2 containing gas flow at 80 wt.% (mixture of CO_2 with N_2). This concentration of CO_2 was selected in accordance with a previous study [26]. Weight loss of the char sample due to gasification was monitored and recorded against the reaction time. The experiment was ended when weight loss no longer occurred. The starting time of CO_2 inflow was taken as the initial time (t_0) and the sample weight as the initial weight.

The fractional carbon conversion was determined according to the following equation:

$$X = \frac{W_0 - W_t}{W_0 - W_f} \tag{1}$$

where, W_0 is the initial sample weight at time t_0. W_t is the sample weight at any gasification time t, W_f is the final weight.

2.3. Biomass and char characterization

The elemental analysis was carried out by LECO CHNS 932 elemental analyzer according to ASTM D5291-96. The proximate analysis of chars and biomasses was done according to ASTM D3174-04 for ash analysis and ASTM D3175-89a for volatile matter. Component analysis (extractives, lignin, hemicellulose and cellulose) of biomasses was carried out according to literature [27]. The metal analysis of ashes in

Table 1
Properties of lignocellulosic biomasses.

	PC	PB	PD	GS	SS
Proximate analysis (as received, wt.%)					
Moisture	9.6	7.7	7.4	8.1	11.2
Volatile matter	77.8	68.5	75.4	69.5	70.3
Fixed carbon	21.4	21.7	16.9	19.1	15.6
Ash	0.8	1.1	0.3	3.3	2.92
Ultimate analysis (dry, wt.%)					
C	42.6	48.9	46.8	53.0	49.8
H	5.6	5.0	5.4	5.7	5.8
N	0.8	0.2	0.3	1.8	3.4
S	0.1	0.2	0.2	0.2	0.2
Component analysis, (dry, wt.%)					
Cellulose	32.7	17.1	42.6	45.3	22.5
Hemicellulose	37.6	16.5	22.9	22.9	39.5
Lignin	24.9	32.9	25.1	31.1	33.5
Extractives	4.8	33.5	9.4	0.7	4.5

Table 2
Properties of chars.

	Elemental analysis, wt.%			Surface area, m²/g	Pore volume, cm³/g	Ash, wt.%
	C	H	N			
PC	81.0	3.0	0.5	213	0.40	2.3
WPC	79.6	3.2	0.4	224	0.42	1.3
PB	77.3	2.7	0.3	220	0.41	5.3
WPB	79.0	3.0	0.2	230	0.43	1.4
PD	81.7	3.1	0.6	210	0.40	0.7
WPD	79.7	3.3	0.4	223	0.43	0.5
GS	81.9	3.1	1.2	5	0.07	5.3
WGS	82.7	3.0	1.7	23	0.07	1.3
SS	69.5	2.7	3.9	5	0.04	10.9
WSS	80.0	3.1	3.2	11	0.08	2.8

chars was performed with XRF analyzer (SPECTRO IQ II). Metals in chars were detected in oxide forms. The specific surface area of the chars was measured by conventional N_2 adsorption BET method (Micromeritics Gemini 2375). Surface morphology of the chars was confirmed by scanning electron microscope (SEM) (HITACHI S-4700).

3. Results

3.1. Char properties

The ash content of the raw and demineralized chars is compared in Table 2. As it is seen from Table 2, the raw pine dust char has the lowest ash content and the safflower seed char exhibits the highest one. The acid treatment significantly reduces the ash content of chars.

It is obvious that the extent of mineral matter removal is dependent on char type. Acid washing of chars (except PC and PD) resulted in about 74% removal of ash. But, the ash content of PC and PD decreased about 45% and 30%, respectively by acid treatment.

The inorganic element distributions in ash of chars before and after the acid treatment showed that substantial reductions were achieved in different main elements (Table 3). It is clearly seen from Table 3 that Ca and K were significantly decreased. The fact that the percent of Na and Mg in ashes (except GS and SS) was increased by acid washing shows that these metals were present in minerals, of which are relatively insoluble in HCl.

The BET surface areas of the biochars are generally related to their gasification activity, as well as their ash content. Table 2 also presents the nitrogen surface area obtained for biomass chars. It is evident from Table 2 that biomass chars showed varied surface area characteristics. The surface area and porosity of chars obtained from woody biomass were much higher than that of chars obtained from agricultural waste biomass. It is known that carbonization conditions (such as soaking time, temperature, heating rate, and pressure) greatly influence the surface area of chars generated from biomass. Keeping in mind that all chars were obtained in same carbonization conditions, it is clear that the differences can be related to the biomass origins namely, agricultural industrial waste and woody biomass.

Table 3
Metal content of chars; wt.%.

	Na	K	Ca	Mg	Al	P	Mn	Fe
PC	0.23	0.05	0.83	0.10	0.08	0.02	0.01	0.21
WPC	0.24	–	0.26	0.09	0.04	–	0.01	0.02
PB	0.23	0.23	2.96	0.11	0.04	0.01	0.02	0.05
WPB	0.27	–	0.33	0.09	0.03	–	0.01	0.01
PD	0.07	0.04	0.25	0.03	0.01	–	0.04	0.02
WPD	0.10	–	0.11	0.03	0.01	–	–	0.02
SS	0.72	0.77	1.48	0.23	0.05	0.36	0.01	0.02
WSS	0.27	0.09	0.20	0.07	0.03	0.04	0.01	0.01
GS	1.73	2.03	1.47	0.73	0.19	0.58	0.02	0.29
WGS	0.60	0.10	0.27	0.21	0.10	0.09	0.01	0.06

The fact that the chars from woody biomass have higher surface area than that from agricultural biomass may be attributed to ash contents. Higher amount of inorganics in biomass led to formation of char having low surface area due to the filling up pores by fusion of molten ash [28]. Similarly, due to the lower ash content, black wattle biochar showed higher surface area (241 g/m^2) than vineyard (92 g/m^2) [29]. Guerrero et al. also observed that chars from rice husk devolatilization have lower surface areas compared with those from eucalyptus obtained under similar conditions [30]. On the other hand, the demineralization with acid washing slightly affected surface characteristics of chars, leading to less increase.

Fig. 1, presents a series of SEM images recorded for raw- and washed chars. It is evident in the SEM images that the mineral matters were partially removed from the char by acid washing and the surface texture of acid-washed char became comparatively rougher except for WPD char.

3.2. Char reactivity

The rates of char conversion are mainly determined by surface area, surface accessibility, carbon active sites and catalytic active sites created by indigenous or added inorganic matter, and the gaseous reactant concentration. It was postulated that the reactivity depends on three main characteristics of the char: chemical structure, inorganic constituents and porosity [17]. It was possible in this work to differentiate between these effects.

The curves of gasification time versus carbon conversion of chars are shown in Fig. 2(a) and (b). As seen in Fig. 2 the general shape of the conversion curves (except PC and PB) versus time is globally almost linear, as observed in previous studies [19,21,31,32].

The times observed for complete gasification were 321 min, 182 min, 202 min, min, 419 min, and 476 min for the PC, PB, PD, GS and SS, respectively. These differences in the overall gasification rate are significant for industrial process. They indicate that depending on the type of biomass, the gasification time will vary. In brief, the gasification of chars with higher surface area was found to be faster (Fig. 2) than that of chars having lower surface area (Table 2).

As could be expected, the acid treatment decreased the overall gasification rate of raw chars. The times for complete gasification were 494, 210 and 673 min for the WPC, WPB and WPD, respectively. The most notable differential is that the gasification was very slow for WGS and WSS, although their ash contents were higher than some chars (WPB, PD and WPD). The results from WGS and WSS had not been presented in Fig. 2(b) since the gasification experiments were lasted after 11 h at that time weight loss was less than 50%. It should be noted that demineralization did not have considerable effect on overall gasification rate of char obtained from pine bark, although ash content of char was reduced by acid treatment. In addition, it is interesting that overall gasification rate of WPB is higher than that of WPC, although both their surface area and ash contents are similar. The obtained results showed that there is no exact relationship between the ash content and overall gasification rate as independently char types.

3.3. Gasification rate

Fig. 3 shows reactivity profiles of char samples. Kinetic models which were summarized by Gomez-Bareaet al. [4] have been used to fit with the reactivity data by using least square method using Excel. The best description of experimental data depicts in Fig. 3. Three types of kinetic models were fitted with our experimental data; namely random pore model, extended pore random model and modified volume model.

Modified Volume Model (MVM) which is a semi-empirical model, assumes a homogenous reaction throughout a char particle [33]. The reaction rate equation is describes as follows;

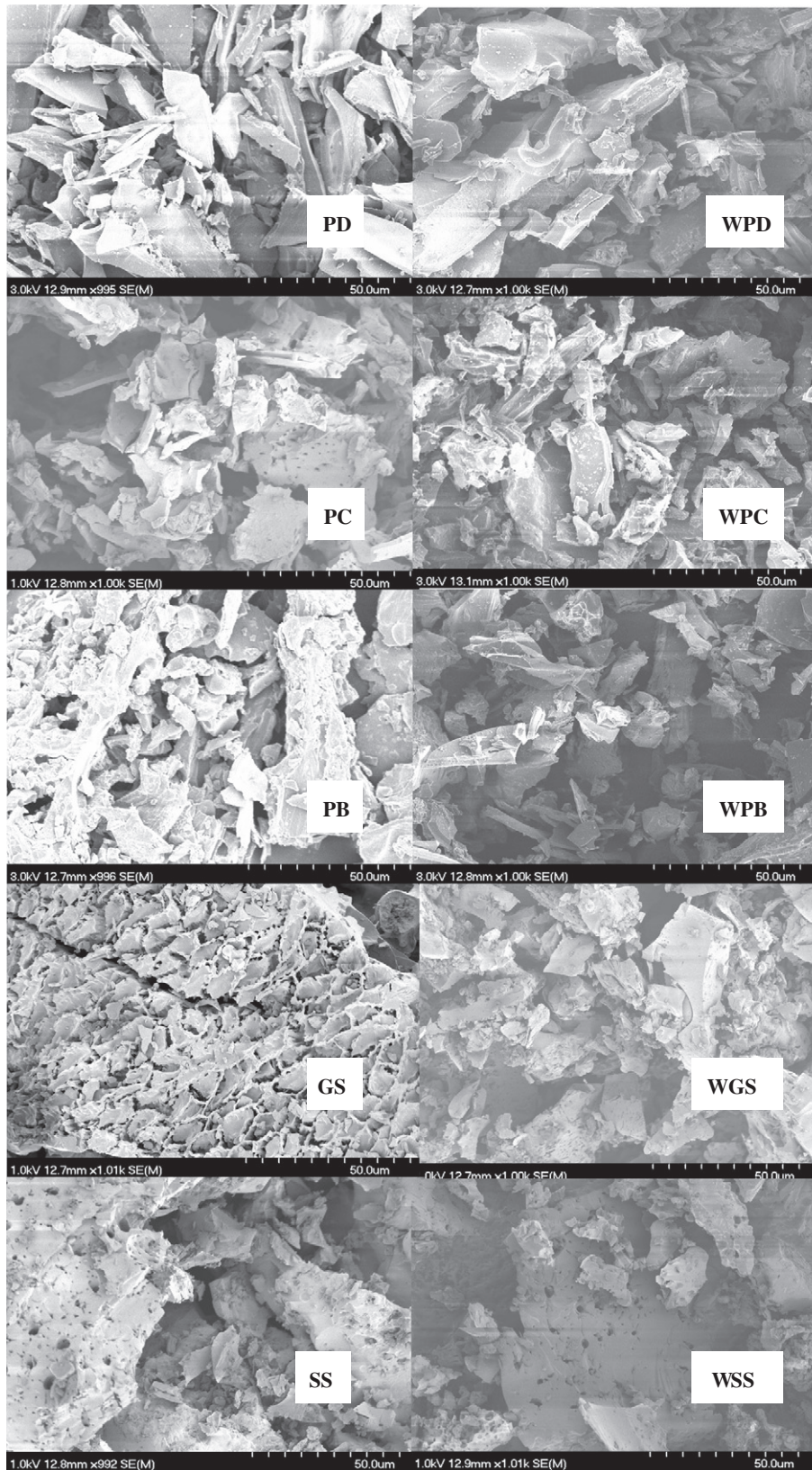$$\frac{dX}{dt} = k_{MVM}a^{(1/b)}b[-In(1-X)]^{(b-1)/b} \qquad (2)$$

Fig. 1. SEM images of chars.

where k_{MVM} is rate constant. a and b are two constants which are determined from the conversion (X) versus apparent reaction rate (dX/dt) data by least-squares method.

Random pore model (RPM) represents the change of nonuniform cylindrical pore structures within a solid during gasification as a function of conversion X. Although the RPM considers the internal structural
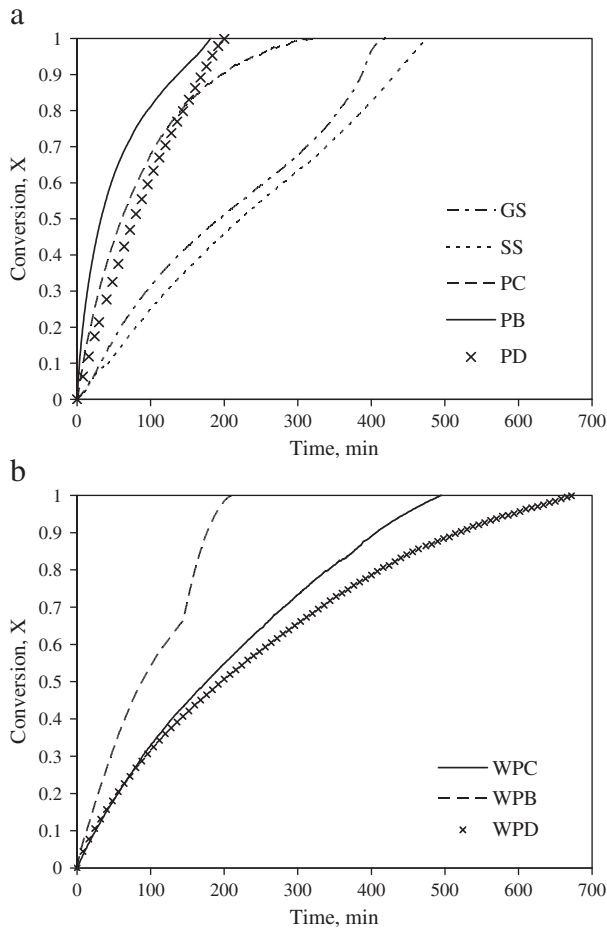
a

b

Fig. 2. Plot of carbon conversion of different char samples vs. time.

changes resulting from pore growth and coalescence with gasification progress, it does not consider the random pore overlapping and neglects all diffusion resistances in the char reaction.

$$\frac{dX}{dt} = k_{PRM}(1-X)\sqrt{1-\Psi In(1-X)} \qquad (3)$$

where k_{PRM} is the rate constant and Ψ is the structural parameter which are determined from the conversion (X) versus apparent reaction rate (dX/dt) data by least-square method.

The RPM has successively applied to most of coal chars. However, it is not adequate to describe the systems in which the reactivity increases with increasing conversion or exhibits a maximum in high conversion range, for most of biomass chars or alkali catalyzed carbons. For this reason, the original random pore model has been modified for more extensive application, which can either be structural or catalytic in nature. A new model (extended random pore model, ERPM) was developed by introducing a new conversion term with two dimensionless parameters into the original random pore model, as indicated in the following:

$$\frac{dX}{dt} = k_{ERPM}(1-X)\sqrt{1-\Psi In(1-X)}\left(1-(cX)^p\right) \qquad (4)$$

where; c denoting a constant with dimension [time^{-1}] and p a dimensionless power law constant [8]. As seen from Eq. (4), when c = 0, it will be the same as the random pore model.

As seen in Fig. 3, reactivity curves of SS, GS, PD, WPB and WPC showed a better fitting with ERPM while the original random pore model provided approximate fittings for the profile of PC. On the other hand, PB and WPD reactivity curves were fitted with MVM.

In the case of chars from woody biomass, reactivities decreased with increasing conversion, similar to those of chars reported in literature [5,8,12,24,34]. It was postulated that the catalytic action varies during conversion owing to the chemical occurrence of the catalysts (for example, deactivation resulting from sintering and agglomeration) and char structure [17].

Due to the high alkali and earth alkaline metal content, the gasification rates of raw chars were more than that of demineralized chars in the conversion ranges of X < 0.7 for PB, X < 0.9 for PC and X < 1 for PD. For WPB, at high conversions, its' reactivity is higher than raw chars'. This may be due to the change in active surface sites of WPB during gasification process. It was proposed that as progressing of gasification, a geometrical change in char pore structure can be occurred which affects the reaction rate [5]. The fact that gasification kinetic of WPB was ERPM also supports above results.

Keeping in mind that Na and Mg in chars could not be removed by acid washing, it can be mentioned that K and Ca were the most active sites for char gasification. A notable fact is that, although literature reported the catalytic activity of Na for the gasification of biomass chars [8,9,22], it did not show effect on reactivity. The reason is most probably the fact that Na was inactive form. For agricultural industrial wastes, reactivity profiles presented an irregular variation: initially increasing and then decreasing and again increasing at higher conversion. This might be due to the alterations in active surface sites during gasification. As conclusion, the above results showed that the effect of ash alone is not sufficient to explain the reactivity of the different chars to CO_2. Since biomass char gasification is a surface-initiated process, both the active site concentration and mineral dispersion are important in determining gasification reactivity as well as mineral concentration [1]. Indeed, reactive surfaces can be changed along the gasification, and it is not possible to distinguish these two effects.

As reported in many literatures, during gasification, the char properties are changed; sintering of inorganic constituents, collapse of pores etc. Because of this, both initial surface area and inorganic constituents have mainly effect on gasification rate at the beginning of gasification. To observe the effect of initial char properties on gasification rates, the initial rates (rate at X = 0.05) have been calculated and the results have been presented in Fig. 4. Alkali index (AI) is a parameter used to describe the overall influence of catalytically active species within the ash and is defined as the ratio of the sum of basic oxide contents in the ash to the sum of acidic and amphotheric oxides, multiplied by the ash amount in sample [35].

The initial rates for chars from woody biomass decreased with acid treatment. By considering chars from woody biomass, a correlation between reactivity and alkali index may be established: the high alkali index value shows the high reactivity. However, the surface area of char also must be considered. Although the AI values of chars obtained from agricultural biomasses have equal or higher than that of woody biomass chars, their initial rates are considerably lower. In contrast, Blasi postulated that water- or acid soluble minerals have a higher influence on char reactivity than the surface area does [17].

4. Conclusion

Gasification reactivity of various biomass chars was investigated in CO_2 atmosphere. The gasification reactivity of the chars from woody biomass was higher than that of the chars from than that of chars obtained from agricultural waste biomass. Washing of chars with HCl resulted in the removal of K and Ca salts, as well as the creation of some small pores.

The decrease in indigenous mineral matters in char led to a markedly decreased gasification reactivity as compared with that of the original one. But, a comparison of the observed gasification reactivity among all chars showed that the surface areas have a higher influence on char reactivity than mineral matter.
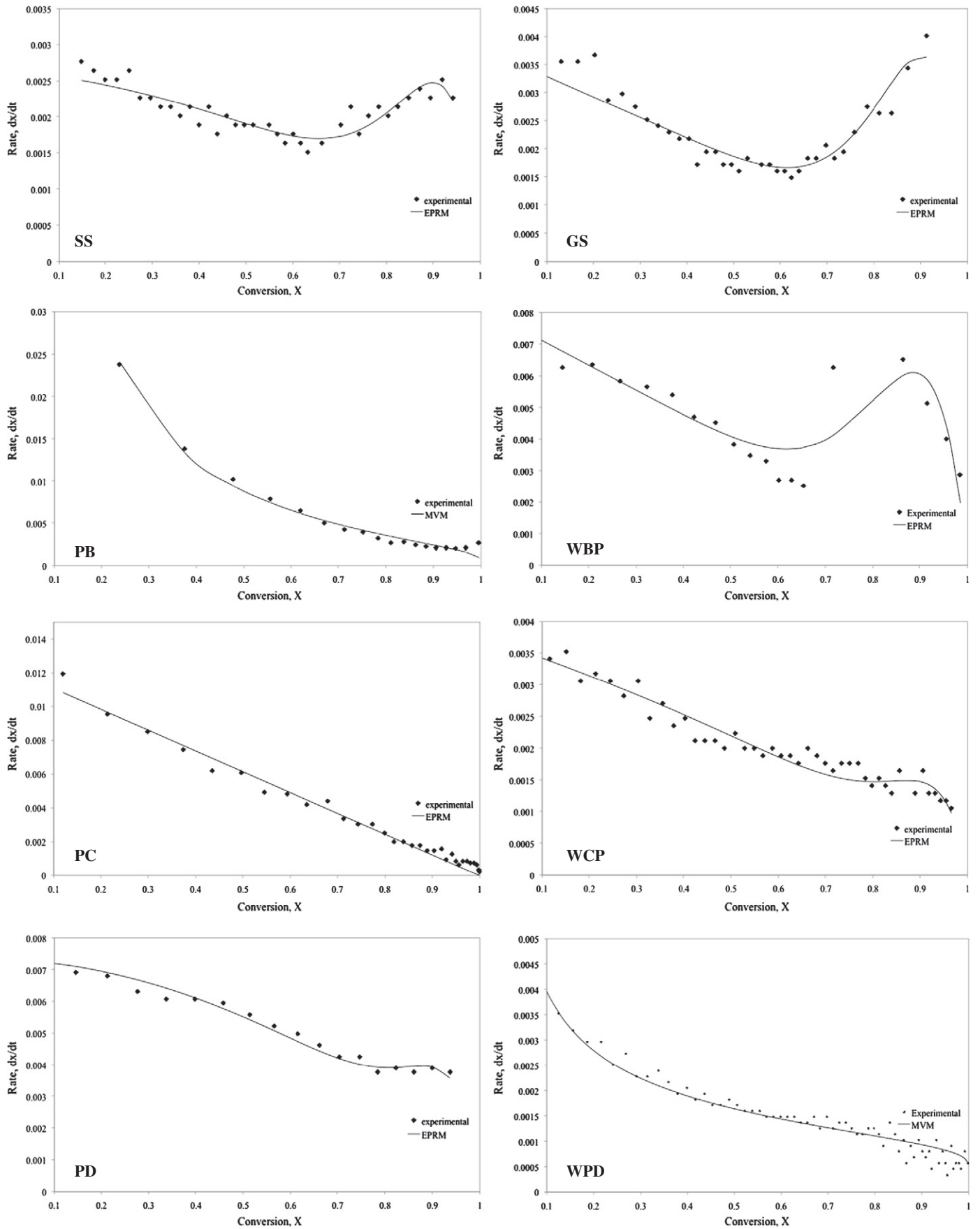
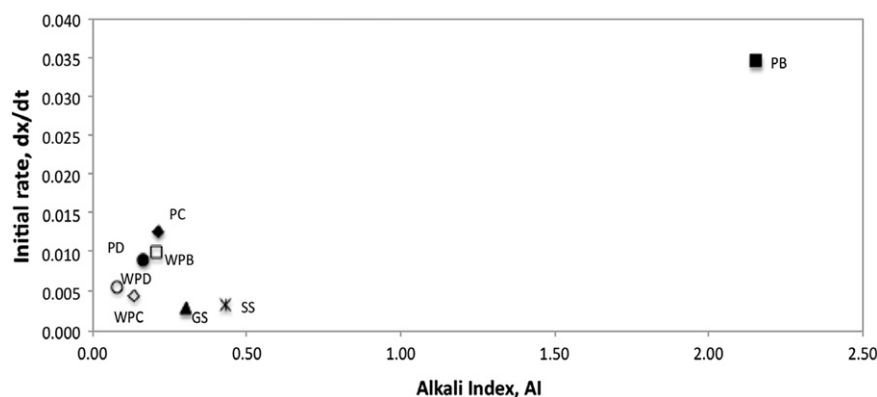**Fig. 3.** Gasification rate versus conversion.

Fig. 4. Initial rates of chars against alkali index.

Acknowledgments

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