39

Contribution of Volatile Interactions During Co-Gasification of Biomass with Coal

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Abstract: Thermo-gravimetric behavior during steam co-gasification of Japanese cedar and coal was investigated. The difference between co-gasification behavior and the average gasification behavior of cedar and coal indicates two synergetic peaks. The first peak occurred between 300 °C and 550 °C while the second peak was observed above 800 °C. The first peak coincides with volatile release and therefore associated with volatile interactions while the second peak is linked with catalytic effect of alkali and alkaline earth metal (AAEM). Acid washed cellulose and Na rich lignin chemicals were used as artificial biomass components. In reference to Japanese cedar, mixture of cellulose and lignin i.e. *simulated biomass*, was also investigated. Co-gasification of cellulose with coal and co-gasification of lignin with coal, demonstrates contribution of volatile interactions and AAEM catalysis respectively. Morphology of partially gasified blends, shows hastened pore development and physical cracking on coal particles. Brunauer–Emmett–Teller (BET) surface area of the charred blend was lower than the average surface area for charred biomass and coal.

Keywords: Co-gasification, synergy, biomass, cellulose, lignin.

INTRODUCTION

Co-gasification of biomass and coal has several advantages including benefits of biomass as a renewable energy in addition to utilization of abundant coal [1]. Further advantages of co-gasification consist of the reduction of overall energy production cost as well as the reduction of environmental consequences resulting from coal utilization [2]. When biomass and coal are co-gasified, the resulting behaviors covering occurrence of synergy and mechanism of interaction are not clearly understood. Enhanced reactivity which occur during co-gasification have widely been linked with catalytic effects of AAEM [3-5]. In addition to that, some researchers have also reported that volatiles interactions also affects conversion characteristics [1, 2, 6]. To demonstrate the effect of AAEM catalysis, comparison of co-gasification of coal with biomass against co-gasification of coal with acid washed biomass have been used [4, 5]. Acid washing is possibly an effective method of AAEM removal, however some researchers have argued on its effects on the morphology and inherent chemical characteristics of the acid washed samples [7].

Compositions of lignin and cellulose are crucial factors in biomass reactivity during gasification [5, 8, 9]. Biomass with high cellulose content is relatively more reactive than biomass with higher lignin content [5, 10]. Besides moisture removal process, decomposition of

biomass volatiles can be divided into two stages; cellulose decomposition and lignin decomposition. Cellulose decomposes fast between 300 °C and 400 °C while lignin decomposes slowly from 250 °C to 500 °C [5, 8, 11]. If biomass is co-processed with coal, decomposition of volatile matters lowers the actual biomass-to-coal mass ratio in the charred blend since biomass has higher volatile matters in comparison to coal. Consequently, the resulting mass loss leads to relatively higher ash concentration within the charred blend and therefore AAEM catalysis is more effective at higher conversion stages [4, 5].

Japanese cedar and coal were used as primary parent fuels for studying co-gasification characteristics. In order to differentiate between the interactions phenomena and AAEM catalysis, acid washed cellulose [12] that has high volatile matters and Na rich lignin chemicals were used as artificial biomass components. As reference to Japanese cedar, gasification characteristics of simulated biomass, i.e. the mixture of 70% cellulose and 30% lignin by weight, was also investigated. In addition to that, cogasification of cellulose with coal and co-gasification of lignin with coal were also conducted. After partial gasification to 800°C, BET surface area and morphology of the charred samples were also investigated.

EXPERIMENTAL METHODS

Samples and Blending Ratios

Japanese cedar (*cryptomeria japonica*) and coal were milled to 150 μ m and stored in a desiccator to

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avoid moisture contamination. lignin made by Kanto Chemical Co. Inc, and acid washed microcrystalline cellulose prepared by Sigma-Aldrich Chemie GmbH [12], were used as artificial biomass constituents. Proximate and ultimate analyses of these samples are shown in Table **1** while Table **2** shows analysis of inorganic matters contents. Separate gasification experiments were conducted for; cedar, cellulose, lignin and coal. In reference to cellulose and lignin contents in Japanese cedar [13, 14], *simulated biomass* was made by mixing cellulose and lignin at 70% and 30% dry and ash free (d.a.f.) mass basis. Cogasification of the samples mixed at 1:1 d.a.f. mass basis was conducted for the blend of cedar with coal, lignin with coal and cellulose with coal.

Gasification Experiments

Steam gasification of about 10 mg samples was conducted by using Shimadzu Thermo-Gravimetric Analyzer (TGA). WORKlab water pump was used to supply distilled water to a steam generator set at 300 °C. Heating rate from ambient temperature to 1,000 °C was set at 20 °C min⁻¹, however holding at 107 °C for 10 min to ensure complete removal of moisture contents from the samples. When 1,000 °C was attained, constant temperature gasification was allowed to proceed until no mass loss was observed. To avoid steam condensation within TGA reactor at lower temperature ranges, only N₂ at 150 mL_N min⁻¹ was supplied from ambient temperature to 200 °C. Thereafter, N₂ flow was reduced to 75 mL_N min⁻¹, and

steam at 75 $mL_N min^{-1}$ was supplied to allow gasification reactions to proceed. N₂ supplied at 75 $mL_N min^{-1}$ was maintained throughout the gasification process as purging gas and as a steam carrier.

Analysis of Conversion Ratios and Extent of Synergy

Conversion ratio X (wt %) was derived from mass decomposition data by TGA as follows;

$$X = 1 - m/m_o \tag{1}$$

where m and m_o (both in g) represent mass of the sample on d.a.f. basis at a certain gasification temperature and at initial condition, respectively.

Average conversion ratio X_{avg} (wt %) was calculated from conversion ratios for cedar, lignin, cellulose or simulated biomass X_{bio} and conversion of coal X_{col} multiplied with mass ratio of the respective samples in the blend;

$$X_{avg} = (X_{bio} \times m_{bio}/m_{bld}) + (X_{col} \times m_{col}/m_{bld})$$
(2)

where m_{col} and m_{bld} (both in g) represents initial d.a.f. mass of coal and the blend while m_{bio} (g) represents d.a.f. mass of cedar, lignin, cellulose or simulated biomass.

Extent of synergy Y (%), was calculated as the difference between conversion ratio for blend X_{bld} from the calculated average conversion X_{avg} at the same temperature;

	Pro	Ultimate analysis (wt, %)							
Sample	As received	Dry basis				Balance			
	Moisture	VM	FC	Ash	С	н	N	S	0
Coal	2.00	30.30	56.00	13.60	80.97	1.47	9.32	0.45	7.79
Cedar	3.90	86.09	11.79	2.13	47.56	5.66	0.27	-	46.51
Cellulose	4.96	85.14	14.86	<0.01	45.34	6.97	0.08	-	51.39
Lignin	2.23	38.62	55.64	5.74	60.58	5.14	0.27	-	33.99

Table 1: Proximate and Ultimate Analyses of the Samples

 Table 2:
 Ash Analysis for Inorganic Compounds

Sample	Inorganic compounds in the ash (wt, %)											
	SiO ₂	Al ₂ O ₃	CaO	TiO₂	Fe ₂ O ₃	MgO	Na₂O	K₂O	P ₂ O ₅	MnO	V ₂ O ₅	SO₃
Coal	65.90	22.90	1.08	1.37	4.58	0.79	0.47	1.37	0.31	0.03	0.07	0.62
Cedar	24.51	4.67	25.99	0.26	4.98	5.89	3.13	19.13	1.66	-	-	3.32
Lignin	10.05	1.33	0.44	<0.01	0.15	0.81	47.18	1.17	<0.01	-	-	32.25

 $Y = X_{bld} - X_{ava}$

Investigation of Morphology and BET Surface Area

(3)

Morphology of the samples dried at 60 °C for 24 hours as well as the samples partially gasified at 20 °C min⁻¹ to 800 °C was investigated by using Scanning Electron Microscope (SEM). BET surface area of the partially gasified samples was done by using Shimadzu Flowsorb Micrometrics whereby samples were degassed at 200 °C prior to adsorption of N₂. During partial gasification, temperature profile as well as flow rates for N₂ and gasifying agents, were similar to those applied during gasification experiments. However, when the target temperature of 800 °C was attained, heat supply and steam supply was terminated. Mean while the residues were allowed to cool under 150 mL_N min^{-1} supply of N₂. It can be noted that due to high temperature and possible presence of residual steam, it is most likely that further conversion of the residues occurred at initial stage of the cooling process to affect their morphology.

RESULTS AND DISCUSSION

Conversion Behaviors and Extent of Synergy

Conversion ratios during gasification at 20 °C min⁻¹ were calculated from mass decomposition data by using Equation (1). Conversion characteristics for Japanese cedar, coal and their blend is presented in Figure **1**. It was observed that initial conversion of cedar, coal and the blend is marked by rapid change due to volatile decomposition. These rapid changes ended-up at around 400 °C, 700 °C and 450 °C

respectively, corresponding to about 61%, 36% and 45% conversion. Thereafter, gasification of fixed carbon started at 750 °C, 950 °C and 800 °C for cedar, coal and the blend, respectively. Average conversion was calculated from separate biomass gasification and coal gasification by using Equation (2). As from 400 °C and notably above 800 °C, co-gasification characteristics shows improved trend in comparison to the calculated average. This improvement is an indication of occurrence of conversion synergy. Considering the slow heating rate of 20 °C min⁻¹ used, the synergy occurring above 800 °C can be related to AAEM catalytic effect [3-5] since volatile release will be less significant above this temperature range. However, synergy at the lower temperature range, can be also be associated with volatile interactions [1, 2, 6].

In order to investigate AAEM catalysis and volatile interactions, we conducted experiments on cogasification of coal with Na rich lignin in addition to cogasification of coal with acid washed cellulose that has with high volatile matter content (Table 1 and Table 2). Firstly, we checked gasification characteristics of cellulose and lignin (Figure 2a). Gasification of cellulose is characterized by sharp devolatilization which occurs between 350 °C and 450 °C, after which cellulose attain about 87% conversion corresponding to its high volatile matter contents (see Table 1). Lignin shows relatively slow volatilization limited to about 38% at 450 °C. Gasification behavior of the simulated biomass compares well with that of Japanese cedar. However, simulated biomass shows the narrow temperature ranges for volatile decomposition and char gasification processes which occur at around 400 °C



Figure 1: Conversion behavior of Japanese cedar, coal and the blend during steam gasification at 20 °C min⁻¹.

Conversion, X (%)

20%



Figure 2: (a): Conversion of cellulose, lignin, simulated biomass and cedar during steam gasification at 20 °C min⁻¹.

(b): Conversion behavior of simulated biomass, coal and the blend during steam gasification at 20 °C min⁻¹.

and 800 °C respectively. These patterns correspond to cellulose gasification and lignin gasification characteristics.

Co-gasification characteristic of simulated biomass with coal is presented in Figure 2b. Two synergetic regions were observed as it was the case for cogasification of Japanese cedar with coal (Figure 1). Under both cases, it is difficult to demarcate between domination of the catalytic effect of AAEM and volatile interactions. Nevertheless, Figure 2b demonstrates the suitability of cellulose and lignin chemicals as artificial biomass components.

Co-gasification behavior of lignin with coal and cogasification of cellulose with coal are presented in Figures 3a and 3b, respectively. For the case of cogasification of lignin with coal, two synergetic regions were observed as it was the case for co-gasification of coal with either Japanese cedar or simulated biomass (Figures 1 and 2b). Similarly, contribution of catalytic effect of AAEM and volatile interactions cannot be differentiated. On the other side, co-gasification of acid washed cellulose with coal shows synergetic pattern between 350 °C and 450 °C but no significant synergy is observed at temperatures above 800 °C (Figure 3b). This result indicates that synergy occurred during decomposition of cellulose volatiles and therefore associated with volatile interactions [1, 2, 6].



The extent of the synergy for co-gasification of coal with Japanese cedar, simulated biomass, lignin or

Figure 3: (a): Conversion behavior of lignin, coal and the blend during steam gasification at 20 °C min⁻¹. (b): Conversion behavior of cellulose, coal and the blend during steam gasification at 20 °C min⁻¹.





cellulose, was derived by using Equation (3). Two synergetic peaks were observed, the first one extending from 300 °C to 550 °C for all blends (Figure 4). The second peak occurred above 800 °C, except for the blend of coal and acid washed cellulose. The first peak coincides with volatile release from Japanese cedar, simulated biomass, lignin and cellulose. The corresponding synergy can therefore be associated with volatile interactions [1, 2, 6]. Under slow heating TGA conditions used, most of volatiles decompose below 500 °C therefore the synergy which occurs at temperature ranges above 800 °C can be linked with AAEM catalysis. This figure suggests and demarcates two possible synergy mechanism; volatile interactions and AAEM catalysis which dominate at higher conversion stages [4, 5].

Morphology Changes

Morphology changes were investigated by comparing morphology of raw samples to the morphology of samples partially gasified to 800 °C. SEM images of raw Japanese cedar, coal, cellulose and lignin are shown in Figure **5**. Figure **5a** shows that raw cedar has fiber based structure with multiple tubelike cells in contrast to coal which has solid structure and shiny surface (see Figure **5b**). Cellulose has solid fiber structure while lignin has lumpy solid structure (Figure **5c** vs. Figure **5d**).

After gasification to 800 °C, samples indicate diverse morphological changes dependent to their intrinsic structures as well as conversion attained (Figure 6). Japanese cedar demonstrates remarkable morphology change (Figure 6a) owing to about 90% conversion attained at this stage (see Figure 1). The rectangular structure shown is indicative of the lignin based primary plant wall structure that is visible after decomposition of cellulose rich secondary wall [15].



Figure 5: Morphology of the raw samples; (a) cedar, (b) coal, (c) cellulose, (d) lignin.



Figure 6: Surface structures after gasification to 800 °C; (a) cedar, (b) coal, (c) cellulose, (d) lignin.

Coal surface indicate pores development and slight physical cracking (Figure 6b). Nevertheless, coal particle seems to maintain its solid shape due to its low conversion of about 41% (Figure 1). Morphology change on cellulose is mainly based on fiber shrinkage basis (see Figure 6c). This shrinkage is attributed to decomposition of volatile matters which accounts for 85% of cellulose mass (Table 1). This is not the case with lignin which attained 46% conversion at 800 °C (Figure 2a). Despite of maintaining its solid shape as it is the case with coal, surface structure of a lignin particle shows spongy surface as shown in Figure 6d. Probably, spongy surface offers less steam diffusion resistance and therefore enhancing the gasification process [2, 16, 17] as observed from 800 °C onwards (see Figure 2a).

Morphology investigation was also conducted for partially gasified blends; cedar with coal, lignin with coal and cellulose with coal. Since reactivity of cedar, cellulose and even lignin is higher than that of coal, we focused on indication of the enhanced reactivity for coal particles. Figure **7** shows surface structures of coal particles taken from the co-gasified blends. After co-gasification with Japanese cedar, coal surface shows further pores development and physical cracking (Figure **7a**). Enhanced pores and physical cracking on coal surface also applies for the case of the cellulose and coal as shown in Figure **7b**. However this effect is less pronounced in the case of cogasification of lignin with coal (Figure **7c**). It can be noted that low extent of synergy was also observed for co-gasification of lignin with coal at temperature below 800 °C (Figure **4**). Development of pores and physical cracking on coal surface may indicate enhanced conversion [16, 17]. In addition to that, these features may also play a significant role in enhancing intrinsic reactions through the resulting increase in reactive surface area and improved diffusion of steam into the coal matrix [2, 16, 17].

BET Surface Area

BET surface areas for the samples partially gasified to 800 °C under steam gasification are shown in Figure **8**. Inevitably, gasified cedar sample has higher BET surface areas than gasified coal sample as suggested by morphology presented in Figures **6a** and **6b**. Average surface area for cedar and coal is shown as $373 \text{ m}^2 \text{ g}^{-1}$ while the surface area of the blend is 308 m^2 g^{-1} . This result shows that average of the surface areas for coal and cedar is higher than the surface area of blend. It is known that BET surface area follows a bellytype profile against conversion, i.e. initially increases to a peak and hence decreases slightly at higher conversion stages [18, 19]. As opposed to that,



Figure 7: Surface structures after co-gasification to 800 °C; (a) coal surface from coal and cedar blend, (b) coal surface from coal and cellulose blend, (c) coal surface from coal and lignin blend.

conversion ratios increase to around 100% (Figure 1 through Figure 4). Although it is difficult to explain synergy aspects by using this result, consideration of corresponding lower biomass to coal ratio at 800 °C suggests significant morphology improvement for coal particles as suggested by Figure 7a.



Figure 8: BET surface areas for Japanese cedar, coal and the blend gasified to 800 °C.

CONCLUSIONS

Improved co-gasification conversion characteristic was observed in comparison to average conversion characteristics from separate gasification of cedar and gasification of coal. Two conversion synergetic peaks were observed, one extending from 300 °C to 550 °C while the other peak occurred above 800 °C. The first peak coincides with volatile release and therefore associated with volatile interactions while the second peak can be linked with catalytic effect of AAEM species from biomass. In order to differentiate between the interactions phenomena and AAEM catalysis, acid washed cellulose that has high volatile matters and Na rich lignin chemicals were used as artificial biomass components. Co-gasification of cellulose with coal and co-gasification of lignin with coal elucidate volatile phenomena and AAEM interactions catalysis, respectively. Morphology of partially gasified blends, shows hastened pore development and physical cracking on coal particles. Average surface area for cedar and coal was about 373 m² g⁻¹ while the surface area of the blend was 308 m² g⁻¹.

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