

Gasification reactivity of biomass chars with CO₂

Dong Kyun Seo¹, Sun Ki Lee², Min Wong Kang³, Jungho Hwang^{4*},
Tae-U Yu⁵

¹ Department of Mechanical Engineering, Yonsei University, Seoul, Korea
(dkseo@yonsei.ac.kr)

² Department of Mechanical Engineering, Yonsei University, Seoul, Korea
(dltjsrl8@yonsei.ac.kr)

³ Department of Mechanical Engineering, Yonsei University, Seoul, Korea
(hwangjh @nate.com)

⁴ Department of Mechanical Engineering, Yonsei University, Seoul, Korea
(@yonsei.ac.kr)

⁵ Manufacturing System Division, Korea Institute of Industrial Technology,
Chunan, Korea (ytu@kitech.re.kr)

ABSTRACT: This paper studied on the CO₂ gasification reactivity for biomass, wood chip, using a fixed bed reactor at the gasification temperature ranging from 850 °C to 1050 °C. After applying two models to experimental data, it was found that the activation energies (E) of biomass char-CO₂ reaction, obtained from the two models, were almost same as those reported in literatures. Overall, the shrinking un-reacted core model (SUCM) was superior to the volume reaction model (VRM). The BET surface area of biomass chars increased with the temperature, but slightly decreased after 950 °C, which implied that the maximum gasification temperature of CO₂ reactivity in this study was around 950 °C.

Keywords: CO₂ gasification, VRM, SUCM, activation energy, BET

NOMENCLATURE

A	pre-exponential factor
E	activation energy
ΔH^0	standard state enthalpy change
k_s	rate constant (SUCM)
k_v	rate constant (VRM)
R	universal gas constant
R_v	correlative index (VRM)
R_s	correlative index (SUCM)
T	wall temperature
t	time
t_i	initial time

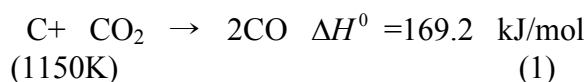
x carbon conversion

1. INTRODUCTION

Among the renewable energies, biomass is expected to be one of the most important in the near future [1]. Biomass energy currently represents approximately 14% of world final energy consumption, a share higher than that of coal (12%) and comparable to those of gas (15%) and electricity (14%) [2]. Environmentally large quantities of agricultural and forestry residual wastes are generated over the world annually. A careful use of these biomasses

could contribute to relieve the environmental impacts such as global warming and acid rain. [3]

The thermal processing of biomass offers the potential transition from a fossil fuel driven global economy [4]. Pyrolysis and gasification have been identified as the most favourable thermo-chemical biomass conversion processes to renewable energy are environmental friendly due to low sulphur and nitrogen content of biomass. [3] The gasification of biomass begins with devolatilization, leaving chiefly a char composed of carbon and ash. The gasification reaction of char with a few gases is important in any gasification scheme [5]. Generally there are two routines regarding biomass gasification. One is the gasification with H₂O, and the other is with CO₂ (Eq.(1))[6].



Comparing to steam (H₂O) gasification, the gasification with CO₂ has the following advantages. (i) CO₂ gas can be fed easily to the reactor through as simple line, (ii) more energy can be stored per mol of carbon, and (iii) CO₂ emission to the atmosphere could be reduced by its recycling [6].

So far, there have been numerous studies on the CO₂ gasification [1,5-9]. Mathieu and Dubuisson presented a CO₂ gasification modelling of the biomass and particularly the wood gasification based on the minimisation of the Gibbs free energy [1]. Scott et al. investigated the rate of CO₂ gasification of chars from dried sewage sludge, car tyres, bituminous coal, and activated carbon at 800-1050°C. On the basis of BET area or mass, they observed that the sewage sludge char was the most reactive, while the activated carbon had the lowest reactivity per unit BET surface area, indicating that the area in its micro-pores is comparatively unreactive [5]. Jin et al. studied the waste paper gasification in CO₂ atmosphere with molten alkali carbonates

which is capable of facilitating a desired reaction (C+ CO₂→CO) [6]. Liu et al. studied the gasification activity of three kinds of coal chars with CO₂ at 1000-1300°C under atmospheric pressure, with the specific surface area determined with BET method during gasification. The results showed that the reaction rate of the rapid pyrolysis chars increased at the beginning and decreased subsequently with increasing carbon conversion at relatively high temperature [7]. Kajitani et al. gasified four types of coal chars with CO₂ using a pressured drop tube furnace or TGA at high temperature and pressure. They also applied the kinetics model, the rate equations of the *n*th order and Langmuir-Hinshelwood type to the char gasification reaction with the random pore model and the effectiveness factor, and the applicability of these rate equations to air-blown and oxygen-blown entrained flow gasifiers evaluated [8]. Bhat et al. investigated the gasification of rice husk char in CO₂ for determining the kinetics parameters [9].

In the present work, wood chip, one of biomass fuels, were selected to examine the CO₂ gasification reactivity and determine the kinetic parameters. The data were analysed by two widely accepted models; the volume reaction model (VRM) and the shrinking un-reacted core model (SUCM).

2. KINETIC MODELING

Gasification of char particles is usually classified as an irreversible gas-solid reaction, which is commonly described using the volume reaction model (VRM) or the shrinking un-reacted core model (SUCM) [10,11].

The VRM proposed by Wen(1968) assumes that the gas reactant reacts with char in all possible places, both outside and inside the particle surface[11]. The rate equation is as follows:

$$\frac{dx}{dt} = k_v(1-x) \quad (2)$$

where x is the carbon conversion and k_v is the rate constant for carbon conversion. Solving equation (2), k_v is represented as follows:

$$-\ln(1-x) = k_v t \quad (3)$$

The SUCM also proposed by Wen(1968) represents that the reaction initially occurs at the external surface of char, and gradually moves inside. At the intermediate conversion of the solid, there is a shrinking core of unreacted solid [11]. The reaction is described as follows:

$$\frac{dx}{dt} = k_s(1-x)^{2/3} \quad (4)$$

where k_s is the rate constant for carbon conversion.

Solving equation (4), k_s becomes:

$$1 - (1-x)^{1/3} = k_s t / 3 \quad (5)$$

k_v and k_s are represented as Arrhenius equation

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (6)$$

where A , R , E , T are the pre-exponential factor, universal gas constant, activation energy, and gas temperature, respectively.

3. EXPERIMENTAL METHOD

3.1 Preparation of biomass samples

Samples were prepared after grinding and sieving commercial products of biomass (DONGYANG HI TECH CO., LTD, Korea). The size of samples ranged between 250 μ m ~ 300 μ m. The proximate analysis was

carried out using the method described in American Society for Testing Material (ASTM) D5142. The ultimate analysis was conducted using an element analyzer (EA1110, CE instrument). The calorific value of the sample (LHV) was calculated by the Dulong's equation

$$LHV = HHV - 600(9H + W) \quad (7)$$

where

$$HHV = 8100C + 34000\left(H - \frac{O}{8}\right) + 2500S \quad (8)$$

The characteristics of biomass samples are summarized in Table 1.

Table 1: Characteristics of biomass samples

Proximate analysis(wt%)	
moisture	9.55
volatile matter	40.40
fixed carbon	22.68
ash	0.44
ultimate analysis(wt%)	
C	49.60
H	9.22
O	44.32
N	0.10
Calorific value (kcal kg ⁻¹)	
LHV	6116.12

3.2 Experimental apparatus and procedures

The schematic of experimental set up is shown in Figure 1. Experiments were conducted using a fixed-bed reactor, which was made of a dense alumina ceramic tube with 50mm in ID and 450mm in length. Three R-type thermocouples were inserted into the reactor to monitor the local gas temperatures.

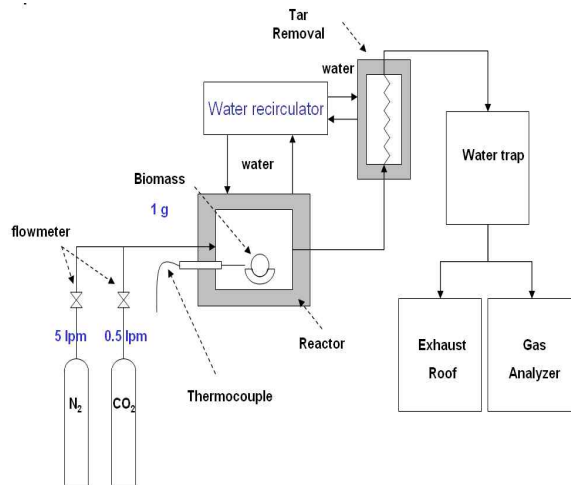


Figure 1: Schematic of experimental apparatus.

At the beginning of each experiment, 1g of biomass samples were placed into the reactor and at the same time the reactor was electrically heated at a heating rate of 10°C up to the desired wall temperature for gasification. When the desired temperature was reached, CO₂ was injected for 30min at a rate of 0.5 lpm with a purging gas of N₂ at 5 lpm. Five different temperatures of 850, 900, 950, 1000, and 1050°C were tested. After gasification products exited the reactor, they passed through a tar removal system and a water trap system, where tar was condensing and any moisture was removed, before entering a real time gas analyzer (GreenLine 9000). The sampling flow rate of the gas analyzer was 3 lpm. After each test, the analysis of BET surface area of remaining biomass char was conducted by N₂ adsorption technique using the pore structure analyzer (ASAP 2020) produced by Micrometrics Instrument CO.

4. RESULTS AND DISCUSSION

4.1 Gasification kinetics

In this study, the carbon conversion at any time is defined as follows:

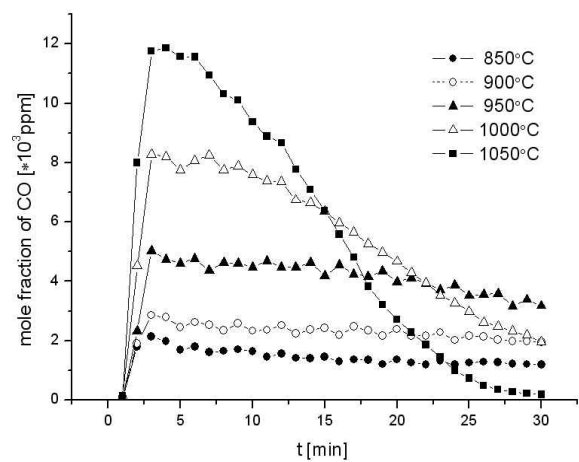


Figure 2: Effect of reaction temperature on the production of CO.

$$x = \frac{\sum_{j=1}^{j=t} [CO]_j}{\sum_{j=t_i}^{total} [CO]_j} \quad (9)$$

where $[CO]$ is the concentration of $[CO]$.

In this study, experimental runs of the CO₂ gasification reaction were conducted at temperatures ranging from 850°C to 1050°C. Figure 2 shows that the carbon conversion was sensitive to the temperature, which implied that the chemical reaction was probably the rate controlling step.

The results of the VRM and the SUCM were compared with the experimental data in Figures 3 and 4, respectively. Table 2 shows the correlative indexes, R_v and R_s . The results show that the SUCM was better for modelling CO₂ gasification at temperatures ranging from 900°C to 1050°C.

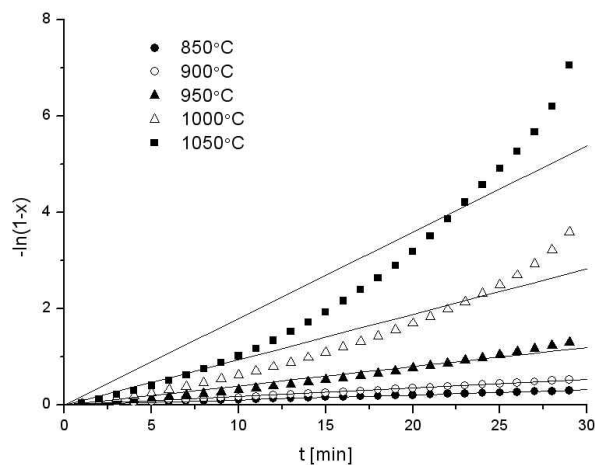


Figure 3: $-\ln(1-x)$ versus t at different temperature (VRM)

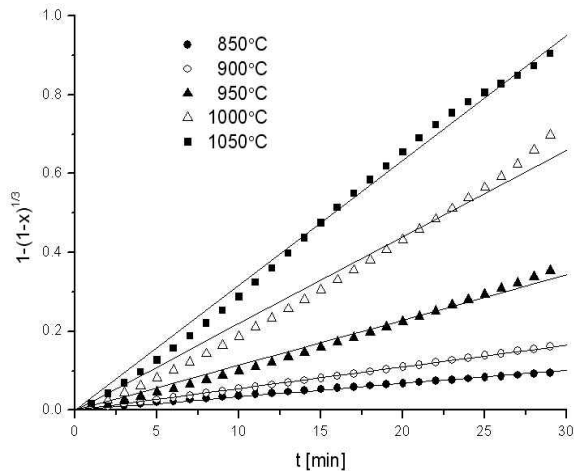


Figure 4: $1-(1-x)^{1/3}$ versus t at different temperature (SUCM)

Table 2: Correlative indexes obtained using the VRM(R_V) and SUCM(R_S)

Gasification temperatures	R_V	R_S
850°C	0.9995	0.9981
900°C	0.9995	0.9999
950°C	0.9932	0.9963
1000°C	0.9752	0.9951
1050°C	0.9694	0.9971

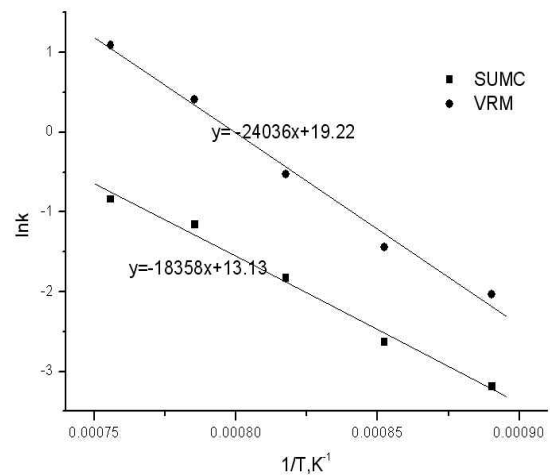


Figure 5: Arrhenius plots for A and E

For the CO₂ gasification, the values of activation energy were reported by many researchers, as shown in Table 3. Figure 5 represents the Arrhenius plots of VRM and SUCM for obtaining pre-exponential factors (A, min^{-1}) and activation energies ($E, \text{J/kmol}$). The results are summarized in Table 4. Thus, the activation energies obtained in this study were almost same as those reported in literatures.

Table 3: Activation energy reported by some literatures

Samples	Activation Energy (J/kmol)	reference
Rice husk	2.00×10^8	[9]
Wood chip	2.59×10^8	[2]
Paper	2.21×10^8	[6]

Table 4: Activation energy and pre-exponential factor estimated from the SUCM and the VRM, respectively

	VRM	SUCM
A, min^{-1}	1.78×10^8	4.24×10^5
$E, \text{J/kmol}$	1.92×10^8	1.53×10^8

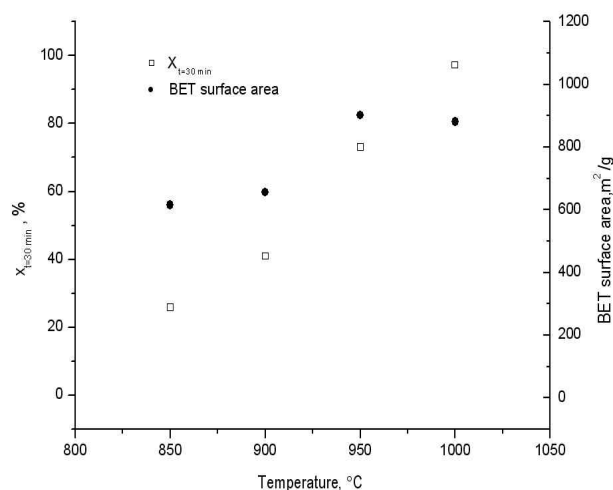


Figure 6: Changes of BET surface area and carbon conversion at different gasification temperatures

4.2 Changes of BET surface area and reaction rate

It has been reported that the BET surface of char, which represents the degree of porosity, changes as the reaction proceeds [5,7]. The effects of temperature on BET surface area as well as carbon conversion for 30 minutes of gasification were plotted in Fig. 6. The results show that the BET surface area increased and then slightly decreased with carbon conversion. Therefore, it was expected that the porosity of chars increased at low carbon conversions due to the pores being opened and enlarged, simultaneously, while it decreased at high carbon conversions due to amalgamation of the neighbouring pores [10].

Thus, it can be seen that the reactivity increased in the beginning with the increase of carbon conversion, reached a maximum at a certain conversion value, and declined thereafter.

4. CONCLUSIONS

The following conclusions were obtained through this work.

(1) For the calculation of CO₂ gasification reaction, the SUCM was superior to the VRM.

(2) Activation energies obtained for CO₂ gasification reaction are 1.92×10^8 J/kmol for VRM and 1.53×10^8 J/kmol for SUCM.

(3) BET surface area of biomass chars increased with the temperature but slightly decreased after 950°C, which implied that the maximum gasification temperature of CO₂ reactivity in this study was around 950°C.

ACKNOWLEDGEMENT

This work was financially supported by the Korea Energy Management Corporation project (PNS07210), Korea. This work is also an outcome of the fostering project of the Specialized Graduate School of Hydrogen & Fuel Cell supported by the Ministry of Commerce, Industry and Energy (MOCIE).

REFERENCES

- [1] Mathieu, P, Dubuisson, R. 2002. Performance analysis of a biomass gasifier. Energy Conversion and Management. Vol 43. pp1291-1299. Belgium.
- [2] Senneca, O. 2007. Kinetics of pyrolysis, combustion and gasification of three biomass fuels. Fuel Processing Technology. Vol 88. pp87-97. Italy.
- [3] Chaudhari, S. T, Dalai, A. K, & Bakhshi, N. N. 2003. Production of Hydrogen and/or Syngas(H₂+CO) via Steam Gasification of Biomass-Derived. Vol 17. pp1062-1067. Energy & Fuels. Canada.
- [4] Buttermann, H. C, Castaldi, M. J. 2007. Influence of CO₂ injection on biomass gasification. Ind. Eng. Chem. Res. Vol 46. pp8875-8886. USA.
- [5] Scott, S. A, Davidson, J. F, Dennis J. S, Fennell P. S, & Hayhurst A. N. 2005. The rate of gasification by CO₂ of chars from waste. Proceedings of the Combustion Institute. Vol 30. pp2151-2159. UK.
- [6] Jin, G, Iwaki, H, Arai, N, & Kitagawa, K. 2005. Study on the gasification of wastepaper/carbon dioxide catalyzed by

molten carbonate salts. Energy. Vol 30.
pp1192-1203. Japan.

- [7]Liu, T, Fang, Y, & Wang, Y. 2008. An experimental investigation into the gasification reactivity of chars prepared at high temperatures. Fuel. Vol 87. pp460-466. China.
- [8]Kajitani, S. Suzuki, N, Ashizawa, M, & Hara, S. 2006. CO₂ gasification rate analysis of coal char in entrained flow coal gasifier. Fuel, Vol 85. pp163-169. Japan.
- [9]Bhat, A. Bheemarasetti, J. V. R, & Rao, T. R, S. 2006. Kinetics of rice husk char gasification. Energy Conversion and Management, Vol 42. pp2061-2069. India.
- [10]Wu, S, Gu, J, Li, L, Wu, Y, & Gao, J. 2006. The reactivity and kinetics of Yanzhou coal chars from elevated pyrolysis temperatures during gasification in steam at 900-1200 °C. Trans IChemE. Vol 84(B6). pp420-428. China.
- [11]Wen, C. Y, Gu, J, Li, L, Wu, Y, & Gao, J. 1968. Non-catalytic heterogeneous solid-fluid reaction models. Ind. Eng. Chem., Vol 60(9). pp34-54. USA.