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Water Gas Shift Reaction Characteristics Using Syngas from Waste Gasification

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Abstract: *The characteristics of a high temperature water gas shift reaction over a commercial Fe-based catalyst using syngas from waste gasification were investigated using lab equipment tests and found to be feasible for producing valuable chemical products. The CO conversion and H_2/CO ratio were observed using various values for the gas hourly space velocity(GHSV), steam/CO ratio, and temperature. The CO conversion and H_2/CO ratio increased with increasing temperature, increasing steam/CO ratio and decreasing SV. The CO conversion values were 32.95% and 46.84% and the H_2/CO ratios were 1.8 and 2.09 with temperatures of 350 ℃ and 400℃, respectively, when the steam/CO ratio was 2.4 and SV was 458 h^{-1}. The H_2/CO ratio and CO conversion were 1.42 and 30.14%, respectively, when the steam/CO ratio was 1.45, and increased with an increase in the steam/CO ratio. The H_2/CO ratio increased to 2.36 and the CO conversion increased to 51.70% when the steam/CO ratio was 3.44. However, the increase in the CO conversion was insignificant when the steam/CO ratio was greater than 2.9.*

Keywords: *H_2/CO Ratio, Syngas, Waste gasification, Water gas shift reaction*

I. Introduction

Gasification is the conversion of any carbonaceous fuel to a gaseous product with a useable heating value and is widely used for energy conversion from coal, waste and biomass all over the world[1]. Gasification has several potential advantages over the traditional combustion of solid wastes, mainly related to the possibility of combining the operating conditions (in particular, temperature and equivalence ratio) and the features of the specific reactor (a fixed bed, fluidized bed, or entrained bed) to obtain a syngas suited for use in different applications[2]. Such a syngas can be utilized as a fuel gas that can be combusted in a conventional burner, connected to a boiler and steam turbine, or in a more efficient energy conversion device, such as a gas reciprocating engine or gas turbine. Its main components, CO and H_2, can also offer the basic building blocks for producing valuable chemical and fuel products through catalytic synthesis, among other methods, to diesel, gasoline, naphtha, methanol, dimethyl ether(DME), and synthetic natural gas(SNG) and hydrogen[3]. Moreover, the ability to produce biomass or waste-derived fuels on a large scale will help to reduce greenhouse gases and pollution, increase the security of energy supplies, and enhance the use of renewable energy[4]. Various kind of research on biomass and waste gasification technologies have been conducted in the EU, Japan and the U.S. and some are in the lab- or demonstration phase[2, 3, 5, 6]. In Japan, numerous gasification plants for municipal solid waste(MSW), including gasification and melting processes, are under commercial operation for energy and material recovery[1] . Gasification is a process that converts a solid or liquid combustible feedstock into a partially oxidized gas called syngas(essentially a mixture of CO, H_2, CO_2 ,and H_2O). The composition of the syngas derived from gasification can vary with the type and properties of the feedstock, type of gasifier and operating conditions. In the case of the waste gasification of Korean municipal solid waste and industrial waste, the syngas composition shown in Table 1 was investigated using the operation data for a 3 ton/d fixed-bed pilot plant gasification system. The syngas composition was approximately 10~40% hydrogen, 20~42% carbon monoxide, and 20~45% carbon dioxide, and the range for the H_2/CO ratio was 0.54~1.56. Because the value for the H_2/CO ratio was lower than the required ratio for various chemical products as listed in Table 2, an adjustment process is needed for the H_2/CO ratio to utilize the syngas derived from waste gasification as useful chemical products. In general, a water gas shift reaction is used to adjust the H_2/CO ratio. The water gas shift process is the process where the ratio between hydrogen and carbon monoxide in the synthesis gas can be turned[7].

Table 1. Syngas compositions of pilot-scale waste gasification system

		Municipal solid waste				Industrial waste			
		S-city	Y-city	K-city	B-city	D company			A company
Syngas Composition (vol.%)	CO	20~35	25~35	27~40	24~27	20~30	27~33	25~34	39~46
	H2	18~35	20~35	36~40	30~36	20~30	22~30	20~28	25~30
	CO2	20~45	28~40	24~30	20~27	20~45	28~32	15~35	19~25
H_2/CO ratio		0.9~ 1.15	0.68~ 1.30	1.04~ 1.15	1.19~ 1.56	0.56~ 0.99	0.6~ 0.97		0.54~ 0.69

Table 2. H_2/CO ratios for synthesis of various products

Process	Catalyst	Operation condition			CO conversion(%)	Product
		Temperature(℃)	Pressure(bar)	H_2 : CO		
Fischer-Tropsch Synthesis	Fe	300~350	10~40	1.7 : 1	50~90%	Olefins Gasoline
	Co	200~240	7~12	2.15 : 1		Waxes Diesel
Methanol Synthesis	ZnO/Cr_2O_3	350	250~350	2 : 1	99%	Methanol
	$Cu/ZnO/Al_2O_3$	220~270	50~100			
DME Synthesis	$Cu/ZnO/Al_2O_3$ + γ-Al_2O_3	240~280	60	1 : 1		DME
SNG Synthesis	NiO	300~350	Atmosphere ~50	3 : 1		SNG

The WGS reaction is a chemical reaction in which carbon monoxide reacts with water vapor to form carbon dioxide and hydrogen. The WGS process is a commercial process that is used to convert carbon monoxide to hydrogen in an ammonia synthesis plant or hydrogen production plant. Conventionally, the WGS reaction is employed in a two-stage reactor that consists of a high temperature shift (HTS) unit and a low temperature shift (LTS) unit coupled with a cooling system to cool the hot gases to optimum reaction temperatures. The HTS reaction is performed using a Fe–Cr catalyst in a working temperature range of 300~450 °C, while the LTS reaction is performed using a Cu–Zn catalyst at 180-270°C. A fixed bed reactor is generally used for WGS. The reaction is A moderate exothermic reaction, as shown by equation (1), and high conversion rates are facilitated at a low temperature and high steam to dry gas ratio. The pressure has no significant effect on the equilibrium because there is no change in moles.

$$CO + H_2O(g) \Leftrightarrow CO_2 + H_2 \qquad \Delta H^{\circ}_{298} = -41.2\ kJ/mol \quad (1)$$

Syngas derived from waste gasification can be utilized to produce chemical products by adjusting the H_2/CO ratio using the WGS unit as shown in Fig. 1.

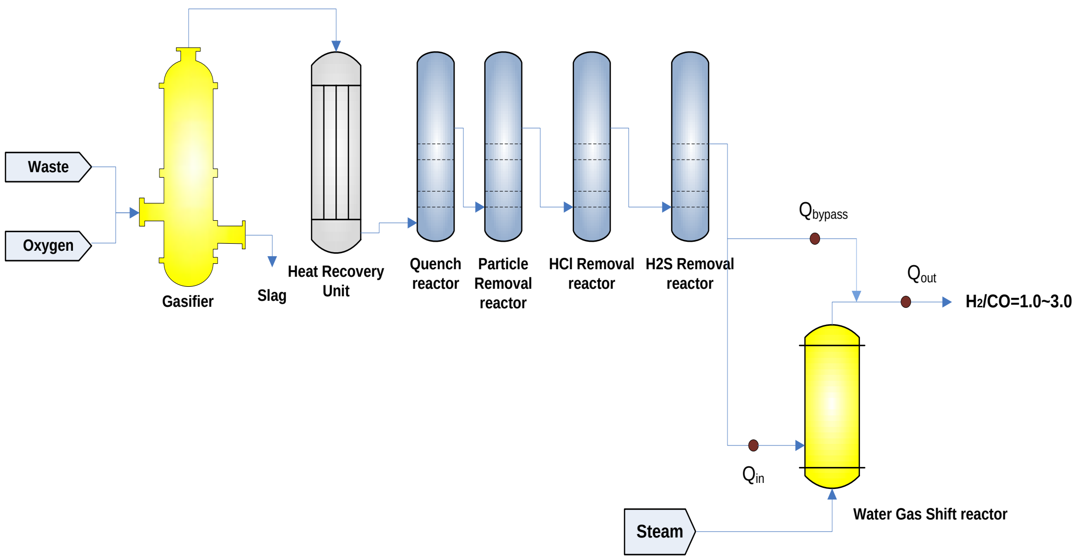

Fig. 1. Waste gasification system including WGS unit

The mechanism and kinetics of the individual WGS reaction have systemically and extensively been studied using many methods[8-14]. However, the kinetics study or characteristics study of WGS under syngas derived from waste gasification has received relatively little attention.

In this study, the characteristics of a high temperature WGS reaction were investigated by using lab equipment tests. The CO conversion and H_2/CO ratio were observed with various values for gas hourly space velocity(GHSV), steam/CO ratio, and temperature using simulated syngas derived from waste gasification.

II. Experiment

2.1 Equipment and catalyst

The lab-scale equipment shown in Fig. 2 and Fig. 3 was used to investigate the characteristics of a WGS reaction in the case of syngas from waste gasification. We simulated syngas with concentrations similar to the syngas from a 3 ton/d pilot-scale waste gasification system operated by IAE, and conducted tests with various values for the GHSV, steam/CO ratio, and temperature. The lab-scale equipment consisted of the following parts : a WGS reactor, electric heater, water pump, preheater for converting water into steam, condenser, gas meter, and portable online gas analyzer. The WGS reactor, which consisted of a 2-in-diameter stainless steel pipe, was located inside a horizontal electric furnace. The syngas flow rates were controlled by a mass controller, and the catalyst was taken in at the reactor, which was kept inside the heating zone during the experiment. The reactor was operated at atmospheric pressure and the syngas flow rate was 0.25 ~ 0.43 m^3/h. The H_2/CO ratio of syngas was 0.78 and syngas composition listed in Table 3. Fe-based commercial high temperature WGS catalysts were used for this test. The catalyst had a diameter of 5.4 mm of diameter, length of 3.6 mm as a pellet type, and bulk density of 1,250 kg/m^3.

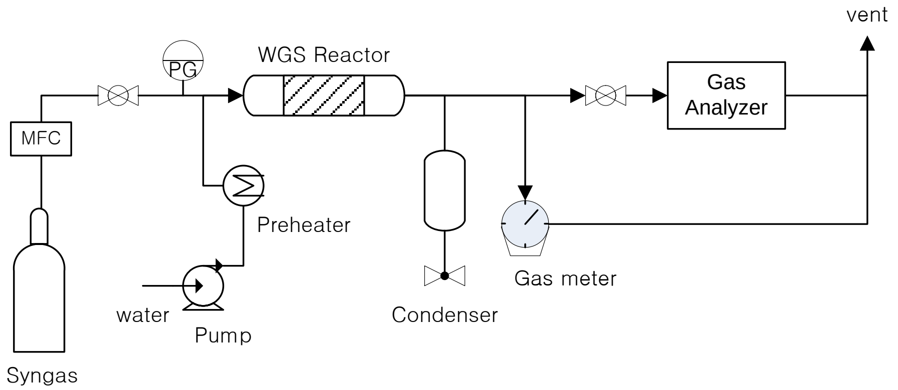

Fig. 2. Schematic diagram of lab-scale WGS reactor

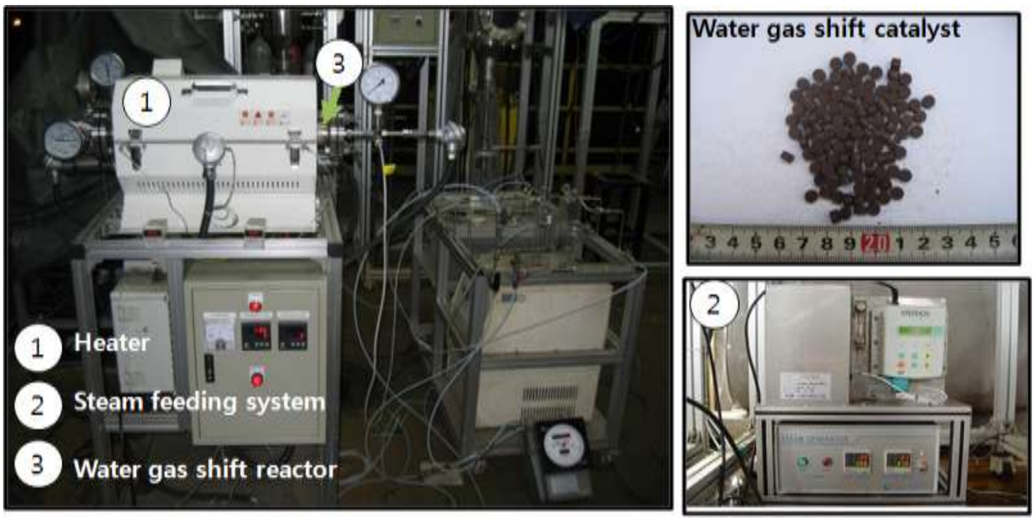

Fig. 3. Picture of lab-scale WGS reactor

Table 3. Inlet syngas compositions

Content	Condition	
	CO	36.35%
	H_2	25.73%
	CO_2	37.57
	CH_4	0.06
Input syngas H_2/CO ratio		0.70

Table 4. Chemical composition of catalyst

Content	
Chemical composition (provided by catalyst company)	Fe_2O_3 88 wt% Cr_2O_3 9wt% CuO 2.6 wt% S < 0.025 wt% Cr^{6+} < 10 ppmw
Chemical composition (By X-ray fluorescence analysis)	Fe 80.7 wt% Cr 12.8 wt% Cu 1.93 wt%
BET*	27 m^2/g
Pore volume*	0.20 cm^3/g
Pore size*	297 Å

* By analysis

During the WGS reaction, the gas composition was analyzed using a portable muilti-component NDIR gas analyzer(model : Delta 1600 S-IV). The chemical composition of the catalyst used for the WGS reactions is listed in Table 4 and the experimental conditions are presented in Table 5.

Table 5. Experimental conditions for WGS reactor

Case	H_2/CO ratio of syngas	Reactor temperature	Syngas flow rate	Steam flow rate	Steam/CO ratio (mole basis)	SV (STP)
		°C	m^3/h	ml/min		1/h
1	0.70	350	0.432	4.7	2.4	458
2		400	0.432	4.7	2.28	458
3			0.432	3.07	1.45	458
4			0.432	5.2	2.45	458
5			0.432	6.25	2.95	458
6			0.432	7.3	3.44	458
7			0.384	5.5	2.92	407
8			0.384	6.48	3.44	407
9			0.252	6.48	5.24	267

The definition of the CO conversion, H_2/CO ratio, steam/CO ratio and SV are shown below.

CO conversion (%)

$$= \frac{\left(Q_{IN}\left(\frac{m^3}{h}\right)\times \text{CO concentration before WGS reaction(\%)}\right)-\left(Q_{OUT}\left(\frac{m^3}{h}\right)\times \text{CO concentration after WGS reaction(\%)}\right)}{Q_{IN}\left(\frac{m^3}{h}\right)\times \text{CO concentration before WGS reaction(\%)}} \times 100$$

$$H_2/\text{CO ratio} = \frac{\text{Hydrogen concentration(dry vol.\%)before or after shift reaction}}{\text{Carbon monoxide concentration(dry vol.\%)before or after shift reaction}}$$

$$\text{Steam/CO ratio} = \frac{\text{Steam flow rate}\left(\frac{ml}{min}\right)\times\frac{60\ min}{1\ h}\times\frac{1\ g}{1\ ml}\times\frac{1\ kmol}{18\ kg}\times\frac{1\ kg}{1000\ g}}{Q_{IN}\left(\frac{m^3}{h}\right)\times\frac{\text{CO concentration befor shift reaction(dry vol.\%)}}{100}\times\frac{1\ kmol}{22.4\ m^3}}$$

$$\text{SV (space velocity)}(h^{-1}) = \frac{Q_{IN}\left(\frac{m^3}{h}\right)}{\frac{\text{catalyst loading weight(kg)}}{\text{catalyst bulk denxity}\left(\frac{kg}{m^3}\right)}}$$

2.2 Catalyst reduction

It is known that the activity and the useful life of catalysts depend mainly on the activation process. In the high temperature WGS process, as previously mentioned, Fe_3O_4-Cr_2O_3 catalysts are used, and the active agent is Fe_3O_4, which is obtained from a partial reduction of Fe_2O_3[15]. Metallic Fe formation must be avoided in the reduction step because it can catalyze the highly exothermic methanation reaction, which can damage the catalyst. One of the ways to avoid this risk is adding steam to the reduction mixture[15]. According to the operating manual provided by the catalyst manufacturing company, it is very important that steam is present during the reduction procedure in order to prevent the over-reduction of the catalyst. In this study, the catalyst reduction was carried out as shown below, and the reduction temperature profile of the catalyst was as shown in Fig. 4.

(a) Temperature of reactor increased to 100°C using nitrogen at 0.5 m^3/h by heating at 50°C per h.
(b) Temperature of reactor increased to 150°C using nitrogen at 0.5 m^3/h with steam of 1.0 ml/min by heating at 50°C per h.
(c) Temperature of reactor increased up 300°C using syngas at 0.5 m^3/h by heating at 50°C per h.

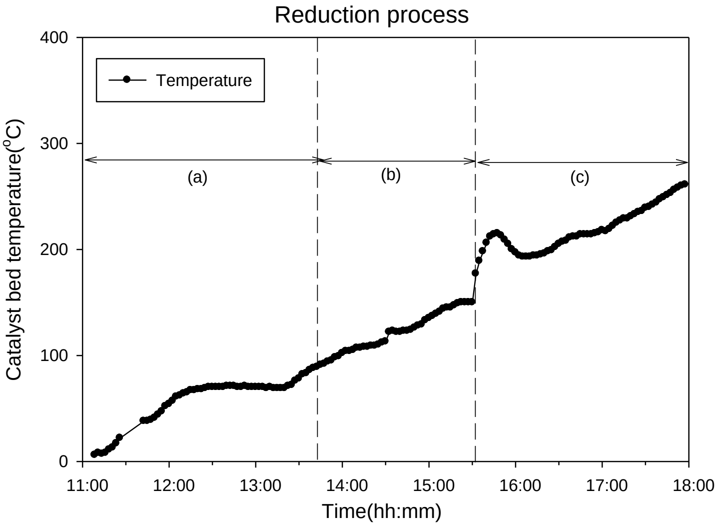

Fig. 4. Temperature profile during reduction process

III. Result And Discussion

3.1 Gas composition for WGS reaction

The gas composition for the WGS reaction in each experiment was measured using an online gas analyzer. The gas compositions for the experiments(CASE 1-CASE 9) are shown in Fig. 5~Fig. 8. CASE 1 used a temperature of 350°C, steam/CO ratio of 2.4 and SV of 458 h^{-1}, CASE 2-CASE 6 used a temperature of 400°C and SV of 458 h^{-1} with various steam/CO ratios, and CASE 7-CASE 9 used a temperature of 400°C with various values for SV and the steam/CO ratio. At a temperature of 350°C, the composition of the syngas after the WGS reaction was 19.25% CO, 34.74% H_2, 45.95% CO_2, while the H_2/CO ratio and CO conversion were 1.18, and 32.98%, respectively. At a temperature of 450°C, the composition of the syngas after the WGS reaction varied with the steam/CO ratio and SV, the H_2/CO ratio after the reaction was in the range of 1.42~3.9, and the CO conversion was in the range of 30.14~64.66%. The initial concentration of CO in the syngas was 36.65%. However the CO concentration after the reaction decreased wigh the increasing steam/CO ratio under the conditions of 400°C and 458 h^{-1}, and the final concentration of CO for CASE 6 was 15.93%. According to the results, if the syngas from waste gasification was used for methanol synthesis using a process based on a ZnO/Cr_2O_3 catalyst, CASE 4 in this study could be the possible operation condition. If the syngas was used for SNG synthesis, CASE 7 or CASE 8 could be available for the WGS process operating condition without adjusting the H_2/CO ratio.

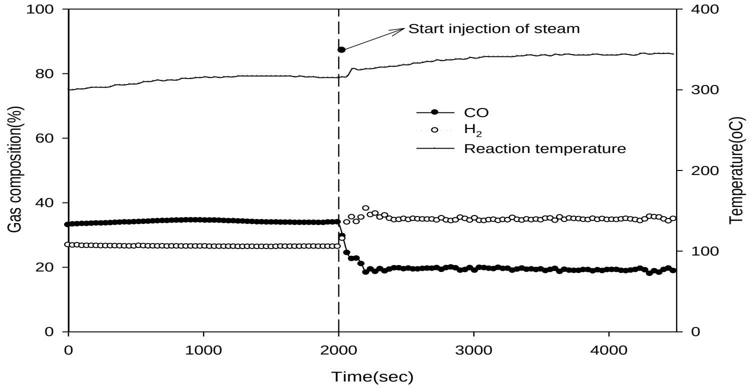

Fig. 5. Gas composition after reaction of CASE 1

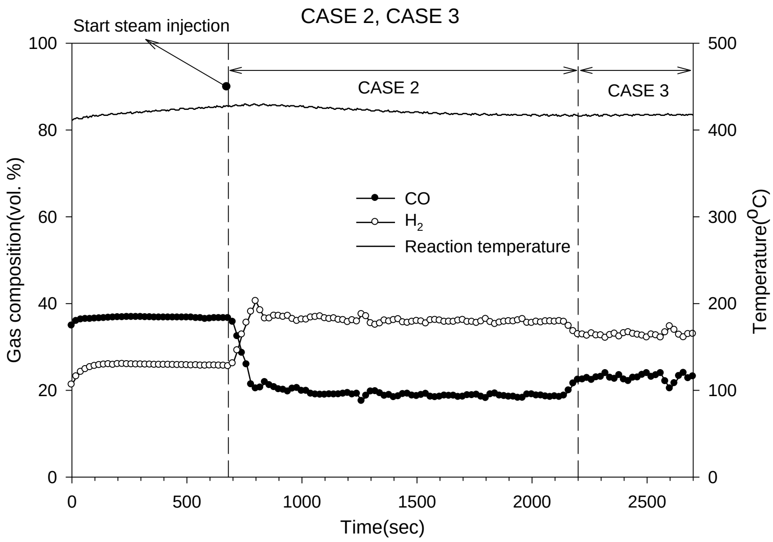

Fig. 6. Gas composition after reaction of CASE 2 and CASE 3

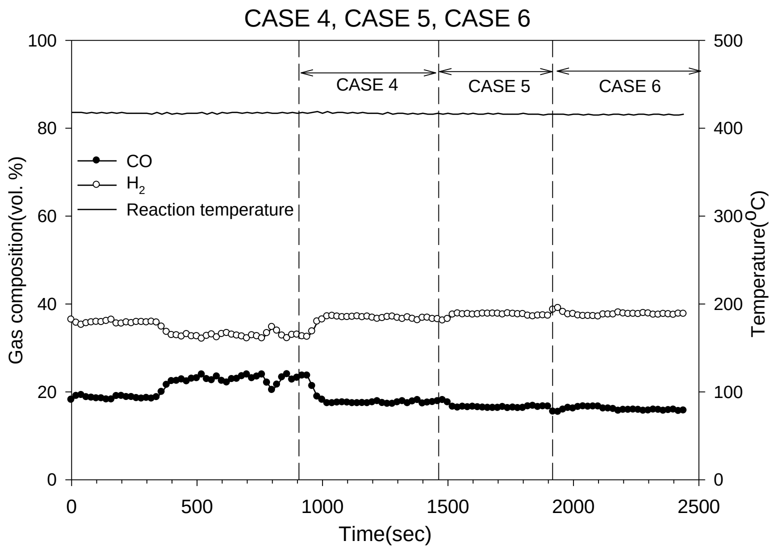

Fig. 7. Gas composition after reaction of CASE 4~CASE 6

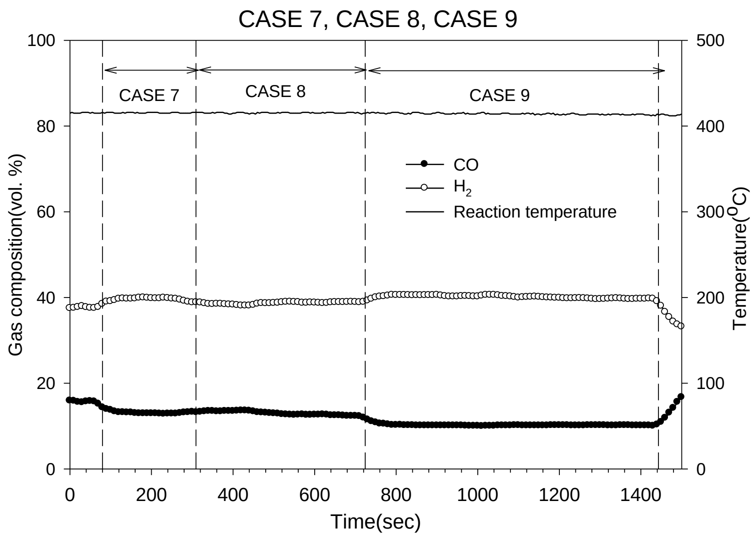

Fig. 8. Gas composition after reaction of CASE 7~CASE 9

3.2 Influence of temperature, steam/CO ratio, and SV

Based on the results of the WGS reaction using syngas from waste gasification, the influences of the reaction temperature, steam/CO ratio, and SV observed in this study are shown in Fig. 9 ~ Fig.11. Fig. 9 shows the influence of the temperature on the H_2/CO ratio and CO conversion when the steam/CO ratio is 2.4 and SV is 458 h^{-1}. At 350°C, the gas composition was 19.25% CO and 49.95% H_2, with a H_2/CO ratio of 1.80 and a CO conversion of 32.98%. At 400°C, the gas composition was 17.54% CO and 45.68% H_2, with a H_2/CO ratio of 2.09 and a CO conversion of 46.84%. The H_2/CO ratio and CO conversion increased with an increase in temperature. The reaction temperature has been reported to be a critical parameter for a WGS reaction[16-21].
It is known that the WGS reaction is thermodynamically unfavorable at high temperatures, and according to stoichiometry, the WGS reaction requires a H_2O/CO molar ratio of 1 to proceed[16] .

For this reason, it is usual to operate with excess vapor water(H_2O/CO equal or higher than 2)[22-23] because this allows a high WGS catalytic performance, avoiding the appearance of side and undesired reactions such as methanation or CO disproportionation[16]. In order to investigate the influence of the steam/CO ratio, tests with steam/CO ratios of 1.45 to 3.44 were conducted. The effect of the steam/CO ratio on the WGS reaction is shown in Fig. 10. This figure shows the results of a WGS reaction with reaction temperature of 400 °C and SV of 458 h^{-1}. The H_2/CO ratio and CO conversion were 1.42 and 30.14%, respectively, when the steam/CO ratio was 1.45. The H_2/CO ratio and CO conversion increased with an increase in the steam/CO ratio, with a H_2/CO ratio of 2.36 and a CO conversion of 51.70% when the steam/CO ratio was 3.44. However, the increase in the CO conversion was insignificant when the steam/CO ratio was greater than 2.9. The influence of SV was investigated at steam/CO ratios of 2.9 and 3.4. Fig. 11 presents the effect of the SV on the H_2/CO ratio and CO conversion at a temperature of 400°C. In terms of the CO conversion, the commercial Fe- based catalyst used in this study seemed to be influenced by the SV at a temperature of 400°C. It has been reported that the CO concentration relies on the GHSV under the same operating condition, so it may influence both the reaction extension and the product distribution[16,22, 24-26].

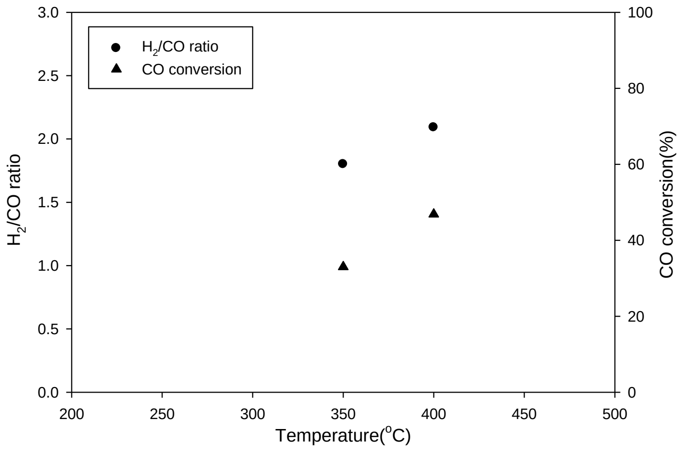

Fig. 9. Influence of temperature on H_2/CO ratio and CO conversion

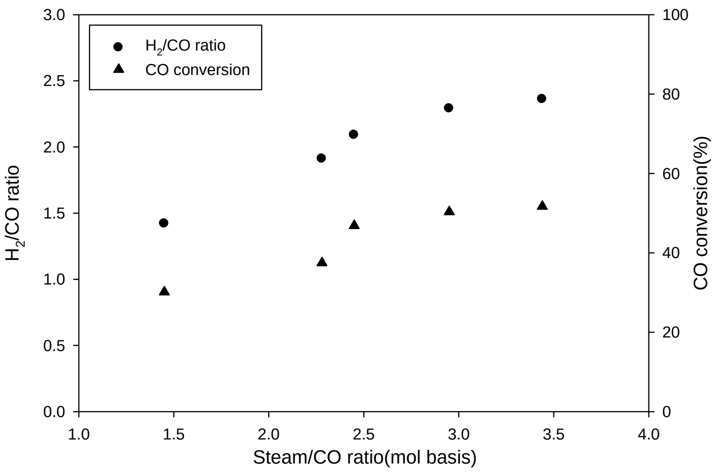

Fig. 10. Influence of steam/CO ratio on H_2/CO ratio and CO conversion

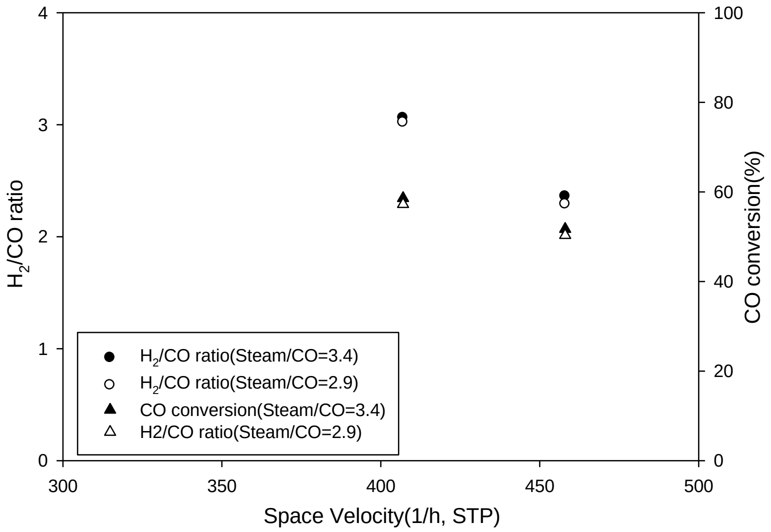

Fig. 10. Influence of space velocity on H_2/CO ratio and CO conversion

IV. Conclusion

As previously mentioned, the WGS reaction is very commonly used for converting carbon monoxide to hydrogen and carbon dioxide, and various studies have been conducted by numerous researchers. However, studies have been conducted related to the WGS reaction using syngas from waste gasification. In this study, the characteristics of a high temperature WGS reaction over a commercial Fe-based catalyst using syngas from waste gasification were investigated and found to be feasible for producing valuable chemical products using lab equipment tests. The CO conversion and H_2/CO ratio were observed with various values for GHSV, steam/CO ratio, and temperature. The WGS reaction performance was found to be influenced by the reaction conditions. An increase in the reaction temperature, an increase in the steam/CO ratio, and a decrease in the SV led to a higher CO conversion rate and H_2/CO ratio. However, the space velocity had a more significant influence on the CO conversion than did the steam/CO ratio when the steam/CO ratio was greater than 2.9.

V. List Of Acronyms & Symbols

Nm^3/h : Normal cubic meter per hour
SNG : Synthesis natural nas or substitute natural nas
SV : Space velocity

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References

[1]. Nobuhiro Tanigaki, Kazutaka Manako, Morihiro Osada, 2012, Co-gasification of municipal solid waste and material recovery in a large-scale gasification and melting system, *Waste Management*, 32, pp667-675
[2]. Arena, U., Zaccariello, L., Mastellone, M.L., 2010. Fluidized bed gasification of waste-derived fuels, *Waste Managemen*t, 30, 1212–1219
[3]. Arena, U., 2012, Process and technological aspects of municipal solid waste gasification. A review, *Waste Management*. 32, 625–639.
[4]. Albertazzi. S, Basile. F., Brandin. J., Einvall. J., Hulteberg. C., Fornasari. G., Rosetti. V., Sanati. M., Trifiro. F., Vaccari. A., 2005, The technical feasibility of biomass gasification for hydrogen production, *Catalysis Today*, 106, pp297-300
[5]. Koppatz, S., Pfeifer, C., Rauch, R., Hofbauer, H., Marquard-Moellenstedt, T., Specht, M., 2009. H2 rich product gas by steam gasification of biomass with in situ CO2 absorption in a dual fluidized bed system of 8 MW fuel input. *Fuel Process Technology*, 90, 914–921.
[6]. Aigner, I., Pfeifer, C., Hofbauer, H., 2011. Co-gasification of coal and wood in a dual fluidized bed gasifier. *Fuel* 90, 2404–2412.
[7]. Einvall, J., Parsland. C., Benito. P., Basile. F., Brandin. J., 2011, High temperature water-gas shift step in the production of clean hydrogen rich synthesis gas from gasified biomass. *Biomass Bioenergy* 35, S123–S131
[8]. Rethwisch. D.G., Dumesic. J.A., 1986, Adsorption and catalytic properties of supported oxide : III. Water-gas shift over supported iron and zinc oxide, *Journal of Catalysis*, 101, 35-42
[9]. Ovesen. C.V., Stoltze. P., Nørskov. J.K., Campbell. C.T., 1992, A kinetic model of the water gas shift reaction, *Journal of catalysis*, 134, 445-468

[10]. Callaghan. C., Fishtik. I., Datta. R., Carpenter. M., Chmielewski. M., Lugo. A., 2003, An improved microkinetic model for the water gas shift reaction on copper, *Surface Science*, 541, 21–30.

[11]. Fishtik I, Datta R., 2002, A UBI-QEP microkinetic model for the water-gas shift reaction on Cu(111), *Surface Science*, 512, 229–254

[12]. Ovesen. C.V., Clausen. B.S., Hammershøi. B.S., Steffensen. G., Askgaard. T., Chorkendorff. I., Nørskov. J.K., Rasmussen. P.B., Stoltze. P., Taylor. P., 1996, A Microkinetic analysis of the water-gas shift reaction under industrial conditions, *Journal of catalysis*, 158, 170-180

[13]. Wang. G., Jiang. L., Zhou. Y., Cai. Z., Pan. Y., Zhao. X., Li. Y., Sun. Y., Zhong. B., Pang. X., Huang. W., Xie. K., 2003, Investigation of the kinetic properties for the forward and reverse WGS reaction by energetic analysis, *Journal of Molecular Structure(Theochem)*, 634, 23-30

[14]. Burcu Selen C, Ahmet Erhan A, 2009, Water-gas shift reaction over Bimetallic Pt-Ni/Al_2O_3 Catalysts, *Turk J Chem* 33, 249-256

[15]. Gonzalez, J.C., Gonzalez. M.G., Laborde. M.A., Moreno. N., 1986, Effect of temperature and reduction on the activity of high temperature water gas shift catalyst, *Applied Catalysis*, 20, 3-13

[16]. Osa, A.R. de la, Lucas A. De, Romero. A, Casero. P, Valverde. J.L., Sanchez. P., 2012, High pressure water gas shift performance over a commercial non-sulfide CoMo catalyst using industrial coal-derived syngas, *Fuel* 97, 428–434

[17]. Yu. J., Tian FJ, Mckenzie LJ, Li CZ. 2006, Char-supported nano iron catalyst for water–gas-shift reaction: hydrogen production from coal/biomass gasification, *Process Safety Environmental protection* ,84:125–30.

[18]. Maiya PS, Anderson TJ, Mieville RL, Dusek JT, Picciolo JJ, Balachandran U.Maximizing, 2000, H2 production by combined partial oxidation of CH4 and water gas shift reaction. *Applied Catalysis A: General* ,196:65–72.

[19]. Luengnaruemitchai A, Osuwan S, Gular E. 2003, Comparative studies of lowtemperature water–gas shift reaction over Pt/CeO2, Au/CeO2, and Au/Fe2O3 catalysts. *Catalysis Communications*, 4, 215–21.

[20]. Djinovic P, Batista J, Pintar A., 2008, Calcination temperature and CuO loading dependence on CuO–CeO2 catalyst activity for water–gas shift reaction, *Applied Catalysis A: General*, 347:23–33.

[21]. Gunawardana PVDS, Lee HC, Kim DH. 2009, Performance of copper-ceria catalysts for water gas shift reaction in medium temperature range. *International Journal of Hydrogen Energy*, 34, 1336–1341.

[22]. Hakkarainen, R., Salmi, T., 1993. Water–gas shift reaction on a cobalt-molybdenum oxide catalyst. *Applied Catalysis A: General*, 99, 195–215.

[23]. Tavasoli A, Malek Abbaslou RM, Dalai AK. 2008, Deactivation behavior of ruthenium promoted Co/c-Al2O3 catalysts in Fischer–Tropsch synthesis. *Appled Catalysis A: General*, 346:58–64.

[24]. Roberts GW, Chin P, Sun X, Spivey JJ. 2003, Preferential oxidation of carbon monoxide with Pt/Fe monolithic catalysts: interactions between external transport and the reverse water–gas-shift reaction. *Applied Catalysis B: Environmental* ,46:601–11

[25]. Barbieri G, Brunetti A, Tricoli G, Drioli E., 2008, An innovative configuration of a Pdbased membrane reactor for the production of pure hydrogen: experimental analysis of water gas shift, *Journal of Power Sources*, 182, 160–167

[26]. Pradhan S, Satyanarayana Reddy A, Devi RN, 2009, Satyanarayana Chilukuri. Copperbased catalysts for water gas shift reaction: influence of support on their catalytic activity. *Catalysis Today*,141:72–6.