

The Comparison Study of Hydrogen Production Derived from Gasification System with CO₂ Reduction with Various Feedstocks

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ABSTRACT: Gasification technology is recognized as next generation power plant technology which can replace conventional fossil fuel power plant. It produces not only electricity but also chemical energy as a form of syngas. The syngas can be further transformed into valuable chemicals such as H₂, DME and liquid fuel etc. It is focused on hydrogen and power (Co-gen) gained by gasification system which is based on 300MW_{th} scale gasification plant with various feedstocks such as Illinois#6 coal, heavy residue oil (bunker-C, naphtha) and bitumen of oil sand in this study. Besides it is considered gasification system with options of CO₂ capture technology. The simulation model of the gasification plant is composed of sub-process such as fuel preparing, gasification, ash removal, acid gas removal (AGR) and H₂ production process model based on ASPEN plus. Then adding CO₂ capture models to the base model of gasification system, its models are compared with their performance of the systems. To research performance of these models, evaluating parameters are chosen as cold gas efficiency and carbon conversion of gasifier, carbon dioxide capture efficiency and production rate of H₂ and plant net efficiency.

Keywords: gasification, hydrogen, CO₂ capture, poly-feedstock, ASPEN plus

Nomenclature

<i>BC</i>	bunker-C	<i>LHV</i>	lower heating value [kcal]
<i>BT</i>	bitumen	<i>M_C</i>	molecular weight of carbon
<i>C_i</i>	mole fraction of <i>i</i> component	<i>M_{CO2}</i>	molecular weight of carbon dioxide
<i>CC</i>	carbon conversion [%]	<i>NP</i>	naphtha
<i>CGE</i>	cold gas efficiency [%]	<i>P_{net}</i>	net power [MW]
<i>CWS</i>	coal water slurry	<i>PDC</i>	pulverized dry coal
<i>F_t</i>	flow rate of product gas [kmol/hr]	<i>U_C</i>	carbon content of ultimate analysis
<i>HV_f</i>	higher heating value of fuel per unit mass [kcal/kg]	<i>m_c</i>	mass flow rate of carbon [ton/hr]
<i>HV_i</i>	higher heating value of component <i>i</i>	<i>m_f</i>	mass flow rate of input fuel [ton/hr]
<i>HHV_f</i>	higher heating value of fuel [kcal]	<i>p_{H2}</i>	hydrogen production rate [ton/hr]
<i>IC6</i>	Illinois #6 coal	<i>ε_{CO2}</i>	CO ₂ capture ratio
		<i>η_H</i>	hydrogen production efficiency [%]
		<i>η_P</i>	net power efficiency [%]

1. Introduction

In these days we have been facing high price of crude oil since oil shock in 1970's and crisis of climate change, so it need to get over crisis of energy and environment are required to be developed alternative technologies which considered clean and low fuel cost. Hydrogen is high quality energy carrier, contains no carbon and generates little or no polluting emissions at the point of use. A hydrogen based energy system is an advantageous option for delivering efficient, clean and safe energy in a wide range of application [1]. However it has clean and renewable characteristics, hydrogen infra such as production, storage, transportation and safety technology are still lacking in common utilization at present society. Most of the hydrogen is made by steam reforming of natural gas (CH_4), but the price of natural gas is also increased to accompanying with oil price. According to statistics data of AEO2008, price of natural gas has almost three times higher than industrial coal [2]. That hasn't an attractive method of hydrogen production. So the use of raw rank energy such as coal, heavy residue oil, and bitumen is desirable, being a low cost fuel and guaranteeing long-term availability. Gasification is well-established technology, has broad flexibility of feedstocks and operation, and is the most environmentally friendly route for handling these feedstocks for producing hydrogen.

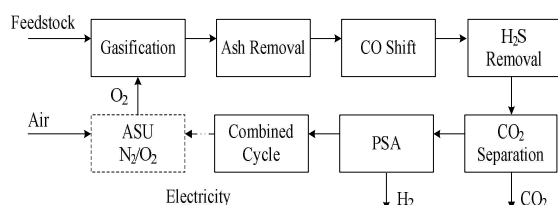


Figure 1. Flow scheme of hydrogen production process with gasification

For producing hydrogen with gasification technology, it follows to proceeding technology such as acid gas (H_2S and CO_2)

removal and gas separation from syngas. It is focused on flow scheme of hydrogen production process with gasification technology like Fig.1 in this study.

The concept of hydrogen production process states that syngas (mainly CO and H_2) is passed through CO shift process; CO converted into CO_2 with increasing H_2 of syngas. Then both H_2S and CO_2 are captured from shifted syngas, high purity of H_2 is obtained from PSA (pressure swing adsorption) process. And tail-gas from PSA is used for generating power which can supply required power for producing H_2 in the plant.

2. Simulation Assumption and Condition

To research characteristics of H_2 production process with gasification dependent on various feedstock, base model of H_2 production process is developed with coal amounts (approximately 2,500 ton/day) of 300 MW_{th} scale IGCC power plant using ASPEN plus. Then constructed base model is composed of preparing fuel, gasification, ash removal, acid gas removal (AGR), CO shift process, CO_2 capture and H_2 separation with PSA.

Feedstocks for the gasification were selected pulverized and slurry type based on Illinois #6 coal, naphtha, bunker-C and bitumen, characteristics such as ultimate, proximate analysis and heating value of each feedstock were presented in Table 1. Illinois#6 coal has lower carbon (71.72%) and hydrogen (5.06%) content than carbon (84.4~86.9%) and hydrogen (12.1~15.6%) of heavy residue oil. On the other hand, the coal has higher oxygen (8.08%) and ash (10.91%) content than oxygen (~0.15%) and ash (~0.05%) of heavy residue oil. Both HHV and LHV of feedstocks are calculated by modified Dulong's equation with values of ultimate analysis.

Table. 1. Proximate, ultimate analysis and heating values of fed fuels

		IC6	BC	NP	BT
Proximate Analysis (wt %)	M	11.2	-	-	-
	V.M	34.99	-	-	-
	F.C	44.19	-	-	-
	Ash	9.7	-	-	-
Ultimate Analysis (wt %)	C	71.72	84.4	86.9	83.2
	H	5.06	15.6	12.1	10.8
	O	8.08	<0.01	0.15	1.36
	N	1.41	<0.5	0.5	0.72
	S	2.82	142ppm	0.3	3.95
	Ash	10.91	20ppm	0.05	0.00
¹)HHV (kcal/kg)		7,217	10,659	11,432	10,033
²)LHV (kcal/kg)		6,951	10,024	10,613	9,466

1) $HHV \text{ (kcal/kg)} = 83.43 \times C + 281.6 \times H - 24.71 \times O - 3.61 \times N + 24.02 \times S - 5.04 \times \text{Ash}$

2) $LHV \text{ (kcal/kg)} = 83.43 \times C + 281.6 \times H - 24.71 \times O - 3.61 \times N + 24.02 \times S - 5.04 \times \text{Ash} - 52.53 \times H$

1), 2) heating values are calculated by modified Dulong's equation

For comparing hydrogen production efficiency (η_H) of base model, input of fuels and utilities are equivalently calculated at the base model of gasification plant for each feedstock. Supplying conditions of input fuels and utilities are presented in Table 2. ASU is abbreviated in this study. It is assumed that utility gases such as O₂, N₂ and air are separated from ASU.

Table. 2. Input conditions of each feedstock

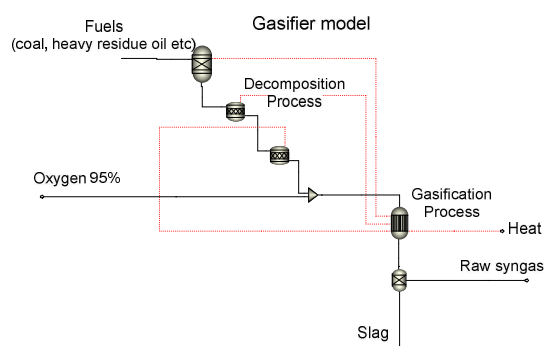
Flow rate (tons/hr)	IC6	BC	NP	BT
Fuel	87.5	65.9	61.5	70
Oxygen	75.1	74.5	69.5	79
Nitrogen	6.65	-	-	-
Water (steam)	-	-	-	-
	(2.6)	(30.2)	(30.1)	(30.1)
O ₂ /Fuel	0.858	1.131	1.130	1.128
(H ₂ O+O ₂)/Fuel	0.89	1.59	1.62	1.56

3. Simulation of Unit Process

3.1. Gasification process

The gasifier model is divided by 4 sections such as decomposition, gasification, soot and slag generation, its process model is shown in Figure 2. The gasifier model is composed of thermal decomposition process which changed organic materials such as H₂, N₂, O₂, C and S from char coal particles and gasification process which proceeded to

partial combustion of carbon particle and organic materials.

**Figure 2.** Simulation model of gasifier

It is assumed that PDC, BC, NP and BT gasifier is identically operated at 28 kg/cm², 1420°C. CWS gasifier is operated at 43 kg/cm², 1370°C in this study. However gasification mechanism complexes with various reactions, those are simplified to limit 11 major reactions in this model [3].



Ahead of 11 reactions are calculated by approaching minimization of Gibbs free energy in the RGibbs block of ASPEN plus. RGibbs model assumes to approach to an equilibrium state, but actual gasification reaction happens to react in non-equilibrium state under short resident time inner gasifier.

So the gasifier block is reflected inert effect as considering non-equilibrium reaction between reactants of syngas in the

gasifier model. For describing degree of participation between syngas components inner gasifier, it is defined inert fractions for each components inner gasifier model.

3.2. Gas clean up process

Gas clean-up section is composed of ash removal and acid gas removal process. For removing solid particles such as fly-ash inner syngas, this syngas is passed through the cyclone and metal filter by turns, fly-ash on the inside syngas is removed to near the 99% of removal efficiency.

Then ash-free syngas lead to acid gas removal (AGR) process which can be captured acid gases (CO_2 , H_2S) by absorbent as 20 wt% of MEA absorbent, this MEA absorption process is operated at the range of 40~110°C. The absorbent is recycled between absorber and regenerator column, absorbent has 95~99% of acid gas removal efficiency.

3.3. CO shift / H_2 separation process

Before producing hydrogen from syngas is mainly composed of CO and H_2 gas, CO component inner syngas is led in high purity of H_2 with generating CO_2 by water gas shift reaction. Water gas shift reaction (WGSR) is an important reaction in extra H_2 production from syngas. The WGSR is carried out in two reactors high-temperature (HT-SR) and low-temperature shift reactors (LT-SR) in series [4].

CO shift reaction is respectively derived from Cu/ZnO/ Al_2O_3 catalyst be used in LT-SR, whereas Fe_2O_3 - Cr_2O_3 catalyst be used in HT-SR. However, it is assumed that two CO shift reactions are approaching equilibrium state without catalyst effects in this process model. CO shift process is largely composed of 450°C, 3.5 kg/cm² of HT-SR and 220°C, 3.5 kg/cm² of LT-SR [4]. Steam adding to both shift reactors are passing through two heat exchangers, syngas mixed with steam is individually fed to diverged 25% stream of HT-SR and 75% of LT-SR like Figure 3.

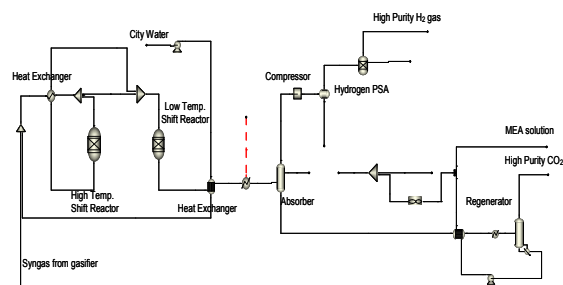


Figure 3. Simulation model of hydrogen production process

After being shifted syngas in CO shift process, syngas has mainly both H_2 and CO_2 component in shifted syngas. Next, the gas is passed through CO_2 removal process with 20 wt% of MEA absorbent. At last syngas is separated by PSA tower which can obtain H_2 with 99.9% of purity. The driving force for H_2 separation is the difference has a minimum pressure ratio of approximately 4:1 in impurity partial pressure between feed and tail-gas in hydrogen purification. However, the absolute pressure of the feed and tail-gas is also important, particularly for hydrogen recovery. Specially, the optimum tail-gas pressure is as low as possible. Because vacuum is normally avoided, tail-gas pressures of 0.3~0.7 kg/cm² are typically used when high hydrogen recovery is desired [5]. Typically, a multi-step, multi-column PSA process consisting of 4 to 12 adsorbers is used in industrial site [8]. But PSA model of this study is simplified to assume one PSA block through Ryield block which set performance of hydrogen yield.

3.4. Power generation

Tail-gas from hydrogen PSA is used for generating power which being required to supply in power plant. A co-generation power plant is modelled by combined cycle which has been operated at Shell Pernis in Netherlands. That power island was composed of 2 gas turbines (GE MS 6541B) and 2 steam turbines. The specification of gas turbine is shown in Table 3. NO_x emission from the gas turbine is controlled

by steam injection. The steam generated by the gasification effluent boilers is directly fed into the steam drum of the gas turbine [6]. The two combined cycle generate 131 MW of net plant output by provided specification of performance.

Table. 3. Comparison between reference (M6581B) and simulation model of gas turbine

Parameters	M6581B	GT model
Exhaust Temp(°C)	544	490-600
Pressure ratio	12.0:1	12.0:1
Diluent	steam	steam
Generating power (MW)	43.5	40

It is assumed that real plant has two combined cycles, but simulation model has one combined cycle which can indicate power output in this study.

4. Results and Discussions

Before discussing the results of simulation model for H₂ production with gasification, it is defined in following Eq.12 ~ Eq.14 of gasification performance such as cold gas efficiency (*CGE*), carbon conversion (*CC*) and net power efficiency (η_p). Product gas is limited by combustible component (*i*= CO, H₂, CH₄) at Eq.12.

$$CGE(\%) = \frac{\sum_i (C_i \times HV_i) \times F_i \text{ [kcal]}}{HV_f \times m_f \times 10^{-3} \text{ [kcal]}} \times 100 \quad (12)$$

Total generated carbon in product gas (syngas) is calculated by components included carbon such as CO, CO₂ and CH₄ in Eq.13.

$$CC(\%) = \frac{\sum_i C_i \times F_i \text{ [kmol / h]}}{0.833 \times m_f \times U_c \text{ [kmol / h]}} \times 100 \quad (13)$$

$$\eta_p = \frac{P_{net} \text{ [MW]}}{HHV_f \text{ [kcal]}} = \frac{P_{net}}{HV_f \times m_f \times 10^{-3}} \quad (14)$$

After simulating hydrogen production process models for 5 cases of feedstock (pulverized dry coal; PDC, coal water slurry; CWS, bunker-C; BC, naphtha; NP, bitumen; BT), it were obtained gasification characteristics of gasifier for each case like Table 4. The H₂/CO ratio of syngas was individually appeared H₂ lean atmosphere of PDC (0.507) and CWS (0.892), the other side heavy residue oil such as BC (1.231), NP (1.168) and BT (1.223) were appeared H₂ rich.

Table. 4. Operating conditions of gasifier and gasification characteristics by various feedstock

		PDC	CWS	BC	NP	BT
T _{gasifier} (°C)		1420	1370	1420	1420	1420
P _{gasifier} (kg/cm ²)		28	43	28	28	28
O ₂ /fuel		0.858	0.616	1.131	1.130	1.129
(H ₂ O+O ₂)/fuel		0.888	1.222	1.589	1.620	1.559
H ₂ /CO		0.507	0.892	1.231	1.168	1.223
F _{syngas} (kmol/h)		7,528	8,392	11,148	10,525	11,729
Syngas Composition mole fraction	CO	0.605	0.408	0.376	0.363	0.386
	CO ₂	0.047	0.055	0.032	0.041	0.026
	H ₂	0.307	0.364	0.450	0.424	0.472
	CH ₄	350ppm	58ppb	110ppm	72ppm	162ppm
	O ₂	trace	32ppm	trace	trace	trace
	N ₂	0.038	0.007	0.008	0.008	0.007
	H ₂ S	trace	253ppm	107ppm	105ppm	108ppm
	COS	51ppm	18ppm	4ppm	4ppm	4ppm
	NH ₃	151ppm	4ppm	27ppm	26ppm	29ppm
	H ₂ O	0.003	0.165	0.130	0.160	0.105

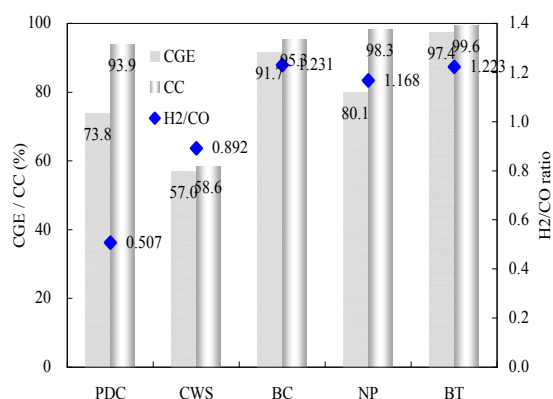
For increasing H₂ concentration of syngas, syngas was shifted from CO to CO₂ at CO shift reactor. Then CO₂ component of shifted syngas was captured by 20 wt% of MEA absorbent in AGR process. The captured CO₂ gas in MEA absorbent is separated by adding heat at regenerator column. This CO₂ is equal to CO₂ avoidance. For indicating CO₂ capture ratio in this section, it was defined in following Eq.15 [7].

$$\varepsilon_{CO_2} = \frac{m_{CO_2 \text{ removal}}}{m_{C, \text{ fuel}} \times (M_{CO_2} / M_C)} \quad (15)$$

Table. 5. CO₂ capture performance by various feedstock (acid gas stream at regenerator column in AGR process)

	PDC	CWS	BC	NP	BT
CO ₂ conc. (wt%, captured gas)	64.4	50.9	84.9	84.8	84.8
Carbon of fuel (ton/h)	230.1	291.9	209.9	190.3	213.5
CO ₂ avoidance (ton/h)	214.8	100.4	123.2	125.4	121.1
CO ₂ capture ratio (ϵ_{CO_2})	93.3	34.4	58.7	65.9	56.7

The CO₂ capture performances for each feedstock were shown in Table 5. By this result, PDC was relatively shown 93.3% of CO₂ capture ratio with 64.4% of CO₂ concentration. CWS, on the other hand, was shown 34.4% of lowest CO₂ capture ratio. CO₂ capture ratios of the others such as BC, NP and BT were indicated at the range of 56.7~65.9%.

**Figure 4.** Gasification performances (CGE, CC, H₂/CO ratio) dependent on various feedstocks

The factors of both CGE and CC can explain gasification performance of gasifier. So gasification performances dependent on feedstock are shown in Fig 4. BT has the highest value of CGE (97.4%) and CC (99.6%). But so CWS has included extra 35% of H₂O in fed fuel, it hasn't only lower CC (58.6%) but also CGE (57%) than PDC (CGE: 73.8%, CC: 93.9%). The CGE has had a tendency of rise as the oxygen ratio fed to gasifier increased [9].

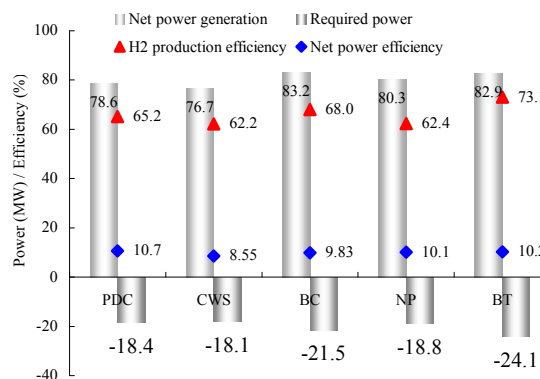
For comparing H₂ production efficiency between 5 cases of feedstock, it was defined as hydrogen production efficiency (η_H) like Eq.16.

$$\eta_H = \frac{P_{H_2} \times HHV_{H_2}}{m_f \times HV_f} \quad (16)$$

It was considered that H₂ and power were simultaneously produced by co-generation concept. So those results for each feedstock were respectively indicated at Table 6 and Figure 5. According to results of Table 6, 5 cases could produce average 328 ton/day of hydrogen approximately. BT had the highest value of H₂ production efficiency as 73%. H₂ production efficiency was appeared higher value, however, it was shown that tendency of power required for producing H₂ was increasing.

Table. 6. Hydrogen production and power generation (Co-gen) dependent on various feedstocks

	PDC	CWS	BC	NP	BT
H ₂ Production (ton/day)	291	340	338	311	364
H ₂ production efficiency (η_H , %)	65.2	62.2	68.0	62.4	73.1
Required power of H ₂ production (MW)	18.4	18.1	21.5	18.8	24.1
Net Power Generation (MW)	78.6	76.7	83.2	80.3	82.9
Net Power efficiency (η_P , %)	10.7	8.55	9.83	10.1	10.2

**Figure 5.** H₂ production performances dependent on various feedstocks

5. Conclusion

It was performed comparison study for hydrogen and power generation system which have co-generation concept with gasification technology applied to 5 cases of feedstock such as pulverized dry coal and coal water slurry (from Illinois#6 coal), bunker-C, naphtha and bitumen. Simulation models of hydrogen production process were based on Shell Pernis refinery plant, simulated by ASPEN plus. It could be evaluated H₂ production system dependent on 5 cases of feedstock under equivalent conditions through gasification performance parameters such as cold gas efficiency, carbon conversion and H₂/CO ratio of syngas in gasification section. In the process of H₂ production, CO₂ capture performance and H₂ production efficiency were respectively suggested.

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