CHEMICAL ENGINEERING TRANSACTIONS
VOL. 52, 2016

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Peng-Yen Liew, Jun-Yow Yong, Jiří Jaromír Klemeš, Hon Loong Lam

ISBN 978-88-95608-42-6; **ISSN** 2283-9216

DOI: 10.3303/CET1652079

Warm Syngas Clean-up Processes Applied in Synthetic Natural Gas (SNG) Production with Coal and Biomass

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In Taiwan, the Greenhouse Gas Reduction Act has been issued since 2015, which sets the target to reduce greenhouse gas (GHG) emissions to 50 % of the 2005 level by 2050. Natural gas is one of the options to reduce the GHG emissions due to lower CO_2 emission in electricity generation. The value discharged from NGCC (natural gas combined-cycle) is near half of that from coal-fired power plant. The price of natural gas in Taiwan is substantially higher than that of coal, which results in the situation that near 50 % of electricity is generated from coal and the capacity factor of NGCC units is relatively low. If cheaper gas fuel could be provided to domestic NGCC units, their capacity factor could be increased; then, the CO_2 emission in power sector could be decreased to help meet the GHG reducing target. Synthetic natural gas (SNG) from solid fuel via gasification is possible to provide a relatively lower price than that of natural gas to NGCC units in Taiwan. The price of SNG from coal has been studied in 2012, and the results showed that the mean price of SNG is US$ 12.27 /MMBtu, while the liquefied natural gas (LNG) is US$ 14.32 /MMBtu. It shows the possibility to decrease the CO_2 emission with relatively lower cost of electricity in Taiwan.
The SNG production processes have been built with the commercial chemical process simulator, Pro/II® V8.1.1, to analyse the efficiency improvement with warm gas clean-up processes. The four major blocks, consisted of air separation unit (ASU), gasification island, gas clean-up unit, and methanation processes, were built in a previous study. Two different parts in the study, i.e., warm syngas clean-up processes and another kind of biomass that is possibly used in Taiwan. The warm gas clean-up process is implemented to keep the temperature of syngas in the range of 400 °C to increase the available energy which is compared with typical one with lower temperature. A series of sorbents are selected for the processes: e.g., Na_2CO_3-based sorbent to remove HCl and ZnO-based sorbent to deminish sulphur contained in syngas, while CaO-based sorbent for removal of CO_2 to enhanced the methanation processes. The results show that the energy penalty of CO_2 capture could be improved as warm gas clean-up processes are adopted in the system. Biomass could further reduce the CO_2 emission, due to the advantage of carbon neutral feature. The effect of biomass blended with coal shows the similar trend with previous study, i.e., the system performance is slightly decreased with the blend percentage of biomass.

1. Introduction

British Petroleum (2015) reported that the world primary energy consumption increased by just 0.9 % in 2014 and well below the 10-y average of 2.1 %. Although the energy consumption looks like slowing growth, it still means the growth in global CO_2 emission from energy use accelerated. The world reserves of oil, natural gas and coal at the end of 2014 are 1, $700.1 \cdot 10^9$ bbl, $181.1 \cdot 10^9$ m^3 and 891,531 Mt, while the reserve-to-production ratios for oil, natural gas and coal are 52.5, 54.1 and 110 years, respectively.
Taiwan is an isolated island with dense population and limited natural resources. In 2014, the dependence on imported energy in Taiwan is 97.75 %, which means that Taiwan is highly dependent on fossil fuels. The status of energy supply in Taiwan, by primary energy statistics, is described as follows: the percentages of crude oil, coal, natural gas, nuclear and others are 48.52 %, 29.20 %, 12.23 %, 8.33 % and 1.72 %,

Please cite this article as: Chen P.-C., Chiu H.-M., Chyou Y.-P., Svoboda K., 2016, Warm syngas clean-up processes applied in synthetic natural gas (sng) production with coal and biomass, Chemical Engineering Transactions, 52, 469-474 DOI:10.3303/CET1652079

respectively. The portfolio of electricity generation spreads over coal, gas, oil, nuclear, pumped hydro and renewable (conventional hydro, wind, solar, biomass and waste), with the portions of 46.94 %, 28.97 %, 2.79 %, 16.3 %, 1.2 % and 3.8 %, respectively (Bureau of Energy, 2015). It could be expected that the power generated from fossil plants will be increased to cover the shortage of electricity supply in Taiwan.

Taiwan government has inaugurated the Greenhouse Gas Reduction Act to reduce greenhouse gas (GHG) emission to 50 % of the 2005 level by 2050. One of the activities is increasing the amount of natural gas in electricity generation due to less carbon footprint and the present lower capacity factor of NGCC (natural gas combined-cycle) units. It is possible to convert solid fuel which has lower price to synthetic natural gas (SNG) via gasification to provide the relative lower price than that of natural gas to decrease the cost of electricity. Chen et al. (2014) reported the efficiency study of NGCC plant fed with SNG as well as mixture gas of syngas and SNG in Taiwan. Biomass was introduced to blend with coal for converting to SNG in a later study by Chen et al. (2015), and the results showed that the major advantage of biomass introduced in the SNG production is the reduction of CO_2 emission. The purposes of the present study are to introduce the warm syngas clean-up processes in the system, and to perform analyses on the system efficiency and CO_2 emission for the blend of coal and biomass to convert SNG based on gasification.

2. Process description

Blending two or more fuels as feedstock and feeding to gasifier is generally used to handle coal, biomass, and waste (André et al. 2014). The kaltim prima coal (KPC), wood chip, and Empty Fruit Bunches (EFB) are investigated in the previous study to understand the effect on the system efficiency from solid fuel to SNG (Chen et al., 2015). Another kind of biomasses that are possibly used in Taiwan was employed to compare with the previous study. The proximate and ultimate analyses of the three solid fuels are shown in table 1. Warm syngas clean-up processes were also introduced to keep the temperature of syngas higher than that in typical cleaning processes to increase the available energy in the system.

Table 1: The proximate and ultimate analyses of KPC, wood chip and EFB

	kaltim prima coal (KPC)	wood chip	EFB
Total Moisture % as received	10.5	-	
Proximate Analysis % air dried basis			
Moisture	5	15.67	5.18
Ash	5	4.51	3.45
Volatile Matter	41		82.58
Fixed Carbon	49		8.97
Calorific Value kcal/kg			
Air dried	7,100	3,974.70	4,067.9
Gross as received	6,689		
Net as received	6,389		
Ultimate Analysis (DAF)%			
Carbon	80	45.22	46.62
Hydrogen	5.5	5.56	6.45
Nitrogen	1.6	0.50	1.21
Sulfur	0.7	0.27	0.035
Oxygen	12.2	48.46	45.66

There are four major blocks in the solid fuels to SNG production system; they are air separation unit (ASU), gasification island, gas clean-up unit, and methanation processes. The simulated model was built with commercial chemical process simulator, Pro/II® V8.1.1. The process flow diagram is shown as Figure 1, and processes are described in the following sections.

2.1 Air separation unit (ASU)

Cryogenic air separation technology is the most common technology with efficiency and cost-effectiveness to produce large quantities of oxygen and nitrogen. A conventional, multi-column cryogenic rectifying process, which produces oxygen from compressed air at high recoveries and purities, is used in ASU. There are five major unit-operations to cryogenically separate air into useful products. Oxygen with purity of 95% by volume is produced as gasification agent and delivered to the gasification island to avoid the nitrogen in the syngas that will decrease the purity of SNG in the study.

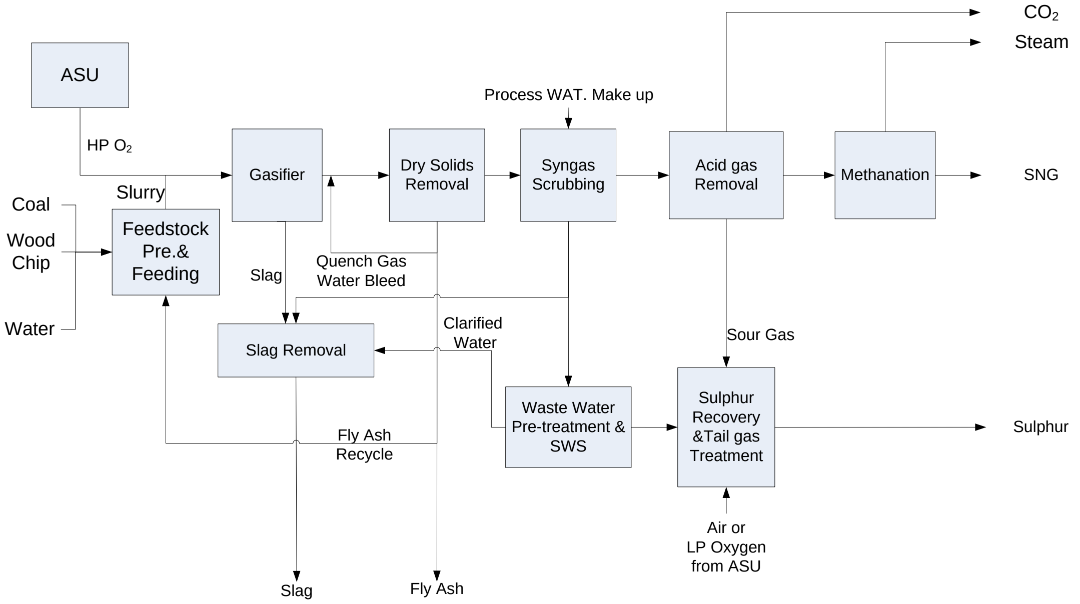

Figure 1: Process flow diagram of solid fuels to synthetic natural gas Gasification island

Solid fuel can be converted to gaseous fuel with a useable heating value via gasification. Gasification is a complicated process consisted of partial-oxidation reactions in gasifier that is operated at a high temperature in the range of 800 °C to 1,800 °C. The temperature is affected by the type of gasifier, characteristics of the feedstock and operation conditions (Higman and Burgt, 2003).

The main compositions of syngas are H_2, CO, CO_2 and H_2O. There are three major reaction equations for gasification, which are listed as follows. Eqs(1) and (2) are endothermic gasification reactions, to which the heat is supplied from pyrolysis. Eq(3) is the CO shift reaction that can decide the ratio of H_2 and CO in the syngas.

$$C + CO_2 \rightarrow 2\,CO \qquad \Delta h_r^0 = 167 \text{ kJ/mol} \tag{1}$$

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta h_r^0 = 125.4 \text{ kJ/mol} \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta h_r^0 = -42 \text{ kJ/mol} \tag{3}$$

where Δh_r^0 is the heat of reaction at standard temperature and pressure, i.e. 298 K and 1 atm.

The entrained-bed gasification technology of GE (General Electric) is adopted to convert coal to syngas in this study. The temperature level in an entrained-bed gasifier (the designated reactor in the present study) is well above the kinetics-controlled threshold. Hence, the reduced reactor, i.e. Gibbs reactor, could be employed and gives acceptable simulated data of equilibrium approach (Syed et al., 2012).

The flow rate of typical coal feed to gasifier is set as 2,000 t/d, and kept the total energy in feedstock as the same for the blended fuel cases in the study. It means that the mass flow rate increases due to the lower heating vale of biomass than that of coal. In general, 10 % flow rate increase is acceptable for commercial gasifier in the study. The maximum percentages of biomass in blended cases are set to the value of 10 %.The slurry concentration and the mass ratio of oxygen from ASU to feedstock are set as 66.5 % and 0.88, respectively.

2.2 Gas clean-up unit

The typical gas clean-up process, consisted of water-gas shift reaction, Selexol-based absorption process, and sulfur recovery processes, was adopted in the previous study (Chen et al., 2015). The warm gas clean-up process is implemented to keep the temperature of syngas at a higher level to increase the available energy which is compared with typical one with lower temperature. Figure 2 is a flow diagram of the warm gas clean-up unit. The raw syngas is sent to HCl removal unit to remove HCl (if syngas produced from biomass). Then, the syngas is sent to desulfurization for sulfur removal. The solid sorbent is regenerated, and the recycled to the desulfurization unit. The sulfur-free syngas is then sent to water-gas shift reactor and CO_2 removal unit to produce clean syngas to the methanation unit. A series of sorbents are selected for the processes: e.g., Na_2CO_3-based sorbent to remove HCl and ZnO-based sorbent to diminish sulphur contained in syngas, while

CaO-based sorbent for removal of CO_2 to enhance the methanation processes. Due to the specific ratio among H_2, CO, CO_2 to meet the requirement from methanation processes, water-gas shift reaction is used to adjust the syngas composition to meet the specific ratio before the CO_2 removal.

The H_2 content in syngas could be increased by going through the water-gas shift reactor. If the ratio of CO converted to H_2 is lower than the typical equilibrium value in water-gas shift reaction, only partial syngas will go through the water-gas shift reactor to increase H_2 content, and the other one goes bypass. Then, the two streams are mixed into one for adjusting the gas composition to meet the requirement of methanation processes.

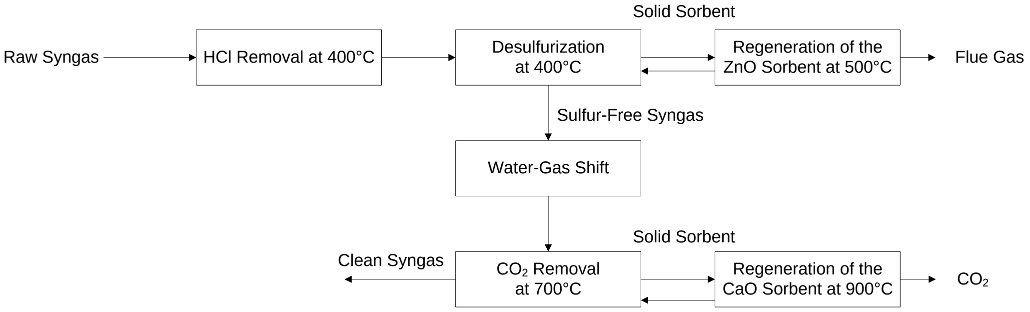

Figure 2: Process flow diagram of warm gas clean-up

2.3 Methanation processes

Syngas after gas conditioning processes is delivered to methanation processes to generate methane. Methanation is generally used for years in the final purification step in ammonia plant or H_2 plant. Carbon monoxide and hydrogen are the main components used to generate methane and shown in Eq(4). The stoichiometric ratio between H_2 and CO is 3. The CO_2 content in the feeding gas affects the production rate of methane based on Eq(5). For SNG production application, it is at a different level due to the higher content of CO and CO_2. The ruthenium, cobalt, nickel and iron are the main catalysts used for this reaction (Mills et al. 1974). In order to take the effect of CO_2 in methanation, the specified parameter “M” is adopted and shown as Eq(6). In general, the value of M is from 2.9 to 3.1 and the best one is 3.

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta h_r^0 = -206 \text{ kJ/mol} \tag{4}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \Delta h_r^0 = -165 \text{ kJ/mol} \tag{5}$$

where Δh_r^0 is the heat of reaction at standard temperature and pressure, i.e. 298 K and 1 atm

$$M = \frac{H_{2,mol\%} - CO_{2,mol\%}}{CO_{mol\%} + CO_{2,mol\%}} \tag{6}$$

The four reactors were built in the model to convert syngas to methane. Partial product gas is needed to recycle back to the reactor in the first reactor to maintain the temperature in a setting temperature due to exothermic methanation reaction and heat recovery. The compression power and the size of reactor could be reduced with decreasing recycle gas flow rate. It means that the first methanation reactor operated with a higher temperature to decrease the flow rate of recycle gas is beneficial.

3. Results and discussion

The coal and blend cases converted to SNG were simulated with the software, Pro/II® V8.1.1. Table 2 shows the raw syngas composition after the gasification in the three cases. Two cases were published last year (Chen et al., 2015) and the warm-temperature gas clean-up is applied in the study to evaluate the impact on the system efficiency. Because the slurry concentration and ratio of mass of oxygen from ASU to mass of feedstock are set as 66.5 % and 0.88, the atomic oxygen content in the feedstock increases with the percentage of wood chip in feedstock increases, as the oxygen content in wood chip is higher than that in coal. As increasing the percentage of wood chips in the feedstock, the more atomic oxygen in the gasifier results in the more CO_2 and H_2O generated and higher temperature. It means that lower CO and H_2 content in the syngas and the cold gas efficiency could be found in the results.

Table 2: The raw syngas composition after the gasification

		kaltim prima coal (KPC)	10 % wood chip blending	10 % EPB blending
Feedstock Flow Rate	t/d	2,000	2,092.09	2,089.22
Temperature	°C	1,187	1,345	1,295
Flow Rate	kmol/h	9,564	9,742	9,825
Composition	%			
H_2		29.38	26.15	26.97
CO		42.36	40.74	40.52
CO_2		9.81	10.29	10.40
H_2O		16.34	20.73	20.04
H_2S		0.16	0.15	0.15
N_2		1.89	1.91	1.91
Cold Gas Efficiency	%	77.64	74.35	75.15

Table 3 shows the system performance analysis from solid fuels to SNG. Due to the fact that CO and H_2 content in the syngas are slight different in the three cases, the specified parameter, M, in the three cases are set around 3. The CO_2 capture ratios in the three cases are 63.51 %, 64.97 % and 65.00 %,respectively. It means that over 60 % of carbon in feedstock is removed in the processes. The biomass could further reduce the CO_2 emission due to the advantage of carbon neutral. The energy of CO is released as heat and reacted with H_2O to form H_2 in water-gas shift reaction. It means that the energy of CO converted to CO_2 is stored in H_2 and the H_2 is used to form CH_4 in later processes. And, partial product gas after the first methanation reactor is recycled back to the reactor to maintain the temperature, the heat generated in the reaction could be reused to increase the system efficiency.

The system efficiency is defined as the ratio of energy of SNG to energy of feedstock. The efficiency in three cases is 61.26 %, 57.57 % and 59.14 %, respectively. The major advantage of biomass introduced in the SNG production is the reduction of CO_2 emission. If the cost of biomass is lower than coal, it will be another benefit for the system.

The energy penalty for CO_2 capture with chemical absorbents is in the range of 4-5 GJ/ t CO_2 (Pellegrini et al., 2009). There is potential that the energy penalty for CO_2 capture with warm gas clean-up in this study could be lower than 2.3 GJ/ t CO_2, when the processes are optimized. It could eliminate cold gas clean-up thermal penalty to improve efficiency.

Table 3: The performances of SNG production with coal and blending cases

		kaltim prima coal (KPC)	10 % wood chip blending	10 % EFB blending
Ambient Temperature (Site Condition)	°C		25	
Feedstock Flow Rate	t/d	2,000	2,092.09	2,089.22
Thermal Energy of Feedstock (Based on Coal HHV) (A)	MWt		687.65	
Specified Parameter, M			3	
CH_4 Production	kg/h	27,410	25,981	26,461
CH_4 High Heating Value	kJ/kg		55,331.73	
CH_4 High Heating Value Production (B)	MWt	421.28	399.32	406.71
Efficiency (B/A *100) (Based on Coal HHV)	%	61.26	58.07	59.14

4. Conclusions remark

The effects of blending fuels cases and the warm gas clean-up process on the system efficiency of solid fuels converted to SNG were shown in the study. The cold gas efficiency is slight decreased as blending biomass in feedstock. The CO_2 capture ratios in the three cases are 63.51 %, 64.97 % and 65.00 %, respectively. The system efficiency in three cases is 61.26 %, 58.07 % and 59.14 %, respectively. The energy penalty for CO_2 capture in this study is improved due to the warm gas clean-up process adopted in the system. The effect of various feedstock, operation parameters such as ratio of oxygen to carbon, pressure, temperature, recycle flow rate, steam integrated, and others could be employed in the further work to find out the proper operation condition.

Acknowledgements

The authors appreciate financial support from the Grant Agency of Czech Republic (GAČR), bilateral grant project of GAČR and Ministry of Science and Technology (MOST) Taiwan, Registr. No. in CR: 14-09692J (Registr. No of foreign project 102WBS0300011) and Grant No. in Taiwan: NSC 103-2923-E-042A-001 -MY3.

References

André R.N., Pinto F., Miranda M., Carolino C., Costa P., 2014, Co-gasification of Rice Production Wastes, Chemical Engineering Transactions, 39, 1633-1638.

British Petroleum, 2015, BP Statistical Review of World Energy, British Petroleum.

Bureau of Energy, 2015, Energy Statistical Hand Book 2014, Bureau of Energy, R.O.C., Taipei, Taiwan. (in Chinese)

Chen P.C., Chiu H.M., Chyou Y.P., 2015, Synthetic Natural Gas (SNG) Production via Gasification Process with Blend of Coal and Wood Chip as Feedstock, Chemical Engineering Transactions, 45, 601-606.

Chen P.C., Chiu H.M., Chyou Y.P., 2014, Efficiency Analysis of Advanced G Class Gas Turbine Feed with Synthetic Natural Gas (SNG) and Mixture Gas of Syngas and SNG, Chemical Engineering Transactions, 39, 1717-1722.

Higman C., van der Burgt M., 2003, Gasification, Elsevier, Burlington, USA.

Lim C.H., Lam H.L., 2013, Biomass Demand-Resources Value Targeting, Chemical Engineering Transactions, 35, 631-636.

Pellegrini G., Strube R., Manfrida G., 2010, Comparative study of chemical absorbents in postcombustion CO2 capture, Energy, 35, 851-857.

Mills, G. A., Steffgen F. W., 1974, Catalytic Methanation, Catalysis Reviews: Science and Engineering, 8, 159-210.

Syed S., Janajreh I., Ghenai C., 2012, Thermodynamics Equilibrium Analysis within the Entrained Flow Gasifier Environment, International Journal of Thermal & Environmental Engineering, 4(1), 47-54.