

Processes Simulation Study of Coal to Methanol Based on Gasification Technology

Po-Chuang Chen, Hsiu-Mei Chiu, Yau-Pin Chyou, Chiou-Shia Yu

Abstract—This study presents a simulation model for converting coal to methanol, based on gasification technology with the commercial chemical process simulator, Pro/II® V8.1.1. The methanol plant consists of air separation unit (ASU), gasification unit, gas clean-up unit, and methanol synthetic unit. The clean syngas is produced with the first three operating units, and the model has been verified with the reference data from United States Environment Protection Agency. The liquid phase methanol (LPMEOH™) process is adopted in the methanol synthetic unit. Clean syngas goes through gas handling section to reach the reaction requirement, reactor loop/catalyst to generate methanol, and methanol distillation to get desired purity over 99.9 wt%. The ratio of the total energy combined with methanol and dimethyl ether to that of feed coal is 78.5% (gross efficiency). The net efficiency is 64.2% with the internal power consumption taken into account, based on the assumption that the efficiency of electricity generation is 40%.

Keywords—Gasification, Methanol, LPMEOH, System-level simulation.

I. INTRODUCTION

METHANOL is a chemical with formula CH_3OH and often simply abbreviated as MeOH. It is also named as methyl alcohol, wood alcohol, wood naphtha or wood spirits. It is a toxic, light, volatile, colorless and flammable liquid with a distinctive odor that is very similar to but slightly sweeter than ethanol material. People will suffer blindness with drinking 10 ml and death with 100 ml [1].

MeOH may be applied in three directions, i.e. hydrogen carrier, fuel and chemical synthesis. It can be a hydrogen carrier for direct methanol fuel cell or fuel-cell-powered vehicle in the future. For fuel and power applications, it can be mixed with conventional petrol to feed vehicle without technical modifications. This mixture fuel has advantages in improving

security of energy supply and reducing the dependency on importing crude oil. For the power industry, fuel-grade MeOH is a back-up and clean alternative fuel for gas turbine. For the chemical synthesis, various processes can be implemented for the production of formaldehyde, methyl tertiary-butyl ether (MTBE), acetic acid, dimethyl ether (DME) and so on [2]–[4].

The global MeOH demand is increasing, from 31,447,000 metric tons in 2001 to 44,763,000 metric tons in 2008. It means that the market for MeOH is growing. Formaldehyde is still the major demand of MeOH, and it takes about one-third global demand. MTBE is the second after the formaldehyde, but the demand is decreasing, from 27.69% in 2001 to 13.33% in 2008. The third is the acetic acid, which increases from 8.78% in 2001 to 11.69% in 2008. Formaldehyde, MTBE and acetic acid take over 70% and 60% world-wide demand in 2001 and 2008, respectively. The reason is the decreasing demand of MTBE, which is taken by others, such as fuels and DME. MeOH for fuel and DME application has a great increase over 10 times from 2001 to 2008. For fuel, it is from 0.94% to 10.02%. For DME, it is from 0.47% to 5.14%. The combination of fuel and DME is over 15%, it means that MeOH has a potential to be an alternative fuel in the future [5], [6].

Fossil fuels still play a major role of energy generation and chemical production in the 21st century. British Petroleum estimated that the world reserves of oil, natural gas, and coal are 1,258 trillion barrels, 185.02 trillion cubic meters and 826,001 million tons in the end of 2008, and the reserves-to-production ratio for oil, natural gas and coal are 42, 60.4 and 147 years, respectively [7]. The whole world is trying to find other ways to avoid the shortage of fossil fuels in the future. There are several ways to reduce the dependence on fossil fuels, such as renewable energy, multiple fuel supply, alternative fuel, efficiency improvement of fuel utilization, etc. Conversion of solid fuel to gas fuel, liquid fuel or chemical products by adopting gasification technology is a better way to achieve the replacement of oil and natural gas by solid fuel.

The ratio of global syngas output from gasification by feedstock of coal, petroleum, gas, petcoke and biomass are 55%, 32%, 8%, 3% and 2%, respectively. The production of world gasification capacity in 2007 consists of chemicals (45%), liquid fuel (30%), power (19%) and gaseous fuel (6%) [8]. It shows that although coal is the major part of feedstock, while the major product is chemicals. It is possible to replace oil by coal with gasification technology.

In the system-level simulation, Zhao et al. performed a simulation model based on ASPEN Plus to compare with the experimental study of co-gasification with coke and natural

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gas. Their results showed that the co-gasification reactions operate at quasi-equilibrium [9]. Zheng and Furinsky built an IGCC model to compare the effect of four gasification technologies, i.e. Shell, Texaco (now GE), BGL, KRW, and three coals, such as bituminous, sub-bituminous, lignite, on efficiency [10]. Although the gasification phenomena are complicated to get exact simulation, it is reasonable to mimic final gas compositions with gasification reactions under higher temperature by employing ideal thermodynamics in system-level simulation models [11]-[15]. For detailed simulation investigation and reactor design, it can be performed by computational fluid dynamics coupling with chemical reactions.

In the studies of chemical production, Kumabe et al. discussed three process design cases of woody biomass converting to methanol with PRO/II simulator. The better case is a process independent of heat and power for CO₂ reduction in the results of three cases [16]. Vaswani built a liquid phase methanol (LPMEOH) model via ASPEN Plus, and utilized syngas as starting material for MeOH production [17]. Ju et al. used ASPEN Plus to simulate a single-step process of DME synthesis with woody biomass gasification. The DME yield in the study is 0.37 with assuming that the DME selectivity was 0.91 and that CO was totally converted. In summary, it is able to produce power, chemical products and synthetic fuels simultaneously or alternatively by employing gasification fed with fossil fuels, renewable biomass and mixture of them. It is a promising future prospect that is attracting increasing interest [18].

The MeOH import in Taiwan is 978,524 metric tons, and export is 7,202 metric tons in 2008. It means MeOH is almost dependent on import. Thus, this study presents a feasible choice to reduce the dependence on MeOH, i.e. converting coal to MeOH. The purpose of this study is to simulate a MeOH plant, based on gasification process shown in Fig.1, which illustrates the main flow chart of gasification process and the applications of syngas. The simulated results of the four process blocks will be compared with several reference data [17], [19]-[20] to verify the simulation model. Then, the MeOH production plant will be performed to evaluate the MeOH production rate and efficiency.

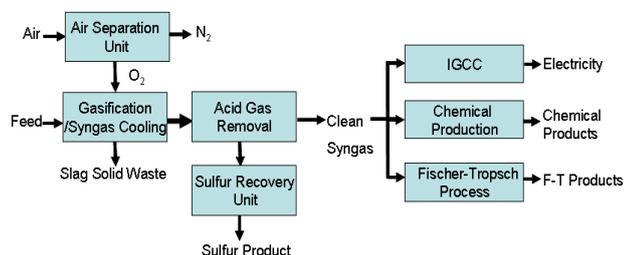


Fig. 1 Block diagram of gasification process and syngas applications

II. PROCESS DESCRIPTION

The four major blocks for converting coal to MeOH with the gasification technology are described in the following sections.

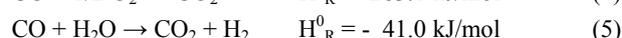
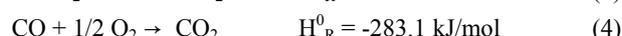
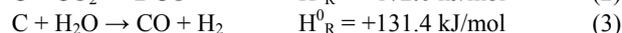
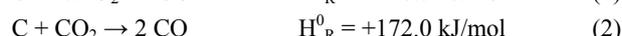
A. Air Separation Unit (ASU)

To produce large quantities of oxygen and nitrogen as gaseous or liquid, cryogenic air separation is the most common technology to reach the requirement with efficiency and cost-effectiveness. A conventional, multi-column cryogenic rectifying process, which produces oxygen from compressed air at high recoveries and purities, is used in ASU. First, air is introduced into an air pre-purification unit which located in the downstream of the air compression and after cooling. The process contaminants, including water, carbon dioxide, and hydrocarbons are removed in the unit. Then, the air is cooled to cryogenic temperatures and delivered to distillation processes for separating oxygen and nitrogen. Numerous configurations of heat exchange and rectifying equipment can separate air into the required product streams [21].

B. Gasification Unit

Gasification is a manufacturing process that converts carbonaceous solid fuel such as coal, biomass and mixture of them into gas fuel which is called synthesis gas or syngas. The gasifier operates at a high temperature in the range of 800 °C to 1,800 °C. The exact temperature depends on the characteristics of the feedstock and gasifier types [22]. In general, gasification technology consists of three chemical reaction processes: pyrolysis, combustion and gasification. The volatile materials are released from coal in pyrolysis procedure. Combustion is oxygen burning with volatile gas generated from the pyrolysis. It is an exothermic reaction, and the generated heat is supplied to the endothermic gasification reaction to convert solid fuel to gas fuel.

The oxygen demand in gasification reaction is in the range of 1/5 to 1/3 as the stoichiometric value with complete combustion. In other words, it is a partial-oxidation process and sometimes called incomplete combustion reaction. The main compositions of syngas in the gasification reaction are H₂ and CO [23]. The main global reactions in a gasification process are shown as follows [24]:



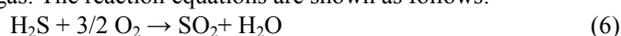
The compositions of outlet gas (raw syngas) are decided from the feedstock composition, gasifying agent (oxygen or air), steam and actual gasification temperature.

C. Clean-Up Unit

The two parts of sulfur compounds removal and sulfur recovery processes are included in the clean-up system in this study. The sulfur removal process is adopted to remove H₂S in the raw syngas generated from gasification. The H₂S is usually removed by absorption using ethanolamine such as Methyldiethanolamine (MDEA) [25]. The MDEA solvent has higher selectivity for H₂S than CO₂ [26]. MDEA is a

cost-effective choice in the case without handling CO₂. If CO₂ handling is taken into consideration, another solvent named selexol is better than MDEA [27]. For the MeOH synthetic process, the concentration of CO₂ is an effective parameter in the reaction. Thus, the MDEA is built in the model to verify with reference data, and then the selexol is used for replacing the MDEA to reach the requirement of CO₂ concentration in the MeOH synthetic process. The sulfur recovery process is used to produce elemental sulfur from H₂S stream which is stripped by steam. The process includes Claus process, Shell Claus off-gas treatment (SCOT) process and combustion of tail-gas.

The major point in the Claus process is that the molar ratio of H₂S/SO₂ must be controlled to 2 after combusting excess sulfur gas. The reaction equations are shown as follows:



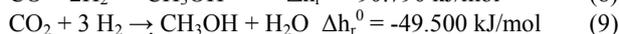
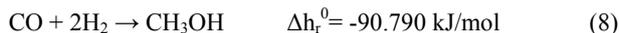
From Equation (6), 1/3 of H₂S is oxidized to SO₂ and generates heat to supply the energy needed in Equation (7). Then, elemental sulfur can be yielded by the remaining 2/3 of H₂S which reacts with SO₂ [28]. The overall sulfur conversion is about 94 ~ 97% in the Claus process [25].

To increase the total recovery rate of elemental sulfur, SCOT process is a general choice which is used to clean up the tail gas from the Claus sulfur recovery unit. The overall sulfur recovery efficiency can be higher than 99.8% with standard Claus and SCOT unit. The tail gas of SCOT unit contains rare H₂S which can be treated by a burner to form SO₂.

D. Methanol Synthetic Unit

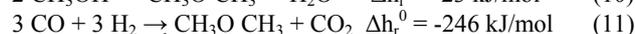
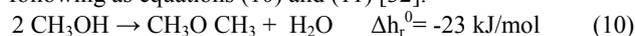
As mentioned in the introduction, MeOH is a world-wide demand chemical product and the market is continuously growing up. MeOH shows a potential to be an alternative fuel in the future, due to the fact that the combined percentage of fuel and DME in 2008 is over 15%, while in 2001 it is only 1.41% [5].

Methanol can be produced from carbonaceous materials such as natural gas, coal, municipal wastes, woody biomass, and so on. Syngas which consists primarily of H₂ and CO is the first step in the production of MeOH. The process for natural gas is named reforming and for coal or solid feed is named gasification. Although MeOH is primarily produced from natural gas in this moment, natural gas supply in Taiwan is not very sufficient. Hence, methanol production in Taiwan is needed to find another way to replace natural gas; a feasible choice is to use coal as feedstock with gasification technology. The LPMEOH process is developed by industry. Air Products and Chemicals Company built a commercial-scale demonstration plant employing the liquid phase methanol process technique where the catalyst is mixed with mineral oil. The project is partially funded by U.S. Department of Energy (DOE) [29]. The LPMEOH process represents a major departure from traditional gas-phase routes to MeOH in the method of removing the heat of reaction. The reactions of H₂, CO and CO₂ to form MeOH are highly exothermic. Two main representative reactions in the synthesis of MeOH are listed in the following as equations (8) and (9) [30], [31]:



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

In the MeOH synthetic reactor, the side reactions of DME production occur and the two major reactions are shown in the following as equations (10) and (11) [32].



The typical operating condition for the LPMEOH process reactor is 50 atm to 100 atm pressure, and near 250 °C temperature.

The production of methanol can be further divided into a series of steps including removal of water and mineral oil to produce dry syngas, methanol production, methanol condensation, unreacted gas recycle, and methanol distillation to desired purity. The purity of methanol in the top product is over 99.9 weight percent [33].

III. SIMULATION MODEL

The present study builds the MeOH plant simulation models based on gasification with a chemical process simulator, Pro/II® V8.1.1. The details of model construction and parameters are described as follows.

A. Air Separation Unit

The separation process of nitrogen and oxygen is based on high pressure (HP) and low pressure (LP) rectifying columns. In the commercial application, the two columns are built in a single tower, in which the upper side is LP column and the down side is HP one, because the condenser in the HP column is equivalent to the reboiler in the LP one. The air after purification and compression feeds to the bottom side of the HP column to produce gaseous oxygen. The bottom product of HP column feeds to LP column to produce gaseous nitrogen. The overhead liquid products of HP column are delivered to LP column as reflux. Table I shows the main simulation parameters in the ASU.

TABLE I
THE SIMULATION PARAMETERS IN ASU

Item	Value
Air flow rate (kg/hr)	535,641
Air temperature (K)	298.15
Air pressure (kPa)	101.3
Air composition (mole %)	
Nitrogen	79
Oxygen	21
Pressure of HP column (kPa)	603.9
Pressure of LP column (kPa)	162.5

B. Gasification Unit

The feedstock to gasifier consists of oxygen, coal and water, while the output includes raw syngas and solid waste slag. The Gibbs reactor is used as gasifier to simulate the gasification process since it is reasonable to simulate the raw syngas with ideal thermodynamics when gasification reactions are at higher temperature [11]–[15]. Solid waste slag is cooled down by two heat exchangers to the room temperature. Table II shows the

main simulation parameters in the gasification process. The operating conditions and the ultimate analysis of coal are referred to the reference data [19].

TABLE II
THE SIMULATION PARAMETERS IN GASIFICATION

Item	ASU	Coal	Water
Temperature (K)	426	343	343
Pressure (kPa)	3,703	4,199	4,199
Flow rate (kg/hr)	129,231	141,000	71,030
Composition (kg/hr)			
O ₂	123,799	10,929	-
N ₂	5,435	1,988	-
C	-	101,123	-
H ₂	-	7,135	-
S	-	3,977	-
SiO ₂	-	15,848	-
H ₂ O	-	-	71,030

C. Clean-Up Unit

The sulfur removal process consists of a COS hydrolysis reactor, a H₂S absorption column and a stripper column. The two solvents, MDEA and selexol, are used in the simulation model for clean-up unit. The MDEA built in the simulation case is to verify with the reference data [19], while selexol is used for capturing more CO₂ than MDEA to meet the MeOH synthetic requirement under the same condition of H₂S removal. The raw syngas from gasifier contains COS, thus a COS hydrolysis reactor should be built to convert COS to H₂S for increasing the final sulfur recovery rate. Downstream the absorber column there are clean syngas and rich absorption solution in the top and bottom columns, respectively; then, the rich absorption solution is fed into the stripper column where almost pure H₂S stream can be obtained. Due to the fact that CO₂ capability of selexol is higher than MDEA, the CO₂ composition in the output gas from the top of stripper column is different between the selexol and MDEA processes. For selexol process, an additional CO₂ separation processes is needed to reduce the CO₂ composition and increase the H₂S counterpart in the mixture gas before entering the Claus process.

The Claus unit consists of a combustion reactor and two stages of conversion reactors with two sulfur condensers to generate liquid sulfur. The SCOT unit consists of a heater, a hydrolysis/hydrogenation reactor, a H₂S absorption column, a stripper column and a burner. The overall simulation parameters in the clean-up process are shown in Table III and Table IV.

D. Methanol Synthetic Unit

Methanol is one of the basic feedstock in the chemical industry and the market of demand is growing. Methanol can be produced from mixture gas (syngas) of CO and H₂ with three methods, which are high pressure with Zn/Cr catalyst, medium pressure with Cu/Zn/Al catalyst and low pressure with Cu/Zn/Cr catalyst, respectively. This study adopts the low pressure method with Cu/Zn/Cr catalyst to build the simulation

model due to the fact that the pressure of feeding mixture gas is near the pressure level of the requirement, i.e. 6.89 MPa, and the activity and selectivity of Cu-base catalyst are better than Zn-base counterpart.

TABLE III
THE SIMULATION PARAMETERS IN SULFUR REMOVAL PROCESS

Item	Value	Item	Value
COS hydration reactor, Temperature (K)		503.15	
MDEA absorber column		Selexol absorber column	
Temperature (K)	308.15	Temperature (K)	273.15
Pressure (kPa)	3,103	Pressure (kPa)	6,890
MDEA solution (%)	50		
Number of stages	20	Number of stages	20
Stripper column		Stripper column	
Temperature (K)	388.15	Temperature (K)	273.15
Pressure (kPa)	101.32	Pressure (kPa)	101.32
Number of stages (include condenser and reboiler)	21	Number of stages (include condenser and reboiler)	20
Pressure swing adsorption (PSA)			
High Pressure (kPa)		2,026.5	
Low Pressure (kPa)		101.32	

TABLE IV
THE SIMULATION PARAMETERS IN SULFUR RECOVERY PROCESS

Claus unit	
Combustion reactor, Temperature (K)	1,574.11
1 st Sulfur convert reactor, Temperature (K)	576.04
1 st Sulfur condenser, Temperature (K)	438.15
2 nd Sulfur convert reactor, Temperature (K)	479.14
2 nd Sulfur condenser, Temperature (K)	438.15
SCOT unit	
Heater, Temperature (K)	573.15
Sulfur convert to H ₂ S reactor, Temperature (K)	573.15
MDEA absorber column	
Temperature (K)	298.15
Pressure (kPa)	101.32
MDEA solution (%)	50
Number of stages	20
Stripper column	
Temperature (K)	388.15
Pressure (kPa)	101.32
Number of stages	8

The benchmark model adopts clean syngas as feedstock. First, the pressure and temperature of syngas are increased to 50 atm and 533 K by compressor and heat exchanger, respectively. Then, syngas is fed to methanol reactor to product methanol. The outlet gas goes through the purification processes, i.e. flash, distillation column, condenser, to yield the 99.9wt% methanol [1], [29].

In the MeOH synthetic reactor, the stoichiometry indicates that the desired molar composition of reactor feed is controlled by the ratio of H₂/CO and the equation is shown as follows:

$$R = (\text{H}_2 - \text{CO}_2) / (\text{CO} + \text{CO}_2) \quad (12)$$

In general, the ratio of H₂/CO and R value are set slightly higher than the balance value of 2. Mixture gas with R=2.0 to 2.1 is balanced stoichiometrically. For a liquid-phase reactor, it has an advantage over traditional reactor because CO-rich mixture can be fed in, i.e. R value between 0.3 and 0.4. It means the demand of water gas shift (WGS) reaction and CO₂ removal process can be reduced [29], [33].

In the simulation model, the R value and ratio of H₂/CO

come from the reference data, which are set as 1.1 and 2.5, respectively [29]. Thus, the WGS and CO₂ removal sections are employed in the model to adjust the composition of syngas to meet the two values. The selexol instead of MDEA is used in H₂S absorption process in order to reduce the additional CO₂ removal section. The major process unit setting parameters are shown in Table V.

TABLE V
SIMULATION PARAMETERS IN METHANOL SYNTHETIC PROCESS

Item	Value	
Methanol Reactor	Temperature (K)	533
	Pressure (kPa)	5,066.25
Methanol Distillation Column	Temperature (K)	378.06
	Operating Pressure (kPa)	344.51
	Number of stage	20

IV. RESULTS OF BENCHMARK MODEL

The simulation results for the basic case model are described in the following, and some works are introduced from previous study [35]. The processes to provide clean syngas, i.e. ASU, gasification and clean-up, are verified with the report published by U.S. environmental protection agency (EPA) [19]. Methanol synthetic process is verified with the project of commercial-scale demonstration plant which is partially funded by U.S. DOE [29].

A. Air Separation Unit

In the ASU, the present study adopts different pressure setting in the HP column and LP column to meet the state of air in the bubble point and dew point. In real plants, the LP and HP columns are built in a single tower, the upper side is LP column and the down side is HP one. It means that the needed energy at the condenser of HP column is equal to that at the reboiler of LP column. The energy needed in the simulation result is 94.8 GJ/h, and the temperatures at the condenser of HP column and the reboiler of LP column are 96.1 K and 94.6 K, respectively. The difference of the two temperatures conforms to the principle of heat transfer.

To keep the pressure drop between the HP and LP columns, it is needed to compress air. Hence, a main compressor for air and the others for oxygen and nitrogen are needed in the ASU process. Table 6 shows the properties of compressors in the simulation.

TABLE VI
COMPRESSORS' PROPERTIES IN THE SIMULATION RESULTS

Compressor	Main	O ₂	N ₂ (1)	N ₂ (2)
Pressure (kPa)	608	3,040	430	1,823
Temperature (K)	543	745	427	487
Actual Work (kW)	37,375	14,126	15,207	22,447

In the ASU, the input stream contains 529,200 kg/h air, and the output streams contain high purity oxygen and nitrogen, of which the flow rates are 129,001 kg/h and 400,199 kg/h, respectively. The high purity oxygen contains 95% oxygen and 5% nitrogen and feeds to gasifier, while the high purity nitrogen can be applied in other fields such as feeding to gas turbine as dilution stream for NO_x reduction.

B. Gasification Unit

The present study uses the conditions of modifying the effect on the feedstock energy compensation, with reactor heat loss 1.5% and carbon conversion rate 99.51%, to perform the gasification process.

Table VII shows the results of raw syngas properties. The mass balance in the gasification model coincides very well with the reference data [19]. The input data in the Pro/II refers to the reference data, so the simulated result from Pro/II shows certain accuracy on the mass balance. The input includes three streams which contain 141,000 kg/h coal, 71,030 kg/h water and 129,001 kg/h oxygen from ASU, respectively. The output streams contain 324,686 kg/h raw syngas and 16,345 kg/h slag.

TABLE VII
RESULTS OF SYNGAS IN THE GASIFICATION

	EPA[19]	Pro/II	Error (%)
Flow rate (kg/h)	324,678	325,086	0.004
Temperature (K)	1,703	1,839.5	7.08
Syngas composition (mole %)			
CO	42.25	45.05	6.41
CO ₂	9.62	6.89	-30.04
H ₂	30.76	27.80	-9.08
H ₂ O	14.90	17.93	18.53
N ₂	1.70	1.56	-0.17
H ₂ S	0.71	0.70	1.59
COS	0.05	0.06	7.06
CO+H ₂	73.01	72.85	-0.11

There is no detailed description on the setting of every system in the reference data, so the energy compensation of reactor should be reasonably modified in the present model. The total energy input to the gasification in the result is 4,305 GJ/h, which is comparable with the reference data (4,308 GJ/h). The deviation of the input total energy is only 0.07%. The output energy in the results is 4,250 GJ/h, which is slightly lower than the reference data (4,273 GJ/h). The deviation of the output energy is higher than input one and the value is 0.54%.

The main components of the output gas are CO, H₂, CO₂ and H₂O. Although the temperature of raw syngas in the results is a little higher than the reference data, the amount of CO and H₂ in weight percent in the output gas, which is an important value in industry applications, coincides well with the reference data. The values of CO and H₂O are 2% higher than those in reference data, while the values of H₂ and CO₂ are 2% lower. It means that the water-shift reaction, in which CO and H₂O result in H₂ and CO₂, is retarded by the elevated temperature in gasification reactions. The main sulfur compounds in the syngas are H₂S and COS, of which the weight percents are stable in the simulation results.

C. Clean-Up Unit

In the clean-up unit, this study first uses raw syngas data from the reference [19] to build the clean-up unit with MDEA solution. The final sulfur recovery efficiency is close to the reference result, so that the simulation model is verified. Then, the clean-up unit model can be used to clean the raw syngas produced from the gasification model. Table VIII shows the syngas results before and after cleaning. Upstream the MDEA

absorber column, it contains 0.91% H₂S and 0.01% COS. The H₂S absorption efficiency can be achieved exceeds 99%. It should be noted that clean syngas needs to be preheated before entering gas turbine for power generation. The data from EPA [19] seems to be in the condition after preheating (T ≈ 300 °C), while this study only focuses on H₂S removal (around room temperature). This discrepancy would cause substantial deviations in H₂O content, temperature and the total energy of clean syngas. In the final simulated MeOH product plant, the absorbent will be replaced by selexol.

TABLE VIII
RESULTS OF CLEAN SYNGAS

Stream Name	Before absorber column	clean syngas
Flow rate (kg-mole/h)	13,280.96	12,715.78
Temperature (K)	308.15	308.15
Syngas composition (mole %)		
CO	54.66	56.49
CO ₂	8.39	5.76
H ₂	33.83	35.21
H ₂ O	0.20	0.46
N ₂	2.00	2.1
H ₂ S	0.91	0.01
COS	0	0
CO+H ₂	88.49	91.71

The overall sulfur recovery efficiency achieved is around 99% via two stages Claus reactions and SCOT processes, as shown in Table IX.

TABLE IX
RESULTS OF OVERALL SULFUR RECOVERY EFFICIENCY

Stream Name	input Claus unit	1 st S recovery	2 nd S recovery
Rate (kg-mole/h)	622.89	116.45	6.71
Flow rate (kg-mole/h)			
H ₂ S	120.07	0.00	0.00
COS	0.45	0.00	0.00
SO ₂	1.06	0.00	0.00
S	0	114.23	6.58
S recovery efficiency (%)	–	93.95	5.41
Overall S recovery efficiency (%)	–		99.36

In the clean-up unit, the main input stream contains 324,686 kg/h raw syngas from gasification, while the main output streams amount to 341,169 kg/h, containing 247,417 kg/h clean syngas, 3,839 kg/h sulfur, 38,637 kg/h SCOT tail gas and 51,276 kg/h discharge water, respectively. The discharge water is generated from condensing the raw syngas due to the temperature difference. This is the major mass difference between the raw syngas and the clean syngas. The other discrepancy between input and output streams comes from the additional input streams in the process, such as introducing air

for combustion with H₂S in Claus unit, water stream for hydrolysis and MDEA solution, etc.

D. Methanol Synthetic Unit

The simulation results are shown in the Table X. The parameters of feeding gas, temperature and pressure are set from the reference [29]. Because the conversion parameters in the reactor are not shown in reference data, the parameters are determined by comparing the gas composition from input and output of MEOH synthetic reactor. The conversion parameters are thus verified in terms of the minor deviation between the simulation results and reference data. The purity of methanol is 99.95wt% and higher than the requirement from reference case. Thus, the MeOH synthetic model can be applied to convert syngas from gasification to MeOH in the model of coal to MeOH model. Before entering the MeOH reactor, syngas is needed to go through WGS and CO₂ removal sections to adjust the two parameters of the H₂/CO ratio and R value. This will increase the conversion rate and the efficient in the system.

TABLE X
RESULTS OF METHANOL SYNTHETIC UNIT

Item	Ref[29]	Pro/II	Error%
Output gas from reactor			
Fluid Rates kg-mol/hr			
N ₂	133.45	133.45	-0.00
H ₂	1,347.43	1,346.58	-0.06
CO	509.28	512.57	0.65
CO ₂	635.18	635.89	0.11
H ₂ O	9.83	9.55	-2.84
MeOH	337.98	339.52	0.45
DME	2.30	2.51	9.13
Final MeOH purity wt%			
MeOH	99.98	99.96	-0.02

V. CASE STUDY OF METHANOL PRODUCT PLANT

The simulation model of methanol production plant is shown in Fig. 2. The model combines the clean syngas providing process and MeOH synthetic process form two verified reference cases. The clean syngas providing process, i.e. ASU, gasification island and clean-up unit, in the reference delivers syngas to feed the combined-cycle for generating electricity. However, it is not appropriate to directly feed the said syngas to the MeOH synthetic process due to some unturned parameters, such as pressure of mixture gas, the ratio of H₂/CO, R value and so on. The necessary modification is employed in the simulation model, to make the specification of clean syngas complied with the requirement in the MeOH production unit.

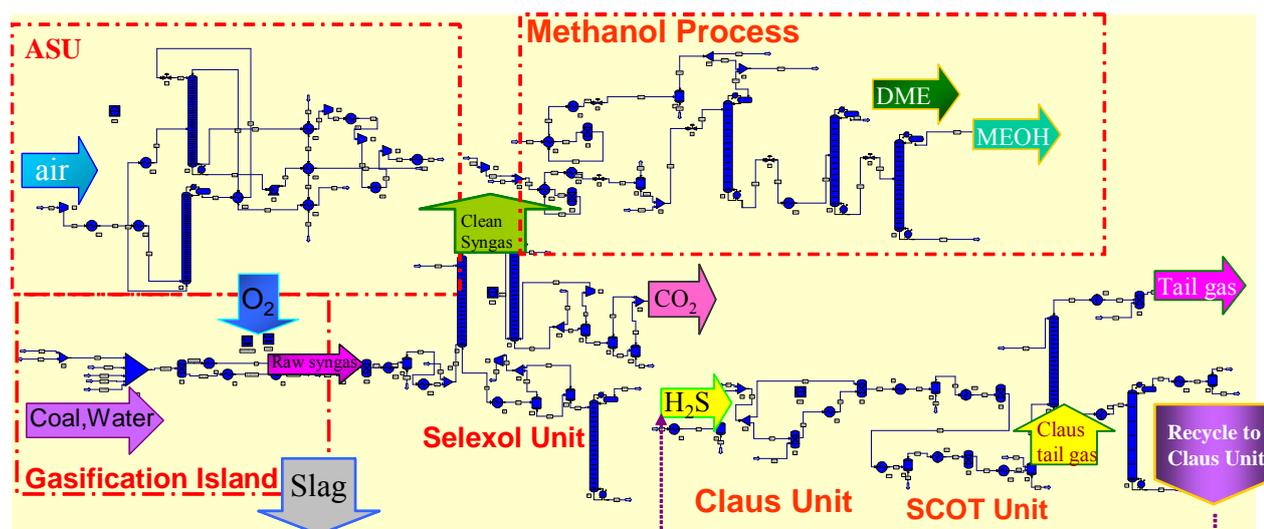


Fig.2 Simulation model of methanol product plant built with Pro/II

Table XI shows the differences between the reference and the modified setting with description in the model. The pressure in the present gasifier is 68 atm, which is higher than the level of 30 atm in the reference. The relative higher pressure not only co-operates well with the MeOH synthetic reactor, but also requires lower sorbent flow rate than the reference. Due to the growing demand of DME in recent years, the DME separation unit is added in this case study, in which DME is obtained as the byproduct to increase the plant efficiency rather than being burned as in the traditional process. The other modification and description are shown in this table and discussed in the previous section.

TABLE XI
MODIFICATIONS FROM THE BENCHMARK MODEL AND THE DESCRIPTIONS IN
THE METHANOL PRODUCT PLANT SIMULATION MODEL

Item	Benchmark	MeOH plant	Description
Pressure of O ₂ feeds to gasifier	30 atm	68 atm	To meet the requirement of MeOH synthetic.
Pressure of N ₂ as dilute gas feeds to gas turbine	18 atm	NA	Combined-cycle in the MeOH plant is not employed, the internal power consumption is reduced.
Gasifier pressure	30 atm	68 atm	To meet the requirement of MeOH synthetic.
WGS	NA	Add WGS	To control H ₂ : CO equal to 2.1
H ₂ S absorbent	MDEA	Selexol	1. selexol is replaced the MDEA to reach the requirement of CO ₂ concentration in the MeOH synthetic process. 2. To control the R value equal to 1.5.
PSA	NA	Add PSA	PSA unit locates between the downstream of H ₂ S stripper and upstream of Claus to remove the remainder of the CO ₂ .
MeOH Reactor	One Reactor	Two Reactors	Increase MeOH productions.
DME Distillation column	NA	One DME Distillation column	To separate DME from the mixture gas.

The simulation results of performances of the methanol production plant are arranged in Table XII. The ASU is still the major part of power needed in the whole process. The internal power consumption is 54.3 MWe, based on 40% efficiency in the power block, or 137.75 MW in terms of thermal energy. The overall production includes 2,784 t/day MeOH and 7.2 t/day DME. The gross and net efficiency in the case study are 77.7% and 63.3%, respectively. It is relative higher than the counterparts in traditional IGCC plants [19] by 20% points and the poly-generation plant of electricity and MeOH simulation study [36] by 17%. Although the simulation results show that coal to liquid fuel, MeOH and DME, process provides a better way to utilize coal more efficiently. If the liquid fuel is applied to generate the electricity, the efficiency of electricity generation from coal in the case study may be lower than the case of traditional IGCC plants. The utilization of coal is not only taking efficiency into consideration, but also identifying the best way is to use it sufficiently with the whole demand in the region or country. For example, Taiwan is import dependent on MeOH; thus, it is possible to choose coal to MeOH plants in Taiwan to reduce the import dependency, if the process is efficient and cost-effective.

VI. CONCLUSIONS

A conversion process of coal to methanol with system-level simulation model has been performed. The four major processes include ASU, gasification process, gas clean-up modules, and methanol synthetic unit. The simulation procedures are performed in benchmark models and a case study of methanol production. The benchmark models are built to verify the reference data in clean syngas providing and methanol synthetic processes, respectively. The deviations compared with the reference data are relatively reasonable in general. Thus, the model of methanol production plant employs the verified model and takes some necessary modification to make the processes co-operate well. The results show that gross

and net efficiency in the case study are 77.7% (HHV) and 63.3% (HHV), respectively. It is relatively higher than the counterparts in traditional IGCC plants and the poly-generation plant of electricity and MeOH. Taiwan is import dependent on methanol; thus, it is an alternative choice to reduce the dependence on methanol importing in Taiwan with plants converting coal to methanol, if the process is efficient and cost-effective.

TABLE XII

PERFORMANCES OF THE METHANOL PRODUCT PLANT IN SIMULATION MODEL

Item	Unit	Value
Ambient Temperature	°C	25
Coal Flowrate (Dry Basis)	t/h	125.3
Coal HHV (including Inh. Moisture and Ash)	kJ/kg	27,137.0
Thermal Energy of Feedstock (Based on Coal HHV) (A)	MWt	944.5
Process Units Consumption	MWe	6.5
ASU Consumption	MWe	47.3
LPMEOH System	MWe	0.5
Electric Power Consumption	MWe	54.3
Power Consumption in Thermal energy (B)*	MW	137.75
Methanol Production	t/h	116.0
Methanol Heating Value	kJ/kg	22,691.6
Methanol Heating Value Production (C)	MW	731.2
DME Production	t/h	0.3
DME Heating Value	kJ/kg	31,681
DME Heating Value Production (D)	MW	2.6
Gross Efficiency ((C+D)/A *100) (Based on Coal HHV)	%	77.7
Net Efficiency ((C+D-B)/A*100) (Based on Coal HHV) ^a	%	63.3

^aBased on the assumption that the efficiency of electricity generation is 40%.

REFERENCES

- [1] F. Gallucci, A. Basile, and E. Drioli., "Methanol as an energy source and/or energy carrier in membrane processes," *Separ. Purif. Rev.*, vol. 36, no. 2, pp. 175–202, 2007.
- [2] P. Galindo Cifre, and O. Badr, "Renewable hydrogen utilisation for the production of methanol," *Energy Convers. Manage.*, vol. 48, no. 2, pp. 519–527, 2007.
- [3] E. Fiedler, G. Grossmann, D. B. Kersebohm, G. Weiss, and C. Witte, *Methanol*. 7th ed. Ullmann's encyclopedia of industrial chemistry, Weinheim, Germany: Wiley-VCH Verlag GmbH & Co, 2005.
- [4] P. L. Spath, and D. C. Dayton, "Preliminary screening - technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas," Technical report NREL/TP- 510-34929, 2003.
- [5] PCI - Ockerbloom & Co., Inc., "Global methanol supply and demand," Available: <http://www.methanol.org/pdfFrame.cfm?pdf=WrlSD.pdf> [accessed Jan. 25, 2010]
- [6] General Electric Company, "Feasibility of methanol as a turbine fuel," Available: <http://www.methanol.org/pdfFrame.cfm?pdf=GEWhitePaper.pdf> [accessed Jan. 25, 2010]
- [7] BP. *BP Statistical Review of World Energy*, British Petroleum, 2009.
- [8] Gasification Technology Council, *Gasification: Redefining Clean Energy*. Gasification Technology Council, 2008.
- [9] Y. Zhao, H. Wen, and X. Xu, "Conceptual design and simulation study of a co-gasification technology," *Energy Convers. Manage.*, vol. 47, pp. 1416–1428, 2006.
- [10] L. Zheng, and E. Furinsky, "Comparison of Shell, Texaco, BGL and KRW gasifiers as part of IGCC plant computer simulations," *Energy Convers. Manage.*, vol. 46, pp. 1767–1779, 2005.
- [11] P. Kuchonthara, S. Bhattacharya, and A. Tsutsumi "Combination of thermochemical recuperative coal gasification cycle and fuel cell for power generation," *Fuel.*, vol.84, pp.1019–1021, 2005.
- [12] C. H. Frey, and N. Akunuri, "Probabilistic modeling and evaluation of the performance, emissions, and cost of Texaco gasifier-based integrated gasification combined cycle systems using ASPEN," Prepared by North Carolina State University for Carnegie Mellon University and U.S. Department of Energy, Pittsburgh, 2001. Available: http://www4.ncsu.edu/~frey/reports/Frey_Akunuri_2001.pdf [accessed Oct. 06, 2009]
- [13] D. Brown, T. Fuchino, and F. Mare'chal., "Solid fuel decomposition modeling for the design of biomass gasification systems." in *Proc. ESCAPE16*, Garmisch-Partenkirchen. Germany, 2005, pp.1661–1666. Available: <http://www.nt.ntnu.no/users/skoge/prost/proceedings/escape16-pse2006/Part%20B/Volume%201B/N52257-Topic4/Topic4-%20Oral/1445.pdf> [accessed Oct. 06, 2009].
- [14] P. J. Robinson, and W. L. Luyben, "Simple dynamic gasifier model that runs in ASPEN dynamics," *Ind. Eng. Chem. Res.*, vol. 47, pp. 7784–7792, 2008.
- [15] S. V. Nathen, R. D. Kirkpatrick, and B. R. Young, "Gasification of New Zealand coals: a comparative simulation study," *Energy Fuels*. vol. 22, pp. 2687–2692, 2008.
- [16] K. Kumabe, S. Fujimoto, Y. Yanagida, M. Ogata, T. Fukuda, A. Yabe, and T. Minowa, "Environmental and economic analysis of methanol production process via biomass gasification," *Fuel*, vol. 87, pp. 1422–1427, 2008.
- [17] S. Vaswani, "Development of models for calculating the life cycle inventory of methanol by liquid phase and conventional production processes," M.S. Thesis, Dep. Civil. Eng., North Carolina State University, U.S., 2000.
- [18] F. Ju, H. Chen, X. Ding, H. Yang, X. Wang, S. Zhang, and Z. Dai, "Process simulation of single-step dimethyl ether production via biomass gasification," *Biotechnol. Adv.*, vol. 27, pp. 599–605, 2009.
- [19] Nexant, Inc., *Environmental Footprints and Costs of Coal-Based Integrated Gasification Combined Cycle and Pulverized Coal Technologies*. United States Environmental Protection Agency (EPA), EPA Contract No. 68-W-03-33, Work Assignment 2-02, 2006.
- [20] Aspen Plus, "Aspen plus model of the CO₂ capture process by DEPG," Available: <http://www.cadfamily.com/download/chemical/aspen-meoh/Aspen%20Plus%20DEPG%20Model.pdf> [accessed Jan. 13, 2010].
- [21] A. R. Smith, and J. Klosek, "A review of air separation technologies and their integration with energy conversion processes," *Fuel Process. Technol.*, Vol. 70, pp. 115–134, 2001.
- [22] C. Higman, and M.V.D. Burtg, *Gasification*. Elsevier Science, Massachusetts, 2003.
- [23] J. Philips, "Gasification combined cycle 101," presented at gasification technology conference, San Francisco, Oct. 9–12, 2005.
- [24] L. D. Smoot and P. J. Smith, *Coal Combustion and Gasification*, Plenum Press, New York, 1985.
- [25] E. B. Ribbi, and N. Haimour, "Claus recycle with double combustion process," *Fuel Process. Technol.*, Vol. 86, pp. 245–260, 2004.
- [26] JN.J. Lammers, J. Haringa, and R. J. Little, "Effect of Polyhydroxyalcohols on COS Absorption in Aqueous Methyl-diethanolamine," *Chem. Eng. J.*, Vol. 60, pp. 123–129, 1995.
- [27] W. Breckenridge, A. HolidayJames, O. Y. Ong, and C. Sharp, "Commercial-scale demonstration of the liquid phase methanol (LPMEOH) process," Laurance Reid Gas Conditioning Conference, February 27–March 1, 2000, The University of Oklahoma, Norman, Oklahoma, Available:

- <http://www.uop.com/search/cherche.asp?target=selexol> [accessed Jan. 13, 2010]
- [28] W. D. Monnery, K. A. Hawboldt, A. Pollock, and W. Y. Svrcek, "New experimental data and kinetic rate expression for the Claus reaction," *Chem. Eng. Sci.*, vol. 55, pp. 5141-5148, 2000.
- [29] E. C. Heydorn, and B. W. Diamond, "Commercial-Scale Demonstration of the Liquid Phase Methanol (LPMEOH™) Process," Final report, vol. 2: Project performance and economics, No. DE-FC22-92PC90543, 2003.
- [30] E. C. Heydorn, B. W. Diamond, and R. D. Lilly, "Commercial-scale Demonstration of the Liquid Phase Methanol (LPMEOH) Process," DOE/METL-2004/1199, No. DE-FC22-92PC90543, 2003.
- [31] W. Cheng, and H. H. Kung, *Methanol Production and Use*, Marcel Dekker, Inc. New York, 1994.
- [32] T. Ogawa, N. Inoue, T. Shikada, and Y. Ohno, "Direct Dimethyl Ether Synthesis," *J. Nat. Gas Chem.*, vol. 12, pp. 219-227, 2003.
- [33] C. P. Marion, "Production of Methanol," US Patent 3,920,717, 1975.
- [34] A. K. Perka, T. S. Hsiung, J. Klosek, and R. B. Moore, "IGCC processes with combined methanol synthesis/water gas shift for methanol and electrical power production," U.S. Patent 3,946,477, 1990.
- [35] P. C. Chen, H. M. Chiu, Y. P. Chyou, "A gasification island and clean-up system model based on system-level simulation," in *Proc. 2008 Taiwan/Korea/Japan Chemical Engineering Conference and 55th Taiwan Institute of Chemical Engineers Annual Conference*, Nov. 21-22, Taipei, Taiwan, 2008.
- [36] P. C. Chen, H. M. Chiu, Y. P. Chyou and C. S. Yu, "A System-Level Simulation Model of Poly-Generation Plant Based on Gasification Technology with Methanol and Power Generation," in *Proc. ASME 2010 4th Int Conf on Energy Sustainability*, submitted for publication.