

ABSTRACT

Vaswani, Sudeep. Development of Models for Calculating the Life Cycle Inventory of Methanol by Liquid Phase and Conventional Production Processes. (Under the direction of Drs. Morton A. Barlaz and H. Christopher Frey).

This study deals with the development of an ASPEN PLUS process model for the liquid phase methanol (LPMEOH) process, which is in the demonstration phase at Eastman Chemical Company, TN. The model will ultimately be integrated with MSW gasification model being modeled separately and used in an integrated gasification combined cycle (IGCC) system to co-produce methanol and power from syngas obtained from MSW gasification. The LPMEOH process uses syngas as a starting material for methanol production. Model results for an example case are presented and the life cycle inventory (LCI) of methanol has been calculated starting from syngas.

When methanol is produced from the LPMEOH process, its production by conventional processes is avoided. Thus, an EXCEL spreadsheet model of methanol production using conventional process has also been developed. This model calculates the LCI of methanol from conventional process which is used to calculate the emissions avoided per kg of methanol produced by the LPMEOH process.

For LPMEOH process model, it is found that the performance of the model is dependent on syngas conversion in methanol reactor. Syngas conversion is a function of reactor pressure, syngas space velocity in methanol reactor, molar ratio of recycle gases

to fresh syngas feed, and H_2/CO molar ratio in syngas feed. The syngas composition mainly depends on the source from which it is obtained (e.g. coal gasification, MSW gasification). LPMEOH process model has the capability to process syngas of varying compositions.

Sensitivity analysis of LPMEOH process model has been presented. Based on the sensitivity analysis, it is shown that for syngas compositions limited in hydrogen content, the reactor pressure of or higher than 750 psig must be used. Further it is shown that recycling the unreacted gases has an advantage of more methanol production compared to the case with no recycle. It is also shown that the syngas feed with low H_2/CO ratio has lower methanol production than syngas with higher H_2/CO ratio. It therefore recommended that the syngas with low H_2/CO ratio be adjusted via water-gas shift reaction such that the H_2/CO ratio increases thereby resulting in a higher methanol production. It is also learnt that net steam demand in the LPMEOH process increases as the syngas becomes limited in its hydrogen content. This is expected to have some implications when the LPMEOH process is combined with an IGCC system.

The LCI of methanol produced by LPMEOH process varies widely with change in syngas composition and process conditions such as reactor pressure, space velocity in methanol reactor, and recycle ratio. The main contribution to the LCI occurs from the combustion of purge gases to produce steam in a boiler. The steam generated offsets the emissions from other contributors of the LCI. The sensitivity analysis of the LCI of methanol production from LPMEOH reveals that the methanol LCI is quite sensitive to

the changes in syngas composition, reactor pressure, syngas space velocity and the recycle ratio.

The sensitivity analysis of conventional methanol production has also been discussed. It is found that the LCI of conventional process is not very sensitive to changes in natural gas composition, which is used as a raw material for methanol production. The change in syngas conversion in methanol reactor also does not cause the overall LCI of methanol to change significantly.

The ultimate objective of the study is to compare the LCI of methanol produced by conventional process with that by LPMEOH process to determine if there is any advantage to methanol production by using LPMEOH technology on syngas derived from MSW gasification. The effect of an LPMEOH process on a gasification system would be an incremental increase in fuel use. Because of the incremental fuel use there would be an increase in elemental sulfur recovered, slag production, and some pollutant emissions. However, an overall LCI of methanol for LPMEOH process would require the calculation of the LCI associated with gasification.

**DEVELOPMENT OF MODELS FOR CALCULATING THE LIFE CYCLE
INVENTORY OF METHANOL BY LIQUID PHASE AND CONVENTIONAL
PRODUCTION PROCESSES**

by

SUDEEP VASWANI

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APPROVED BY:

Co-chair of Advisory Committee

Co-chair of Advisory Committee

BIOGRAPHY

Sudeep Vaswani was born on 31st August 1975 in Mumbai (Bombay), India. He earned a Bachelor of Engineering degree in Chemical Engineering from University of Roorkee (UOR), India in November 1998. His areas of interest upon graduation included Process Modeling and Simulation of Chemical Processes, Air Pollution Control, Air Quality and Process Thermodynamics.

He joined Marine, Earth and Atmospheric Science (MEAS) department at North Carolina State University in August 1998 to pursue an M.S. in Air Quality. In January 1999, he transferred to Civil Engineering department at NC State to pursue an M.S. in Environmental Engineering. Drs. Morton A. Barlaz and H. Christopher Frey advised him. He pursued a minor in Chemical Engineering along with his major in Environmental Engineering. He completed his M.S. thesis research in June 2000.

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1.0 INTRODUCTION AND BACKGROUND INFORMATION

Management of municipal solid waste (MSW) continues to be a high priority issue for many communities as we enter the new century. Landfilling has been the most common method of solid waste management in the U.S. (Tchobanoglous, 1993). As the space available for landfilling MSW continues to shrink, alternative methods for its management are being sought. Another popular way of treating MSW is by thermal processing. Thermal processing is used both for volume reduction and energy recovery. The two most focused ways of thermal processing are incineration and gasification of MSW. Due to recently demonstrated benefits of gasification over incineration, as described in the following paragraph, gasification technology is under great attention (Simbeck *et al.*, 1983; Stiegel, 2000).

Gasification can be defined as the process of partial combustion in which a fuel (e.g. MSW) is partially combusted with less than stoichiometric air (Tchobanoglous, 1993). The product gas, referred to as synthesis gas or syngas, consists mainly of hydrogen (H₂), carbon monoxide (CO), and carbon dioxide (CO₂). After cleaning, this synthesis gas can be split and used for the production of wide variety of chemicals such as methanol, hydrogen, ammonia, sulfuric acid, formaldehyde, and others or saturated with water and combusted in a gas turbine for power production. The main advantage of gasification over incineration is that gasification allows for the conversion of a wide-range of fuels such as coal, petroleum cokes, natural gas, heavy oils, biomass and wastes into a product gas that can be used for power generation or as a feed stock for the

production of chemicals. Also, gasification technology, when used in an integrated gasification combined cycle (IGCC) system, has higher thermal efficiency and lower pollutant production compared to conventional power generation systems (Frey and Rubin, 1992; Stiegel, 2000).

The work described here is a part of a larger project that will develop novel assessment methodologies for evaluation of the risks and potential pay-offs of new technologies that avoid pollutant production. The methodology will be demonstrated via a detailed case study of one promising new pollution prevention technology – gasification of MSW for the production of syngas to generate power and produce chemicals (e.g., methanol). The approach will utilize process simulation and optimization in ASPEN PLUS to simulate the chosen technology. Life cycle analysis will then be applied leading to the development of a life cycle inventory (LCI) of chemicals produced by MSW gasification technology. A parallel LCI will also be developed to calculate the benefits of chemical production via gasification relative to conventional production process.

This study deals with developing models for calculating the LCI of methanol produced by a conventional method and the liquid phase methanol (LPMEOHTM) process. The model for conventional production of methanol has been developed in MS EXCEL and that of LPMEOH process has been developed in ASPEN PLUS in conjunction with EXCEL. Since the LCI of methanol uses the LCI of steam and electricity, they are also described.

While LCI of steam was developed in this project, the LCI of electricity was directly used from the electric energy process model developed by Dumas (1998).

The following subsection presents the motivating questions of this study. An overview of MSW management is presented next followed by the commercial status of gasification systems and MSW gasification technology. Production of methanol is then described. Information on LCI analysis and its need is presented next. Objectives of the study are then presented.

1.1 Motivating Questions

In order to evaluate the risks and potential pay-offs of a new technology, the LPMEOH process, there is a need to develop a systematic approach for its assessment. The performance and emissions of the technology need to be characterized on a basis such that comparison can be made with conventional methanol technology. The current study deals with the development of models for calculating the LCI of methanol production from LPMEOH and conventional process and has following motivating questions:

1. What are the methanol production rates and the emissions from LPMEOH process using the synthesis gas obtained from various sources (e.g. coal gasification, MSW gasification)?

2. What are the emissions from the alternative conventional process of methanol production for calculation of emission offsets?
3. What are the key design variables that affect the performance of LPMEOH process and the LCI associated with it?
4. What is the sensitivity of LPMEOH process model and conventional process model LCI to changes in key design variables?
5. How does the LCI of methanol obtained from LPMEOH process compare with that obtained from conventional process?
6. What are the main issues/key parameters involved in combining the LPMEOH process with an IGCC system for coproduction of methanol with power?

The following section presents an overview of MSW management.

1.2 Overview of MSW Management

Solid waste management may be defined as the discipline associated with the control of generation, storage, collection, transfer and transport, processing, and disposal of solid wastes in a manner that is in accord with the best principles of public health, economics, engineering, conservation, aesthetics, and other environmental considerations (Tchobanoglous, 1993). Ultimate disposal of solid waste is one of the most important aspects of solid waste management. Historically, landfills have been the most economical and environmentally acceptable method for the disposal of solid wastes, both in the U.S. and throughout the world (Tchobanoglous, 1993).

Landfills are the physical facilities used for the disposal of residual solid wastes in the surface soils of the earth. Chief advantages of landfilling are low cost, and production of landfill gas consisting mainly of methane which can be used for energy recovery. Disadvantages of landfills include: (1) the uncontrolled release of landfill gases that might migrate off-site and cause odor and other potentially dangerous conditions; (2) the uncontrolled release of leachate that might migrate down to underlying groundwater or to surface water; and (3) limited availability of space for construction of landfills. As available land continues to decrease, landfilling is becoming a less desirable alternative for waste disposal. Alternatives are being considered and one of the most widely focused methods is thermal conversion of solid waste which results in significant volume reduction prior to burial.

Thermal conversion of solid waste management includes: (1) combustion systems or incinerators; (2) pyrolysis systems; and (3) gasification systems. Combustion or incineration can be defined as the thermal processing of solid waste by chemical oxidation with greater than stoichiometric air whereas pyrolysis is thermal processing of waste in complete absence of oxygen. The main advantages of solid waste incineration are volume and weight reduction of solid waste, less space required and energy recovery. The main limitations are high capital cost, skilled operators required for the incinerator operation, and public disapproval. Due to these limitations, gasification, although discovered in nineteenth century, is being studied with renewed interest. The main advantages of solid waste gasification are production of synthesis gas which can be used

for wide variety of applications and potential to achieve low air pollution emissions with simplified air pollution control devices (Tchobanoglous, 1993). The following section briefly describes gasification technology.

1.3 Gasification Systems and MSW Gasification Technology

Gasification is an energy efficient technique for reducing the volume of solid waste and for recovery of energy. The process involves partial combustion of carbonaceous fuel to generate a combustible gas rich in CO, H₂, and some saturated hydrocarbons, principally methane. The combustible fuel gas can then be combusted in an internal combustion engine, gas turbine, or boiler under excess-air conditions. One method of utilizing gasification to produce power is an integrated gasification combined cycle (IGCC) system. Besides the production of electricity, a gasification plant can also produce several chemicals such as methanol, hydrogen, ammonia, sulfuric acid, formaldehyde, and others (Simbeck *et al.*, 1983)

MSW gasification is a relatively new concept. There are several research projects investigating the process. Various demonstration plants using solid waste gasification technology include Thermoselect (Italy), ThermoChem (Ontario, CA), Proler (Houston, TX), and Lurgi/Shwarze Pumpe (Dresden, Germany) (Niessen *et al.*, 1996). The only commercially demonstrated IGCC system fueled by solid waste is the Shwarze Pumpe plant near Dresden, Germany. The Dresden plant processes wastes including plastics, sewage sludge, rubber, auto waste, contaminated wood, residues of paint, household

waste and coal. The plant produces 120,000 tons per year of grade AA methanol (>99.85 percent purity by weight) and 75 MW electricity. The following section briefly describes the production of methanol starting from synthesis gas.

1.4 Methanol Production

There are 18 methanol production plants in the United States with a total annual capacity of over 2.6 billion gallons per year (American Methanol Institute, 1998). Worldwide, over 90 methanol plants have the capacity to produce over 11 billion gallons of methanol annually. The typical feedstock used in the production of methanol is natural gas. Methanol also can be made from renewable resources such as wood, municipal solid wastes and sewage. In either case the starting material is syngas. In syngas, CO, CO₂ and H₂ react over a copper-based catalyst to produce methanol, which is then condensed and finally refined in a distillation column.

Various methanol production technologies are available for production of methanol from syngas. The most popular of these technologies are ICI low-pressure and Lurgi low-pressure processes. Both these conventional technologies require the H₂/CO ratio near 2 to 2.1 for optimum methanol production. Most methanol plants built all over the world use natural gas for generation of syngas to produce methanol (American Methanol Institute, 1998; Cheng and Kung, 1994).

The current thrust in the methanol process industry is to produce methanol using a syngas that is obtained from wastes i.e. MSW. The Lurgi Shwarze Pumpe plant described in the previous section is one example, where methanol is being produced using syngas obtained from solid waste. Syngas produced by dirty fuels such as coal and MSW is high in CO content and requires a shift conversion to achieve an H_2/CO ratio near two in order for the conventional methanol plant to operate optimally (Cheng and Kung, 1994). A new technology of methanol production, the liquid phase methanol (LPMEOH) process, currently undergoing demonstration at Eastman Chemical Company, TN, is expected to produce methanol from syngas richer in CO without having to perform a shift reaction. This technology is therefore expected to perform well on the syngas produced by MSW gasification. Other advantages of this process over conventional processes (ICI and Lurgi) are described in Chapter 4.

The following section presents a brief description of the need to develop the LCI of chemicals.

1.5 Life Cycle Inventory Analysis of Chemicals

Life cycle is defined as consecutive and interlinked stages of a system that extend from raw material acquisition or generation of natural resources to final disposal. Life cycle analysis involves compilation and evaluation, according to systematic procedure, of the inputs and outputs of materials and energy and the associated environmental impacts directly attributable to the function.

A complete life cycle study consists of three complementary components: (1) inventory analysis, which is a compilation of all material and energy requirements associated with each stage of product manufacture, use and disposal; (2) impact analysis, a process in which the effects of the inventory on the environment are assessed; and (3) improvement analysis, which is aimed at reducing the product impact on the environment (Pistikopulos *et al.*, 1994). LCI can be used in process analysis, material selection, product evaluation, product comparison, and policy making.

1.6 Objectives

The objectives of the current work are:

1. To develop the models for calculating the LCI of methanol from LPMEOH and conventional production technologies.
2. To perform the sensitivity analysis on models developed in (1) to understand the key parameters affecting their performance and the LCI of methanol.
3. To compare the LCI of methanol produced by the LPMEOH and conventional production technologies.

Chapter 2 presents the methodology for calculating the LCI of steam, which is used in calculating the overall LCI of methanol production, both for the LPMEOH and conventional processes. Chapter 3 presents the methodology for calculating the LCI of electricity to be used in calculating the overall LCI of methanol production, both for the LPMEOH and conventional process. Chapter 4 elaborates on various methods of methanol production with their advantages and disadvantages. It also presents the

methodology to model LPMEOH process in ASPEN PLUS, the model results for the base case and calculation of the LCI of methanol from the results. Chapter 5 describes the development of an EXCEL spreadsheet to calculate mass and energy balances of a conventional process of methanol production. The spreadsheet model also calculates the LCI of methanol produced by a conventional process based on its mass and energy balance. Chapter 6 presents the conclusions of this study.

2.0 LIFE CYCLE INVENTORY OF STEAM

The objective of this chapter is to present a methodology to calculate the life cycle inventory (LCI) of steam. Steam is used in many process industries as a heating medium, in the process itself or for the generation of electricity. Production of nearly all the chemicals in a process industry requires the use of steam in some manner (Babcock and Wilcox, 1972). Thus, in order to develop an overall LCI of a particular chemical, the LCI of steam is typically required as a key component. The methodology described in this section considers emissions that result from fuel combustion in a boiler for the generation of steam. Pre-combustion emissions associated with fuel production such as surface and underground mining, transportation, fugitive emissions and others are also included. Emission factors are calculated for particulate matter (PM), SO₂, NO_x, CO, hydrocarbons (HC), CH₄, HCl, VOCs and trace metals. Water emissions and solid waste generation as a result of boiler feed water pretreatment and use of materials in air pollution control equipment are also considered. Emission factors are calculated in units of kg pollutant per MJ of steam produced and lb pollutant per million Btu (MMBtu) of steam produced.

The next section presents background information on steam and its generation in boilers, followed by Section 2.2, which presents the design basis for developing the LCI of steam and key assumptions, made therein. The methodology used to calculate the LCI parameters is then described in Section 2.3. Finally, the values of LCI parameters associated with generation of steam based on design assumptions are presented in Section 2.3.8.

2.1 Background

Steam is a vapor form of water. It plays a pivotal role in industrial plants because of its availability and advantageous properties for use in heating processes and power cycles. When steam is used for process heating, it provides an excellent rate of heat transfer and control of process temperature. It is a good way of conveying heat released from the combustion of a fuel to the place where heat is needed. Over 45 percent of all the fuel burned by U.S. manufacturers is consumed to produce steam. It costs approximately \$18 billion (1997 dollars) annually in fuel costs to feed the boilers generating the steam (U.S. DOE, 1999).

The fuel burned in the boiler or steam-generating unit produces hot combustion products that supply the heat to convert water to steam. The most commonly used fuels are coal, fuel oils (residual and distillate) and natural gas (U.S. EPA, 1998). While carbon dioxide and water vapor are produced as a result of combustion, some atmospheric pollutants are also produced depending on the type and composition of fuel combusted. The hot exhaust gas is treated to remove these pollutants using appropriate pollution control technologies before releasing it to the atmosphere. Typical industrial steam boilers vary in size range from 2.9 MW to 29 MW heat input (U.S. EPA, 1982). Boiler emissions are a function of fuel type, fuel composition, boiler type, boiler heat rate and combustion efficiency. It is therefore important to understand the various types of boilers and their heat input rate.

Boilers can be classified by type, fuel, and method of construction. Boiler types are identified by heat transfer method (watertube, firetube, or cast iron), the arrangement of heat transfer surfaces (horizontal, vertical, straight or bent tube), and in the case of coal, the fuel feed system (pulverized or stoker). The major distinguishing characteristic of a boiler is its heat transfer mechanism. Based on this classification, boilers can be divided into 3 major groups (U.S. EPA, 1982): (1) watertube boilers; (2) firetube boilers; and (3) cast iron boilers. Each is described in the following sections.

(1) Watertube boilers: Watertube boilers are used in a variety of applications ranging from supplying large amounts of process steam to providing space heat for industrial facilities. In these types of boilers, water passes through the inside of heat transfer tubes while the outside of the tube is heated by direct contact with hot combustion gases. This process results in generation of high pressure, high temperature steam. Watertube boilers are available, as packaged or field-erected units, in capacities ranging from less than 2.9 MW to over 200 MW (10×10^6 Btu/hr to 700×10^6 Btu/h) thermal input. Industrial watertube boilers can burn coal, residual oil, distillate oil, natural gas, liquefied petroleum gas and other fossil and nonfossil fuels.

(2) Firetube boilers: Firetube boilers are used primarily for heating systems, industrial process steam, and portable power boilers. Essentially all firetube boilers are packaged units with some being portable rather than stationary. In these types of boilers, the hot gas flows through the tubes and the water being heated circulates

outside of the tubes. Firetube boilers are usually limited in size to less than 5.9 MW (20×10^6 Btu/h) thermal input. Most of the installed capacity of firetube units is oil- and gas-fired.

(3) Cast Iron boilers: In cast iron boilers, the hot gas is contained inside the tubes and the water being heated circulates outside the tubes. The units are constructed of cast iron rather than steel. Cast iron boilers are used to produce either low-pressure steam or hot water. Generally, boiler capacity ranges from 0.001 MW to 2.9 MW (0.003×10^6 Btu/h to 10×10^6 Btu/h) thermal input with pressure ratings up to 690 kPa (100 psi) for hot water units and 100 kPa (15 psi) for steam units. Thus, cast iron boilers are most commonly used in domestic or small commercial application.

Table 2-1 shows the population distribution for industrial boilers in the U.S. by design type in 1982 (U.S. EPA, 1982). Table 2-2 shows the relative distribution by capacity. As evident from Table 2-2, watertube boilers are available over a larger size range than the other types.

Table 2-1. Boiler Population Distribution by Heat-transfer Configuration

Heat-transfer Configuration	Total Boiler Capacity	
	MW Thermal Input	Percent of Total
Watertube	638,665	70.0
Firetube	219,360	24.2
Cast Iron	52,570	5.8

Table 2-2. Relative Distribution by Capacity of the Three Types of Industrial Boilers

Heat transfer Configuration	Population Based on MW Heat Input (Percentage in each category)				
	<i>0-2.9</i>	<i>2.9-14.7</i>	<i>14.7-29.3</i>	<i>29.3-73.3</i>	<i>>73.3</i>
<i>Size Range, MW thermal input</i>					
Watertube	19737 ^a (10.64 ^b)	113158 (51.8)	118421 (100)	171053 (100)	213158 (100)
Firetube	110526 (59.57)	105263 (48.2)	0 (0)	0 (0)	0 (0)
Cast Iron	55263 (29.78)	0 (0)	0 (0)	0 (0)	0 (0)

^a Units: MW (e.g., 19737 MW)

^b Percent (e.g., 10.64 %)

For low pressure to medium pressure steam generation, the heat-input rate of a process boiler is typically in the range of 2.9 MW_t to 29.3 MW_t heat input to the boiler (U.S. EPA, 1982). In this range, overall installed capacity (in MW_t thermal input) of watertube boilers in US fairly exceeds the installed capacity of firetube or cast iron boilers, which are used for relatively small steam demand (U.S. EPA, 1982). Furthermore watertube boilers are structurally more stable to variations in steam demand than firetube boilers (U.S. EPA, 1998). Thus, watertube boilers are chosen as representative boilers for the generation of an LCI of steam in a process industry.

2.2 System Boundaries and Design Basis

The steam LCI includes all activities associated with the production of steam starting from water. The LCI of boiler feed water (BFW) conditioning/pretreatment is restricted to hardness removal using ion exchange and resin regeneration for simplicity

(Gonzalez and Overcash, 1999). LCI parameters associated with removal of other trace impurities and contaminants from BFW are insignificant, and are not considered (Gonzalez and Overcash, 1999).

One Mega-joule (MJ) of steam produced has been used as a basis for the calculation of LCI parameters. It is assumed that saturated steam at 100 psia is generated from water entering the boiler at 50°C. Raw water is typically available at 20 °C. During BFW treatment, the raw water is heated to 50 °C for the removal of dissolved gases to avoid boiler corrosion (Nunn, 1997). The energy used in raising a kg of water from 20 °C to 50 °C is less than five percent of the energy carried by a kg of 100-psia saturated steam produced, therefore, the energy associated with BFW treatment is neglected.

The amount of saturated steam generated at 100-psia is calculated to be 0.392 kg for 1 MJ steam demand using Equation (2-1).

$$m_{Steam} = \frac{\Delta H_{Steam}}{(h_v - h_l)} \quad (2-1)$$

where: m_{Steam} = Mass of steam produced (kg)

ΔH_{Steam} = Enthalpy associated with steam (= 1 MJ).

h_v = Enthalpy per kg of 100 psia steam (= 2.76 MJ/kg).

h_l = Enthalpy per kg of 50 °C BFW (= 0.209 MJ/kg)

Amount of steam generated is determined to calculate the LCI associated with BFW treatment. It will be demonstrated later that the LCI associated with BFW is quite small and therefore as the flowrate of steam changes for the same total enthalpy due to

changing pressure, there is almost no effect on the overall LCI of steam. Thus only the enthalpy associated with steam is required to determine the LCI associated with steam use in a process.

The emissions from a fuel-fired boiler depend on fuel type, fuel composition, boiler type, boiler heat rate, and combustion efficiency. As explained in the previous section, a watertube boiler was selected as a model boiler for the development of an LCI for steam.

Watertube boilers in the 2.9 MW_t to 29.3 MW_t heat-input category can be further subdivided based on the fuel type used. Table 2-3 shows various categories, based on fuel type, of watertube boilers and their installed capacity in the U.S (U.S. EPA, 1982). Only coal, fuel oil (distillate and residual) and natural gas are considered here since they are the only fuels used in the industrial steam boilers. Table 2-4 shows typical ultimate analyses and heating values of coal, residual oil, distillate oil and natural gas used in developing combustion emission factors (Pechtl and Chen, 1992; Perry, 1997; U.S. EPA, 1982). Pre-combustion emissions for coal, distillate oil, residual oil and natural gas have been calculated for 1 MJ of steam production from the emission factors (given in per 1000 units of fuel basis) in an electric energy process model developed by Dumas (1998). Pre-combustion emissions are presented in Table 2-6.

Table 2-3. Percentage of Installed Capacity of Various Fuel Type Watertube Boilers in 2.9 MW_t to 29.3 MW_t Heat-input Category (U.S. EPA, 1982)

Fuel Type		Percentage of Watertube Boilers
COAL	Pulverized coal	0
	Spreader-stoker coal	4.2
	Underfeed-stoker coal	12.16
	Overfeed-stoker coal	3.07
OIL	Residual Oil	32.49
	Distillate Oil	4.87
NATURAL GAS		43.21
Total		100.00

Table 2-4. Ultimate Analysis and Heating Values of Fuels Used in Developing the Emission Factors (Pechtl and Chen, 1992; Perry, 1997; U.S. EPA, 1982)

Fuel	Coal (Bituminous)	Distillate Oil (No. 2)	Residual Oil (No.6, Low sulfur)	Natural Gas
Element	Wt%	Wt%	Wt%	Wt%
C	73.21	87.3	87.26	69.28
H	4.94	12.6	10.49	22.67
N	1.38	0.006	0.28	8.05
O	4.85	0.04	0.64	Trace
S	3.3	0.22	0.84	Trace
Ash	12.23	Trace	0.04	0
Cl	0.09	-	-	-
Heating Value	12350 Btu/lb	19500 Btu/lb	18500 Btu/lb	1020 Btu/ft ³

Steam produced is distributed among watertube boilers based on the percentage of their installed capacity as in Table 2-3. Thus, steam with total enthalpy of 1 MJ would be divided as 0.4321 MJ being produced by natural gas fired, 0.0487 MJ being produced by distillate oil fired, 0.3249 MJ being produced by residual oil fired, 0.0307 MJ being produced by overfeed stoker coal fired, 0.1216 MJ being produced by underfeed stoker coal fired, and 0.042 MJ being produced by spreader stoker coal fired watertube boilers.

Table 2-5 presents the regulatory emission limits, as reported in Code of Federal Regulations (CFR, 1999), for steam generating units that commenced construction, modification, or reconstruction after June 9, 1989 and have a heat input capacity from fuels combusted in the steam generating unit of 2.9 to 29 MW_t (10 to 100 million Btu/hour).

Table 2-5. Code of Federal Regulations Emissions Limit for Boilers Heat Rate in the Range of 2.9 MW_t to 29 MW_t (from 40 CFR Part 60 – As revised on July 1999)

Fuel Type	SO₂ ng/J (lb/10 ⁶ Btu)	PM ng/J (lb/10 ⁶ Btu)
Overfeed stoker coal	520 (1.2)	22 (0.05)
Spreader stoker coal	520 (1.2)	22 (0.05)
Pulverized coal	520 (1.2)	22 (0.05)
Underfeed stoker coal	520 (1.2)	22 (0.05)
Distillate Oil	215 (0.5)	- ^a
Residual Oil	215 (0.5)	- ^a
Natural Gas	-	- ^a

^a Standard applies when gas or oil is fired in combination with coal (40 CFR Part 60, subpart Dc)

Carbon dioxide, CO, organic compounds, trace metals, acid gases such as hydrogen chloride and fugitive emission are some of the other products of combustion of fuels. Uncontrolled emission factors for pollutants (PM, SO₂, CO, CO₂, NO_x, and others) based on boiler are fuel type were available from AP-42 (U.S. EPA, 1998). Air pollution control (APC) equipment assumed to be present includes: (1) a spray dryer for acid gas control (SO₂ and HCl) for acid emissions from coal fired and residual oil fired boilers (U.S EPA, 1998); (2) a low NO_x burner for NO_x control in case of coal fired boilers except stoker boilers, residual and distillate oil fired boilers, and natural gas fired boilers; and (3) a fabric filter for particulate matter (PM) control in case of coal fired, residual oil

fired and distillate oil fired boilers. NO_x control technology used for stoker coal fired boilers is low excess air (LEA) technology. Spray dryer is used for the removal of acid gases generated by low and medium sulfur fuels fired in steam generating industrial boilers (U.S. EPA, 1998). Typical control efficiency of SO₂ in a spray dryer ranges from 70 to 90 percent. A low NO_x burner is a combustion modification technique commonly used for controlling the NO_x emissions in steam generating boilers. Low NO_x burner has a NO_x reduction potential ranging from 35 to 55 percent. LEA technology typically has NO_x reduction potential of 25 percent for coal fired stoker boilers (U.S. EPA, 1998). Fabric filters are commonly used for the removal of PM with a typical removal efficiency ranging from 99 to 99.9 percent. After APC, the flue gas is released to the atmosphere.

The LCI parameters considered includes gaseous and liquid releases as well as solid waste. Although it is assumed that there are no water releases or solid waste production other than ash, these parameters are included because such releases are associated with the fuel pre-combustion emissions, LCI of BFW pretreatment and that of materials consumed in APC equipment.

For LCI of BFW conditioning, ionic exchange pretreatment is considered. A total hardness of 100 mg Ca²⁺/liter and 155 mg Mg²⁺/ liter was assumed to be present in the water to be pretreated (Gonzalez and Overcash, 1999).

One hundred percent hardness removal efficiency is assumed in calculations. The regenerant for the ion exchange resin is sodium chloride.

2.3 Calculation of the LCI of Steam

The LCI of steam considers the emission associated with generation of steam from various boilers based on fuel types, pre-combustion emissions associated with fuels, the LCI of sodium chloride used in BFW pretreatment, and the LCI of lime used in spray drying for the removal of acid gases. The overall LCI parameters considered include PM, PM-10, SO₂, SO₃, NO_x, CO, CO₂, CH₄, HCl, VOCs, hydrocarbons, NH₃, 12 metals, liquid emissions and solid waste. The methodology used to calculate and allocate emissions is described in this section.

2.3.1 Pre-combustion Emissions from the Fuels Fired

Pre-combustion emissions in the units of lb per 1000 units of fuel (lbs. for coal, gals. for distillate and residual oil, and standard cuft. for natural gas) are presented in Table 2-6 (Dumas, 1998). Knowing these emission factors, heating values of fuels in consideration and total enthalpy of steam produced (1 MJ), the emission factors per MJ of steam can be calculated as follows:

$$E_i = \left(\frac{EF_i}{HV_j} \right) \times \frac{\Delta H_{Steam}}{1000} \quad (2-2)$$

where: E_i = Emission of pollutant 'i' (lb/Btu Steam)

EF_i = Emission factor of pollutant 'i' (lb/1000 fuel units)

HV_j = Heating value of the fuel (Btu/fuel unit)

Fuel unit = lb for coal, gal for residual and distillate oil, and standard. cuft. for natural gas

$\Delta H_{\text{Steam}} = 1 \text{ MJ (in Btu's)}$

The emission (E_i) calculated in above equation can be then converted to kg emissions per MJ steam produced. Table 2-7 presents the calculated pre-combustion emissions in kg per MJ of steam.

Table 2-6. Pre-Combustion Emissions per 1000 Units of Fuel (Dumas, 1998)

Atmospheric Emissions	Coal (lb/1000 lbs coal)	Residual Oil (lb/1000 gal)	Distillate Oil (lb/1000 gal)	Natural Gas (lb/1000 cuft)
PM	2.56E+00	1.80E+00	1.66E+00	3.80E-03
PM-10	no data	no data	no data	no data
SO ₂	2.30E-01	2.81E+01	2.58E+01	1.97E+00
SO ₃	no data	no data	no data	no data
NO _x	2.30E-01	9.20E+00	8.47E+00	1.20E-01
CO	1.80E-01	6.90E+00	6.36E+00	2.30E-01
CO ₂ (Fossil)	4.07E+01	2.86E+03	2.63E+03	1.57E+01
CO ₂ (Biomass)	3.00E-01	6.64E+00	6.10E+00	2.80E-02
CH ₄	4.69E+00	4.41E+00	4.05E+00	3.80E-01
HCl	1.10E-03	2.70E-02	2.50E-02	9.80E-05
VOC	no data	no data	no data	no data
NH ₃	2.00E-05	4.40E-02	4.00E-02	9.50E-06
Hydrocarbons	8.50E-02	5.50E+01	5.02E+01	5.30E-01
Metals				
Antimony (Sb)	no data	no data	no data	no data
Arsenic (As)	no data	no data	no data	no data
Beryllium (Be)	no data	no data	no data	no data
Cadmium (Cd)	no data	no data	no data	no data
Chromium (Cr)	no data	no data	no data	no data
Cobalt (Co)	no data	no data	no data	no data
Copper (Cu)	no data	no data	no data	no data
Lead (Pb)	2.70E-06	1.50E-04	1.40E-04	2.87E-07
Mercury (Hg)	no data	no data	no data	no data
Nickel (Ni)	no data	no data	no data	no data
Selenium (Se)	no data	no data	no data	no data
Zinc (Zn)	no data	no data	no data	no data
Liquid Emissions				
Dissolved Solids	8.20E-02	3.79E+01	3.48E+01	3.04E+00
Suspended Solids	1.41E+00	8.60E-01	7.90E-01	5.40E-03
BOD	1.20E-04	1.40E-01	1.30E-01	2.70E-03
COD	1.30E-03	9.50E-01	8.70E-01	1.90E-02
Oil	1.50E-03	8.90E-01	8.10E-01	5.40E-02
Sulfuric Acid	2.50E-04	7.50E-03	6.90E-03	2.10E-05
Iron	1.20E-01	2.10E-02	1.90E-02	7.30E-05
Ammonia	1.40E-05	1.50E-02	1.40E-02	4.90E-06

Table 2-6 continued on next page

Table 2-6 continued

Liquid Emissions	Coal (lb/1000 lbs coal)	Residual Oil (lb/1000 gal)	Distillate Oil (lb/1000 gal)	Natural Gas (lb/1000 cuft)
Cadmium	3.60E-06	1.40E-03	1.30E-03	1.40E-04
Arsenic	0.00E+00	no data	no data	no data
Mercury	2.80E-10	1.10E-07	9.80E-08	1.10E-08
Phosphate	1.20E-04	3.80E-03	3.50E-03	1.10E-05
Selenium	0.00E+00	no data	no data	no data
Chromium	3.60E-06	1.40E-03	1.30E-03	1.40E-04
Lead	5.70E-09	1.60E-05	1.50E-05	1.10E-09
Zinc	1.30E-06	7.10E-04	6.50E-04	4.80E-05
Solid Waste	3.45E+02	1.44E+02	1.33E+02	5.80E+00
Energy (Btu)	2.64E+05	2.10E+07	1.93E+07	1.29E+05

Table 2-7. Pre-Combustion Emissions for 1 MJ of Steam Produced^a

Atmospheric Emissions	Coal (kg/MJ Steam)	Distillate Oil (kg/MJ Steam)	Residual Oil (kg/MJ Steam)	Natural Gas (kg/MJ Steam)	Total (kg/MJ Steam)
PM	2.17E-05	3.19E-07	2.00E-06	8.66E-07	2.48E-05
PM-10	no data	no data	no data	no data	
SO ₂	1.95E-06	4.95E-06	3.12E-05	4.49E-04	4.87E-04
SO ₃	no data	no data	no data	no data	
NO _x	1.95E-06	1.63E-06	1.02E-05	2.73E-05	4.11E-05
CO	1.52E-06	1.22E-06	7.67E-06	5.24E-05	6.28E-05
CO ₂ (Fossil)	3.44E-04	5.05E-04	3.18E-03	3.58E-03	7.61E-03
CO ₂ (Biomass)	2.54E-06	1.17E-06	7.38E-06	6.38E-06	1.75E-05
CH ₄	3.97E-05	7.78E-07	4.90E-06	8.66E-05	1.32E-04
HCl	9.31E-09	4.80E-09	3.00E-08	2.23E-08	6.64E-08
VOC	no data	no data	no data	no data	
NH ₃	1.69E-10	7.68E-09	4.89E-08	2.16E-09	5.89E-08
Hydrocarbons	7.19E-07	9.64E-06	6.11E-05	1.21E-04	1.92E-04
Metals					
Antimony (Sb)	no data	no data	no data	no data	
Arsenic (As)	no data	no data	no data	no data	
Beryllium (Be)	no data	no data	no data	no data	
Cadmium (Cd)	no data	no data	no data	no data	
Chromium(Cr)	no data	no data	no data	no data	
Cobalt (Co)	no data	no data	no data	no data	
Copper (Cu)	no data	no data	no data	no data	
Lead (Pb)	2.28E-11	2.69E-11	1.67E-10	6.54E-11	2.82E-10
Mercury (Hg)	no data	no data	no data	no data	
Nickel (Ni)	no data	no data	no data	no data	
Selenium (Se)	no data	no data	no data	no data	
Zinc (Zn)	no data	no data	no data	no data	
Liquid Emissions					
Dissolved Solids	6.94E-07	6.68E-06	4.21E-05	6.93E-04	7.42E-04
Suspended Solids	1.19E-05	1.52E-07	9.56E-07	1.23E-06	1.43E-05
BOD	1.02E-09	2.50E-08	1.56E-07	6.15E-07	7.97E-07
COD	1.10E-08	1.67E-07	1.06E-06	4.33E-06	5.56E-06
Oil	1.27E-08	1.56E-07	9.89E-07	1.23E-05	1.35E-05
Sulfuric Acid	2.12E-09	1.33E-09	8.34E-09	4.78E-09	1.66E-08
Iron	1.02E-06	3.65E-09	2.33E-08	1.66E-08	1.06E-06
Ammonia	1.18E-10	2.69E-09	1.67E-08	1.12E-09	2.06E-08
Copper	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

Table 2-7 continued on next page

Table 2-7 continued

Liquid Emissions	Coal (kg/MJ Steam)	Distillate Oil (kg/MJ Steam)	Residual Oil (kg/MJ Steam)	Natural Gas (kg/MJ Steam)	Total (kg/MJ Steam)
Arsenic	0.00E+00	no data	no data	no data	
Mercury	2.37E-15	1.88E-14	1.22E-13	2.51E-12	2.65E-12
Phosphate	1.02E-09	6.72E-10	4.22E-09	2.51E-09	8.42E-09
Selenium	0.00E+00	no data	no data	no data	
Chromium	3.05E-11	2.50E-10	1.56E-09	3.19E-08	3.37E-08
Lead	4.82E-14	2.88E-12	1.78E-11	2.51E-13	2.10E-11
Zinc	1.10E-11	1.25E-10	7.89E-10	1.09E-08	1.19E-08
Solid Waste	2.92E-03	2.55E-05	1.60E-04	1.32E-03	4.43E-03
Energy (MJ)^B	5.19E-03	8.61E-03	5.42E-02	6.83E-02	1.36E-01

^a Heating values used for the fuels are presented in Table 2-4.

2.3.2 Combustion of Coal to Generate Steam

This section presents the emission factors of various pollutants associated with the combustion of coal for the generation of steam in various types of boilers. Four types of coal fired boilers, namely pulverized coal wall fired (dry bottom), spreader stoker, overfeed stoker and underfeed stoker boilers are considered. The boilers are assumed to fire bituminous coal (Bituminous high volatile – A), which is mainly used for the generation of steam in industrial boilers (U.S. EPA, 1998). A typical ultimate analysis of Bituminous coal is presented in Table 2-4. Thermal efficiency of these boilers is assumed to be 80 percent, which is typical of coal fired boilers (U.S. EPA, 1982). AP-42 lists the uncontrolled emission factors of PM, SO₂, CO, NO_x, CO₂, CH₄ and HCl in the units of lb per ton of coal combusted for various boiler configurations firing bituminous coal. It also lists the controlled emissions for 12 metals.

The spray dryer used in case of all coal fired boilers is assumed to operate with 90 percent SO₂ removal efficiency as required by the Code of Federal Regulations (40 CFR Part 60 subsection Dc, July 1999). A low NO_x burner is assumed to have a NO_x control efficiency of 50 percent for all coal fired boilers except the coal fired stoker boiler (U.S. EPA, 1998). LEA technology used for coal fired stoker boilers is assumed to have NO_x control efficiency of 25 percent (U.S. EPA, 1998). A fabric filter with 99 percent PM removal efficiency is assumed for all coal fired boilers, as is typical of bag filters (U.S. EPA, 1998).

Emission control factors are applied to uncontrolled SO₂, NO_x, and PM emission factors. Emission control factors, defined by Equation (2-3), are the factors based on control efficiency of APC by which uncontrolled emission factors are multiplied to get controlled emission factors.

$$ECF_i = \left(1 - \frac{h_i}{100} \right) \quad (2-3)$$

where: ECF_i = Emission control factor

η_i = Control Efficiency of APC equipment (e.g., 90 percent removal for SO₂)

i. = Pollutant (e.g., SO₂, NO_x, etc.)

Metal emissions are controlled emissions as reported in AP-42 so they are presented as such. CO and CH₄ emissions are quite low and therefore no control factor is applied to them. Table 2-8 presents the emission factors of various pollutants after APC for all four kinds of boilers firing bituminous coal. The emission factors are reported in lb/MMBtu heat input. It is assumed that no liquid emissions are generated. Bottom ash and fly ash generated occur as a solid waste. Roughly, 80 percent of ash content of coal occurs as fly ash and 20 percent as bottom ash (Frey, 2000). For LCI purposes, no differentiation is made between bottom ash and fly ash (Harrison *et al.*, 1999.). Ninety nine percent of total fly ash (80 percent of total ash content) was assumed to be collected as PM in APC. The collected PM was added to bottom ash (20 percent of total ash content) to calculate the solid waste generated.

Table 2-8. Emission Factors of Various Pollutants After APC for Different Coal Fired Boilers Firing Bituminous Coal

Air Emissions	Pulverized Coal (lb/MMBtu input)	Spreader stoker (lb/MMBtu input)	Overfeed Stoker (lb/MMBtu input)	Underfeed Stoker (lb/MMBtu input)
PM	4.95E-02	2.67E-02	6.48E-03	6.07E-03
PM-10	1.14E-02	5.34E-03	2.43E-03	2.51E-03
SO ₂	5.08E-01	5.08E-01	5.08E-01	4.14E-01
SO ₃	no data	no data	no data	no data
NO _x	4.45E-01	3.34E-01	2.28E-01	2.88E-01
CO	2.02E-02	2.02E-01	2.43E-01	4.45E-01
CO ₂ (Fossil)	2.15E+02	2.15E+02	2.15E+02	2.15E+02
CO ₂ (Biomass)	no data	no data	no data	no data
CH ₄	1.62E-03	2.43E-03	2.43E-03	3.24E-02
HCl	2.43E-03	2.43E-03	2.43E-03	2.43E-03
VOC	no data	no data	no data	no data
NH ₃	no data	no data	no data	no data
Hydrocarbons	no data	no data	no data	no data
METALS				
Antimony (Sb)	7.29E-07	7.29E-07	7.29E-07	7.29E-07
Arsenic (As)	1.66E-05	1.66E-05	1.66E-05	1.66E-05
Beryllium (Be)	8.50E-07	8.50E-07	8.50E-07	8.50E-07
Cadmium (Cd)	2.06E-06	2.06E-06	2.06E-06	2.06E-06
Chromium (Cr)	1.05E-05	1.05E-05	1.05E-05	1.05E-05
Cobalt (Co)	4.05E-06	4.05E-06	4.05E-06	4.05E-06
Copper (Cu)	no data	no data	no data	no data
Lead (Pb)	1.70E-05	1.70E-05	1.70E-05	1.70E-05
Mercury (Hg)	3.36E-06	3.36E-06	3.36E-06	3.36E-06
Nickel (Ni)	1.13E-05	1.13E-05	1.13E-05	1.13E-05
Selenium (Se)	5.26E-05	5.26E-05	5.26E-05	5.26E-05
Zinc (Zn)	no data	no data	no data	no data
Solid Waste	9.81E+00	9.81E+00	9.81E+00	9.81E+00

2.3.3 Combustion of Fuel Oil for the Generation of Steam

This section presents the emission factors of various pollutants associated with the combustion of fuel oil for the generation of steam in a boiler. Two major categories of fuel oils are burned in steam generating boilers: distillate oils and residual oils. These oils are further distinguished by grade numbers, with Numbers 1 and 2 being distillate oils and Numbers 5 and 6 being residual oils. Number 2 oil is chosen to represent the distillate oils and low sulfur Number 6 is chosen to represent the residual oil for LCI purpose since they represent the distillate and residual oils, respectively, most commonly used in industry (U.S. EPA, 1998). Typical ultimate analyses of distillate and residual oils are presented in Table 2-4. Thermal efficiency of distillate oil fired boiler is assumed to be 80 percent for steam generation and that of residual oil fired boiler is assumed to be 85 percent (U.S. EPA, 1982). AP-42 lists the uncontrolled emission factors of PM, SO₂, CO, NO_x, CO₂, CH₄, HCl, and 12 metals in units of lb per 1000 gallons of fuel combusted for boilers burning distillate oil and residual oil.

Sulfur dioxide control using a spray dryer is applied to SO₂ emissions from residual oil as they exceed code of federal regulation limit (215 ng/J heat input) where as no control factor is applied to SO₂ emissions from distillate oil because they are low. Spray drier (in case of residual oil) is assumed to operate with 90 percent SO₂ removal efficiency as required by code of federal regulations (40 CFR Part 60 subpart Dc, July 1999).

Low NO_x burner control technique is assumed to control 50 percent of NO_x, both in case of distillate and residual oil (U.S. EPA, 1998). A bag filter with 99 percent PM removal efficiency is assumed as is typical of bag filters (U.S. EPA, 1998).

The control factors (as calculated by Equation 2-3) are applied to SO₂, PM and NO_x emissions. CO and CH₄ emissions are quite low and therefore no control factor is applied to them. For metal emissions, it is assumed that the metals are removed with PM in the APC equipment (bag filter), therefore 99 percent removal efficiency is used for metal emissions. Ninety nine percent removal efficiency for metals is not a good assumption as it ranges from 99 percent to 99.9 percent (U.S. EPA, 1998). Removal efficiency of metals is a user input and can be changed if an accurate data is available. For the residual and distillate oil fired boilers in the heat input range of 2.9 MW_t to 29 MW_t, there is no solid waste generation except the PM collected in APC equipment. Solid waste generation because of PM collection is very low for Number 2 and Number 6 oils considered, and is neglected (U.S. EPA, 1982). Table 2-9 presents the emission factors of various pollutants after APC equipment for boilers firing distillate and residual oil.

Table 2-9. Emission Factors for Various Pollutants After APC Equipment for Distillate and Residual Oil Fired Industrial Boilers

Air Emissions	Distillate Oil (lb/MMBtu input)	Residual Oil (lb/MMBtu input)
PM	1.47E-04	7.39E-04
PM-10	3.08E-05	6.64E-05
SO ₂	2.29E-02	8.91E-02
SO ₃	3.22E-04	1.13E-03
NO _x	7.33E-02	1.86E-01
CO	3.66E-02	3.38E-02
CO ₂ (Fossil)	1.58E+02	1.65E+02
CO ₂ (Biomass)	no data	no data
CH ₄	3.81E-04	6.76E-03
HCl	no data	no data
VOC	no data	no data
NH ₃	no data	no data
Hydrocarbons	no data	no data
METALS		
Antimony (Sb)	no data	3.55E-07
Arsenic (As)	4.00E-08	8.92E-08
Beryllium (Be)	3.00E-08	1.88E-09
Cadmium (Cd)	3.00E-08	2.69E-08
Chromium (Cr)	3.00E-08	5.71E-08
Cobalt (Co)	no data	4.07E-07
Copper (Cu)	6.00E-08	1.19E-07
Lead (Pb)	9.01E-08	1.02E-07
Mercury (Hg)	3.00E-08	7.63E-09
Nickel (Ni)	3.00E-08	5.71E-06
Selenium (Se)	1.50E-07	4.61E-08
Zinc (Zn)	4.00E-08	1.97E-06
Solid waste	0.00E+00 ^a	0.00E+00 ^a

^a Solid waste generation is very low and is therefore neglected (U.S. EPA, 1982)

2.3.4 Combustion of Natural Gas for Generation of Steam

This section presents the emission factors of various pollutants associated with the combustion of natural gas for the generation of steam in a boiler. The emissions from natural gas fired boilers include NO_x, CO, CO₂, CH₄, VOCs, trace amounts of SO₂, particulate matter and metals. The ultimate analysis of natural gas is presented in Table 2-4. Thermal efficiency of natural gas fired boiler is assumed to be 80 percent for steam generation (U.S. EPA, 1982). AP-42 lists the uncontrolled emission factors of PM, SO₂, CO, NO_x, CO₂, CH₄, HCl, and 12 metals in the units of lb per million standard cubic feet of natural gas combusted. Because the SO₂ and PM emissions are very low, no control technology is applied. APC equipment commonly used for NO_x control in natural gas fired steam boilers is a low NO_x burner. A typical NO_x control efficiency for a low NO_x burner is 50 percent (U.S. EPA, 1998). Carbon monoxide, CH₄, and VOC emissions being small are not controlled. For metals, a removal efficiency of 99 percent is assumed as a default as no data on the control efficiencies could be found for metal emissions from natural gas fired boilers. The removal efficiency for metals is a user input and can be altered if an accurate data is available. No liquid and solid wastes are generated (U.S. EPA, 1982). Table 2-10 presents the emission factors of various pollutants after APC equipment for boilers firing natural gas for the generation of steam. The emission factors are reported in lb/MMBtu heat input.

Table 2-10. Emission Factors for Various Pollutants After APC Equipment for Natural Gas fired Industrial Boilers

Air Emissions	Natural Gas (lb/MMBtu input)
PM	7.73E-03
PM-10	no data
SO ₂	6.10E-04
SO ₃	no data
NO _x	5.09E-02
CO	8.54E-02
CO ₂ (Fossil)	1.22E+02
CO ₂ (Biomass)	no data
CH ₄	2.34E-03
HCl	no data
VOC	5.59E-03
NH ₃	no data
Hydrocarbons	no data
METALS	
Antimony (Sb)	no data
Arsenic (As)	2.03E-09
Beryllium (Be)	1.22E-10
Cadmium (Cd)	1.12E-08
Chromium (Cr)	1.42E-08
Cobalt (Co)	8.54E-10
Copper (Cu)	8.65E-09
Lead (Pb)	5.09E-09
Mercury (Hg)	2.64E-09
Nickel (Ni)	2.14E-08
Selenium (Se)	2.44E-10
Zinc (Zn)	2.95E-07

2.3.5 Overall Weighted Emission Factors from Boilers Generating Steam

As described in Section 2.2, the total enthalpy carried by steam was allocated to various boiler types based on the percentage of installed boiler capacity given in Table 2-3. The respective boiler heat inputs are then calculated by dividing the above-allocated enthalpy by the boiler efficiency as described by Equation (2-4). Table 2-12 presents the heat input to each boiler type.

$$H_{Boiler, j} = \frac{H_{Allocated, j}}{h_{Boiler, j}} \quad (2-4)$$

where: $H_{Boiler, j}$ = Heat input to boiler 'j' (J/MJ steam)

$H_{Allocated, j}$ = Enthalpy allocated to boiler 'j' based on the boiler percentage (J/MJ steam)

$\eta_{Boiler, j}$ = Boiler thermal efficiency (fraction)

Finally, a particular emission for respective boiler types is calculated (Equation 2-5) and summed across.

$$E_i = EF_i \cdot H_{Boiler, j} \quad (2-5)$$

where: E_i = Emission of pollutant 'j' per MJ steam produced (kg/MJ steam)

EF_i = Emission factor of pollutant 'j' per J heat input (kg/J)

Table 2-11 presents the emission factors for various boilers in units of lb/MMBtu heat input. Table 2-12 presents the respective boiler emissions for the generation of 1 MJ of steam. Total emissions are calculated by summing across in Table 2-12.

Table 2-11. Emissions from Various Boilers (units: lb/MMBtu heat input).

Air Emissions	PC^a	SS^b	OS^c	US^d	DO^e	RO^f	NG^g
PM	4.95E-02	2.67E-02	6.48E-03	6.07E-03	1.47E-04	7.39E-04	7.73E-03
PM-10	1.14E-02	5.34E-03	2.43E-03	2.51E-03	3.08E-05	6.64E-05	no data
SO ₂	5.08E-01	5.08E-01	5.08E-01	4.14E-01	2.29E-02	8.91E-02	6.10E-04
SO ₃	no data	no data	no data	no data	3.22E-04	1.13E-03	no data
NO _x	4.45E-01	3.34E-01	2.28E-01	2.88E-01	7.33E-02	1.86E-01	5.09E-02
CO	2.02E-02	2.02E-01	2.43E-01	4.45E-01	3.66E-02	3.38E-02	8.54E-02
CO ₂ (Fossil)	2.15E+02	2.15E+02	2.15E+02	2.15E+02	1.58E+02	1.65E+02	1.22E+02
CO ₂ (Biomass)	no data	no data	no data	no data	no data	no data	no data
CH ₄	1.62E-03	2.43E-03	2.43E-03	3.24E-02	3.81E-04	6.76E-03	2.34E-03
HCl	2.43E-03	2.43E-03	2.43E-03	2.43E-03	no data	no data	no data
VOC	no data	no data	no data	no data	no data	no data	5.59E-03
NH ₃	no data	no data	no data	no data	no data	no data	no data
Hydrocarbons	no data	no data	no data	no data	no data	no data	no data
METALS							
Antimony (Sb)	7.29E-07	7.29E-07	7.29E-07	7.29E-07	no data	3.55E-07	no data
Arsenic (As)	1.66E-05	1.66E-05	1.66E-05	1.66E-05	4.00E-08	8.92E-08	2.03E-09
Beryllium (Be)	8.50E-07	8.50E-07	8.50E-07	8.50E-07	3.00E-08	1.88E-09	1.22E-10
Cadmium (Cd)	2.06E-06	2.06E-06	2.06E-06	2.06E-06	3.00E-08	2.69E-08	1.12E-08
Chromium (Cr)	1.05E-05	1.05E-05	1.05E-05	1.05E-05	3.00E-08	5.71E-08	1.42E-08
Cobalt (Co)	4.05E-06	4.05E-06	4.05E-06	4.05E-06	no data	4.07E-07	8.54E-10
Copper (Cu)	no data	no data	no data	no data	6.00E-08	1.19E-07	8.65E-09
Lead (Pb)	1.70E-05	1.70E-05	1.70E-05	1.70E-05	9.01E-08	1.02E-07	5.09E-09
Mercury (Hg)	3.36E-06	3.36E-06	3.36E-06	3.36E-06	3.00E-08	7.63E-09	2.64E-09
Nickel (Ni)	1.13E-05	1.13E-05	1.13E-05	1.13E-05	3.00E-08	5.71E-06	2.14E-08
Selenium (Se)	5.26E-05	5.26E-05	5.26E-05	5.26E-05	1.50E-07	4.61E-08	2.44E-10
Zinc (Zn)	no data	no data	no data	no data	4.00E-08	1.97E-06	2.95E-07
Solid Waste	9.81E+00	9.81E+00	9.81E+00	9.81E+00	0.00E+00	0.00E+00	0.00E+00

^a PC: Pulverized coal wall fired (dry bottom) boiler

^b SS: Spreader stoker coal fired boiler

^c OS: Overfeed stoker coal fired boiler

^d US: Underfeed stoker coal fired boiler

^e DO: Distillate oil fired boiler

^f RO: Residual oil fired boiler

^g NG: Natural gas fired boiler

Table 2-12. Emissions From Various Boilers Based on Steam Allocation for the Production of 1 MJ Steam (units: kg/MJ Steam Produced).

Watertube Firing Method & Fuel	SS^b	OS^c	US^d	DO^e	RO^f	NG^g	Total
Boiler Percentage, %	4.20	3.07	12.16	4.87	32.49	43.21	100
Typical Boiler Efficiency, %	80	80	80	80	85	80	
Heat Input to Boiler (J)	5.24E+04	3.84E+04	1.52E+05	6.09E+04	3.82E+05	5.40E+05	1.23E+06
Air Emissions	kg/MJ Steam	kg/MJ Steam	kg/MJ Steam	kg/MJ Steam	kg/MJ Steam	kg/MJ Steam	(kg/MJ Steam)
PM	6.03E-07	1.07E-07	3.97E-07	3.84E-09	1.21E-07	1.80E-06	3.03E-06
PM-10	1.21E-07	4.01E-08	1.64E-07	8.07E-10	1.09E-08	no data	
SO ₂	1.15E-05	8.39E-06	2.71E-05	6.00E-07	1.47E-05	1.42E-07	6.23E-05
SO ₃	no data	no data	no data	8.45E-09	1.87E-07	no data	
NO _x	5.03E-06	2.51E-06	1.26E-05	1.92E-06	3.06E-05	1.18E-05	6.44E-05
CO	4.57E-06	4.01E-06	2.91E-05	9.60E-07	5.56E-06	1.99E-05	6.41E-05
CO ₂ (Fossil)	4.86E-03	3.56E-03	1.41E-02	4.13E-03	2.71E-02	2.84E-02	8.21E-02
CO ₂ (Biomass)	no data	no data	no data	no data	no data	no data	
CH ₄	5.48E-08	4.01E-08	2.12E-06	9.99E-09	1.11E-06	5.44E-07	3.88E-06
HCl	5.48E-08	4.01E-08	1.59E-07	no data	no data	no data	
VOC	no data	no data	no data	no data	no data	1.30E-06	
NH ₃	no data	no data	no data	no data	no data	no data	
Hydrocarbons	no data	no data	no data	no data	no data	no data	
METALS							
Antimony (Sb)	1.64E-11	1.20E-11	4.77E-11	no data	5.83E-11	no data	
Arsenic (As)	3.75E-10	2.74E-10	1.09E-09	1.05E-12	1.47E-11	4.73E-13	1.75E-09
Beryllium (Be)	1.92E-11	1.40E-11	5.56E-11	7.86E-13	3.09E-13	2.84E-14	9.00E-11
Cadmium (Cd)	4.66E-11	3.41E-11	1.35E-10	7.87E-13	4.42E-12	2.60E-12	2.24E-10
Chromium (Cr)	2.38E-10	1.74E-10	6.88E-10	7.87E-13	9.39E-12	3.31E-12	1.11E-09
Cobalt (Co)	9.14E-11	6.69E-11	2.65E-10	no data	6.69E-11	1.99E-13	
Copper (Cu)	no data	no data	no data	1.57E-12	1.96E-11	2.01E-12	
Lead (Pb)	3.84E-10	2.81E-10	1.11E-09	2.36E-12	1.68E-11	1.18E-12	1.80E-09
Mercury (Hg)	7.58E-11	5.55E-11	2.20E-10	7.87E-13	1.26E-12	6.15E-13	3.54E-10
Nickel (Ni)	2.56E-10	1.87E-10	7.41E-10	7.87E-13	9.39E-10	4.96E-12	2.13E-09
Selenium (Se)	1.19E-09	8.70E-10	3.44E-09	3.94E-12	7.59E-12	5.67E-14	5.51E-09
Zinc (Zn)	no data	no data	no data	1.05E-12	3.23E-10	6.86E-11	
Solid Waste	2.21E-04	1.62E-04	6.42E-04	0.00E+00	0.00E+00	0.00E+00	1.02E-03

^a PC: Pulverized coal wall fired (dry bottom) boiler

^b SS: Spreader stoker coal fired boiler

^c OS: Overfeed stoker coal fired boiler

^d US: Underfeed stoker coal fired boiler

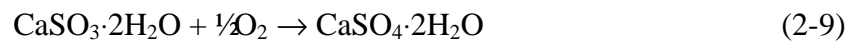
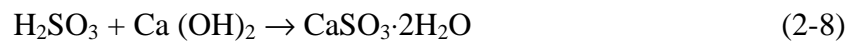
^e DO: Distillate oil fired boiler

^f RO: Residual oil fired boiler

^g NG: Natural gas fired boiler

2.3.6 LCI of Lime consumed for the Removal of SO₂ in a Spray Dryer

In lime spray drying, a lime slurry is sprayed into the absorption tower, and SO₂ is absorbed by the slurry, forming CaSO₃/CaSO₄. However, the liquid-to-gas ratio is such that the water in the slurry evaporates before the slurry droplets reach the bottom of the tower. The following equations represent the chemistry of lime spray drying process (Cooper and Alley, 1994):



The overall equation therefore is:



From Equation 2-10, a minimum of 1 mole (56 gm) of lime is required in order to remove 1 mole (64 gm) of SO₂ removed. Therefore 0.875 kg of CaO is required for the removal of 1 kg of SO₂ from stoichiometry. It is assumed that 5 percent in excess of the stoichiometric amount of CaO is needed for SO₂ removal (Cooper and Alley, 1994). The amount of SO₂ removed can be calculated from controlled SO₂ emissions occurring in various boilers by multiplying the controlled emissions by 9 since 90 percent removal efficiency was assumed. The CaO consumption rate (in kg) is then calculated by

multiplying total SO₂ removal (kg) by 0.918 kg (5 percent excess of stoichiometric amount, 0.875 kg per kg of SO₂ removed). Further it is assumed that the only products of SO₂ removal reaction are calcium sulfate (CaSO₄·2H₂O) and unreacted CaO. The amount of calcium sulfate produced is stoichiometrically equal to 2.687 kg per kg of SO₂ removed. Table 2-13 presents the LCI associated with removal of SO₂ using lime in a spray dryer. The LCI of lime was obtained from Franklin Associates (1998).

Table 2-13. LCI of Lime Associated with Removal of SO₂ for 1MJ Steam Production

Air Emissions	kg/mT of Lime^a	kg/MJ Steam Produced
PM	2.70E+00	1.39E-06
PM-10	no data	no data
SO ₂	3.70E+00	1.90E-06
SO ₃	no data	no data
NO _x	1.30E+00	6.68E-07
CO	3.50E-01	1.80E-07
CO ₂ (Fossil)	1.30E+03	6.68E-04
CO ₂ (Biomass)	4.80E-02	2.47E-08
CH ₄	9.50E-01	4.88E-07
HCl	1.20E-06	6.17E-13
VOCs	no data	no data
NH ₃	2.00E-04	1.03E-10
Hydrocarbons	3.00E-01	1.54E-07
Metals		
Antimony	7.30E-07	3.75E-13
Arsenic	1.50E-04	7.71E-11
Beryllium	no data	no data
Cadmium	5.00E-05	2.57E-11
Chromium	3.10E-04	1.59E-10
Cobalt	no data	no data
Copper	no data	no data
Lead	1.90E-05	9.77E-12
Mercury	4.30E-06	2.21E-12
Nickel	2.10E-04	1.08E-10
Selenium	8.00E-07	4.11E-13
Zinc	no data	no data
Liquid Emissions		
Dissolved Solids	1.10E+00	5.66E-07
Suspended Solids	4.30E-02	2.21E-08
BOD	1.20E-03	6.17E-10
COD	1.60E-02	8.23E-09
Oil	1.90E-02	9.77E-09
Sulfuric Acid	3.90E-03	2.01E-09
Iron	2.10E-02	1.08E-08
Ammonia	5.90E-05	3.03E-11
Copper	no data	no data
Cadmium	5.20E-05	2.67E-11
Arsenic	no data	no data
Mercury	4.00E-09	2.06E-15
Phosphate	1.90E-03	9.77E-10
Selenium	no data	no data
Chromium	5.00E-05	2.57E-11
Lead	1.50E-08	7.71E-15
Zinc	1.70E-05	8.74E-12
Solid Waste	8.30E+01	1.57E-03
Energy (BTUs)	5.11E+06	2.62E+00

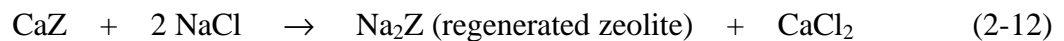
^a This column presents the LCI of lime obtained from Franklin Associates (1998)

2.3.7 LCI Associated with Boiler Feed Water (BFW) Pretreatment

For the LCI of BFW conditioning, ionic exchange pretreatment is considered. Calcium and magnesium hardness can be removed by passing the water through a bed of resin mixed with a natural mineral known as zeolite enabling the calcium or aluminum base to be exchanged for sodium (Nunn, 1997):



As a result of the above reaction, calcium and magnesium ions become bound and the sodium ions are solubilized. The ion exchange reaction is nonselective and will remove any soluble cations, including iron and manganese, and will remove noncarbonate hardness as well as carbonate hardness. When the exchange material becomes depleted of sodium ions, no further exchange of cations can occur until the bound cations are replaced with sodium ions. The exchange material can be regenerated by contact with brine solution according to the following reaction:



The concentration of the brine is high enough to provide an excess of sodium ions, so that all the cations are replaced by sodium ions. This so-called “sodium cycle” can be repeated over and over again and is an economical method of softening because of the low cost of salt brine.

A total hardness of 100 mg Ca²⁺/liter and 155 mg Mg²⁺/ liter was assumed in the water to be pretreated. One hundred percent hardness removal efficiency is assumed in calculations. Because ion exchange resin is regenerated, its replacement is ignored in the life cycle inventory. Based on the above assumptions, 555 mg of NaCl is required per liter of water treated. In addition, 4.92 g of sludge (consisting of 5.6 % w/w of CaCl₂ and 4.4 % w/w of MgCl₂) are produced per liter of water treated. The LCI of sodium chloride is presented in Table 2-14 (Gonzalez and Overcash, 2000).

It is assumed that saturated steam at 100 psia is generated from water entering the boiler at 50°C. Amount of saturated steam at 100-psia was calculated to be 0.392 kg (Equation 2-1) for the 1 MJ steam, which is the basis of the LCI of steam. Assuming no evaporation losses, the amount of steam generated is equal to the amount of BFW treated and entering the boiler. Since 555 mg of NaCl is required for treating one liter of water, the total NaCl consumption (0.217 gm) can be calculated using Equation 2-13.

$$m_{NaCl} = \frac{m_{NaCl} V_{BFW}}{1000} \quad (2-13)$$

where: m_{NaCl} = Amount of NaCl consumed (gm)

m_{NaCl} = NaCl consumed per liter of BFW treated (= 555 mg/liter)

V_{BFW} = Volume of BFW equivalent to 0.392 kg (= 0.392 liters approximately)

Table 2-14 presents the LCI associated with BFW treatment for producing steam with 1 MJ total enthalpy.

Table 2-14. LCI of BFW Treatment for 1 MJ Steam Generation

Air Emissions	mg/kg NaCl^a	Total Emissions (kg/MJ Steam)
PM	3.20E+02	6.96E-08
PM-10	no data	no data
SO ₂	1.10E+03	2.39E-07
SO ₃	no data	no data
NO _x	1.50E+03	3.26E-07
CO	90	1.96E-08
CO ₂ (Fossil)	1.75E+05	3.80E-05
CO ₂ (Biomass)	no data	no data
CH ₄	3.70E+02	8.04E-08
HCl	1.00E+01	2.17E-09
VOCs	1630	3.54E-07
NH ₃	no data	no data
Hydrocarbons	no data	no data
Metals		
Antimony (Sb)	no data	no data
Arsenic (As)	no data	no data
Beryllium (Be)	no data	no data
Cadmium (Cd)	no data	no data
Chromium (Cr)	no data	no data
Cobalt (Co)	no data	no data
Copper (Cu)	no data	no data
Lead (Pb)	no data	no data
Mercury (Hg)	no data	no data
Nickel (Ni)	no data	no data
Selenium (Se)	no data	no data
Zinc (Zn)	no data	no data
Liquid Emissions		
Dissolved Solids	no data	no data
Suspended solids	1290	2.80E-07
BOD	1	2.17E-10
COD	14	3.04E-09
Oil	no data	no data
Sulfuric acid	no data	no data
Iron	no data	no data
Ammonia	no data	no data
Copper	no data	no data
Cadmium	no data	no data
Arsenic	no data	no data
Mercury	no data	no data
Phosphate	no data	no data
Selenium	no data	no data

Table 2-14 continued on next page

Table 2-14 continued

Liquid Emissions	mg/kg NaCl^a	Total Emissions (kg/MJ Steam)
Chromium	no data	no data
Lead	no data	no data
Zinc	no data	no data
Solid waste	2.11E+04	1.93E-03 ^b
Energy (BTUs)	2.88E+03	6.26E-01

^a LCI of NaCl production (Gonzalez and Overcash, 2000)

^b Includes the sludge produced as a result of BFW pretreatment (4.92 g/liter of water treated).

2.3.8 Overall LCI of Steam production

All the LCI parameters associated with different operations for the generation of steam are finally summed up to yield the overall LCI of steam production. The emission factors or the LCI parameters are based on 1 MJ steam produced (0.392 kg of saturated steam at 100 psia). Table 2-15 presents the overall LCI of steam in kg of pollutant per MJ of steam produced. Table 2-16 presents the overall LCI of steam in lb of pollutants per MMBtu of steam produced.

Looking at Table 2-15, it is clear that the overall LCI of steam consists of PM, SO₂, NO_x, CO, CO₂, CH₄, suspended solids, BOD, COD, and solid waste as the LCI parameters which have quantitative information. Where no data was available for any one component, the sum is not reported to emphasize that the absence of data does not necessarily mean that the correct value is zero. Particulate matter, SO₂, NO_x are the most important parameters since these are regulated in code of federal regulations (CFR, 1999). The most uncertain parameters seem to be PM, SO₂, and NO_x since they have been calculated from uncontrolled emission factors based on assumed control efficiencies as per guidelines in the literature (U.S. EPA, 1998).

As can be seen in Table 2-15, pre-combustion emissions associated with fuels fired in the boilers contribute most to PM, SO₂, CH₄, suspended solids, BOD, COD and solid waste in the total LCI of steam. NO_x and CO contributions from boiler emissions component are slightly higher in magnitude than the pre-combustion emissions

component. Carbon dioxide contribution from boiler emissions component is higher than pre-combustion emissions component by an order of magnitude. The LCI of lime and BFW are very small contributors to the overall LCI of steam. In the overall LCI of steam, both pre-combustion emissions and boiler emissions are significant and are both important than lime and BFW LCI. The LCI of steam developed in this chapter can be used as a component LCI in the LCI of other chemicals.

Table 2-15. LCI of Steam (Units: kg/MJ of steam)

Air Emissions	Pre-Combustion Emissions	Boiler Emissions	Lime LCI	BFW LCI	Total (kg/MJ Steam)
PM	2.48E-05	3.03E-06	1.39E-06	6.96E-08	2.93E-05
PM-10	no data	no data	no data	no data	
SO ₂	4.87E-04	6.23E-05	1.90E-06	2.39E-07	5.51E-04
SO ₃	no data	no data	no data	no data	
NO _x	4.11E-05	6.44E-05	6.68E-07	3.26E-07	1.07E-04
CO	6.28E-05	6.41E-05	1.80E-07	1.96E-08	1.27E-04
CO ₂ (fossil)	7.61E-03	8.21E-02	6.68E-04	3.80E-05	9.04E-02
CO ₂ (Biomass)	1.75E-05	no data	2.47E-08	no data	
CH ₄	1.32E-04	3.88E-06	4.88E-07	8.04E-08	1.36E-04
HCl	6.64E-08	no data	6.17E-13	2.17E-09	
VOCs	no data	no data	no data	3.54E-07	
NH ₃	5.89E-08	no data	1.03E-10	no data	
Hydrocarbons	1.92E-04	no data	1.54E-07	no data	
METALS					
Antimony (Sb)	no data		3.75E-13	no data	
Arsenic (As)	no data	1.75E-09	7.71E-11	no data	
Beryllium (Be)	no data	9.00E-11	no data	no data	
Cadmium (Cd)	no data	2.24E-10	2.57E-11	no data	
Chromium (Cr)	no data	1.11E-09	1.59E-10	no data	
Cobalt (Co)	no data	no data	no data	no data	
Copper (Cu)	no data	no data	no data	no data	
Lead (Pb)	2.82E-10	1.80E-09	9.77E-12	no data	
Mercury (Hg)	no data	3.54E-10	2.21E-12	no data	
Nickel (Ni)	no data	2.13E-09	1.08E-10	no data	
Selenium (Se)	no data	5.51E-09	4.11E-13	no data	
Zinc (Zn)	no data		no data	no data	
Liquid Emission					
Dissolved Solids	7.42E-04	0.00E+00	5.66E-07	no data	
Suspended Solids	1.43E-05	0.00E+00	2.21E-08	2.80E-07	1.46E-05
BOD	7.97E-07	0.00E+00	6.17E-10	2.17E-10	7.98E-07
COD	5.56E-06	0.00E+00	8.23E-09	3.04E-09	5.57E-06
Oil	1.35E-05	0.00E+00	9.77E-09	no data	
Sulfuric Acid	1.66E-08	0.00E+00	2.01E-09	no data	
Iron	1.06E-06	0.00E+00	1.08E-08	no data	
Ammonia	2.06E-08	0.00E+00	3.03E-11	no data	
Copper	0.00E+00	0.00E+00	no data	no data	
Cadmium	3.37E-08	0.00E+00	2.67E-11	no data	

Table 2-15 continued on next page

Table 2-15 continued

Liquid Emission	Pre-Combustion Emissions	Boiler Emissions	Lime LCI	BFW LCI	Total (kg/MJ Steam)
Mercury	2.65E-12	0.00E+00	2.06E-15	no data	
Phosphate	8.42E-09	0.00E+00	9.77E-10	no data	
Selenium		0.00E+00	no data	no data	
Chromium	3.37E-08	0.00E+00	2.57E-11	no data	
Lead	2.10E-11	0.00E+00	7.71E-15	no data	
Zinc	1.19E-08	0.00E+00	8.74E-12	no data	
		0.00E+00			
Solid Waste	4.43E-03	1.02E-03	1.57E-03	1.93E-03	8.95E-03
Energy (MJ)	1.36E-01	1.23E+00	2.76E-03	6.59E-04	1.37E+00

Table 2-16. LCI of Steam (Units: lb/MMBtu of steam)

Air Emissions	Pre-Combustion Emissions	Boiler Emissions	Lime LCI	BFW LCI	Total (lb/MMBtu Steam)
PM	5.77E-02	7.04E-03	3.23E-03	1.62E-04	6.82E-02
PM-10			no data	no data	
SO ₂	1.13E+00	1.45E-01	4.42E-03	5.56E-04	1.28E+00
SO ₃			no data	no data	
NO _x	9.56E-02	1.50E-01	1.55E-03	7.59E-04	2.48E-01
CO	1.46E-01	1.49E-01	4.18E-04	4.55E-05	2.95E-01
CO ₂ (fossil)	1.77E+01	1.91E+02	1.55E+00	8.85E-02	2.10E+02
CO ₂ (Biomass)	4.06E-02		5.74E-05	no data	
CH ₄	3.07E-01	9.01E-03	1.14E-03	1.87E-04	3.17E-01
HCl	1.54E-04		1.43E-09	5.06E-06	
VOCs		3.02E-03	no data	8.24E-04	
NH ₃	1.37E-04		2.39E-07	no data	
Hydrocarbons	4.47E-01		3.58E-04	no data	
METALS					
Antimony (Sb)			8.72E-10	no data	
Arsenic (As)		4.07E-06	1.79E-07	no data	
Beryllium (Be)		2.09E-07	no data	no data	
Cadmium (Cd)		5.20E-07	5.97E-08	no data	
Chromium (Cr)		2.59E-06	3.70E-07	no data	
Cobalt (Co)			no data	no data	
Copper (Cu)			no data	no data	
Lead (Pb)	6.55E-07	4.18E-06	2.27E-08	no data	
Mercury (Hg)		8.22E-07	5.14E-09	no data	
Nickel (Ni)		4.95E-06	2.51E-07	no data	
Selenium (Se)		1.28E-05	9.56E-10	no data	
Zinc (Zn)			no data	no data	
Liquid Emissions					
Dissolved Solids	1.72E+00	0.00E+00	1.31E-03	no data	
Suspended Solids	3.32E-02	0.00E+00	5.14E-05	6.53E-04	3.39E-02
BOD	1.85E-03	0.00E+00	1.43E-06	5.06E-07	1.85E-03
COD	1.29E-02	0.00E+00	1.91E-05	7.08E-06	1.30E-02
Oil	3.13E-02	0.00E+00	2.27E-05	no data	
Sulfuric Acid	3.85E-05	0.00E+00	4.66E-06	no data	
Iron	2.46E-03	0.00E+00	2.51E-05	no data	
Ammonia	4.79E-05	0.00E+00	7.05E-08	no data	
Copper	0.00E+00	0.00E+00	no data	no data	
Cadmium	7.84E-05	0.00E+00	6.21E-08	no data	
Arsenic		0.00E+00	no data	no data	
Mercury	6.16E-09	0.00E+00	4.78E-12	no data	

Table 2-16 continued on next page

Table 2-16 continued

Liquid Emissions	Pre-Combustion Emissions	Boiler Emissions	Lime LCI	BFW LCI	Total (lb/MMBtu Steam)
Phosphate	1.96E-05	0.00E+00	2.27E-06	no data	
Selenium		0.00E+00	no data	no data	
Lead	4.87E-08	0.00E+00	1.79E-11	no data	
Zinc	2.76E-05	0.00E+00	2.03E-08	no data	
Solid Waste	1.03E+01	2.37E+00	3.65E+00	4.49E+00	2.08E+01
Energy (MMBtu)	1.36E-01	1.23E+00	2.76E-03	6.59E-04	1.37E+00

3.0 LIFE CYCLE INVENTORY OF ELECTRICITY

Electricity is one of our most widely used forms of energy. We get electricity, which is a secondary energy source, from the conversion of other sources of energy, such as coal, natural gas, oil, nuclear power and other natural sources, which are called primary sources. Electricity is used in a process industry for a variety of functions such as driving compressors and pumps, running process equipment, and many other applications (EIA, 1995). Any life cycle evaluation in which electric energy is consumed must consider the energy consumption and emissions associated with the production of electrical energy.

An electric energy process model for calculating the life cycle inventory (LCI) of electricity was developed by Dumas (1998). This section describes the methodology developed by Dumas to calculate the LCI of electricity production. The section starts with a brief description of the electric energy process model followed by energy conversion processes involved in the production of electricity. Information concerning electric grid definition and fuel usage, generation efficiencies, fuel heating values, fuel pre-combustion energy, and total fuel energy is then presented. Finally emissions or LCI parameters associated with generation of electricity are presented with the methodology used for their calculations.

3.1 Design Basis and System Boundaries

This section presents the design basis for calculating the LCI of electricity. The processes of energy conversion to electricity are briefly described including the types of fuels considered. The national grid for the generation of electricity from various fuels is described. Generation efficiencies are defined and described including the fuels heating values. Pre-combustion and combustion energy consumption and emissions on a per unit fuel basis are used in conjunction with unit efficiencies, transmission and distribution line losses, and electric generation fuel usage percentages to allocate energy consumption and emissions to the usage of an electric kilo-watt hour (kWh) based on the contribution to the generation of that kWh by each fuel type (Dumas, 1998). Emissions and energy consumption per kWh are calculated for national grid fuel mix. Regional grid fuel mix are not considered since the primary purpose of LCI of electricity is to calculate burdens or offsets associated with the production of a chemical which is assumed be produced at several locations across the U.S., as opposed to in a particular region. The emissions and energy consumption associated with facility construction are assumed to be negligible.

The majority of electrical energy in the U.S. is derived from seven major fuel sources: coal, natural gas, residual oil, distillate oil, uranium, hydroelectric and wood (Franklin Associates, 1998). Sources such as solar, wind, geothermal and other emerging technologies make insignificant contributions. Thus seven major fuel types are considered in the LCI of electricity.

Pre-combustion energy and emissions for each of the above fuels are associated with surface and underground mining operations (coal and uranium), oil well operations (natural gas and oil), pumping (oil and natural gas), fugitive emissions (coal, oil, natural gas, uranium), cleaning (all fuels), transportation (all fuels) and production facilities. The default assumption is that there are no pre-combustion emissions associated with hydroelectric power generation and wood fuel. The following subsection defines the electric grid considered for calculating the LCI of electricity.

3.2 Electric Grid Definition

To calculate the emissions associated with the generation of electricity it is necessary to define fuel usage by type for the national grid. Table 3-1 presents the national default generation percentages by fuel type (Dumas, 1998).

Table 3-1. National Electric Generation by Fuel Type (Dumas, 1998)

Fuel Type	Percent
Coal	56.45
Natural Gas	9.75
Residual Oil	2.62
Distillate Oil	0.23
Nuclear	22.13
Hydro	8.58
Wood	0.24
Other	-
Total	100.00

The electric energy process model was imported into an electrical energy spreadsheet. The above default percentage splits can be changed by the user in EXCEL spreadsheet environment in which the LCI of electricity is implemented.

3.3 Generation Efficiencies of Electricity Generation

Generation weighted national efficiencies for each fuel type are based on Energy Information Administration (EIA) data (EIA, 1995). Table 3-2 presents default electrical generation efficiencies by fuel type on a national basis.

Table 3-2. National Grid Generation Efficiencies (Dumas, 1998)

Fuel Type	Default National Unit Efficiency
Coal	0.325
Natural Gas	0.311
Residual Oil	0.326
Distillate Oil	0.260
Nuclear	0.314
Hydro	1.000
Wood	0.325
Other	0.325

3.4 Fuel Heating Values

Table 3-3 presents the heating values of various types of fuels used in electricity generation (Franklin Associates, 1998). Hydroelectric power is unique from an LCI standpoint in that there is no heating value associated with use of hydroelectric power. The default energy consumption associated with the use of 1 kWh of hydroelectric power is fixed at 3413 Btu/kWh.

Table 3-3. National Grid Fuel Heating Values (Dumas, 1998)

Fuel Type	Btu/fuel unit
Coal	10,402 Btu/lb
Natural Gas	1,022 Btu/ft ³
Residual Oil	149,700 Btu/gal
Distillate Oil	138,700 Btu/gal
Uranium	985,321,000 Btu/lb
Wood	10,350 Btu/lb
Other	10,350 Btu/lb

3.5 Fuel Pre-Combustion Energy

Pre-combustion energy is the energy expended in operations required to prepare the fuel for use in an electrical generating facility. An example of this type of energy would be the gasoline and diesel fuel used in coal mining and transportation. The emissions associated with this type of energy are known as pre-combustion emissions. Since hydroelectric power is unique from an LCI standpoint, there is no pre-combustion energy associated with the use of hydroelectric power. Table 3-4 presents the default pre-combustion energy by fuel type (Franklin Associates, 1998). Total energy is obtained by adding combustion and pre-combustion energies and total emissions are obtained by adding combustion and pre-combustion emissions. Pre-combustion emissions by fuel type are presented in the electric energy process model documentation (Dumas, 1998).

Table 3-4. Fuel Pre-Combustion Energy (Dumas, 1998)

Fuel Type	Value
Coal	264 Btu/lb
Natural Gas	129 Btu/ft ³
Residual Oil	21,000 Btu/gal
Distillate Oil	19,300 Btu/gal
Uranium	50,600,000 Btu/lb
Wood	0 Btu/lb
Other	0 Btu/lb

3.6 Total Fuel Emissions and LCI calculation

Combustion and pre-combustion emissions generated per 1000 fuel units combusted (e.g., lbs. for coal, ft³ for natural gas) on a national basis have been reported by Franklin Associates (1998). For calculating the total emissions per kWh of electricity, 1 kWh is allocated to be generated by various fuels based on the national grid energy generation by fuel types as in Table 3-1 (e.g., 0.5645 kWh generated by coal, 0.0975 kWh generated by natural gas, 0.0262 kWh generated by residual oil).

The kWh value allocated to the each fuel type is divided by its default national energy generation efficiency and heating value to calculate the amount of fuel units combusted to generate that energy. The following equation relates the fuel units combusted to electric energy generated.

$$F_i = \left(\frac{F_i'}{h_{Fi} HV_i} \right) \times \left(\frac{3412.14 \text{ Btu}}{\text{kWh}} \right) \quad (3-1)$$

where: F_i = Fuel units of type 'i' combusted (e.g., lbs. for coal, gal. for oil)

F_i = kWh allocated to fuel of type 'i' (kWh)

HV_i = Heating value of fuel of type 'i' (Btu/fuel units)

The fuel combusted, as calculated in Equation (3-1), is then multiplied by the total emissions (kg/fuel unit) from that fuel to obtain the emissions for the generation of electrical energy allocated to that fuel (Equation 3-2).

$$FE_{j,i} = FE'_{j,i} F_i \quad (3-2)$$

where: FE_{j,i} = Emission of type 'j' from fuel type 'i' (kg)

FE' _{j,i} = Emission factor of pollutant 'j' from fuel type 'i' (kg/fuel unit)

Emission j can then be summed across all the fuels combusted to generate the total 1 kWh of electricity. Equation (3-3) represents the total emission of type j in generation of 1 kWh of electricity.

$$E_j = \sum_{i=1}^n FE_{j,i} \quad (3-3)$$

where: E_j = Emission of 'j' per kWh of electricity produced (kg/kWh of electricity)

The results of Equation (3-3) i.e. emissions (both in lb and kg) per kWh of electricity generated are shown in Table 3-5. These emissions include the pre-combustion emissions. The data in Table 3-5 represents the LCI of electricity on 1 kWh basis. Pre-combustion and combustion emissions for each fuel type for a total generation of 1 kWh of electric energy can be found in Electric Energy Process model documentation by Dumas (1998).

Table 3-5. Emissions produced per kWh of Electricity generated (LCI of Electricity)^a

Air Emissions	lb/kWh generated	kg/kWh generated
Particulates (PM ₁₀)	0.00E+00	0.00E+00
Particulates (Total)	1.76E-03	7.98E-04
Nitrogen Oxides	5.41E-03	2.45E-03
Hydrocarbons (non CH ₄)	7.54E-04	3.42E-04
Sulfur Oxides	1.07E-02	4.86E-03
Carbon Monoxide	6.19E-04	2.81E-04
CO ₂ (Biomass)	4.85E-03	2.20E-03
CO ₂ (non Biomass)	1.45E+00	6.57E-01
Ammonia	6.50E-06	2.95E-06
Lead	6.77E-08	3.07E-08
Methane	3.13E-03	1.42E-03
Hydrochloric acid	1.06E-04	4.80E-05
Solid Waste		
Solid Waste #1	2.65E-01	1.20E-01
Solid Waste #2	0.00E+00	0.00E+00
Solid Waste #3	0.00E+00	0.00E+00
Solid Waste #4	0.00E+00	0.00E+00
Solid Waste #5	0.00E+00	0.00E+00
Waterborne Emissions		
Dissolved Solids	3.42E-03	1.55E-03
Suspended Solids	9.52E-04	4.32E-04
BOD	3.54E-06	1.60E-06
COD	4.86E-05	2.20E-05
Oil	6.03E-05	2.73E-05
Sulfuric Acid	1.29E-05	5.86E-06
Iron	7.94E-05	3.60E-05
Ammonia	9.17E-07	4.16E-07
Copper	0.00E+00	0.00E+00
Cadmium	1.54E-07	7.00E-08
Arsenic	0.00E+00	0.00E+00
Mercury	1.21E-11	5.50E-12
Phosphate	6.46E-06	2.93E-06
Selenium	0.00E+00	0.00E+00
Chromium	1.54E-07	7.00E-08
Lead	3.75E-11	1.70E-11
Zinc	5.34E-08	2.42E-08

^a From Electric Energy Process Model (Dumas, 1998)

4.0 LIQUID PHASE METHANOL PROCESS

This chapter describes a systems model for a new and promising technology for methanol production known as the Liquid Phase Methanol (LPMEOHTM) process, which is in the demonstration phase at Eastman Chemical's Kingsport process demonstration facility. The chapter focuses on modeling of the LPMEOHTM process in ASPEN PLUS, a steady state chemical process simulator. The systems model of LPMEOHTM process will enable the evaluation of performance of the LPMEOH production process under varying synthesis gas feed conditions as might be expected from the municipal solid waste (MSW) gasification.

An overview of methanol production is presented in the next section (Section 4.1), followed by a brief description of methanol production technologies and their commercial status in Section 4.2, including the LPMEOH process technology. Modeling of processes in ASPEN PLUS is then described in Section 4.3. Technical basis for the LPMEOHTM process, including process chemistry and major process equipment, is presented in Sections 4.4. Section 4.5 presents the major process sections in the LPMEOH process model in ASPEN PLUS. Design specification and FORTRAN blocks used in the LPMEOH process model are presented in Section 4.6. Convergence sequence of LPMEOH process model is presented in Section 4.7. LPMEOH process model verification and validation is presented in Section 4.8. Implementation of a LPMEOH process model in ASPEN PLUS is presented in Section 4.9.

The life cycle inventory (LCI) of methanol produced by LPMEOH technology is calculated based on an example case in Section 4.10. Finally, the sensitivity analysis of LPMEOH process model is presented in Section 4.11.

4.1 Overview of Methanol production

Methanol, CH₃OH, is a major feedstock for the chemical industry. About 85 percent of the methanol produced is used in the chemical industry as a starting material or solvent for chemical synthesis. The remainder is used in the fuel and energy sector. It is a colorless, neutral, polar liquid that is miscible with water, alcohols, esters, and most other organic solvents. Synthesis gas, known as syngas for short, is a major precursor for methanol production. Table 4-1 lists the various processes, feedstocks, and catalysts for the production of methanol and its precursor syngas (Cheng and Kung, 1994).

Table 4-1. Processes and Feedstocks for Methanol Production

Feedstocks	Processes and main reactions	Catalysts
<i>Formation of syngas</i>		
Natural Gas	Steam Reforming: $\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$	Ni on Al ₂ O ₃
Natural Gas	Autothermal Reforming 1) $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ 2) $\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$ 3) $\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$	-- Ni on refractory supports
Natural Gas	Partial oxidation: $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$	Non-catalytic or lanthanide/Ru, supported Ru, Ni, Pd
Coal	Gasification (in presence of H ₂ O/O ₂)	--

Table 4-1 continued on next page

Table 4-1 continued

Feedstocks	Processes and main reactions	Catalysts
<i>Formation of syngas</i>		
Biomass	Gasification	--
Others (e.g., liquefied petroleum gas, naphtha, heavy fuel oil)	Steam reforming (light hydrocarbons)	Alkalized Ni on Al ₂ O ₃ or on Ca/Al ₂ O ₃
<i>Formation of Methanol</i>		
Syngas	Methanol synthesis: CO + 2H ₂ ↔ CH ₃ OH, CO ₂ + 3H ₂ ↔ CH ₃ OH + H ₂ O	Cu/ZnO/Al ₂ O ₃ Cu/ZnO/Cr ₂ O ₃ , or Zn/Cr
Syngas	Two-step methanol synthesis: CH ₃ OH + CO ↔ HCOOCH ₃ , then HCOOCH ₃ + 2H ₂ ↔ 2CH ₃ OH	Potassium methoxide, Cu chromite
Methane	Direct Oxidation: CH ₄ + 1/2O ₂ (or N ₂ O) ↔ CH ₃ OH	Metal oxides (e.g. MoO ₃)
Methane	Bioprocessing	Enzymes (e.g., cytochrome P ₄₅₀), methanotrophs

The first step in the production of methanol is generation of synthesis gas consisting mainly of H₂, CO, and CO₂. Synthesis gas can be produced by any of the processes listed in Table 4-1. The next step is syngas compression, if it is not already produced at high pressure, to the pressure at which methanol synthesis occurs. Methanol synthesis is the most important step in the process of methanol manufacture. The feature that is most useful in distinguishing commercial methanol processes from one another is the type of reactor used for methanol synthesis as described in Section 4.2. Unreacted gases downstream of the methanol reactor are separated in a flash drum and recycled back to the methanol reactor after compression. The methanol exit from the reactor has water, higher alcohols and other products of side reactions as impurities. These impurities are separated in a distillation column where a high purity (nearly 99.9 percent by weight) methanol is distilled as a top product.

Methanol production processes are classified according to the pressure used in the methanol synthesis reactor as:

- 1) High Pressure Process: 25-30 Mpa
- 2) Medium Pressure Process: 10-25 Mpa
- 3) Low Pressure Process: 5-10 Mpa

The main advantages of the low-pressure process are lower investment and production costs, improved operational reliability, and greater flexibility in the choice of plant size. The technology for the commercial manufacture of methanol has become fairly standard with the advent of the copper-based catalyst in the 1960s, and several large plants based on the so-called low-pressure methanol-synthesis process are currently in operation all over the world. Most current research is to seek alternate processes for methanol synthesis such as by the liquid-phase methanol synthesis process and the low-temperature, homogeneous, catalysis process. The syngas used in all low-pressure processes using copper-based catalysts needs purification and conditioning. Purification of syngas involves the removal of gaseous (or solid) components that which are harmful to the process route and/or methanol catalyst. The conditioning of syngas involves providing proper stoichiometric conditions for producing methanol from CO, CO₂, and H₂. The stoichiometric number is expressed by the formula:

$$S = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]} \quad (4-1)$$

where, the square brackets represent the number of moles of each component in the reactor feed. For higher single pass conversion of the syngas and high methanol yield, the value of S should be as close to 2 as possible. As reported in literature (Chen, 1995), the optimum value of S is 2.1.

As stated earlier, the type of methanol synthesis reactor is the main distinguishing feature in methanol synthesis technologies. The four basic reactor types in use are shown in Figure 4-1. There are a variety of proprietary reactor designs commercially available from licensors, all of which utilize one of these four types or a combination of two among them. ICI low-pressure (using quench type reactor) and Lurgi low-pressure (using steam raising type reactor) methanol synthesis processes are the two most widely used, commercially proven, and successful technologies. Most of the methanol plants built in last 20 to 25 years use the ICI or Lurgi processes. Other commercial technologies in use include Mitsubishi Gas Chemical (MGC) low-pressure process, Nissui-Topsoe methanol synthesis process, Variobar^(R) process by Linde AG, Germany and Japan Gas-chemical Company process (JGC). Since ICI and Lurgi low-pressure are the most commonly used commercial processes, only these will be described in detail. The following subsections present the detailed process descriptions on ICI, Lurgi and LPMEOH processes. A brief description of the MGC methanol process is also presented.

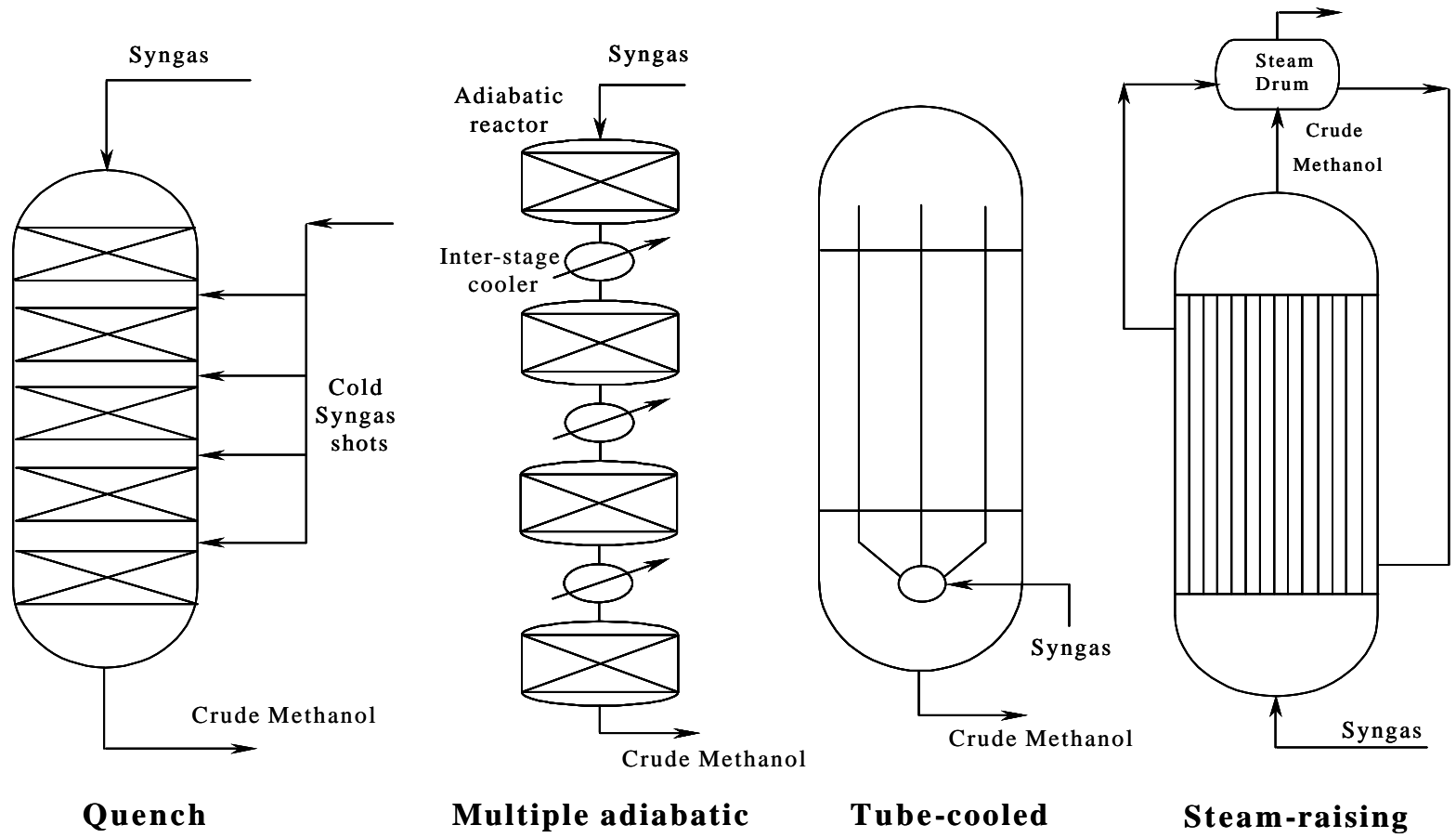


Figure 4-1. Methanol Converter Types

4.1.1 The ICI Low-Pressure Methanol Synthesis Process

ICI, Ltd. of the United Kingdom began manufacturing methanol with the new low-pressure technology in 1966. The plant, with 400 tons per day (TPD) capacity, operated at 5 Mpa (50 atm) and used centrifugal compression equipment. As of 1997, 53 methanol plants had been built using the ICI low-pressure methanol process and three plants were under construction (SRI, 1999). The principal feedstock used to produce synthesis gas for methanol synthesis is natural gas, although naphtha, heavier oil fractions and coal are also used. African Explosives and Chemical Industries of South Africa built the first coal-based plant using the ICI low-pressure process, with a capacity of 25,000 metric tons (8 million gallons) per year in 1976. There are two ways to produce syngas from the above said feedstocks: steam reforming of the feedstock and the partial oxidation of the feedstock.

The hydrocarbon feedstock is desulfurized by catalytic or absorptive processes, mixed with steam and passed forward to a tubular reformer. This is the process of steam reforming. The reformed gas (syngas) is cooled to ambient temperature and the heat is recovered in heat recovery section. Alternatively, syngas may be produced by partial oxidation of heavy fuel oil or coal by oxygen and steam. The product gas mostly consists of H₂ and CO, together with some CO₂ and trace impurities. It is treated to remove sulfur compounds and then adjusted via water-gas shift reaction, in a water-gas shift reactor by water addition, to achieve the optimum ratio of H₂ to CO before sending it to the

converter (Equation 4-2). Figure 4-2 shows a simplified process flowsheet for the ICI low-pressure process.



Where: Δh_r° = Enthalpy of reaction at standard conditions (T=298K, P = 1 atm; Twigg, 1989)

Syngas produced by either of two routes is compressed by a turbine driven centrifugal compressor to a pressure between 50 and 100 atm. The synthesis gas is added to the synthesis loop, which is comprised of the following process units: circulator; converter; heat exchanger; heat recovery exchanger; cooler and separator. The crude product is distilled in two or three columns. Synthesis catalyst operates in the pressure range of 50 atm to 100 atm at 200 °C to 300 °C and has a life of up to four years. The converter is a pressure vessel containing a single bed of catalyst. The reaction is quenched at several levels by cold syngas feed gas injections (called cold shots) through specially designed spargers. Reaction heat is recovered from the converter effluent to preheat the high-pressure boiler feed-water or to heat water for feedstock saturation. The product stream is cooled and methanol is condensed out. Crude methanol is then sent to a distillation column to achieve the desired purity.

The main advantages of the ICI low-pressure process are high methanol synthesis rates and selectivity (Dry, 1988). The main limitations of the ICI process are:

- 1) Maximum size is limited by multi-stage quenches in view of the pressure drop across the catalyst beds.
- 2) Due to high-pressure drop across the catalyst beds, the recycle compressor duty is high.
- 3) Methanol production is very sensitive to reactor bed temperatures. This is because the different parts of the catalyst beds are required to operate at different temperatures, and these temperatures depend critically on feed temperatures to each bed.
- 4) A small deviation in feed temperature tends to be amplified in the system, and catalyst life is reduced by thermal swings that occur during plant upsets.
- 5) The reaction heat is largely used to bring the quench gas to the reaction temperature and therefore the steam generation from the waste heat of the reactor exit gas is quite low. The maximum attainable steam pressure is limited to about 10 atm.

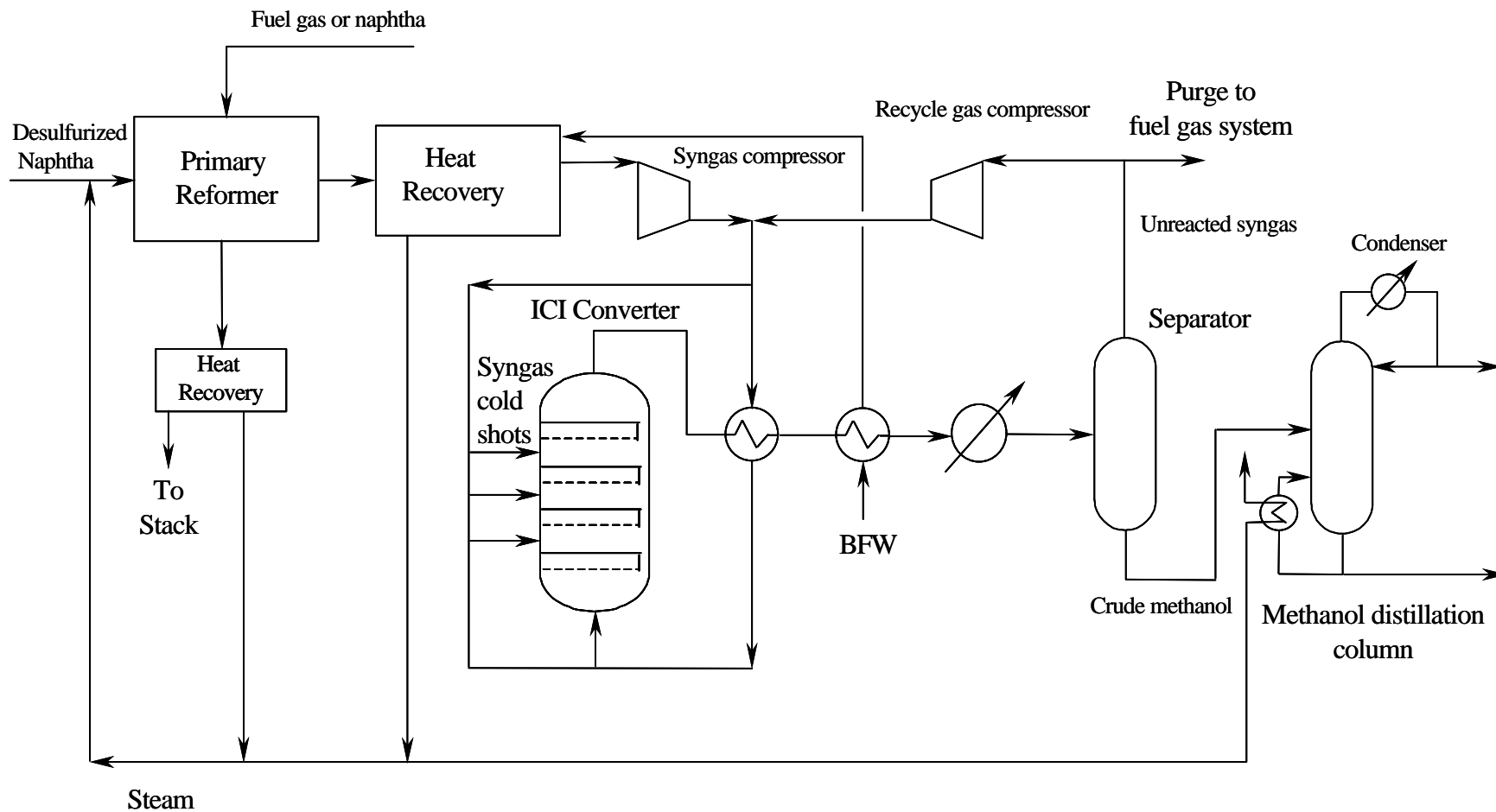


Figure 4-2. The ICI Low Pressure Process

4.1.2 The Lurgi Low-Pressure Methanol Synthesis Process

The first low-pressure Lurgi plants using tubular reactors went onstream between 1970 and 1973 (Supp, 1981). In early 1980, Lurgi had almost 40 percent of the market for low-pressure methanol plants. The process can handle synthesis gas obtained from a wide variety of feedstocks from natural gas to coal. Twenty-nine methanol plants had been built using Lurgi's methanol technology as of 1997 (SRI, 1999). Eastman Chemical Company in Kingsport, Tennessee has the only coal-based commercial plant in the United States.

The converter or the synthesis reactor is operated at temperatures ranging from 250 °C to 260 °C. The operating pressure is 50 atm to 60 atm. The design of the converter is different from that of ICI. In the ICI design, the catalyst forms a bed in which gas is introduced at various locations all along the length of the bed to get a uniform temperature distribution. The Lurgi design is comprised of a shell and tube reactor where the tubes are packed with catalyst and the heat of reaction is removed by circulating water on the shell side thereby generating high-pressure steam on the shell side.

The synthesis gas is generated either by the steam-reforming route or by the partial oxidation route. The steam reformer is typically operated at 850 °C to 880 °C where the previously desulfurized naphtha is contacted with steam to produce syngas (Twigg, 1989). Figure 4-3 shows the simplified flowsheet for the Lurgi low-pressure process. The syngas is compressed in a centrifugal compressor to 50 atm to 80 atm and

fed to the reactor. In the second route of partial oxidation, the heavy residues are fed into the furnace along with oxygen and steam. The feedstock gets partially oxidized at 1400 °C to 1450 °C. The operating pressure of the partial oxidizer is 55 atm to 60 atm and there is no need for syngas compression (Supp, 1981). The gas is cleaned to remove H₂S and free carbon, and a shift conversion is necessary to adjust the hydrogen to carbon monoxide ratio. The remaining process after the reactor involves cooling of the reactor effluent to condense the methanol, which is then sent to a separator and finally to a distillation column for methanol purification. The process after the methanol reactor is similar to the ICI low-pressure process. The major advantages of the Lurgi process are:

- 1) High heat-transfer area to catalyst bed volume ratio (ca. 80 m²/m³) and the resulting low temperature drop across the tube wall imply that temperature and hence selectivity control is easy.
- 2) The system is relatively insensitive to changes in feed gas temperature and features direct bed temperature control via shell pressure.
- 3) Largely complete utilization of reaction heat for the generation of high-pressure steam. When preheating feed water to boiling, 40 atm steam at a rate of 1.4 ton/ton methanol can be produced.
- 4) For the tube diameters chosen, the maximum temperature differential between the water and tube centerline is calculated to be about 11 °C because of the intensive cooling with boiling water around the tubes, thereby giving the reactor nearly isothermal operation and hence better equilibrium.

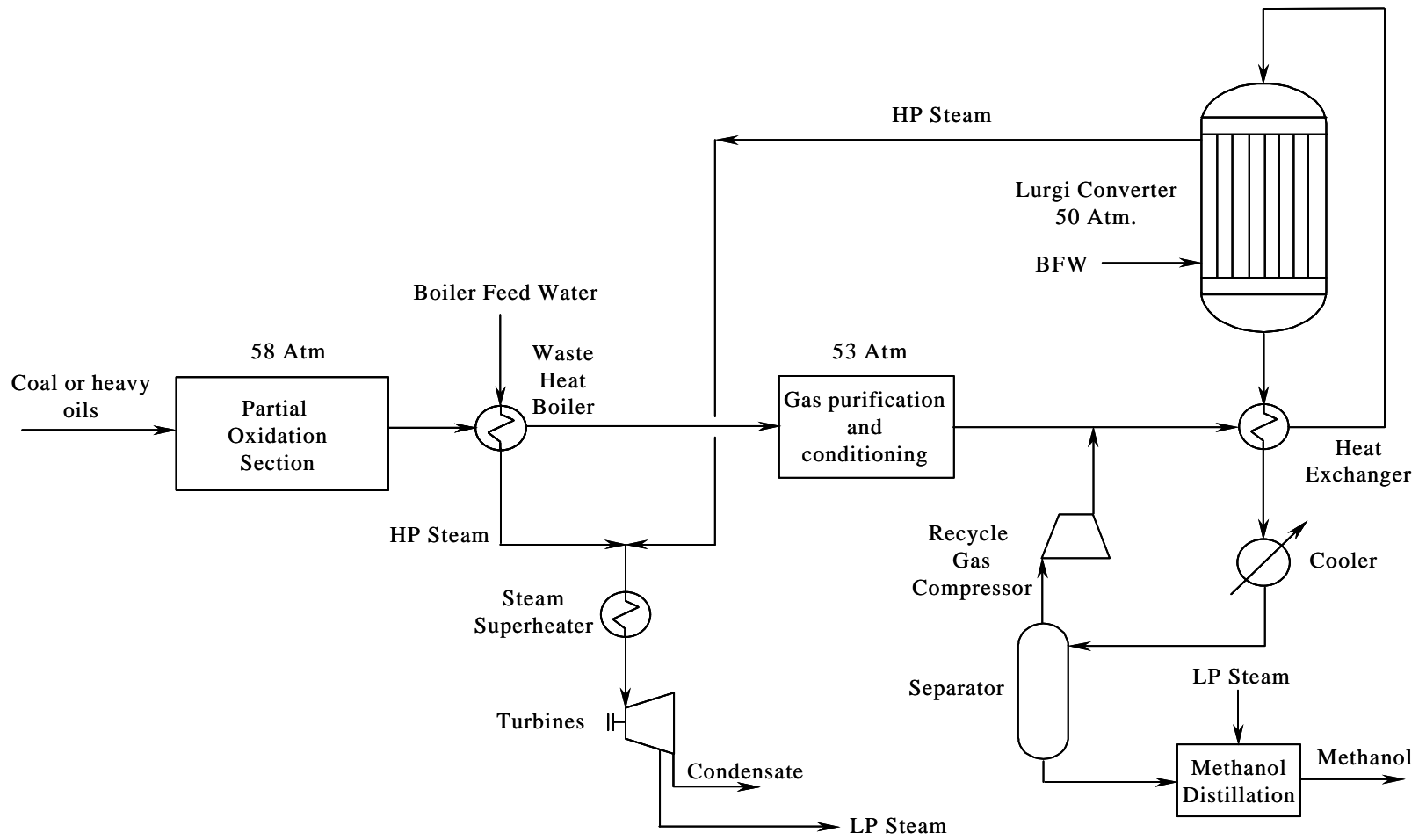


Figure 4-3. The Lurgi Low Pressure Process

The main limitation of the Lurgi low-pressure process is intractability of the system as far as scale-up beyond a certain limit is concerned. The problem stems from mechanical design of the tube-sheet, and its integrity becomes questionable at diameters greater than about 6 m. Maximum unit capacity is 900 ton/day to 1250 ton/day of methanol (Zardi, 1982). This is well short of the single train capacities envisaged for synfuel plants.

4.1.3 The MGC Low-Pressure Process

Mitsubishi Gas Chemical Company developed MGC low-pressure process. This process uses a copper-based methanol-synthesis catalyst and is operated at temperatures of 200 °C to 280 °C over a pressure range of 50 atm to 150 atm. The temperature in the catalyst bed is controlled by using a quench-type converter design, as well as by recovering some of the reaction heat in an intermediate stage boiler. The process uses a hydrocarbon feedstock. The feed is desulfurized and then fed into a steam reformer at 500 °C. The exit stream from the reformer contains hydrogen, carbon monoxide, and carbon dioxide at a temperature of 800 °C to 850 °C. The gases are then compressed in a centrifugal compressor and mixed with the recycled stream before being fed into the methanol reactor (converter).

4.1.4 Liquid Phase Methanol Process

In a conventional methanol production process, methanol is synthesized in a gas phase reaction over a heterogeneous catalyst from a synthesis gas that consists primarily of hydrogen, carbon monoxide and carbon dioxide. Newer processes for methanol are focused on the use of CO-rich synthesis gas instead of H₂ rich synthesis gas, thereby utilizing cheaper synthesis gas for the production of methanol. One of the promising technologies utilizing CO-rich synthesis gas is liquid phase methanol synthesis process (also known as LPMEOHTM process) that was conceived by Chem Systems, Inc., in 1975. The LPMEOHTM technology has been developed by Air Products and Chemicals Inc. Since the 1980's, the process has been successfully demonstrated on a bench-scale in a Department of Energy (DOE) – owned process and hydrodynamics development unit in LaPorte, Texas.

The LPMEOH process is not commercialized yet. However, a commercial scale demonstration plant began operation in April 1997 at Eastman Chemical Company, Kingsport, TN. It has a four year operating program scheduled to end in 2001 during which the demonstration plant intends to meet or exceed the design production capacity of 260 TPD of methanol, and will simulate operation of the integrated gasification combined cycle (IGCC) coproduction of power and methanol.

The test plan will also seek to establish commercial acceptance of the technology and verify the fitness of the as-produced methanol product (ranging from 97.5 weight percent to 99.99 weight percent purity depending on purification conditions chosen) through a series of off-site, product-use test.

The production of methanol by a LPMEOH process involves three phases: (1) the catalyst (solid phase); (2) inert hydrocarbon oil (liquid phase); and (3) the synthesis gas (gas phase). The process is illustrated in Figure 4-4. The reaction takes place in a fluidized bed reactor within the synthesis section of the methanol plant. The synthesis gas containing CO, H₂, and CO₂ is passed upward into the reactor concurrent with the inert liquid hydrocarbon. At the top of the reactor, product gases separate leaving behind the catalyst and liquid hydrocarbon. The heat generated in the reactor is used to generate high-pressure steam in the reactor's internal heat exchanger. The effluent gases from the reactor are then cooled and condensed. The unreacted gases are recycled after compression in a recycle gas compressor. The methanol produced can be purified by distillation to produce chemical grade methanol.

The single pass conversion of syngas in LPMEOH reactor, though higher than the conventional gas phase technology, is limited (Brown and Frenduto, 1992). For the syngas richer in hydrogen, there is lot of unconverted hydrogen after the methanol reaction in LPMEOH reactor. The unconverted syngas therefore needs to be recycled back to the reactor in order to produce additional methanol. This scenario of methanol production is known as LPMEOH process with recycle. Alternative scenario, once-

through-methanol (OTM) production, is the case in which unreacted syngas after single pass through LPMEOH reactor is sent to combustion facility for the generation of steam (Street, 1999). In an IGCC system combined with LPMEOH process, the unconverted syngas would be returned to the IGCC power plant's combustion turbines (Heydorn *et al.*, 1998). The following sub-section presents the main advantages of the LPMEOH process over current technologies.

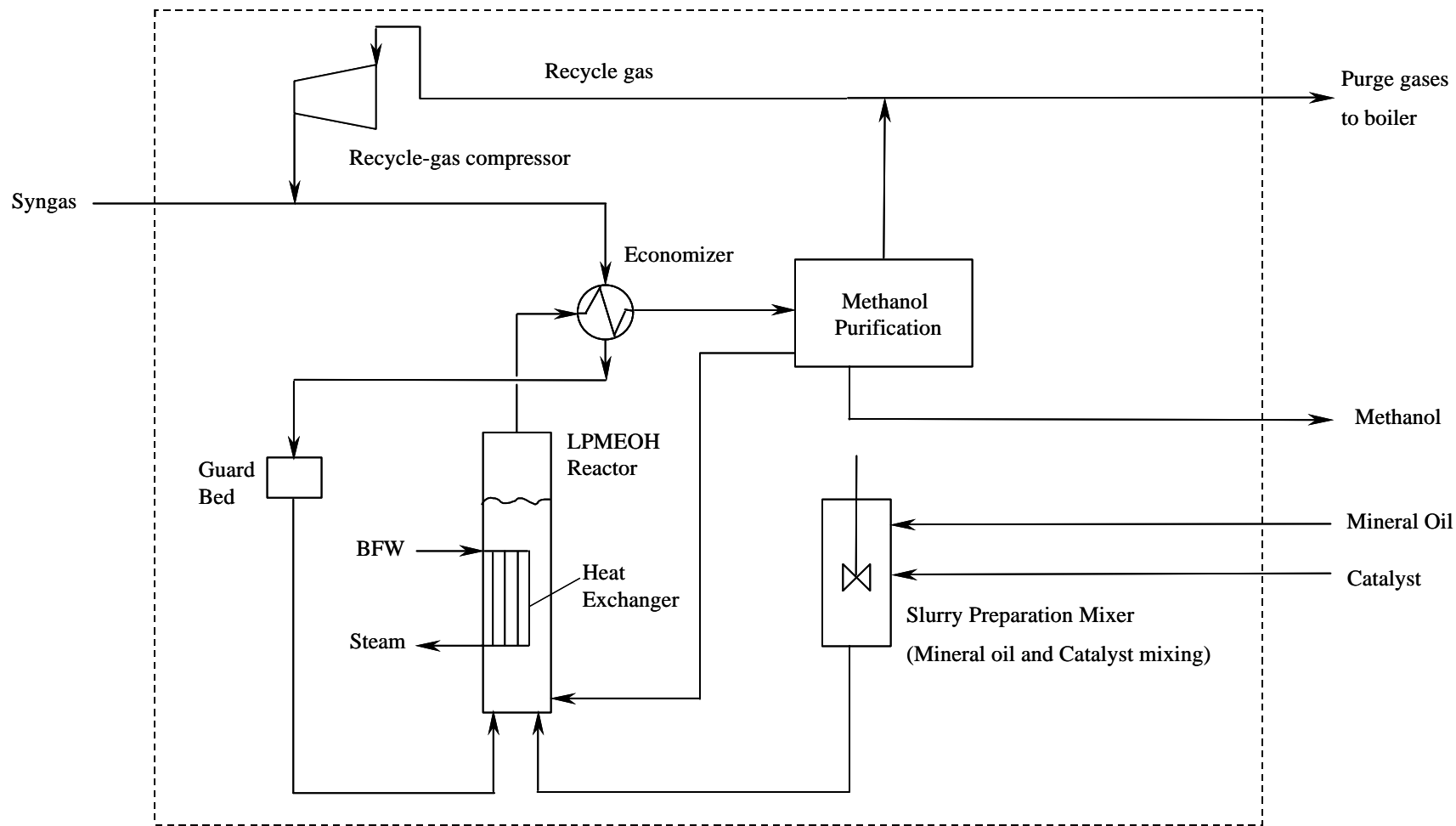


Figure 4-4. Simplified Process Flowsheet for Liquid Phase Methanol (LPMEOH™) Process

4.1.4.1 Advantages of Liquid Phase Process over Current Technologies

This section presents the advantages of LPMEOH process technology over the conventional gas phase methanol production process. The main advantages of LPMEOH process over the gas phase technology are (Cook, 1995; Heydorn *et al.*, 1998):

- 1) Because of the LPMEOH reactor's ability to control temperature, it is able to directly process syngas that is rich in CO and CO₂. The gas phase methanol technology would require such a feedstock to undergo stoichiometric adjustment by water-gas shift reaction, described in Section 4.1.5, to increase the H₂ content and achieve temperature moderation by recycling large amounts of H₂ rich syngas since H₂ has higher heat capacity as compared to CO.
- 2) Due to good control of reaction temperature, it is possible to achieve high per pass conversion economically such that the methanol concentration in the exit gas attains the 15 to 20 volume percent range as compared to normal value of 5 to 6 volume percent for the syngas with H₂/CO ratio of equal to or greater than two. This greatly reduces recycling and compression requirements.
- 3) The heat of reaction can be effectively used to generate high-pressure steam.
- 4) The reactor design allows for liquids and gases to be readily distributed across the reactor cross-sectional area without the necessity for redistribution and quench along the reactor length.
- 5) Catalyst can be added and withdrawn from the system while on-stream without the necessity of shut-down.

- 6) A smaller catalyst size can be used which leads to higher rates of reaction as compared to larger catalyst particles.
- 7) Because of the near isothermal temperature of the reactor, nearly optimum conditions prevail in the system favoring the reaction kinetics.
- 8) The axial diffusivity of the gas in three-phase process is relatively low as compared to gas-solid fluidized bed, making high per pass conversion easier to achieve.

4.1.4.2 Drawbacks of the Liquid Phase Methanol Process

This section presents the main limitations of the LPMEOH process technology with respect to conventional gas phase technologies. The main limitations of LPMEOH process are:

- 1) Liquid phase diffusivities of the reactants are lower than those in the vapor phase.
- 2) The solubility of the reactants in the liquid medium must be sufficiently high for the process to be efficient.
- 3) The liquid chosen for the reaction system should be chemically inert and thermally stable and have low vapor pressure at operating conditions.
- 4) Problems of catalyst attrition may occur due to fluidization of catalyst in mineral oil.

4.1.5 Water-gas Shift Reaction

The water-gas shift reaction, as described by Equation 4-2, is employed to stoichiometrically adjust the H_2/CO ratio of syngases that are rich in CO. The

conventional gas phase process does not have a capability to operate on raw material syngas that has less than a stoichiometric amount of H₂. Therefore the syngas which is rich in CO (e.g. syngas obtained from coal gasification) needs to be sent to a water-gas shift converter to adjust the H₂/CO ratio to near stoichiometric (2 to 2.1) for higher methanol yields (Twigg, 1989).

LPMEOH methanol process has a capability to operate on CO rich syngas and the syngas feed does not require any water gas shift reaction for stoichiometric adjustment. However, the conversion per pass in the LPMEOH reactor for CO-rich syngas is low and the methanol yield is also low. One methanol production option using high CO syngas is the once-through-methanol (OTM) process described in Section 4.1.4, where the unreacted syngas after a single reactor pass can be sent to steam boiler for steam generation or it can be returned to IGCC power plant combustion turbines if an integrated methanol plant with IGCC is used. In another option, the LPMEOH reactor design can be altered to generate additional H₂ via water-gas shift reaction in the LPMEOH reactor. The inherent shift activity of the methanol reactor can be utilized to accommodate a modest amount of shift activity within the reactor. This can be done by the addition of water, as steam, to the syngas before it passes through the LPMEOH reactor. Within the reactor, the steam is converted to H₂, which is in turn converted to methanol. In the case of water addition, the increase in conversion would be accompanied with a modest increase of water in the crude methanol product and of CO₂ in the reactor effluent gas (Tijm *et al.*, 1997).

This option is being thought of and being simulated in a proprietary model by Air Products and Chemical, Inc but no operational experience of this option is available in literature.

4.2 Commercial Status of Liquid Phase Methanol (LPMEOHTM) Technology

Coal is the most abundant domestic energy resource in the United States. The Fossil Energy division within the U.S. Department of Energy (DOE) has been supporting a coal liquefaction program to develop improved technologies for converting coal to clean and cost-effective liquid fuels to complement the supply of petroleum crude. Indirect and direct liquefaction routes are the two technologies being pursued under the DOE coal liquefaction program. In indirect liquefaction, coal is gasified in the presence of steam and oxygen to produce a synthesis gas containing mostly carbon monoxide and hydrogen. This synthesis gas, after being cleaned of impurities and adjusted to the desired H₂/CO ratio (if required), is converted to liquid fuels in the presence of catalysts. The conversion of syngas to motor fuels is known as Fischer-Tropsch (F-T) synthesis. Commercial indirect liquefaction plants in operation since 1955 have included coal based plants in South Africa and the U.S. In all these plants, the syngas is converted in gas phase reactors (Shen, 1996). Because of the highly exothermic reactions, it has long been known that a liquid phase reactor could offer cost and operational advantages over gas phase reactors due to its effective heat transfer capabilities.

Chem Systems Inc. conducted bench-scale development of the liquid phase methanol process in the mid-1970s, with support from the Electric Power Research Institute (EPRI). The project involved bench-scale and process development unit (PDU) testing of a new liquid-phase reactor. While it was demonstrated that methanol could be produced from coal-derived syngas, attempts to produce an active, attrition resistant catalyst were not completely successful as judged by low catalyst life during catalyst testing. Table 4-2 summarizes the project results.

TABLE 4-2. Chem Systems Inc, Bench-scale Testing of LPMEOH PDU^a

Objectives	Results	Problems Faced
<ul style="list-style-type: none"> ◆ Demonstration of concept feasibility. ◆ Bench-scale and PDU testing of a new liquid-phase reactor. Reactor was 1-inch in diameter and 6 feet in length ◆ Catalyst development ◆ Process variable studies ◆ Scale-up in a larger process development unit. ◆ Long term continuous runs. ◆ Engineering studies 	<ul style="list-style-type: none"> ◆ Concept feasibility studies were successful; methanol could be produced from high CO containing feed gas (K-T) as well as from Lurgi. ◆ Active, attrition resistant catalyst could not be produced. ◆ Best catalyst formulation available was 3/32 inch mini-tablet. ◆ Methanol concentration in the reactor exit gases found to be 2.3 to 4 times greater than conventional processes. ◆ The reaction temperature for maximum catalyst productivity was found to be 220-250 °C. ◆ The presence of small quantities of CO₂ was found to enhance catalyst productivity. 	<p>No problems reported except catalyst attrition and catalyst activity loss during the catalyst testing.</p>

^a Sherwin and Blum, 1979

In 1981, DOE, in cooperation with industrial organizations, began to support a research and development program to advance the liquid phase reactor technology for coal based syngas. Air Products and Chemicals, Inc. (APCI), with the support of DOE, began a research and development project in September 1981 as a part of DOE's indirect liquefaction program to further develop LPMEOHTM at a process demonstration unit (PDU) scale. The PDU scale development began in 1981 with the construction of a 5-ton per day (TPD) nameplate capacity methanol plant located in LaPorte, Texas (Shen, 1996). Chem Systems Inc., being the inventor of the process, was the key subcontractor in the program. Industrial cost sharing participants were APCI, EPRI, and Fluor Engineers, Inc. The primary function of the LaPorte PDU was to acquire data at a small, representative engineering scale for testing the feasibility of the LPMEOH process. The process was successfully demonstrated and extensively proven in over 7,400 hours of test operation (Shen, 1996). Table 4-3 presents a summary of the operational experience at LaPorte PDU.

TABLE 4-3. LPMEOH™ PDU, LaPorte, Texas^a

Objectives	Overall Results	Problems
<ul style="list-style-type: none"> ◆ To acquire data at a small representative engineering scale for testing the feasibility. ◆ Test the plant over the range of operating conditions. <p>Five major runs were conducted.</p> <ol style="list-style-type: none"> 1) 10-day shakedown run. 2) 40-day continuous run on CO-rich syngas. 3) Use of commercially available catalyst powder at high slurry concentration. 4) 40-day run to demonstrate improved activity using catalyst powder that had been reduced in-situ. 5) 10-day run to demonstrate in-situ reduction of a high slurry concentration and to obtain performance data with high solids loading. 	<ul style="list-style-type: none"> ◆ 7,400 hours of successful operation. ◆ 99+ % onstream factor. ◆ Confirmation of simple reactor design. ◆ Easy accommodation of shutdowns/restarts/ load increase. ◆ Long catalyst life. ◆ Successful operation at high slurry concentration (50 wt%) ◆ High production rates, 12+ TPD of fuel grade methanol at 97.5 wt % methanol product purity (as produced) ◆ Maintenance of production rate with online addition of fresh catalyst. ◆ Good laboratory-to-pilot plant agreement on scale-up. 	<p>No problems were reported.</p>

^a Frank, 1989

The first commercial-scale demonstration plant for the technology has been constructed and operating at Eastman Chemical Company's coal gasification facility in Kingsport, Tennessee with the help of a \$92.7 million award under the DOE's Clean Coal Technology Program. The estimated total cost of the project including the four-year demonstration test program is \$213.7 million. Air Products and Eastman formed the "Air Products Liquid Phase Conversion Co., L.P." partnership to execute this demonstration project. The plant has been in operation since April 1997. The demonstration plant has a design capacity of 80,000 gallons of methanol per day (260 TPD). The partnership will own and operate the facility for the four-year demonstration period.

As documented in the DOE reports on the commercial scale demonstration of the LPMEOHTM process, the demonstration plant, during its four-year operating program is intended to meet or exceed the design production capacity of 260 TPD of methanol, and simulate operation for the integrated gasification combined cycle (IGCC) coproduction of power and methanol application (Air Products and Chemicals, Inc, 1997). The project, as reported, is intended to establish the commercial acceptance of the technology and verify the suitability of the as-produced methanol product (approximately 98-weight percent purity) through a series of off-site, product-use tests. The ultimate goal of the demonstration period is to reach a stable, optimized operating condition, with the best combination of the operating parameters. The operational experience and the results to date are included in Table 4-4.

TABLE 4-4. Commercial Scale Demonstration of LPMEOHTM Process, Kingsport (260 TPD Plant)^a

Objectives	Results as of Oct. 1999	Problems
<p>The ultimate goal of the demonstration period is to reach a stable, optimized operating condition, with the best combination of the most aggressive operating parameters.</p> <p>The test plan outline for 4 years will be:</p> <p><u>Year 1:</u></p> <ul style="list-style-type: none"> ◆ Studies on catalyst aging. ◆ Process Optimization using parameters such as catalyst slurry concentration, reactor slurry level and gas superficial velocity. <p><u>Year 2 and 3:</u></p> <ul style="list-style-type: none"> ◆ Catalyst Attrition/poisons/activity/aging tests. ◆ Simulation of IGCC coproduction for various commercial gasifiers. ◆ Studies of maximum throughput and production rate. <p><u>Year 4:</u></p> <ul style="list-style-type: none"> ◆ Test for 99% availability. ◆ Potential alternative catalysts test and additional industry user test 	<ul style="list-style-type: none"> ◆ Methanol production reached nameplate capacity of 260 TPD and a stable test period at over 300 TPD of methanol revealed no system limitations in reactor or distillation areas. ◆ During initial operating period, the plant achieved an availability in excess of 92%. ◆ Availability during 1998 has been reported to be above 99%. ◆ Higher levels of iron and arsenic were found on catalyst that could not be correlated to presence of iron carbonyl in feed gas. ◆ Fresh charge of catalyst was introduced in December 1997. ◆ Variability in catalyst performance attributed to presence of trace levels of catalyst poisons (iron, sulfur, arsenic, etc.). 	<ul style="list-style-type: none"> ◆ Two high-pressure oil make-up pumps failed to generate the differential pressure required for their service due to which connection at the reactor was blocked. ◆ The catalyst samples showed higher levels of iron and arsenic. ◆ The catalyst showed variability in its performance due to which reactor temperature varied from 220 °C to 250 °C during 8 months period after the fresh catalyst charge was introduced.

^a Heydorn *et al.*, 1998

^b Tijm *et al.*, 1999

4.3 Modeling Process Flowsheets in ASPENPLUS

ASPEN PLUS is a process simulation package that solves steady-state material and energy balances, estimates physical properties of a large number of species, calculates phase and chemical equilibria, and sizes and costs various types of process units (Aspen Technology, Inc., 1996). ASPEN stands for Advanced Systems for Process Engineering. It was originally developed under government contract for the Department of Energy (DOE) by Massachusetts Institute of Technology in 1987. ASPEN PLUS is a commercial version developed by Aspen Technology, Inc. (AspenTech) and is widely used in process industries.

AspenTech developed ModelManager, a graphical user interface (GUI) program to simplify building a flowsheet and running process simulation. The user creates a schematic process flowsheet using ModelManager which then translates the flowsheet into the equivalent ASPEN PLUS input file and runs the simulation. (AspenTech, 1996).

The ASPEN PLUS framework includes a number of generalized unit operations “blocks”, which are models of specific process operations or equipment (e.g., chemical reactions, pumps, compressors, distillation columns, etc.). By specifying configurations of unit operations and the flow of material, heat, and work streams it is possible to represent a process plant in ASPEN PLUS. In addition to a varied set of unit operation blocks, ASPEN PLUS also contains an extensive physical property database and

convergence algorithm for calculating results in closed loop systems, all of which make ASPEN PLUS a powerful tool for process simulation (Akunuri, 1999).

ASPEN PLUS uses a sequential-modular approach to flowsheet convergence. In this approach, mass and energy balances for individual unit operation blocks are computed sequentially, often in the same order as the sequencing of mass flows through the system being modeled. However, when there are recycle loops in an ASPEN PLUS flowsheet, stream and block variables have to be manipulated iteratively in order to converge upon the mass and energy balance. ASPEN PLUS has a capability for converging recycle loops using a feature known as “tear streams”.

In addition to calculations involving unit operations, there are other types of block used in ASPEN PLUS to allow for iterative calculations or incorporation of user-created code. These include Design Specifications and FORTRAN blocks.

A Design Specification is used for feedback control. The user can set any flowsheet variable or function of flowsheet variables to a particular design value. A stream variable or block input variable is designated to be manipulated in order to achieve the design value. FORTRAN statements can be used within the design specification block to compute design specification values.

FORTRAN blocks are used for feedforward control. Any FORTRAN operation can be carried out on flowsheet variables by using in-line FORTRAN statements that

operate on these variables. FORTRAN blocks are one method for incorporating user code into the model. It is also possible to call any user-provided subroutine from either a design specification or FORTRAN block.

4.4 Technical Description of the Liquid Phase Methanol (LPMEOHTM) Process

This section discusses the technical basis for the liquid phase methanol (LPMEOHTM) process. First, the general description and process flow sheet is presented. The process chemistry and the issues related to it are then discussed. Finally, the unit operations involved in the process and design variables are presented with their typical values, many of which were based on a visit to the LPMEOHTM process demonstration facility at Kingsport, TN (October 14, 1999).

4.4.1 LPMEOHTM Process Description

Eastman Chemical uses the Texaco gasification process to convert about 1,000 tons-per-day of high sulfur, eastern bituminous coal to syngas for the manufacture of methanol, acetic anhydride, and associated products. The crude syngas is quenched, partially shifted via water gas shift reaction (Equation 4-2), treated for acid gas removal (hydrogen sulfide, carbonyl sulfide, and CO₂) via the Rectisol® process, and partially processed in a cryogenic separation unit to produce separate H₂ and CO streams. The H₂ stream is combined with clean syngas to produce a stoichiometrically balanced feed for a conventional gas-phase Lurgi methanol synthesis unit that was already present at the

facility, which is further polished in an arsine- and sulfur-removal guard bed. Approximately 50 percent of the balanced gas fresh feed to the existing methanol unit is diverted to the LPMEOHTM PDU.

Figure 4-5 shows a simplified process flow diagram of the LPMEOHTM demonstration plant at Kingsport. The balanced gas fresh feed is passed through an activated carbon guard bed. This bed removes iron and nickel carbonyls, which are poisons to the methanol synthesis catalyst, down to ppb levels. Because the third feed stream (H₂ gas) is at lower pressure than the other two streams, it can be combined when appropriate with the recycle gas stream, made up of unconverted syngas from the LPMEOHTM reactor, and compressed in the recycle gas compressor. These streams are then combined to form one high-pressure (nearly 750 psia) reactor feed gas stream that is preheated in the feed/product economizer against the reactor effluent to a temperature of 330 °F. The feed gas is then sparged into the LPMEOHTM reactor (7.5 ft in diameter) operating at a temperature of 481 °F and approximately 721 psia pressure, where it gets mixed with the catalyst slurry and is partially converted to methanol vapor, liberating the heat of reaction in the slurry (Air Products and Chemicals, Inc., 1997). Varying the steam temperature within the heat exchanger tubes controls the temperature inside the reactor, which in turn is controlled by adjusting the steam pressure. Saturated steam at 300 psia is produced from boiler feed water (BFW) in the internal heat exchanger of the reactor (Street, 1999).

Disengagement of the effluent gas (methanol vapor and unreacted syngas) from the catalyst/oil slurry occurs in the freeboard region of the reactor. Any entrained slurry droplets leaving the top of the reactor are collected in the cyclone separator, where a pressure drop of approximately 6 psia occurs (Street, 1999). The product gas passes through the tubeside of the feed/product economizer, where it is cooled against the reactor inlet gas stream. Any condensed oil droplets are collected in the high-pressure oil separator and then returned to the reactor with the entrained slurry from the cyclone separator.

The product gas is cooled further in a series of air-cooled and cooling water exchangers to a temperature of approximately 100 °F, where product methanol condenses and collects in the high-pressure methanol separator (Street, 1999). Most of the unreacted synthesis gas returns to the reactor after undergoing compression in the recycle compressor. The balance of the unreacted syngas is purged to the fuel gas system.

The condensed methanol contains dissolved gases, water, trace oil, and some higher alcohols. These impurities are removed in a two-column distillation train that produces a methyl acetate feed-grade methanol product. The bottom draw from the second column is a crude methanol stream heavy in higher alcohols, water, and any oil carried over from the reactor.

Catalyst slurry is activated in the catalyst reduction vessel, which is equipped with a heating/cooling jacket, utility oil skid, and agitator. Pure CO, diluted with nitrogen, acts as the reducing agent for the activation of the catalyst.

For a commercial plant, it would be desirable to use the water-gas shift reaction for syngas compositions lower in hydrogen content (Tijm *et al.*, 1997). This can be done in the manner explained in Section 4.1.5. However, the LPMEOH process model developed in this study does not include the option of water-gas shift reaction.

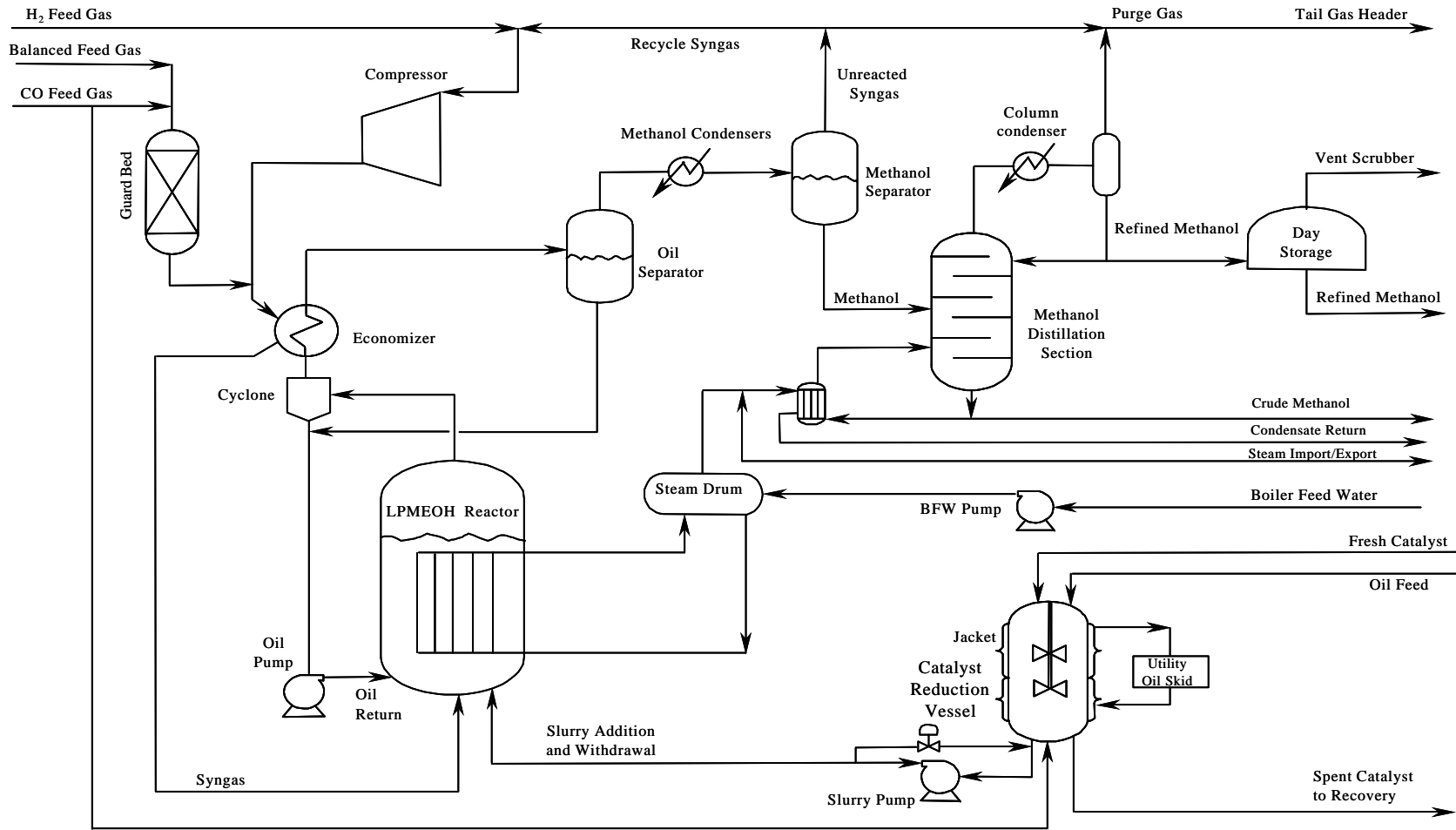
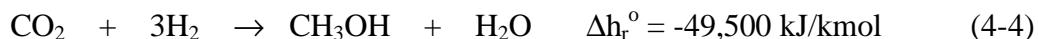


Figure 4-5. Simplified Process Diagram (LPMEOH™ Process Demonstration Facility, Kingsport)

4.4.2 Process Chemistry of Methanol Synthesis

Two main reactions taking place in the synthesis of methanol are listed below as Equations 4-3 and 4-4 (Cheng and Kung, 1994).

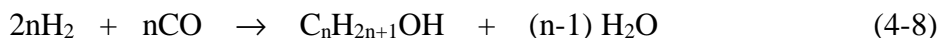


A third relatively less important reaction, known as the reverse water gas shift reaction also occurs (Cheng and Kung, 1994).



Δh_r° is the heat of reaction at standard temperature and pressure (298 K and 1 atm; Cheng and Kung, 1994). The first two reactions are exothermic while the third reaction is endothermic. The reaction heat generated during methanol formation is considerable, and as the temperature increases, the backward reaction is favored. Thus there is need for maintenance of a thermodynamically optimum temperature of 250°C to maintain catalyst activity high enough and to favor the forward reaction. This concept is explained in detail in the catalyst activity section, Section 4.4.3. A temperature increase may lead to the reverse reaction and at the same time the chances for the competing side reactions increase. Side reactions can lead to the formation of methane, dimethyl ether, methyl formate, higher alcohols, and acetone. The heat of reaction must therefore be removed quickly to maintain the temperature near optimum as far as possible to achieve higher

conversion and yield. In LPMEOHTM process, this is accomplished by an inert mineral oil, which acts as a heat carrier. The common side reactions that may take place are (Meyers, 1984):



The typical operating condition for the LPMEOHTM process reactor is 50 atm to 100 atm pressure, and near 250 °C temperature. The composition of the catalyst is proprietary but it consists of copper and zinc oxides in their reduced form.

4.4.3 Catalyst Activity

The role of the catalyst is to increase the rate(s) of the desired reaction(s) under favorable thermodynamic conditions. The reaction of H₂ with carbon monoxide and carbon dioxide is exothermic and relies on the catalyst. For exothermic reactions, which are favored at lower temperature, it is the catalyst that determines the lowest practical operating temperature. The limitation imposed by low temperature catalysts is that their activity is also a function of temperature. Thus if the reactor temperature drops too low, the catalyst itself becomes inactive and the reaction proceeds at very slow pace. At higher temperatures the catalyst may be very active but again thermodynamics will favor CO

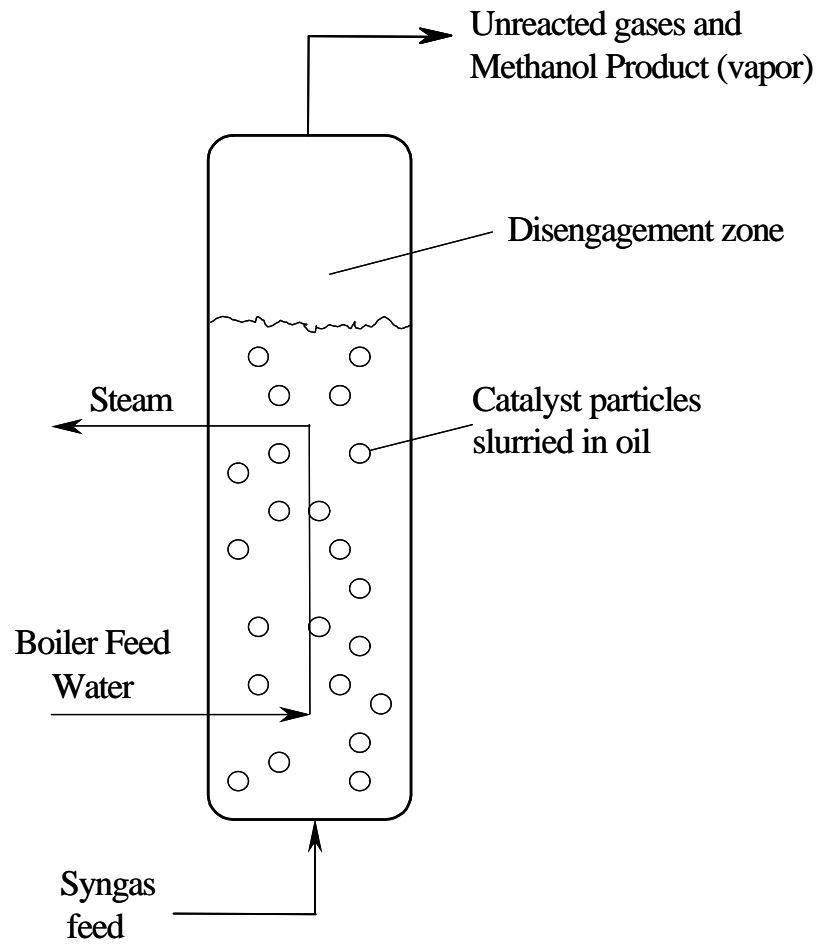
formation so that the rate of the desired reaction is again slow. At the same time, the temperature should not be so high that it damages or degrades the catalyst activity. Thus a reactor should be designed to operate in a regime where the desired reaction is thermodynamically favored and catalyst activity is high. In such a case the driving force of thermodynamics is fully utilized given the limitations of the catalyst. This regime refers to the optimum range of temperature and leads to the definition of optimum temperature as the temperature at which reaction rate(s) and catalyst life are optimized.

4.4.4 Major Process Equipment

The major process equipment used in the LPMEOHTM process are described in this section.

4.4.4.1 Reactor

The heart of the LPMEOHTM plant is the reactor. The reactor size being used in the Kingsport demonstration facility is based on the scale-up of the DOE-owned Alternate Fuels Process Development Unit at LaPorte, Texas. The reactor is a stainless steel clad carbon steel vessel designed for 1000 psig and 600 ° F. The reactor at Kingsport, along with supports, is 84-feet tall. Within the reactor, the copper/zinc oxide-based catalyst is suspended in an inert mineral oil, which serves as the heat transfer medium. The reactor has an internal heat exchanger for removal of the heat of reaction. The general reactor schematic is presented in Figure 4-6. The feed gas is sparged into the



TYPICAL METHANOL SYNTHESIS CONDITIONS

Pressure : 50-100 Atm (725-1450 psia)

Temperature : 250 °C (482 °F)

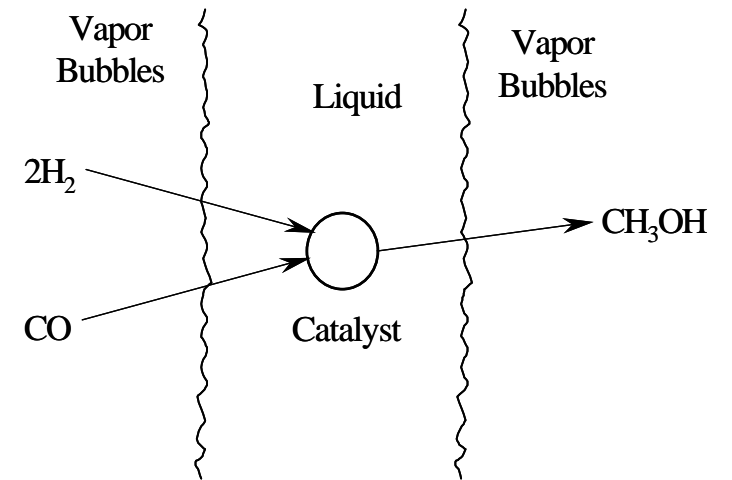


Figure 4-6. LPMEOH™ Reactor and Reaction Schematics

LPMEOHTM reactor, where it mixes with the catalyst slurry and is partially converted to methanol, releasing the heat of reaction to the slurry. A typical pressure drop of 10 psi occurs in the LPMEOH reactor sparger (Street, 1999).

The removal of heat of reaction is of prime importance. The rise of temperature above the optimum temperature (approximately 250 °C) may reduce the catalyst activity and lead to formation of undesirable products via side reactions. The feed gas pressure is a prime determinant of the degree of syngas conversion. Reaction pressure for methanol synthesis design is usually 750 psia or higher. The conversion increases as the operating pressure increases but the capital cost of the reactor and the syngas compression cost also increase with pressure.

The exit gases consist of methanol vapor, unconverted syngas and other byproduct impurities produced by the side reactions within the reactor. The heat generated in the reactor is used to produce steam in the internal heat exchanger, which is supplied with boiler feed water (BFW).

Typical operating conditions of the reactor as evident from DOE quarterly and topical reports on commercial scale demonstration of Liquid Phase Methanol (LPMEOHTM) process are: (1) temperature of 250 °C; (2) pressure of 710 psig to 750 psig; and (3) syngas space velocity of 4000 to 8000 standard liters/kg-hr (Air Products and Chemicals, Inc., 1997).

Depending on the reactor pressure, temperature, composition of the feed syngas, the per pass conversion of syngas to methanol may typically vary from 15 percent to as high as 60 percent. The variation of syngas conversion with pressure, syngas space velocity and H₂/CO ratio (composition of syngas) has been described in Section 4.5.4.1.

4.4.4.2 Guard Bed

The guard bed consists of two beds in series called the sections of the guard bed. The first section consists of MnO as packing for the removal of H₂S and arsenic. The second section consists of activated carbon as packing for the removal of iron and nickel carbonyls to ppb levels, which are poisons to methanol catalyst. The overall pressure drop across the guard bed is approximately 6 psia (Street, 1999).

4.4.4.3 Economizer

The LPMEOHTM process includes an economizer to conserve the heat energy within the process. The economizer is a heat exchanger, which allows for heat exchange between the cold feed to the reactor and the hot product gas exiting the reactor. The cold feed is on the shell side of the feed/product economizer and the hot product gas stream passes through the tubeside.

4.4.4.4 Cyclone Separator

After the reaction has taken place on the surface of the catalyst, the products diffuse back to the liquid phase. The disengagement of the effluent gas, which includes methanol and unreacted gas, from the catalyst/oil slurry occurs in the freeboard region of the reactor. A cyclone removes any entrained slurry droplets leaving the top of the reactor. A pressure drop of approximately 6 psia occurs in the cyclone separator (Street, 1999). The collected slurry droplets from the cyclone are then returned to the reactor. The exit gas from the cyclone then enters the tubeside of the feed/product economizer to exchange heat with cold feed.

4.4.4.5 Oil Separator

After cooling of the hot exit gas from the reactor in feed/product economizer, the gas is sent to a high-pressure oil separator. The function of this oil separator is to remove any condensed oil droplets from the gas stream. The condensed oil collected is then returned to the reactor with the entrained slurry from the cyclone separator.

4.4.4.6 Pre-Methanol Separator Condensers

The product gas from the oil separator is cooled by passing it through a series of air-cooled and cooling water heat exchangers. These heat exchangers are known as pre-methanol separator condensers.

4.4.4.7 Pre-Methanol Separator Valve

The function of the pre-methanol flash valve is to allow for the reduction of pressure in the stream such that flashing of non-condensables can take place. The stream after flashing enters the methanol separator for vapor-liquid phase separation.

4.4.4.8 Methanol Separator

Methanol and water condensed in a series of condensers enter the methanol separator along with unreacted gases. Simple phase separation takes place in the methanol separator, in which condensed liquid phase consisting mostly of methanol and water is separated at the bottom and unreacted gases leave the top of separator in the gas phase.

4.4.4.9 Pre-distillation Pressure Relief Valve

The condensed and phase separated liquid stream, consisting mainly of methanol, enters the pre-distillation pressure relief valve for the reduction of pressure before it enters the vapor distillation column for the removal of light gases/impurities.

4.4.4.10 Methanol Distillation and Purification Section

The purpose of the methanol distillation section is to produce high purity methanol (>99 percent by weight). The distillation section consists of a two-column distillation train. The first column is just a vapor recovery column and is used to remove light impurities and gases. No methanol is taken out as a top product from this column. The bottoms from the first distillation column flows as a feed to second distillation column where 75 percent of the methanol in the feed is distilled to chemical grade methanol (99.99 percent by weight) in the top product (Street, 1999). The bottom product from the second column has methanol with 80 to 90 percent purity by weight, with the balance being water, higher alcohols, and traces of oil. The bottom product is sent to a third distillation column (not a part of LPMEOH process facility at Kingsport) for the recovery of remaining methanol with 99.99 percent purity by weight as top product (Street, 1999). The bottoms from this third column are sent to a wastewater treatment facility. Use of three distillation columns for methanol purification is a site-specific issue at Kingsport. In a chemical plant, 99.99 percent purity of methanol can be achieved using two distillation columns as modeled in this study (Street, 1999).

4.4.4.11 Recycle Gas Compressor

The unreacted gas from the methanol separator is recycled back to the reactor to increase the conversion of syngas. This recycled gas is sent to the recycle gas compressor to raise the pressure of the recycle gas such that it reaches the pressure required for

methanol synthesis reactor. A typical inlet pressure of recycle gases to the compressor is 700 psia and typical compressor outlet pressure is approximately 738 psia. Thus the recycle gas compressor overcomes the overall pressure drop of 38 psi in the LPMEOH process (Street, 1999).

4.4.4.12 Catalyst Reduction Vessel

In addition to the equipment already discussed, the LPMEOHTM plant has catalyst activation facilities, consisting of an agitated catalyst reduction vessel, where powdered catalyst in oxide form is combined with mineral oil to produce a slurry containing 30 percent catalyst by weight. After the agitator is stopped, reducing gas, consisting of a blend of nitrogen and carbon monoxide, is introduced into the reduction vessel via a gas distributor. The carbon monoxide reacts with the oxide form of the catalyst to convert it to the active metallic form.

During the reduction, slurry temperature is carefully increased while the consumption of carbon monoxide is monitored to determine when complete reduction has occurred. After reduction, the catalyst is pumped to the LPMEOHTM reactor. Before fresh slurry is added to the reactor, an equivalent amount of spent slurry is removed and sent to metals recovery for safe disposal.

4.5 Major Process Sections in the LPMEOHTM Process Model in ASPENPLUS

Each major flowsheet section is described below. In the flowsheet, unit operation models represent specific components of that process area. There are user-specified inputs regarding key design assumptions for each unit operation model. The numerical values of the design assumptions are presented in this section. Figure 4-7 presents the LPMEOH process flowsheet as modeled in ASPEN PLUS with stream numbers. Table 4-5 presents the description of various stream numbers used in Figure 4-7.

4.5.1 Guard Bed

The feed syngas flows through a guardbed, modeled as a unit operation of the type “VALVE” with a block identification of “GRDBED”. The purpose of the guard bed, as described previously, is to remove trace contaminants such as carbonyls and arsenic from the feed stream. There is a pressure drop across the guard bed as the feed syngas passes through it. For modeling purposes, we assume that the mass flow rate of the feed gas is not altered due to removal of trace contaminants and the only change in the feed gas is its exit pressure because of pressure drop. A pressure drop of approximately 6 psia occurs across the guard bed (Street, 1999).

4.5.2 Feed-Recycle Mixer

After exiting the guard bed, the syngas mixes with the recycle stream of unreacted gases in the process. The mixing of the fresh feed and the recycle gas is simulated by a

unit operation of the type “MIXER” with a block identification of “FRMIX”. The combined feed from this block then enters the economizer.

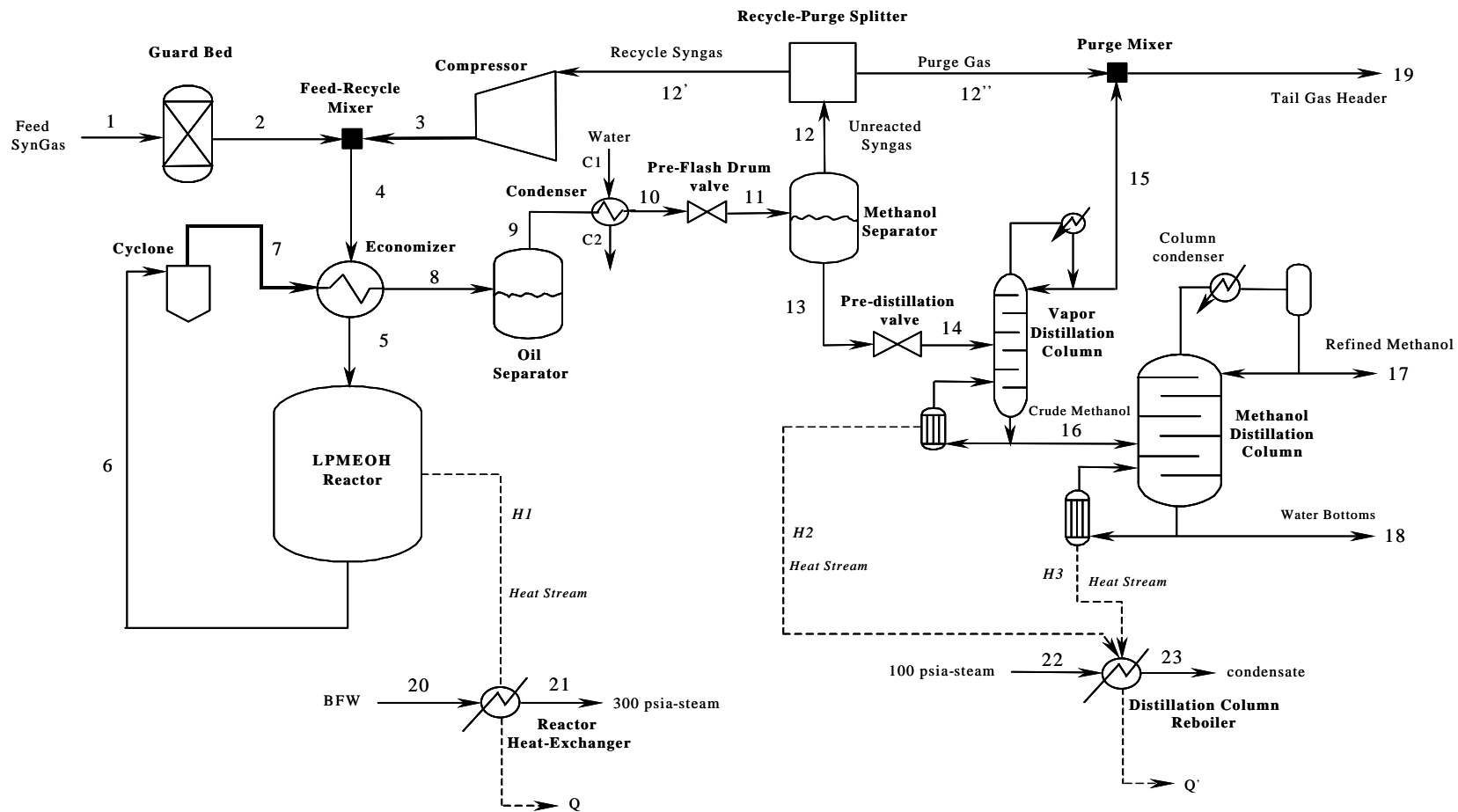
Table 4-5 Description of Stream Numbers Used in the Process Flowsheet of LPMEOH Process as Modeled in ASPEN PLUS (Figure 4-7)

Stream Number	Description
1	Fresh syngas feed to guard bed
2	Clean syngas exit from guard bed
3	Recycle gas from compressor
4	Combined fresh syngas and recycle gas feed to economizer (cold side)
5	Combined heated feed exiting the economizer (cold side)
6	LPMEOH reactor exit products
7	Hot products gases entering the economizer (hot side)
8	Cooled product gases leaving the economizer (hot side)
9	Oil free product gases entering the condenser
10	Condensed methanol and water leaving the condenser with uncondensed gases
11	Condensed methanol, water and uncondensed gases entering the methanol separator
12	Uncondensed (unreacted) gases leaving the methanol separator in vapor phase
12R	Unreacted gases recycled to methanol reactor via compressor
12P	Unreacted gases purged
13	Liquid phase consisting mainly of methanol and water leaving methanol separator
14	Crude methanol feed entering the vapor distillation column
15	Vapors removed in vapor distillation column
16	Crude methanol feed entering methanol distillation column for purification
17	Refined methanol product (99.99 wt percent purity)
18	Wastewater bottoms from methanol distillation column
19	Total purge gas to process boiler

Table 4-5 continued on next page

Table 4-5 continued

20	BFW entering the internal heat exchanger of the LPMEOH reactor
21	Saturated steam at specified pressure (300 psia) produced in the LPMEOH reactor's internal heat exchanger
22	100 psia saturated steam used in methanol distillation column reboiler
23	Reboiler condensate
C1	Cooling water entering the methanol condenser
C2	Cooling water leaving the methanol condenser
H1	Heat stream from LPMEOH reactor to reactor's internal heat exchanger
H2	Heat stream from vapor distillation column to the distillation column reboiler
H3	Heat stream from methanol distillation column to the distillation column reboiler



Note: Interpretation of Stream Numbers is presented in Table 4-5

Figure 4-7. LPMEOH™ Process Flowsheet as Modeled in ASPEN PLUS

4.5.3 Economizer

The purpose of the economizer is to allow for heat exchange between cold combined feed gas and the hot product gas coming from the LPMEOH reactor. The economizer or feed-product heat exchanger is modeled as a unit operation of the type “HEATX” with a block identification of “ECONM” in ASPENPLUS. HEATX is a simple countercurrent heat exchanger unit operation in ASPEN PLUS that allows for heat exchange between hot and cold stream. The temperature of cold feed to ECONM is the temperature of the mixer, FRMIX, exit gas, which is the combined temperature of fresh feed and the recycle gas. The exit temperature from ECONM’s cold side is specified as 330 °F based on DOE topical reports (Air Products and Chemicals, Inc., 1997) and a visit to the Kingsport demonstration facility (Street, 1999).

4.5.4 LPMEOHTM Reactor

The heated syngas from ECONM is fed to the LPMEOH reactor, which is modeled as unit operation of type “RSTOIC” with a block identification of “LPMREACT”. RSTOIC is a stoichiometric reactor unit operation in ASPEN PLUS and is used to simulate chemical reactions when the reaction stoichiometry is known, conversion of one of the reactant is known but the kinetics is unknown. The main reactions taking place in the LPMEOH reactor are reactions given by Equations (4-3) and (4-4) as given in Section 4.4.2. Both of these reactions are modeled in LPMREACT by specifying the reaction conditions, including: (1) temperature (T); (2) pressure (P); and

the conversion of a specific reactant in each reaction. The conversion of CO in Equation (4-3) is specified by a FORTRAN block CONV described in Subsection 4.5.4.1, which calculates the conversion of CO as a function of reactor pressure (P), syngas space velocity (SV) and the H₂ to CO molar ratio (R) in the syngas fed to the reactor. The conversion of CO₂ in reaction given by Equation (4-4) is specified as a fraction by the user to be equal to 0.089 (8.9 percent), and does not vary with P, SV and R (Twiggs, 1989; Street, 1999). Carbon dioxide conversion in Equation (4-4) varies only with the reactor temperature and since the reactor temperature in LPMEOH reactor is held nearly constant at 250°C, the conversion of CO₂ is almost fixed at 8.9 percent. A third, less important, reaction known as the reverse water gas shift reaction given by Equation (4-5), also occurs. Equation (4-5) has a very low conversion of CO, which is one of the equilibrium products, and is not modeled in the reactor (Twiggs, 1989; Air Products and Chemicals, Inc., 1997).

4.5.4.1 FORTRAN Block CONV

The purpose of the FORTRAN block, CONV, is to calculate the conversion of CO in the LPMEOH reactor using the parameters upon which the conversion of CO is dependent. The key parameters include: (1) the reactor pressure (P); (2) syngas space velocity (SV) in the reactor; (3) molar ratio of H₂ to CO (R) in the reactor feed; and (4) reactor temperature. The temperature in LPMEOH reactor is assumed to be 250 °C. This is the preferred temperature for reasons given in Section 4.4.3. Furthermore, the available

data for CO conversion are typically only for this temperature. Thus the parameters considered in developing the equation for CO conversion are P, SV and R.

Data for once through (H₂ +CO) conversion in the LPMEOH reactor as a function of P, SV, and R are available in an economic analysis report of LPMEOH process in the form of graphs (Air Products and Chemicals, Inc., 1998). The data presented in the report are based on the proprietary model of the LPMEOH process developed by Air Products and Chemicals, Inc. For developing the equation to predict the (H₂+CO) conversion as a function of P, SV, and R, a data set was developed by reading values from the graphs presented in the Air Products. This data set is presented in Table 4-6.

A regression analysis was done on the data in Table 4-6. Three models given by Equations (4-10) to (4-12) were fit to the data to find out the most appropriate equation relating the (H₂ + CO) conversion (C) to P, SV and R. The models considered include the linear (Equation 4-10), quadratic (Equation 4-11) and logarithmic (Equation 4-12) relationship between the dependent and the independent variables. Table 4-7 presents the results of the regression analysis on data in Table 4-6 considering the 3 models as given by Equations (4-10) to (4-12).

$$\text{Model 1:} \quad C = a + b P + c SV + d R \quad (4-10)$$

$$\text{Model 2:} \quad C = a + b P + c P^2 + d SV + e SV^2 + f R + g R^2 \quad (4-11)$$

$$\text{Model 3:} \quad C = A (P)^B (SV)^C (R)^D \quad (4-12)$$

Table 4-6. Data Set Used in Regression Analysis to Develop a (H₂+CO) Conversion Model (C) for the LPMEOH Reactor as a Function of Pressure, P, Space Velocity, SV, and H₂/CO ratio, R^a

C	P	SV	R	ln(C)	ln(P)	ln(S)	ln(R)
<i>percent</i>	<i>psig</i>	<i>sL/kg-hr</i>	<i>(moles H₂/moles CO)</i>				
28.1	500	2000	2	3.33	6.21	7.60	0.693
42.2	750	2000	2	3.74	6.62	7.60	0.693
51.8	1000	2000	2	3.94	6.90	7.60	0.693
58.75	1250	2000	2	4.07	7.13	7.60	0.693
22.8	500	4000	2	3.12	6.21	8.29	0.693
34.4	750	4000	2	3.53	6.62	8.29	0.693
44.4	1000	4000	2	3.79	6.90	8.29	0.693
51.8	1250	4000	2	3.94	7.13	8.29	0.693
15.6	500	8000	2	2.74	6.21	8.98	0.693
24.3	750	8000	2	3.19	6.62	8.98	0.693
31.9	1000	8000	2	3.46	6.90	8.98	0.693
38.4	1250	8000	2	3.64	7.13	8.98	0.693
17.5	500	2000	0.97	2.86	6.21	7.60	-0.0305
26.87	750	2000	0.97	3.29	6.62	7.60	-0.0305
35	1000	2000	0.97	3.55	6.90	7.60	-0.0305
41.56	1250	2000	0.97	3.72	7.13	7.60	-0.0305
23.12	500	4000	0.97	3.14	6.21	8.29	-0.0305
34	750	4000	0.97	3.52	6.62	8.29	-0.0305
42.18	1000	4000	0.97	3.74	6.90	8.29	-0.0305
48.12	1250	4000	0.97	3.87	7.13	8.29	-0.0305
17.81	500	2000	0.68	2.87	6.21	7.60	-0.385
26.87	750	2000	0.68	3.29	6.62	7.60	-0.385
33.12	1000	2000	0.68	3.50	6.90	7.60	-0.385
37.5	1250	2000	0.68	3.62	7.13	7.60	-0.385

^a Air Products and Chemicals, Inc., 1998

Table 4-7. Results of Regression Analysis on Data in Table 4-6 Applied to the 3 Models Considered

Model	n (No. of data points)	R ²	Standard Error
Model 1 (4-10)	24	0.86	4.54
Model 2 (4-11)	24	0.88	3.7
Model 3 (4-12)	24	0.89	1.60

Equation (4-12) developed by linear regression applied to the logarithms of P, SV, and R on the data in Table 4-6 is found to be the most appropriate based on the results of regression because it has highest R² value and lowest standard error compared to other model equations. The parameters of Equation 4-12 are found to be:

$$C = 0.501 (P)^{0.88} (SV)^{-0.225} (R)^{0.30} \quad (4-13)$$

where: C = (H₂+CO) conversion in percent

P = Reactor pressure (psig)

SV = Syngas space velocity in the reactor (standard liters/kg-hr)

R = H₂ to CO molar ratio in the feed entering the reactor

Equation (4-13) is valid for P ranging from 500 psig to 1250 psig; SV ranging from 2000 standard liters/kg-hr to 8000 standard liters/kg-hr; and R ranging from 0.68 to 2. Figure 4-8 presents the graph of (H₂+CO) conversion predicted by Equation (4-13) versus the actual (H₂+CO) conversion as in Table 4-6. This graph shows that the conversion predicted by Equation (4-13) compares quite well with the actual conversion data.

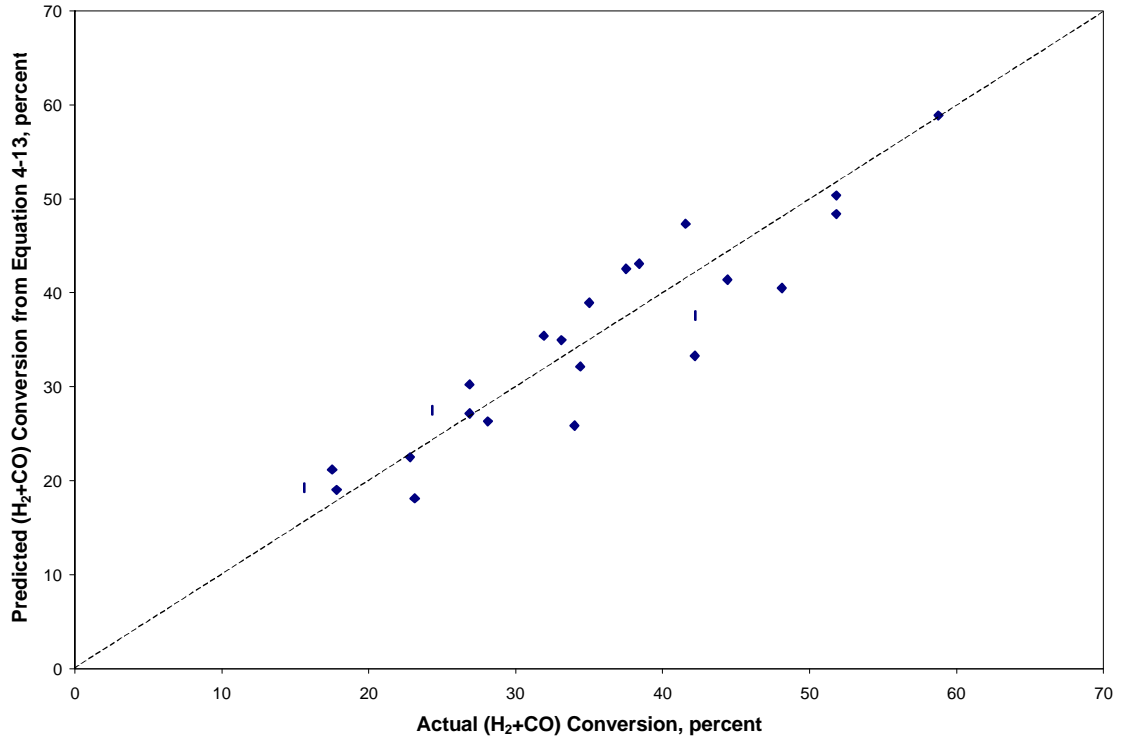


Figure 4-8. Graph of (H₂+CO) Conversion Predicted by Equation 4-13 versus Actual (H₂+CO) Conversion as in Table 4-6

According to Equation (4-13), as the reactor pressure increases the (H₂+CO) conversion will increase because of the positive exponent. This is reasonable because at higher reactor pressure a higher syngas conversion is expected. As the space velocity in the reactor increases, the syngas has less residence time in the reactor and therefore the conversion of syngas must decrease, which is predicted by Equation (4-13) since SV has a negative exponent. Also, as the H₂/CO ratio increases, the syngas conversion must increase, which is predicted by Equation (4-13) since H₂/CO ratio (R) has positive exponent. Therefore, the fitted equation reflects appropriate qualitative behavior.

Table 4-8 presents the actual plant data for (H₂+CO) conversion based on P, SV and R. Equation (4-13) was applied to P, SV and R data of the actual plant to predict the

(H₂+CO) conversion. It was found that Equation (4-13) overpredicts, on average, the (H₂+CO) conversion with respect (H₂+CO) conversion in the actual plant data. A modified equation for (H₂+CO) conversion was therefore desired. Actual plant data could not be used for developing the (H₂+CO) conversion equation. This was because the various regression models, such as Equations (4-10) to (4-12), when fitted on actual plant data, predicted an increase in conversion as the space velocity increased, which is contrary to what is expected.

Since the Equation (4-13) over predicted the (H₂+CO) conversion with respect to the actual data set, the predicted conversion, C, from the above equation based on P, SV, and R was divided by the actual (H₂ + CO) conversion available from plant data. This provided the ratio of predicted to actual conversion for 13 cases. A mean of the ratios of these 13 cases is calculated and called a mean ratio. The mean ratio (1.384) is the number by which the conversion in Equation 4-14 should be divided to form a modified equation of (H₂ + CO) conversion (C^{*}). The exponents associated with P, SV, and R remain unchanged. The modified equation, as obtained, is:

$$C^* = 0.362 (P)^{0.88} (SV)^{-0.225} (R)^{0.30} \quad (4-14)$$

where: C^{*} = Modified (H₂+CO) conversion

Table 4-8 presents the comparison of (H₂+CO) conversion from actual plant data with that predicted by Equation (4-13). It presents the ratio of conversion predicted by Equation (4-13) to that of actual plant data. Table 4-8 also presents the conversion

predicted by Equation (4-14) i.e. after modification. Figure 4-9 presents the graphical comparison between the (H₂+CO) conversions as in Table 4-9.

Table 4-8. Comparison of (H₂+CO) Conversion from Actual Plant Data with that Obtained From Equation 4-13 (before modification) and Equation 4-14 (after modification).

Case	P psig	SV Sl/kg-hr	H ₂ /CO	(H ₂ +CO) Conversion, percent			
				Actual Plant Data	Before Modification	Ratio ^a (Before Modification/ Actual Plant)	After Modification
1	707	8827	3.46	21.9	30.1	1.37	21.8
2	701	6507	0.77	21.9	20.3	0.93	14.7
3	700	6537	3.22	21.2	31.2	1.47	22.6
4	675	5047	3.95	20.3	34.1	1.69	24.7
5	675	4596	3.14	18.0	32.5	1.81	23.5
6	674	4598	3.49	18.8	33.5	1.79	24.2
7	680	9625	4.05	28.9	29.9	1.03	21.6
8	680	9601	3.70	27.6	29.1	1.05	21.1
9	710	7216	0.74	21.5	19.9	0.92	14.4
10	710	6295	4.32	24.9	34.9	1.40	25.2
11	710	5646	3.39	20.7	33.2	1.61	24.0
12	710	5537	4.73	25.6	36.9	1.44	26.7
13	709	4942	4.29	26.0	36.7	1.41	26.5

^a This column presents the ratio of conversion predicted by Equation 4-13 to actual plant conversion for same conditions of P, SV and R.

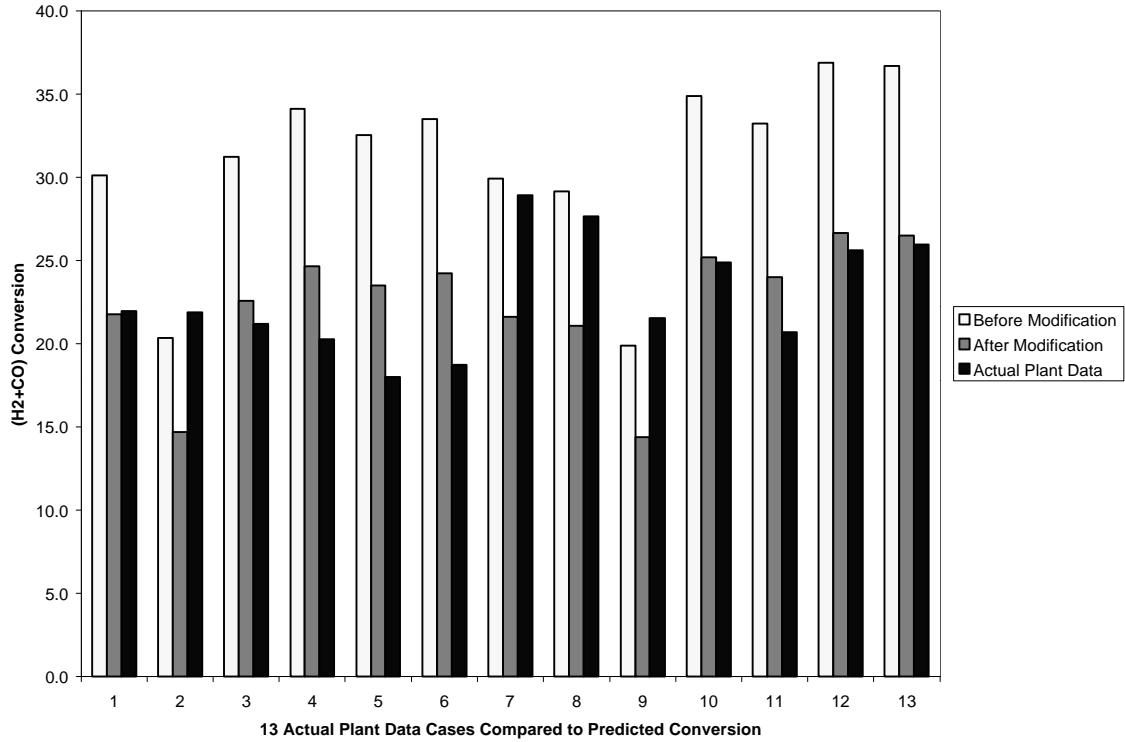


Figure 4-9. (H₂+CO) Conversion From Actual Plant Data Compared with that Obtained by Using Equation (4-13) and Equation (4-14)

Equation (4-14) is valid for P ranging from 500 psig to 1250 psig; SV ranging from 2000 standard liters/kg-hr to 8000 standard liters/kg-hr; and R ranging from 0.68 to 2. The conversion of CO, θ , is related to modified (H₂ + CO) conversion, C^* , by following equation using a simple mass balance:

$$q = C^* \frac{(R+1)}{3} - Z S \quad (4-15)$$

where,

R = molar ratio of H₂ to CO in the reactor feed, moles H₂/moles CO

Z = conversion of CO₂ (8.9 percent)

S = molar ratio of CO₂ to CO in the reactor feed, moles CO₂/moles CO

Conversion of CO is required separately because (H₂+CO) conversion cannot be specified in the RSTOIC reactor, LPMREACT since the conversion of only one component per reaction can be specified in RSTOIC (AspenTech, 1996). Thus in FORTRAN block CONV, Equation 4-14 is defined first to calculate the (H₂+CO) conversion based on P, SV, and R followed by Equation 4-15 to calculate the CO conversion from the calculated (H₂+CO) conversion. A pressure drop of approximately 10 psi occurs in the LPMEOH reactor sparger (Street, 1999).

4.5.5 Cyclone Separator

The cyclone separator is modeled as a unit operation of type “VALVE” with a block identification of “CYCLONE” in ASPEN PLUS through which a pressure drop of approximately 6 psia occurs in the reactor exit gas (Street, 1999). VALVE is the common unit operation in ASPEN PLUS that can be used to simulate the pressure drop in a process equipment in which no reaction takes place (AspenTech, 1996). Since the cyclone separator primarily removes oil droplets entrained in the reactor exit gases, it does not significantly alter the flow rate for the reactor exit gas.

4.5.6 Oil Separator

The oil separator, like the cyclone separator, is modeled as a unit operation of type “VALVE” with a block identification of “OILSEP” through which a pressure drop of approximately 2 psia occurs (Street, 1999). VALVE is used to simulate the pressure

drop that occurs in oil separator because no reaction takes place. Also, the oil separator removes one gallon to two gallons per minute (gpm) of oil, which is very small compared to the total mass flow through the oil separator. Therefore, it is assumed that the oil separator does not alter the gaseous flow rate of the feed stream.

4.5.7 Pre-Methanol Separator Condensers

For the methanol to condense, a series of heat exchangers and air coolers is employed prior to the methanol separator unit. For purposes of simplicity, the train of condensers is approximated by a single condenser modeled as a unit operation of type “HEATX” with a block identification of “CONDSR”. HEATX is a simple counter-current heat exchanger unit operation in ASPEN PLUS that is used to simulate the heat exchange between hot and cold stream (AspenTech, 1996). CONDSR uses water at 68 °F for condensing methanol and water vapor in the product gas, which comes from OILSEP. CONDSR is specified with product gas exit temperature of 100 °F and pressure of 713 psia (Street, 1999). The mass flow rate of water is calculated by design specification, CONDWAT, described later, which manipulates the flow rate of water such that the exit temperature of cooling water is 25 °C higher than its inlet temperature (68 °F).

4.5.8 Pre-Methanol Separator Flash Valve

The pre-methanol separator flash valve is modeled as a unit operation of the type “VALVE” with a block identification of “FLVALVE”. In this block, a pressure drop

occurs such that there is a vapor-liquid phase separation. A pressure drop of approximately 10 psia occurs in FLVALVE (Street, 1999).

4.5.9 Methanol Separator

The stream from pre-methanol flash valve enters the methanol separator. Methanol separator separates methanol and other condensable material as a liquid phase while non-condensable gases leave at the top. The methanol separator is modeled as a unit operation of the type “FLASH2” with a block identification of “MEOHSEP” in ASPEN PLUS. MEOHSEP is a simple flash drum where the vapor and liquid phase separate. MEOHSEP block has temperature and pressure specifications of 100 °F and 700 psia, respectively (Street, 1999).

4.5.10 Recycle and Purge Gas Splitter

In this section of the process model, exit gases from the methanol separator are split into two streams: recycle gas and purge gas. The amount of reactor exit gases split to be recycled depends on a specified recycle ratio, which is the molar ratio of recycled gas to fresh feed to the process. The recycle and purge gas splitter is modeled as a unit operation of the type “FSPLIT” with a block identification of “RPSPLIT” in ASPEN PLUS. The flowrate of recycle gas is calculated using the desired recycle ratio and is specified in RPSPLIT. A typical value of the recycle ratio is 3 moles recycle gas per

moles fresh syngas feed for the syngas being used at Kingsport to achieve higher conversion of syngas in methanol reactor (Street, 1999).

4.5.11 Pre-Distillation Pressure Relief Valve

The pre-distillation pressure relief valve is modeled as a unit operation of the type “VALVE” with a block identification of “DISTVAL” in ASPENPLUS. The phase separated liquid stream from MEOHSEP enters the DISTVAL and undergoes a pressure reduction such that the exit pressure from the DISTVAL is 35 psia, which is near the pressure at which the methanol distillation column operates (Street, 1999).

4.5.12 Methanol Distillation and Purification Section

There are two distillation columns in the methanol purification section. The first distillation column is modeled as a unit operation of the type “SEP2” with a block identification of “VPDISTCO” in ASPEN PLUS. SEP2 is a unit operation in ASPEN PLUS in which component separation operation such as vapor distillation occurs (AspenTech, 1999). Since the function of the first distillation column is to purge all of the gases and vapors, it is specified to remove 100 percent of the H₂, CO, N₂, CO₂ and CH₄ as a purge stream. All of the methanol and water flow from the bottom of VPDISTCO is a feed to a second distillation column.

The second distillation column is modeled as unit operation of the type “DSTWU” with a block identification of “MEOHDIST” in ASPENPLUS. DSTWU is a simplified distillation column unit operation in ASPEN PLUS and is used to simulate distillation of a light component such as methanol and a heavy component such as water from their mixture (AspenTech, 1999). The number of trays specified in MEOHDIST is 40 (Street, 1999). Recovery of the light key component is specified as 99.99 percent. The light key component is the one which has the highest vapor pressure and it is methanol in this case. The recovery of the heavy key component in the top product is set by a design specification, MOHPURIT. The heavy key component is the one which has the lowest vapor pressure and water in this case. The design specification MOHPURIT determines the recovery of the heavy key component, water, such that the distilled methanol has a purity of 99.99 percent on weight basis. The top and bottom pressures of MEOHDIST are specified to be 30 and 33 psia, respectively (Street, 1999).

4.5.13 Distillation Column Reboiler

The distillation column reboiler is modeled for the purpose of calculating the steam consumption in the distillation column. It is modeled as a unit operation of type “HEATER” with a block identification of “REBHTR”. It has two input heat streams: one heat stream is from VPDISTCO, which as described before, is a distillation column for vapor removal; and the other heat stream is from MEOHDIST. The heat stream from VPDISTCO is its heat duty and the heat stream from MEOHDIST column is its reboiler duty. The amount of 100-psia steam used in the reboiler is calculated by the design

specification, STMCON. STMCON sets the heat loss from the REBHTR equal to zero by manipulating the flow rate of 100-psia steam such that saturated water at 100 psia is produced at the exit.

4.5.14 Recycle Gas Compressor

The recycle gas compressor is modeled as a unit operation of the type “COMPR” with a block identification of “RECCOMP”. RECCOMP is an isentropic compressor with which has typical inlet recycle gas pressure of 700 psia and the typical outlet pressure of 738 psia (Street, 1999). Therefore, the recycle gas compressor overcomes a process pressure drop of 38 psi, approximately. The purpose of RECCOMP is to raise the pressure of the recycle gas and make it compatible with the pressure of the fresh syngas before they mix in FRMIX.

4.5.15 Reactor’s Internal Heat Exchanger

The LPMEOH reactor has an internal heat exchanger for the removal of the heat of reaction. It is modeled as unit operation of type “HEATER” with a block identification of “REACTHX” in ASPEN PLUS. REACTHX receives a heat stream from the RSTOIC reactor (LPMREACT) unit operation block and uses that heat to model the conversion of boiler feed water (BFW) at 160 °F and 200 psia into saturated steam at 300 psia. The amount of BFW fed to REACTHX is calculated by a design specification, STMPRO.

STMPRO sets the heat loss from the REACTHX to surroundings equal to zero by manipulating the flow rate of BFW through REACTHX.

4.5.16 Fresh and Recycle Syngas Mixer

Fresh syngas mixes with the recycle gas from recycle compressor in a mixer before entering the economizer. Fresh and recycle syngas mixer is modeled as unit operation of type “MIXER” with a block identification of “FRMIX” in ASPEN PLUS. MIXER is a simple unit operation block in ASPEN PLUS which allows for mixing of two different streams to produce one combined stream. The combined feed from FRMIX enters the cold side of ECONM for heat exchange with hot product gases coming from the LPMEOH reactor (LPMREACT).

4.5.17 Purge Mixer

The purge gases coming from splitter and vapor distillation column are mixed in a purge mixer. Purge mixer is modeled as a unit operation of type “MIXER” with a block identification of “PURGEMIX” in ASPEN PLUS.

Table 4-9 presents the description of process unit operation blocks used in ASPEN PLUS to simulate the various unit operations involved in the LPMEOH process. This table also contains the default values for key inputs to the model.

TABLE 4-9. LPMEOH™ Process Unit Operation Block Description for ASPEN PLUS Model

NO	BLOCK ID (ASPENPLUS BLOCK NAME)	BLOCK PARAMETERS	DESCRIPTION
1.	GRDBED (VALVE)	Pressure drop (ΔP) = 6 psia	Simulates the guardbed for the removal of impurities in feed
2.	FRMIX (MIXER)		Simulates the mixing of fresh syngas and recycle gas
3.	ECONM (HEATX)	Cold feed Outlet temperature = 330 °F Pressure drop = 0 psia	Simulates the feed/product heat exchanger
4.	LPMREACT (RSTOIC)	Temperature = 481 °F Pressure = 721 psia	Simulates two stoichiometric reactions, reaction 4-2 and 4-3 for methanol production
5.	CYCLONE (VALVE)	Pressure drop = 6 psia	Simulates the cyclone separator for the removal of entrained oil/catalyst particles in the reactor exit gases
6.	OILSEP (VALVE)	Pressure drop = 2 psia	Simulates the oil separator for the removal of oil from reactor exit gases
7.	CONDSR (HEATX)	<u>Hot side</u> (Product gas) Outlet temperature = 100 °F <u>Cold side</u> (Cooling Water) Inlet temperature = 68 °F Inlet pressure = 14.7 psia	Simulates the series of fan cooled and water cooled condensers for condensing methanol and water
8.	FLVALVE (VALVE)	Pressure drop = 10 psia	Simulates the flash valve for flashing non-condensables from the liquid phase formed in the condenser
9.	MEOHSEP (FLASH2)	Temperature = 100 °F Pressure = 700 psia	Simulates the flash drum for phase separation into liquid and vapor
10.	RPSPLIT (FSPLIT)	Recycle flow = (Specified Recycle Ratio) x (Molar flow of fresh feed)	Simulates the splitting of vapor phase from the methanol separator into a recycle stream and a purge stream
11.	DISTVAL (VALVE)	Outlet Pressure = 35 psia	Simulates the pre-distillation pressure release valve

Table 4-9 continued on next page

Table 4-9 continued

NO	BLOCK ID (ASPENPLUS BLOCK NAME)	BLOCK PARAMETERS	DESCRIPTION
12.	VPDISTCO (SEP2)	Separation Efficiency of H ₂ , CO, CO ₂ , N ₂ , and CH ₄ = 100 percent	Simulates first distillation column of methanol purification section for the complete removal of gases and vapors
13.	MEOHDIST (DSTWU)	Light key recovery = 0.9999 Heavy key recovery: manipulated by design specification, MOHPURIT Top tray pressure = 30 psia Bottom tray pressure = 33 psia	Simulates the second distillation column for 99.99 percent recovery of methanol with 99.99 weight percent purity
14.	RECCOMP (COMPR)	$\Delta P = 38$ psi	Simulates the recycle gas compressor
15.	PURGEMIX (MIXER)		Simulates the mixing of the main purge from the splitter and first distillation column
16.	REACTHX (HEATER)	Outlet Pressure = 300 psia Outlet Vapor fraction = 1.0	Simulates the internal heat exchanger in the reactor for calculation of steam generation.
17.	REBHTR	Outlet Pressure = 100 psia Outlet Liquid fraction = 1.0	Simulates the reboilers of both distillation columns (1 and 2) for calculation of steam consumption.

4.6 Design Specification and FORTRAN blocks used in LPMEOH Process Model

The design specifications used in the LPMEOHTM process model are STMPRO, CONDWAT, STMCON, and MOHPURIT.

STMPRO is used to calculate the amount of saturated steam produced at 300 psia in the reactor's internal heat exchanger. The internal heat exchanger is used to keep the reactor temperature at 250°C. Because the overall reaction in the reactor is exothermic, heat must be removed from the reactor and it is used to generate steam. The heat lost to the surroundings (Q) from the REACTHX should be zero. The product steam is specified to be saturated at 300 psia in REACTHX. This design specification is achieved by varying the flow rate of boiler feed water entering the REACTHX at 160 °F and 200 psia. This in turn gives the amount of boiler feed water used in the REACTHX and therefore the amount of saturated steam produced at 300 psia in the REACTHX.

STMCON operates in a very similar way as STMPRO. STMCON is used to calculate the amount of 100 psia saturated steam used in the distillation column reboiler for methanol recovery. The heat loss to the surroundings (Q') from REBHTR should be zero. The product water is specified to be saturated water at 100 psia in the REBHTR. This design specification is achieved by varying the flow rate of 100 psia saturated steam entering REBHTR.

The purpose of design specification CONDWAT is to manipulate the flow rate of cooling water, used in methanol condenser for condensing methanol, such that its temperature rise upon exit is limited to 25 °C.

The purpose of design specification, MOHPURIT, is to specify the purity of the methanol top product from the second distillation column to 99.99 percent (on weight basis) by varying the recovery of the heavy key component (water) in top product. Recovery of the heavy key component is manipulated because the methanol distillation column is specified as unit operation of type DSTWU. In this unit operation model, the only the variable that directly corresponds to the reflux ratio is the heavy key component recovery. Also, since the number of stages, the top pressure and the bottom pressure are fixed, the only variable left to be manipulated is the heavy key component recovery. The initial guess supplied for the water recovery in top product is arbitrarily set to 0.005 moles reflux/moles distillate.

FORTTRAN block CONV is used to calculate the conversion of CO in the reactor based on pressure (P), space velocity (SV) and the molar ratio of H₂ to CO entering the reactor as explained in Section 4.5.4.1.

4.7 Convergence Sequence of LPMEOH Process Model

The convergence sequence for the model is based on 17 unit operation blocks, 2 tear streams, 4 design specifications and one FORTRAN block. All of the unit operation blocks have been described individually in Section 4.5. Here, the calculation sequence for

the simulation is described. The design specification STMPRO, STMCON, CONDWAT, and MOHPURIT and FORTRAN block CONV are described in Section 4.6.

The convergence sequence starts with the initialization of key input variables in the unit operations. The physical property data set RKSOAVE (Redlich-Kwong-Soave) is then invoked to specify the physical properties of the components used in the simulation. RKSOAVE is specified by the user when specifying the input values of process parameters. RKSOAVE is specified because it is recommended for methanol production process simulation based on the thermodynamic parameter estimation method (AspenTech, 1996). The fresh feed, Stream 1 in Figure 4-7, first enters the GRDBED. The fresh feed exit from GRDBED then mixes with the recycle stream, Stream 3 in Figure 4-7, whose composition and flowrate is unknown at this point. Therefore Stream 3 is defined as a tear stream. Convergence block MOH-TER1 is defined to converge the tear stream 3 before the Stream 2 mixes with it in FRMIX.

MOH-TER2 is a convergence block that is specified to tear Stream 7. Stream 7 leaves the ECONM which requires a temperature specification for streams entering and leaving it. However the temperature of Stream 7 is not known initially and therefore an initial guess must be used. Stream 2 is mixed with Steam 3 to form Stream 4. The combined syngas stream, Stream 4 enters the ECONM for heat exchange with the hot product gases from the reactor. Stream 5 is the heated stream that enters the LPMEOH reactor, LPMREACT. Before Stream 5 enters the LPMREACT, FORTRAN block CONV is executed to specify the conversion of CO in the LPMREACT. LPMREACT is

executed next. After LPMREACT, the product gases, Stream 6, enters CYCLONE, which is then executed. Here some pressure drop in Stream 6 occurs. Stream 7 is calculated and compared with its initial guess. If the steam parameters don't match, MOH-TER2 convergence block updates the Stream 7 and repeats the calculation starting at ECONM. When the simulated value of Stream 7 exiting the CYCLONE agrees with the previous value of Stream 7 used when going to ECONM, then there is convergence and the simulation continues to other unit operations. After MOH-TER2 has converged for a particular pass, OILSEP is executed the next. The exit stream from OILSEP, Stream 9, consist of vapors of methanol, water and unreacted gases, enters the CONDSR where CONDWAT (a design specification) is specified to calculate the flowrate of cooling water required in CONDSR cold side.

After CONDSR is executed, the CONDSR exit stream, Stream 10, enters FLVALVE. FLVALVE and MEOHSEP are then executed. MEOHSEP produces Stream 12 and Stream 13. Stream 13 needs to be recycled and therefore RPSPLIT is executed next which splits Stream 12 into Stream 12R and 12P. Stream 12R is recycled back via RECCOMP, which is executed next. Stream 3 exiting from RECCOMP is compared with its initial guess. If the temperature, pressure and flowrate do not match, MOH-TER1 convergence block updates the tear stream parameters and repeats through same process steps as earlier until the Stream 3 is converged.

After MOH-TER1 has converged, DISTVAL, VPDISTCO, MOHPURIT (a Design Specification), MEOHDIST, and PURGEMIX are executed. After the tear

streams converge, two design specifications MOH-DS1 (convergence block for design specification STMPRO) and MOH-DS2 (convergence block for design specification STMCON) operating on REACTHX and REBHTR, respectively, are executed. MOH-DS1 is executed last because the heat generation in the reactor for steam generation is dependent on reactor conversion. The final value of the reactor conversion is not available until the simulation ends. Also, methanol production in the distillation column does not occur until the tear streams converge, so the steam consumed is calculated at the end by STMCON based on the distillation column reboiler duty. STMPRO and STMCON can be any order. In the process modeled, STMCON is implemented the last. The results of the entire simulation are then generated in the RESULTS window. Table 4-10 shows the main convergence blocks and the method of convergence used. Figure 4-10 shows the convergence sequence as described above. Table 4-11 describes the convergence sequence presented above.

Table 4-10. Convergence Blocks and the Methods used for Convergence

Convergence Blocks	Method	Tear/Design Spec.
MOH-TER1	WEGSTEIN	t3 (tear Stream 3)
MOH-TER2	WEGSTEIN	t7 (tear Stream 7)
MOHDS1	SECANT	STMPRO
MOHDS2	SECANT	STMCON
MOHDS3	SECANT	CONDWAT
MOHPUR	SECANT	MOHPURIT

Table 4-11. Summary of Convergence Sequence

GRDBED

Table 4-11 continued on next page

Table 4-11 continued

MOH-TER1 (begin)^{a1}

FRMIX,

MOH-TER2 (begin)^{b1}, ECONM, CONV^c, LPMREACT, CYCLONE, MOH-TER2
(return)^{b2}

OILSEP, *MOH-DS3 (begin)^{d1}* CONDSR, *MOH-DS3 (return)^{d2}*, FLVALVE, MEOHSEP,
RPSPLIT, RECCOMP

MOH-TER1 (return)^{a2}

DISTVAL, VPDISTCO, *MOHPUR (begin)^{e1}*, MEOHDIST, *MOHPUR (return)^{e2}*,
PURGEMIX

MOH-DS1 (begin)^{f1}, REACTHX, *MOH-DS1 (return)^{f2}*

MOH-DS2 (begin)^{g1}, REBHTR, *MOH-DS2 (return)^{g2}*

^{a1} Stream 3 initialized as term stream, t3 (convergence loop starts)

^{a2} Stream 3 returns for comparison (convergence loop returns)

^{b1} Stream 7 initialized as tear stream, t7 (convergence loop starts)

^{b2} Stream 7 returns for comparison (convergence loop returns).

^c FORTRAN block, CONV

^{d1} Design specification CONDWAT initialized (convergence loop begins)

^{d2} Design specification CONDWAT returns for comparison (convergence loop returns)

^{e1} Design specification MOHPURIT initialized (convergence loop begins)

^{e2} Design specification MOHPURIT returns for comparison (convergence loop returns)

^{f1} Design specification STMPRO initialized (convergence loop begins)

^{f2} Design specification STMPRO returns for comparison (convergence loop returns).

^{g1} Design specification STMCON initialized (convergence loop begins)

^{g2} Design specification STMCON returns for comparison (convergence loop returns)

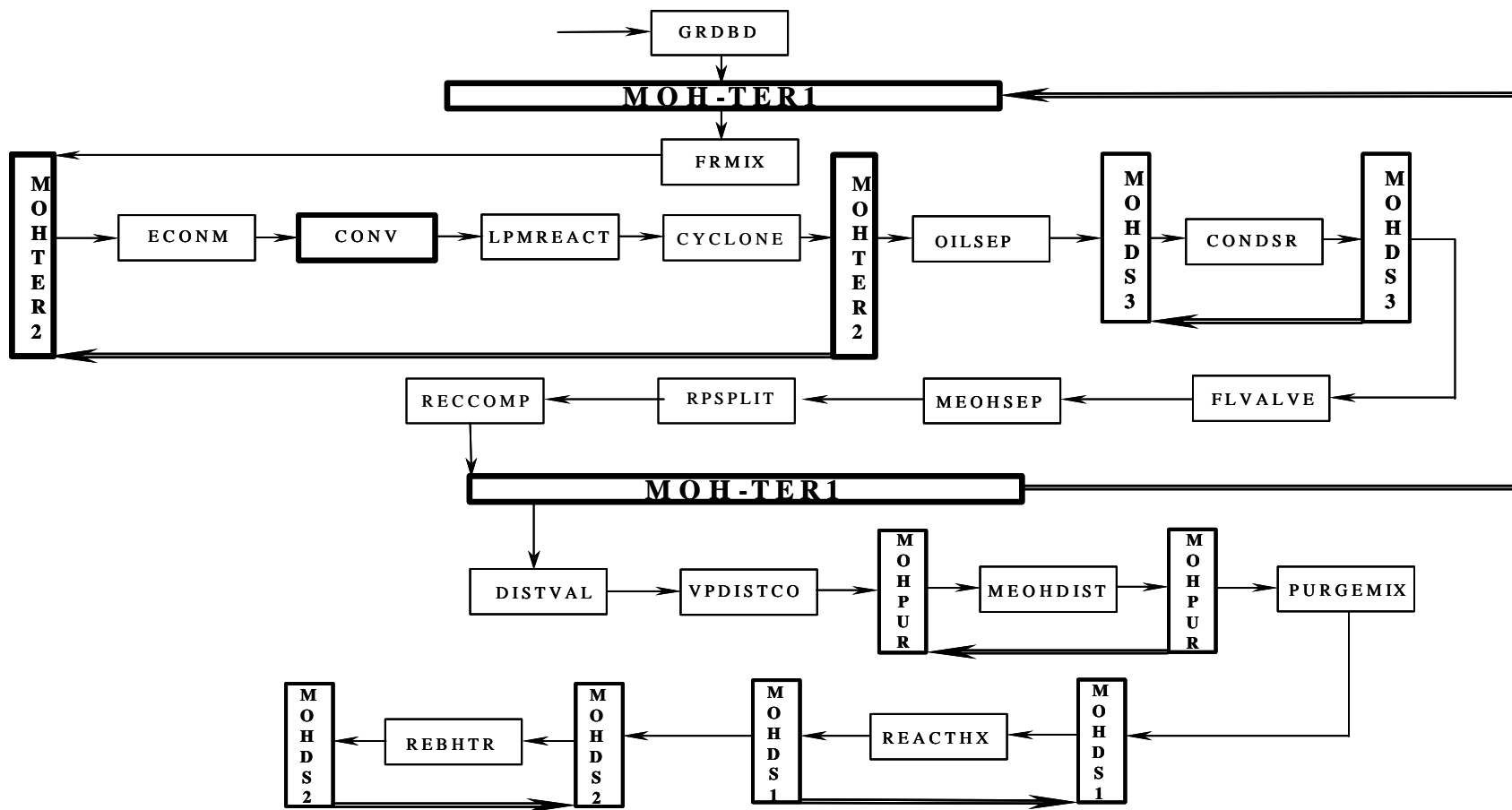


Figure 4-10. Convergence Sequence for the LPMEOH™ Process Model in ASPEN PLUS

4.8 LPMEOH Process Model Verification and Validation

The LPMEOH process model is developed in ASPEN PLUS, a chemical process simulator. ASPEN PLUS can perform mass and energy balance of the entire LPMEOH process in a clock time of less than 5 minutes. It is however important to verify that the results produced by ASPEN PLUS are reasonable and in agreement with what is expected in a real plant. The following sections describe the steps taken to verify and validate the LPMEOH process model implemented in ASPEN PLUS.

4.8.1 Comparison of the Model Results with the Actual Plant Results

The LPMEOH process model results such as methanol produced, steam produced in methanol reactor, steam consumed in the methanol distillation column, and purge gas production were compared with the same results from an actual plant run using similar operating conditions. Section 4.9 discusses the base case run of the LPMEOH process model and compares the results with the actual plant results. The results produced by ASPEN PLUS model are found to be in close agreement with that from actual plant. Thus the analysis provides some proof that model behaves appropriately and resembles the actual plant.

4.8.2 Sensitivity Analysis on the LPMEOH Process Model

The sensitivity analysis of LPMEOH process model is presented in Section 4.11. Based on the sensitivity runs it is observed that for increasing reactor pressure, the production of methanol increases because there is more syngas conversion in the reactor. Similarly, the variation of syngas space velocity, recycle ratio and syngas composition produces the results that are expected if an actual plant operated on similar conditions. This provides some proof that the LPMEOH process model is correctly implemented in ASPEN PLUS. The results of sensitivity analysis are discussed in detail in Section 4.11.

4.9 Application of the Liquid Phase Methanol (LPMEOH) Process Model to a Base Case.

In this section an example case is presented to illustrate the use of the LPMEOH process model in ASPEN PLUS. The main application of the model is to determine, quantitatively, the life cycle inventory parameters associated with the process. The key steps in running the ASPENPLUS simulation model of the LPMEOH process are: (1) specify input assumptions; (2) execute the model; and (3) collect results. The results obtained after running the ASPEN PLUS model of LPMEOH process are used in an EXCEL spreadsheet to calculate the LCI of methanol produced by the LPMEOH process.

4.9.1 Input Assumptions

Model input assumptions were developed for the LPMEOH process by the review of samples of material balance available in DOE topical reports on the commercial scale demonstration of LPMEOH process at Kingsport (Air Products and Chemicals, Inc., 1998) and a visit to Kingsport. The inlet temperature, pressure, and composition of the syngas, as available from a particular base case (actual plant run at Kingsport) are given in Table 4-12.

Table 4-13 summarizes a number of the input assumptions for this case study, with a focus on the key inputs for the LPMEOH reactor and FORTRAN block, CONV. Many of these assumptions have been previously described in the technical description of the technology. Conversion of (H_2+CO) in the LPMEOH reactor is a function of reactor pressure (P), reactor temperature (T), syngas space velocity (SV), and the molar ratio of H_2 to CO (R) entering the reactor, as stated earlier. Since P, T, and SV are fixed for a particular base case, the conversion of CO in the reactor depends on R for a specified simulation. During an ASPEN PLUS run of the model for a specified case, the conversion of CO is modified continuously due to changing R in each iteration, until the tear streams converge thereby satisfying the mass and energy balance across all the process equipment.

4.9.2 Running the Model and Model Results

The first step in making an ASPENPLUS model of a process is to assemble the various unit operations involved into a flowsheet of the process in ASPENPLUS. This is done by selecting the unit operation block from the vertical tool bar at the left. The user then clicks in the flowsheet area where the unit operation is desired. After building the entire flowsheet, the user then connects the blocks by double clicking on one block and choosing the outlet stream. By double clicking on the block, the ports for that unit operation block are displayed and labeled. After choosing the outlet port, ASPENPLUS reveals all of the options where the stream can inlet the other blocks. After building the model, the streams can be labeled by selecting the stream, right clicking and choosing *Rename Stream*.

Once the flowsheet connectivity is complete, the user is asked to specify the set of components that will be used in the model. The next thing to do is to specify the unit operation blocks (block's operating conditions like temperature, pressure, pressure drop etc.) for the block to run. The user then has an opportunity to choose the physical property data set from various equation of state (EOS) models built in ASPENPLUS like Redlich-Kwong-Soave, Peng-Robinson, NRTL, UNIFAC, Pitzer, Ideal Gas etc. The choice is based on the type of vapor-liquid interaction expected between the components involved in the model. FORTRAN blocks and any design specification, if needed, are then included in the model. In the end, the sequence must be specified to indicate to ASPENPLUS what block should be executed and in what order. If no sequence is

specified, then ASPENPLUS specifies its own sequence based on its understanding of the process. When all the inputs are complete, ASPENPLUS plus displays “Required Input Complete” on top left corner of the ASPENPLUS window indicating that model is ready to run.

Our main interest lies in obtaining the mass flowrates of the process streams, which are related to LCI parameters, like steam produced in LPMEOH reactor, steam consumed in the methanol distillation columns, methanol produced, and any waste or purge stream leaving the process. The results of ASPENPLUS base case simulation are summarized in Table 4-14. It is observed that ASPENPLUS converges to a slightly different mass and energy balance than the base case if Equation (4-14) is used for the conversion of (H₂+CO) as a function of P, SV, and R. The final conversion of CO, θ , at the end of simulation is 28.6 percent, whereas in base case it is reported as 30.6 percent. An investigation was conducted to understand why ASPENPLUS produces different results when all the input parameters and equipment operating conditions were the same as the base case.

Equation 4--14 was developed from the graphical data obtained from the process economic report (Air Products and Chemicals, Inc, 1998). The equation relating (H₂+CO) conversion to P, SV, and R was in form:

$$C^* = A (P)^b (SV)^c (R)^d \quad (4-16)$$

where, A was equal to 0.362.

It is found that the conversion of (H_2+CO) and therefore CO is sensitive to a change in the value of A. For example, if the value of A is 0.380 instead of 0.362, CO conversion in the end of simulation is slightly different. On performing simulations using hit and trial values of A, it was found that for a value of $A = 0.402$, ASPENPLUS converged to mass and energy balance which closely resembled the base case. Looking at the results that influence the LCI parameters (steam produced, steam consumed, electricity consumed, etc.), it is seen that there is not a significant difference in them even when the final conversion of CO is 29.2 percent as opposed to the actual base case value of 30.6 percent. Table 4-15 shows a comparison of the results produced by both simulations.

Thus the parameters which are of concern in terms of developing the LCI of methanol are not sensitive to small changes in value of factor A. The following section presents the LCI of methanol based on the results produced by ASPENPLUS process model for the base case.

Table 4-12. Temperature, Pressure and Composition of Fresh Syngas Feed Used in the Base Case (Air Products and Chemicals, Inc., 1997)

Description	Value
Temperature, °F	95
Pressure, psia	738
Composition	
Component	Mole percent
H ₂	67.14
CO	29.89
N ₂	0.46
CH ₄	0.03
CO ₂	2.48
Dimethyl ether (DME)	0.00
Methanol (MeOH)	0.00
Ethanol (EtOH)	0.00
H ₂ O	0.00
TOTAL	100

Table 4-13. Summary of Selected Base Case Input Values for the LPMEOH Process (Air Products and Chemicals, Inc., 1997)

Description	Value
Pressure Drop (ΔP) or Outlet Pressure (P_{outlet}), psia	
Guard Bed (GRDBED), ΔP	6
Methanol Reactor Sparger, ΔP	10
Cyclone (CYCLONE), ΔP	6
Oil Separator (OILSEP), ΔP	2
Methanol Condenser (CONDSR), ΔP	4
Flash Valve (FLVALVE), ΔP	10
Pre-distillation Valve (DISTVAL), P_{outlet}	35
LPMEOH Reactor Conditions	
Pressure, psia	721.7
Temperature, °F	481
Gas Space Velocity, Std. Liter/kg-hr	8827
Reactions taking place:	
$\text{CO} + 2 \text{H}_2 \rightarrow \text{CH}_3\text{OH} \quad (1)$	
$\text{CO}_2 + 3 \text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad (2)$	
CO conversion (θ) in reaction (1), percent	30.6
CO ₂ conversion (Z) in reaction (2), percent	8.9
Recycle Ratio , molar ratio (moles recycle/ moles fresh feed)	3.22
Temperatures, °F	
Economizer (ECONM), Coldside Outlet Temperature	330
Condenser (CONDSR), Hotside Outlet Temperature	100
Recycle Gas Compressor	
<i>Isentropic compressor</i>	
Inlet Pressure, psia	700
Outlet Pressure, psia	738
Vapor Distillation Column	
Percentage separation (in top product) of: H ₂ , CO, N ₂ , CO ₂ and CH ₄	100
Methanol Distillation Column	
Top tray pressure, psia	30
Bottom tray pressure, psia	33
Top product (methanol) purity, wt. Percent	99.99
Reactor's Internal Heat Exchanger	
Boiler feed water (BFW) conditions	160 °F, 387.7 psia
Saturated steam conditions	441.55 °F, 387.7 psia
Distillation column Reboiler	
Saturated steam inlet conditions	329.41 °F, 100 psia
Saturated water outlet conditions	329.41 °F, 100 psia

Table 4-13 continued on next page

Table 4-13 continued

Methanol Separator (MEOHSEP)	
Temperature, °F	100
Pressure, psia	700
(CO+H ₂) conversion, $C^* = 0.362 (P)^{0.88} (SV)^{-0.225} (R)^{0.30}$	(4-14)
CO conversion, $q = C^* \frac{(R+1)}{3} - Z \cdot S$	(4-15)

Table 4-14. Summary of the Results Produced by LPMEOH Model in ASPEN PLUS for the Base Case^a.

Description	Value
Power Consumed in Recycle gas compressor, kW	115
Steam Produced in LPMEOH Reactor	
Temperature, °F	441.55
Pressure, psia	387.7
Mass flow rate, lb/hr	11150
Methanol Produced in Distillation Column	
<u>Purified Methanol (Top Product)</u>	
Temperature, °F	182
Pressure, psia	30
Mass flow rate, lb/hr	15900
Methanol Purity, wt. Percent	99.99
<u>Water (Bottom Product)</u>	
Temperature, °F	258
Pressure, psia	33
Mass flow rate, lb/hr	447.9
Methanol content, wt. Percent	0.34
Steam Consumed in methanol Distillation Column Reboiler	
Temperature, °F	327.82
Pressure, psia	100
Mass flow rate, lb/hr	12550
Purge Gases to flue gas boiler	
Temperature, °F	99
Pressure, psia	700
Mass flow rate, lb/hr	3200

^a Only the results that influence the LCI of methanol are presented.

Table 4-15. Comparison of Simulation Results of the Same Base Case with Two Different Values of ‘A’ in Equation (4-16)^a

Description	Base Case (Actual)	Simulation 1	Simulation 2
Value of A in Equation 4-12	-	0.36222	0.40185
Conversion of CO at the end of Simulation	30.6	29.2	30.6
Power Consumed in Recycle gas compressor, kW	- ^b	115	118
Steam Produced in LPMEOH Reactor			
<i>Temperature, °F</i>	441.55	441.55	441.55
<i>Pressure, psia</i>	387.7	387.7	387.7
<i>Mass flow rate, lb/hr</i>	11250	11150	11200
Methanol Produced in Distillation Column			
<u>Purified Methanol (Top Product)</u>			
<i>Temperature, °F</i>	-	182	182
<i>Pressure, psia</i>	-	30	30
<i>Mass flow rate, lb/hr</i>	16100	15900	16050
<i>Methanol purity, wt. Percent</i>	99.99	99.99	99.99
<u>Bottom Product</u>			
<i>Temperature, °F</i>	-	258	258
<i>Pressure, psia</i>	-	33	33
<i>Mass flow rate, lb/hr</i>	495	448	502
<i>Methanol content, wt. Percent</i>	-	0.34	0.332
Steam Consumed in Methanol Distillation			
<i>Temperature, °F</i>	329.41	329.41	329.41
<i>Pressure, psia</i>	100	100	100
<i>Mass flow rate, lb/hr</i>	12600	12550	12600
Purge Gases to flue gas boiler			
<i>Temperature, °F</i>	100	99	99
<i>Pressure, psia</i>	700	700	700
<i>Mass flow rate, lb/hr</i>	2960	3200	3050

^a Only the results that influence the LCI of methanol are presented and compared.

Note: In above table, specified input conditions are indicated in *italics*.

^bNo data presented for the base case.

4.10 Life Cycle Inventory of LPMEOH Process

A methodology to calculate emissions associated with the LPMEOH process is presented here. The methodology considers emissions at a LPMEOH facility as well as emissions that are generated due to electricity and steam consumption. The LCI of steam and electricity is used directly from Chapters 2 and 3, respectively. Emissions are calculated in units of kg pollutant per kg of methanol produced.

4.10.1 System Boundaries and Design Basis

The LPMEOH LCI modeling includes all activities associated with the operating LPMEOH facility starting with the syngas. The LCIs of steam and electricity are considered in separate spreadsheet models, the results from which are then imported into the overall spreadsheet model for the LCI of methanol from the LPMEOH process. It was assumed that emissions associated with construction of the LPMEOH facility were not significant and these emissions are not considered in the LCI. Energy recovered from thermal oxidation of purge gases from the LPMEOH system was assumed to be in the form of heat, which raises steam in steam boiler. The emissions that are avoided because of this steam generation were subtracted from the LPMEOH process emissions to calculate the overall LCI of methanol from LPMEOH process.

The LCI of methanol produced in the LPMEOH process is a function of syngas composition, temperature and pressure. It is also a function of reactor pressure, gas space

velocity in the reactor and the recycle to fresh feed molar ratio. The process as described in previous sections is modeled in ASPENPLUS and the model results are directly used in an EXCEL spreadsheet in conjunction with the LCIs of steam and electricity to develop the overall LCI of methanol. The results produced by the LPMEOH model that are of concern for developing the LCI of methanol are: steam generated in the methanol reactor, steam consumed in methanol distillation section, electric power consumed by the recycle gas compressor, purge gases produced from the process that are then combusted to generate steam in a boiler, and the amount of methanol produced. Information on fugitive emissions and other wastes that could not be modeled in ASPENPLUS is derived from the environmental information volume on the LPMEOH process (Air Products and Chemicals, Inc., 1995).

LCI parameters considered include gaseous and liquid releases as well as solid waste. Although it is assumed that there are no water releases or solid waste production in the LPMEOH process, these parameters are included because such releases are associated with the LCI of electrical energy and steam. Table 4-16 lists the parameters that are considered in the LCI of the LPMEOH process. Individual components of the overall LCI like steam, electricity, purge gas emissions, fugitive emissions also have the same LCI parameters. Wherever the information regarding a particular LCI parameter is not available, it is left blank indicating that “no data” is available for that parameter. The methodology used to calculate and allocate emissions from each part of LPMEOH process is described in the following section.

Table 4-16. LCI Parameters considered in the LCI of LPMEOH Process

<u>Air Emissions</u>	<u>Liquid Emissions</u>
PM	Dissolved Solids
PM-10	Suspended Solids
SO ₂	BOD
SO ₃	COD
NO _x	Oil
CO	Sulfuric Acid
CO ₂ (fossil)	Iron
CO ₂ (Biomass)	Ammonia
CH ₄	Copper
HCl	Cadmium
VOCs	Arsenic
NH ₃	Mercury
Hydrocarbons	Phosphate
Methanol	Selenium
Mineral Oil	Chromium
<u>METALS</u>	Lead
Antimony (Sb)	Zinc
Arsenic (As)	
Beryllium (Be)	Solid Waste
Cadmium (Cd)	
Chromium (Cr)	
Cobalt (Co)	
Copper (Cu)	
Lead (Pb)	
Mercury (Hg)	
Nickel (Ni)	
Selenium (Se)	
Zinc (Zn)	

4.10.2 Calculation of LPMEOH Process LCI

The LCI of the LPMEOH process considers the emissions due to LCI of electricity, LCI of steam, fugitive emissions and wastes from the process. Purge gases from the process are sent to an onsite boiler where 99% of the gases present are assumed to be combusted. The remaining one percent of the purge gas is assumed to be released to the atmosphere. The heat generated in the boiler is used to generate 100-psia saturated

steam. The methodology used to calculate and allocate energy used and associated emissions are described in this section.

4.10.2.1 Emissions associated with LCI of Steam

The LPMEOH process produces the 387.7 psia-saturated steam in the reactor's internal heat exchanger for the base case. The methanol purification section of the process uses 100 psia-saturated steam in distillation column's reboiler. Again the LPMEOH process model reports the amount of steam consumed in the distillation column reboiler. The steam produced in the reactor's heat exchanger can be blown down to 100-psia steam to meet the steam demand for distillation. If steam generated in the reactor is more than steam required in distillation, the balance can be used elsewhere in the process plant but if the steam required in distillation is more than steam generated in the reactor, the difference must be supplied. It is found that 387.7 psia saturated steam when blown down to 100 psia saturated steam, produces 900 kWh per day in a steam turbine with 75 percent efficiency. This would result in revenue of \$18 per day based on an electricity price of 2 cents per kWh. Further it is found that bare module capital cost of a turbine is more than \$100,000 (Ulrich, 1984). Since the cost of a steam turbine is very high, the steam at 387.7 psia is assumed to be blown down to 100 psia in pressure relief valve with no energy recovery.

Thus 100-psia steam required in the process is obtained from 387.7 psia steam generated in the process. The difference is supplied from a steam boiler. Since the only

steam now required in the process is the difference between the 100 psia steam used and 387.7-psia steam generated, the LCI conducted on this steam difference would give the LCI of steam emissions associated with the LPMEOH process. Table 4-17 presents the steam generated and the steam consumed in the LPMEOH process for the base case and the difference. It also presents the LCI of steam, as applicable to LPMEOH process, for the base case. The documentation for the LCI of steam can be found in Chapter 2. The only inputs required in the LCI of steam spreadsheet are the total enthalpy carried by the steam (MJ/hr) and the amount of methanol produced.

Table 4-17. LCI of Steam in LPMEOH Process for the Base Case^a

Methanol Produced (kg/hr)	7210	
Pressure of Steam (psia):	1.00E+02	
Initial Enthalpy (kJ/kg), 50 °C water:	2.09E+02	
<i>Final Enthalpy (kJ/kg), 100 psia steam:</i>	2.76E+03	
<i>Enthalpy change (kJ/kg):</i>	2.55E+03	
Steam Consumed (kg/hr) – 100 psia:	12550	
Steam Produced (kg/hr) – 387.7 psia:	11150	
Net Steam Consumed (kg/hr) – 100 psia:	1400	
Enthalpy Carried by Steam (MJ/hr):	1.62E+03	
Air Emissions	Steam LCI (kg/MJ Steam)	Emissions (kg/kg of Methanol)
PM	2.93E-05	6.87E-06
PM-10		
SO ₂	5.51E-04	1.29E-04
SO ₃		
NO _x	1.07E-04	2.50E-05
CO	1.27E-04	2.98E-05
CO ₂ (fossil)	9.04E-02	2.12E-05
CO ₂ (Biomass)		
CH ₄	1.36E-04	3.20E-05
HCl	3.22E-07	7.56E-08
VOCs		
NH ₃		
Hydrocarbons		
Methanol	0.00E+00	0.00E+00
METALS		
Antimony (Sb)		
Arsenic (As)		
Beryllium (Be)		
Cadmium (Cd)		
Chromium (Cr)		
Cobalt (Co)		
Copper (Cu)		
Lead (Pb)		
Mercury (Hg)		
Nickel (Ni)		
Selenium (Se)		
Zinc (Zn)		
Liquid Emissions		
Dissolved Solids		
Suspended Solids	1.46E-05	3.41E-06
BOD	7.98E-07	1.87E-07
COD	5.57E-06	1.31E-06
Oil		
Sulfuric Acid		

Table 4-17 continued on next page

Table 4-17 continued

Liquid Emissions	Steam LCI (kg/MJ Steam)	Emissions (kg/kg of Methanol)
Iron		
Ammonia		
Copper		
Cadmium		
Arsenic		
Mercury		
Phosphate		
Selenium		
Chromium		
Lead		
Zinc		
Solid Waste	7.93E-03	1.86E-03

^a Blank cells represent “no data” available.

4.10.2.2 Emissions associated with LCI of Electricity

Electricity is used in the LPMEOH process in the recycle gas compressor. The compressor has a pressure ratio of 1.07 and is assumed to be isentropic. The LCI documentation for electricity has been presented in Chapter 3 with emissions calculated for a kWh of electricity. The only inputs required are power consumed by the compressor (kW) and the flowrate of methanol produced (kg/hr). The emissions are calculated per kg of methanol produced using following equation:

$$Emission_j, kg / kg \text{ methanol} = \frac{(Emission_j, kg / kWh) \times (Compressor_Work, kW)}{(Methanol_produced, kg / hr)} \quad (4-17)$$

where: j = emission of type 'j' (PM, SO₂, CO, etc.)

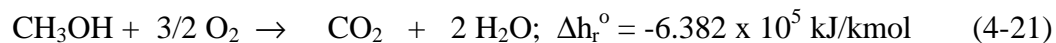
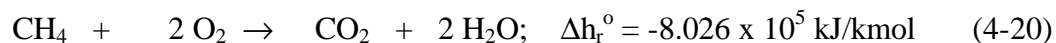
Table 4-18 presents the LCI of electricity for the LPMEOH process base case.

Table 4-18. LCI of Electricity for LPMEOH Process Base Case**Electric Power Consumed (kW): 115****Methanol Produced (kg/hr): 7210**

Air Emissions	LCI of Electricity (kg/kWh)	Emissions (kg/kg of Methanol)
PM ₁₀	0.00E+00	0.00E+00
PM	7.98E-04	1.44E-01
NO _x	2.45E-03	4.41E-01
Hydrocarbons (non CH ₄)	3.42E-04	6.15E-02
SO ₂	4.86E-03	8.74E-01
CO	2.81E-04	5.05E-02
CO ₂ (biomass)	2.20E-03	3.95E-01
CO ₂ (non biomass)	6.57E-01	1.18E+02
NH ₃	2.95E-06	5.30E-04
Lead	3.07E-08	5.52E-06
CH ₄	1.42E-03	2.55E-01
HCl	4.80E-05	8.62E-03
Solid Waste #1	1.20E-01	2.16E+01
Solid Waste #2	0.00E+00	0.00E+00
Solid Waste #3	0.00E+00	0.00E+00
Solid Waste #4	0.00E+00	0.00E+00
Solid Waste #5	0.00E+00	0.00E+00
Dissolved Solids	1.55E-03	2.79E-01
Suspended Solids	4.32E-04	7.76E-02
BOD	1.60E-06	2.88E-04
COD	2.20E-05	3.96E-03
Oil	2.73E-05	4.92E-03
Sulfuric Acid	5.86E-06	1.05E-03
Iron	3.60E-05	6.47E-03
Ammonia	4.16E-07	7.48E-05
Copper	0.00E+00	0.00E+00
Cadmium	7.00E-08	1.26E-05
Arsenic	0.00E+00	0.00E+00
Mercury	5.50E-12	9.88E-10
Phosphate	2.93E-06	5.27E-04
Selenium	0.00E+00	0.00E+00
Chromium	7.00E-08	1.26E-05
Lead	1.70E-11	3.06E-09
Zinc	2.42E-08	4.36E-06

4.10.2.3 Emissions associated with Burning of Purge Gas (Purge gas LCI)

The purge gases from LPMEOH process, which consist of CO, CH₄, N₂, CO₂, H₂, CH₃OH vapors, N₂ and some water vapor are sent to an on-site boiler for combustion. The composition of the purge gas is presented in Table 4-19. It is assumed that 99 percent combustion of the combustible gases takes place. The enthalpy generated by the combustion of these gases is used for the generation of 100 psia saturated steam. Further, it is assumed that the boiler operates with 80 percent efficiency. Thus, the amount of energy carried by steam can be calculated. Following are the reactions of combustion that take place in the boiler:



Δh_r° is the heat of reaction at standard temperature and pressure (298 K and 1 atm; Perry and Green, 1997). CO₂, H₂O and N₂ do not take part in combustion reactions. Steam produced from the purge gas is used to offset steam production in an industrial boiler.

The LCI of the purge gas, including the uncombusted purge gas (one percent of total) and the avoided steam production offsets are presented in Table 4-20. Table 4-20

shows the total enthalpy of the steam generated (80 percent of heat generated due to purge combustion) and the emissions associated with purge gas combustion including the emissions avoided due to steam generation, for the base case.

Table 4-19. Composition of Purge Gas for the Base Case

Gases	Mole percent	Flowrate (lbmol/hr)
H ₂	65.93	215
CO	24.53	70
CH ₄	2.45	8
CH ₄ O	0.17	0.5
N ₂	6.07	19.8
CO ₂	0.74	2.42
H ₂ O	0.11	0.35
Total	100.00	316

Table 4-20. LCI of Purge Gas for the Base Case^a

Total Enthalpy of the Steam Generated (MJ/hr): -2.60E+04^b

Air Emissions	Purge Gas^c	Steam^c	Emissions (kg/kg of methanol)
PM	no data	-1.10E-04	-1.10E-04
PM-10	no data		
SO ₂	no data	-2.07E-03	-2.07E-03
SO ₃	no data		
NO _x	no data	-4.00E-04	-4.00E-04
CO	1.47E-03	-4.77E-04	9.92E-04
CO ₂ (fossil)	2.60E-01	-3.39E-01	-7.93E-02
CO ₂ (Biomass)	no data		
CH ₄	8.39E-05	-5.12E-04	-4.28E-04
HCl	no data	-1.21E-06	-1.21E-06
VOCs			
NH ₃			
Hydrocarbons			
Methanol	1.13E-05	0.00E+00	1.13E-05
METALS			
Antimony (Sb)			
Arsenic (As)			
Beryllium (Be)			
Cadmium (Cd)			
Chromium (Cr)			
Cobalt (Co)			
Copper (Cu)			
Lead (Pb)			
Mercury (Hg)			
Nickel (Ni)			
Selenium (Se)			
Zinc (Zn)			
Liquid Emissions^d			
Dissolved Solids	0.00E+00 ^e		
Suspended Solids	0.00E+00 ^e	-5.47E-05	-5.47E-05
BOD	0.00E+00 ^e	-2.99E-06	-2.99E-06
COD	0.00E+00 ^e	-2.09E-05	-2.09E-05
Oil	0.00E+00 ^e		
Sulfuric Acid	0.00E+00 ^e		
Iron	0.00E+00 ^e		
Ammonia	0.00E+00 ^e		
Copper	0.00E+00 ^e		
Cadmium	0.00E+00 ^e		
Arsenic	0.00E+00 ^e		
Mercury	0.00E+00 ^e		
Phosphate	0.00E+00 ^e		

Table 4-20 continued on next page

Table 4-20 continued

Liquid Emissions	Purge Gas^c	Steam^c	Emissions (kg/kg of methanol)
Selenium	no data		
Chromium	no data		
Lead	no data		
Zinc	no data		
Solid Waste	0.00E+00 ^e	-2.98E-02	-2.98E-02

^a Blank cells in above table represent “no data” available

^b Negative sign indicates that steam is produced

^c In units of kg/kg of methanol produced

^d Liquid emissions and solid waste from purge gas emissions are expected to be none and therefore judged to be zero

4.10.2.4 Fugitive Emissions from the LPMEOH process

LPMEOH process model in ASPENPLUS does not have a capability to estimate the fugitive emissions. The fugitive emissions were calculated for the LPMEOH process demonstration facility at Kingsport before the plant began operation and have been reported in the Environmental Information Volume on the LPMEOH process (Air Products and Chemicals, Inc., 1995). The emissions were reported on annual basis with a plant capacity of 260 tons per day (TPD) of methanol production based on 320 days of operation per annum. The fugitive emission can thus be calculated on per kg methanol produced basis. Table 4-21 presents the fugitive emissions from LPMEOH process.

Table 4-21. Fugitive Emissions from LPMEOH Process

Fugitive Emissions	Tons/annum	kg/kg CH₃OH
CO	2.1	2.52E-05
CH ₃ OH (VOC)	5.4	6.49E-05
Other VOCs	1.9	2.28E-05

4.10.2.5 Emissions from Storage tanks

There are small emissions of methanol and mineral oil from their respective storage tanks. Methanol storage tanks are covered at the top but the vapor space above the liquid methanol has some methanol vapors, which are passed through an absorber before venting to atmosphere. Mineral oil storage tanks are uncovered and there is small emission of mineral oil vapors because of its low volatility as compared to methanol. Table 4-22 presents emissions of methanol and mineral oil from their respective storage

tanks as obtained from Environmental Information Volume on the LPMEOH process (Air Products and Chemicals, Inc., 1995).

Table 4-22. Emissions from Storage Tanks

Emission from Storage Tanks	Tons/annum	kg/kg CH₃OH
Methanol (2 tanks)	0.072	8.65E-07
Mineral Oil (3 tanks)	0.015	1.80E-07

4.10.2.6 Waste water emissions

The only water emission estimated and documented in the environmental information volume of LPMEOH process (Air Products and Chemicals, Inc., 1995) is biochemical oxygen demand (BOD) in the wastewater stream from the process. It was estimated that the LPMEOH process facility would add about 4180 lb/day of BOD to existing wastewater at Kingsport. BOD added per kg of methanol produced can thus be calculated. It is assumed that BOD can be removed with 92 percent efficiency. It takes 0.001 kWh of electricity to remove a gram of BOD. Also, 0.5 gm solid waste and 3.6 gm CO₂ are produced per gm of BOD (Ecobalance, Inc; 1999). The electricity used in treating the BOD, solid waste generated, and CO₂ produced can be calculated using the following equations:

$$BOD_Electricity_used \left(\frac{kWh}{kg \text{ methanol}} \right) = \left(\frac{0.001 kWh}{gm \text{ BOD treated}} \right) \times \left(\frac{gm \text{ BOD present}}{kg \text{ methanol}} \right) \times (BOD_removal_efficiency) \quad (4-22)$$

$$BOD_Solidwst_gen \left(\frac{kg}{kg \text{ methanol}} \right) = \left(\frac{0.5 \times 10^{-3} kg}{gm \text{ BOD treated}} \right) \times \left(\frac{gm \text{ BOD present}}{kg \text{ methanol}} \right) \times (BOD_removal_efficiency) \quad (4-23)$$

$$BOD_CO_2_gen \left(\frac{kg}{kg \text{ methanol}} \right) = \left(\frac{3.6 \times 10^{-3} kg}{gm \text{ BOD treated}} \right) \times \left(\frac{gm \text{ BOD present}}{kg \text{ methanol}} \right) \times (BOD_removal_efficiency) \quad (4-24)$$

Table 4-23 shows the amount of electricity used, solid waste generated and CO₂ produced in BOD treatment. Table 4-24 shows the overall emissions due to BOD removal including the emissions from electricity generation (LCI of electricity).

Table 4-23. Emissions Associated With BOD Removal from Wastewater

Chemical/Electricity produced	kg/g BOD treated	kg/kg methanol
CO ₂	3.60E-03	2.66E-02
Solid Waste	5.00E-04	3.70E-03
	kWh/g BOD treated	kWh/kg methanol
Electricity Produced	0.001	0.0074

Table 4-24. Overall Emissions Due to BOD Removal Including the Emissions from Electricity Generation (LCI of Electricity)

Air Emissions	Emissions Due to Electricity (kg/kg of methanol)	Emissions (kg/kg methanol)
PM ₁₀	0.00E+00	0.00E+00
PM	5.90E-06	5.90E-06
NO _x	1.81E-05	1.81E-05
Hydrocarbons (non CH ₄)	2.53E-06	2.53E-06
SO ₂	3.59E-05	3.59E-05
CO	2.08E-06	2.08E-06
CO ₂ (biomass)	1.63E-05	1.63E-05
CO ₂ (non biomass)*	4.86E-03	3.15E-02
NH ₃	2.18E-08	2.18E-08
Lead	2.27E-10	2.27E-10
CH ₄	1.05E-05	1.05E-05
HCl	3.55E-07	3.55E-07
Solid Waste #1*	8.88E-04	4.59E-03
Solid Waste #2	0.00E+00	0.00E+00
Solid Waste #3	0.00E+00	0.00E+00
Solid Waste #4	0.00E+00	0.00E+00
Solid Waste #5	0.00E+00	0.00E+00
Water Emissions		
Dissolved Solids	1.15E-05	1.15E-05
Suspended Solids	3.19E-06	3.19E-06
BOD*	1.19E-08	6.43E-04
COD	1.63E-07	1.63E-07
Oil	2.02E-07	2.02E-07
Sulfuric Acid	4.34E-08	4.34E-08
Iron	2.66E-07	2.66E-07
Ammonia	3.08E-09	3.08E-09
Copper	0.00E+00	0.00E+00
Cadmium	5.18E-10	5.18E-10
Arsenic	0.00E+00	0.00E+00
Mercury	4.06E-14	4.06E-14
Phosphate	2.17E-08	2.17E-08
Selenium	0.00E+00	0.00E+00
Chromium	5.18E-10	5.18E-10
Lead	1.26E-13	1.26E-13
Zinc	1.79E-10	1.79E-10

* Only these parameters change in overall emissions due to BOD removal with respect to emissions from electricity

4.10.2.7 Overall LCI of Methanol (LPMEOH Process Base Case)

All the LCI parameters associated with different operations in production of methanol as documented in previous sections are finally summed across to yield the overall LCI of methanol production. The LCI parameters are presented in units of kg pollutant/kg of methanol produced. Table 4-25 presents the LCI associated with various sections of methanol production (steam, electricity, etc.) and the overall LCI of methanol for the base case.

Looking at the overall LCI table with various contributing components present, it is evident that purge gas LCI drives most LCI parameters in the overall LCI of methanol starting from syngas. The negative LCI parameters in the overall LCI are due to steam production offsets. The second largest contributor to the overall LCI is the LCI associated with steam consumption and the third largest contributor is the LCI associated with electricity consumption. The contribution of the LCI associated with BOD removal is lower than above three but is higher for one LCI parameter, BOD. The contribution from the LCI associated with fugitive emissions and storage tank emissions is quite low in most LCI parameters.

Table 4-25. Overall LCI of Methanol (LPMEOH Process Base Case, in kg/kg of methanol produced)^a

Air Emissions	Steam	Electricity	Purge	BOD Removal	Fugitive	Storage Tanks	TOTAL
PM	6.87E-05	2.08E-05	-1.10E-04	5.90E-06	0.00E+00	0.00E+00	-7.65E-05
PM-10		0.00E+00		0.00E+00	0.00E+00	0.00E+00	
SO2	1.29E-03	1.26E-04	-2.07E-03	3.59E-05	0.00E+00	0.00E+00	-1.78E-03
SO3					0.00E+00	0.00E+00	
NOx	2.50E-04	6.38E-05	-4.00E-04	1.81E-05	0.00E+00	0.00E+00	-2.93E-04
CO	2.98E-04	7.29E-06	9.92E-04	2.08E-06	2.52E-05	0.00E+00	1.06E-03
CO2 (fossil)	2.12E-01	1.71E-02	-7.93E-02	3.15E-02	0.00E+00	0.00E+00	-9.56E-03
CO2(Biomass)		5.72E-05		1.63E-05	0.00E+00	0.00E+00	
CH4	3.20E-04	3.69E-05	-4.28E-04	1.05E-05	0.00E+00	0.00E+00	-3.48E-04
HCl	7.56E-07	1.25E-06	-1.21E-06	3.55E-07	0.00E+00	0.00E+00	4.67E-07
VOCs					2.28E-05	0.00E+00	
NH3		7.66E-08		2.18E-08	0.00E+00	0.00E+00	
Hydrocarbons		8.89E-06		2.53E-06	0.00E+00	0.00E+00	
Methanol	0.00E+00	0.00E+00	1.13E-05	0.00E+00	6.49E-05	8.65E-07	7.71E-05
Mineral Oil					0.00E+00	1.80E-07	
METALS							
Antimony (Sb)					0.00E+00	0.00E+00	
Arsenic (As)					0.00E+00	0.00E+00	
Beryllium (Be)					0.00E+00	0.00E+00	
Cadmium (Cd)					0.00E+00	0.00E+00	
Chromium (Cr)					0.00E+00	0.00E+00	
Cobalt (Co)					0.00E+00	0.00E+00	
Copper (Cu)					0.00E+00	0.00E+00	
Lead (Pb)		7.98E-10		2.27E-10	0.00E+00	0.00E+00	
Mercury (Hg)					0.00E+00	0.00E+00	
Nickel (Ni)					0.00E+00	0.00E+00	
Selenium (Se)					0.00E+00	0.00E+00	
Zinc (Zn)					0.00E+00	0.00E+00	
Liquid Emissions							
Dissolved Solids		4.03E-05		1.15E-05	0.00E+00	0.00E+00	
Suspended Solids	3.41E-05	1.12E-05	-5.47E-05	3.19E-06	0.00E+00	0.00E+00	-3.68E-05
BOD	1.87E-06	4.17E-08	-2.99E-06	6.43E-04	0.00E+00	0.00E+00	6.40E-04
COD	1.31E-05	5.73E-07	-2.09E-05	1.63E-07	0.00E+00	0.00E+00	-1.89E-05
Oil		7.11E-07		2.02E-07	0.00E+00	7.81E-05	
Sulfuric Acid		1.52E-07		4.34E-08	0.00E+00	0.00E+00	
Iron		9.36E-07		2.66E-07	0.00E+00	0.00E+00	
Ammonia		1.08E-08		3.08E-09	0.00E+00	0.00E+00	
Copper		0.00E+00		0.00E+00	0.00E+00	0.00E+00	
Cadmium		1.82E-09		5.18E-10	0.00E+00	0.00E+00	
Arsenic		0.00E+00		0.00E+00	0.00E+00	0.00E+00	
Mercury		1.43E-13		4.06E-14	0.00E+00	0.00E+00	
Phosphate		7.62E-08		2.17E-08	0.00E+00	0.00E+00	
Selenium		0.00E+00		0.00E+00	0.00E+00	0.00E+00	
Chromium		1.82E-09		5.18E-10	0.00E+00	0.00E+00	

Table 4-25 continued on next page

Table 4-25 continued

Liquid Emissions	Steam	Electricity	Purge	BOD Removal	Fugitive	Storage Tanks	TOTAL
Lead		4.42E-13		1.26E-13	0.00E+00	0.00E+00	
Zinc		6.30E-10		1.79E-10	0.00E+00	0.00E+00	
Solid Waste	1.86E-02	3.12E-03	-2.98E-02	4.59E-03	0.00E+00	0.00E+00	-2.02E-02

^a Blank cells represent “no data” available.

4.11 Sensitivity Analysis of LPMEOH Process Model in ASPEN PLUS

This section documents the sensitivity analysis results of the LPMEOH process model implemented in ASPEN PLUS. The main objective of doing a sensitivity analysis is to evaluate the effect of change in one or more model inputs on the values of selected model outputs. One form of sensitivity, which is used here, is to vary only one model input at a time over a nominal range while all other model inputs are held constant. The purpose of the sensitivity analysis of the LPMEOH process model is to evaluate the model performance under varying conditions of reactor pressure, syngas space velocity, and recycle ratio. These parameters are considered because the (H₂ + CO) conversion, which is a significant parameter in the LPMEOH process, depends on them. All other process conditions such as temperatures and pressure drops in all of the process equipment, are held at their constant values as in the base case. The base case assumptions are presented in Table 4-13. The main model results that are considered are: (1) methanol production; (2) steam production in the methanol reactor; (3) steam consumption in methanol distillation; (4) net steam consumption in the process; (5) electricity consumption in the recycle gas compressor; and (6) purge gas production. These results are tracked because they affect the LCI of methanol starting from syngas. These are also key indicators of overall process performance. Furthermore, these outputs are important when considering integration issues with an IGCC power plant.

The sensitivity analysis is focused on three sets of cases based upon three different syngases. These syngases are: (1) syngas obtained from Texaco gasifier at Kingsport; (2)

syngas gas obtained from a British Gas/Lurgi (BGL) gasifier firing coal; and (3) syngas obtained from a BGL gasifier firing a mixture of coal and MSW. For each of the three syngases, the following sensitivity cases are considered:

- (1) Varying the reactor pressure (P), keeping space velocity (SV) and recycle ratio (R) constant. The cases considered for pressure are 500, 750, 1000, 1250 psig while SV is held constant at 8827 standard liters/kg-hr and R is held constant at 3.22 moles recycle gas/moles fresh syngas feed.
- (2) Varying SV, keeping P and R constant. The cases considered for SV are 2000, 4000, and 8000 standard liters/kg-hr while P is held constant at 707 psig and R is held constant at 3.22 moles recycle gas/moles fresh feed.
- (3) Varying R, keeping P and SV constant. The cases considered for the recycle ratio are 0 (no recycle), 1, 2, and 3 moles recycle gas/moles fresh feed, while P is held constant at 707 psig and SV is held constant at 8827 standard liters/kg-hr.

The reactor pressure is held constant at 707 psig, space velocity is held constant at 8827 standard liters/kg-hr, and the recycle ratio is held constant at 3.22 moles recycle gas/moles fresh syngas feed because these values are the base case values.

4.11.1 Syngases Considered in the Sensitivity Analysis

This section presents the description of syngases considered in the sensitivity analysis of LPMEOH process model. Three syngas compositions are described: (1)

Syngas obtained from Texaco gasifier at Kingsport; (2) syngas obtained from a coal fired BGL gasifier; and (3) syngas obtained from a BGL gasifier firing mixture of coal and MSW. The composition of the three syngases considered is presented in Table 4-26.

Table 4-26. Temperature and Composition of Texaco Gasifier Syngas (Air Products and Chemicals, Inc., 1997)

Syngas Type	Texaco Syngas	Coal Fired BGL Syngas	Coal and MSW co-fired BGL Syngas
<i>Component</i>	<i>Mole Percent</i>	<i>Mole Percent</i>	<i>Mole Percent</i>
H ₂	67.14	29.90	38.20
CO	29.89	58.60	48.80
N ₂	0.46	1.80	2.60
CH ₄	0.03	7.80	8.40
CO ₂	2.48	2.01	2.00
CH ₃ OH	0.00	0.00	0.00
H ₂ O	0.00	0.00	0.00

It is clear in the above table that the three syngases mainly differ in their H₂ and CO content. As discussed in section 4.5.4.1, the H₂/CO ratio is one of the key parameters affecting the performance of the LPMEOH process because syngas conversion in methanol reactor depends on it. In Table 4-26, the Texaco syngas has highest H₂/CO ratio of 2.25 and coal fired BGL syngas has the lowest H₂/CO ratio of 0.51. The syngas obtained from co-firing coal and MSW in a BGL gasifier has lower H₂/CO content than Texaco syngas but higher than the coal fired BGL syngas. Based on the H₂/CO ratio, it can be said that the Texaco syngas will produce maximum amount of methanol for given syngas flowrate and process conditions. The following section presents the sensitivity analysis results of the LPMEOH process model using Texaco syngas as feed.

4.11.2 Sensitivity Analysis on Texaco Syngas used at LPMEOH Process Demonstration Facility at Kingsport

This section presents the sensitivity analysis results of individually changing pressure, space velocity, and recycle ratio in LPMEOH process operating on Texaco syngas the same as that being used at Kingsport, TN. The composition of syngas is presented in Table 4-26. Flowrate of syngas considered is 1805.2 lbmol/hr as in base case. This is held constant for all of the sensitivity cases considered. Saturated steam is produced in the methanol reactor whose pressure is held constant at 387.7 psia as in base case. Saturated steam at 100 psia is used in methanol distillation and its pressure is also held constant in all the sensitivity cases.

Table 4-27 presents the results of the sensitivity analysis with P, SV and R as sensitive inputs. It should be noted that in varying reactor pressure, the pressure drops and temperatures across various process equipment are held constant as in Table 4-13. The following section presents the interpretation of the results of the sensitivity analysis on pressure. The sensitivity analysis of space velocity and recycle ratio are discussed in Sections 4.11.2.2 and 4.11.2.3, respectively.

4.11.2.1 Effect of Change in Reactor Pressure

This section presents the interpretations of the results of sensitivity analysis on pressure. In doing the sensitivity analysis on pressure, a FORTRAN block PRESSURE is defined which specifies the pressure, at the beginning of the simulation, in various process equipment based on the pressure drop across them. For example, if a reaction

pressure of 500 psig is specified for simulation, the FORTRAN block PRESSURE sets the fresh syngas pressure to 516 psig based 6 psia pressure drop in guard bed and 10 psia pressure drop in reactor sparger. It sets the operating pressure of methanol separator to 478 psig to account for the pressure drops from reactor until methanol separator. It also sets the compressor outlet pressure as 516 psig to match the pressure of fresh syngas feed. The following subsections present the interpretation of results obtained in Table 4-27.

Table 4-27. Results of Sensitivity Analysis for Varying Pressure, Space Velocity, and Recycle Ratio in LPMEOH Process Operating on Texaco Syngas Being Used at Kingsport^a

Parameters	Variation of P (psig) SV = 8827 SI/kg-hr (Constant) R = 3.22 (Constant)				Variation of SV (SI/kg-hr) P = 707 psig (Constant) R = 3.22 (Constant)			Variation of R P = 707 psig (Constant) SV = 8827 SI/kg-hr (Constant)			
	500	750	1000	1250	2000	4000	8000	0	1	2	3
Parameter Value											
CO Conversion per pass, %	16.8	33.4	48.7	52.1	48.9	40.7	34.5	21.1	22.9	24.7	26.5
Electricity Consumption (kW)	160	108	82	67	189	189.2	189.5	0	60.4	120.7	181
MeOH Production (lb/hr)	11800	16700	17900	18100	18100	17900	16300	3430	7270	11100	15100
Steam Production (lb/hr)	6610	11900	13300	13550	13350	13200	11400	2610	5180	7730	10400
Steam Consumption (lb/hr)	9160	12900	13850	14100	14000	13850	12590	2650	5600	8550	11700
Net Steam Consumption (lb/hr)	2550	1000	550	550	600	650	1190	40	420	820	1300
<i>Purge Gas</i>											
Temperature (F)	99	99	99	99	99	99	99	99	99	99	99
Pressure (psia)	492.7	742.7	992.7	1242.7	699.7	699.7	699.7	699.7	699.7	699.7	699.7
Flowrate (lbmol/hr)											
H ₂	440	137	60.2	58.5	52.6	62.5	163	972	730	490	239
CO	182.9	43	8.1	5.1	6.8	10.8	54.9	425	310	202	88
N ₂	8.3	8.1	8	7.8	8	8	8.4	8.31	8.32	8.33	8.36
CH ₄	0.54	0.54	0.54	0.54	0.56	0.55	0.55	0.55	0.53	0.53	0.53
CO ₂	24.2	17	15.5	15	13.1	13.6	17.7	40.7	35.8	29.4	20.6
CH ₃ OH	6.2	1.34	0.5	0.32	0.5	0.6	1.7	10.5	7.9	5.2	2.5
H ₂ O	0.1	0.02	0.007	0.004	0.007	0.009	0.02	0.1	0.08	0.07	0.03
Total (lbmol/hr)	662	207	93	87	81.6	96.1	246	1460	1090	736	359.0

^a Flowrate of syngas used is 1805.2 lbmol/hr for all the cases presented

4.11.2.1.1 Effect of Reactor Pressure on Electricity Consumption in the Recycle Gas Compressor

The purpose of the recycle gas compressor is to compress the recycle gases to overcome the pressure drop across the process such that recycle gas is at the pressure at which fresh syngas is available. The total pressure drop starting from fresh syngas through the methanol separator is approximately 38 psia. This total pressure drop is assumed to remain the same even if the pressure in the reactor changes. As an example, for the reactor pressure of 1250 psig, fresh syngas needs to be supplied at 1266 psig to account for pressure drops in guardbed and reactor sparger. The recycle gases entering the compressor would be at a pressure of 1228 psig. The compressor has to compress the recycle gas to 1266 psig, which results in a compression ratio of 1.03. Thus the compressor has to do less work in compressing the recycle gases for the case in which high pressure fresh syngas is used. Therefore, when the reactor pressure is increased from 500 to 1250 psig, the work done by the recycle gas compressor decreases. This trend is clear in Table 4-27.

4.11.2.1.2 Effect of Reaction Pressure on Methanol Production

As the pressure in the reactor increases, the CO conversion in the reactor increases, leading to more production of methanol (Equation 4-14). Although the production of methanol increases with an increase in pressure, the increase in methanol production is not in same proportion as the pressure increase because the CO conversion does not increase in the same proportion as the pressure. As the pressure increases from 500 psig to 750 psig, an increment of 250 psi, methanol production increases by 4900

lb/hr. When the pressure is further increased from 750 psig to 1000 psig, the methanol production increases by only 1200 lb/hr, and when the pressure increases from 1000 psig to 1250 psig, the methanol production only increases by 200 lb/hr. This can be explained on the basis that at higher and higher reactor pressure, higher conversion of syngas to methanol is already achieved so further increase in pressure does not increase the methanol production at the specified process conditions. So as the pressure increases past 1000 psig, there is not much change in methanol production at specified process conditions of space velocity and recycle ratio.

4.11.2.1.3 Steam Production in the Methanol Reactor

Steam production in methanol reactor is a function of amount of syngas converted in methanol reactor. Steam production in the reactor increases as the syngas conversion increases due to increase in pressure. Steam production does not increase in the same proportion as the reactor pressure for the reason same as that for methanol production. (Table 4-27).

4.11.2.1.4 Steam Consumption in Methanol Distillation

Steam consumption in methanol distillation increases as the reactor pressure increases. Steam consumption in the methanol distillation depends on the amount of methanol to be distilled and hence is dependent on methanol production. Thus steam consumption follows similar trend as methanol production. Net steam consumption in the process decreases with increase in reactor pressure as shown in Table 4-27.

4.11.2.1.5 Effect of Pressure on Purge Gas Production

As the reactor pressure increases, the syngas conversion in the methanol reactor increases and therefore less amount of purge gas is generated. Thus amount of purge gases decreases with increase in reactor pressure (Table 4-27).

Figures 4-11 and 4-12 present the results of sensitivity analysis of pressure for the Texaco syngas being used at Kingsport, graphically. The following section presents the interpretation of results of sensitivity analysis on space velocity.

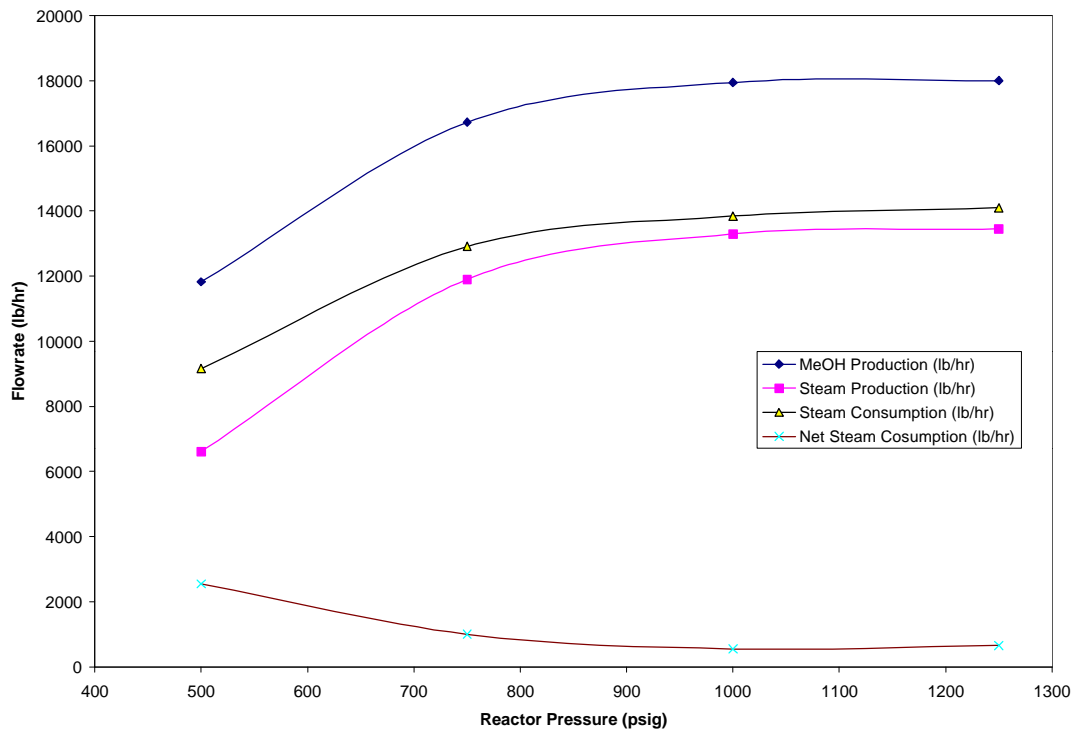


Figure 4-11. Results of Sensitivity of Reactor Pressure on Methanol Production, Steam Production, Steam Consumption, and Net Steam Consumption for Texaco Syngas Being Used at Kingsport.

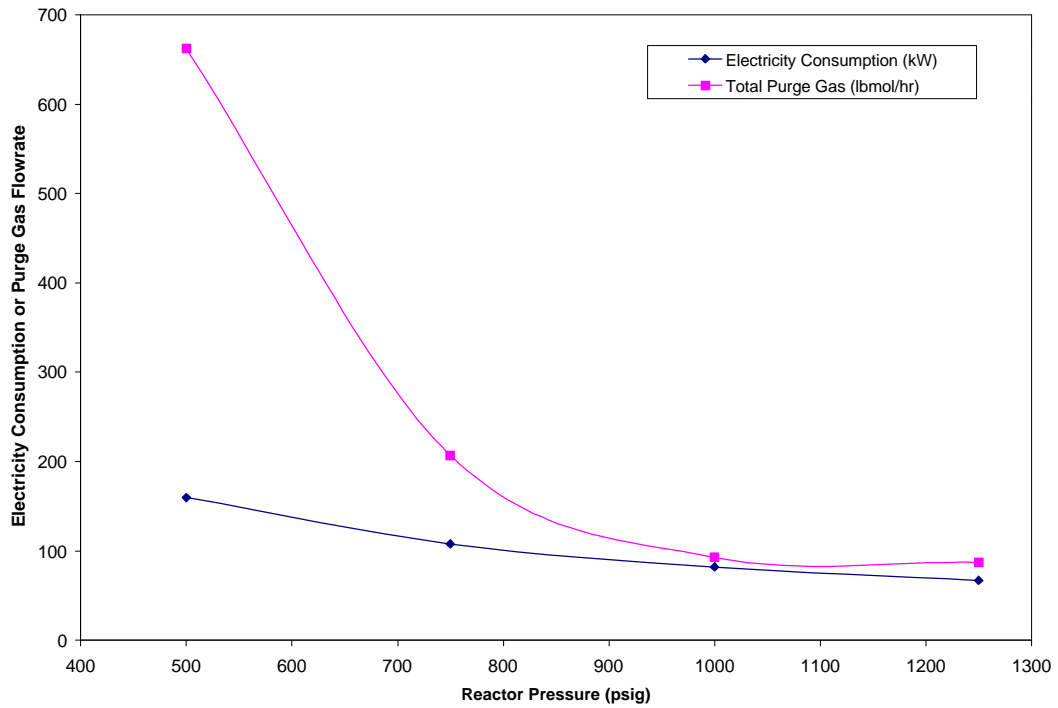


Figure 4-12. Results of Sensitivity of Reactor Pressure on Electricity Consumption in Recycle Gas Compressor and Purge Gas Flowrate for Texaco Syngas Being Used at Kingsport.

4.11.2.2 Effect of Change in Syngas Space Velocity in Methanol Reactor

This section presents the interpretation of the results of sensitivity analysis on space velocity for the Texaco syngas being used at Kingsport.

4.11.2.2.1 Effect of Reactor Space Velocity on Electricity Consumption in the Recycle Gas Compressor

The electric power consumed in the recycle gas compressor does not change as the syngas space velocity inside the reactor changes. The compressor power depends on the process pressure drop that the compressor has to overcome based on the fresh syngas supply pressure and the recycle gas flowrate and since neither of these changes, the power consumed in the compressor remains approximately constant (Table 4-27).

4.11.2.2.2 Effect of Syngas Space Velocity on Methanol Production

As the space velocity in the reactor increases, the CO conversion in the methanol reactor decreases as shown in Table 4-27, thus less methanol is produced. As space velocity of syngas in the reactor increases, there is less residence time for contact with the catalyst so the syngas conversion decreases.

4.11.2.2.3 Effect of Space Velocity on Steam Production in the Methanol Reactor

Steam production in the methanol reactor is a function of the amount of syngas converted in methanol reactor. Steam production decreases as the syngas conversion decreases due increasing space velocity. Hence Table 4-27 shows a decrease in steam production with increasing space velocity in the methanol reactor.

4.11.2.2.4 Effect of Space Velocity on Steam Consumption in Methanol Distillation

As the space velocity increases from 2000 to 8000 standard liters/kg-hr, the methanol production decreases and therefore the steam consumption in methanol distillation also decreases. Table 4-27 shows the decrease in steam consumption as the syngas space velocity in methanol reactor increases. Net steam consumption in the process increases slightly with increase in syngas space velocity as seen in Table 4-27.

4.11.2.2.5 Effect of Space Velocity on Purge Gas Production

As the space velocity increases, the conversion of syngas in methanol reactor decreases so there is more production of purge gas. Table 4-27 shows the increase in production of syngas due to increasing space velocity in the methanol reactor.

Figures 4-13 and 4-14 present the results of sensitivity analysis of syngas space velocity for the Texaco syngas being used at Kingsport, graphically. The following section presents the interpretation of the results of sensitivity analysis on recycle ratio.

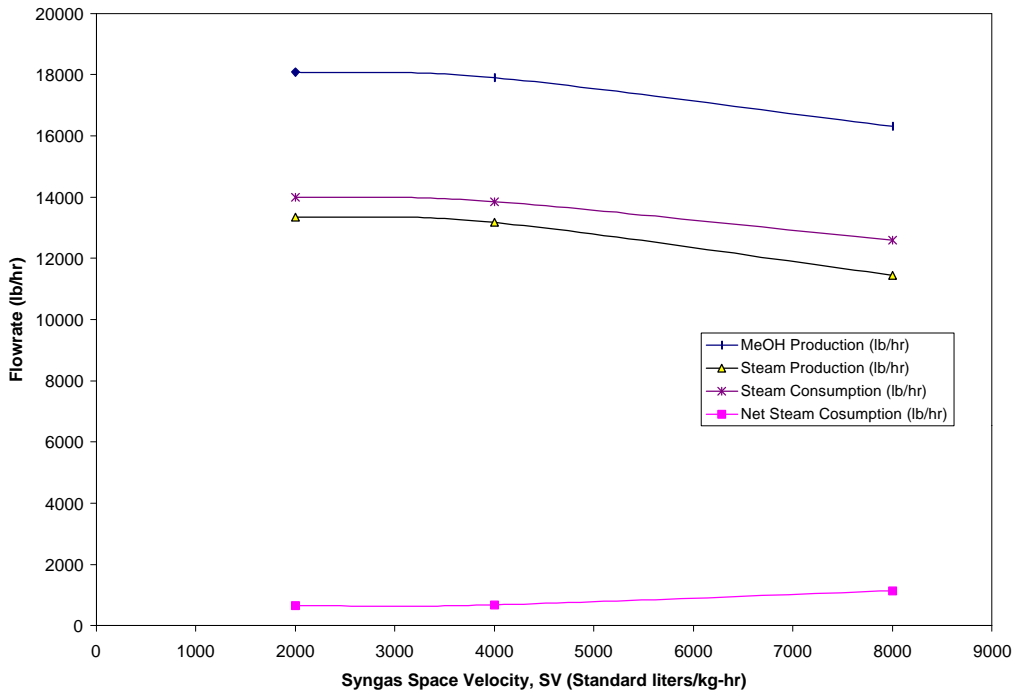


Figure 4-13. Results of Sensitivity of Syngas Space Velocity on Methanol Production, Steam Production, Steam Consumption, and Net Steam Consumption for Texaco Syngas Being Used at Kingsport

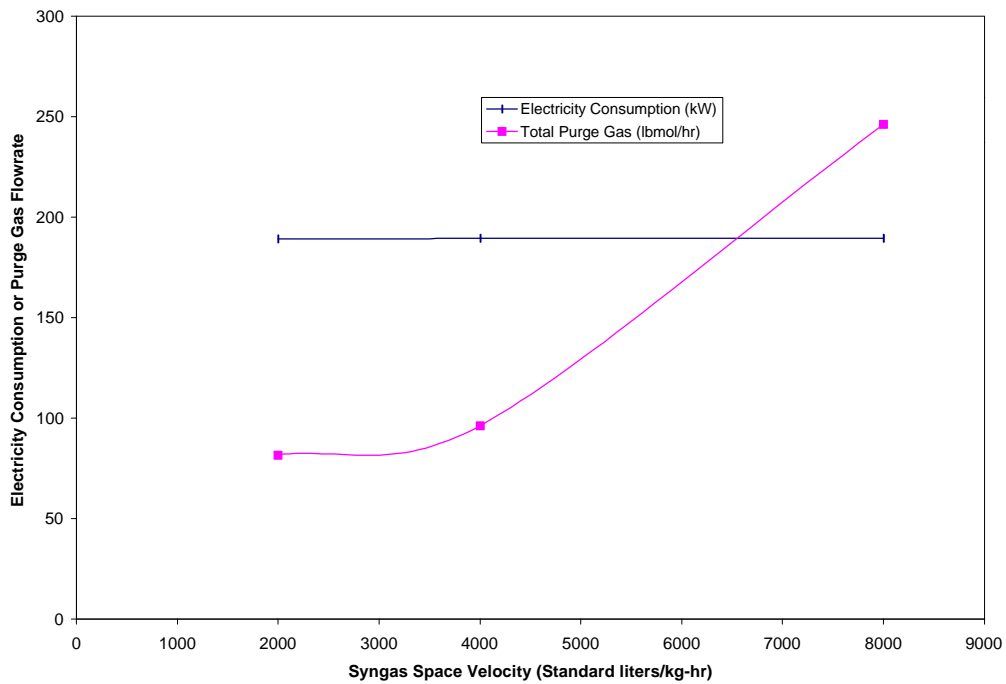


Figure 4-14. Results of Sensitivity of Syngas Space Velocity on Electricity Consumption in Recycle Gas Compressor and Purge Gas Flowrate for Texaco Syngas Being Used at Kingsport

4.11.2.3 Effect of Change in Recycle Ratio

This section presents the interpretation of the results of the sensitivity analysis of the recycle ratio. Table 4-27 presents the results of the sensitivity analysis with recycle ratio as a variable.

4.11.2.3.1 Effect of Recycle Ratio on Electricity Consumption in Recycle Gas Compressor

As the flowrate of the recycle gases through the recycle gas compressor increases, the electric power consumed in the compressor also increases because the compressor has to do more work to compress the higher mass of recycle gas. For the case of no recycle, the power consumed in compressor is zero and as the recycle ratio increases from 1 to 3 the compressor power increases linearly because of the linear increase in flowrate of recycle gas with increase in recycle ratio.

4.11.2.3.2 Effect of Recycle Ratio on Methanol Production

Methanol production increases as the recycle ratio is increased. For the fresh syngas richer in H_2 , the H_2/CO ratio in the combined feed (fresh syngas and recycle gas) would increase with the recycle ratio since the recycle gas would have higher H_2/CO ratio than fresh feed. Due to increase in H_2/CO ratio in combined feed, the conversion of syngas in methanol reactor increases. More amount of syngas flows through the methanol reactor because of higher recycle ratio due to which methanol production increases. Table 4-27 shows increasing methanol production with increasing recycle ratio.

4.11.2.3.3 Effect of Recycle Ratio on Steam Production in Methanol Reactor

Steam production in the methanol reactor is a function of amount of syngas converted in methanol reactor. Steam production increases as the syngas conversion increases due to increasing recycle ratio. Hence Table 4-27 shows an increase in steam production with increasing recycle ratio.

4.11.2.3.4 Effect of Recycle Ratio on Steam Consumption in Methanol Distillation

As the recycle ratio increases from 0 to 3, the methanol production increases and therefore the steam consumption in methanol distillation also increases. Table 4-27 shows the increase in steam consumption as the recycle ratio increases. Net steam consumption in the process increases with recycle ratio as seen in Table 4-27.

4.11.2.3.5 Effect of Recycle Ratio on Purge Gas Production

As the recycle ratio increases, the conversion of syngas in methanol reactor increases so there is less production of purge gas. Table 4-27 shows the decrease in production of syngas due to increasing recycle ratio.

Figures 4-15 and 4-16 present the results of sensitivity analysis of recycle ratio for the Texaco syngas being used at Kingsport, graphically. The following section presents the sensitivity analysis of P, SV, and R for the syngas obtained from coal fired BGL gasifier.

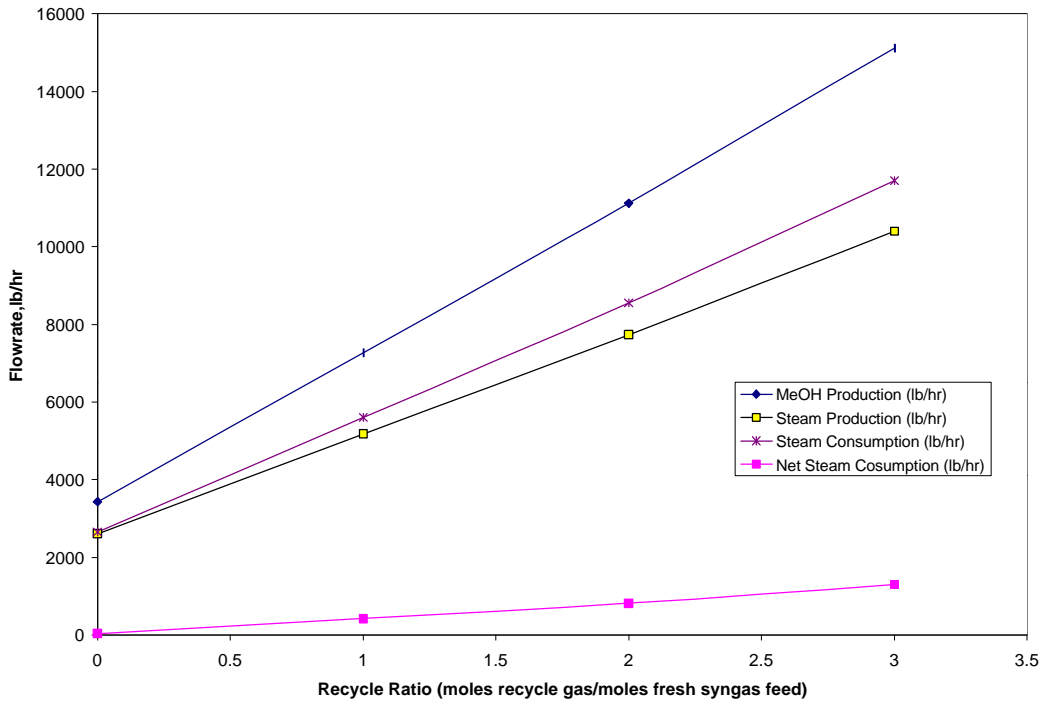


Figure 4-15. Results of Sensitivity of Recycle Ratio on Methanol Production, Steam Production, Steam Consumption, and Net Steam Consumption for Texaco Syngas Being Used at Kingsport

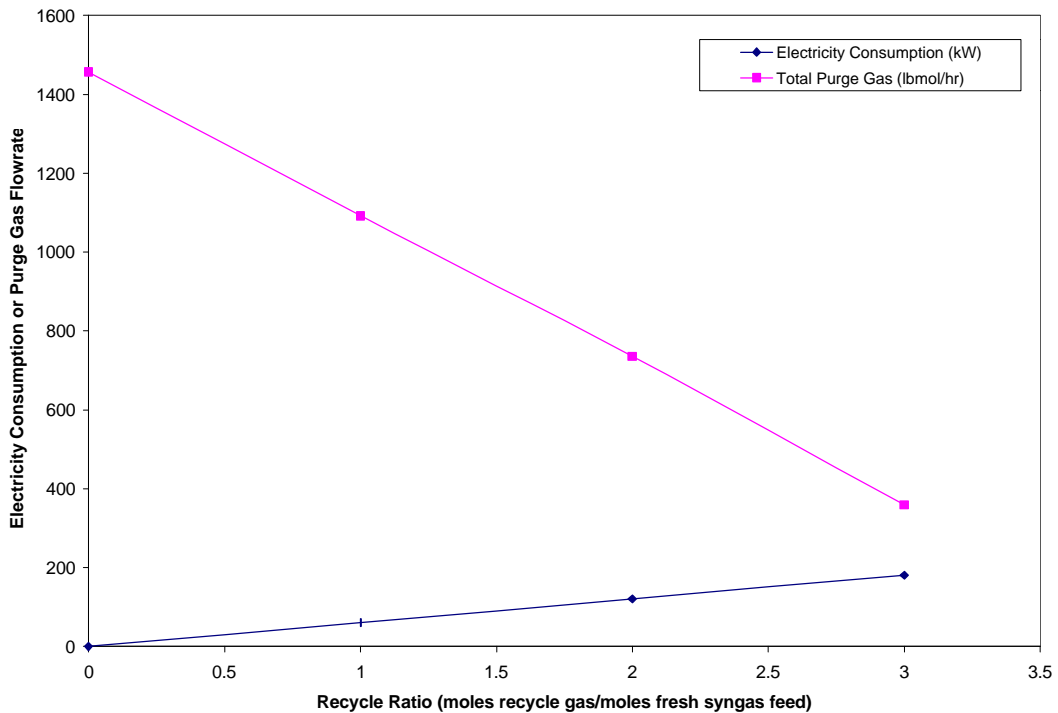


Figure 4-16. Results of Sensitivity of Recycle Ratio on Electricity Consumption in Recycle Gas Compressor and Purge Gas Flowrate for Texaco Syngas Being Used at Kingsport

4.11.3 Sensitivity Analysis on Syngas Produced by British Gas and Lurgi (BGL) Gasifier Fired with Coal

This section presents the sensitivity analysis results of individually changing P, SV, and R in LPMEOH process operating on syngas obtained from coal fired BGL gasifier, whose composition is presented in Table 4-26. Flowrate of syngas considered is 1805.2 lbmol/hr as in base case. A saturated steam is produced in methanol reactor whose pressure is held constant at 387.7 psia as in base case. Saturated steam at 100 psia is used in the methanol distillation whose pressure is also held constant during all the sensitivity cases.

Table 4-28 presents the results of the sensitivity analysis with P, SV and R as a variable. It should be noted that in varying reactor pressure, the pressure drops and temperatures across various process equipment are held constant as in Table 4-13. Following section presents the interpretation of the results of sensitivity analysis on pressure.

Table 4-28. Results of Sensitivity Analysis for Varying Pressure, Space Velocity, and Recycle Ratio in LPMEOH Process Operating on Syngas Obtained from Coal Fired BGL Gasifier^a

Parameters	Variation of P (psig) SV = 8827 SI/kg-hr (Constant) R = 3.22 (Constant)				Variation of SV (SI/kg-hr) P = 707 psig (Constant) R = 3.22 (Constant)			Variation of R P = 707 psig (Constant) SV = 8827 SI/kg-hr (Constant)			
	500	750	1000	1250	2000	4000	8000	0	1	2	3
Parameter Value											
CO Conversion per pass, %	3.11	3.82	4.22	4.46	4.26	4.04	3.76	6.19	5.30	4.50	3.81
Electricity Consumption (kW)	212	141	106	85	247.1	247.6	248.1	0	79.6	158.7	237.4
MeOH Production (lb/hr)	4920	6510	7550	8200	7590	7010	6370	1770	3620	5075	6150
Steam Production (lb/hr)	0	320	1390	2075	1490	850	160	750	1020	810	210
Steam Consumption (lb/hr)	3830	5030	5815	6300	5850	5410	4920	1360	2790	3920	4760
Net Steam Consumption (lb/hr)	3830	4710	4425	4225	4360	4560	4760	610	1770	3110	4550
<i>Purge Gas</i>											
Temperature (F)	99	99	99	99	99	99	99	99	99	99	99
Pressure (psia)	492.7	742.7	992.7	1242.7	692.7	699.7	699.7	699.7	699.7	699.7	699.7
Flowrate (lbmol/hr)											
H ₂	195	101	40	5	33	69.1	110	399	285	191	122
CO	901	850	820	800	820	844	860	991	930	895	861
N ₂	32.5	32.5	32.5	32.4	32.5	32.5	32.5	32.5	32.5	32.5	32.5
CH ₄	139	139	139	139	140	141	141	140.7	140.8	140.8	140.7
CO ₂	23.8	23.2	22.8	22.6	22.6	23	23.3	32.8	29.6	26.5	23.6
CH ₃ OH	13.9	9.8	8.1	7.3	9.6	9.9	10.3	13.4	12.2	11.2	10.4
H ₂ O	0.3	0.2	0.1	0.1	0.15	0.16	0.18	0.2	0.2	0.2	0.2
Total (lbmol/hr)	1305	1155	1062	1006	1058	1120	1177	1610	1430	1297	1190

^a Flowrate of syngas used is 1805.2 lbmol/hr for all the cases presented

4.11.3.1 Effect of Change in Reactor Pressure

This section presents the interpretation of the results of sensitivity analysis on pressure for the syngas obtained from coal fired BGL gasifier. Table 4-28 presents the results of the sensitivity analysis with reactor pressure as a variable. Since the syngas obtained from BGL gasifier firing coal has low H_2/CO ratio (0.51), the conversion of CO in the methanol reactor is quite small. There is a small increase in CO conversion with increase in pressure. However, methanol production increases because of large amount of combined feed entering the reactor. Because of increase in methanol production with reactor pressure, the amount of steam consumed in methanol distillation increases (Table 4-28)

At 500 psig reactor pressure, the conversion of syngas in the methanol reactor is very low because of low H_2/CO ratio in the syngas feed (Table 4-28). The amount of heat produced by the reactions taking place in the reactor is less than the amount of heat required in raising the reactants to the reactor temperature. As a result, the reactor requires a heat supply to sustain the reactions. Thus there is no steam production in the case of 500 psig reactor pressure as the reactor requires heat to raise the reactants to reactor temperature. Hence the reactor would not be operated at 500 psig pressure for the syngas obtained from coal fired BGL gasifier. At the pressure of 750 psig, the steam production is 320 lb/hr and increases with an increase in reactor pressure because the amount of syngas converted in the reactor increases. Net steam consumption in the

process first increases until the reactor pressure of 750 psig and then continues to decrease with increase in reactor pressure beyond 750 psig.

As the reactor pressure increases, the electricity consumption in the recycle gas compressor decreases for the same reason described in the case of Texaco syngas. Purge gas production decreases with the increase in reactor pressure because of increase in syngas conversion with pressure (Table 4-28).

Figures 4-17 and 4-18 present the results of sensitivity analysis of reactor pressure for the syngas obtained from coal fired BGL gasifier, graphically. The following section presents the interpretation of the results of sensitivity analysis on syngas space velocity.

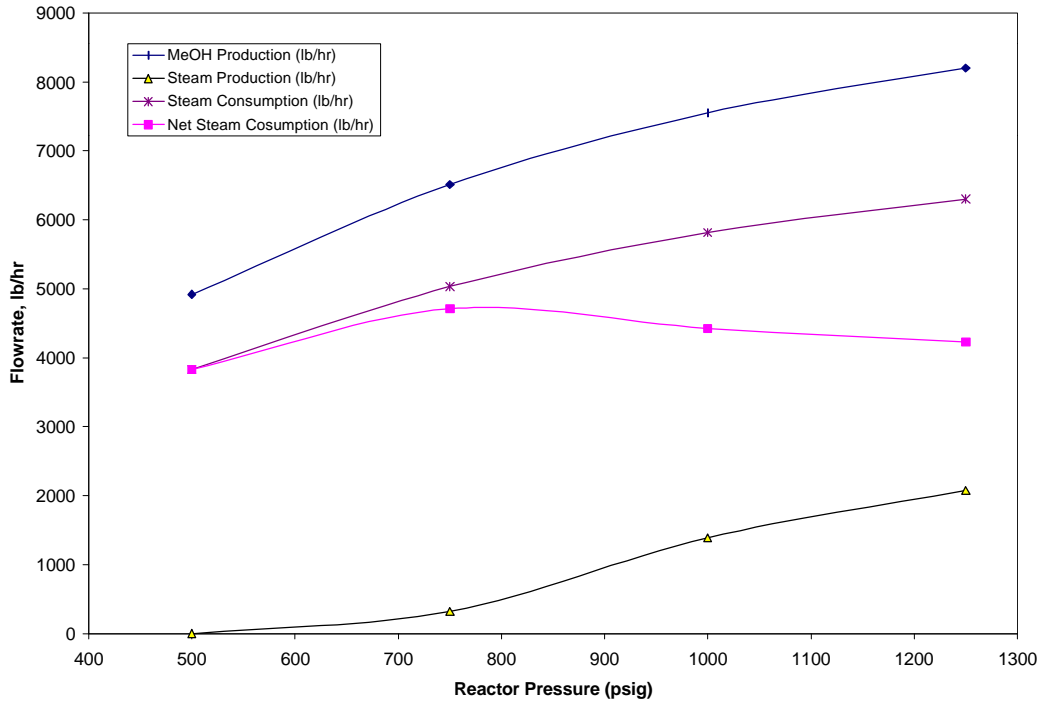


Figure 4-17. Results of Sensitivity of Reactor Pressure on Methanol Production, Steam Production, Steam Consumption, and Net Steam Consumption for the Syngas Obtained from Coal Fired BGL Gasifier

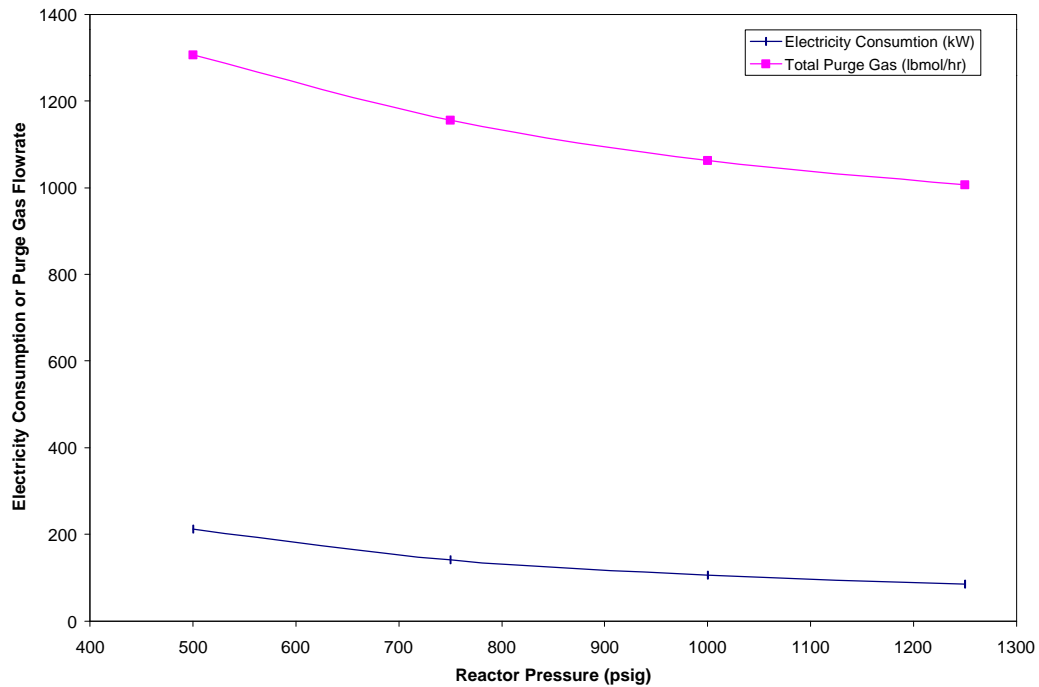


Figure 4-18. Results of Sensitivity of Reactor Pressure on Electricity Consumption in Recycle Gas Compressor and Purge Gas Flowrate for the Syngas Obtained from Coal Fired BGL Gasifier

4.11.3.2 Effect of Change in Syngas Space Velocity in Methanol Reactor

This section presents the interpretation of the results of sensitivity analysis on syngas space velocity for the syngas obtained from coal fired BGL gasifier. Table 4-28 presents the results of the sensitivity analysis with syngas space velocity as a variable.

As the syngas space velocity increases, the conversion of CO in methanol reactor decreases due to which the methanol production decreases. The amount of steam produced in the reactor decreases with increase in syngas space velocity because of decreasing syngas conversion. The steam consumption in methanol distillation decreases with increase in space velocity because of decreasing methanol production. The net consumption of steam increases with increasing space velocity (Table 4-28).

Electricity consumed in recycle gas compressor does not change with increases in space velocity primarily because the flowrate of recycle gas through the compressor remains the same. Purge gas production increases with increase in syngas space velocity because of decreasing syngas conversion in methanol reactor (Table 4-28).

Figures 4-19 and Figure 4-20 present the results of sensitivity analysis of syngas space velocity for the syngas obtained from coal fired BGL gasifier, graphically. The following section presents the interpretation of the results of sensitivity analysis on recycle ratio.

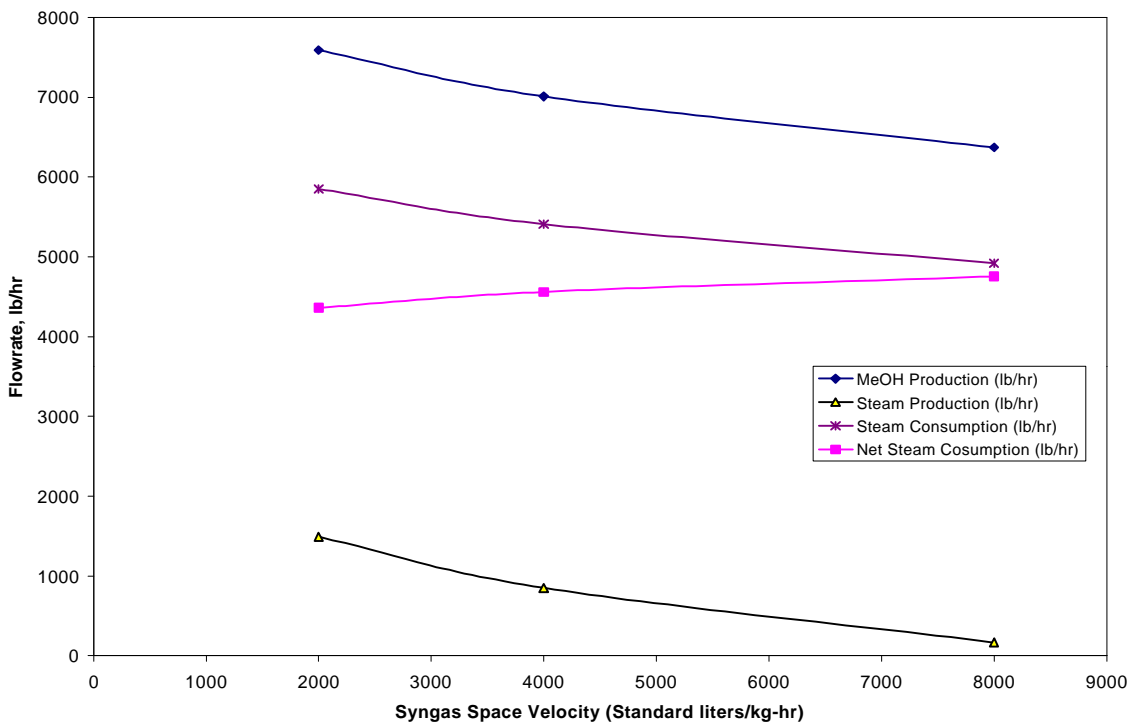


Figure 4-19. Results of Sensitivity of Syngas Space Velocity on Methanol Production, Steam Production, Steam Consumption, and Net Steam Consumption for the Syngas Obtained from Coal Fired BGL Gasifier

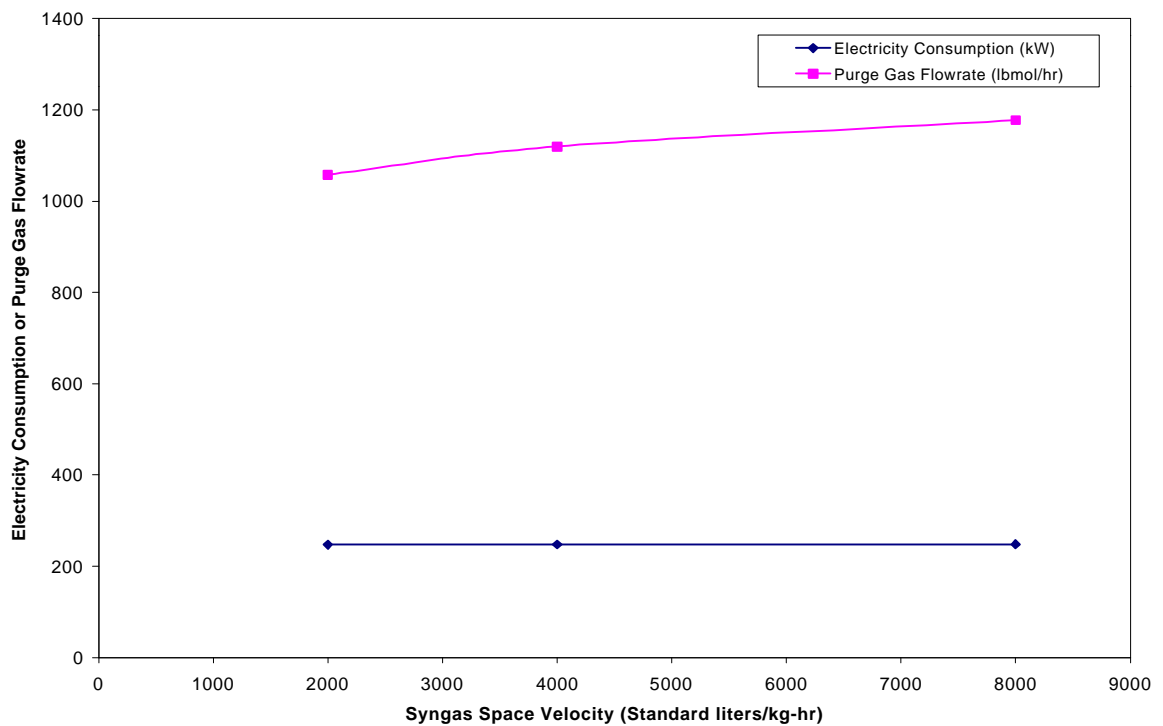


Figure 4-20. Results of Sensitivity of Syngas Space Velocity on Electricity Consumption in Recycle Gas Compressor and Purge Gas Flowrate for the Syngas Obtained from Coal Fired BGL Gasifier

4.11.3.3 Effect of Change in Recycle Ratio

This section presents the interpretation of the results of sensitivity analysis on recycle ratio for the syngas obtained from coal fired BGL gasifier. Table 4-28 presents the results of the sensitivity analysis with recycle ratio as a variable.

As the recycle ratio increases, the conversion of CO in methanol reactor decreases because of lower H₂/CO ratio combined syngas entering the reactor. Although the syngas conversion decreases with increasing recycle ratio, methanol production increases because of increasing amount of syngas entering the reactor (Table 4-28). The amount of steam consumed in distillation increases as the methanol production increases with increasing recycle ratio (Table 4-28)

The amount of steam produced in the reactor is highest for the recycle ratio of 1 because the conversion of syngas does not decrease much when recycle ratio increases from 0 to 1 but the flowrate of syngas through the reactor increases so more amount of syngas is converted and steam production increases. As the recycle ratio increases beyond 1, the conversion of syngas decreases and its flowrate through the reactor increases. A part of heat produced in the reactor is used in raising the temperature of reactants to the reactor temperature and with the increasing flow rate this part increases. As a result less heat is available for steam production, which therefore decreases as the recycle ratio increases from 1 to 3. Net steam consumption in the process increases with increasing recycle ratio (Table 4-28).

Electricity consumed in recycle gas compressor increases with increase in the recycle ratio because of increasing amount of recycle gas flowing through it (Table 4-28). Purge gas production decreases with increase in recycle ratio because the amount of syngas converted in methanol reactor to produce methanol increases due to increasing flowrate (Table 4-28).

Figures 4-21 and 4-22 present the results of sensitivity analysis of recycle ratio for the syngas obtained from coal fired BGL gasifier, graphically. The following section presents the sensitivity analysis of P, SV, and R for the syngas obtained from MSW fired BGL gasifier.

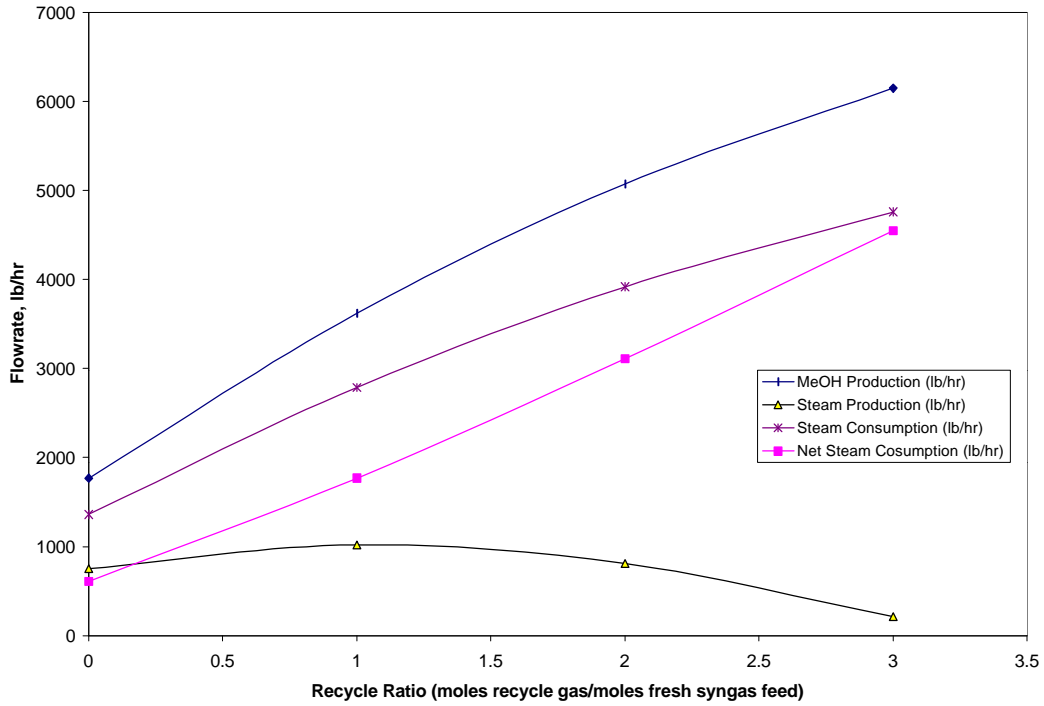


Figure 4-21. Results of Sensitivity of Recycle Ratio on Methanol Production, Steam Production, Steam Consumption, and Net Steam Consumption for the Syngas Obtained from Coal Fired BGL Gasifier

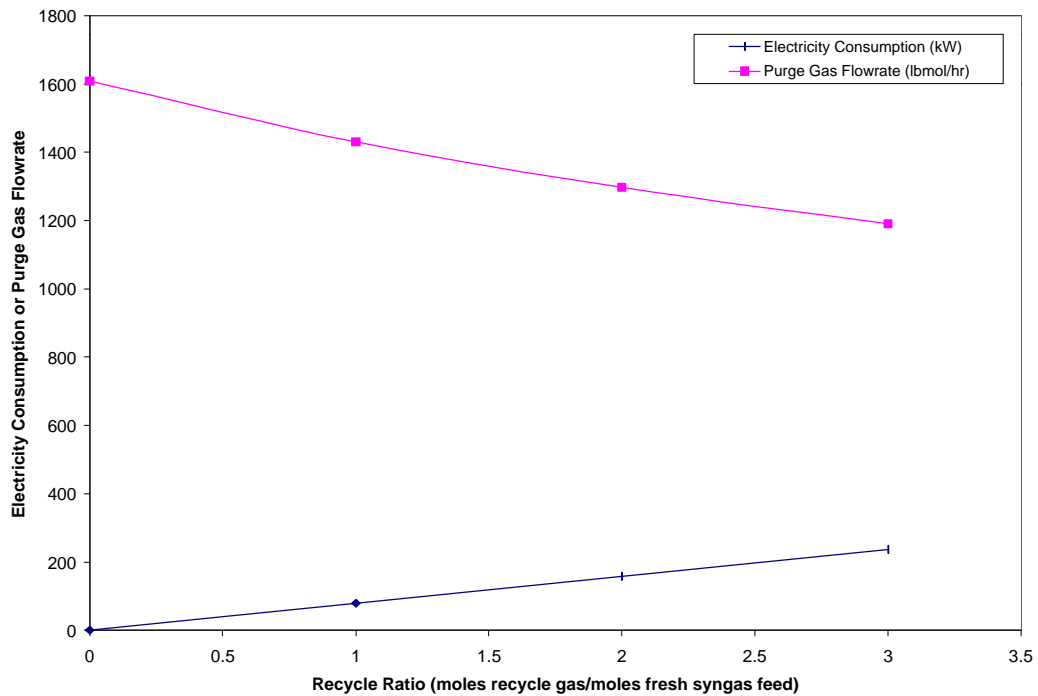


Figure 4-22. Results of Sensitivity of Syngas Recycle Ratio on Electricity Consumption in Recycle Gas Compressor and Purge Gas Flowrate for the Syngas Obtained from Coal Fired BGL Gasifier

4.11.4 Sensitivity Analysis on Syngas Produced by Municipal Solid Waste (MSW) Fired British Gas and Lurgi (BGL) Gasifier

This section presents the sensitivity analysis results of individually changing P, SV, and R in LPMEOH process operating on syngas obtained from a blend of coal and refuse derived fuel (RDF), which is referred to here as the MSW fired BGL gasifier. The composition of the syngas derived from MSW is presented in Table 4-26. Flowrate of syngas considered is 1805.2 lbmol/hr as in base case. A saturated steam is produced in methanol reactor whose pressure is held constant at 387.7 psia as in base case. Saturated steam at 100 psia is used in the methanol distillation whose pressure is also held constant during all the sensitivity cases.

Table 4-29 presents the results of the sensitivity analysis with P, SV and R as a variable. It should be noted that in varying reactor pressure, the pressure drops and temperatures across various process equipment are held constant as in Table 4-13. Following section presents the interpretation of the results of sensitivity analysis on pressure

Table 4-29. Results of Sensitivity Analysis for Varying Pressure, Space Velocity, and Recycle Ratio in LPMEOH Process Operating on Syngas Obtained from MSW Fired BGL Gasifier^a

Results of Simulation	Variation of P (psig)				Variation of SV (SI/kg-hr)			Variation of R			
	SV = 8827 SI/kg-hr (Constant) R = 3.22 (Constant)				P = 707 psig (Constant) R = 3.22 (Constant)			P = 707 psig (Constant) SV = 8827 SI/kg-hr (Constant)			
Parameter Value	500	750	1000	1250	2000	4000	8000	0	1	2	3
CO Conversion per pass, %	4.37	5.39	5.96	6.29	6.03	5.72	5.33	8.35	7.3	6.29	5.38
Electricity Consumption (kW)	205	137	102	82	242	242.4	243	0	76.5	153	230
MeOH Production (lb/hr)	5780	7690	8980	9860	9070	8320	7520	2050	4180	5910	7250
Steam Production (lb/hr)	0	1570	2930	3870	3060	2260	1400	1050	1630	1730	1360
Steam Consumption (lb/hr)	4480	5930	6910	7560	6980	6410	5800	1570	3210	4550	5600
Net Steam Consumption (lb/hr)	4480	4360	3980	3690	3920	4150	4400	520	1580	2820	4240
<i>Purge Gas</i>											
Temperature (F)	99	99	99	99	99	99	99	99	99	99	99
Pressure (psia)	492.7	742.7	992.7	1242.7	699.7	699.7	699.7	699.7	699.7	699.7	699.7
Flowrate (lbmol/hr)											
H ₂	291	178	100	47	92	139	187	532	399	290	205
CO	701	647	611	583	606	628	652	807	745	696	659
N ₂	47	46.9	46.8	46.8	46.8	46.8	46.8	46.9	46.9	46.9	46.9
CH ₄	151	151	151	151	151.8	151.6	151.2	151	151	151	151
CO ₂	23.5	22.6	22.1	21.7	21.8	22.3	22.7	32.9	29.5	26.2	23.13
CH ₃ OH	12.9	8.8	7	6.1	8.3	8.7	9.2	12.9	11.5	10.3	9.4
H ₂ O	0.2	0.1	0.08	0.07	0.11	0.12	0.13	0.16	0.15	0.14	0.14
Total (lbmol/hr)	1226	1054	938	856	927	997	1069	1580	1380	1220	1090

^a Flowrate of syngas used is 1805.2 lbmol/hr for all the cases presented

4.11.4.1 Effect of Change in Reactor Pressure

This section presents the interpretation of the results of sensitivity analysis on pressure for the syngas obtained from MSW fired BGL gasifier. Table 4-29 presents the results of the sensitivity analysis with reactor pressure as a variable.

As the syngas obtained from BGL gasifier firing MSW has low H_2/CO ratio (0.78), the conversion of CO in the methanol reactor is quite small but greater than that for syngas derived from coal fired BGL gasifier. The trends in the sensitivity results with varying reactor pressure in case of syngas obtained from MSW are similar to that for syngas derived from coal discussed in previous section and are not detailed here.

Figures 4-23 and 4-24 present the results of sensitivity analysis of reactor pressure for the syngas obtained from MSW fired BGL gasifier, graphically. The following section presents the interpretation of the results of sensitivity analysis on syngas space velocity.

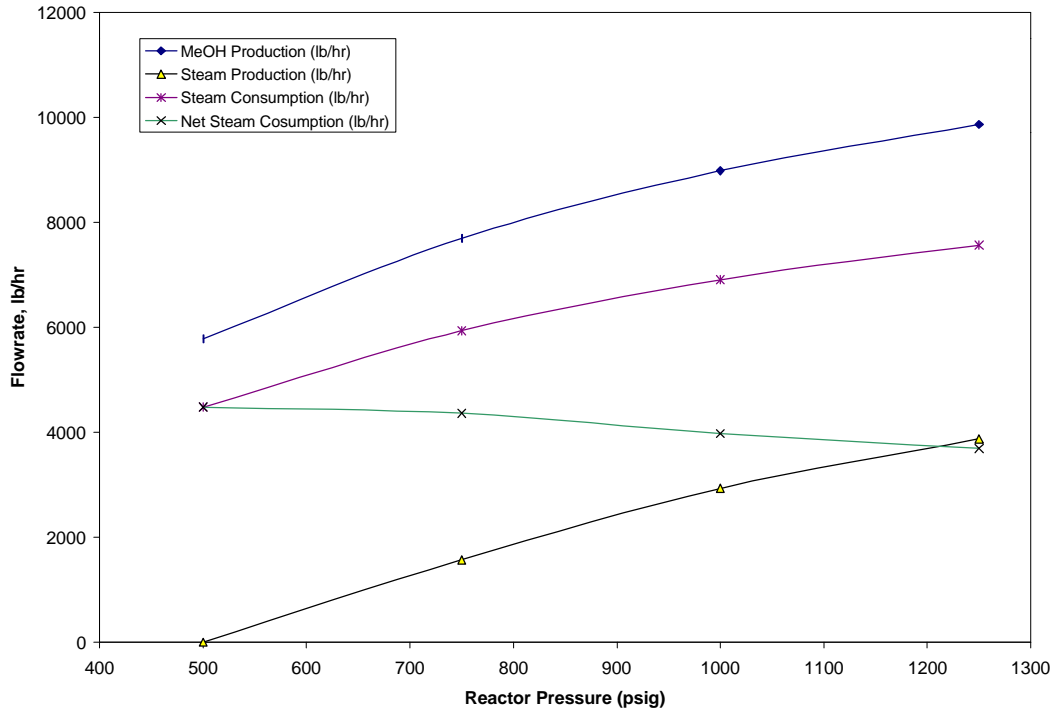


Figure 4-23. Results of Sensitivity of Reactor Pressure on Methanol Production, Steam Production, Steam Consumption, and Net Steam Consumption for the Syngas Obtained from MSW Fired BGL Gasifier

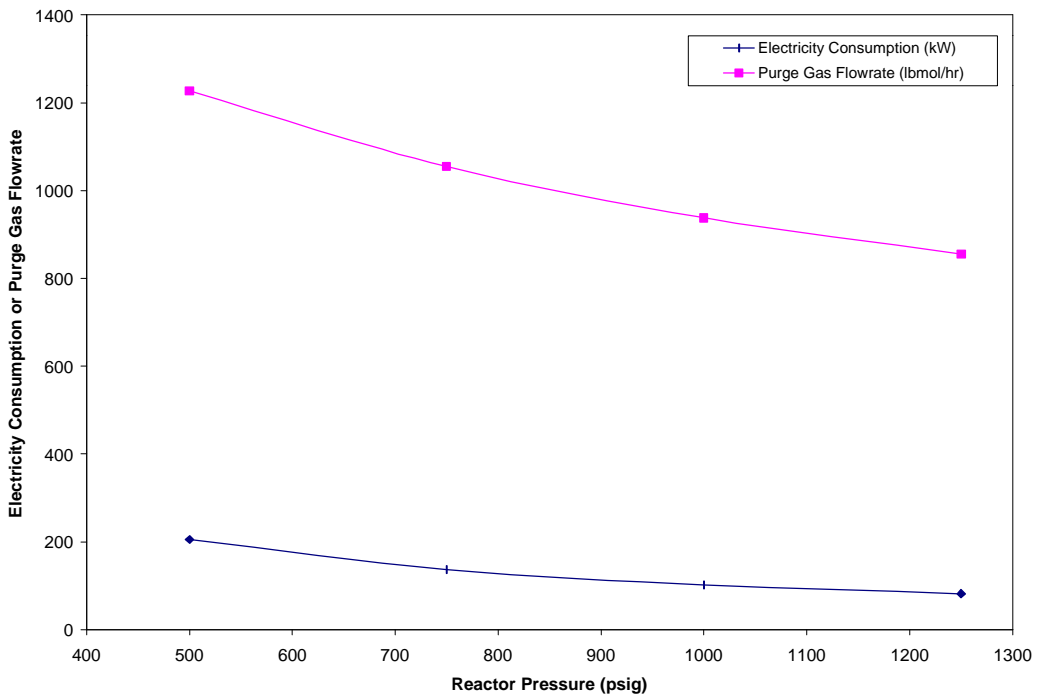


Figure 4-24. Results of Sensitivity of Reactor Pressure on Electricity Consumption in Recycle Gas Compressor and Purge Gas Flowrate for the Syngas Obtained from MSW Fired BGL Gasifier

4.11.4.2 Effect of Change in Syngas Space Velocity in Methanol Reactor

This section presents the interpretation of the results of sensitivity analysis on syngas space velocity for the syngas obtained from MSW fired BGL gasifier. Table 4-29 presents the results of the sensitivity analysis with syngas space velocity as a variable.

As the syngas space velocity increases, the conversion of CO in methanol reactor decreases due to which the methanol production decreases. The amount of steam produced in the reactor decreases with increase in syngas space velocity because of decreasing syngas conversion. The steam consumption in methanol distillation decreases with increase in space velocity because of decreasing methanol production. The net consumption of steam increases with increasing space velocity (Table 4-29).

Electricity consumed in recycle gas compressor does not change with increases in space velocity primarily because the flowrate of recycle gas through the compressor remains the same (Table 4-29). Purge gas production increases with increase in syngas space velocity because of decreasing syngas conversion (Table 4-29).

Figures 4-25 and 4-26 present the results of sensitivity analysis of syngas space velocity for the syngas obtained from MSW fired BGL gasifier, graphically. The following section presents the interpretation of the results of sensitivity analysis on recycle ratio.

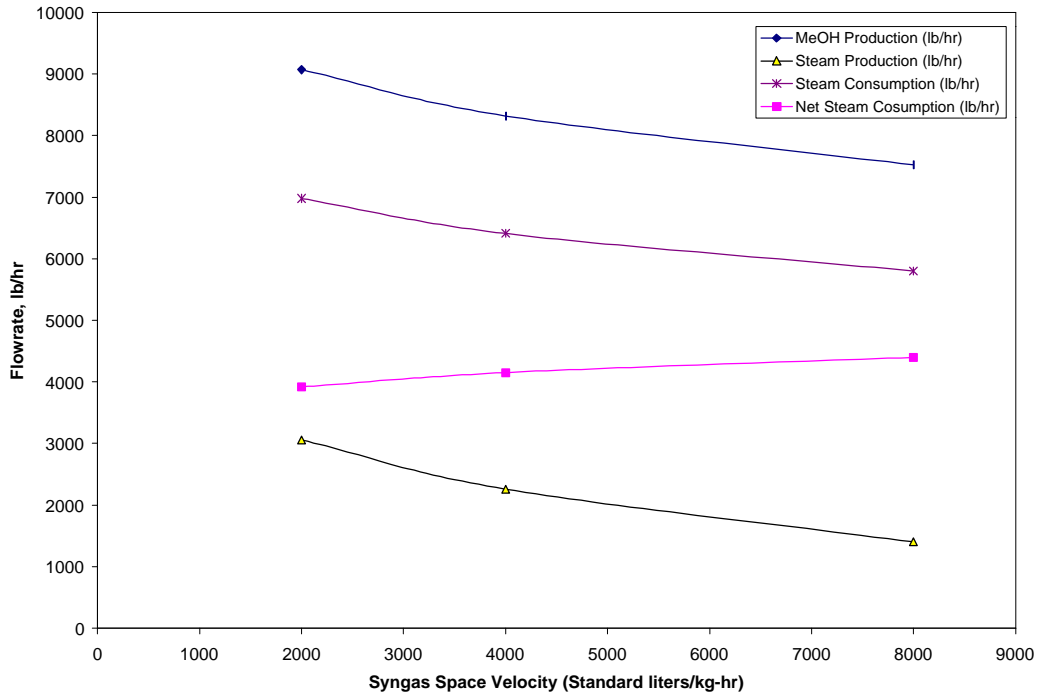


Figure 4-25. Results of Sensitivity of Syngas Space Velocity on Methanol Production, Steam Production, Steam Consumption, and Net Steam Consumption for the Syngas Obtained from MSW Fired BGL Gasifier

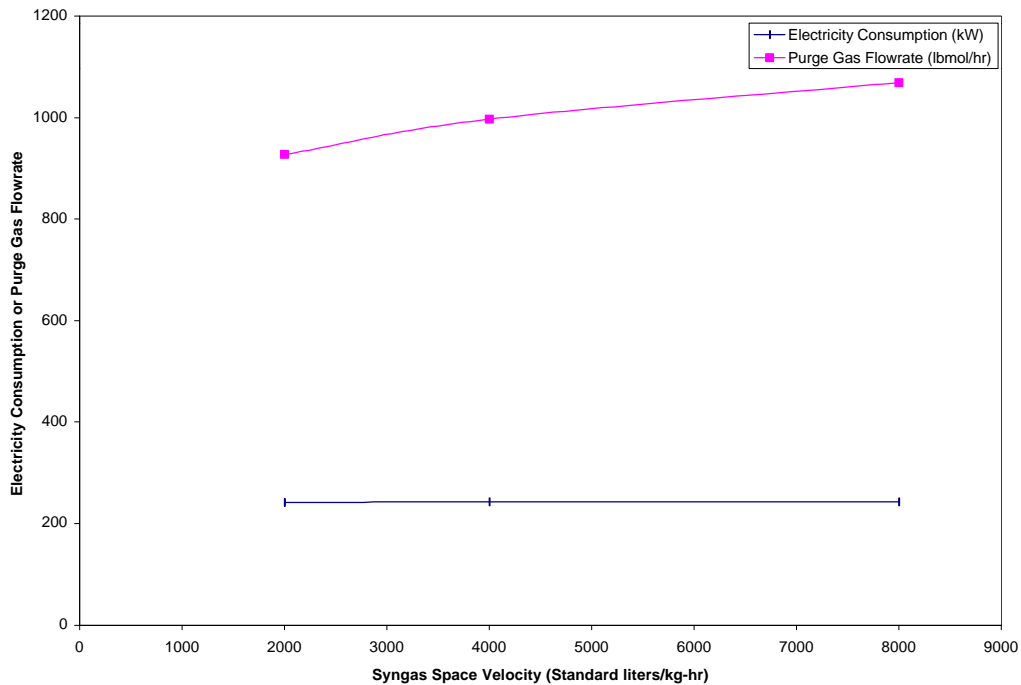


Figure 4-26. Results of Sensitivity of Reactor Pressure on Electricity Consumption in Recycle Gas Compressor and Purge Gas Flowrate for the Syngas Obtained from MSW Fired BGL Gasifier

4.11.4.3 Effect of Change in Recycle Ratio

This section presents the interpretation of the results of sensitivity analysis on recycle ratio for the syngas obtained from MSW fired BGL gasifier. Table 4-29 presents the results of the sensitivity analysis with recycle ratio as a variable.

As the recycle ratio increases, the conversion of CO in methanol reactor decreases because of lower H₂/CO ratio in combined syngas entering the reactor. Although the syngas conversion decreases with increasing recycle ratio, methanol production increases because of increasing amount of syngas entering the reactor (Table 4-29). The amount of steam consumed in distillation increases as the methanol production increases with increasing recycle ratio (Table 4-29)

The amount of steam produced in the reactor first increases until certain recycle ratio and then decreases as the recycle ratio increase beyond that. This is explained on the same reasoning as for the syngas derived from coal fired BGL gasifier. Net steam consumption in the process increases with increasing recycle ratio (Table 4-29). Electricity consumption and purge gas production show similar trends as obtained for syngas derived from coal fired BGL gasifier (Table 4-29).

Figures 4-27 and 4-28 present the results of sensitivity analysis of recycle ratio for the syngas obtained from MSW fired BGL gasifier, graphically.

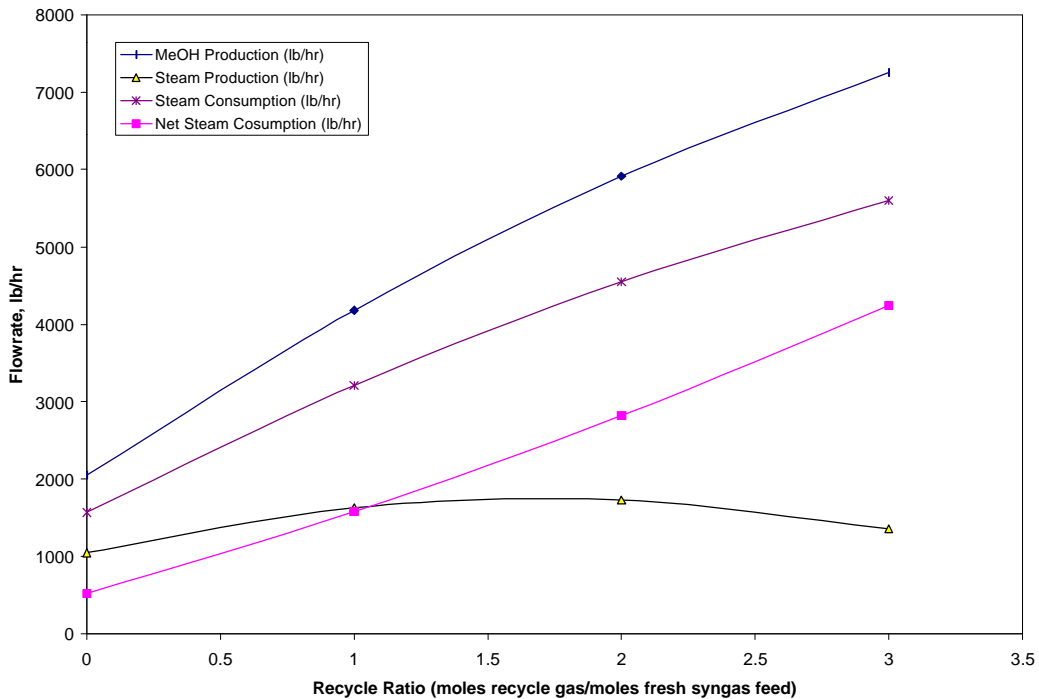


Figure 4-27. Results of Sensitivity of Recycle Ratio on Methanol Production, Steam Production, Steam Consumption, and Net Steam Consumption for the Syngas Obtained from MSW Fired BGL Gasifier

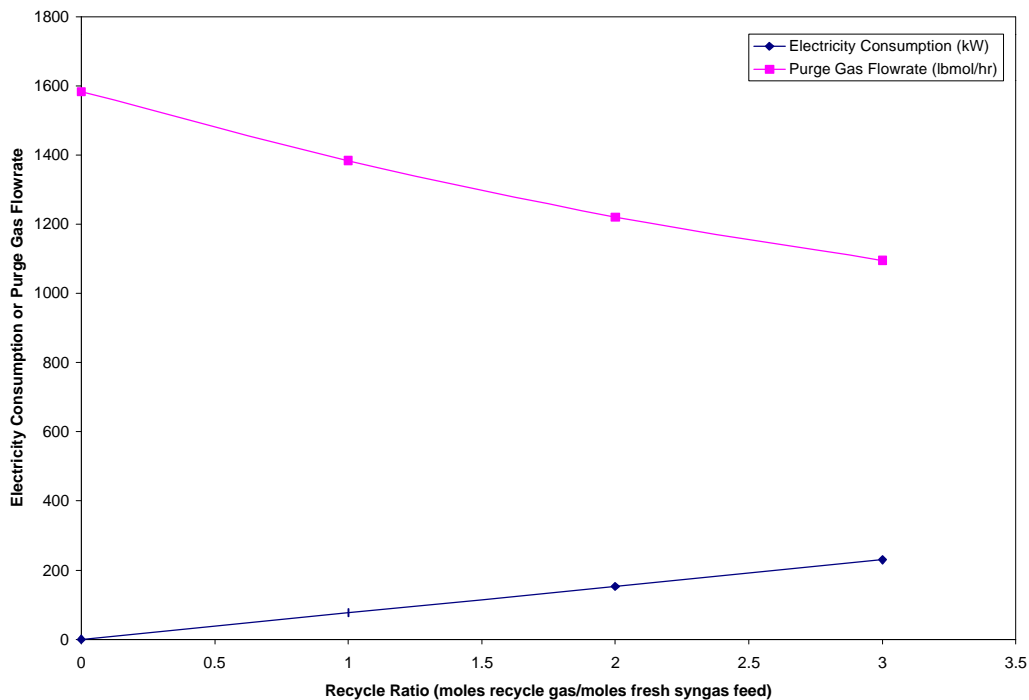


Figure 4-28. Results of Sensitivity of Syngas Recycle Ratio on Electricity Consumption in Recycle Gas Compressor and Purge Gas Flowrate for the Syngas Obtained from MSW Fired BGL Gasifier

4.11.5 Comparison of Sensitivity Results Among Various Syngas Compositions Considered

This section compares the results of sensitivity analysis obtained for 3 different syngas compositions considered for a single case of reactor pressure, syngas space velocity and recycle ratio. The case is chosen arbitrarily to be the one with reactor pressure equal to 750 psig, space velocity equal to 8827 standard liters/kg-hr, and recycle ratio equal to 3.22 moles recycle gas/moles fresh syngas feed. Three syngas compositions considered are: (1) Texaco syngas being used at Kingsport; (2) syngas obtained from a coal fired BGL gasifier; and (3) syngas obtained from a MSW fired BGL gasifier.

Sections 4.11.2 to Section 4.11.4 present the sensitivity analysis on the above three syngas compositions including the case with reactor pressure of 750 psig, syngas space velocity of 8827 standard liters/kg-hr and recycle ratio of 3.22 moles recycle gas/moles fresh syngas feed. Figures 4-29 and 4-30 present the comparison of results obtained for three syngas compositions considered.

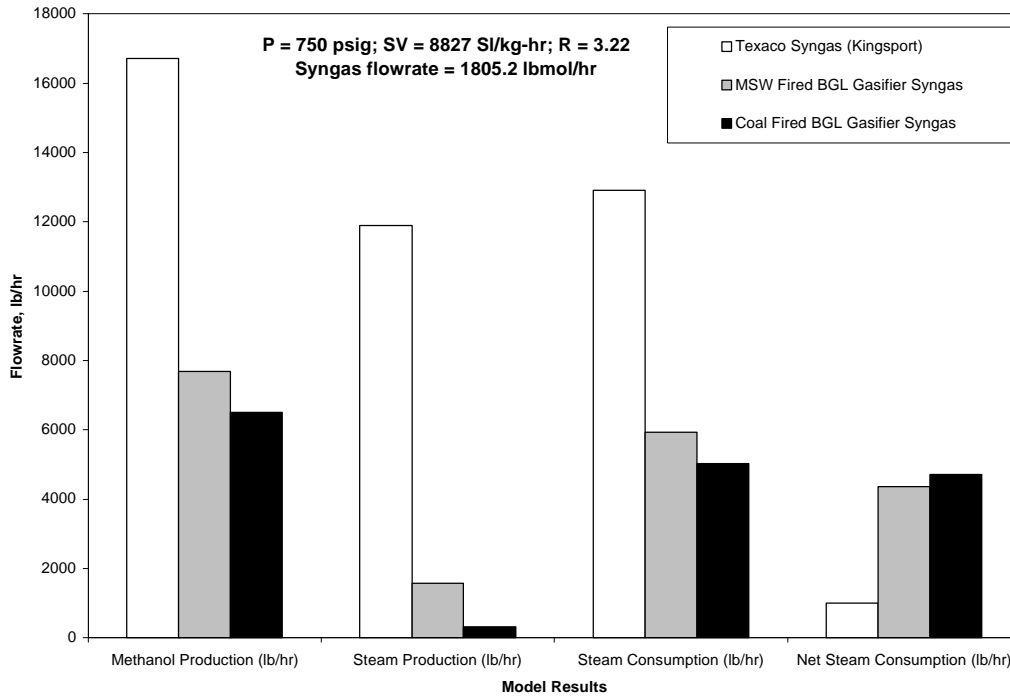


Figure 4-29. Comparison of Methanol Production, Stream Production, Steam Consumption, Net Steam Consumption for: (1) Texaco Syngas (Kingsport); (2) MSW Fired BGL Gasifier Syngas; and (3) Coal Fired BGL Gasifier Syngas

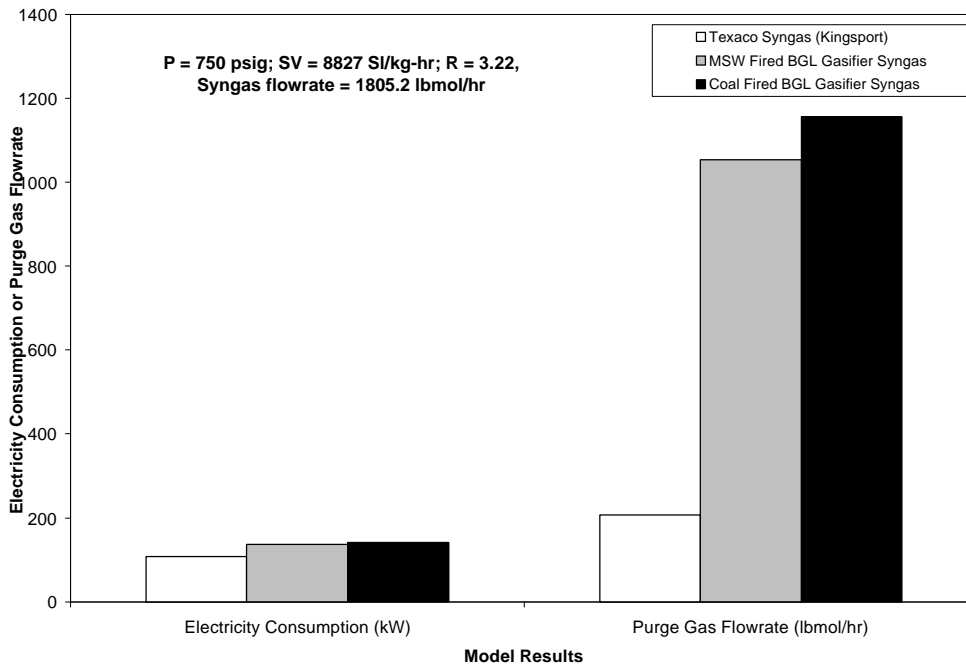


Figure 4-30. Comparison of Electricity Consumption and Purge Gas Production for: (1) Texaco Syngas (Kingsport); (2) MSW Fired BGL Gasifier Syngas; and (3) Coal Fired BGL Gasifier Syngas

The main difference between the three syngas compositions is their H_2/CO molar ratio. Texaco syngas has the H_2/CO ratio of 2.25 (highest), syngas derived from MSW has H_2/CO ratio of 0.78, and syngas derived from coal has H_2/CO ratio of 0.51 (lowest). From Figure 4-29, it is clear that for same fresh syngas flowrate (1805.2 lbmol/hr) and same conditions of reactor pressure, syngas space velocity, and recycle ratio, the Texaco syngas produces the most methanol and the syngas derived from coal produces the least amount of methanol. Thus as the H_2/CO ratio of the fresh syngas feed decreases, the methanol production decreases because there is less syngas conversion in the methanol reactor due to decreasing H_2/CO ratio of syngas feed. Also the steam consumption in methanol reactor decreases as the H_2/CO ratio of the syngas decreases because methanol production decreases. Steam production in the methanol also decreases with decreasing H_2/CO ratio in the fresh syngas feed for the same reason as that in methanol production. Net steam consumption, however, increases with decreasing H_2/CO ratio of the fresh syngas feed.

In Figure 4-30, it is clear that electricity consumption in the recycle gas compressor increases with decrease in H_2/CO ratio because for the same molar flowrate through the compressor, the syngas with higher H_2/CO has lower mass flowrate, so the compressor has to do less work in compressing it than the recycle gas with lower H_2/CO ratio. Purge gas flowrate increases with decreasing H_2/CO ratio because the syngas conversion in the reactor decreases.

Based on the sensitivity analysis of LPMEOH process model, it is found that methanol production, steam consumption, steam production, electricity consumption, and purge gas production are sensitive to reactor pressure, syngas space velocity, and recycle ratio. For the syngas compositions with lower H_2/CO ratio such as coal and MSW derived syngas, it is recommended that the reactor be operated at or above 750 psig pressure since at lower pressure such as 500 psig, the syngas conversion in the reactor is very limited and reactions would not occur unless the reactor is supplied with heat. Also there is no steam production in the LPMEOH reactor at pressure of 500 psig for coal and MSW derived syngas which defeats the purpose of having internal heat exchanger in the reactor for heat removal.

The sensitivity analysis indicate that there is a clear advantage to recycling the unconverted syngas to the methanol reactor, since there is more production of methanol for the case with a recycle than the case with no recycle. This holds true for all three syngas compositions considered. Also as the H_2/CO ratio of the fresh syngas decreases from Texaco syngas (2.25) to that of coal derived syngas (0.51), there is a decrease in methanol production. Thus it would be desirable to adjust the H_2/CO ratio of the fresh syngas feed through a water-gas shift reaction so that the H_2/CO ratio increases and there is higher methanol production. This would require inclusion of a water-gas shift reactor prior to the LPMEOH process section or some modification within the LPMEOH methanol reactor itself to incorporate water gas shift reaction for the syngas feeds limited in hydrogen content. The actual steps to be incorporated will require detailed economic analysis and is beyond the scope of this study.

The following section presents the sensitivity analysis of the LCI of methanol produced by LPMEOH process.

4.11.6 Sensitivity Analysis of the LCI of Methanol

This section presents the results of sensitivity analysis of LCI of methanol based on the results obtained from LPMEOH process model. Four main cases considered for the sensitivity analysis on the LCI of methanol are: (1) effect of reactor pressure; (2) effect of syngas space velocity; (3) effect of recycle ratio; (4) effect of syngas composition. Texaco syngas is arbitrarily chosen to demonstrate the sensitivity analysis on 2 cases of reactor pressures, 750 psig, and 1000 psig; 2 cases of syngas space velocities, 4000 standard liters/kg-hr and 8000 standard liters/kg-hr; and 2 cases of recycle ratio, 2 moles recycle gas/moles fresh syngas feed and 3 moles recycle gas/moles fresh syngas feed. For the case of sensitivity analysis on syngas composition, reactor pressure of 750 psig, syngas space velocity of 8827 standard liters/kg-hr, and a recycle ratio of 3.22 moles recycle gas/moles fresh syngas feed are chosen, arbitrarily.

The following section presents the results of sensitivity analysis on LCI of methanol with change in reactor pressure. The results that are relevant from LCI standpoint are: (1) electricity consumption; (2) net steam consumption in the process; (3) steam production from 99 percent purge gas combustion in boiler; (4) purge gas emissions after 99 percent purge gas combustion, and (5) methanol production. Since the LPMEOH process model does not have a capability to calculate fugitive emissions, storage tank emissions, and BOD removal emissions, they are assumed to be constant.

4.11.6.1 Effect of Change in Reactor Pressure on the LCI of Methanol

This section presents the results of sensitivity analysis on the LCI of methanol with change in reactor pressure for the Texaco syngas being used at Kingsport. Two reactor pressures considered are: (1) 750 psig, and (2) 1000 psig. Table 4-30 presents the results as obtained in Section 4.11.2.1 on per kg of methanol produced basis for reactor pressure of 750 psig and 1000 psig.

From Table 4-30, it is clear that as pressure increases from 750 psig to 1000 psig, the electricity consumed per kg of methanol decreases. Net steam consumption per kg of methanol also decreases with an increase in pressure. As the pressure increases from 750 psig to 1000 psig, purge gas production per kg of methanol decreases so the purge gas emissions (one percent of total purge gas produced) also decrease. As the purge gas production decreases with increasing pressure, less steam per kg of methanol is produced by 99 percent combustion of purge gases.

Table 4-31 presents the overall LCI of methanol for both the reactor pressures of 750 psig and 1000 psig.

Table 4-30. Sensitivity Results for Texaco Syngas on per kg of Methanol Produced Basis for Reactor Pressure of 750 psig and 1000 psig.

Model Results per kg of Methanol Produced	Reactor Pressure (psig)	
	750	1000
Electricity Consumption (kWh/kg methanol)	1.43E-02	1.01E-02
Net Steam Consumption in Process (kg/kg methanol)	5.99E-02	3.07E-02
Purge Gas Steam Production (MJ/kg methanol) ^a	1.95E+00	6.88E-01
Purge Gas Emissions (kg/kg methanol) ^b		
H ₂	1.64E-04	6.73E-05
CO	7.21E-04	1.27E-04
CH ₄	5.17E-06	4.83E-06
CH ₃ OH	2.57E-05	8.94E-06
N ₂	8.81E-02	2.67E-02
CO ₂ ^c	1.62E-01	6.03E-02
H ₂ O	1.50E-01	6.20E-02

^aSteam produced in boiler due to 99 percent purge gas combustion

^bPurge gas emissions are based on 99 percent combustion efficiency in steam boiler

^cIncludes CO₂ produced after 99 percent purge gas combustion in steam boiler

Table 4-31. The LCI of Methanol for Reactor Pressures of 750 psig and 1000 psig in LPMEOH Process Using Texaco Syngas

Air Emissions	P = 750 psig	P = 1000 psig
PM	-3.55E-05	-3.91E-06
SO ₂	-8.88E-04	-2.51E-04
NO _x	-1.39E-04	-2.20E-05
CO	5.23E-04	7.94E-05
CO ₂ (fossil)	3.99E-02	4.33E-02
CH ₄	-2.10E-04	-5.35E-05
HCl	4.58E-07	6.42E-07
Methanol	9.14E-05	7.47E-05
Liquid Emissions		
Suspended Solids	-1.69E-05	-1.33E-06
BOD	6.42E-04	6.43E-04
COD	-9.56E-06	-3.01E-06
Solid Waste	-7.98E-03	9.65E-04

In Table 4-31, it is clear that as reactor pressure increases from 750 psig to 1000 psig, the LCI parameters that are positive in sign increase in magnitude except that for CO and methanol. The CO and methanol emissions are higher in case of 750 psig case because of a higher amount of CO and methanol (per kg of methanol produced) are present in the uncombusted purge gas emitted from boiler. Some of the LCI parameters are negative which means that they are avoided. The avoided emissions in case of 750 psig case are more than 1000 psig case. For example 750 psig pressure case avoids one order of magnitude more PM emissions than 1000 psig case. For the case of 750 psig pressure, steam production (per kg of methanol produced) by purge gas combustion is higher than that for 1000 psig pressure case. Higher steam production due to purge gas combustion causes more emission offsets in case of 750 psig case than 1000 psig case.

4.11.6.2 Effect of Change in Syngas Space Velocity on the LCI of Methanol

This section presents the results of sensitivity analysis on the LCI of methanol with change in syngas space velocity for the Texaco syngas being used at Kingsport. Two syngas space velocities considered are: (1) 4000 standard liters/kg-hr, and (2) 8000 standard liters/kg-hr. Table 4-32 presents the results as obtained in Section 4.11.2.2 on per kg of methanol produced basis for space velocities of 4000 standard liters/kg-hr and 8000 standard liters/kg-hr.

From Table 4-32, it is clear that as syngas space velocity increases from 4000 standard liters/kg-hr to 8000 standard liters/kg-hr, the electricity consumed per kg of methanol increases because the methanol production decreases. Net steam consumption per kg of methanol increases with increase in pressure. As the space velocity increases from 4000 standard liters/kg-hr to 8000 standard liters/kg-hr, purge gas production per kg of methanol increases so the purge gas emissions (one percent of total purge gas produced) also increases. As the purge gas production increases with increasing space velocity, more steam per kg of methanol is produced by 99 percent combustion of purge gases in boiler.

Table 4-33 presents the overall LCI of methanol for both the space velocities of 4000 standard liters/kg-hr and 8000 standard liters/kg-hr.

Table 4-32. Sensitivity Results for Texaco Syngas on per kg of Methanol Produced Basis for Syngas Space Velocities of 4000 standard liters/kg-hr and 8000 standard liters/kg-hr

Model Results per kg of Methanol Produced	Syngas Space Velocity (Standard liters/kg-hr)	
	4000	8000
Electricity Consumption (kWh/kg methanol)	2.33E-02	2.56E-02
Net Steam Consumption in Process (kg/kg methanol)	3.63E-02	7.30E-02
Purge Gas Steam Production (MJ/kg methanol) ^a	7.43E-01	2.42E+00
Purge Gas Emissions (kg/kg methanol) ^b		
H ₂	6.98E-05	2.00E-04
CO	1.69E-04	9.43E-04
CH ₄	4.92E-06	5.40E-06
CH ₃ OH	1.07E-05	3.34E-05
N ₂	3.10E-02	1.12E-01
CO ₂ ^c	6.25E-02	2.01E-01
H ₂ O	6.45E-02	1.83E-01

^aSteam produced in boiler due to 99 percent purge gas combustion

^bPurge gas emissions are based on 99 percent combustion efficiency in steam boiler

^cIncludes CO₂ produced after 99 percent purge gas combustion in steam boiler

Table 4-33. The LCI of Methanol for Syngas Space Velocities of 4000 SI/kg-hr and 8000 SI/kg-hr in LPMEOH Process Using Texaco Syngas

Air Emissions	SV = 4000 SI/kg-hr	SV = 8000 SI/kg-hr
PM	5.44E-06	-3.93E-05
SO ₂	-2.09E-04	-1.07E-03
NO _x	6.03E-06	-1.58E-04
CO	1.20E-04	6.93E-04
CO ₂ (fossil)	5.05E-02	4.64E-02
CH ₄	-4.02E-05	-2.53E-04
HCl	1.26E-06	8.62E-07
Methanol	7.65E-05	9.91E-05
Liquid Emissions		
Suspended Solids	3.78E-06	-1.84E-05
BOD	6.43E-04	6.41E-04
COD	-2.95E-06	-1.18E-05
Solid Waste	2.23E-03	-1.01E-02

In Table 4-33 it is clear that as syngas space velocity increases, the CO and methanol emission per kg of methanol produced increase because of increases in purge gas production. Some of the LCI parameters are negative which means that they are avoided. The avoided emissions in case of 8000 SI/kg-hr space velocity case are more than 4000 SI/kg-hr case. For the case of 8000 SI/kg-hr space velocity, steam production (per kg of methanol produced) by purge gas combustion is higher than that for 4000 SI/kg-hr space velocity case. Higher steam production due to purge gas combustion causes more emission offsets in case of 8000 SI/kg-hr space velocity. Carbon dioxide emission in case of 8000 SI/kg-hr space velocity is less than that of 4000 SI/kg-hr space velocity case because of more avoided CO₂ emissions due to higher steam production from purge gas combustion. Other LCI parameters are similarly explained.

4.11.6.3 Effect of Change in Recycle Ratio on the LCI of Methanol

This section presents the results of sensitivity analysis on the LCI of methanol with change in recycle ratio for the Texaco syngas being used at Kingsport. Two recycle ratios considered are: (1) 2 moles recycle gas/moles fresh syngas feed, and (2) 3 moles recycle gas/moles fresh syngas feed. Table 4-34 presents the results as obtained in Section 4.11.2.3 on per kg of methanol produced basis for the recycle ratio of 2 moles recycle gas/moles fresh syngas feed and 3 moles recycle gas/moles fresh syngas feed.

From Table 4-34, it is clear that as recycle ratio increases from 2 to 3, the electricity consumed per kg of methanol increases because the compressor has to recycle more unreacted gases where as the methanol production does not increased in same proportion. Net steam consumption per kg of methanol increases with increase in recycle ratio. As the recycle ratio increases from 2 to 3, purge gas production per kg of methanol decreases because of higher syngas conversion in methanol reactor. Therefore the purge gas emissions (one percent of total purge gas produced) also decrease. As the purge gas decreases with increasing recycle ratio, less amount of steam per kg of methanol is produced by 99 percent combustion of purge gases in boiler.

Table 4-35 presents the overall LCI of methanol for the recycle ratio of 2 moles recycle gas/moles fresh syngas feed and 3 moles recycle gas/moles fresh syngas feed.

Table 4-34. Sensitivity Results for Texaco Syngas on per kg of Methanol Produced Basis for Recycle Ratios of 2 moles recycle/moles fresh feed and 3 moles recycle/moles fresh feed

Model Results per kg of Methanol Produced	Recycle Ratio (moles recycle/moles fresh feed)	
	2	3
Electricity Consumption (kWh/kg methanol)	2.39E-02	2.64E-02
Net Steam Consumption in Process (kg/kg methanol)	7.39E-02	8.61E-02
Purge Gas Steam Production (MJ/kg methanol) ^a	1.13E+01	3.93E+00
Purge Gas Emissions (kg/kg methanol) ^b		
H ₂	8.83E-04	3.17E-04
CO	5.10E-03	1.63E-03
CH ₄	7.64E-06	5.62E-06
CH ₃ OH	1.50E-04	5.30E-05
N ₂	5.40E-01	1.83E-01
CO ₂ ^c	9.32E-01	3.23E-01
H ₂ O	8.05E-01	2.89E-01

^aSteam produced in boiler due to 99 percent purge gas combustion

^bPurge gas emissions are based on 99 percent combustion efficiency in steam boiler

^cIncludes CO₂ produced after 99 percent purge gas combustion in steam boiler

Table 4-35. The LCI of Methanol for Recycle Ratios of 2 moles recycle gas/moles fresh feed and 3 moles recycle gas/moles fresh feed in LPMEOH Process Using Texaco Syngas

Air Emissions	Recycle Ratio = 2	Recycle Ratio = 3
PM	-3.02E-04	-8.18E-05
SO ₂	-5.99E-03	-1.88E-03
NO _x	-1.11E-03	-3.12E-04
CO	3.71E-03	1.19E-03
CO ₂ (fossil)	-2.76E-02	3.61E-02
CH ₄	-1.47E-03	-4.52E-04
HCl	-2.09E-06	4.26E-07
Methanol	2.16E-04	1.19E-04
Liquid Emissions		
Suspended Solids	-1.49E-04	-3.95E-05
BOD	6.34E-04	6.40E-04
COD	-6.14E-05	-1.99E-05
Solid Waste	-8.08E-02	-2.17E-02

In Table 4-35 it is clear that as recycle ratio increases, the CO and methanol emissions per kg of methanol produced decrease because of decrease in purge gas production. Most of the other LCI parameters are negative in case of recycle ratio of 2 and have higher avoided emissions as compared to case with recycle ratio of 3. This is because the case with recycle ratio of 2, produces more steam in boiler combusting 99 percent purge gases. The emissions are therefore avoided thereby offsetting the other contributors to the overall LCI.

4.11.6.4 Effect of Change in Syngas Composition on the LCI of Methanol

This section presents the results of sensitivity analysis on the LCI of methanol with change in syngas composition. Three syngas compositions considered are: (1) Texaco syngas being used at Kingsport; (2) syngas obtained from coal fired BGL gasifier; and (3) syngas obtained MSW fired BGL gasifier. Table 4-36 presents the results as obtained in Section 4.11.2 to Section 4.11.4 on per kg of methanol produced basis. All the three cases considered have same reactor pressure ($P = 750$ psig), syngas space velocity ($SV = 8827$ standard liters/kg-hr), and recycle ratio ($R = 3.22$ moles recycle gas/moles fresh syngas feed).

As stated earlier in Section 1.1.4, the main difference between the three syngas compositions considered is their H_2/CO molar ratio. From Table 4-36, it is clear that as H_2/CO ratio decreases from Texaco syngas (2.25) to coal syngas (0.51), the electricity consumed per kg of methanol increases. Net steam consumption per kg of methanol also increases with decrease in H_2/CO ratio of fresh syngas feed. Amount of purge gas increases as H_2/CO ratio decreases because the syngas conversion in methanol reactor decreases. Thus purge gas production increases per kg of methanol produced when H_2/CO ratio decreases from Texaco syngas to coal derived syngas. As the purge gas production increases with decreasing H_2/CO ratio, amount of steam produced per kg of methanol by 99 percent combustion of purge gases in boiler also increases and is highest for coal derived syngas. Table 4-37 presents the overall LCI of methanol for 3 syngas compositions considered.

Table 4-36. Sensitivity Results for Different Syngas Compositions on per kg of Methanol Produced Basis for Reactor Pressure of 750 psig, Syngas Space Velocity of 8827 standard liters/kg-hr and Recycle Ratio of 3.22 moles recycle gas/moles fresh syngas feed

Model Results per kg of Methanol Produced	Syngas Compositions		
	Texaco Syngas	MSW Syngas	Coal Syngas
H ₂ /CO molar ratio in Fresh Syngas Feed ^a	2.24	0.78	0.51
Electricity Consumption (kWh/kg methanol)	1.43E-02	3.92E-02	4.77E-02
Net Steam Consumption in Process (kg/kg methanol)	5.99E-02	5.67E-01	7.24E-01
Purge Gas Steam Production (MJ/kg methanol) ^b	1.95E+00	3.27E+01	4.20E+01
Purge Gas Emissions (kg/kg methanol) ^c			
H ₂	1.64E-04	4.63E-04	3.10E-04
CO	7.21E-04	2.36E-02	3.66E-02
CH ₄	5.17E-06	3.14E-03	3.42E-03
CH ₃ OH	2.57E-05	3.66E-04	4.82E-04
N ₂	8.81E-02	3.08E+00	4.39E+00
CO ₂ ^d	1.62E-01	4.70E+00	6.84E+00
H ₂ O	1.50E-01	1.15E+00	1.09E+00

^aH₂/CO ratio is not a model result.

^bSteam produced in boiler due to 99 percent purge gas combustion

^cPurge gas emissions are based on 99 percent combustion efficiency in steam boiler

^dIncludes CO₂ produced after 99 percent purge gas combustion in steam boiler

Table 4-37. The LCI of Methanol for Different Syngas Compositions Using Reactor Pressure of 750 psig, Syngas Space Velocity of 8827 standard liters/kg-hr and Recycle Ratio of 3.22 moles recycle gas/moles fresh syngas feed

Air Emissions	Texaco Syngas	MSW Derived Syngas	Coal Derived Syngas
PM	-3.55E-05	-8.83E-04	-1.13E-03
SO ₂	-8.88E-04	-1.71E-02	-2.19E-02
NO _x	-1.39E-04	-3.23E-03	-4.14E-03
CO	5.23E-04	1.96E-02	3.15E-02
CO ₂ (fossil)	3.99E-02	1.92E+00	3.27E+00
CH ₄	-2.10E-04	-1.07E-03	-1.98E-03
HCl	4.58E-07	-7.87E-06	-1.03E-05
Methanol	9.14E-05	4.32E-04	5.47E-04
Liquid Emissions			
Suspended Solids	-1.69E-05	-4.37E-04	-5.61E-04
BOD	6.42E-04	6.18E-04	6.11E-04
COD	-9.56E-06	-1.74E-04	-2.22E-04
Solid Waste	-7.98E-03	-2.39E-01	-3.08E-01

In Table 4-37, it is clear that as syngas composition changes from Texaco syngas to coal fired syngas, there is a wide variation in the magnitude of LCI parameters. As H₂/CO ratio decreases from Texaco syngas to coal derived syngas, CO and methanol emissions increase due to increasing purge gas production. Carbon dioxide emissions also increase with decreasing H₂/CO ratio because of more purge gas production and therefore higher production of CO₂ when that purge gas is combusted. All other parameters decrease in magnitude with decreasing H₂/CO ratio since the increasing production of steam from purge gas combustion offsets the contributions from other LCI contributors.

Based on the sensitivity analysis on the LCI of methanol with varying reactor pressure, space velocity, recycle ratio, and syngas composition, it is clear that the LCI of

methanol is sensitive to changes in them. In most of the cases considered above, steam production from 99 percent purge gas combustion offsets the contributions from other sources such as electricity, net steam consumption in the process, BOD removal, fugitive emissions and methanol storage tank emissions. A sensitivity analysis of LCI of methanol by varying pressure, space velocity and recycle ratio for two other syngas compositions (MSW derived syngas and coal derived syngas) can be conducted in a similar way as done for Texaco syngas in Sections 4.11.6.1 to 4.11.6.3. Although the results would be widely different from the Texaco syngas, but trends within the same syngas composition are expected to be similar as trends in Texaco syngas.

5.0 LIFE CYCLE INVENTORY OF METHANOL PRODUCED BY CONVENTIONAL PROCESS

MSW gasification is a potentially new technology for MSW management. Gasification is defined as the thermochemical conversion of a solid carbonaceous feed to a combustible gas product (Chen, 1995). The product gas, referred to as synthesis gas or syngas, is usually rich in hydrogen, H₂, carbon monoxide, CO, carbon dioxide, CO₂, and various low-weight hydrocarbons. There has been lot of experience with coal gasification for the generation of power and chemicals and the technology has been successfully demonstrated commercially (Cheng and Kung, 1994; Supp 1990). MSW gasification is similar to coal gasification in a sense that the unit operations involved in its gasification are similar.

MSW gasification results in generation of synthesis gas (syngas), which is the main raw material for the production of methanol. Thus we can utilize the syngas generated from MSW to produce methanol and therefore avoid some conventional methanol production.

To evaluate the environmental burdens of MSW gasification relative to alternate MSW management strategies, it is necessary to develop a life cycle inventory (LCI) of methanol production based on conventional feedstock and production. This will enable us to take credit for avoided methanol production when methanol is produced from syngas obtained from MSW gasification.

The objective of this chapter is to develop a model for calculation of the LCI of methanol production based on conventional feedstock (Natural gas). The previous chapter, Chapter 4, presented the LCI of methanol based on the Liquid Phase Methanol (LPMEOHTM) technology.

This chapter is divided into 4 sections. Section 5.1 presents an overview of methanol production by the conventional process in which natural gas is used as a feedstock in a syngas generator (steam reformer). The major sections of the process are identified and described. Section 5.2 presents the methodology of performing a LCI. A spreadsheet model for the LCI of methanol is developed in EXCEL, which consists of mass and energy balances of the conventional process. The manner in which the model was assembled is described. Section 5.3 is divided into several subsections. The mass balance, energy balance, and the LCI calculation documentation of the process are presented. Section 5.4 presents the sensitivity analysis of the conventional methanol process.

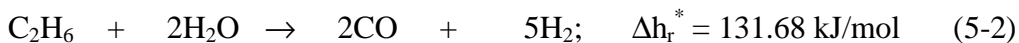
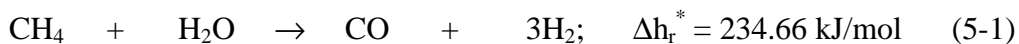
5.1 Overview of Methanol Production by Conventional Process

An overview of a conventional methanol production process is presented in this section. The major factors that will affect the LCI of methanol production include the generation and consumption of steam, consumption of electrical energy, natural gas production and consumption, purge gas combustion, and fugitive emissions.

Methanol is produced from syngas, which consists primarily of H₂ and CO. Generation of syngas is the first step in the production of methanol. Carbonaceous materials such as coal, coke, natural gas, petroleum, and fractions obtained from petroleum (asphalt, gasoline, gaseous compounds) can be used as starting materials for syngas production. Most methanol produced worldwide is derived from natural gas (Elvers *et al.*, 1989). The production of methanol using conventional industrial processes involves the following three steps:

- 1) Natural gas (mostly methane) is converted to syngas using steam. This process is known as steam cracking or steam reforming. The syngas produced consists of CO, H₂ and CO₂ as its major components. The reactions that occur in a syngas generator (steam reformer) are:

Reforming reactions

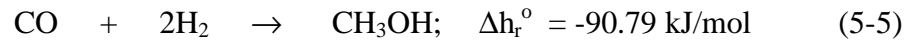


Shift reaction



(Δh_r^* indicates the heat of reaction at typical reformer operating conditions: 2.0 MPa and 870 °C – Elvers *et al.*, 1989).

- 2) In the second step, water is removed from the syngas and the components (mainly CO, H₂, and CO₂) of dry syngas are catalytically reacted to produce methanol. Two major reactions taking place are:



A side reaction producing dimethyl ether also occurs to a limited extent



The water-gas shift reaction (reaction 5-4) also occurs. Δh_r° is the heat of reaction at standard temperature and pressure (298K and 1 atm; Cheng and Kung, 1994).

- 3) The methanol is distilled and purified to the desired purity.

The production of methanol can be further divided into a series of steps including natural gas compression, production of syngas, heat recovery in waste heat boiler (WHB), removal of water to produce dry syngas, methanol production, methanol condensation, unreacted gas recycle, and methanol distillation to desired purity. Figure 5-1 represents the process flow diagram of the process. Each step is described in the following subsections.

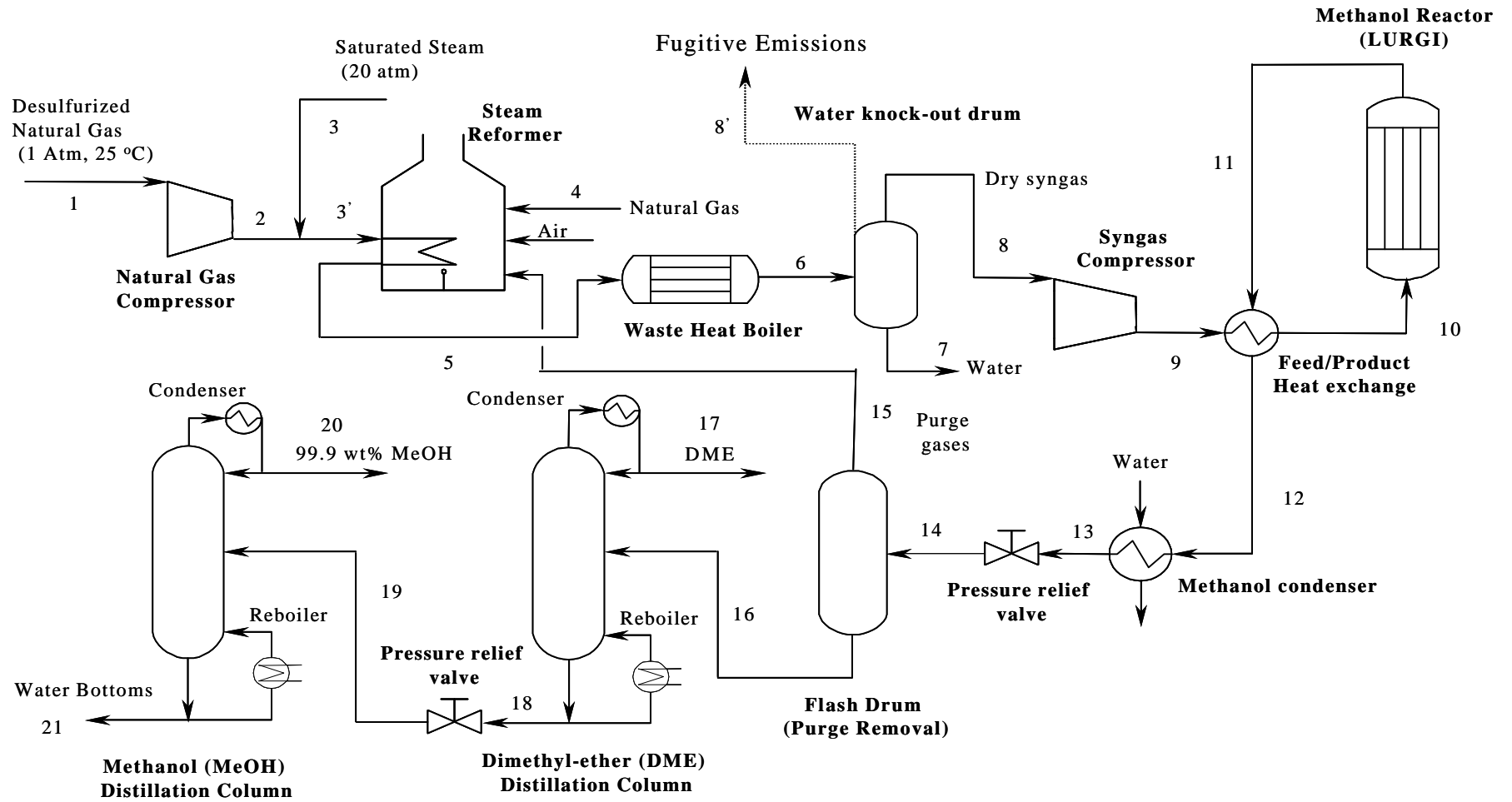


Figure 5-1. Simplified Flowsheet for the Production of Methanol by a Conventional Process (e.g., Lurgi Low Pressure Process)

5.1.1 Natural Gas Compression and Steam Supply

Natural gas varies in its composition. Table 5-1 presents the percentage range of various components present in natural gas (Kirk and Othmer, 1990). The desulfurized natural gas available at 25 °C and 1 atmosphere (atm) is compressed to 20 atm., the pressure at which the steam reformer operates. Compressed natural gas is mixed with saturated steam at 20 atm and sent to steam reformer. With methane, which comprises major portion of natural gas, the stoichiometric requirement for steam per carbon atom is 1.0 (moles steam/moles carbon). However, it has been demonstrated that this is not practicable because all catalysts developed so far tend to promote carbon forming under steam reforming condition. In practice steam to carbon ratios of 3.0-3.5 are commonly used (Twiggs, 1989).

Table 5-1. Typical Natural Gas Compositions^a

Component	Value
Methane, vol. %	45.6 -96.8
Ethane, vol. %	0.21-11.1
Propane, vol. %	0.14-5.8
Butanes and heavier gaseous hydrocarbons, vol. %	0.1-2.3
Nitrogen, vol. %	0.1-25.6
Carbon dioxide, vol. %	0-53.9

^a This is a typical composition range of natural gas (Kirk and Othmer, 1990). The composition can widely vary within this range.

5.1.2 Syngas Generation

Generation of syngas takes place in steam reformer or syngas generator. A combined feed of natural gas and saturated steam enter the steam reformer. Steam

reforming reactions are endothermic (equations 5-1 to 5-3) and are favored at high temperatures. The heat for maintaining this high temperature is supplied by combustion of purge gases (generated in methanol production process) external to the tubes in which reactants (natural gas and steam) flow. The heat is also supplied by natural gas combustion. Typical operating pressure and temperature in steam reformer tubes are 20 atm and 880 °C (Twigg, 1989). Typically 80 to 95 percent of CH₄ is converted to CO and H₂. All C₂H₆ and C₃H₈ are reformed to CO and H₂ (US patent 4,407,973). The water-gas shift reaction (reaction 5-4) also occurs in the steam reformer. Hot product gases comprising of H₂, CO, CO₂, unconverted CH₄, N₂ and water vapor leave the steam reformer at 20 atm and 880 °C.

5.1.3 Waste Heat Boiler (WHB)

The exit gases from the syngas generator are at a temperature of 880 °C and enter the waste heat boiler (WHB) for the recovery of excess process heat. In addition to heat recovery, the gases need to be cooled in order to condense the water for its removal from the syngas. Typically, the hot gases are cooled to 110 °C (Dry, 1988). Saturated steam is generated as a result of process heat exchange. Water vapor in the syngas condenses in this process section as a result of heat exchange. The cooled syngas enters the water knockout drum.

5.1.4 Water Removal and Knock-out Drum

In water knockout drum, the condensed water and trace solid impurities (carbon particles) produced in the steam reformer are removed to produce clean dry syngas. The exit syngas from this section consists of H₂, CO, CO₂, CH₄, and N₂. One half percent loss of syngas as fugitive emission is estimated to occur in this process section (Overcash, 1999).

5.1.5 Syngas Compressor

Clean and dried syngas from the water knockout drum enters the syngas compressor. The syngas is compressed to an exit pressure of 50 atm, which is a typical operating pressure for a low-pressure methanol reactor (Cheng and Kung, 1994).

5.1.6 Methanol Reactor

In the methanol reactor CO, CO₂ and H₂ are catalytically converted to methanol and dimethyl ether in accordance with Equations (5-5), (5-6) and (5-7). The reactions taking place in the methanol reactor are all exothermic and heat must be removed to maintain an optimum reaction temperature in the reactor. Typical operating conditions in methanol reactor are 50 atm. and 260 °C (Cheng and Kung, 1994; Lurgi Corp., 1979; ICI Ltd., 1979; Supp 1973). The catalyst used consists of copper oxide, zinc oxide and alumina in varying proportions. At higher temperatures, the catalyst gets deactivated and the potential for side reactions to produce undesirable products increases.

Various reactor configurations are available for the synthesis of methanol. ICI quench bed reactors and Lurgi tubular reactors are the most widely used reactors for methanol synthesis (Elvers *et. al.*, 1989). The ICI design employs cold syngas injections at various catalyst beds to maintain the temperature in the reactor around 260 °C. Lurgi design employs a tubular reactor in which high-pressure steam (40 atm) is generated on the shell side of the reactor (Cheng and Kung, 1994). By controlling the pressure of steam generated on the shell side, it is possible to control the temperature in the tubes of the reactor and maintain it in the vicinity of 260 °C.

CO conversion is dependent on the temperature and pressure inside the reactor, the H₂ to CO ratio, gas space velocity, catalyst composition, and CO₂ content. Since CO and CO₂ conversion to methanol is normally only 40 to 60 percent complete per pass, economics usually dictate that excess unreacted gas be recycled. The common recycle ratio (recycle to fresh feed) ranges from 3 to 8 moles recycle gas per moles fresh feed (US patent 3,920,717; Dry, 1988). Overall conversion of the carbon content in syngas to methanol is typically 95 percent (US patent 4,407,973) and may be as high as 99.5 percent (Cheng and Kung, 1994).

The Lurgi low-pressure reactor is assumed to be a typical representative technology for methanol synthesis primarily because it is more commonly used than ICI methanol reactor in the process industry in U.S. In Lurgi methanol reactor, a high-pressure steam at 40 atm is generated from the enthalpy of reactions taking place (Cheng

and Kung, 1994). 95 percent of carbon in syngas (CO and CO₂) conversion to methanol takes place (US patent 4,407,973) and CH₄ does not react under the reaction conditions since the catalyst is highly selective to CO and CO₂ for methanol synthesis. The amount of Dimethyl ether (DME) produced is 2 percent of the weight of methanol produced (US patent 3,920,717). The actual reactor in the process has a recycle stream mixing with the fresh syngas feed in a ratio ranging from 3 to 8 (moles recycle gas/moles fresh feed) to achieve the overall conversion of 95 percent for both CO and CO₂. No recycle stream is shown in Figure 5-1 since the reactor is modeled to achieve 95 percent conversion of CO and CO₂ to methanol in a single pass. Unreacted gases are taken out as purge after the methanol condenser described in section 5.1.1.8. They have the same flowrate and composition as the purge from the actual process (compared with US patent 4,407,973). This simplification does not affect the steam generation on shell-side in the reactor and therefore the LCI parameters associated with it are not affected. Product gas from the methanol reactor consists of CH₃OH, H₂O, CO, CO₂, DME, N₂ and CH₄.

5.1.7 Syngas Feed/Methanol Product Heat Exchanger (Feed-Preheater)

The product gases from the methanol reactor leave at 260 °C. The enthalpy carried by this stream can be utilized to preheat the syngas from the syngas compressor to 250 °C, typically, before sending it to the methanol reactor (Chen, 1995). The cooled product gases are then sent to the methanol condenser. The exit temperature of the product gas depends on the inlet temperature of fresh feed and can be evaluated by simple energy balance.

5.1.8 Methanol Condenser

The cooled product gas from the feed/product heat exchanger enters a series of methanol condensers. Cooling water at 20 °C is used to cool the product gas for methanol condensation. The exit temperature of water is set at 50 °C (Overcash, 1999). The saturation temperature of methanol at 50 atm is 45 °C; therefore, the product gas is cooled to 45 °C to condense all methanol, DME, and water present. Unreacted H₂, CO, CO₂, CH₄ and N₂ do not condense at this temperature and remain in gas phase.

5.1.9 Pre-Flash Drum Pressure Relief Valve

The exit stream from the methanol condenser is a two-phase mixture with methanol, DME and water in the liquid phase. The pressure of this stream is 50 atm, assuming that there is no pressure drop in feed/product heat exchanger and methanol condenser. The pressure is reduced using a pressure relief valve so that liquid and gas phase separation can take place in flash drum. For DME distillation to occur in the DME distillation column, the pressure should be reduced to 11.2 atm (US patent 3,920,717). The exit stream from pressure relief valve has a pressure of 11.2 atm.

5.1.10 Flash Drum for Removal of Uncondensed Gases

The next step in methanol production is vapor-liquid phase separation. The gaseous phase comprised of unreacted CO, CO₂, H₂, CH₄, N₂ is removed as a purge at the

top of the flash drum and sent to a steam reformer furnace for combustion (thermal oxidation) to supply the heat required for the steam reforming process. The liquid phase, comprised of methanol, DME and water, is taken out at the bottom of the flash drum. The liquid stream at 11.2 atm and 45 °C is then sent to a DME distillation column.

5.1.11 DME Distillation

Dimethyl ether can be separated from crude methanol by extractive distillation. Extractive distillation is a process in which a third component is added to alter the relative volatility of a binary mixture which is difficult to separate so that distillation can proceed with ease. The extractive distillation of DME involves addition of water in a 15 to 45 tray column at approximately 11.2 atm pressure and a reflux ratio of 20 (moles recycle liquid/moles distillate) (US patent 3,920,717). In this column, almost complete recovery of DME is accomplished as a top product, while methanol and water leave as bottoms. DME recovered has various uses including as an aerosol and as a diesel additive. Since the amount of DME produced is very small, it is not considered in the LCI of methanol.

5.1.12 Pre-Methanol Distillation Pressure Relief Valve

Liquid bottoms from the DME distillation column at 11.2 atm enter the pressure relief valve, where the pressure is reduced to 3.4 atm, which is the pressure at which

distillation of methanol in the methanol distillation column takes place (US patent 3,920,717).

5.1.13 Methanol Distillation

Feed entering the methanol distillation column consists of methanol and water at 3.4 atm and 45 °C. Methanol distillation takes place in a 45 to 75 tray distillation column at a pressure of 3.4 atm and a reflux ratio of 1.5 (moles recycle liquid/moles distillate) (US patent 3,920,717). The boiling point of methanol at 3.4 atm is approximately 90 °C. Methanol recovery of 99.9 percent takes place in the top product with 99.9 percent purity by weight (US patent 3,920,717). Water leaves as bottoms with a trace amount of methanol and is sent to a wastewater treatment facility.

5.2 Overview of LCI Model

The LCI of methanol based upon a conventional process is comprised of:

- 1) The mass and energy balance of the process;
- 2) Calculation of the amount of energy used in the process and in what form (e.g., steam, electricity);
- 3) The emissions associated with the methanol production process (e.g., fugitive emissions, purge emissions);
- 4) The emissions associated with the form of energy usage in the process (e.g., steam, electricity); and

- 5) LCI parameters associated with the production and consumption of raw material for the process (e.g., pre-combustion emissions for natural gas).

The information required for the LCI of methanol production includes the amount of raw materials used in the process, process utilities required, energy used or generated in the process, emissions and wastes produced, the emissions produced in production of the inputs to the process. Thus, a mass and energy balance of the entire process is required.

Mass and energy balances of the process are performed in MS EXCEL. MS EXCEL is a spreadsheet-based model in which various cells are defined to represent the inputs used in the process. Inputs such as feed composition, flow rates, reaction conversion, removal efficiency, efficiency of operation, percentage losses, and others, are set up such that they can be altered by a user to create alternate scenarios. Such flexibility in altering the input parameters will permit the user to perform sensitivity analysis of parameters involved in the process. The details of the process conditions and assumptions made in performing the mass and energy balance are discussed in sections 5.3.1 and 5.3.2.

The EXCEL spreadsheet model consists of various sub-sheets called “sub-models” linked together to calculate the LCI of methanol production. The entire spreadsheet model, as presented in Figure 5-2, consists of following sub-models:

5.2.1 Mass Balance Sub-Model

The mass balance sub-model contains quantitative information on mass flow rates of raw materials, intermediate streams, utility streams and product streams. It is linked to the energy balance sub-model (described next) to represent the process as a whole.

5.2.2 Energy Balance Sub-Model

The energy balance sub-model presents an energy balance across all the components of the process. It contains quantitative information on temperatures, pressures, enthalpy flow rates of process streams, and energy generation and consumption in process units. The energy balance sub-model is linked to the mass balance sub-model to represent the complete process.

5.2.3 Physical Property Sub-Model

The physical property sub-model contains the values of physical properties and constants that are used repetitively in energy balance calculations. It is linked with energy balance sub-model wherever required. It consists of heat capacity constants, Antoine's equation constants, specific heat capacities of liquids, and heats of vaporizations. Table 5-2 presents the values of these constants.

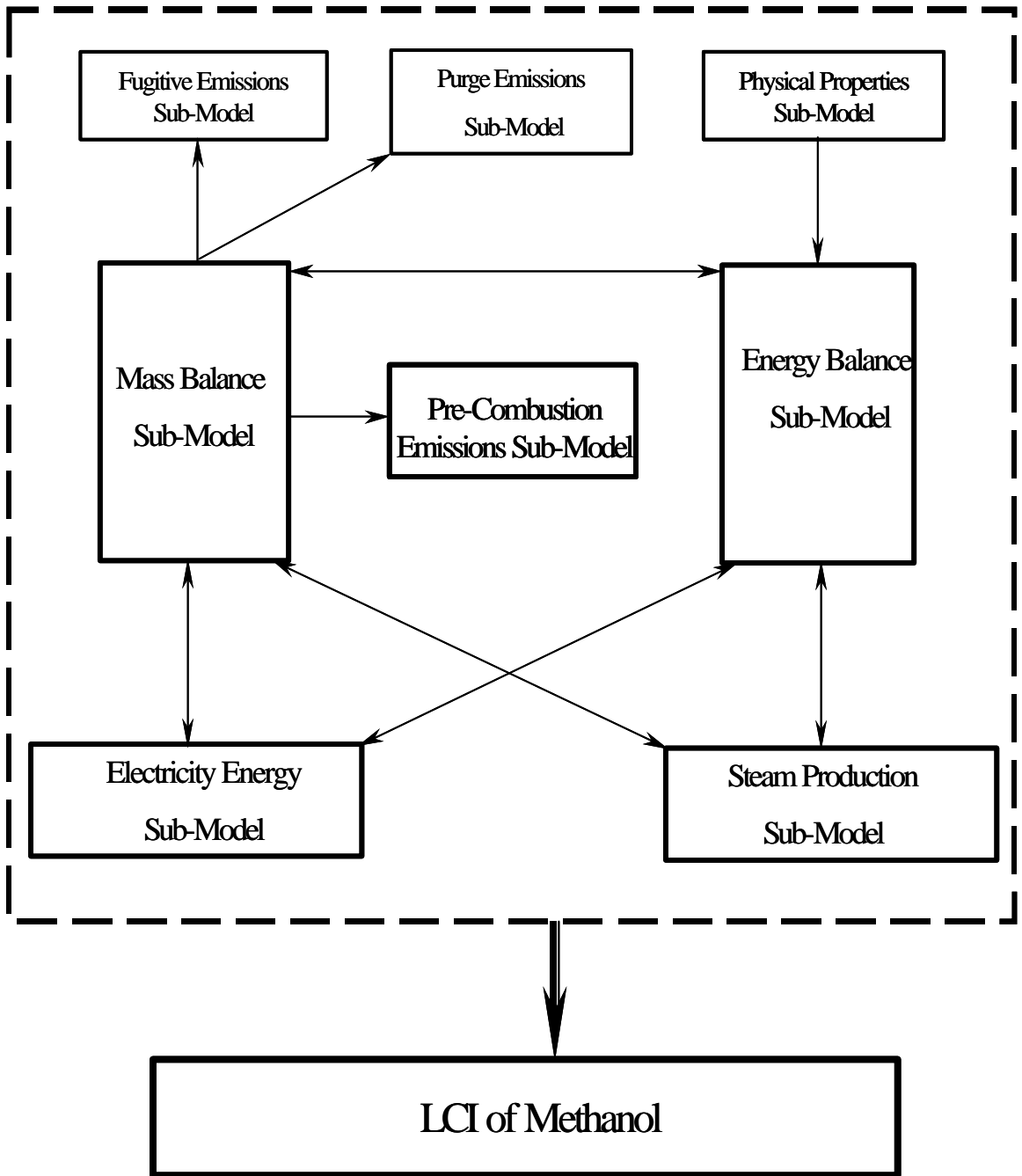


Figure 5-2. Design on Spreadsheet for Conventional Methanol LCI Calculation

Table 5-2. Physical Properties of Compounds used in Physical Property Sub-Model

(a) Heat Capacity Constants in equation, $C_{pi}/R = A_i + B_iT + C_iT^2 + D_i/T^2$, $R = 8.314$ J/mol-K (Felder and Rousseau, 1986)

Compound	A_i	B_i	C_i	D_i
CH4	1.702E+00	9.081E-03	-2.16E-06	0
C2H6	1.131E+00	1.92E-02	-5.56E-06	0
C3H8	1.213E+00	2.88E-02	-8.82E-06	0
N2	3.28E+00	5.93E-04	0	4.00E+03
H2	3.249E+00	4.22E-04	0	8.3E+03
CO	3.376E+00	5.57E-04	0	-3.10E+03
CO2	5.457E+00	1.05E-03	0	-1.16E+05
H2O	3.47E+00	1.45E-03	0	1.21E+04
DME ^b	2.0465E+00	2.15E-02	-6.29E-06	-2.31E-10
CH3OH	2.211E+00	1.22E-02	-3.45E-06	0.00E+00

^b(Perry and Green, 1997)

(b) Specific Heat Capacity of Liquids ($C_{pLiquid}$, in J/mol-K)^c

Compound	$C_{pLiquid}$
CH ₃ OH	82.59
H ₂ O	75.4

^c(Felder and Rousseau, 1986)

(c) Antoine's Equation Constants^c in equation^d, $\ln(P) = A_o - B_o/(T+C_o)$ (where, P = partial pressure in mm Hg, and T = temperature in K)

Compound	A_o	B_o	C_o
H2O	7.966	1668.21	228
CH3OH	7.878	1473.11	230
DME	16.846	2361.44	-17.1

^d(Sinnott, 1996)

(d) Heat of Vaporizations (H_v)^e

Compound	$T_{boiling}$ (K)	$(H_v)^o$, kJ/mol ^f
H2O	373	40.657
DME	248	27.032
CH3OH	338	36.842

^e(Perry and Green, 1997)

^f $(H_v)^o$ = Standard heat of vaporization (at 298K and 1 atm).

5.2.4 Purge Emissions Sub-Model

The purge emissions sub-model consists of mass flow rates of the purge streams generated in the process. Since the purge stream is combusted in the steam reformer furnace to supply the heat for steam reforming of natural gas, this sheet also calculates the balance fuel (natural gas) required to be burned in the steam reformer furnace to maintain steam reforming conditions (20 atm, 880 °C). Emissions due to combustion of fuel (natural gas) and unconverted purge gas (one percent of total) described in section 5.3.3.4 are also calculated in this sub-model.

5.2.5 Fugitive Emissions Sub-Model

The fugitive emissions sub-model consists of fugitive emissions obtained from the mass balance sub-model to be included in the overall LCI of methanol. It calculates the loss of chemicals from the water knockout drum in the methanol production process.

5.2.6 LCI of Steam Sub-Model

The LCI of steam developed in Chapter 2 is directly used in this sub-model. It consists of quantitative information on the total energy of steam consumed or produced in various process sections of methanol production. The process section where steam is produced is assigned a negative sign indicating that energy is recovered. The process section where steam is consumed is assigned positive sign indicating that energy is

consumed. All these energies are summed together to calculate the net steam energy consumed or produced. This sub-model then calculates the emissions associated with steam generation or consumption using the LCI of steam imported from Chapter 2.

5.2.7 LCI of Electricity Sub-Model

The LCI of electricity sub-model provides an accounting of the total energy consumed in the form of electricity in the process. This sub-model is linked to the total energy consumed in two compressors (natural gas compressor and syngas compressor) as calculated in energy balance sub-model. The LCI of electricity as presented in Chapter 3 is directly imported into this sub-model to calculate the total emissions due to consumption of electricity in the process.

5.2.8 Pre-Combustion Sub-Model

The pre-combustion sub-model presents the pre-combustion emissions associated with the raw material, specifically natural gas, used in the methanol production process. Pre-combustion emissions for natural gas were obtained from an electric energy process model (Dumas, 1998).

5.2.9 Overall LCI of Methanol Model

The overall LCI of methanol model calculates overall LCI of methanol production using the Lurgi process. The results of all sub-models are imported into the overall LCI of methanol model where they are divided by the quantity of methanol produced to calculate the LCI parameters per kg of methanol produced.

The following section presents the manner in which the overall LCI of methanol was developed. It describes the mass and energy balance calculations and the assumptions made therein. It also presents the equations coded in the EXCEL spreadsheet.

5.3 LCI of Methanol Production

The LCI of methanol is developed by performing a mass and energy balance across the entire methanol production process. The mass balance includes all mass streams entering and leaving the process. The energy balance evaluates the amount of energy associated with each stream and the energy supplied to the process in the form of electricity, steam, and heat. Results from both the mass balance and energy balance are used to calculate the LCI parameters of the entire process.

The following sub-section presents documentation of the mass balance across the entire process. Mass balance calculations and all other calculations described were

implemented in an EXCEL spreadsheet. Section 5.3.2 describes the energy balance and section 5.3.3 presents the methodology for calculation of the LCI associated with production of conventional methanol.

5.3.1 Mass Balance across the Conventional Methanol Process

This section documents the mass balance across each process section including all assumptions and relevant equations. One thousand kmol/hr of desulfurized natural gas is assumed as a starting raw material for methanol production. US patents 4,407,973 and 4,443,560 present the mass balance for conventional process of methanol production starting with 3865 lbmoles/hr and 6957 lbmoles/hr of desulfurized natural gas, respectively. Both of these patents result in same mass balance per kmol of natural gas used so either of them can be used to represent the mass balance of the conventional process. The mass balance presented in this section has been scaled down, with a scale down factor of 3.865, from the mass balance of conventional methanol production as presented in US patent 4,407,973.

5.3.1.1 Natural Gas Compressor

Desulfurized natural gas at 1 atm and 25 °C is sent to natural gas compressor to achieve the outlet pressure of 20 atm. The compressor is assumed to operate isentropically for simplicity (Overcash, 1999). This is the pressure at which the steam reformer operates. Since the composition of natural gas used is not presented in US patent 4,407,973, it is calculated by trial and error based on reforming reactions taking

place in the syngas generator (steam reformer), using a simple mass balance involving reactions 5-1, 5-2, 5-3 and 5-4. The method used in calculating the composition is described in Appendix A. The composition of natural gas thus determined is 90.6 percent CH₄, 7 percent C₂H₆, 2.1 percent C₃H₈, 0.17 percent N₂ and 0.13 percent CO₂, on mole basis. The percentage of each component is within the range of the typical compositions presented in Table 5-1. Since there is no reaction occurring in the compressor, the mole flow rate and composition of natural gas remain the same. Electric power consumed is calculated in Section 5.3.2.1.

5.3.1.2 Synthesis Gas Generator

Natural gas with the above-mentioned composition at 20 atm is mixed with saturated steam at 20 atm at a steam to natural gas ratio of 3.681 kmol H₂O/kmol natural gas (US patent 4,407,973) before entering the syngas generator. Steam reforming reactions (5-1), (5-2), and (5-3) take place at 20 atm. and 880 °C (Twigg, 1989). C₂H₆ and C₃H₈ are completely reformed to produce CO and H₂, while 81.46 percent of the CH₄ is reformed to produce CO and H₂, as calculated from mass balance presented in US patent 4,407,973. A water-gas shift reaction also occurs in the syngas generator producing CO₂. The CO conversion to produce CO₂ in reaction 5-4 was estimated to be 40.2 percent based upon US patent 4,407,973. The percentage conversions of reactants are specified as user inputs in the spreadsheet to provide the user with the flexibility to change these values in case the reaction conditions change and the default values are based on the information in US patent 4,407,973. The flow rates of products leaving the syngas

generator can be calculated by the following equations. Flowrates of all the components are in kgmol/hr (kmol/hr).

$$m_{CH_4,5} = \left(1 - \frac{f_{CH_4}}{100}\right) x m_{CH_4,5} \quad (5-8)$$

$$m_{H_2,5} = 3 \left(\frac{f_{CH_4}}{100}\right) m_{CH_4,3} + 5 \left(\frac{f_{C_2H_6}}{100}\right) m_{C_2H_6,3} + 7 \left(\frac{f_{C_3H_8}}{100}\right) m_{C_3H_8,3} \quad (5-9)$$

$$m_{CO,5} = \left\{ \left(\frac{f_{CH_4}}{100}\right) m_{CH_4,3} + 2 \left(\frac{f_{C_2H_6}}{100}\right) m_{C_2H_6,3} + 3 \left(\frac{f_{C_3H_8}}{100}\right) m_{C_3H_8,3} \right\} \left[1 - \left(\frac{f_{CO}}{100}\right) \right] \quad (5-10)$$

$$m_{CO_2,5} = m_{CO_2,3} + \left\{ \left(\frac{f_{CH_4}}{100}\right) m_{CH_4,3} + 2 \left(\frac{f_{C_2H_6}}{100}\right) m_{C_2H_6,3} + 3 \left(\frac{f_{C_3H_8}}{100}\right) m_{C_3H_8,3} \right\} \left(\frac{f_{CO}}{100}\right) \quad (5-11)$$

$$m_{H_2O,5} = m_{H_2O,3} - \left\{ \left(\frac{f_{CH_4}}{100}\right) m_{CH_4,3} + 2 \left(\frac{f_{C_2H_6}}{100}\right) m_{C_2H_6,3} + 3 \left(\frac{f_{C_3H_8}}{100}\right) m_{C_3H_8,3} + m_{CO_2,5} \right\} \quad (5-12)$$

Where: ϕ_i = percentage conversion of component 'i' (CH₄, C₂H₆, C₃H₈, and CO)

Number subscript = stream number as identified in Figure 5-1.

$m_{i,j}$ = molar flowrate of the component 'i', kmol/hr in stream j. (Applies throughout the mass balance)

The flowrates of C₂H₆ and C₃H₈ have been defined by equations similar to Equation (5-8). Since N₂ is inert, its flowrate is the same at the inlet and outlet of the

syngas generator. The flowrate of fuel (natural gas) used in the syngas generator furnace to supply the heat for reforming reactions has been calculated with the energy balance. The product gases from syngas generator leave at 20 atm and 880 °C.

5.3.1.3 Waste Heat Boiler

The products from the syngas generator are sent to waste heat boiler (WHB) for recovery of excess process heat. The syngas is cooled to 110°C but no change in mole flow rate of any component occurs.

$$m_{i,6} = m_{i,5} \quad (5-13)$$

where, i = represents all the components present in syngas (CH₄, N₂, CO₂, CO, H₂, and H₂O).

5.3.1.4 Water Removal and Knock-out Drum

Since the syngas is cooled to 110 °C, which is 55 °C below the dew point of water in syngas at 20 atm., complete condensation of water takes place. The condensed water is removed from the syngas to produce dry syngas. Also, a small amount of carbon particles produced in syngas generator due to coking are removed with the water. It is assumed that a 0.5 percent loss of syngas as fugitive emission takes place in this section (Overcash, 1999). Hence, the molar flowrates of gaseous components leaving the section are 0.995 times of that entering the section. Since all the water is in liquid state, no loss of water takes place as fugitive emissions.

$$m_{i,8} = 0.995 m_{i,6} \quad (5-14)$$

$$m_{i,8} = 0.005 m_{i,6} \quad (\text{Fugitive Emissions}) \quad (5-15)$$

where, $i = \text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8, \text{N}_2, \text{H}_2, \text{CO}, \text{and } \text{CO}_2$

$$m_{\text{H}_2\text{O},6} = m_{\text{H}_2\text{O},7} \quad (5-16)$$

5.3.1.5 Syngas Compressor

After leaving the water knockout drum, dry syngas enters the syngas compressor where it is compressed to 50 atm, the pressure at which the methanol synthesis reactor operates. For simplicity, it is assumed that the compressor operates isentropically (Overcash, 1999). No reaction takes place in syngas compressor so the flowrate of components in is equal to their exit flowrate.

$$m_{i,9} = m_{i,8} \quad (5-17)$$

where, $i = \text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8, \text{N}_2, \text{H}_2, \text{CO}, \text{and } \text{CO}_2$

5.3.1.6 Syngas Feed/Product Heat Exchanger (Feed Preheater)

Before sending the syngas to the methanol reactor, it is passed through a feed/product heat exchanger, where the hot product gases from the methanol reactor exchange heat with the syngas feed thereby heating them close to the temperature in the methanol reactor (260°C). The syngas feed is heated to a temperature of 250 °C (Chen, 1995). No reaction takes place in this process section and therefore the flowrates of components going in is equal to their flowrate out.

$$m_{i,10} = m_{i,9} \quad (5-18)$$

where, $i = \text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8, \text{N}_2, \text{H}_2, \text{CO}, \text{and } \text{CO}_2$

5.3.1.7 Methanol Reactor

Feed syngas enters methanol reactor at 250 °C and 50 atm. The Lurgi tubular reactor operates at 260 °C and 50 atm. (Cheng and Kung, 1994; Lurgi Corp., 1979; Supp, 1973). Reactions 5-5, 5-6 and 5-7 take place in the reactor and since all of them are exothermic reactions, heat removal from the reactor is a critical issue.

In the Lurgi tubular reactor design, a high-pressure steam at 40 atm is generated from boiler feed water on the shell side while the exothermic reaction takes place in tubeside filled with catalyst (Cheng and Kung, 1994). The main component of the Lurgi methanol catalyst is copper. As with all copper catalysts, this one tends to recrystallize and deactivate at a temperature above 270 °C (Supp, 1981). Use of catalyst filled tubes in the Lurgi methanol reactor system ensures an extremely quick transfer of the reaction heat from the catalyst to a cooling medium (Meyers, 1984). Per pass conversion in the methanol reactor ranges from 40 to 60 percent of CO and CO₂. To increase the conversion, the unreacted gases after methanol condensation are recycled back to the reactor with a result that above 95 and up to 99.5 percent overall conversion can be achieved (Meyers, 1984).

For simplicity, an overall conversion of 95 percent of CO and CO₂ to methanol (US patent 4,407,973 and 4,443,560) is specified as a default for the reactor and no recycle stream is considered since the primary purpose of recycle stream is to increase the conversion as compared to single pass reactor. This simplification is not expected to alter the overall LCI of methanol (Overcash, 1999). A third reaction in methanol reactor, reaction 7, is considered which produces DME equal to 2 percent by weight of the methanol produced in the reactor (US patent 3,920,717). Unreacted gases are removed from process as a purge. Conversions of CO and CO₂ are user-specified parameters as defined in EXCEL. The amount of DME produced is based upon a percentage of methanol produced and is also a user-specified parameter with a default value of 2 percent (US patent 3,920,717). CH₄ is inert under methanol synthesis conditions and so is N₂. The outlet flowrates of various components from methanol reactor are calculated by following equations.

$$m_{CO_2,11} = \left(1 - \frac{f_{CO_2}}{100}\right) m_{CO_2,10} \quad (5-19)$$

$$m_{CH_3OH,11} = \left(\frac{f_{CO_2}}{100}\right) m_{CO_2,10} + \left(\frac{f_{CO}}{100}\right) m_{CO,10} \quad (5-20)$$

$$m_{DME,11} = m_{CH_3OH,11} \left(\frac{MW_{CH_3OH}}{MW_{DME}}\right) \left(\frac{Wt\%_{CH_3OH_{DME}}}{100}\right) \quad (5-21)$$

$$m_{CO,11} = \left(1 - \frac{f_{CO}}{100}\right) m_{CO,10} - 2(m_{DME,11}) \quad (5-22)$$

$$m_{H_2,11} = m_{H_2,10} - 2\left(\frac{f_{CO}}{100}\right) m_{CO,10} - 3\left(\frac{f_{CO_2}}{100}\right) m_{CO_2,10} - 4(m_{DME,11}) \quad (5-23)$$

$$m_{H_2O,11} = m_{DME,11} + \left(\frac{f_{CO_2}}{100} \right) m_{CO_2,10} \quad (5-24)$$

$$m_{CH_4,11} = m_{CH_4,10} \quad (5-25)$$

$$m_{N_2,11} = m_{N_2,10} \quad (5-26)$$

where: ϕ_i = percent conversion of “i” to methanol (i = CO, CO₂)

MW = Molecular weight (CH₃OH = 32; DME = 46)

Wt%_CH₃OH_DME = Wt. Of DME produced as user-defined percentage of methanol production

Product gases from methanol reactor are passed through feed/product heat exchanger. No reaction occurs in heat exchanger and therefore the flowrates in and out of the heat exchanger remains the same.

$$m_{i,12} = m_{i,11} \quad (5-27)$$

where: i = CH₄, N₂, H₂, CO, CO₂, H₂O, CH₃OH, and DME

5.3.1.8 Methanol Condenser

In methanol condenser, syngas from the feed/product heat exchanger is cooled to 45 °C (Overcash, 1999). CH₃OH, DME and H₂O condense out of the product gases. It is assumed that complete condensation of these components takes place. Other components entering the condenser leave as gases. Cooling water at 20°C is used for condensing methanol. The exit temperature of water is limited to 50 °C (Overcash, 1999). No

reaction takes place in this process section and therefore the flowrates of component in and out remain the same.

$$m_{i,14} = m_{i,13} \quad (5-28)$$

where: $i = \text{CH}_4, \text{N}_2, \text{H}_2, \text{CO}, \text{CO}_2, \text{H}_2\text{O}, \text{CH}_3\text{OH},$ and DME

5.3.1.9 Pre-Flash Drum Pressure Relief Valve

In pre-flash drum pressure relief valve, the pressure of the outlet stream from the condenser is reduced from 50 atm to 11.2 atm for the removal of uncondensed gases in a flash drum to follow (US patent 3,920,717). Since no reaction occurs in this process section, the flowrate of components in and out remains the same.

$$m_{i,14} = m_{i,13} \quad (5-29)$$

where: $i = \text{CH}_4, \text{N}_2, \text{H}_2, \text{CO}, \text{CO}_2, \text{H}_2\text{O}, \text{CH}_3\text{OH},$ DME

5.3.1.10 Flash Drum for Removal of Uncondensed Gases

Uncondensed gases $\text{CH}_4, \text{N}_2,$ unreacted $\text{CO},$ unreacted CO_2 and unreacted H_2 are removed in a flash drum at the top as a purge. This purge is sent for combustion in steam reformer furnace to generate the heat required for steam reforming reactions. The liquid fraction is taken out at bottom and consists of $\text{CH}_3\text{OH},$ DME and $\text{H}_2\text{O}.$ The following equations represent the mass balance across this section

$$m_{i,15} = m_{i,14} \quad (5-30)$$

$$m_{j,16} = m_{j,14} \quad (5-31)$$

where: $i = \text{CH}_4, \text{N}_2, \text{H}_2, \text{CO}, \text{and } \text{CO}_2$

$j = \text{CH}_3\text{OH}, \text{DME}, \text{and } \text{H}_2\text{O}$

5.3.1.11 DME Distillation Column

DME is distilled by extractive distillation with water. Since water is already present in the mixture to be separated and the feed to the distillation column is at the boiling point of DME (45°C) at 11.2 atm, it is assumed that complete recovery of DME takes place in the top product. Water and methanol are assumed to leave as bottoms of DME distillation column at 45°C for simplicity (Overcash, 1999). The steam used in the reboiler section of distillation column is assumed to be saturated steam at 100 psia. This column operates at 11.2 atm and 45 °C (Overcash, 1999). The column operates with a reflux ratio of 20 (moles recycle/moles distillate). The following equations represent the mass balance across this process section.

$$m_{DME,17} = m_{DME,16} \quad (5-32)$$

$$m_{j,18} = m_{j,16} \quad (5-33)$$

where: $j = \text{CH}_3\text{OH} \text{ and } \text{H}_2\text{O}$

5.3.1.12 Pre-Methanol Distillation Pressure Relief Valve

The bottom exit from the DME distillation column consists of CH₃OH and H₂O at 11.2 atm and 45 °C. This process section reduces the pressure from 11.2 atm to 3.4 atm, the pressure at which methanol distillation occurs (US patent 3,920,717). No reaction takes place in this process section so the flowrate of the components remains the same.

$$m_{j,19} = m_{j,18} \quad (5-34)$$

where: j = CH₃OH and H₂O

5.3.1.13 Methanol Distillation Column

The exit stream from pre-methanol distillation column valve enters methanol distillation column at 45°C and 3.4 atm. The column operates at a pressure of 3.4 atm. and a reflux ratio of 1.5 (US patent 3,920,717). It is assumed that 99.9 percent recovery of methanol in top product takes place producing 99.9 percent pure methanol on weight basis. Water with a trace quantity of methanol is recovered at the bottom and sent to wastewater treatment facility. Following equation present the mass balance across the methanol distillation column.

$$m_{CH_3OH,20} = 0.999(m_{CH_3OH,19}) \quad (5-35)$$

$$m_{H_2O,20} = (m_{CH_3OH,20}) \left(\frac{100}{\text{Methanol Purity}_{in_mole\%}} \right) \quad (5-36)$$

$$m_{CH_3OH,21} = m_{CH_3OH,19} - m_{CH_3OH,20} \quad (5-37)$$

$$m_{H_2O,21} = m_{H_2O,19} - m_{H_2O,20} \quad (5-38)$$

where: Number subscript = stream numbers as identified in process flow diagram (PFD).

Table 5-3 presents the default values of the process variables used in the process. Table 5-4 presents the mass balance for the conventional methanol production process based on the default values. It shows the temperatures, pressures and flowrates of components in various streams of the process.

Table 5-3. Default Input Values of Process Variables Used for Conventional Methanol Production

	Process Unit	Process Variable (Units)	Value
1.	Natural Gas Compressor (Isentropic)	Inlet Temperature (K) Outlet Pressure (atm.) Compressor Efficiency (%)	298 20 75
2.	Syngas Generator	Reaction Temperature (K) Reaction Pressure (atm.) Steam to Natural Gas Ratio Steam Reformer Furnace Efficiency (%) CH ₄ conversion (%) C ₂ H ₆ and C ₃ H ₆ conversion (%) CO conversion in water-gas shift (%)	1153 20 3.681 92 81.46 100 40.2
3.	Waste Heat Boiler (WHB)	Outlet Temperature (K) Steam Generation Pressure (atm.) BFW Inlet Temperature (K) WHB Efficiency (%)	383 6.8 323 85
4.	Syngas Compressor (Isentropic)	Outlet Pressure (atm.) Compressor Efficiency (%)	50 75
5.	Feed/Product Heat Exchanger	Coldside Outlet Temperature (K) Exchanger Efficiency (%)	523 100

Table 5-3 continued on next page

Table 5-3 continued

	Process Unit	Process Variable (Units)	Value
6.	Methanol Reactor	Reactor Temperature (K)	533
		Reactor Pressure (atm.)	50
		Steam Generation Pressure (atm.)	40
		Reactor Steam Boiler Efficiency (%)	85
		CO and CO ₂ conversion (%)	95
		DME Production (% of methanol production)	2
7.	Condenser	Outlet temperature (K)	318
		Condenser Efficiency (%)	85
8.	Pre-Flash Drum Pressure Relief Valve	Outlet Pressure (atm.)	11.2
9.	DME Distillation Column	Operating Pressure (atm.)	11.2
		Feed Temperature (K)	318
		Reflux Ratio	20
		Steam Pressure Used in Reboiler (atm.)	6.8
10.	Pre-Methanol Distillation Pressure Relief Valve	Outlet Pressure (atm.)	3.4
11.	Methanol Distillation Column	Operating Pressure (atm.)	3.4
		Feed Temperature (K)	318
		Reflux Ratio	1.5
		Steam Pressure Used in Reboiler (atm.)	6.8

Table 5-4. Mass Balance Across Methanol Production Process^a (All flowrates are in kmol/hr).

Stream No.	T (K)	P (atm)	Total Flow	CH ₄	C ₂ H ₆	C ₃ H ₈	N ₂	H ₂	CO	CO ₂	Steam/H ₂ O	DME	CH ₃ OH
1	298	1	1000	906	70	21	1.7	0	0	1.3	0	0	0
2	605.47	20	1000	906	70	21	1.7	0	0	1.3	0	0	0
3	486.1	20	3681	0	0	0	0	0	0	0	3681	0	0
4	298	1	62.7	NG ^b	NG	NG	NG	NG	NG	NG	NG	NG	NG
5	1153	20	6563	168	0	0	1.7	3088	564.3	378.0	2363	0	0
6	383	20	6563	168	0	0	1.7	3088	564.3	378.0	2363	0	0
7	383	20	2363	0	0	0	0	0	0	0	2363	0	0
8'	383	20	21.00	0.84	0	0	0.01	15.44	2.82	1.89	0	0	0
8	383	20	4179	167	0	0	1.69	3072	561.5	376.1	0	0	0
9	492.9	50	4179	167	0	0	1.69	3072	561.5	376.1	0	0	0
10	523	50	4179	167	0	0	1.69	3072	561.5	376.1	0	0	0
11	533	50	2348	167	0	0	1.69	884.0	3.29	18.81	369.7	12.39	890.7
12	495.3	50	2348	167	0	0	1.69	884.0	3.29	18.81	369.7	12.39	890.7

Table 5-4 continued on next page

Table 5-4, Continued

Stream No.	T (K)	P (atm)	Total Flow	CH ₄	C ₂ H ₆	C ₃ H ₈	N ₂	H ₂	CO	CO ₂	Steam/H ₂ O	DME	CH ₃ OH
13	318	50	2348	167	0	0	1.69	884.0	3.29	18.81	369.7	12.39	890.7
14	318	11.2	2348	167	0	0	1.69	884.0	3.29	18.81	369.7	12.39	890.7
15	318	11.2	1075	167	0	0	1.69	884.0	3.29	18.81	0	0	0
16	318	11.2	1273	0	0	0	0	0	0	0	369.7	12.39	890.7
17	318	11.2	12.39	0	0	0	0	0	0	0	0	12.39	0
18	318	10.5	126	0	0	0	0	0	0	0	369.7	0	890.7
19	318	3.4	1260	0	0	0	0	0	0	0	369.7	0	890.7
20	363	3.4	891.4	0	0	0	0	0	0	0	1.58	0	889.8
21	363	3.4	369.0	0	0	0	0	0	0	0	368.1	0	0.89

^a For 28503.5 kg/hr methanol production

^b NG implies Natural Gas combusted in Steam Reformer Furnace and is calculated in Energy Balance Section

5.3.2 Energy Balance Across the Process

Energy balance section documents the energy balance across each process section including all assumptions and relevant equations implemented in an EXCEL spreadsheet. As stated in mass balance section, 1000 kmol/hr of desulfurized natural gas was assumed as a starting raw material for methanol production. From mass balance, 891.43 kmol/hr (28503.5 kg/hr) of 99.9 percent methanol by weight is produced from that much natural gas. Since the function of each process unit has been discussed in the overview of the process and the mass balance section, only the information pertaining to energy will be addressed in this section. The following subsections present the energy balance across each process unit.

5.3.2.1 Natural Gas Compressor

The compressor used in the process utilizes electrical energy for its operation. The energy used in the compressor can be calculated by obtaining the work required in compressing the natural gas feed from 1 atm to 20 atm, the pressure at which steam reformer operates (Twigg, 1989). Work done in compressing the natural gas can be then divided by a user defined compressor efficiency, η , to obtain the power consumption by the compressor. Equations 5-39 through 5-43 were used to calculate compressor power requirements. The compressor is assumed to operate isentropically with a default compressor efficiency of 75 percent (Overcash, 1999)

The work done in compressing a gaseous component 'i' from pressure P_1 to P_2 at initial temperature T_1 (in K) is given by:

$$-W_i = \frac{R T_1}{M} \left(\frac{g_i}{g_i - 1} \right) \left[\left(\frac{P_2}{P_1} \right)^{(g_i - 1)/g_i} - 1 \right] \quad (5-39)$$

where: W_i = work done in compressing component 'i', W

i = CH₄, C₂H₆, C₃H₈, N₂, CO₂, etc.

M = Molecular Wt. (g/mole)

R = Universal Gas Constant (= 8.314 J/mol/K)

$\gamma_i = C_{pi}/C_{vi}$

γ_i is obtained from specific heat at constant pressure C_p , and specific heat capacity at constant volume, C_v , C_p and C_v are related as follows:

$$C_p - C_v = R \quad (5-40)$$

C_p is a function of temperature. The following equation relates C_p with temperature:

$$\left(\frac{C_{p_i}}{R} \right) = A_i + B_i T + C_i T^2 + \frac{D_i}{T^2} \quad (5-41)$$

where: A, B, C, D are constants characteristic of a particular gas. The values of A, B, C, D for the compounds involved in the process are presented in Table 5-2.

C_p can be obtained once the temperature is known. C_{pi} and C_{vi} can thus be used to find ' γ_i ' for a particular gas. Using Equation (5-39), the work done in compressing the gas component 'i' from pressure P_1 to pressure P_2 can be calculated. This work done is calculated individually for all components comprising the natural gas. Power required by

the compressor can be calculated from the flow rate, in kg/s, of the component by using Equation (5-42).

$$BHP_i = \frac{-W_i m_i^c}{1000 h_{compressor}} \quad (5-42)$$

where: m_i^c = mass flow rate of component in kg/s

$\eta_{compressor}$ = Efficiency of compressor (Default value = 0.75).

The total power requirement of the compressor is given by Equation (5-43)

$$(Compressor_Power)_{TOTAL} = \sum_{i=1}^n (BHP, kW)_i \quad (5-43)$$

where: n = number of components

Compressor_Power = Compressor power in kW.

The temperature of the natural gas rises as it is compressed from 1 atm to 20 atm under isentropic conditions assumed. The exit temperature of natural gas, T_2 , is given by Equation 5-44

$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{\frac{\gamma_{av} - 1}{\gamma_{av}}} \quad (5-44)$$

where: γ_{av} = average $\gamma \cong \gamma$ of major component (CH_4)

Total electrical power calculated in Equation 5-43 is linked to the electricity sub-model to calculate the LCI parameters associated with power consumption.

5.3.2.2 Synthesis Gas Generator (Steam Reformer)

Natural gas with a composition given in section 5.3.1.1 enters the steam reformer at the exit temperature and pressure of compressor. Saturated steam at 20 atm is mixed with natural gas and the combined feed is sent to steam reformer. The reaction products formed leave the reactor at the reaction temperature and pressure inside the steam reformer (880 °C, 20 atm., Twigg, 1989). Based on inlet temperature and composition of inlet gas and outlet temperature and composition of products, the enthalpy change within the reactor is calculated, including the heat of reaction. Equations 5-45 through 5-48 are used to calculate the total enthalpy change within the reactor.

$$(\Delta H)_p = \sum_{i=1}^n m_{i,5} \left[A_i (T_{out} - T_R) + B_i \frac{(T_{out}^2 - T_R^2)}{2} + C_i \frac{(T_{out}^3 - T_R^3)}{3} - D_i \left(\frac{1}{T_{out}} - \frac{1}{T_R} \right) \right] \quad (5-45)$$

where: $(\Delta H)_p$ = Total enthalpy of products at T_{out} (K) with respect to T_R , kJ/hr

$m_{i,5}$ = molar flowrate of component 'i' out of the reactor, kmol/hr

T_{out} = Temperature of the product gases, K

T_R = Reference temperature, 298 K

A_i, B_i, C_i, D_i = Constants for component 'i' in specific heat capacity equation.

i = CH₄, N₂, CO₂, H₂O, CO, H₂

$$(\Delta H)_R = \sum_{j=1}^m m_{j,3} \left[A_j (T_{in} - T_R) + B_j \frac{(T_{in}^2 - T_R^2)}{2} + C_j \frac{(T_{in}^3 - T_R^3)}{3} - D_j \left(\frac{1}{T_{in}} - \frac{1}{T_R} \right) \right] \quad (5-46)$$

where: $(\Delta H)_R$ = Total enthalpy of reactants at T_{in} (K) with respect to T_R , kJ/hr

$m_{j,3}$ = molar flowrate of component 'j' in to the reactor, kmol/hr

T_{in} = Temperature of the inlet reactants, K

T_R = Reference temperature, 298 K

A_j, B_j, C_j, D_j = Constants for component 'j' in specific heat capacity equation.

j = $CH_4, C_2H_6, C_3H_8, N_2, CO_2, H_2O$

$$(\Delta H)_{RXN} = \sum_{k=1}^l m_k [\Delta H_{RXN}]_k \quad (5-47)$$

where: $(\Delta H)_{RXN}$ = Total enthalpy of Reactions $k=1$ to l , kJ/hr

m_k = moles of the reactant 'k' consumed in reaction 'k', kmol/hr

$[(\Delta H)_{RXN}]_k$ = enthalpy of reaction 'k', kJ/mole 'k' reacted

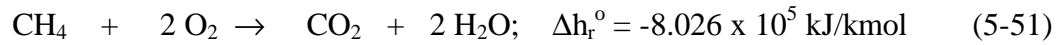
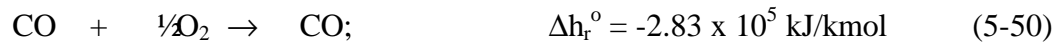
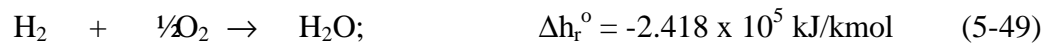
k = reactions 5-1 to 5-4 (CH_4 conversion, C_2H_6 conversion, C_3H_8 conversion, and water gas shift).

$$(\Delta H)_{SR} = (\Delta H)_P + (\Delta H)_{RXN} - (\Delta H)_R \quad (5-48)$$

where: $(\Delta H)_{SR}$ = Enthalpy change in Steam Reformer (SR), kJ/hr

Since the reactions occurring in the steam reformer are endothermic, $(\Delta H)_{SR}$ is positive and this much energy must be supplied, externally, for reforming reactions to occur. Purge gases are combusted in the steam reformer furnace to supply this heat. If the required heat is more than the heat available after purge combustion, then the remaining heat is supplied by natural gas combustion. The furnace is assumed to operate at 980°C,

100 °C higher than the temperature inside the steam reformer, which is a typical steam reformer furnace firebox temperature (Cheng and Kung, 1994). The combustion heat raises the temperature of reactant gases and supplies the heat for the reforming reactions. The following purge combustion reactions occur in the furnace. N₂ and CO₂ just undergo the change in enthalpy.



Δh_r° is the enthalpy of reaction at standard temperature and pressure (298K and 1 atm; Perry and Green, 1997). Ninety nine percent thermal oxidation of purge gases (separated in flash drum) is assumed to occur in steam reformer furnace. One percent unconverted purge gases are included in the overall LCI. Overall furnace heat transfer efficiency of 92 percent is assumed as a default value (Cheng and Kung, 1994).

$$(\Delta H)_{Purge} = \sum_{p=1}^q m_p (\Delta H)_p \quad (5-52)$$

where: $(\Delta H)_{Purge}$ = Total heat supplied by purge gas combustion, kJ/hr

m_p = kmol of reactant 'p' in purge combusted in reaction 'p', kmol/hr

$(\Delta H)_p$ = Heat of reaction of reaction 'p', kJ/kmol.

p = H₂, CH₄, CO

This heat with certain efficiency (default = 92 percent), η_f , is available to steam reforming reactions inside the steam reformer tubes. The enthalpy difference between the heat required and heat supplied by purge is given by Equation 5-53.

$$(\Delta H)_{Balance} = (\Delta H)_{SR} - \eta_f (\Delta H)_P \quad (5-53)$$

where: η_f = Furnace efficiency.

The remaining heat is supplied by natural gas combustion (Cheng and Kung, 1994). The amount of natural gas (in 10^6 ft^3) combusted to supply this heat with furnace efficiency of η_f is calculated by Equation (5-54).

$$V_{NG} = \frac{(\Delta H)_{Balance}}{\eta_f (HV)_{NG}} \quad (5-54)$$

where: V_{NG} = amount of natural gas to be combusted, $10^6 \text{ ft}^3/\text{hr}$

HV_{NG} = Heating value of natural gas ($=1.0752 \times 10^9 \text{ kJ}/10^6 \text{ ft}^3$)

Mass flowrate of natural gas can be calculated by multiplying the volumetric flowrate by the density ($=19051.2 \text{ kg}/10^6 \text{ cuft.}$). The flowrate of natural gas will be used to calculate the pre-combustion and combustion emissions for the purpose of the LCI of methanol. If $(\Delta H)_{Balance}$ is negative, then no natural gas is required to be burned in steam reformer furnace and the additional heat generated by purge gases can be used as appropriate.

5.3.2.3 Waste Heat Boiler

Hot product gases from the steam reformer at 880 °C enter the waste heat boiler for excess process heat recovery. Saturated steam at 100-psia is assumed to be generated from BFW at 50°C as a result of non-contact heat exchange with hot gases. The temperature of the product gases is reduced to 110 °C. Change in enthalpy of the product gases in going from 880 °C to 110 °C can be calculated by Equation 5-55. It should be noted that water undergoes a phase change at its saturation temperature (T^{sat}) at 50 atm. Therefore its enthalpy change is evaluated separately.

$$(\Delta H)_{\text{WHB,G}} = \sum_{j=1}^m m_j \left[A_j (T_o - T_i) + B_j \frac{(T_o^2 - T_i^2)}{2} + C_j \frac{(T_o^3 - T_i^3)}{3} - D_j \left(\frac{1}{T_o} - \frac{1}{T_i} \right) \right] \quad (5-55)$$

where: $(\Delta H)_{\text{WHB,G}}$ = Enthalpy change associated with non-condensables, kJ/hr

m_j = flowrate of component 'j' through WHB, kmol/hr.

T_o = Outlet temperature of gases from WHB, K (default value = 383 K)

T_i = Inlet temperature of gases into WHB, K (default value = 1153 K)

j = CH₄, N₂, H₂, CO, CO₂ (H₂O considered separately).

In order to evaluate the enthalpy change of H₂O, its saturation temperature (T^{sat}) is required. Enthalpy change for water occurs in two parts: H₂O going from 880 °C to its T^{sat} in vapor phase and from T^{sat} to 110 °C in liquid phase. Both of these enthalpies are added to calculate the enthalpy change associated with H₂O. Saturation temperature of

water is calculated using Antoine's equation, which is inverted to find the saturation temperature (in K):

$$T^{sat} = \left(\frac{A_{oi} C_{oi} - B_{oi} - C_{oi} \log_{10} (760 P)}{\log_{10} (760 P) - A_{oi}} \right) + 273 \quad (5-56)$$

where: P = Partial pressure of the component in mm of Hg

A_{oi} , B_{oi} , are C_{oi} = constants depending on the component (H_2O in this case).

Based on above equation, it can be determined that no other component undergoes a phase change and therefore their change in enthalpy is accounted in Equation 5-55. Enthalpy change associated with water is given by equations 5-57 to 5-59

$$(\Delta H)_{H_2O_v} = m_i \left[A_i (T_{sat} - T_i) + B_i \frac{(T_{sat}^2 - T_i^2)}{2} + C_i \frac{(T_{sat}^3 - T_i^3)}{3} - D_i \left(\frac{1}{T_{sat}} - \frac{1}{T_i} \right) \right] \quad (5-57)$$

$$(\Delta H)_{H_2O_L} = m_i C_{PL} (T_o - T_{sat}) \quad (5-58)$$

where: m_i = molar flowrate of water, kmol/hr

C_{PL} = liquid specific heat capacity of water, kJ/kmol/K

$$(\Delta H)_{H_2O} = (\Delta H)_{H_2O_v} + (\Delta H)_{H_2O_L} \quad (5-59)$$

The total enthalpy change of syngas in WHB is given by Equation 5-60.

$$(\Delta H)_{WHB} = (\Delta H)_{WHB,G} + (\Delta H)_{H_2O} \quad (5-60)$$

Equation 5-61 calculates the enthalpy carried by the steam generated. Amount of 100-psia steam generated is calculated by Equation 5-62.

$$H_{WHB_Steam} = \eta_{WHB} (\Delta H)_{WHB} \quad (5-61)$$

$$S_{WHB} = \frac{H_{WHB_Steam}}{(h_v - h_l)} \quad (5-62)$$

where: H_{WHB_Steam} = Enthalpy carried by steam, kJ/hr

η_{WHB} = Efficiency of heat exchange in WHB (default value = 85 percent).

h_v = Enthalpy of 100 psia saturated steam, kJ/kg

h_l = Enthalpy of water at 50°C, kJ/kg

S_{WHB} = Flowrate of steam generated, kg/hr.

The steam produced in WHB is avoided being produced by conventional means and therefore offsets the LCI emissions due to steam.

5.3.2.4 Water Removal and Knock-out Drum

In this process section, condensed water is removed from the syngas to produce dry syngas. No significant enthalpy change takes place. Thus the enthalpy change is assumed to be zero for this process section.

5.3.2.5 Syngas Compressor

In this section, dry syngas is compressed to 50 atm from 20 atm. The compressor used in the process utilizes electrical energy for its operation. Power consumed by the compressor and the outlet temperature of syngas are calculated using Equations 5-39 through 5-44. The components, i 's, in this case are CH₄, N₂, H₂, CO, and CO₂. γ_{av} for the calculation of compressor outlet temperature is taken as a weighted average based on mole fractions of the components. The default compressor efficiency is 75 percent (Overcash, 1999). For simplicity, the compressor is assumed to operate isentropically. Total electrical power calculated by Equation 5-43 is linked to the electricity sub-model to calculate LCI parameters associated with it.

5.3.2.6 Syngas Feed/Product Heat Exchanger (Feed-Preheater)

In this process section, hot product gases from the methanol reactor at 260 °C and 50 atm exchange heat with exit gases from syngas compressor to heat them to 250 °C before sending them to methanol reactor. The cold side inlet temperature is fixed by the outlet temperature from the syngas compressor. The hot side outlet temperature is determined by an enthalpy balance. Since gas-gas non-contact heat exchange can occur at very high efficiency, it is assumed that heat supplied by hot stream is completely transferred to the cold stream. Following equations present the enthalpy balance across this process section.

Hot-side (Product gases from methanol reactor)

$$(\Delta H)_H = \sum_{i=1}^n m_i \left[A_i (T_{Ho} - T_{RC}) + B_i \frac{(T_{Ho}^2 - T_{RC}^2)}{2} + C_i \frac{(T_{Ho}^3 - T_{RC}^3)}{3} - D_i \left(\frac{1}{T_{Ho}} - \frac{1}{T_{RC}} \right) \right] \quad (5-63)$$

where: $(\Delta H)_H$ = Enthalpy change of hot product side, kJ/hr

m_i = molar flowrate of component 'i' in hot product gases, kmol/hr

T_{Ho} = Hotside outlet temperature, K (to be determined)

T_{RC} = Hotside inlet temperature = Reactor temperature (Default value = 533 K)

'i' = CH₄, N₂, H₂, CO, CO₂, CH₃OH, DME, and H₂O.

Cold-side (Syngas from syngas compressor)

$$(\Delta H)_C = \sum_{j=1}^m m_j \left[A_j (T_{in} - T_{RI}) + B_j \frac{(T_{in}^2 - T_{RI}^2)}{2} + C_j \frac{(T_{in}^3 - T_{RI}^3)}{3} - D_j \left(\frac{1}{T_{in}} - \frac{1}{T_{RI}} \right) \right] \quad (5-64)$$

where: $(\Delta H)_C$ = Enthalpy change of cold syngas side, kJ/hr

m_j = molar flowrate of component 'j' in syngas, kmol/hr

T_{RI} = coldside outlet temperature, K (default value = 523 K)

T_{in} = coldside inlet temperature = Compressor exit temperature, K

'j' = CH₄, N₂, H₂, CO, CO₂

Using the enthalpy balance, $(\Delta H)_H = (\Delta H)_C$, hotside outlet temperature, T_{Ho} , is calculated using goal seek function in EXCEL. The goal seek solver function used is not automatic and the user must re-run the solver if any change is made in process conditions.

5.3.2.7 Methanol Reactor

Preheated syngas from the feed/product heat exchanger at 250 °C is sent to the methanol reactor, which operates at 50 atm and 260 °C. Reactions as presented by Equations 5-5 through 5-7 take place in the methanol reactor. All of these reactions are exothermic so the heat generated in the reactor and must be removed. This heat is removed by generating high-pressure steam on the shell side. Boiler feed water at 50°C is used to generate 40 atm saturated steam (Cheng and Kung, 1994). Based on inlet temperature and the composition of the inlet gas and the outlet temperature and composition of products, enthalpy change within the reactor is calculated in Equations (5-65) to (5-68) are used to calculate the total enthalpy change within the reactor.

$$(\Delta H)_P = \sum_{i=1}^n m_i \left[A_i (T_{out} - T_R) + B_i \frac{(T_{out}^2 - T_R^2)}{2} + C_i \frac{(T_{out}^3 - T_R^3)}{3} - D_i \left(\frac{1}{T_{out}} - \frac{1}{T_R} \right) \right] \quad (5-65)$$

where: $(\Delta H)_P$ = Total enthalpy of products at T_{out} (K) with respect to T_R , kJ/hr

m_i = molar flowrate of component 'i' out of the reactor, kmol/hr

T_{out} = Temperature of the product gases, K (Default value = 533 K)

T_R = Reference temperature, 298 K

A_i, B_i, C_i, D_i = Constants for component 'i' in specific heat capacity equation given in Table 5-2.

i = CH₄, N₂, H₂, CO, CO₂, H₂O, CH₃OH, and DME.

$$(\Delta H)_R = \sum_{j=1}^m m_j \left[A_j (T_{in} - T_R) + B_j \frac{(T_{in}^2 - T_R^2)}{2} + C_j \frac{(T_{in}^3 - T_R^3)}{3} - D_j \left(\frac{1}{T_{in}} - \frac{1}{T_R} \right) \right] \quad (5-66)$$

where: $(\Delta H)_R$ = Total enthalpy of reactants at T_{in} (K) with respect to T_R , kJ/hr

m_j = molar flowrate of component 'j' in to the reactor, kmol/hr

T_{in} = Temperature of the inlet reactants, K (Default value = 523 K)

T_R = Reference temperature, 298 K

A_j, B_j, C_j, D_j = Constants for component 'j' in specific heat capacity equation given in Table 5-2.

j = CH₄, N₂, H₂, CO, and CO₂.

$$(\Delta H)_{RXN} = \sum_{k=1}^l m_k [\Delta H_{RXN}]_k \quad (5-67)$$

where: $(\Delta H)_{RXN}$ = Total enthalpy of Reactions $k=1$ to l , kJ/hr

m_k = moles of the reactant 'k' consumed in reaction 'k', kmol/hr

$[(\Delta H)_{RXN}]_k$ = enthalpy of reaction 'k', kJ/mole 'k' reacted

k = reactions 5-5 to 5-7 (CO conversion to CH₃OH, CO₂ conversion to CH₃OH, DME production).

$$(\Delta H)_{MeOH} = (\Delta H)_P + (\Delta H)_{RXN} - (\Delta H)_R \quad (5-68)$$

where: $(\Delta H)_{MeOH}$ = enthalpy change in methanol (MeOH) reactor, kJ/hr

Equation 5-69 calculates the enthalpy carried by the steam generated. The amount of 588-psia (40atm) saturated steam generated is calculated by Equation 5-70.

$$H_{MR_Steam} = h_{MeOH} (\Delta H)_{MeOH} \quad (5-69)$$

$$S_{MR} = \frac{H_{MR_Steam}}{(h_v - h_l)} \quad (5-70)$$

where: H_{MR_Steam} = enthalpy carried by steam, kJ/hr

η_{WHB} = Efficiency of heat exchange in MeOH reactor (default value = 0.85)

h_v = Enthalpy of 588 psia (40 atm) saturated steam, kJ/kg

h_l = Enthalpy of water at 50°C, kJ/kg

S_{WHB} = Flowrate of steam generated, kg/hr.

5.3.2.8 Methanol Condenser

Product gases from the methanol reactor enter the methanol condenser after heat exchange with feed syngas. In methanol condenser, water at 20 °C is used for condensing methanol, DME, and water. Exit temperature of cooling water is limited to 50 °C (Overcash, 1999). The outlet temperature of product gases is 45 °C (Overcash, 1999). At this temperature, complete condensation of methanol, DME and water takes place. It should be noted that the enthalpy change in the condenser is calculated using similar set of equations as used for the WHB in Equations (5-55) to (5-60). The enthalpy change for non-condensable gases, CH₄, N₂, H₂, CO, CO₂ is calculated using Equation (5-55) taking regard of changed components. The enthalpy change associated with CH₃OH, DME and H₂O is calculated using equations 5-56 to 5-59. The saturation temperature, T^{sat} , for methanol, DME, and water is calculated at their respective partial pressures. Equation 5-71 calculates the total enthalpy change occurring in the condenser.

$$(\Delta H)_{\text{Condenser}} = (\Delta H)_{\text{Condenser,G}} + (\Delta H)_{\text{CH}_3\text{OH}} + (\Delta H)_{\text{DME}} + (\Delta H)_{\text{H}_2\text{O}} \quad (5-71)$$

where: $(\Delta H)_{\text{Condenser,G}}$ = Enthalpy change associated with non-condensables, kJ/hr

$(\Delta H)_{\text{CH}_3\text{OH}}$ = Enthalpy change associated with CH₃OH, kJ/hr

$(\Delta H)_{\text{H}_2\text{O}}$ = Enthalpy change associated with H₂O, kJ/hr

$(\Delta H)_{\text{DME}}$ = Enthalpy change associated with DME, kJ/hr

The flowrate of water required for the removal of this enthalpy is calculated by Equation 5-72.

$$W_{\text{Condenser}} = \frac{(\Delta H)_{\text{Condenser}}}{h_{\text{Condenser}} C_{P_{\text{H}_2\text{O}}} (\Delta T)_{\text{H}_2\text{O}}} \quad (5-72)$$

where: $W_{\text{Condenser}}$ = Flowrate of cooling water, kg/hr

$C_{p_{\text{H}_2\text{O}}}$ = Specific heat capacity of water (4.18 J/kg/K)

$(\Delta T)_{\text{H}_2\text{O}}$ = Change in temperature of water (Default value = 50-20 = 30 K)

$\eta_{\text{Condenser}}$ = Condenser heat exchange efficiency (Default value = 0.85)

It should be noted that the heat removed by cooling water in methanol condenser is not recoverable and therefore does not contribute to the LCI of methanol. The flowrate of water is calculated just for the sake of completeness of energy balance.

5.3.2.9 Pre-Flash Drum Pressure Relief Valve

In pre-flash drum pressure relief valve, the pressure of the condenser outlet is reduced from 50 atm to 11.2 atm before sending it to flash drum for the removal of non-condensable gases. No useful work is recovered and therefore energy change in this process section does not contribute to the LCI of methanol.

5.3.2.10 Flash Drum

The flash drum is a simple gas liquid separator. Non-condensable gases, CH₄, N₂, H₂, CO, and CO₂ are removed at the top and sent to steam reformer furnace for combustion while liquid fraction consisting of CH₃OH, DME and H₂O is sent to DME distillation column. No significant energy changes occur in this section.

5.3.2.11 DME Distillation Column

The liquid fraction from flash drum enters this column at 45 °C and 11.2 atm. As stated in mass balance section, it is assumed that complete recovery of DME takes place as top product. Methanol and water leave as the bottoms of the distillation column. Reflux ratio used in the column is 20 (US patent 3,920,717). If 'D_{DME}' is the distillate (DME) flowrate of this distillation column, then the flowrate of vapor to the condenser of distillation column is given by:

$$V_{DME} = (R + 1) D_{DME} \quad (5-73)$$

where: V_{DME} = vapor flowrate of DME at the top, kmol/hr

R = Reflux ratio of the distillation column (Default value = 20)

D_{DME} = Distillate product DME flowrate, kmol/hr

Heat removal in the distillation column condenser is calculated by Equation 5-74.

$$(\Delta H)_{DME_Condenser} = V_{DME} (H_V)_{DME} \quad (5-74)$$

where: $(H_V)_{DME}$ = Heat of vaporization of DME at 45 °C, kJ/kmol

Since the feed enters the distillation column at 45°C, which is the boiling point of DME at 11.2 atm, no sensible heat is required in addition to the heat of vaporization. Therefore heat removed by the condenser is approximately equal to heat added by the reboiler.

$$(\Delta H)_{DME_Reboiler} \cong (\Delta H)_{DME_Condenser} \quad (5-75)$$

Saturated steam at 100 psia is assumed to be used in the distillation column reboiler. The steam is assumed to have been generated from 50 °C BFW. The total enthalpy carried by the steam used in the reboiler and its flowrate is calculated in Equations 5-76 and 5-77, respectively.

$$H_{DME_Steam} = \frac{(\Delta H)_{DME_Reboiler}}{h_{Reboiler}} \quad (5-76)$$

$$S_{DME} = \frac{H_{DME_Steam}}{(h_v - h_l)} \quad (5-77)$$

where: H_{DME_Steam} = Total enthalpy carried by steam, kJ/hr

$\eta_{Reboiler}$ = Efficiency of DME distillation column reboiler (default value = 0.85)

h_v = Enthalpy of 100-psia saturated steam, kJ/kg

h_l = Enthalpy of water at 50°C, kJ/kg

S_{DME} = Flowrate of steam used, kg/hr.

5.3.2.12 Pre-Methanol Distillation Relief Valve

In pre-methanol distillation pressure relief valve, the pressure of the bottoms from DME distillation column (CH₃OH and H₂O) is reduced from 11.2 atm to 3.4 atm before sending it to the methanol distillation column for the recovery of methanol. No useful work is recovered and therefore the energy change in this process section does not contribute to the LCI of methanol.

5.3.2.13 Methanol Distillation Column

A liquid stream consisting of methanol and water enters methanol distillation column at 45 °C and 3.4 atm. As stated in mass balance section, it is assumed that 99.9 percent recovery of 99.9 weight percent pure methanol takes place as top product. Water with balance methanol leaves as the bottom product of the distillation column and is sent

to a wastewater treatment facility. The reflux ratio used in the column is 1.5 (US patent 3,920,717). If 'D_T' is the distillate (methanol and water) flowrate of this distillation column, then the flowrate of vapor to the condenser of distillation column is given by:

$$V_T = (R + 1) D_T \quad (5-78)$$

$$\text{or } V_{CH_3OH} = (R + 1) D_{CH_3OH} \quad \text{and} \quad V_{H_2O} = (R + 1) D_{H_2O} \quad (5-79)$$

where: $D_T = D_{CH_3OH} + D_{H_2O}$

V_T = vapor flowrate of methanol and water at the top, kmol/hr

V_{CH_3OH} = vapor flowrate of methanol at the top, kmol/hr

V_{H_2O} = vapor flowrate of water at the top, kmol/hr

R = Reflux ration of the distillation column (Default value = 1.5)

D_T = Distillate product (99.9 percent methanol and 0.1 percent water; wt. basis)
flowrate, kmol/hr

D_{CH_3OH} = Distillate flow rate of methanol, kmol/hr

D_{H_2O} = Distillate flow rate of water, kmol/hr

Heat removal in the distillation column condenser is calculated by Equation 5-80.

$$(\Delta H)_{T_Condenser} = V_{CH_3OH} (H_V)_{CH_3OH} + V_{H_2O} (H_V)_{H_2O} \quad (5-80)$$

where: $(H_V)_{CH_3OH}$ = Heat of vaporization of CH₃OH at 90 °C.

Since the feed enters the distillation column at 45°C and the boiling point of methanol at 3.4 atm. is 90 °C, the sensible heat to take the distillate from 45 °C (feed temperature) to 90 °C is required in addition to the heat of vaporization in a reboiler. Therefore heat added in the reboiler is equal to heat removed in the condenser plus the sensible heat in raising liquid methanol and water from 45 °C to 90 °C. Equation 5-81 calculates the sensible heat supplied to methanol and water by the reboiler.

$$(\Delta H)_{Sensible} = (V_{CH_3OH} C_{P_{CH_3OH}} + V_{H_2O} C_{P_{H_2O}}) (\Delta T)_{Sensible} \quad (5-81)$$

where: C_{PH_2O} = Specific heat capacity of water, kJ/kmol/K

C_{PCH_3OH} = Specific heat capacity of methanol, kJ/kmol/K

$(\Delta T)_{Sensible}$ = Difference of boiling point of methanol and feed temperature, K

Thus enthalpy supplied by the reboiler is calculated by adding sensible heat to the enthalpy removed by condenser and can be calculated using Equation 5-82.

$$(\Delta H)_{T_Reboiler} = (\Delta H)_{T_Condenser} + (\Delta H)_{Sensible} \quad (5-82)$$

Saturated steam at 100-psia is assumed to be used in the distillation column reboiler. The steam is assumed to have been generated from 50 °C BFW. Total enthalpy carried by the steam used in the reboiler and its flowrate is calculated in equations 5-83 and 5-84 respectively.

$$H_{T_Steam} = \frac{(\Delta H)_{T_Reboiler}}{h_{Reboiler}} \quad (5-83)$$

$$S_T = \frac{H_{T_Steam}}{(h_v - h_l)} \quad (5-84)$$

where: H_{T_Steam} = Total enthalpy carried by steam used in methanol distillation column reboiler, kJ/hr

$\eta_{Reboiler}$ = Efficiency of DME distillation column reboiler (default value = 0.85)

h_v = Enthalpy of 100-psia saturated steam, kJ/kg

h_l = Enthalpy of water at 50°C.

S_T = Flowrate of steam used in methanol distillation column, kg/hr.

Table 5-5 presents the various parameters that affect the life cycle inventory of conventional methanol production process as obtained from the energy balance.

Table 5-5. Energy Balance Results of Process Units that Affect the LCI of Methanol^a (28,500 kg/hr of Methanol Production)

	Process Unit	Energy Type	Value	Units
1.	Natural Gas Compressor	Electricity	3.97E+03	kWh
2.	Steam Reformer	Steam (20 atm. Saturated)	1.72E+08	kJ/hr
3.	Steam Reformer	Natural Gas Combustion Enthalpy (Steam Reformer Furnace)	5.74E+07	kJ/hr
4.	Steam Reformer	Purge Gas Combustion Enthalpy (Steam Reformer Furnace)	-2.85E+08 ^b	kJ/hr
5.	Waste Heat Boiler	Steam (6.8 atm. Saturated)	-8.80E+06	kJ/hr
6.	Synthesis Gas Compressor	Electricity	5.14E+03	kWh
7.	Methanol Tubular Reactor (Steam Generation)	Steam (40 atm. Saturated)	-6.36E+07	kJ/hr
8.	Condenser (Heat Removal)	Heat ^c	-2.22E+07	kJ/hr
9.	DME Distillation Column Reboiler	Steam (6.8 atm. Saturated)	7.22E+06	kJ/hr
10.	MeOH Distillation Column Reboiler	Steam (6.8 atm. Saturated)	1.18E+08	kJ/hr
	TOTAL ELECTRICITY USED	Electricity	9.11E+03	KWh
	TOTAL STEAM CONSUMED/PRODUCED	Steam	2.25E+05	MJ/hr
	NATURAL GAS CONSUMED	Heat	62.7	kmol/hr

^a Negative sign in “value” column implies that energy is produced in the system and therefore a credit

^b Negative sign indicates that this energy is produced by combustion of purge gases and supplied to the steam reformer furnace.

^c This parameter does not influence the LCI of methanol but is presented for the sake of completeness of process unit.

5.3.3 Calculation of the LCI of Methanol Production from a Conventional Process

This section presents the methodology by which the LCI parameters are calculated using the results obtained from mass and energy balance of the process which are based on 891.4 kmol/hr (28500 kg/hr) of methanol produced. The methodology considers emissions from the process as well as the emissions that are associated with the LCI of electricity and steam used in the process. The LCI parameters associated with steam and electricity are imported from Chapters 2 and 3, respectively.

The LCI of methanol using a conventional process includes all activities associated with the process starting from desulfurized natural gas. The LCI parameters considered include gaseous and liquid releases as well as solid waste. The LCI parameters considered include particulate matter (PM), SO₂, NO_x, CO, CO₂, hydrocarbons (HCs), CH₄, HCl, VOCs and 12 trace metals, liquid emissions and solid waste. The emission factors are presented in units of kg pollutant/kg methanol produced. The following subsections present the various components of overall LCI of methanol.

5.3.3.1 Emissions Associated with LCI of Steam used in the Process

Steam production/consumption has been calculated in the energy balance section of the process for the total production of 28,500 kg/hr of methanol. Steam is consumed in the steam reformer (20 atm, saturated), DME distillation column (6.8 atm, saturated) and methanol distillation column (6.8 atm, saturated). Steam is produced in the WHB (6.8

atm, saturated) and methanol reactor (40 atm, saturated). Enthalpy associated with each of these has been calculated in the energy balance section. Enthalpy associated with steam produced is considered negative while enthalpy associated with steam consumption is considered positive. All of the energy contributions from these are added to calculate the net steam energy consumed or produced. Equation 5-85 calculates the net enthalpy of steam (in MJ/hr) in the methanol process for 28,500 kg/hr methanol production.

$$H_{Overall} = \frac{(H_{SR} + H_{WHB} + H_{MR_Steam} + H_{DME_Steam} + H_{T_Steam})}{1000} \quad (5-85)$$

where: $H_{Overall}$ = Net enthalpy of steam, MJ/hr

H_{SR} = Enthalpy associated with steam to steam reformer, kJ/hr (*Positive*)

H_{WHB} = Enthalpy associated with steam generated in WHB, kJ/hr (*Negative*)

H_{MR_Steam} = Enthalpy associated with steam generated in methanol reactor, kJ/hr
(*Negative*)

H_{DME_Steam} = Enthalpy associated with steam used in DME distillation column,
kJ/hr (*Positive*)

H_{T_Steam} = Enthalpy associated with steam used in methanol distillation column,
kJ/hr (*Positive*)

Chapter 2 presents the emissions associated with steam (LCI of steam) in the units of kg/MJ of steam. Emissions due to net enthalpy of steam in Equation 5-85 are calculated by Equation 5-86.

$$m'_j = (m'_j)_{\text{Steam_LCI}} (H_{\text{Overall}}) \quad (5-86)$$

where: j = Emission of type 'j' (PM, SO₂, CO, NO_x, etc.)

m'_j = Emission of type 'j', kg/hr

$(m'_j)_{\text{Steam_LCI}}$ = Emission of type 'j' from LCI of steam, kg/MJ steam.

Emissions due to steam usage/generation in the process per kg of methanol produced are calculated using Equation 5-87.

$$m_j = \frac{m'_j}{CH_3OH_Produced} \quad (5-87)$$

where: m_j = Emission of type 'j' per kg of methanol produced, kg/kg methanol

CH₃OH_Produced = Methanol production, kg/hr

Table 5-6 presents the emissions due to steam usage/production in the process per kg of methanol produced.

Table 5-6. LCI of Steam Used in the Conventional Methanol Synthesis Process

Atmospheric Emissions	kg/kg methanol produced
PM	2.31E-04
PM-10	no data
SO ₂	4.34E-03
SO ₃	no data
NO _x	8.38E-04
CO	9.99E-04
CO ₂ (Fossil)	7.11E-01
CO ₂ (Biomass)	no data
CH ₄	1.07E-03
HCl	2.53E-06
VOC	no data
NH ₃	no data
Hydrocarbons	no data
Metals	no data
Antimony (Sb)	no data
Arsenic (As)	no data
Beryllium (Be)	no data
Cadmium (Cd)	no data
Chromium (Cr)	no data
Cobalt (Co)	no data
Copper (Cu)	no data
Lead (Pb)	no data
Mercury (Hg)	no data
Nickel (Ni)	no data
Selenium (Se)	no data
Zinc (Zn)	no data
Liquid Emissions	
Dissolved Solids	no data
Suspended Solids	1.15E-04
BOD	6.27E-06
COD	4.38E-05
Oil	no data
Sulfuric Acid	no data
Iron	no data
Ammonia	no data
Copper	no data
Cadmium	no data
Arsenic	no data
Mercury	no data
Phosphate	no data
Selenium	no data
Chromium	no data
Lead	no data
Zinc	no data
Solid Waste	6.23E-02

5.3.3.2 Emissions Associated with Electricity Used in the Process

Electrical energy is used in the methanol production process in the natural gas and syngas compressors. The electrical power used in each compressor was calculated based on 28,500 kg/hr methanol of production. Electrical power used in both the compressors is added to calculate the total electrical power consumed in the process.

$$E_{TOTAL} = (Compressor_Power)_{NG} + (Compressor_Power)_{Syngas} \quad (5-88)$$

where: E_{TOTAL} = Total electrical energy used in the process, kWh (based on 1-hr)

$(Compressor_Power)_{NG}$ = Electrical power used in natural gas compressor, kW

$(Compressor_Power)_{Syngas}$ = Electrical power used in syngas compressor, kW

Chapter 3 presents the emissions associated with electricity (LCI of electricity) in the units of kg/kWh of electricity. Emissions due to electricity consumption in Equation 5-88 are calculated by Equation 5-89.

$$m'_i = (m'_i)_{Electricity_LCI} (E_{TOTAL}) \quad (5-89)$$

where: i = Emission of type 'i' (PM, SO₂, CO, NO_x, etc.)

m'_i = Emission of type 'i', kg

$(m'_i)_{Electricity_LCI}$ = Emission of type 'i' from LCI of Electricity, kg/kWh

Emissions due to electricity usage in the process per kg of methanol produced are calculated using equation 5-90.

$$m_i = \frac{m_i}{CH_3OH_Produced} \quad (5-90)$$

where: m_i = Emission of type 'i' per kg of methanol produced, kg/kg methanol

$CH_3OH_Produced$ = Methanol production, kg (1-hr basis).

Table 5-7 presents the emissions due to electricity usage in the process per kg of methanol produced.

Table 5-7. LCI of Electricity used in the Conventional Methanol Synthesis Process

Atmospheric Emissions	kg/kg methanol produced
PM	2.55E-04
PM-10	no data
SO ₂	1.55E-03
SO ₃	no data
NO _x	7.84E-04
CO	8.97E-05
CO ₂ (Fossil)	2.10E-01
CO ₂ (Biomass)	7.03E-04
CH ₄	4.53E-04
HCl	1.53E-05
VOC	no data
NH ₃	9.42E-07
Hydrocarbons	1.09E-04
Metals	
Antimony (Sb)	no data
Arsenic (As)	no data
Beryllium (Be)	no data
Cadmium (Cd)	no data
Chromium (Cr)	no data
Cobalt (Co)	no data
Copper (Cu)	no data
Lead (Pb)	9.81E-09
Mercury (Hg)	no data
Nickel (Ni)	no data
Selenium (Se)	no data
Zinc (Zn)	no data
Liquid Emissions	
Dissolved Solids	4.95E-04
Suspended Solids	1.38E-04
BOD	5.13E-07
COD	7.04E-06
Oil	8.74E-06
Sulfuric Acid	1.87E-06
Iron	1.15E-05
Ammonia	1.33E-07
Copper	0.00E+00
Cadmium	2.24E-08
Arsenic	no data
Mercury	1.76E-12
Phosphate	9.36E-07
Selenium	no data
Chromium	2.24E-08
Lead	5.43E-12
Zinc	7.74E-09
Solid Waste	3.84E-02

5.3.3.3 Emissions Associated with Fugitive Emissions from the Process

Mass balance section of the process calculates the fugitive emissions from H₂O knockout drum for 28500 kg/hr of methanol production. The emissions per kg of methanol production are calculated by following equation.

$$m_k = \frac{m'_k}{CH_3OH_Produced} \quad (5-91)$$

where: m_k = Emission of type 'k', kg/kg of methanol

m'_k = Emission of type 'k', kg/hr

Table 5-8 presents the emissions due to fugitive emissions in the process per kg of methanol produced.

Table 5-8. LCI for Fugitive Emissions from Conventional Methanol Synthesis Process

Atmospheric Emissions	kg/kg methanol produced
CO	2.77E-03
CO ₂	2.92E-03
CH ₄	4.71E-04

5.3.3.4 Emissions From Methanol Storage Tanks

Due to non-availability of data, the emissions from methanol storage tanks are assumed to be same as that in the LCI of methanol using LPMEOH process. Similar storage tanks are assumed for methanol storage in both cases. The emission factor for methanol is 8.65E-07 kg/kg of methanol produced.

5.3.3.5 Emissions Associated with Purge Gas Combustion

Purge gases are the non-condensable gases removed from flash drum in the process as modeled. As stated in energy balance section of the process, the purge gases are combusted in a steam reforming furnace with assumed 99 percent combustion efficiency (user input) to supply the heat for reforming reactions to take place. In most cases, this heat is less than what is required for the endothermic reactions in steam reformer (Cheng and Kung, 1994). Balance heat required is supplied by natural gas combustion (Cheng and Kung, 1994). Emissions associated with balance natural gas combustion in a process heater such as a steam reformer furnace are considered in a separate section. Emissions due to purge gas combustion are one percent uncombusted purge gases and the products of purge gas combustion (CO_2 and H_2O) as stoichiometrically presented in equations 5-8 to 5-10. Table 5-9 presents the emissions associated with purge combustion in steam reformer furnace. It should be noted that purge gas combustion efficiency may vary and is defined as a user input in the spreadsheet. Ninety nine percent efficiency is used as a default. NO_x emissions are expected but could not be included because of no availability of data.

Table 5-9. Emissions Associated with Purge Gas Combustion

Atmospheric Emissions	kg/kg of methanol produced
CO	3.23E-05
CO ₂	2.89E-01
CH ₄	9.38E-04

5.3.3.6 Emissions Associated with Natural Gas Combustion in the Steam Reformer Furnace

The energy balance section calculates the amount of natural gas combusted in steam reformer furnace. Since the steam reformer furnace operates at 980 °C (Cheng and Kung, 1994), natural gas combustion in it comes under the fired heaters source category. Uncontrolled emissions factors for all combustion sources burning natural gas have been presented in AP-42 (US EPA, 1998). A NO_x emission factor from natural gas combustion in fired heaters, both natural air draft and mechanical air draft, is presented in NO_x Control Options Book (STAPPA and ALAPCO, 1994). CO emission factor for combustion of natural gas in fired heaters is assumed to be same as that in an industrial furnace. Table 5-10 presents the uncontrolled emission factors for natural gas combustion from fired heaters (e.g. steam reforming furnace). Since natural gas is a clean fuel with very low sulfur content, no control factors are applied to SO₂ and PM. Low NO_x burner technology is assumed for NO_x control. 50 percent reduction in uncontrolled NO_x emissions is assumed, which is typical of low NO_x burner (US EPA, 1998). No control factors are applied to CO, CO₂, CH₄, and VOCs. Ninety-nine percent removal of metals is assumed as a default. No liquid discharges and solid residues occur. Table 5-10 also presents the controlled emissions from natural gas combustion for fired heaters. Pre-

combustion emissions associated with natural gas combusted in steam reformer furnace are combined with those of natural gas used for the generation of syngas and are discussed in next section.

Emissions due to natural gas combustion in steam reformer furnace for the production of 28500 kg/hr of methanol are calculated using Equation 5-92.

$$m_l^i = (m_l^i)_{NG_Emissions} (V_{NG}) \quad (5-92)$$

where: l = Emission of type ' l ' (PM, SO₂, CO, NO_x, etc.)

m_l^i = Emission of type ' l ', kg/hr

$(m_l^i)_{NG_Emissions}$ = Emission of type ' l ' from natural gas combustion, kg/10⁶ cuft.

V_{NG} = Natural gas flowrate, 10⁶ cuft/hr

Emissions due to natural gas combustion in the process per kg of methanol produced are calculated using Equation 5-93.

$$m_l = \frac{m_l^i}{CH_3OH_Produced} \quad (5-93)$$

where: m_l = Emission of type ' l ' per kg of methanol produced, kg/kg methanol

$CH_3OH_Produced$ = Methanol production, kg/hr

Table 5-11 presents the emissions associated with natural gas combustion in steam reformer furnace (kg/kg methanol produced).

Table 5-10. Uncontrolled and Controlled Emissions from Fired Heaters Firing Natural Gas^a (AP-42, US EPA, 1998)

Air Emissions	Uncontrolled (lb/10⁶ cuft)	Controlled (lb/10⁶ cuft)
PM	7.6	7.6
PM-10	no data	no data
SO ₂	0.6	0.6
SO ₃	no data	no data
NO _x	142.8	71.4
CO	40	40
CO ₂ (Fossil)	120,000	120,000
CO ₂ (Biomass)	no data	no data
CH ₄	2.3	2.3
HCl	no data	no data
VOC	5.5	5.5
NH ₃	no data	no data
Hydrocarbons	no data	no data
Metals		
Antimony (Sb)	no data	no data
Arsenic (As)	2.00E-04	2.00E-06
Beryllium (Be)	1.20E-05	1.20E-07
Cadmium (Cd)	1.10E-03	1.10E-05
Chromium (Cr)	1.40E-03	1.40E-05
Cobalt (Co)	8.40E-05	8.40E-07
Copper (Cu)	8.50E-04	8.50E-06
Lead (Pb)	5.00E-04	5.00E-06
Mercury (Hg)	2.60E-04	2.60E-06
Nickel (Ni)	2.10E-03	2.10E-05
Selenium (Se)	2.40E-05	2.40E-07
Zinc (Zn)	2.90E-02	2.90E-04

^a A control factor is applied only to NO_x emissions (50% reduction) and trace metals (99% reduction). Controlled emissions for all others are same as their uncontrolled emissions.

Table 5-11. Emissions due to Natural Gas Combustion in Steam Reformer Furnace

Atmospheric Emissions	kg/kg methanol produced
PM	7.01E-06
PM-10	no data
SO ₂	5.54E-07
SO ₃	no data
NO _x	6.59E-05
CO	3.69E-05
CO ₂ (Fossil)	1.11E-01
CO ₂ (Biomass)	no data
CH ₄	2.12E-06
HCl	no data
VOC	5.07E-06
NH ₃	no data
Hydrocarbons	no data
Metals	
Antimony (Sb)	no data
Arsenic (As)	1.85E-12
Beryllium (Be)	1.11E-13
Cadmium (Cd)	1.01E-11
Chromium (Cr)	1.29E-11
Cobalt (Co)	7.75E-13
Copper (Cu)	7.84E-12
Lead (Pb)	4.61E-12
Mercury (Hg)	2.40E-12
Nickel (Ni)	1.94E-11
Selenium (Se)	2.21E-13
Zinc (Zn)	2.68E-10

5.3.3.7 Pre-Combustion Emissions Associated with Natural Gas used in Process

Pre-combustion emissions associated with natural gas are presented in the electric energy process model (Dumas, 1998). Natural gas used in a steam reformer for the production of syngas has a flowrate of 1000 kmol/hr for the production of 28,500 kg/hr methanol. This is the input flowrate of natural gas assumed to calculate the overall LCI of methanol. Natural gas combusted in a steam reformer furnace is calculated in energy balance section of process. Both of these are added to get the total natural gas used in the process assuming that both have approximately same composition and density. Table 5-12 presents the pre-combustion emissions per 1000 cuft of natural gas (Dumas, 1998) It also presents the pre-combustion emissions associated with natural gas used in the process per kg of methanol produced as calculated by Equation 5-94.

$$m_n = \frac{\dot{m}_n (\dot{V}_{FEED} + \dot{V}_{NG})}{CH_3OH_Produced} \quad (5-94)$$

where: m_n = Emission of type 'n', kg/kg of methanol produced

\dot{m}_n = Emission of type 'n', kg/1000 cuft natural gas (Dumas, 1998)

\dot{V}_{FEED} = Natural gas used in generation of syngas, 1000 cuft/hr

\dot{V}_{NG} = Natural gas combusted in steam reformer furnace, 1000 cuft/hr

$CH_3OH_Produced$ = Methanol production, kg/hr

Table 5-12. Pre-Combustion Emissions due to Natural Gas Use in Methanol Process

Atmospheric Emissions	(kg/1000 cuft)^a	kg/kg methanol produced
PM	1.72E-03	5.95E-05
PM-10	no data	no data
SO ₂	8.94E-01	3.08E-02
SO ₃	no data	no data
NO _x	5.44E-02	1.88E-03
CO	1.04E-01	3.60E-03
CO ₂ (Fossil)	7.12E+00	2.46E-01
CO ₂ (Biomass)	1.27E-02	4.38E-04
CH ₄	1.72E-01	5.95E-03
HCl	4.45E-05	1.53E-06
VOC	no data	no data
NH ₃	4.31E-06	1.49E-07
Hydrocarbons	2.40E-01	8.29E-03
Metals		
Antimony (Sb)	no data	no data
Arsenic (As)	no data	no data
Beryllium (Be)	no data	no data
Cadmium (Cd)	no data	no data
Chromium (Cr)	no data	no data
Cobalt (Co)	no data	no data
Copper (Cu)	no data	no data
Lead (Pb)	1.30E-07	4.49E-09
Mercury (Hg)	no data	no data
Nickel (Ni)	no data	no data
Selenium (Se)	no data	no data
Zinc (Zn)	no data	no data
Liquid Emissions		
Dissolved Solids	1.38E+00	4.76E-02
Suspended Solids	2.45E-03	8.45E-05
BOD	1.22E-03	4.22E-05
COD	8.62E-03	2.97E-04
Oil	2.45E-02	8.45E-04
Sulfuric Acid	9.53E-06	3.29E-07
Iron	3.31E-05	1.14E-06
Ammonia	2.22E-06	7.67E-08
Copper	0.00E+00	0.00E+00
Cadmium	6.35E-05	2.19E-06
Arsenic	no data	no data
Mercury	4.99E-09	1.72E-10
Phosphate	4.99E-06	1.72E-07
Selenium	no data	no data
Chromium	6.35E-05	2.19E-06
Lead	4.99E-10	1.72E-11
Zinc	2.18E-05	7.51E-07
Solid Waste	2.63E+00	9.07E-02

^a Pre-combustion emissions (kg/1000 cuft Natural gas) from electric energy process model (Dumas, 1998)

5.3.3.8 Overall LCI of Methanol Production Using Conventional Process

All of the LCI parameters associated with different operations in production of methanol as documented in previous sections are summed to yield an overall LCI of methanol production. The LCI parameters are presented in units of kg pollutant/kg of methanol produced. Table 5-13 presents the LCI associated with various sections of methanol production (steam, electricity, pre-combustion, etc.) and the overall LCI of methanol.

There are three major contributors to the LCI of methanol: (1) the emissions associated with natural gas pre-combustion; (2) the LCI of steam; and (3) the LCI of electricity. For most LCI parameters, emissions associated with natural gas pre-combustions seem to drive the overall LCI of methanol. SO₂, NO_x, CO, CH₄, BOD, COD and solid waste emissions are higher for natural gas pre-combustions than any other contributor. PM emissions due to the LCI of steam and electricity are comparable with each other and higher than any other contributor. CO₂ emissions are more governed by the LCI of electricity. Suspended solid liquid emissions due to the LCI of steam and electricity are comparable with each other and are higher than any other contributor. Thus different contributors govern different LCI parameters; however, natural gas pre-combustions emissions, the LCI of steam, and the LCI of electricity are the main contributors dictating the overall LCI of methanol.

Table 5-13. Overall LCI of Methanol Using Conventional Process (kg/kg methanol produced)

Atmospheric Emissions	NG^a Pre-combustion	Steam LCI	Electricity- LCI	NG Combustion	Purge Gas Combustion^a	Fugitive Emissions	OVERALL- LCI
PM	5.95E-05	2.31E-04	2.55E-04	7.01E-06	no data	0.00E+00	5.52E-04
PM-10	no data	no data	no data	no data		0.00E+00	
SO ₂	3.08E-02	4.34E-03	1.55E-03	5.54E-07	no data	0.00E+00	3.67E-02
SO ₃	no data	no data	no data	no data		0.00E+00	
NO _x	1.88E-03	8.38E-04	7.84E-04	6.59E-05	no data	0.00E+00	3.56E-03 ^b
CO	3.60E-03	9.99E-04	8.97E-05	3.69E-05	3.23E-05	2.77E-03	7.53E-03
CO ₂ (Fossil)	2.46E-01	7.11E-01	2.10E-01	1.11E-01	2.89E-01	2.92E-03	1.57E+00
CO ₂ (Biomass)	4.38E-04	no data	7.03E-04	no data		0.00E+00	
CH ₄	5.95E-03	1.07E-03	4.53E-04	2.12E-06	9.38E-04	4.71E-04	8.88E-03
HCl	1.53E-06	2.53E-06	1.53E-05	no data		0.00E+00	
VOC	no data	no data	no data	5.07E-06		0.00E+00	
NH ₃	1.49E-07	no data	9.42E-07	no data		0.00E+00	
Hydrocarbons	8.29E-03	no data	1.09E-04	no data		0.00E+00	
CH ₃ OH	0.00E+00	0.00E+00	0.00E+00	0.00E+00	no data	8.65E-07	8.65E-07 ^c
Metals							
Antimony (Sb)	no data	no data	no data	no data	no data	0.00E+00	
Arsenic (As)	no data	no data	no data	1.85E-12	no data	0.00E+00	
Beryllium (Be)	no data	no data	no data	1.11E-13	no data	0.00E+00	
Cadmium (Cd)	no data	no data	no data	1.01E-11	no data	0.00E+00	
Chromium (Cr)	no data	no data	no data	1.29E-11	no data	0.00E+00	
Cobalt (Co)	no data	no data	no data	7.75E-13	no data	0.00E+00	
Copper (Cu)	no data	no data	no data	7.84E-12	no data	0.00E+00	
Lead (Pb)	4.49E-09	no data	9.81E-09	4.61E-12	no data	0.00E+00	

Table 5-13 continued on next page

Table 5-13 continued

Atmospheric Emissions	NG Pre-combustion	Steam LCI	Electricity- LCI	NG Combustion	Purge Gas Combustion^a	Fugitive Emissions	OVERALL- LCI
Mercury (Hg)	no data	no data	no data	2.40E-12	no data	0.00E+00	
Nickel (Ni)	no data	no data	no data	1.94E-11	no data	0.00E+00	
Selenium (Se)	no data	no data	no data	2.21E-13	no data	0.00E+00	
Zinc (Zn)	no data	no data	no data	2.68E-10	no data	0.00E+00	
Liquid Emissions^d							
Dissolved Solids	4.76E-02	no data	4.95E-04	0.00E+00	0.00E+00	0.00E+00	
Suspended Solids	8.45E-05	1.15E-04	1.38E-04	0.00E+00	0.00E+00	0.00E+00	3.37E-04
BOD	4.22E-05	6.27E-06	5.13E-07	0.00E+00	0.00E+00	0.00E+00	4.90E-05
COD	2.97E-04	4.38E-05	7.04E-06	0.00E+00	0.00E+00	0.00E+00	3.48E-04
Oil	8.45E-04	no data	8.74E-06	0.00E+00	0.00E+00	0.00E+00	
Sulfuric Acid	3.29E-07	no data	1.87E-06	0.00E+00	0.00E+00	0.00E+00	
Iron	1.14E-06	no data	1.15E-05	0.00E+00	0.00E+00	0.00E+00	
Ammonia	7.67E-08	no data	1.33E-07	0.00E+00	0.00E+00	0.00E+00	
Copper	0.00E+00	no data	0.00E+00	0.00E+00	0.00E+00	0.00E+00	
Cadmium	2.19E-06	no data	2.24E-08	0.00E+00	0.00E+00	0.00E+00	
Arsenic	no data	no data	no data	0.00E+00	0.00E+00	0.00E+00	
Mercury	1.72E-10	no data	1.76E-12	0.00E+00	0.00E+00	0.00E+00	
Phosphate	1.72E-07	no data	9.36E-07	0.00E+00	0.00E+00	0.00E+00	
Selenium	no data	no data	no data	0.00E+00	0.00E+00	0.00E+00	
Chromium	2.19E-06	no data	2.24E-08	0.00E+00	0.00E+00	0.00E+00	
Lead	1.72E-11	no data	5.43E-12	0.00E+00	0.00E+00	0.00E+00	
Zinc	7.51E-07	no data	7.74E-09	0.00E+00	0.00E+00	0.00E+00	
Solid Waste	9.07E-02	6.23E-02	3.84E-02	0.00E+00	0.00E+00	0.00E+00	1.91E-01

^a Based on purge gas combustion efficiency of 99 percent (user input)

^b Does not include NO_x emissions from purge gas combustion

^c Does not include methanol emissions from purge gas LCI

^d No liquid discharges and solid waste are assumed to occur in case of purge gas LCI.

5.4 Sensitivity Analysis of the Conventional Methanol Process Model

This section presents a sensitivity analysis of the conventional methanol process model. Four parameters were selected for study in the sensitivity analysis: (1) natural gas composition; (2) methane conversion in the steam reformer; (3) methanol reactor conversion; and (4) purge gas combustion efficiency. These parameters were selected for study based on a judgment that they had the potential to significantly impact the overall LCI of methanol production by conventional process. Each of these parameters was varied individually over the range considered to be representative of the typical variation. Other parameters, such as process conditions like temperatures and pressures are typically constant for the conventional process (Cheng and Kung, 1994; Twigg, 1989). Furthermore a small change in temperature or pressure was not expected to alter the LCI significantly. The following subsections present the results of the sensitivity analysis for natural gas composition, CH₄ conversion in steam reformer, CO and CO₂ conversion in the methanol reactor, and purge gas combustion efficiency.

5.4.1 Sensitivity of Methanol LCI to Natural Gas Composition

Natural gas composition varies from place to place in the U.S. Table 5-14 represents the composition of natural gas found in various U.S. fields (Babcock and Wilcox, 1972). The conventional methanol process model has the composition of natural gas as a user input. To examine the sensitivity of the overall LCI to natural gas composition, the natural gas composition was varied to represent each of the

compositions in Table 5-14, while all other parameters were held constant. Selected model results for the various natural gas compositions are presented in Table 5-15. It should be noted that only the results that affect the LCI of methanol are presented. Table 5-16 presents the results on per kg of methanol produced basis.

Table 5-14. Natural Gas Compositions from Various U.S. Fields (Babcock and Wilcox, 1972)

Component	Mole percent					
	<i>Base Case (0)</i>	<i>Pennsylvania (1)</i>	<i>S. California (2)</i>	<i>Ohio (3)</i>	<i>Los Angeles (4)</i>	<i>Oklahoma (5)</i>
CH ₄	90.6	83.4	84.0	93.82	90.0	84.1
C ₂ H ₆	7.0	15.8	14.8	0.25	5.0	6.7
C ₃ H ₈	2.1	0.0	0.0	0.00	0.0	0.0
N ₂	0.17	0.8	0.5	3.42	5.0	8.4
H ₂	0.0	0.0	0.0	1.83	0.0	0.0
CO	0.0	0.0	0.0	0.45	0.0	0.0
CO ₂	0.13	0.0	0.7	0.23	0.0	0.8

Table 5-15. Selected Model Results for Various Natural Gas Compositions Given in Table 5-14^a

Model Results	Base Case (0)	Pennsylvania (1)	S. California (2)	Ohio (3)	Los Angeles (4)	Oklahoma (5)
Methanol (kg/hr)	28500	30110	29860	23470	25200	25020
Steam Consumption (kJ/hr) ^b	2.24E+08	2.28E+08	2.27E+08	2.11E+08	2.16E+08	2.15E+08
Electricity Consumption (kWh)	9.11E+03	9.31E+03	9.25E+03	8.44E+03	8.70E+03	8.64E+03
Natural Gas used in Steam Reformer Furnace (10 ⁶ ft ³ /hr)	5.80E-02	5.20E-02	5.51E-02	5.00E-02	5.10E-02	6.00E-02
Fugitive Emissions (kg/hr) ^c	2.07E+02	2.17E+02	2.15E+02	1.78E+02	1.91E+02	1.94E+02
Purge gas Emissions^d	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr
CH ₄	2.67E+01	2.46E+01	2.48E+01	2.77E+01	2.66E+01	2.48E+01
H ₂	1.77E+01	1.80E+01	1.75E+01	1.61E+01	1.67E+01	1.56E+01
CO	9.21E-01	9.84E-01	9.18E-01	7.73E-01	8.24E-01	7.95E-01
CO ₂ ^e	8.25E+03	7.73E+03	7.77E+03	8.34E+03	8.09E+03	7.61E+03

- ^a All Columns are based on 1000 kmol/hr of Natural Gas as a starting material
^b Positive sign means that there is net steam consumption in methanol production process
^c Fugitive emissions are 0.5 percent of syngas leaving the water knockout drum.
^d Based on 99 percent (default) purge gas combustion in steam reformer furnace (User input)
^e Includes CO₂ produced by percent purge gas combustion at 99 percent efficiency

Table 5-16. Selected Model Results for Various Natural Gas Compositions Given in Table 5-14^a on per kg of Methanol Produced Basis

Model Results	Base Case (0)	Pennsylvania (1)	S. California (2)	Ohio (3)	Los Angeles (4)	Oklahoma a (5)
Steam Consumption (kJ/kg) ^b	7.86E+03	7.58E+03	7.62E+03	9.00E+03	8.56E+03	8.61E+03
Electricity Consumption (kWh/kg)	3.20E-01	3.09E-01	3.10E-01	3.60E-01	3.45E-01	3.46E-01
Natural Gas used in Steam Reformer Furnace (10 ⁶ ft ³ /kg)	2.03E-06	1.70E-06	1.85E-06	2.17E-06	2.02E-06	2.42E-06
Fugitive Emissions (kg/kg) ^c	7.25E-03	7.21E-03	7.21E-03	7.60E-03	7.60E-03	7.76E-03
Purge gas Emissions^d	kg/kg	kg/kg	kg/kg	kg/kg	kg/kg	kg/kg
CH ₄	9.38E-04	8.18E-04	8.30E-04	1.18E-03	1.05E-03	9.92E-04
H ₂	6.20E-04	5.98E-04	5.85E-04	6.85E-04	6.63E-04	6.24E-04
CO	3.23E-05	3.27E-05	3.07E-05	3.29E-05	3.27E-05	3.00E-05
CO ₂ ^e	2.89E-01	2.57E-01	2.60E-01	3.55E-01	3.21E-01	3.04E-01

- ^a All Columns are based on 1000 kmol/hr of Natural Gas as a starting material
^b Positive sign means that there is net steam consumption in methanol production process
^c Fugitive emissions are 0.5 percent of syngas leaving the water knockout drum.
^d Based on 99 percent (default) purge gas combustion in steam reformer furnace (User input)
^e Includes CO₂ produced by percent purge gas combustion at 99 percent efficiency

From the results in Table 5-15, it is clear that Pennsylvania natural gas produces the maximum amount of methanol among natural gas compositions considered on per hour basis. This is because it has the maximum amount of ethane, which produces more syngas per mole (two moles of CO and 5 moles of H₂) as opposed to methane which produces only one mole CO and 3 moles H₂ per mole. Ohio natural gas produces the least amount of methanol because of its high methane content and low ethane content.

The amount of steam required in the process increases with methanol production. This increase is not in the same proportion as the methanol production since the net steam required is the difference of steam consumed in steam reformer, methanol and DME distillation; and steam produced in waste heat boiler and methanol reactor. Steam consumed in the steam reformer is constant since the flowrate of raw material natural gas is held constant at 1000 kmol/hr for all the cases. The steam produced in waste heat boiler depends on the flowrate of syngas produced and is maximum in case of Pennsylvania natural gas. Also the steam produced in the methanol reactor is maximum for Pennsylvania natural gas because more syngas is converted to the methanol product. So even though Pennsylvania natural gas has maximum steam demand in methanol distillation, the overall steam demand does not change proportionally with methanol production. Table 5-16 shows that for the case of Pennsylvania natural gas, the steam demand per kg of methanol is less since highest quantity of methanol is produced by it. For the case of Ohio natural gas, there is maximum steam demand per kg of methanol because least amount of methanol is produced by it whereas there is not a major change in its net steam demand as compared with other natural gas compositions.

Electricity is consumed in the natural gas compressor and syngas compressor. The variation in electricity consumption on per hour basis is not wide among various natural gas compositions considered because there is not a major difference in the flowrate of natural gas and syngas. Electricity demand for the case of Pennsylvania natural gas is highest on per hour basis but it is not in same proportion as the methanol production. As a result, the electricity consumption is the least on per kg of methanol produced basis for the case of Pennsylvania natural gas. For the case of Ohio natural gas, there is maximum electricity demand per kg of methanol because least amount of methanol is produced by it whereas there is not a major change in the electricity demand as compared with other natural gas compositions.

Fugitive emissions occur in water knockout drum of the methanol production process and are 0.5 mole percent of the syngas entering the water knock out drum. Thus more the syngas production per hour more would be the fugitive emissions. Since Pennsylvania natural gas produces more syngas (on molar basis) for the same molar flowrate of natural gas, it has highest fugitive emissions on per hour basis. However, on per kg of methanol basis, Pennsylvania natural gas has least amount of fugitive emissions because fugitive emissions do not vary widely among various natural gas compositions whereas methanol production does.

The purge gas combustion efficiency in the steam reformer furnace has been assumed to be 99 percent for all the natural gas compositions considered. This is a user-

defined input and can be altered. The natural gas that has a higher N₂ and CO₂ content also has a higher N₂ and CO₂ content in purge gas on per hour basis. Both of these gases are non-combustible and do not contribute to heating when purge gas is combusted. As a result, the purge gas with higher content of these of N₂ and CO₂ produces less heat on combustion due to which more natural gas has to be supplied to the steam reformer furnace on per hour basis to provide the heat for reforming reactions. Thus, the Oklahoma natural gas with the highest N₂ and CO₂ content uses the highest amount of natural gas in the steam reformer whereas Los Angeles and Ohio natural gases having lower N₂ and CO₂ content use lower amounts of natural gas in the steam reforming furnace on per hour basis. Table 5-16 presents the purge gas emissions and natural gas combustion on per kg of methanol produced basis. The trends in Table 5-16 change from that in Table 5-15 because of wide variation in the methanol production.

Table 5-17 presents the LCI of methanol for the base case natural gas composition. Some of the parameters in the total methanol LCI are blank due to no availability of data for those parameters in the contributing columns. Only the parameters that appear in the total methanol LCI are presented. Table 5-18 presents the LCI of methanol based on Pennsylvania natural gas and the percentage difference with respect to the base case LCI. Pennsylvania natural gas was selected for comparison because its composition varies widely from the base case natural gas composition.

Table 5-17. LCI of Methanol for the Base Case Natural Gas Composition (Units: kg/kg of methanol produced)^a

Air Emissions	NG Pre-combustion	Steam-LCI	Electricity-LCI	NG Combustion (SR)	Purge Gas Combustion	Fugitive Emissions	TOTAL LCI
PM	5.95E-05	2.31E-04	2.55E-04	7.01E-06	no data	0.00E+00	5.52E-04 ^b
SO ₂	3.08E-02	4.34E-03	1.55E-03	5.54E-07	no data	0.00E+00	3.67E-02 ^b
NO _x	1.88E-03	8.38E-04	7.84E-04	6.59E-05	no data	0.00E+00	3.56E-03 ^b
CO	3.60E-03	9.99E-04	8.97E-05	3.69E-05	3.23E-05	2.77E-03	7.53E-03
CO ₂ (Fossil)	2.46E-01	7.11E-01	2.10E-01	1.11E-01	2.89E-01	2.92E-03	1.57E+00
CH ₄	5.95E-03	1.07E-03	4.53E-04	2.12E-06	9.38E-04	4.71E-04	8.88E-03
Liquid Emissions^c							
Suspended Solids	8.45E-05	1.15E-04	1.38E-04	0.00E+00	0.00E+00	0.00E+00	3.37E-04
BOD	4.22E-05	6.27E-06	5.13E-07	0.00E+00	0.00E+00	0.00E+00	4.90E-05
COD	2.97E-04	4.38E-05	7.04E-06	0.00E+00	0.00E+00	0.00E+00	3.48E-04
Solid Waste	9.07E-02	6.23E-02	3.84E-02	0.00E+00	0.00E+00	0.00E+00	1.91E-01

^a The LCI parameters that are blank in the total LCI of methanol are not shown because of “no data” for those parameters in some of the contributing columns.

^b Does not include the corresponding LCI parameter values for purge gas LCI.

^c Liquid discharges and solid waste in purge gas LCI are assumed to be zero.

Table 5-18. The LCI of Methanol for the Pennsylvania Natural Gas Composition and Percentage Difference With Respect to the Base Case LCI (Units: kg/kg of methanol produced)

	NG				Purge Gas	Fugitive	
Air Emissions	Pre-combustion	Steam-LCI	Electricity-LCI	NG Combustion (SR)	Combustion	Emissions	TOTAL-LCI
PM	5.79E-05	2.22E-04	2.47E-04	5.86E-06	no data	0.00E+00	5.33E-04 ^b
SO ₂	3.00E-02	4.18E-03	1.50E-03	4.63E-07	no data	0.00E+00	3.57E-02 ^b
NO _x	1.83E-03	8.07E-04	7.58E-04	5.51E-05	no data	0.00E+00	3.45E-03 ^b
CO	3.51E-03	9.63E-04	8.68E-05	3.09E-05	3.27E-05	2.78E-03	7.40E-03
CO ₂ (Fossil)	2.39E-01	6.85E-01	2.03E-01	9.26E-02	2.57E-01	2.91E-03	1.48E+00
CH ₄	5.79E-03	1.03E-03	4.39E-04	1.77E-06	8.18E-04	4.11E-04	8.50E-03
Liquid Emissions^c							
Suspended Solids	8.23E-05	1.10E-04	1.33E-04	0.00E+00	0.00E+00	0.00E+00	3.26E-04
BOD	4.12E-05	6.04E-06	4.96E-07	0.00E+00	0.00E+00	0.00E+00	4.77E-05
COD	2.90E-04	4.22E-05	6.81E-06	0.00E+00	0.00E+00	0.00E+00	3.39E-04
Solid Waste	8.84E-02	6.01E-02	3.71E-02	0.00E+00	0.00E+00	0.00E+00	1.86E-01
Percentage Difference With Respect to the Base Case^a							
Air Emissions	NG Pre-combustion	Steam-LCI	Electricity-LCI	NG Combustion (SR)	Purge Gas Combustion	Fugitive Emissions	TOTAL-LCI
PM	2.53	3.64	3.24	1.64			3.50
SO ₂	2.53	3.64	3.24	1.64			2.69
NO _x	2.53	3.64	3.24	1.64			3.20
CO	2.53	3.64	3.24	1.64	-1.17	0.14	1.75
CO ₂ (Fossil)	2.53	3.64	3.24	1.64	12.8	0.21	5.72
CH ₄	2.53	3.64	3.24	1.64	14.7	12.9	4.34
Liquid Emissions							
Suspended Solids	2.53	3.64	3.24	1.64			3.2
BOD	2.53	3.64	3.24	1.64			2.68
COD	2.53	3.64	3.24	1.64			2.68
Solid Waste	2.53	3.64	3.24	1.64			3.03

^a Percentage Difference = (Base Case LCI Parameter – Pennsylvania LCI Parameter) x 100/Base Case LCI Parameter

^b Does not include the corresponding LCI parameter value for purge gas LCI.

^c Liquid discharges and solid waste in purge gas LCI are assumed to be zero.

From Table 5-18 it is clear that percentage variation between the components of the overall LCI among base case natural gas composition and Pennsylvania natural gas composition is quite small. The difference occurs due to more steam consumption, more electricity consumption, more natural gas consumption in steam reformer furnace, more purge gas and fugitive emissions per kg of methanol in the base case as compared to Pennsylvania natural gas as presented in Table 5-16. The variation in CH₄ content from purge gas combustion and fugitive emissions is high because base case natural gas has higher CH₄ content as compared to Pennsylvania natural gas that ends up in purge and fugitive emissions. Also variation in CO₂ content from purge gas combustion is high because more CH₄ in purge gases is combusted to produce higher CO₂ in case of the base case. The variation in overall LCI is quite small and within ± 10 to 15 percent. It should be noted that methanol emission from storage tanks has not been included as a LCI parameter in the sensitivity analysis because it remains constant for all the cases considered (8.65E-07 kg/kg methanol produced).

Natural gas pre-combustion emissions (on per 1000 ft³ basis) are assumed to be the same for all the natural gases considered. This is one of the sources of uncertainty. Purge gas combustion efficiency is a user-input as is assumed to be 99 percent. This efficiency may vary thereby contributing another source of uncertainty. Fugitive emissions are estimated to be 0.5 percent of syngas entering the water knockout drum (Overcash, 1999). This is another factor that is uncertain. So given the uncertainties involved in the calculating the LCI of methanol, it can be said that the LCI of methanol is not very sensitive to the natural gas composition used. Table 5-19 presents the overall

LCI of methanol for various natural gas compositions considered and the percentage difference with respect to the base case.

Table 5-19. LCI of Methanol based on Various Natural Gas Compositions as in Table 5-14^{a, b, d}

Air Emissions	Pennsylvania	S. California	Ohio	Los Angles	Oklahoma
PM	5.33E-04	5.36E-04	6.25E-04	5.99E-04	6.06E-04
SO ₂	3.57E-02	3.61E-02	4.12E-02	4.04E-02	4.27E-02
NO _x	3.45E-03	3.49E-03	4.01E-03	3.90E-03	4.05E-03
CO	7.40E-03	7.43E-03	8.13E-03	8.00E-03	8.24E-03
CO ₂ (Fossil)	1.48E+00	1.50E+00	1.80E+00	1.71E+00	1.73E+00
CH ₄	8.50E-03	8.60E-03	1.02E-02	9.80E-03	1.01E-02
Liquid Emissions					
Suspended Solids	3.26E-04	3.28E-04	3.81E-04	3.67E-04	3.74E-04
BOD	4.77E-05	4.83E-05	5.51E-05	5.40E-05	5.71E-05
COD	3.39E-04	3.43E-04	3.91E-04	3.83E-04	4.05E-04
Solid Waste	1.86E-01	1.87E-01	2.16E-01	2.09E-01	2.16E-01

Percentage Variation With Respect to the Base Case^c

Air Emissions	Pennsylvania	S. California	Ohio	Los Angles	Oklahoma
PM	3.50	2.96	-13.24	-8.54	-9.85
SO ₂	2.69	1.54	-12.33	-10.06	-16.19
NO _x	3.20	2.23	-12.62	-9.29	-13.60
CO	1.75	1.32	-7.94	-6.27	-9.49
CO ₂ (Fossil)	5.72	4.53	-14.78	-8.69	-10.40
CH ₄	4.34	3.19	-14.52	-10.36	-14.22
Liquid Emissions					
Suspended Solids	3.2	2.62	-13.08	-8.91	-10.95
BOD	2.68	1.50	-12.34	-10.12	-16.41
COD	2.68	1.51	-12.34	-10.10	-16.33
Solid Waste	3.03	2.21	-12.93	-9.41	-13.03

^a In units of kg/kg of methanol produced

^b All Columns are based on 1000 kmol/hr of Natural Gas as a starting material

^c Percentage Difference = (Base Case LCI Parameter – Test LCI Parameter) x 100/Base Case LCI Parameter

^d The LCI parameters that are blank in the total LCI of methanol are not shown because of “no data” for those parameters in some of the contributing columns

In Table 5-19, for the cases of Ohio, Los Angeles and Oklahoma natural gas, the LCI parameters vary up to 17 percent with respect to the base case. This trend is explained by Table 5-16 which shows higher consumption of steam, electricity, and natural gas in steam reformer for these cases with respect to the base case on per kg of methanol produced basis. The variation can be explained in similar fashion as for the case of Pennsylvania natural gas in Table 5-18.

5.4.2 Sensitivity of Methanol LCI to Methane Conversion in the Steam Reformer

The conversion of CH_4 in a steam reformer is reported to vary from 80 to 95 percent in a conventional methanol production process (Cheng and Kung, 1994; Twigg, 1989). The conversion of CH_4 is defined as a user input in the mass balance sub-model in the EXCEL spreadsheet. The CH_4 conversion in steam reformer was varied from 80 to 95 percent (80, 85, and 95 percent), while holding other process parameters such as temperature and pressures at their default values. The natural gas composition used is the same as in the base case (Section 5.3.1). Table 5-20 presents the results of parameters that affect the LCI of methanol as the CH_4 conversion in steam reformer changes. Table 5-21 presents the same results on per kg of methanol produced basis.

Table 5-20. Model Results for Various CH₄ Conversions in the Steam Reformer^a

Model Results	CH ₄ Conversion in Steam Reformer			
	80 percent	81.46 percent (Base Case)	90 percent	95 percent
Methanol (kg/hr)	28100	28500	30800	32200
Net Steam Consumption (kJ/hr) ^b	2.23E+08	2.24E+08	2.29E+08	2.33E+08
Electricity Consumption (kWh)	9.05E+03	9.11E+03	9.43E+03	9.62E+03
Natural Gas used in Steam Reformer Furnace (10 ⁶ ft ³ /hr)	4.84E-02	5.80E-02	1.14E-01	1.46E-01
Fugitive Emissions (kg/hr) ^c	2.05E+02	2.07E+02	2.16E+02	2.22E+02
Purge Gas Emissions^d	kg/hr	kg/hr	kg/hr	kg/hr
CH ₄	2.88E+01	2.67E+01	1.44E+01	7.21E+00
H ₂	1.74E+01	1.77E+01	1.93E+01	2.03E+01
CO	9.08E-01	9.21E-01	9.98E-01	1.04E+00
CO ₂ ^e	8.81E+03	8.25E+03	4.98E+03	3.06E+03

^a Based on 1000 kmol/hr of natural gas used with the base case composition

^b Positive sign means that there is a net steam consumption in methanol production

^c 0.5 percent of syngas entering the water knockout drum.

^d Based on 99 percent (default) purge gas combustion in steam reformer furnace (user-input)

^e Includes CO₂ produced by purge gas combustion at 99 percent efficiency.

Table 5-21. Model Results for Various CH₄ Conversions in the Steam Reformer on per kg of Methanol Produced Basis

Model Results	CH ₄ Conversion in Steam Reformer			
	80 percent	81.46 percent (Base Case)	90 percent	95 percent
Net Steam Consumption (kJ/kg) ^a	7.94E+03	7.86E+03	7.45E+03	7.24E+03
Electricity Consumption (kWh/kg)	3.22E-01	3.20E-01	3.06E-01	2.99E-01
Natural Gas used in Steam Reformer Furnace (10 ⁶ ft ³ /kg)	1.72E-06	2.03E-06	3.69E-06	4.55E-06
Fugitive Emissions (kg/kg) ^b	7.30E-03	7.25E-03	7.02E-03	6.90E-03
Purge Gas Emissions^c	kg/kg	kg/kg	kg/kg	kg/kg
CH ₄	1.03E-03	9.38E-04	4.68E-04	2.24E-04
H ₂	6.19E-04	6.20E-04	6.26E-04	6.30E-04
CO	3.23E-05	3.23E-05	3.23E-05	3.24E-05
CO ₂ ^d	3.14E-01	2.89E-01	1.61E-01	9.50E-02

^a Positive sign means that there is a net steam consumption in methanol production

^b 0.5 percent of syngas entering the water knockout drum.

^c Based on 99 percent (default) purge gas combustion in steam reformer furnace (user-input)

^d Includes CO₂ produced by purge gas combustion at 99 percent efficiency.

As seen in Table 5-20, methanol production increases with the increase in CH_4 conversion in the reactor due to production of more quantity of syngas. Steam consumption also increases but the variation in steam demand is not large due to the fact that if more steam is consumed in methanol distillation because of higher methanol production, more steam is produced in the waste heat boiler and the methanol reactor so the net effect is a small increase in overall steam demand with CH_4 conversion. Steam demand per kg of methanol produced decreases with increase in CH_4 conversion since variation in steam demand is small whereas variation in methanol production is great (Table 5-21). Electricity demand also increases with more CH_4 conversion since syngas compressor consumes more power to compress higher amount of syngas. However the increase in electricity demand is not in same proportion as methanol production. As a result, the electricity consumed per kg of methanol produced decreases (Table 5-21).

As the CH_4 conversion increases, less amount of CH_4 is available in the purge gas and therefore less heat is produced by purge gas on combustion. Hence more natural gas needs to be supplied in the steam reformer furnace. Thus natural gas increases per kg of methanol produced as the CH_4 conversion increases (Table 5-21). With increasing CH_4 conversion, more syngas is produced and therefore the amount of H_2 in the purge gas increases and CO remains the same per kg of methanol produced (Table 5-21). CO_2 emissions in purge gas decrease because the amount of CH_4 combusted in the steam reformer furnace to produce CO_2 decreases. Fugitive emissions (equal to 0.5 mole percent of syngas entering the water knockout drum) increase because the molar flowrate of syngas increases with increasing CH_4 conversion.

Table 5-22 presents the overall LCI of methanol for various CH₄ conversions and percentage difference with respect to the base case.

Table 5-22. Overall LCI of Methanol for Different CH₄ Conversions and the Percentage Difference With Respect to the Base Case (Units: kg/kg of methanol)

Air Emissions	CH₄ Conversion in Steam Reformer		
	80 Percent	90 Percent	95 Percent
PM	5.56E-04	5.34E-04	5.24E-04
SO ₂	3.69E-02	3.57E-02	3.52E-02
NO _x	3.58E-03	3.50E-03	3.46E-03
CO	7.55E-03	7.42E-03	7.36E-03
CO ₂ (Fossil)	1.59E+00	1.48E+00	1.43E+00
CH ₄	9.05E-03	7.96E-03	7.49E-03
Liquid Emissions			
Suspended Solids	3.40E-04	3.23E-04	3.16E-04
BOD	4.93E-05	4.77E-05	4.70E-05
COD	3.50E-04	3.39E-04	3.34E-04
Solid Waste	1.93E-01	1.84E-01	1.81E-01

Percentage Difference With Respect to the Base Case^a

Air Emissions	80 Percent	90 Percent	95 Percent
PM	-0.63	3.36	5.11
SO ₂	-0.52	2.76	4.19
NO _x	-0.35	1.89	2.87
CO	-0.27	1.46	2.21
CO ₂ (Fossil)	-1.07	5.71	8.67
CH ₄	-1.94	10.35	15.72
Liquid Emissions			
Suspended Solids	-0.77	4.10	6.23
BOD	-0.51	2.73	4.14
COD	-0.51	2.74	4.16
Solid Waste	-0.69	3.66	5.55

^a Percentage Difference = (Base Case LCI Parameter – Test LCI Parameter) x 100/Base Case LCI Parameter

In Table 5-22, as the CH₄ conversion increases the LCI parameters show a small decrease with respect to the base case as can be expected based on Table 5-21. The variation in CH₄ is large mainly because as the CH₄ conversion increases, less CH₄ is available in purge gas and fugitive emissions, so CH₄ emissions decrease with respect to the base case. Overall the LCI parameters vary within ± 10 to 15 percent with respect to the base case LCI.

5.4.3 Sensitivity of Methanol LCI to CO and CO₂ Conversion in Methanol Reactor

The conversion of CO and CO₂ in a methanol reactor is reported to vary from 95 to 99 percent in a conventional methanol production process (Cheng and Kung, 1994). The conversion of CO and CO₂ is defined as a user input in the mass balance sub-model in the EXCEL spreadsheet. The conversion was varied from 95 to 99 percent, while holding other process parameters, such as temperatures and pressures at their default values. The natural gas composition used is the same as in the base case (Section 5.3.1). Table 5-23 presents the results of parameters that affect the LCI of methanol as the reactor conversion changes. Table 5-24 presents the same results per kg of methanol produced.

Table 5-23. Model Results for Various CO and CO₂ Conversions in the Methanol Reactor

Model Results	95 percent	96 percent	97 percent	98 percent	99 percent
Methanol (kg/hr)	28500	28800	29100	29400	29700
Net Steam Consumption (kJ/hr) ^b	2.24E+08	2.25E+08	2.26E+08	2.27E+08	2.28E+08
Electricity Consumption (kWh)	9.11E+03	9.11E+03	9.11E+03	9.11E+03	9.11E+03
Natural Gas used in Steam Reformer Furnace (10 ⁶ scf/hr)	5.80E-02	6.37E-02	6.94E-02	7.52E-02	8.09E-02
Fugitive Emissions (kg/hr)	2.07E+02	2.07E+02	2.07E+02	2.07E+02	2.07E+02
Purge Gas Emissions^c	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr
CH ₄	2.67E+01	2.67E+01	2.67E+01	2.67E+01	2.67E+01
H ₂	1.77E+01	1.72E+01	1.68E+01	1.63E+01	1.58E+01
CO	9.21E-01	7.24E-01	5.36E-01	3.52E-01	1.62E-01
CO ₂ ^d	8.25E+03	7.83E+03	7.41E+03	6.99E+03	6.57E+03

^a All Columns are based on 1000 kmol/hr of Natural Gas as a starting material

^b Positive sign means that there is net steam consumption in methanol production process

^c Based on 99 percent (default) purge gas combustion in steam reformer furnace (User input)

^d Includes CO₂ produced by 99 percent purge gas combustion

Table 5-24. Model Results for Various CO and CO₂ Conversions in the Methanol Reactor on per kg of Methanol Produced Basis

Model Results	95 percent	96 percent	97 percent	98 percent	99 percent
Net Steam Consumption (kJ/kg)	7.86E+03	7.80E+03	7.74E+03	7.69E+03	7.63E+03
Electricity Consumption (kWh/kg)	3.20E-01	3.16E-01	3.13E-01	3.10E-01	3.07E-01
Natural Gas used in Steam Reformer Furnace (10 ⁶ scf/kg)	2.03E-06	2.21E-06	2.39E-06	2.56E-06	2.72E-06
Fugitive Emissions (kg/kg)	7.25E-03	7.18E-03	7.10E-03	7.03E-03	6.96E-03
Purge Gas Emissions	kg/kg	kg/kg	kg/kg	kg/kg	kg/kg
CH ₄	9.38E-04	9.28E-04	9.19E-04	9.09E-04	9.00E-04
H ₂	6.20E-04	5.98E-04	5.76E-04	5.54E-04	5.33E-04
CO	3.23E-05	2.51E-05	1.84E-05	1.20E-05	5.45E-06
CO ₂	2.89E-01	2.72E-01	2.55E-01	2.38E-01	2.21E-01

^a All Columns are based on 1000 kmol/hr of Natural Gas as a starting material

^b Positive sign means that there is net steam consumption in methanol production process

^c Based on 99 percent (default) purge gas combustion in steam reformer furnace (User input)

^d Includes CO₂ produced by 99 percent purge gas combustion

The results of sensitivity analysis with CO and CO₂ conversion as a variable varying from 95 to 99 percent are independent of the unit operations before methanol reactor. Thus, electricity consumed in natural gas and syngas compressors is same since same amount of natural gas with same composition is used for all the 5 cases. As the conversion increases from 95 percent to 99 percent, the methanol production increases (Table 5-23). Also since net steam consumption is controlled by the amount of steam used in distillation of methanol and DME, the net steam consumption increases with small variation as the CO and CO₂ conversion increases from 95 to 99 percent. However, steam consumed per kg of methanol produced decreases (Table 5-24). As the CO and CO₂ conversion increases, less unconverted syngas remains. Therefore the amount of total purge gas decreases and less of it is available for combustion in steam reforming furnace. Hence the amount of natural gas to be supplied to the steam reformer furnace to maintain the heat for steam reforming reactions increases.

Fugitive emissions are a function of the syngas molar flowrate (0.5 mole percent of syngas flowrate) and remain the same since same natural gas flowrate and composition is used for all the cases generating same amount of syngas (Table 5-23). However, the fugitive emissions per kg of methanol produced decrease due to increase in methanol production (Table 5-24). All the components of purge gas except CH₄ decrease with an increase in the conversion since less purge gas remains due to higher conversion. Methane emissions remain constant because it does not take part in the methanol production reaction. However, CH₄ emissions per kg of methanol decrease since more methanol is produced with increasing conversion (Table 5-24).

Table 5-25 presents the overall LCI of methanol for various CO and CO₂ conversions in methanol reactor. The case with 95 percent CO and CO₂ in the reactor is the base case. It can be seen in that as the reactor conversion increases from 95 to 99 percent, the overall LCI parameters decrease with respect to the base case. The reason for this decrease is evident in Table 5-24, where net steam consumption, electricity consumption, fugitive emissions and purge gas emissions decrease with increase in the reactor conversion.

Table 5-25. LCI of Methanol for Various CO and CO₂ Percent Conversions in Methanol Reactor (Units: kg/kg of methanol produced)^a

	95 percent (Base Case)	96 percent	97 percent	98 percent	99 percent
Air Emissions					
PM	5.52E-04	5.48E-04	5.41E-04	5.35E-04	5.30E-04
SO ₂	3.67E-02	3.65E-02	3.61E-02	3.58E-02	3.55E-02
NO _x	3.56E-03	3.55E-03	3.50E-03	3.47E-03	3.44E-03
CO	7.53E-03	7.42E-03	7.38E-03	7.30E-03	7.23E-03
CO ₂ (Fossil)	1.57E+00	1.55E+00	1.53E+00	1.51E+00	1.50E+00
CH ₄	8.88E-03	8.83E-03	8.73E-03	8.65E-03	8.57E-03
Liquid Emissions					
Suspended Solids	3.37E-04	3.34E-04	3.30E-04	3.27E-04	3.23E-04
BOD	4.90E-05	4.88E-05	4.82E-05	4.78E-05	4.74E-05
COD	3.48E-04	3.46E-04	3.42E-04	3.39E-04	3.37E-04
Solid Waste	1.91E-01	1.90E-01	1.88E-01	1.86E-01	1.84E-01

Percentage Difference With Respect to the Base Case

Air Emissions	96 percent	97 percent	98 percent	99 percent
PM	0.74	2.05	3.04	4.01
SO ₂	0.52	1.69	2.51	3.31
NO _x	0.49	1.73	2.57	3.39
CO	1.44	2.01	2.97	3.93
CO ₂ (Fossil)	1.07	2.40	3.57	4.71
CH ₄	0.62	1.77	2.63	3.47
Liquid Emissions				
Suspended Solids	0.80	2.06	3.05	4.03
BOD	0.51	1.68	2.50	3.29
COD	0.51	1.68	2.50	3.30
Solid Waste	0.68	1.94	2.88	3.80

^a Percentage Difference = (Base Case LCI Parameter – Test LCI Parameter) x 100/Base Case LCI Parameter

5.4.4 Sensitivity of Methanol LCI to Purge Gas Combustion Efficiency

To evaluate the effect of purge gas combustion efficiency in the steam reformer furnace on the overall LCI of methanol, the efficiency was adjusted from 99 to 99.99 percent for the base case of natural gas composition. The effect of the purge gas combustion efficiency on the overall LCI is presented in Table 5-26.

Table 5-26. Comparison of the Overall LCI of Methanol with 99 Percent and 99.99 Percent Purge Gas Combustion Efficiency in Steam Reformer Furnace^a

	99 Percent Purge Gas Combustion	99.99 Percent Purge Gas Combustion
Air Emissions		
PM	5.52E-04	5.52E-04
SO ₂	3.67E-02	3.66E-02
NO _x	3.56E-03	3.55E-03
CO	7.53E-03	7.48E-03
CO ₂ (Fossil)	1.57E+00	1.57E+00
CH ₄	8.88E-03	7.93E-03
Liquid Emissions		
Suspended Solids	3.37E-04	3.37E-04
BOD	4.90E-05	4.89E-05
COD	3.48E-04	3.47E-04
Solid Waste	1.91E-01	1.91E-01

^a In units of kg/kg methanol produced

From Table 5-26 it is clear that change in purge gas combustion efficiency from 99 to 99.99 percent does not affect the overall LCI of methanol based on the parameters tracked in this model. The noticeable difference occurs in CH₄ emission since it is contributed in the LCI of methanol mainly by unconverted purge gas emission so changing the purge gas combustion efficiency to 99.99 percent causes it to decrease. The purge gas contains CH₄, H₂, CO, CO₂ and N₂. Methane and CO emissions decrease as

shown in Table 5-26. However the overall effect on the LCI is small because there are other sources of CO and CH₄ as illustrated in Table 5-17.

Based on the above four cases of sensitivity analysis in which natural gas composition, CH₄ conversion in the steam reformer, CO and CO₂ conversion in methanol reactor, and purge gas destruction efficiency was varied, the LCI of methanol varied roughly within ± 10 to 15 percent with respect to the base case. Variation in natural gas composition had the most impact on the overall LCI of methanol as compared to the other sensitivity cases. However, given the uncertainties involved in the LCI parameters such as estimation of fugitive emissions, natural gas pre-combustion emissions, and purge gas destruction efficiency, the variation in overall LCI parameters is quite low.

6.0 CONCLUSIONS

This study documents the development of models for calculating the LCI of methanol production from the LPMEOH and conventional production processes. The LPMEOH process for methanol production has been modeled in ASPEN PLUS and the results obtained from it have been used to calculate the LCI of methanol. The conventional process of methanol production has been modeled in an EXCEL spreadsheet in which the mass and energy balances of the process have been calculated. The LCI of methanol produced by conventional process has been calculated in the same spreadsheet using mass and energy balances.

The LPMEOH process model has syngas as an input to the process model. The process model can be used to simulate methanol production from a wide variety of syngases obtained from different sources ranging from natural gas to MSW. The LCI of methanol is calculated using the results from the process model. The system model for the LPMEOH process can be integrated with an IGCC system model in ASPEN PLUS to represent the complete system for co-generation of power and methanol to study the performance, sensitivity, and LCI of the combined system.

The sensitivity analysis on LPMEOH process model provides some insights about the key process issues associated with it. Based on the sensitivity analysis results, it is found that:

- 1) The performance of LPMEOH process model is sensitive to the syngas conversion in methanol reactor.
- 2) Syngas conversion is shown to be dependent on reactor pressure, syngas space velocity in methanol reactor, H₂/CO molar ratio in the syngas feed, and recycle ratio (moles recycle gas/moles fresh syngas feed).
- 3) For syngas compositions limited in hydrogen content, the methanol reactor must be operated at or above 750 psig.
- 4) Recycling the unreacted gases back to methanol reactor has an advantage of more methanol production compared to the case with no recycle. This is true for all syngas compositions.
- 5) Syngas feeds with low H₂/CO ratio has lower methanol production and higher purge gas production than the syngas composition with high H₂/CO ratio. It is therefore recommended that the syngas compositions with lower H₂/CO ratios be adjusted via water-gas shift reaction such that H₂/CO ratio increases thereby resulting in higher methanol production and lower purge gas emissions.
- 6) Net steam demand in the LPMEOH process increases as the syngas becomes leaner in hydrogen content.

Based on the sensitivity analysis of the LPMEOH process, key parameters that are important in integrating the LPMEOH process model with an IGCC system are: (1) net steam demand in the LPMEOH process; (2) electricity consumption in the LPMEOH process; (3) purge gas production in the LPMEOH process; and (4) the composition of syngas produced in a gasifier. First two parameters are important because electricity and

steam demands of the LPMEOH process are expected to be met by power and steam generation in an IGCC system. Purge gas production becomes important if it is combusted in the IGCC system to generate additional power and steam. Syngas composition depends on the type of fuel gasified in a gasifier and relates directly to the production of methanol as discussed previously. If an IGCC system operates on a fuel that is derived from waste such as refuse derived fuel or RDF, the syngas generated is limited in its hydrogen content. For a syngas limited in its hydrogen content, it is recommended to include a water-gas shift reactor prior to the LPMEOH process so that the H_2/CO ratio of the syngas increases thereby resulting in higher methanol production.

The effect of an LPMEOH process model on gasification system would be an incremental increase in fuel use. The incremental increase in fuel use would cause increase in sulfur recovered, slag production, and perhaps some incremental air pollution emission. The steam usage in the LPMEOH process would be internal to the plant since input to the gasification co-production plant is raw water. The purge gas generated in the LPMEOH process would be combusted with very high combustion efficiency in gas turbine section of the IGCC plant. Electricity demand in the LPMEOH process would be met by gross power production in the combined system.

For the LCI of methanol using LPMEOH process starting with syngas, purge gas LCI controls most LCI parameters. The negative LCI parameters in the overall LCI are due to steam production offsets. The second largest contributor to the overall LCI is the LCI associated with steam consumption and the third largest contributor is the LCI

associated with electricity consumption. The contribution of the LCI associated with BOD removal is lower than the contributions from above three but is higher for one LCI parameter, BOD. The contributions from the LCI associated with fugitive emissions and storage tank emissions are quite low. It should be noted, however, that the LCI of purge gas combustion is highly uncertain since a default combustion efficiency of 99 percent has been assumed for the purge gas. The purge gas combustion efficiency is a user specified input and can be altered if a better combustion efficiency data is available.

The sensitivity analysis of methanol LCI in case of LPMEOH process shows that overall methanol LCI varies widely with change in syngas composition and process conditions such as reactor pressure, syngas space velocity in methanol reactor, and the recycle ratio. The main contribution to the overall LCI occurs from the purge gas combustion to produce steam in a boiler. The steam so generated offsets the emissions from other contributors of LCI. As discussed in previous paragraph, the LCI of purge gas is quite uncertain and therefore the judgment regarding the sensitivity to LCI parameters cannot be based on it.

The EXCEL spreadsheet model for conventional methanol production can be used to calculate the LCI of methanol from conventional process. For the LCI of methanol using the conventional process, there are three main contributors: (1) the LCI parameters associated with natural gas pre-combustion; (2) the LCI of steam; and (3) the LCI of electricity. For most LCI parameters, emissions associated with natural gas pre-combustion drive the overall LCI of methanol. Sulfur dioxide, NO_x, CO, CH₄, BOD,

COD and solid waste emissions are higher for natural gas pre-combustion than any other contributor. Particulate matter emissions due to the LCI of steam and electricity are comparable with each other and are higher than any other contributor. Carbon dioxide emissions are governed by the LCI of electricity. Suspended solid emissions, in liquid discharge, due to the LCI of steam and electricity are comparable with each other and are higher than any other contributor. Thus different contributors govern different LCI parameters; however; natural gas pre-combustion emissions, the LCI of steam, and the LCI of electricity are the main contributors in the overall LCI of methanol by conventional process. Particulate emissions in case of steam are based on the user specified control efficiency and can be expected to be uncertain. PM emissions may therefore be a weak LCI parameter.

Syngas in the conventional process is obtained from steam reforming of natural gas. The model has the capability to calculate the LCI of conventional methanol for a scenario in which natural gas composition, methane conversion, and methanol reactor conversion change. The sensitivity analysis of the conventional methanol process reveals that the LCI parameters are not very sensitive to the variations in natural gas composition, methane conversion in steam reformer, syngas conversion in methanol reactor, and purge gas combustion efficiency. The LCI parameters vary within ± 10 to 15 percent for a typical variation in natural gas composition, methane conversion in steam reformer, syngas conversion in methanol reactor, and purge gas combustion efficiency.

Since the LCI of methanol, both from LPMEOH and conventional process, require the LCI of steam, it is also developed and documented. Watertube boiler was chosen to be the representative boiler for steam generation and coal, fuel oil, and natural gas were the typical fuels considered for steam generation. The controlled emissions were estimated based on steam allocation to various boilers (by fuel type) depending on the boiler population. The LCI associated with boiler feed water pretreatment and air pollution control equipment was included to evaluate the overall LCI of steam. The LCI of electricity has also been presented and can be used wherever electricity is an input or output.

Ultimately it is necessary to compare the LCI of methanol produced by conventional process with that by the LPMEOH process to determine if there is any advantage to methanol production by using LPMEOH technology on syngas derived from MSW gasification. To calculate the overall LCI of methanol by the LPMEOH process, the LCI associated with gasification must be included once it is complete. However, preliminary comparison of the LCI of LPMEOH process (not including gasification) with the LCI of conventional methanol reveals that CO emissions in the case of LPMEOH process have same order of magnitude as CO emissions from conventional process. The BOD emissions in case of LPMEOH process are higher than that from conventional process even when gasification emissions are not included. The key things that need to be known in calculating the LCI associated with gasification are:

- 1) The pre-combustion emissions associated with the fuel gasified.

- 2) The LCI associated with oxygen separation plant for oxygen supply to the gasifier.
- 3) Emission offsets associated with sulfur and slag production.

Carbon monoxide and BOD emissions may compare differently with the conventional LCI once the LCI of overall system is calculated for the LPMEOH process. If the fuel pre-combustion emissions and the LCI associated with oxygen separation plant are not significant, the combined methanol production would prove to be more environmentally benign as compared to the conventional process. Accurate assessment cannot be made because of the non-availability of the LCI associated with the above three contributors in case of gasification

Based on certain limitations of this study, following recommendation/suggestions for future work are made:

- 1) A need for more accurate data for purge gas combustion efficiency. The data can be obtained from industrial sources. Also, the typical NO_x emissions can be estimated from flue gas emissions test for purge gas combustion in a process industry.
- 2) A need for fuel pre-combustion emissions data for fuel gasified in an IGCC system.
- 3) A need for the LCI of sulfur and slag for calculation of emission offset associated with their production.

- 4) It would be important to combine the process model of LPMEOH process and the IGCC system for doing the overall sensitivity analysis of the system. This will provide insights into the overall performance and the LCI of the methanol produced from the LPMEOH process.

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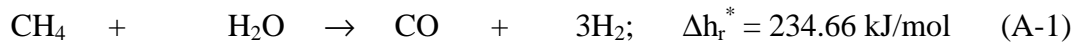
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8.0 APPENDICES

APPENDIX A: CALCULATION OF NATURAL GAS COMPOSITION IN CONVENTIONAL PROCESS OF METHANOL PRODUCTION (US PATENT 4,407,973)

This appendix provides the methodology to calculate the composition of natural gas used in the conventional process of methanol production (in Chapter 5). The following are the four main reactions occurring in the steam reformer process unit of conventional process:

Reforming reactions



Shift reaction



(Δh_r^* indicates the heat of reaction at typical reformer operating conditions: 2.0 MPa and 870 °C – Elvers *et. al.*, 1989).

In US patent 4,407,973, a mass balance across the steam reformer is presented but natural gas composition is not listed. However, it is known that desulfurized natural gas consists of CH₄, C₂H₆, C₃H₈, N₂, and CO₂. In the patent, 3865 lbmol/hr of desulfurized natural gas is mixed with 14228 lbmol/hr of steam and the mixture is fed to a

conventional steam reformer. The composition of dry exit gas (16271 lbmol/hr) from the reformer is reported as: 73.38 mole percent H₂, 13.61 mole percent CO, 8.98 mole percent CO₂, 3.99 mole percent CH₄ and 0.04 mole percent N₂. This mass balance is set-up in an EXCEL spreadsheet. C₂H₆ and C₃H₈ are completely reformed in the steam reformer since they are not present in the reformer exit gas. Thus the CH₄ present in the exit gas is the unconverted CH₄ from natural gas. The product gas from steam reformer consists of CO, H₂, CO₂, CH₄, H₂O and N₂. Nitrogen and CO₂ present in natural gas are inerts in steam reforming reactions. CO and H₂ produced in first three reactions come from CH₄, C₂H₆ and C₃H₈.

An arbitrary composition of natural gas is selected and based on the known percent conversion of reactants in above four reactions, the composition of the exit gas is calculated. The composition of natural gas can be altered in the spreadsheet. By trial and error, that composition of natural gas is calculated, which gives the same mass balance as presented in the patent. Table A-1 shows the EXCEL spreadsheet used for the calculation of composition. In broader sense, this method used to calculate the composition of natural gas is just back calculating the mass of reactants when mass of products is known.

Table A-1. EXCEL Spreadsheet used to Calculate Natural Gas Composition^a

Natural Gas Composition	Mol%	Mol. Flow (lbmol/hr)		
CH ₄	90.6	3501.69		
C ₂ H ₆	7	270.55		
C ₃ H ₈	2.1	81.165		
N ₂	0.17	6.5705		
CO ₂	0.13	5.0245		
<i>Total</i>	100	3865		
Steam Inlet		14228		
Water Condensed		9130		
Syngas Composition		<u>Reported</u>	<u>Calculated</u>	Difference
H ₂	73.38	11939.66	11934.45	5.21
CO	13.61	2214.48	2180.96	33.52
CO ₂	8.98	1461.14	1461.14	0.00
CH ₄	3.99	649.21	649.21	0.00
N ₂	0.04	6.51	6.5705	0.06
<i>Total</i>	100	16271	16232.33	38.67
Reaction (1)	CH ₄	H ₂ O	CO	3H ₂
lbmol/hr	2852.48	2852.48	2852.48	8557.4313
Reaction (2)	C ₂ H ₆	2H ₂ O	2CO	5H ₂
lbmol/hr	270.55	541.1	541.1	1352.75
Reaction (3)	C ₃ H ₈	3H ₂ O	3CO	7H ₂
lbmol/hr	81.165	243.495	243.495	568.155
Reaction (4)	CO	H ₂ O	CO ₂	H ₂
lbmol/hr	1456.11	1456.11	1456.11	1456.11

^a Shaded cells in above table are the ones that are altered to match the calculated syngas composition with the reported composition in the US patent