Methanol Production with Elemental Phosphorus Byproduct Gas: Technical and Economic Feasibility

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R. H. Moore

January 1981

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SUMMARY

In a study sponsored by the U.S. Department of Energy's Office of Industrial Programs, the Pacific Northwest Laboratory (PNL) assessed the technical and economic feasibility of using a typical, elemental, phosphorus byproduct gas stream in methanol production. The purpose of the study was to explore the potential of a substitute for natural gas. When used industrially as a feedstock in the production of chemicals such as methanol, natural gas is subject to curtailments and increasing prices. Using phosphorus byproduct gas as a natural gas substitute could alleviate these problems thus increasing production efficiency.

For the study, PNL developed a description of a typical off-gas stream. The Lummus Company then performed a feasibility-engineering study for PNL that was based on the description. The first part of the Lummus study establishes economic tradeoffs between several alternative methods of supplying the hydrogen which is needed in the methanol synthesis process to react with CO from the off gas. The preferred alternative is one suggested by PNL, the Battelle Process, which uses natural gas in combination with the off gas in an economically sized methanol plant. The second part of the Lummus study presents a preliminary basic design of a plant to 1) clean and compress the off gas, 2) return recovered phosphorus to the phosphorus plant, and 3) produce methanol by the Battelle Process. PNL evaluated the methanol market and performed an economic analyses of the Battelle Process and other alternatives for the final phase of the study.

Use of elemental phosphorus byproduct gas in methanol production appears to be technically feasible. The Battelle Process shows a definite but relatively small economic advantage over conventional methanol manufacture based on natural gas alone. The process would be economically feasible only where natural gas supply and methanol market conditions at a phosphorus plant are not significantly less favorable than at competing methanol plants. If off-gas streams from two or more phosphorus plants could be combined, production of methanol using only offgas might also be economically feasible. The North American methanol market, however, does not seem likely to require another new methanol project until after 1990.

The off-gas cleanup, compression, and phosphorus-recovery system designed for the Battelle Process could be used to produce a CO-rich stream that could be economically attractive for production of several other chemicals besides methanol. The technical feasibility of this system should be demonstrated at the pilot scale. Market conditions for production of CO-based chemicals such, as acetic acid and isocyanates, as well as for methanol should also be carefully assessed in each of the major phosphorus producing regions.

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INTRODUCTION

Carbon monoxide, either alone or mixed with hydrogen in synthesis gas, is an intermediate in the production of several major industrial chemicals. In the United States most intermediate carbon monoxide is produced by reforming natural gas. Several industrial processes, however, generate carbon monoxide in byproduct gases that are either wasted or used only as fuel. Much of this gas could be used as a chemical intermediate, bypassing the reforming step and resulting in the conservation of enough natural gas to equal or exceed the energy content of the byproduct gas consumed. Because chemical producers are facing rising costs and curtailments of natural gas, byproduct gases that can be replaced with energy from a less expensive source or that are not currently utilized are becoming attractive candidates for chemical production.

In 1976 the Pacific Northwest Laboratory (PNL) began a study of the potential for chemical production using carbon monoxide (CO) from industrial waste gases. The study included a comprehensive survey of industrial sources and potential uses of byproduct CO. An updated portion of that survey dealing with potential markets for chemicals is appended to this report. Production of methanol using byproduct CO from an elemental phosphorus plant was identified in the survey as one of the more promising alternatives and has been the subject of detailed analyses.

Substituting byproduct CO for conventional feedstocks in chemical production may reduce 1) operating costs due to hydrocarbon (natural gas) displacement and 2) capital costs due to bypassed manufacturing steps. Both the amount of hydrocarbon displaced and the relative capital investment depend upon the chemical to be produced and the nature of the byproduct gas. At PNL request, the Lummus company prepared capital and operating cost information on methanol production using CO from a typical elemental phosphorus plant. Their report is included as Appendix B.

Drawing upon the Lummus Company Study, PNL determined the potential for operating and capital cost savings from the use of phosphorus plant CO in methanol production. This report explores the conditions under which these savings could justify investment in a chemical plant.

CONCLUSIONS AND RECOMMENDATIONS

Use of elemental phosphorus byproduct gas in methanol production appears to be technically feasible and may be economically feasible under certain conditions. Results of this study include the following:

- Use of byproduct CO in combination with natural gas according to the Battelle Process is the most economical alternative for the production of methanol using byproduct gas from a typically sized elemental phosphorus plant.
- The production of 1200 t/day of methanol by the Battelle Process would require a total investment of \$100 million (December 1979) and would use 335 G•cal/h^(a) of natural gas and 60 G•cal/h of off gas (approximately the output of a 100,000-ton/yr phosphorus plant).
- At price levels representative of the second quarter of 1980, the after-tax discounted cash flow rate of return on investment (100% equity) would be 19.5%/yr while a similar plant based on natural gas alone would return 17.0%/yr under the same conditions.
- The above advantage results largely from the lower cost of off gas relative to natural gas and would become negligible if natural gas was used to replace the off gas in its current use. Because the rate of return is sensitive to natural gas and methanol prices, less favorable supply or shipping costs for a site using the Battelle Process could eliminate its advantage.
- Where off gas can be economically replaced and market conditions are favorable, the Battelle Process may be economically feasible.
- Production of methanol from off gas alone might be economically feasible if off gas from two or more elemental phosphorus plants could be combined to take advantage of the economics of scale in methanol synthesis.

(a) One giga calorie (G•cal) = 1 million kilocalories.

- If elemental phosphorus off gas costs \$2.50/10⁶Btu, the cleanup and compression system from the Battelle Process design would produce a clean, 97% carbon monoxide product at a cost of 3¢/lb. This product would be attractive for production of several other chemicals besides methanol such as acetic acid and isocyanates.
- Technical feasibility of the off-gas cleanup and compression system should be demonstrated at the pilot scale.
- Market conditions for production of methanol and other carbon monoxide based chemicals should be carefully assessed for each of the major elemental phosphorus producing regions. The North American market does not seem likely to require another new methanol project until after 1990.

ELEMENTAL PHOSPHORUS PRODUCTION

The composition and availability of byproduct phosphorus gas is determined primarily by the process and industry producing elemental phosphorus. This section of the report examines elemental phosphorus production processes, current uses of byproduct gases, and the size and location of phosphorus producing industries.

PROCESS

Elemental phosphorus is produced in the United States entirely by the electrothermic reduction of phosphate rock with carbon in the form of coke. Phosphate rock is primarily apatite and fluorapatite, $\text{Ca}_3(\text{PO}_4)_2$ and $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$, but it also contains a variety of other minerals such as silica, clays, iron, limestone and carbonaceous matter.

In this process the charge is heated by an electric arc in an essentially air-tight furnace to high temperatures that assure the reaction of the carbon with the oxygen component of the calcium phosphate mineral in the ore. At these temperatures the elemental phosphorus is produced in gaseous form and is carried from the furnace together with CO, entrained dust, hydrogen sulfide, carbonyl sulfide, phosphine, and nitrogen. The calcium and silica, as well as most other minerals, are discharged as a molten slag.

The reactions that take place for either apatite or fluorapatite are considered to be:

Several side reactions result in the formation of ferrophosphorus alloy, volatile fluorine compounds such as SiF_4 and other gases such as hydrogen sulfide and phosphine. However, with either of the principal reactions shown above, the ratio of the phosphorus and CO products is the same--2.5 moles of CO per mole of phosphorus or, on a weight basis, for every ton of phosphorus

produced, two and a quarter tons of CO are obtained. Phosphorus is condensed from the furnace off gases usually by contact with an aqueous spray at 45°C (Van Wazer 1963). The remaining gas is very rich in CO, usually containing 2% nitrogen or less.

Most phosphorus plants apparently utilize byproduct gas as a fuel for ore preparation steps such as agglomeration. A common agglomeration method is nodulizing in a rotary kiln, fired directly by byproduct gas mixed with coal or oil (Van Wazer 1963). A nodulizing kiln for iron ore has been commercially operated with powdered coal as the only feed (Bennet et al. 1954). Similarly, conversion to all-coal firing in phosphate rock kilns may be a feasible method to make byproduct gas available for chemical production. Plants using certain lump-type ores or agglomeration by sintering with coal (Van Wazer 1963) would be expected to consume little or no byproduct gas for ore preparation. If those plants use their gas for raising steam, then conversion to coal firing would be relatively straight forward.

INDUSTRY

The elemental phosphorus industry is a logical choice for evaluation of byproduct CO utilization because of its size and geographic distribution as well as the quality of byproduct gas produced. Estimated 1980 U.S. production of 450,000 tons (Fallwell and Greek 1980b) represents about one million tons per year of CO. Only the iron and steel industry produces greater amounts of CO in recoverable concentrations, and gases produced by that industry are considerably more dilute (Rohrmann et al. 1977). Capacity use for elemental phosphorus is 88% of nameplate (Fallwell and Greek 1980b). No new construction has been announced, however, as demand is expected to remain stable.

U.S. producers of elemental phosphorus are listed in Table 1 (Kavaler 1978) along with their reported capacities and estimated, maximum CO production rates. Several single plants produce significant amounts of CO; three regions, located in Florida, Idaho and Tennessee, have plants located close enough to consider combining off-gas streams for economics of scale.

TABLE 1. U.S. Phosphorus Producers

<u>Company</u>	<u>Location</u>	<u>Phosphorus Capacity^(a) Short tons/yr</u>	<u>Estimated CO Production Short tons/yr</u>
Electro-Phos	Pierce, FL	20,000	45,000
Mobil	Nichols, FL	7,500	17,000
Stauffer	Tarpon Springs, FL	<u>23,000</u>	52,000
	Florida Region TOTAL	50,500	114,000
FMC	Pocatello, ID	145,000	328,000
Monsanto	Soda Springs, ID	<u>110,000</u>	<u>249,000</u>
	Idaho Region	255,000	576,000
Hooker	Columbia, TN	57,000	129,000
Monsauto	Columbia, TN	120,000	271,000
Stauffer	Mt. Pleasant, TN	<u>45,000</u>	<u>102,000</u>
	Tennessee Region TOTAL	222,000	502,000
Stauffer	Silver Bow, MT	37,000	84,000
	U.S. TOTAL	564,500	1,276,000

(a) at 100% capacity use

METHANOL PRODUCTION

In the United States, the largest direct use of carbon monoxide is in methanol synthesis. This section discusses methanol production technologies and industrial use and growth.

SYNTHESIS

Methanol is produced commercially by the reaction of carbon monoxide (CO) and hydrogen (H₂) over a catalyst at elevated temperatures and pressures:

If CO₂ is present, some may react as follows:

Temperatures and pressures range from 230°C to 350°C and 40 to 350 atm depending upon the catalyst and process economics (Strelzoff 1970; Pinto and Rogerson 1977; Supp 1973).

Equilibrium conversion is favored by high pressure and low temperature, however, elevated temperature must be used to achieve a practical rate of reaction. To obtain high yields at low conversions the reactor is placed within a synthesis loop, as shown in Figure 1, from which crude methanol is removed by condensation. Unreacted gases are recirculated.

A selective catalyst is required for methanol formation which is less favored by equilibrium than several other reactions of carbon oxides and hydrogen. The first synthetic methanol production, in 1923, used a zinc/chrome catalyst requiring temperatures and pressures of about 350°C and 300 atm to obtain practical reaction rates and conversions (Supp 1973). Essentially the same catalyst and conditions are used by many plants today in what is called the high pressure process.

FIGURE 1. Typical Methanol Flow Diagram

As early as 1930, copper-based catalysts were studied that gave high selectivity and activity at lower temperatures which would allow reduced synthesis pressure; however, sensitivity to overheating and to poisoning by sulfur compounds in the synthesis gas precluded their commercialization (Strelzoff 1970). Advances in sulfur removal technology cleared the way for commercial development of a process using a copper/zinc/chrome catalyst by Imperial Chemical Industries (ICI) in the 1960's. Reaction heat is controlled by intermediate quenching with cool feed gas and recovered by using outlet gas to preheat boiler feed water (Pinto and Rogerson 1977). Based on a similar catalyst, Lurgi has developed a process that differs by using steam generation in the reactor for temperature control and heat recovery (Supp 1973). Both processes are referred to as "low pressure" and can operate with synthesis conditions ranging from 40 to 100 atm and 230°C to 270°C.

A three-phase reactor has been the subject of recent development (Sherwin and Frank 1976). It uses a copper/zinc/chrome catalyst under the same range of conditions as the low pressure processes. Higher conversions, credited to efficient heat control by use of an inert circulating liquid, allow reduced power requirements for recycle gas circulation. Developers claim reactor effluent methanol concentrations of 15% to 20% which can be compared to conventional reactor effluent methanol concentrations of 5 to 6 vol%. Favorable economics are projected for the as yet commercially unproven process.

PURIFICATION

Crude methanol condensed in the synthesis loop contains water from the reaction shown in Equation (4), higher alcohols and alkanes, low boilers such as dimethyl ether, and dissolved gases. This stream is purified by de-gasification and a two-column distillation scheme. The first column separates low-boilers by extractive distillation using the water phase from the bottom of the second column as an extractant. Chemical pretreatment and various purge streams may be used depending upon product purity requirements. Methanol recovery ranges from 97% to 99% (Mehta and Pan 1971). Although reboiler energy requirements are substantial, relatively low-value, low-pressure steam or direct heat exchange with process gases can be used with little impact on overall process energy consumption.

FEEDSTOCKS

Synthesis gas is generated by steam reforming of natural gas or naptha as shown in Equations (5) and (6)

where $x \approx 4$ for natural gas, $x \approx 2$ for naptha.

Synthesis gas can also be generated by partial oxidation of heavier petroleum fractions or of coal by the over-all reaction

with side reactions generating CO_2 and water. Methanol synthesis gas can also be generated from biomass such as agricultural residues or from municipal solid waste (Baker et al. 1980; Wan et al. 1979).

If natural gas is the feedstock, more hydrogen is generated than is required by the reactions shown in Equations (3) and (4). This can be remedied by adding CO₂ from an outside source or by purging excess hydrogen from the synthesis loop, in which case most of the heat required for the reforming reaction can be provided by purge gas. A balanced synthesis gas, such as that produced by reforming naptha, allows the purge to be large enough to remove inerts from the loop thus minimizing compression costs. In either case, fuel to drive the strongly endothermic reforming reaction is a major factor in the process energy balance.

Synthesis gas, generated by partial oxidation, usually contains less hydrogen than that required to react with its CO and CO₂ content by the reactions in Equations (3) and (4). Such a gas can be balanced by CO₂ removal which may be preceded by a separate "shift" conversion step to generate additional hydrogen by reaction with steam as follows:

The hydrogen-to-carbon ratio in the feedstock has a marked effect on process efficiency and capital costs. Table 2, developed from published data on the Lurgi low pressure process (Miller and Marschner 1970), compares feed plus fuel consumption per unit production of methanol for different

TABLE 2. Feed Plus Fuel Requirements for Low-Pressure Methanol Synthesis^(a) from Various Feedstocks

<u>Feedstock</u>	<u>Feed Plus Fuel Consumption per 1000 kg of Methanol</u>
Natural Gas	8.49 G•cal
Natural Gas plus CO ₂	7.61 G•cal
Naptha	7.90 G•cal
Bunker-C oil	8.55 G•cal

(a) Lurgi process, 41 to 46 atm.

types of feedstock. The need to 1) process excess hydrogen through the synthesis loop in the natural gas case or 2) remove CO_2 from the synthesis gas, as with heavy oil feed, results in greater energy consumption. Both reforming naphtha, or adding CO_2 from an outside source to natural gas reformat, result in a balanced synthesis gas. The natural gas plus CO_2 case consumes the least energy because derivation of a portion of the synthesis gas from an outside source reduces the reforming requirements.

INDUSTRY

Methanol production in the United States is estimated to reach 1.14 billion gal in 1980 (Fallwell and Greek 1980a). The industry's operating capacity of 1.42 billion gal/yr is located mostly in Texas and Louisiana with one plant in Florida. If 140 million gal/yr of capacity on standby is included, capacity use would be 75% for 1980. Chemical producers have announced new construction that would bring total methanol capacity to 1.66 billion gal/yr by 1982. All of this methanol capacity is based on natural gas reforming except DuPont's 200-million gal/yr plant in Texas which uses partial oxidation of heavy residue oil feedstock (Weismantel 1980). Methanol will be an intermediate in a coal-based route to acetic anhydride announced by Tennessee Eastman in January 1980 (Schultz et al. 1980). Capacity figures were not given but methanol use would apparently be less than 50 million gal/yr.

Short range growth in the methanol industry can be easily predicted based on current uses. The largest single methanol use, which is formaldehyde production, is projected to show little growth next year (Fallwell and Greek 1980a). Two new and rapidly growing uses, however, account for a predicted growth rate for total demand of 6.4%/yr through 1984 (Kavaler 1980). The relatively new use of carbonylation to acetic acid will take 7% of the 1980 methanol production and will grow faster than acetic acid demand as the methanol-based route displaces the ethylene-based acetaldehyde oxidation process. In the other new use, first commercialized in this country in 1979, methanol is reacted with iso-butylene to form methyl-tertiary butyl ether (MtBE), a high-octane additive for unleaded gasoline. Five percent of the 1980 methanol production will go to that use, and continued dramatic growth is likely.

The growth rate for methanol through the remainder of this century may be influenced by new, larger-scale end uses and production routes. One scenario predicts that the use in gasoline blending and in turbines for peak power generation will contribute to a 9%/yr growth rate of demand through 1990 (Weismantel 1980). This would increase methanol demand from 1.14 billion gal/yr in 1980 to 2.70 billion gal/yr (8.1×10^6 t/yr)^(a) in 1990. Growth of North American capacity based on conventional feedstocks (see Table 3) is projected to be adequate to meet demand through that period (Weismantel 1980). Neither of the above new fuel uses would approach saturation by 1990, although skepticism has been expressed over large-scale use of methanol in gasoline blends. A new process, just reaching commercialization, converts methanol to a gasoline-like hydrocarbon at efficiencies approaching 90% (Deutsch 1980). This process would avoid most of the problems cited by the skeptics.

Further dramatic growth in fuel-related methanol uses could occur if large-scale, coal-based plants lower methanol's currently high relative price as a fuel. Some cost projections have shown favorable economics (Leonard 1979; Kermode et al. 1980); however, the projected plant capacities, in the 20,000-ton/day range in most cases, would exceed total current U.S. production capacity. The large potential impact of such an undertaking throws uncertainty on long-range market projections, although a coal-based plant is not expected until after 1990 (Deutsch 1980).

The 1.14 billion gal of 1980 U.S. methanol production will contain about 3.3 million tons of carbon and oxygen derived from carbon monoxide in synthesis gas. This can be compared with the byproduct CO production by the phosphorus industry in 1980 of 1.0 million tons cited earlier. A typical new natural-gas-based plant would produce 130 million gal/yr of methanol, representing 380,000 tons/yr of CO, and the plant could use up to 1.4 million tons/yr if byproduct CO were used to 1) replace the natural gas used as fuel and 2) produce hydrogen as well. Thus, although the amount of byproduct CO, produced by the elemental phosphorus industry, is significant with respect to the size of

(a) t = metric tons or thousands of kilograms.

TABLE 3. Present and Projected North American Methanol Production Capacity
(thousands of t/yr)

<u>Methanol Production Plants</u>	<u>Plant Locations</u>	<u>Feedstock</u>	<u>Present Capacity</u>	<u>Future</u>	<u>Startup</u>
<u>U.S.</u>					
Air Products	Pensacola, FL	Natural gas	150	150	
Allemania ^(a)	Plaquemine, LA	Natural gas	300	300	
Borden	Geismar, LA	Natural gas/offgas	480	570	1980
Celanese	Bishop, TX	Natural gas	435	435	
	Clear Lake, TX	Natural gas	690	690	
DuPont	Beaumont, TX	Natural gas	660	825	1982
	Deer Park, TX	Fuel Oil	--	600	1980
Georgia Pacific	Plaquemine, LA	Natural gas	360	360	
Getty	Delaware City, DE	Raffinate		300	
Monsanto	Texas City, TX	Natural gas	300	300	
Tenneco	Houston, TX	Natural gas/offgas	240	390	
Arco	Gulf Coast	NG/LPG	--	600	1983
			<u>3,615</u>	<u>5,520</u>	
<u>Canada</u>					
Alberta Gas Chemicals	--	Natural gas	360	720	1982
Celanese Canada	--	Naphtha	51	51	
		Natural gas	--	705	1982
Ocelot	--	Natural gas	--	360	1982
Westcoast Transmission	--	Natural gas	--	360	1983
			<u>411</u>	<u>2,196</u>	
<u>Mexico</u>					
Pemex	--	Natural gas	171	825	1985
Total North America			<u>4,197</u>	<u>8,541</u>	

(a) This is a fifty-fifty joint venture of Ashland and IMC.

the methanol industry, a typically sized new methanol project could provide a larger demand for CO than any single phosphorus plant (see Table 1) could fulfill.

The potential for CO use in methanol manufacture is the largest of those chemicals that use CO directly. Potential CO use in the manufacture of other chemicals is discussed in more detail by C. A. Rohrmann et al. (1977) and in Appendix A. Acetic acid is another chemical that represents a potential for CO use at a single site that could match the size of a phosphorus plant source. A 600-million-lb/yr acetic acid plant using the methanol carbonylation process

cited earlier would consume about 150,000 tons/yr of CO. Since only CO would be required and not a CO/H₂ synthesis gas, as in methanol manufacture, acetic acid should also be considered wherever market conditions might favor its manufacture at a phosphorus production site.

EVALUATION OF METHANOL PRODUCTION OPTIONS

Hydrogen as well as carbon monoxide is required for methanol synthesis. PNL supplied The Lummus Company with a description of an off-gas stream from a typical elemental phosphorus plant as a basis for a preliminary study of the economic trade-offs between different methods of supplying the needed hydrogen. The results of that study constitute Section 3 of Appendix B. A brief summary and an analysis of the considered options are given here.

DESIGN BASIS OFF-GAS STREAM

As described earlier in the section on the elemental phosphorus manufacturing process, typical byproduct gas is rich in CO but contains phosphorus and several other impurities resulting from the ore and flux charged to the furnaces. The cost of removing impurities that may interfere with compression of the gas or that may poison the methanol synthesis catalyst must be considered in evaluating a methanol production scheme.

Based on data obtained by sampling at an industrial site, a description was developed of a typical byproduct gas stream from an elemental phosphorus plant. This description is the basis of both the preliminary and detailed studies performed by The Lummus Company and is summarized in Tables 4.2-1, 4.2-3 and 4.2-4 of Appendix B. The flowrate (25,000 kg/h of CO) is equivalent to a 100,000-ton/yr elemental phosphorus operation. The contaminants described are intended to allow realistic cost estimation, although design for any specific site should be based on careful analysis of the actual off gas to be used.

OPTIONS CONSIDERED

Five options were chosen for initial consideration by The Lummus Company. They are Cases 1 through 5 of Table 4. The first case is limited to a 200-t/day capacity by the size of the off-gas stream which is the source of hydrogen as well as CO. Case 5 is limited to 650 t/day because off gas is the only source of carbon while hydrogen is supplied by electrolysis of water. A capacity of 1200 t/day was chosen for the remaining cases as the economic size

TABLE 4. Cases Considered in Preliminary Study

<u>Case</u>	<u>Feed</u>	<u>Fuel</u>	<u>Processing Route to Synthesis Gas</u>	<u>Plant Capacity (t/day)</u>
1	off gas	natural gas	CO shift + CO ₂ removal	200
2	natural gas + off gas	natural gas	steam reforming + CO shift + CO ₂ removal	1200
3	heavy oil + off gas	heavy oil	partial oxidation + CO shift + CO ₂ removal	1200
4	coal + off gas	none ^(a)	partial oxidation + CO shift + CO ₂ removal	1200
5	water + off gas	natural gas	electrolysis + CO shift	650
6	natural gas + off gas	natural gas + off gas	steam reforming	1200
7	natural gas	natural gas	steam reforming	1200

(a) Fuel requirements supplied by process gas streams.

of a single stream methanol plant. Natural gas, heavy oil or coal supply additional carbon as well as the hydrogen required for synthesis. Flowsheets and diagrams for all cases are included in Appendix B.

After review of the first five cases, PNL suggested the option in which only a sufficient amount of off gas is used as feed to balance the excess hydrogen generated by natural gas reforming according to Equations (5) and (6) with the remaining off gas used as fuel. This concept was embodied by Lummus as Case 6 and became known as the Battelle Process. Slightly more natural gas must be reformed than in Case 2, however, the capital and operating costs of the larger reformer tend to be offset by the elimination of the CO shift and CO₂ removal steps.

Case 7 is a conventional natural gas reforming methanol plant. It is included for comparison.

RELATIVE ECONOMICS

Results of the economic trade-off study are summarized in Table 5. All cases are based on production of U.S. Federal Grade A methanol. The high capital cost for Case 1 is due to its small capacity and resultant diseconomies of scale. Case 6 (the Battelle Process) exhibited the lowest capital cost because it involves fewer processing steps than Cases 1 through 5 and requires a smaller reformer than an all natural-gas-based process (Case 7). The low total energy cost for Case 4 is the result of the use of low cost fuels. The low energy costs of Cases 2 and 6 relative to Case 7 are the result of the lower cost of off gas relative to natural gas and also slightly lower total energy requirements (see Appendix B Table 3.1-2) due to the use of a balanced feedstock as demonstrated by Table 2 in the discussion under "Feedstocks."

It is apparent from Table 5 that cost of manufacture for all options is sensitive to energy prices. Figures 2, 3 and 4 illustrate the effect of varying prices from those listed in Table 5 in three ways. In Figure 2, all energy prices vary together, remaining in the same ratios relative to one another. This figure illustrates the relative importance of capital and energy costs and shows that the coal-based option (Case 4) would become most

TABLE 5. Cost of Manufacture for Preliminary Study Cases

Item	Cost Basis	Cost of Manufacture, \$/t						
		Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7
Capital Related	28% TIC/year ^(a)	127.3	50.2	58.0	120.2	122.7	46.7	48.1
Off Gas	\$5.95/G cal ^(b)	43.1	7.1	7.1	7.1	13.2	7.1	--
Natural Gas	\$10.32/G cal ^(b)	19.2	72.4	--	--	10.8	72.1	87.2
Heavy Oil	\$12.70/G cal ^(b)	--	--	97.6	--	--	--	--
Coal	\$3.97/G cal ^(b)	--	--	--	40.0	--	--	--
Electricity	\$0.03/kW	2.3	1.8	1.8	4.4	201.6	1.8	1.8
Cooling Water	\$0.024/m ³	8.1	5.0	7.1	11.7	4.0	5.0	5.2
Total		200.0	136.5	171.6	183.4	352.3	132.7	142.3

(a) 330 on-stream days per year, mid-1979 construction costs.

(b) Higher heating value.

FIGURE 2. Cost of Manufacturing Methanol: Sensitivity to Total Energy Costs

economical only if relative energy costs increased by nearly 200%. In Figure 3, only the cost charged for off gas varies. The cost in Table 5 is based on the cost of converting a gas-fired boiler to coal firing. The most significant point in Figure 3 is that the economic advantage of the best off-gas-based cases over a natural-gas-based plant would be severely reduced if the price of off gas increased by 75% to equal natural gas on an energy basis. Figure 4 illustrates the effect of varying natural gas and oil prices with other costs remaining constant. Although the 50%-to-75% increase required

FIGURE 3. Cost of Manufacturing Methanol: Sensitivity to Off-Gas Cost

to raise the natural gas using options above the coal-based case is very possible (and has occurred for imports during the time span of this study) it would tend to be offset by an increase in coal prices, more like in Figure 2, and by increasing costs of construction.

It was apparent that for the scale of operations considered and the range of prices most likely in the near term, a combination natural gas plus off-gas feed would be the most economical option; in fact, it would be the only option that could produce methanol at a cost competitive with a natural-gas-based plant. The preliminary study showed a lower capital cost and slightly lower operating cost for Case 6 than for Case 2, the other natural gas plus off gas option. Case 6, or the Battelle Process, was therefore chosen as the basis for detailed analysis.

FIGURE 4. Cost of Manufacturing Methanol: Sensitivity to Natural Gas and Oil Cost

DETAILED STUDY OF THE BATTELLE PROCESS

The feasibility of producing methanol with byproduct gas from an elemental phosphorus plant was studied in detail. The study was based upon a combined natural gas and off-gas feedstock scheme known as the Battelle Process. A preliminary basic design for a plant to produce 1200 t/day of U.S. Federal Grade AA methanol was performed by The Lummus Company and constitutes Section 4 of Appendix B. The Lummus study includes equipment lists, capital cost, and operating cost estimates. It should be noted that the design in Section 4 differs from the cases studied in Section 3 in two ways. Grade AA methanol is produced which must meet stricter specifications on contents of water (0.10 wt%), and ethanol and acetone (0.001% each) instead of 0.15% total impurities (Mehta and Pan 1971). Somewhat higher capital and operating costs for distillation would therefore be expected. The method of calculating capital and operating costs also differs as will be explained later.

This section describes the Lummus Study process design considerations, energy balance, environmental impact, capital investment requirements, manufacturing costs, and discounted cash flow return on investment for the Battelle Process.

PROCESS DESIGN CONSIDERATIONS

The Battelle Process, described in Appendix B, includes 1) a cleanup, compression and phosphorus recovery section tailored by Lummus (with input from PNL) to the design-basis off gas, 2) a synthesis gas generation section based on proprietary Lummus steam reforming technology, 3) methanol synthesis and purification sections based on proprietary ICI technology, 4) major utility sections, and 5) general service facilities.

Off-gas cleanup and phosphorus recovery is accomplished by two steps of alkaline scrubbing of the phosphorus--saturated gas followed by compression. Phosphorus is condensed and recovered as a liquid in the coolers following each compressor stage. This scheme was chosen as the most efficient of several alternatives (see Section 4.1.2, Appendix B), however, two potential problems pointed out in the Lummus report should be emphasized. Phosphorus is known to react in alkaline solutions to form phosphite, phosphate, phosphine gas and/or

hydrogen gas. Appendix D comprises a brief discussion of these reactions and shows how kinetic data from the literature (Morgunova and Averbukh 1967; Strezhnev, Morgunova and Gabova 1963) indicate that they may be rate limited to acceptable levels. The other problem is condensation of phosphorus in the compressor casings. The Lummus report indicates that this is unlikely but could result in damage to the compressors. Experimental and pilot-scale tests should be performed to resolve the above problems as well as to verify the efficacy of the entire clean up and recovery scheme.

The steam reforming and methanol synthesis technologies used in this study have been thoroughly developed and optimized for natural gas feedstock. It is possible that use of slightly different reforming conditions, taking into account the availability of a lower cost CO source, or, for example, use of Lurgi low-pressure methanol technology, may have resulted in better economics for this application. Any difference, however, would be expected to be small.

As pointed out in the report (Section 4.2.4, Appendix B), an attractive feature of the Battelle Process, as designed by Lummus, is that an interruption in off-gas supply can be tolerated without shut-down. The plant would be capable of operating on natural gas alone at 68% of capacity.

ENERGY BALANCE

The plant, as designed, consumes 334.68 G•cal/h as natural gas and 60.19 G•cal/h, or 15.2% of total energy consumption, as off gas. Net methanol production is 50,000 kg/h or 252.17 G•cal/h for an overall efficiency of 63.86%. According to J. Chartier of The Lummus Company (personal communication, 1980), a similar plant based on natural gas alone would consume 398.78 G•cal/h for an efficiency of 63.24%. Thus a relatively low-grade feedstock is used with no loss in efficiency relative to the high-value feed it replaces.

ENVIRONMENTAL IMPACT

The feedstock energy not contained in the product would mostly be discharged to the atmosphere from the reformer stack, auxiliary boiler stack and cooling towers. Such thermal discharge is typical for an industrial chemical plant.

Since total evaporation ponds are used for disposal of sludge from off-gas cleanup, no unusual liquid discharge results from the use of byproduct gas feedstock. As pointed out in Section 4.2.3.10 of Appendix B, the plant is designed to meet EPA standards for liquid effluent from a methanol plant.

Air pollution is a potential problem. Any sulfur not removed by the alkaline scrubbing system would exit the process via stack gas either with the portion of the off gas used as fuel or via the methanol wash column purge (stream 112) which is also used as fuel. Attachment A of the Area 100 material balance (Appendix B, Section 4.2.5) shows over 100 ppmv sulfur exiting the caustic scrubbing tower. Pilot tests may show greater removal efficiency but the problem would have to be addressed. In a larger sense, the air quality impact of the fuel (i.e., coal) that would replace the off gas in its current application would also have to be considered.

CAPITAL INVESTMENT

Total installed cost (TIC) was developed on two bases. The first version was for comparison with the preliminary study estimates and the second, more comprehensive version, for economic analysis.

On the first basis, TIC is \$69.8 million (see Table 4.3-2 of Appendix B) compared with \$66 million for the same option (Case 6) in the preliminary study and \$68 million for the all natural gas option (Case 7). Besides being a more in-depth estimate, the detailed study case differs from the preliminary cases in that it produces Grade AA methanol, uses steam-driven cooling water in a recirculated system, and is based on December 1979 construction costs instead of Grade A methanol, electrically pumped cooling water in a once-through system and mid-1979 construction costs. All three differences would tend to increase the TIC. Deflating the detailed estimate by the Chemical Engineering plant cost index to mid-1979 gives \$66.8 million.

The more comprehensive TIC estimate for the detailed study was \$99.6 million (see Table 4.3-1, Appendix B). It includes general service facilities, initial charge of catalysts and chemicals, spare parts, engineering fee, taxes, insurance, and a productivity adjustment for a more

representative, non-Gulf Coast construction site; none of which was included in the \$69.8-million figure. Both versions include a 10% contingency adjustment. Neither figure includes working capital or forward escalation (interest during construction).

In order to allow accurate comparison with an all-natural gas plant, The Lummus Company was asked to prepare capital cost estimates for a plant that would produce Grade AA methanol and would use steam-driven cooling water in a recirculating system based on December 1979 construction costs. The resulting TIC for comparison with the preliminary study was \$73.6 million and the more comprehensive TIC was \$102.4 million (see Tables 1.0 and 2.0 of Appendix C). The above figures include a 15% contingency adjustment (higher because somewhat less accurate methods of estimation were used); it is interesting to note that if that adjustment is reduced to 10%, the TICs for the conventional and off-gas using plants become virtually identical except that the comprehensive TIC for the latter is higher by the \$2 million cost of the off-gas sludge disposal pond.

COST OF MANUFACTURE

Cost of manufacture of methanol, using off gas according to the design developed in the detailed study, is shown in Table 6 along with the last two columns from Table 5 and similar data for the all-natural gas estimate reported in Appendix C. Cooling water and electrical requirements for the all-natural gas based estimate case were estimated from data for the off gas using design. Electrical requirements of the off-gas cleanup system circulating pumps are almost balanced by the larger steam-reformer forced and induced draft fan loads of the all-natural gas case. All capital costs were adjusted to mid-1979 levels from the TIC figures reported by Lummus.

Production of Grade AA methanol increases fuel requirements, and recirculating cooling water increases capital costs; but these effects are more than compensated by reduced cooling water costs compared with the preliminary study estimates. The advantage of using off gas remains about the same for the detailed study as in the preliminary study.

TABLE 6. Cost of Manufacturing Methanol With and Without Byproduct Gas

Item	Cost Basis	Preliminary Study ^(a)		Detailed Study ^(b)	
		With Byproduct Gas (Case 6, \$/t)	Without Byproduct Gas (Case 7, \$/t)	With Byproduct Gas (\$/t)	Without Byproduct Gas (\$/t)
Capital Related	28% TIC/yr ^(c)	46.7	48.1	47.2	49.8
Off Gas	\$5.95/G·cal ^(d)	7.1	--	7.1	--
Natural Gas	\$10.32/G·cal ^(d)	72.1	87.2	76.5	91.2
Electricity	\$0.03/kWh	1.8	1.8	0.7	0.7
Cooling Water	\$0.024/m ³	5.0	5.2	0.1	0.1
TOTAL		132.7	142.3	131.6	141.8

(a) U.S. Federal Grade A Methanol.

(b) U.S. Federal Grade AA Methanol.

(c) 330 on-stream days/yr, mid-1979 construction costs.

(d) Higher heating value.

A detailed operating cost was developed for the Battelle Process by The Lummus Company and is reported in Table 4.3-3 of Appendix B. It includes a credit at full market value for phosphorus recovered from the byproduct gas. Also included is labor and other variable and fixed costs.

DISCOUNTED CASH FLOW RETURN ON INVESTMENT

Based on the capital and operating cost data summarized above, after-tax discounted cash flow rate of return on investment (DCF-ROI) for methanol production with and without byproduct gas is 19.5%/yr and 17.0%/yr, respectively, when calculated as outlined in Table 7. The December 1979 construction cost estimates reported by The Lummus Company and price data representative of the second quarter of 1980 were used. The off-gas price is about equivalent to replacement with \$40/ton coal. Figure 5 shows the sensitivity of the DCF-ROI for the Battelle Process to separate variation of construction cost and of natural gas, off gas and methanol prices.

TABLE 7. Discounted Cash Flow Rate of Return on Investment After Taxes
for Methanol Production With and Without Off Gas^(a)

Item	Basis	Natural Gas Plus Off Gas	Natural Gas Only
Plant Capacity	t/day	1200	1200
Total Installed Cost	\$	99.1 x 10 ⁶	102.4 x 10 ⁶
Working Capital	\$	14.0 x 10 ⁶	14.0 x 10 ⁶
Investment	time zero, \$	113.1 x 10 ⁶	116.4 x 10 ⁶
Methanol Sales	\$/yr @ 71¢/gal, 330 days/yr	93.8 x 10 ⁶	93.8 x 10 ⁶
Phosphorus Credit	\$/yr @ 61¢/lb	0.5 x 10 ⁶	0
Natural Gas Cost	\$/yr @ \$3.50/ million Btu	40.9 x 10 ⁶	48.7 x 10 ⁶
Off Gas Cost	\$/yr @ \$2.50/ million Btu	4.7 x 10 ⁶	0
Other Operating Costs ^(b)	\$/yr	7.9 x 10 ⁶	7.9 x 10 ⁶
Salvage Value	working capital, millions of \$	14.0	14.0
Discounted Cash Flow Rate of Return on Investment After Taxes	%/yr	19.5	17.0

(a) Assuming no debt, 50% tax rate, straight line depreciation, 10-yr life, instant investment and start-up.

(b) Water, electricity, catalysts and chemicals, labor, maintenance, property taxes, and insurance.

Profitability of methanol production by the Battelle Process is quite sensitive to natural gas price as well as to methanol price. Although there is a distinct advantage for its use over all-natural gas-based production at the same price levels, a relatively small difference in prices experienced by plants using the two routes could eliminate that advantage. Given identical

FIGURE 5. Discounted Cash Flow Rate of Return on Investment After Taxes, Sensitivity to Off-Gas, Natural Gas and Methanol Prices, and Total Installed Cost

natural gas and methanol prices, the advantage in DCF-ROI ranges from 3.5% at an off-gas price of \$1.50/10⁶ Btu (the figure used in the Lummus study) to 1.0% at \$3.50/10⁶ Btu (the same as the natural gas price used in the above calculation).

CONDITIONS FOR FEASIBILITY

Three areas are considered in establishing the conditions for an economically feasible application of elemental phosphorus off gas in chemical production. This section discusses market factors, scale of operation, and the use of phosphorus byproduct gas in the production of chemicals other than methanol.

MARKET FACTORS

A process is feasible only with respect to a particular market. Feedstocks and a market for the product(s) must be available in locations, at price levels, and with adequate stability to allow profitable operation over the life of the project.

In the case of methanol production by the Battelle Process, analysis of the market to determine the proper location and time may be all that is required to establish a viable project. The 19.5% DCF-ROI, calculated above, may be only marginally attractive under current financial conditions but was shown to be quickly improved by more favorable natural gas or methanol prices (see Figure 5). One of the large phosphorus plants in the Tennessee area (see Table 1) might be attractive because of the relative proximity of potential markets in several eastern U.S. industrial chemical centers. In spite of the smaller sized streams available, given a suitable supply of natural gas, a methanol plant in Florida might make profitable use of phosphorus plant off gas as well. An Idaho location is not as suitable because of product shipping costs. However, as supply-demand relationships became established for the recent overthrust belt-natural gas discoveries in that area, a viable opportunity may develop.

Two factors, discussed in the section on the methanol industry, indicate that the prospects for new projects are not good. The first is the apparently adequate current and planned capacity for the North American methanol market through 1990. The second is the possible advent of giant coal-based methanol projects that could potentially render even partially natural-gas-based plants obsolete. The large scale of operation apparently required for such projects,

using current technology, may, however, delay (or prevent) implementation. This could allow room for more conventionally sized plants in the 1990 time frame.

SCALE

Selection of the Battelle Process scheme was based on a nominal 100,000-ton/yr elemental phosphorus plant off-gas stream. Figure 6 shows how availability of larger amounts of gas could allow a plant based completely on off gas to compete with natural-gas-based methanol production. The Figure is based on economic data for Case 1 from the first phase of the

FIGURE 6. Cost of Manufacturing Methanol From Byproduct Gas Alone: Effect of Scale

Lummus study. Capital costs are assumed to vary with the 0.5 power of plant capacity as seems consistent with data published for methanol synthesis (Chemical Engineering 1974). Cost of manufacture is calculated as in Tables 5 and 6; except that the cost basis for off gas is the higher second quarter 1980 level, and capital costs have been adjusted to the higher December 1979 level used in the DCF-ROI analysis (Table 7). Case 2 also differs from the curve in that it uses natural gas for fuel, while the curve is based on off-gas fuel as well as feed.

Referring again to Table 1, only Tennessee and Idaho have sufficient total phosphorus capacity to reach favorable sizes with an off-gas-only methanol plant. Projected methanol cost could become competitive with a 1200-t/day natural-gas-based plant at natural gas prices in the range of $\$4/10^6$ Btu to $\$4.50/10^6$ Btu. The combination of off gas from two or more plants would be required and would pose serious problems. The phosphorus producers may be in the best position to judge the feasibility of such a venture.

OTHER CHEMICALS

This study has concentrated on the use of elemental phosphorus byproduct gas in methanol manufacture. The same cleanup and compression scheme could, however, be used to prepare a clean, CO-rich stream for other uses as well. Using economic data from Section 4 of Appendix B, the cost of cleanup and compression for the design basis off-gas stream can be estimated at 1.8¢/lb of CO as shown in Table 8. If byproduct gas is charged in at $\$2.50/10^6$ Btu, then CO would be produced at a total cost of 2.9¢/lb.

CO at 2.9¢/lb would be attractive for use in the production of several other chemicals besides methanol, particularly those such as isocyanates and acetic acid which require CO only and not a CO + H₂ synthesis gas. According to C. J. Forest of Air Products Company, pipeline CO on the Gulf Coast commands a price well above 2.9¢/lb. Markets for the production of the lower volume chemicals, such as isocyanates, in the vicinity of a particular phosphorus plant, would determine whether a project based on off gas would be feasible.

TABLE 8. Summary of CO Cleanup and Compression Costs
for an Elemental Phosphorus Plant

BASIS: 55,000 lb/h CO, 330 days/yr
47% cleaned and compressed to 5.6 atm
54% cleaned, compressed to 33.7 atm, and washed w/CH₃OH

	Annual Cost, <u>million \$</u>
Capital Cost \$13.2 million @ 28%/yr December 1979	3.70
Operating Costs	
Steam, 25 atm and 315°C, 24,000 kg/h @ 1.5¢/kg	2.85
Cooling Water, 44°C, 680 m ³ /h @ 2.4¢/m ³	0.13
Electric Power, 150 kW @ 3¢/kWh	0.04
Methanol, 610 kg/h @ 23¢/kg	1.11
Fuel Credit (Methanol Purge) 1.9 G·cal/h @ \$12/G Cal	<u>(0.18)</u>
Total	7.65
Unit Cost	1.8¢/lb CO

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APPENDIX A

MARKET SURVEY UPDATE

MARKET SURVEY UPDATE

Economic incentives for utilizing byproduct bases for chemical production can be of two types: capital cost savings and operating cost savings. The less tangible incentives such as natural gas conservation are adequately represented by the economic incentives and need not be addressed separately. Capital savings can result if the byproduct gas already has the composition required by the chemical process or requires less expensive equipment for processing to that composition than does the conventional feedstock. For example, reforming followed by cryogenic separation required to produce a hydrogen-free CO stream may be replaced by a simple clean-up operation if a byproduct CO stream is available. Operating cost savings can result from utilizing a byproduct gas if that gas is currently not utilized or can be replaced in its current use at a lower cost than the conventional feedstock it displaces. For example, a CO/H₂ containing off gas currently used as fuel may be replaced by coal and may displace natural gas feedstock on an approximately equivalent-energy basis. The cost per unit energy of coal is one-third that of natural gas, resulting in significant savings.

The savings depend upon the feedstock and energy requirements of a given chemical process and can only be judged in the context of the total costs involved in a chemical venture. Furthermore, success of such a venture depends upon favorable supplies and markets for all feeds and products involved. Market data, including feedstock consumption, prices and production statistics, are therefore required to evaluate the feasibility of any byproduct gas utilization project.

More than two years have elapsed since the report "Chemical Production from Waste Carbon Monoxide - Its Potential for Energy Conservation" by C. A. Rohrmann et al. (1977) was published. This present report serves to update and expand upon some of the market information presented in that report. Thirteen major industrial chemicals that can use carbon monoxide-based feedstocks are discussed; presented here are 1979 U. S. production, estimated West Coast consumption/production, recent new plant sizes, and current conventional feedstock and product price data.

The thirteen chemicals studied are listed in Table A.1. Each will be discussed separately below. They include chemicals and some of their major derivatives, as illustrated in Figure A.1, for which commercial production is based, at least in part, on CO or synthesis gas, $\text{CO} + \text{H}_2$. H_2 can be produced from CO by the water-gas shift reaction. Feeds required by each chemical are indicated in parenthesis and, for derivatives, by arrows. The chemicals considered are generally those that could potentially use more than 100 million lb/yr of CO in the United States. Methyl tert-butyl ether (MtBE) was not included in the original report. From no U.S. production in 1977, it has grown to be one of the major derivatives of methanol in 1980. Acetic anhydride, included in the original report, is primarily an intermediate in the production of cellulose acetate, included here.

AMMONIA

Natural gas, liquid petroleum gas (LPG) or naphtha is steam reformed followed by shift conversion, CO_2 removal, methanation, and high-pressure synthesis to produce ammonia. Capital costs are high forcing the construction of large-scale plants in pursuit of economies of scale. Even a 1-billion-lb/yr plant would cost in the range of \$85 million (current dollars) or 8.5¢/lb/yr (Ricci 1979) indicating poor economics for a plant using the \$3/million Btu natural gas costs assumed in Table A.1. Most U.S. producers are probably operating on lower cost gas. Since CO must be shifted to H_2 for ammonia production, there is little prospect of capital savings through the use of industrial off gases, however, substantial savings in operating cost could result from lower energy costs for byproduct gas compared with natural gas feedstock. A very large source of off gas would be required such as from a major steel mill.

Major derivatives of ammonia are urea, nitric acid and ammonium phosphate with 80% of end uses in fertilizer (Fallwell and Greek 1980). Excess capacity exists in the U.S., and there has been no new construction announced for over a year. 1980 consumption is projected to exceed U.S. operating capacity, however, imports will more than take up the slack. Currently, any new plant would serve primarily to replace old, inefficient capacity.

TABLE A.1. CO-Chemicals, Market Data Summary

Product	1979 U.S. Production, Million lb/yr	West Consumption /Production, Million lb/yr	Typical New Plant Size, Million lb/yr	lb CO/lb Product This Step /Cumulative(a)	2/80 Price \$/lb	Conventional Feeds	
						Feedstock	Cost \$/lb-product
Ammonia	35,000	?/~3200	700-1100	3.6/3.6	6	NG(b)	4.7
Urea	13,000	?/~400	200-1100	2.5/2.5	6.5-8.75	NG	3.2
Methanol "Battelle Process"	7,400	630/0	950	3.5/3.5	9.4	NG	4.6
				0.5/0.5	9.4	NG	4.0
Formaldehyde, 37%	6,500	~1200/~1200	50-250	0/1.6	7	methanol	4.2
Methyl tert-butyl ether	1,460(c)	4000(d)/0	200-600	0/1.4	17	methanol	3.9
						isobutylene	12.(e)
Acetic Acid	3,300	<5/0	300-600	0.5/2.4	26	methanol	5
						CO	?
Vinyl Acetate	2,000	~125/0	100-200	0/1.8	31	acetic acid	19
						C ₂ H ₄	8
Cellulose Acetate	740	<30/0	?	0/2.1	88	cellulose	?
						acetic acid	22
Acrylic Acid + Esters	940	~/0	100-400	0.2-0.4/0.4-1.3	41-46	acetylene	(contract only)
						alcohols	(variable)
						CO	?
Toluene di-isocyanate	680	70(f)/0	50-100	1.4/1.4	74	dinitrotoluene	36
						phosgene	38.(e)
Methylene di-phenyl isocyanate	475	50(f)/0	25-150	0.22/0.65	76	aniline	31
						phosgene	26.(e)
						formaldehyde	1
N-Butanol	730	~/0	100-300	1.3/1.3	29	propylene	10
						NG	2
2-Ethylhexanol	320	neg/0	100-300	1.5/1.5	31	propylene	12
						NG	2

(a) The first figure represents potential CO use in direct manufacture of product; the second represents potential cumulative CO use if other feedstocks are based on CO.

(b) Natural gas, price: \$3/Million Btu

(c) 1980 capacity

(d) Possible demand, 10% of West Coast unleaded gas, 1980

(e) Market price, probably high

(f) Estimated as 10% of U.S. production

FIGURE A.1. Synthesis Gas Based Chemicals and Derivatives

Data on ammonia use in the western United States have not been obtained. Although consumption may exceed capacity by enough to support a world-scale plant, no source of off gas of sufficient size has been located in the West.

UREA

Ammonia and carbon dioxide are reacted under pressure to form ammonium carbonate from which urea is produced by dehydration. Most urea plants are associated with ammonia plants which also provide the required CO_2 . Capital costs for this step are also high resulting in large capacities per stream. The excess CO_2 available if NH_3 is produced from CO is of no apparent advantage to conventional ammonia-urea routes. Two new ammonia processes have different CO_2 removal schemes for which excess CO_2 may show some advantage (Ricci 1979; Cronan 1979b). A new integrated ammonia-urea process (Lagana 1978), which allows savings over the two-step approach, shows less savings for a hydrogen-poor feedstock.

Fertilizer use accounts for 75% of production (Fallwell and Greek 1980) mostly as prills or urea-ammonium nitrate solutions. Smaller uses are urea-formaldehyde and urea-melamine resins and animal feed. Capacity and availability of low-cost CO_2 are currently limiting urea production in the United States. No new capacity is under construction, apparently because urea can be more economically imported.

Western U.S. consumption probably exceeds production by enough to support a new plant. As with ammonia, however, a very large source of off gas would be required for a grass roots urea plant. A large source of byproduct CO_2 might provide incentive for location of a urea plant that would import ammonia.

METHANOL

Synthesis gas from reforming of natural gas or other hydrocarbons is passed over a catalyst in a pressurized synthesis loop to form methanol. Methanol is removed from the loop by condensation, and a purge stream removes inerts such as methane. In the case of natural gas feed, the purge stream is

large, removing excess hydrogen which provides most of the fuel for the reformer. Capital and fuel requirements are similar to ammonia production with large-capacity plants the rule.

A plant based entirely on CO would use shift conversion to reach the 2/1, H₂/CO ratio required for methanol synthesis. Although not as severe a conversion requirement as for ammonia, promise of capital savings over natural gas reforming is still small. If, however, a large enough source of off gas were available at a lower cost per unit energy than natural gas, operating savings could be substantial. Some capital savings can be obtained if CO feed is used only to balance the synthesis gas from natural gas reforming, eliminating the need to purge hydrogen and reducing the size of the reformer. The column labeled "Battelle Process" in Table A.1 shows feed requirements from the preliminary basic design of a plant (see Appendix B) to produce methanol using CO for synthesis gas balancing plus 23% of the fuel requirement of the reformer. The figures in the fourth column of the table for cumulative CO consumption per lb by methanol derivatives are based on methanol produced entirely from CO, that is, using 3.5 lb of CO per pound of methanol.

Major derivatives of methanol are formaldehyde, acetic acid and MtBE with 60% of end use in polymer applications. Current fuel use of methanol is essentially limited to production of MtBE which is expected to reach 10% of U.S. consumption in 1980. Various large-scale fuel uses may develop within the decade greatly expanding the industry (Burke 1979; Meisel et al. 1976; Jonchere 1976). The first commercial venture using Mobil's methanol-to-gasoline process has just been announced (Deutsch 1980). New construction has been announced, however, that would double North American methanol capacity in 5 years and would provide for the most probable growth rate of demand through 1990 (Weismantel 1980).

Western U.S. methanol consumption is nearly large enough to support a world-scale plant, and demand could easily grow to that size in the 1980's. A new plant could displace methanol shipped from outside the region since methanol is currently produced in the west. Prospects for major derivatives are discussed in the following sections of this Appendix.

FORMALDEHYDE

Methanol is catalytically oxidized at ordinary pressures to produce formaldehyde. Capital costs are relatively low allowing economical operation of small-scale plants. Since methanol cost takes 60% of the market price (see Table A.1), lower-cost methanol would have considerable effect on formaldehyde cost.

Major derivatives of formaldehyde (Fallwell and Greek 1980) are urea-formaldehyde, phenolformaldehyde and polyacetal resins, butanediol, and pentaerythrinol. End use is 60% in adhesives and 10% in plastics. Generally, formaldehyde cost represents a relatively small fraction of end product cost. The major adhesive use is in particle board and plywood manufacture which is tied to the housing industry. Since methanol can be shipped more economically than the 37% commercial formaldehyde solution, plants are scattered throughout the lumber-producing regions of the United States. Capacity use is traditionally low with little overall growth projected, although new capacity is under construction in several locations (Cronan 1979a).

The formaldehyde industry in the western United States is almost completely associated with the forest products industry and accounts for nearly all the 630-million-lb/yr estimated methanol consumption in Table A.1. It should provide a stable market for methanol. All of the new formaldehyde construction is in the east.

METHYL TERT-BUTYL ETHER (MtBE)

Methanol is reacted with isobutylene at moderate temperatures and pressure over an ion exchange catalyst to make MtBE. Isobutylene can be removed at good conversions from feed concentrations as low as the 10% to 15% found in C_4 streams from catalytic crackers (Davis and Kohn 1979) although most current projects are based on olefin-plant C_4 streams in which the isobutylene concentration reaches 50%, downstream of butadiene extraction. Capital costs are low, compared with methanol and ammonia plants, but they increase rapidly with feedstock dilution. Depending upon conditions at a given refinery, units as small as 30 million lb/yr can be justified. Cost of the isobutylene feed

is difficult to calculate but methanol probably accounts for 35% to 50% of the feedstock cost which in turn is most of the cost of manufacture.

The only large-scale use of MtBE is as a high-octane blending component for unleaded gasoline where it can be used at concentrations up to 15%. This results in a potential market far exceeding the available supplies of both methanol and isobutylene. Sun Oil Company has proposed the possibility of producing MtBE based entirely on coal feed as well as directly from natural gas (for methanol) and mixed butanes via catalytic dehydrogenation (for isobutylene) (Reynolds et al. 1974); they are currently licensing conventional-feed MtBE technology with no plans for construction (Davis and Kohn 1979). Growth of MtBE is expected to be limited by the availability of olefin plant C_4 streams in the near future with some use of catalytic cracker streams at refineries where economics for the process are particularly attractive.

Catalytic crackers are the only significant source of isobutylene in the western United States. Catalytic crackers in California and Washington currently process 600,000 BPSD of fresh feed (Cantrell 1979). Assuming that 2.4 lb of isobutylene is produced per barrel of feed (industry estimate) and that 50% of that can be economically processed to MtBE, western production of MtBE could reach 360 million lb/yr which would use 150 million lb/yr of methanol.

ACETIC ACID

Three commercial routes exist to acetic acid. Oxidation of acetaldehyde, which is largely ethylene based, oxidation of butanes, and reaction of methanol with carbon monoxide (carbonylation) have all seen recent industrial use but virtually all new construction is based on the third route. Two commercial processes exist for methanol carbonylation, the Reppe process, which uses CO pressures of 7500 psi or more at 250°C , and a new process developed by Monsanto, which can operate at atmospheric pressures and lower temperatures (Grove 1972). Both use liquid-phase reactors, but the Rh-I catalyst of

Monsanto's process gives higher selectivity and yields on both reactants than the Reppe Co-I catalyst system. Although the presence of hydrogen does not lead to side reactions in the Monsanto process as it does in the Reppe, vent losses would increase with any diluent (Roth 1971). Since no hydrogen is required, substantial capital as well as operating cost savings could result for a plant using a relatively concentrated source of byproduct CO compared with a plant using CO obtained by hydrocarbon reforming.

Although capital cost information is not available for methanol carbonylation, it is apparent that the Monsanto acetic acid process should involve considerably lower investment per unit product than ammonia or methanol production. Especially if a CO source is already available, it would seem that smaller plants may be more feasible than the two 600-million-lb/yr plants recently built in the United States or perhaps than Monsanto's pioneer 300-million-lb/yr plant (now expanded to 400 million).

Major derivatives of acetic acid are vinyl acetate, cellulose acetate and acetic esters (Kavaler 1978b; 1979a; 1977a). It is also used as a solvent in terephthalic acid and dimethyl terephthalate manufacture and in textile processing operations such as wool dyeing. Most acetic acid finds its end use in synthetic fibers and resins. Due to recent additions, current capacity is more than adequate; however, U.S. demand is growing steadily and should require new capacity by the mid 1980's. Phasing out of ethylene based capacity could hasten the need for new construction.

No acetic acid is produced in the western United States and consumption is small. One known use is for dyeing by the northwest wool industry. A possible outlet for acetic acid might result from the demand for vinyl acetate in the west as will be discussed further in this Appendix.

Vinyl Acetate

Acetic acid can be reacted with acetylene or with ethylene and oxygen to yield vinyl acetate. Due to the high energy costs of acetylene manufacture, the ethylene route is preferred for new plants in spite of somewhat lower yields. Capital costs is substantial. In early 1978 Celanese announced plans for a 100-million-lb/yr plant to be located in Alberta, Canada at a cost of

\$20 million or 20¢/lb/yr (Vervalin 1978). Recent U.S. capacity additions have been in 200-million-lb/yr increments (Cronan 1979a); 400-million-lb/yr plants have been built. Cost of acetic acid feed for vinyl acetate would be 19¢/lb at current prices; therefore, CO availability could still impact the economics.

Major derivatives of vinyl acetate are polyvinyl acetate and polyvinyl alcohol. End use is almost exclusively in polymeric resins and adhesives. Exports in 1978 were 20% of U.S. production (Kavaler 1978b). Capacity use is projected to approach 95% by 1982 or earlier if older acetylene-based units are shut down.

The western U.S. consumption figure in Table A.1 is a rough estimate. Polyvinyl acetate emulsions and resins production seems to be fairly evenly distributed over the United States and took 47% of vinyl acetate production in 1978 (Kavaler 1978b). A 150-million-lb/yr plant would use about 60 million lb/yr of ethylene which would require a new supply in the west. Two options that might be economically feasible would be cryogenic tank car delivery, from Texas or from a new ethylene unit planned in Alberta, or recovery, from a western refinery off gas via a process such as Cosorb (Schultz et al. 1976).

Cellulose Acetate

Acetic anhydride is produced by high-temperature, low-pressure conversion of acetic acid through ketene. Reaction of acetic anhydride with sulfuric acid-treated cellulose in acetic acid solution yields cellulose acetate and acetic acid for recycle. In 1979, 90% of the acetic anhydride produced in the United States was used in cellulose acetate manufacture (Kavaler 1978a). The overall process of cellulose acetate manufacture is complicated and expensive. There has been no recent construction and the scale-related economics are not easily estimated. As can be seen in Table A.1, acetic acid cost represents only 25% of the product price. CO availability would, therefore, be expected to have somewhat less impact on cellulose acetate than on most of the chemicals discussed above.

Plans for a unique, new route to cellulose acetate have been announced by Tennessee Eastman (Schultz et al. 1980). Methanol will be produced via coal

gasification and reacted with recycle acetic acid to make methyl acetate. Carbon monoxide, separated from the coal synthesis gas, will be reacted with the methyl acetate to make acetic anhydride for cellulose acetate manufacture. Apparently, the route would consume methanol and CO at the same rate as the conventional route using acetic acid from carbonylation of methanol, except that any lower yield of acetate from anhydride than the theoretical 50% (based on acetyl groups) would have to result in excess production of acetic acid or anhydride. Since this route is already based on coal feedstock, the primary potential savings from byproduct CO utilization would be capital savings through elimination of CO separation equipment and reduction in required coal gasification capacity.

The major uses of cellulose acetate are for yarn, cigarette filter tow, and plastics including photographic film. Demand is projected to remain nearly flat due to a declining market for cellulose acetate yarn (Kavaler 1979a). No cellulose acetate is produced in the western United States where the only market that may exist would be for use in plastics.

ACRYLIC ACID AND ESTERS

Carbon monoxide can be reacted with acetylene and water or an alcohol via the Reppe reaction to make acrylic acid or the corresponding acrylate. The data in Table A.1 for CO use and feedstocks are based on that route. Because of the higher energy costs of acetylene manufacture, however, that process has been largely replaced by the propylene-based route, which does not use CO (Kavaler 1979b). Acrylates production, therefore, is no longer a potential consumer of byproduct CO.

TOLUENE DI-ISOCYANATES (TDI)

Phosgene is produced by reaction of CO and chlorine over an activated carbon catalyst. In 1979, 86% of U.S. phosgene production was used in the manufacture of TDI or of methylene di-phenyl isocyanate (MDI) which will be discussed in the next section (Kavaler 1979b; 1979c).

Toluene diamine (mixed isomers) produced by hydrogen reduction of dinitro toluene, is reacted with phosgene in a three stage reactor to make TDI and by-product HCL. Judging from small plant sizes and the small margin between market prices of the product and its required feedstocks (Table A.1), scale-related capital costs are apparently not an overriding factor. The CO utilization figure given in the table includes CO for shift conversion to the H_2 required for reduction of dinitro toluene (1 lb CO/lb TDI), as well as the relatively pure CO required for phosgene manufacture (0.4 lb CO/lb TDI). The latter represents a relatively high value use for byproduct CO although the probable savings would be less than 5% of product price.

TDI is used primarily in manufacture of flexible polyurethane foams. Current capacity use in the industry is high largely due to export demand (Kavaler 1979b). Modest growth of U.S. demand is forecast.

Polyurethane foam is manufactured in the western United States using TDI produced in the east. Sufficient demand probably exists to support a plant. Besides CO, however, sources of the toluene, nitric acid, and chlorine required for TDI manufacture would have to be located, as would a market for byproduct HCL.

METHYLENE DI-PHENYL ISOCYANATE (MDI)

Aniline is reacted with formaldehyde to produce diamino-diphenyl-methane. Reaction of that amine with phosgene, as in TDI manufacture, produces MDI and byproduct HCL. It is noteworthy that a larger gap is apparent in Table A.1 between product price and feedstock costs for MDI rather than the un-reduced nitrate (dinitrotoluene) as for TDI. The use of market prices for intermediates, however, may not be a reliable base for conclusions about manufacturing costs.

The CO use figure in the table for "This Step" includes only CO for the phosgene required to make MDI. The "cumulative" figure includes phosgene CO plus that which would be used if the formaldehyde feed was also CO based. The high-value (phosgene) CO used for MDI is a smaller fraction of product weight than for TDI with cost savings likely to be less than 3% of MDI's price.

The major use of MDI is in manufacture of rigid polyurethane foam, used in the booming insulation industry. Several new markets for MDI are also developing and growth rates of 8%/yr are forecast (Kavaler 1979c). Supply is currently tight, but sufficient capacity is under construction to meet demand into the mid 1980's.

MDI is consumed in the western United States, but, as with TDI, further research would be required to determine if a plant would be feasible. Required feeds would be CO, CO₂, aniline (or benzene, HNO₃ and more reducing gas) and formaldehyde. Byproduct HCl would again have to be marketed.

n-BUTANOL AND 2-ETHYL HEXANOL

Propylene and a synthesis gas composed of CO and H₂ in a 1-to-1 ratio are reacted over a rhodium or cobalt-based catalyst at moderate or high pressure to yield n-butyraldehyde and isobutyraldehyde (the "oxo" reaction). n-Butyraldehyde, the desired product, is further hydrogenated to yield n-butanol or converted via aldol condensation, dehydration and hydrogenation to 2-ethyl hexanol. Isobutyraldehyde produced in 10% yield or less over the rhodium catalyst and 20% to 25% yield over cobalt, is hydrogenated to isobutanol (Cronan 1977). The oxo reaction is used in the commercial synthesis of higher alcohols and other chemicals but not in large enough quantities to be a significant use for byproduct CO.

Shift conversion would be needed to produce the required synthesis gas from a source of byproduct CO. The CO requirements relative to product prices (Table A.1), however, show somewhat greater potential for significant impact of byproduct CO availability on production costs than in the case of isocyanates. Capital costs are probably significant but plant size may be limited by market considerations.

n-Butanol is used as a solvent and as a feedstock for butyl acrylate, glycol ethers and plasticizers (Kavaler 1978c). Seventeen percent of 1978 U.S. production was exported. Plasticizers, primarily dioctylphthalate, consume most 2-ethylhexanol production with 2-ethylhexyl acrylate the only

other major derivative. Adequate capacity exists for both chemicals in the United States and moderate growth is predicted Demand in the western United States alone is probably not adequate to justify a new plant, although existence of an export market indicates that a plant might be considered wherever a favorable feedstock position seems likely.

MARKET SURVEY CONCLUSIONS

- Significant potential impact on production economics of byproduct gas utilization can occur in two ways which seem to operate on separate groups of chemicals. Operating cost savings, resulting when the byproduct gas is less expensive than the natural gas it replaces, have greatest potential impact on large-volume, low unit price chemicals where the cost of natural gas feedstock represents a large fraction of product price. Chemicals, for which capital cost savings (primarily from elimination of processing steps) seem likely to be most significant, tend to be lower-volume, higher unit price commodities.
- Most significant impact of operating cost savings from byproduct gas utilization is possible on the production economics of ammonia and methanol.
- Capital as well as operating cost savings from byproduct gas utilization seem most likely to impact production economics of acetic acid, the isocyanates and, if the Reppe-acetylene-based route were used, the acrylates.
- From a marketing standpoint alone, construction of a major new plant in the United States during the next five years (in addition to those already announced) may be feasible for any of the chemicals discussed with the possible exception of formaldehyde and cellulose acetate.
- From a market standpoint alone, construction of a new plant in the western United States in the next five years may be feasible for ammonia, methanol, TDI and MDI by displacing shipments from outside the region.
- Methanol production may grow dramatically in the next decade as rising fuel prices meet costs for new fuel-use technologies.

- New plants utilizing byproduct gas feed in the western United States appear to be most attractive for methanol and its derivative MtBE, and for acetic acid, dependent for most of its western market on construction of a new vinyl acetate plant.
- Less likely candidates are *n*-butanol and 2-ethylhexanol because of limited markets, and acrylates because of the phasing out of the Reppe process.

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APPENDIX B

METHANOL PLANT FEASIBILITY STUDY

Prepared for the
Pacific Northwest Laboratory
by the Lummus Company
Bloomfield, New Jersey

Lummus Job No. 8852
Special Agreement B-24827-A-E

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1.0 INTRODUCTION

The Pacific Northwest Laboratory (PNL) has been contracted by the U.S. Department of Energy (D.O.E.) to evaluate the technical and economic feasibility of producing chemical commodities from industrial sources of offgases containing carbon monoxide. The work involved requires engineering expertise in the areas of carbon monoxide concentration from gaseous mixtures and the design of chemical synthesis facilities.

The Lummus Company has been contracted by PNL under prime Contract Number EY-76-C-06-1830, to provide preliminary basic engineering and cost estimating services for the design of facilities for the production of chemical commodities from carbon monoxide-containing offgases. Task 1.0 of the contract, Special Agreement No. B-24827-A-E, requires Lummus to provide "Feasibility Engineering and Estimating Services for the Design of Low Pressure Methanol Synthesis Facilities" using CO-rich offgas available from an electric reduction furnace phosphorus plant.

This report presents a preliminary screening study which evaluates the economic feasibility of various process routes to methanol production utilizing the phosphorus plant offgas as a feedstock. Based on results of the screening study, the report also contains the preliminary basic design of a 1200 metric tons per day U.S. Federal Grade AA Methanol plant using the CO-rich offgas and natural gas as feedstocks.

The economic data generated during the study indicate that use of this off-gas for methanol production is an effective method of utilizing the carbon monoxide. It should be noted however, that the attractiveness of the process is very much dependent on the cost of the offgas, assumed for this study. Suggestions for alternate end uses are given in the report.

The design and cost estimate, as well as the screening study, were prepared using Lummus know-how, proprietary information available to Lummus through licensing agreement, and, where necessary, data available in the literature. The methanol synthesis and purification areas are designed based on the ICI (Imperial Chemical Industries, Ltd.) low pressure methanol process. Design and cost data relating to this process, available to Lummus by license, are proprietary information. Design details for this process, such as internal flow rates and compositions, are not included in the report.

2.0 SUMMARY

The purpose of this study, defined as Task 1 in the Contract, is to develop a preliminary basic design and cost estimate of a methanol plant utilizing carbon monoxide as a feedstock. The source of carbon monoxide is a CO-rich offgas from a phosphorus plant electric-reduction furnace.

As methanol production requires a source of hydrogen as well as CO, Task 1 comprises a two-step effort. Task 1.1 is to conduct a preliminary study to evaluate the economic trade-offs between various sources of supplemental hydrogen. Task 1.2 is to utilize the results of Task 1.1 to develop the Preliminary Basic Design of a methanol plant using the phosphorus plant offgas as a feedstock.

The operating and investment costs of methanol plants using the CO-rich offgas as a feedstock, supplemented by hydrogen from five sources, were evaluated. The hydrogen sources were the CO-rich offgas itself (via the water-gas shift reaction), natural gas, oil, coal, and water. To facilitate the screening study by use of in-house "curve-type" investment data, all of the cases were based on producing a methanol product of U.S. Federal Grade A quality. Based upon the economic data generated during this preliminary screening study, the steam-reforming of natural gas was selected as the most economically viable source of supplemental hydrogen.

Based upon the value used in this report for the cost of the CO-rich offgas, it would appear that use of the offgas as a methanol plant feedstock is economically viable. The screening study results show a reduction in manufacturing cost of approximately \$10 per metric ton and a reduction in required investment of \$2 MM when comparing a methanol plant utilizing the offgas with a conventional natural gas-based plant. These savings represent 7% in manufacturing costs and 3% in total installed cost. However, as the difference in manufacturing costs is due mostly to the relative costs of the CO-rich offgas and natural gas, careful consideration must be given to the values assigned to the feedstocks when evaluating the data.

In accordance with Task 1.2, the Preliminary Basic Design of a 1200 metric tons per day plant producing U.S. Federal Grade AA methanol product has been developed. This development included a study for the selection of a phosphorus plant offgas clean-up scheme producing a CO-rich gas suitable for use as a methanol synthesis feedstock. The design includes all necessary chemical processing units and support facilities as required for actual plant operation. Process design information, such as heat and material balances, equipment specifications, process flow diagrams and operating data, has been provided.

A cost estimate of the plant was also developed. Economic data presented in the report includes a breakdown of the required capital investment and an itemized estimate of the operating costs. The estimated total installed cost of a 1200 metric tons per day methanol plant producing U.S. Federal Grade AA Methanol, and using the CO-rich offgas as a feedstock, is \$100 MM. Operating costs for this plant are estimated at \$120 per metric ton.

2.0 SUMMARY - cont'd

A discussion of alternate commodities for which the offgas may also be a suitable feedstock is given in Section 5.0 of this report.

It should be noted that certain restrictions have, of necessity, been imposed upon the disclosure of technical and economic data. The report does not contain any information which is deemed confidential, involves licensing agreements, or is proprietary in nature.

3.0 SELECTION OF SUPPLEMENTARY H₂ SOURCE - TASK 1.1

3.1 Discussion and Results

In compliance with Task 1.1 of the Contract, a preliminary screening study was conducted to evaluate the relative economics of producing hydrogen from various sources. In each case, the hydrogen produced is blended with the carbon monoxide feedstock to generate a synthesis gas suitable for the production of U.S. Federal Grade A Methanol.

The following sources of hydrogen were examined:

- Case 1: Hydrogen produced from the CO-rich offgas by the water-gas shift reaction.
- Case 2: Hydrogen produced by steam-reforming of natural gas followed by shift conversion and CO₂ removal.
- Case 3: Hydrogen produced by partial oxidation of heavy oil.
- Case 4: Hydrogen produced by gasification of coal.
- Case 5: Hydrogen produced by electrolysis of water.

A modification of the steam-natural gas reforming route, defined as Case 6, was also examined. This case is based on supplying hydrogen via natural gas reforming, but blending into the reformer effluent only that portion of the CO-rich offgas which is required to produce a stoichiometrically balanced methanol synthesis gas. By blending the carbon monoxide and reformer effluent in this manner, the need for the shift conversion and CO₂ removal steps is eliminated. The remainder of the offgas supplies a portion of the plant fuel requirement.

Table 3.1-1 defines the various cases studied and the processing routes used for methanol production. Block flow diagrams and terminal material balances for each of the cases are included as Figures 3.1-1 to 3.1-7 and Tables 3.1-3 to 3.1-9, respectively.

A summary of the operating and investment requirements for producing methanol by each of the process routes is given in Table 3.1-2. It is apparent from the data presented in the table that the most economically viable source of supplemental hydrogen is natural gas. Of the two natural gas options (Cases 2 and 6), Case 6 shows a lower capital investment, as well as a lower manufacturing cost. The table does not include the costs of required catalysts and chemicals, nor does it show credit for saleable by-products (such as sulfur in the coal gasification option). However, addition of these items would not be expected to change the relative investment and manufacturing costs significantly. Therefore, based on the preliminary screening study, natural gas was selected as the source of supplemental hydrogen, and Case 6 was selected as the process route for the Preliminary Basic Design of a methanol plant (Task 1.2).

3.1 Discussion and Results - cont'd

Table 3.1-2 also includes economic data for a conventional steam-natural gas reforming based methanol plant. This case (Case 7) is included to provide a reference base against which to judge the relative merits of utilizing CO for methanol production. Comparison of the selected case and the conventional plant shows an advantage for the selected case in terms of lower manufacturing costs. The difference in manufacturing costs, however, is closely related to the relative cost of natural gas and carbon monoxide. The CO-rich offgas is currently being used as fuel. Its value was determined by estimating the cost of replacing it with coal. The attractiveness of utilizing CO as a methanol feedstock is, therefore, highly dependent on the fuel value assigned to the coal replacing it.

TABLE 3.1-1

DEFINITION OF CASES STUDIED

<u>CASE</u>	<u>SUPPLEMENTAL H₂ SOURCE</u>	<u>PROCESSING ROUTE TO H₂</u>	<u>% CO OFFGAS* UTILIZED</u>	<u>PLANT CAPACITY (t/d)</u>
1	None	CO Shift	100	200
2	Natural Gas	Steam Reforming + CO Shift	100	1200
3	Heavy Oil	Partial Oxidation + CO Shift	100	1200
8.7 4	Coal	Partial Oxidation + CO Shift	100	1200
5	Water	Electrolysis + CO Shift	100	650
6	Natural Gas	Steam Reforming (No CO Shift)	56	1200
7	Natural Gas	Steam Reforming + CO Shift	0	1200

*As process feedstock.

TABLE 3.1-2
COMPARISON OF INVESTMENT AND OPERATING REQUIREMENTS

CASE NUMBER	CASE 1	CASE 2	CASE 3	CASE 4	CASE 5	CASE 6	CASE 7
FEEDSTOCK	CO ALONE	CO + NG	CO + OIL	CO + COAL	CO + H ₂ O	CO + NG	NG
PLANT CAPACITY, METHANOL, t/d	200	1200	1200	1200	650	1200	1200
COST DATA (U.S. GULF COAST, MID-1979)							
Estimated TIC ⁽¹⁾ , (ISBL + Boilers)	\$30MM	\$71MM	\$82MM	\$170MM	\$94MM	\$66MM	\$68MM
FEEDSTOCK AND FUEL REQUIREMENTS							
Feed, MM kcal/t ⁽²⁾							
Carbon Monoxide	7.23	1.20	1.20	1.20	2.22	0.68	----
Natural Gas	----	4.57	----	----	----	4.94	7.31
Oil	----	----	6.09	----	----	----	----
Coal	----	----	----	9.17	----	----	----
Fuel, MM kcal/t ⁽²⁾	<u>1.68</u> ⁽³⁾	<u>1.76</u> ⁽³⁾	<u>1.17</u> ⁽⁴⁾	<u>0.00</u> ⁽⁶⁾	<u>0.95</u> ⁽³⁾	<u>1.89</u> ⁽⁵⁾	<u>0.32</u> ⁽³⁾
Total Feed + Fuel, MM kcal/t ⁽²⁾	8.91	7.53	8.46	10.37	3.17	7.51	7.63
MAJOR UTILITY REQUIREMENTS							
Electricity, kW/t	78	60	60	146	6720	60	60
Cooling Water, m ³ /t	340.7	212.0	299.1	492.2	166.6	208.2	219.6
MANUFACTURING COSTS ⁽⁷⁾ , Per Metric Ton							
Capital Related Costs ⁽¹⁾ , (Assumed at 28% TIC Per Year)	\$127.3	\$ 50.2	\$ 58.0	\$120.2	\$122.7	\$ 46.7	\$ 48.1
Feed + Fuel	62.3	79.5	104.7	47.1	24.0	79.2	87.2
Electricity	2.3	1.8	1.8	4.4	201.6	1.8	1.8
Cooling Water	<u>8.1</u>	<u>5.0</u>	<u>7.1</u>	<u>11.7</u>	<u>4.0</u>	<u>5.0</u>	<u>5.2</u>
Total	\$200.0	\$136.5	\$171.6	\$183.4	\$352.3	\$132.7	\$142.3

Notes: (1) TIC = Total Installed Cost.

(2) LHV = Lower Heating Value.

(3) Natural gas used for fuel.

(7) Excluding cost of catalysts and chemicals. Also excluding credit for by-products (e.g., sulfur).

(4) Oil used for fuel.

(5) Carbon monoxide and natural gas used for fuel.

(6) Fuel requirement supplied by synthesis gas.

THE LUMMUS CO.
MATERIAL BALANCE

CASE 1

200 t/d METHANOL VIA SHIFT CONVERSION OF CO-RICH OFFGAS

[illegible]

B.9

E. OR J. NO. _____

DATE _____

SHEET__ OF__

BY _____

CASE 2

1200 t/d METHANOL VIA NATURAL GAS REFORMING + SHIFT CONVERSION OF CO-RICH OFFGAS

1

2

3

4

5

6

[illegible]

NOTE: kg_m/h denotes kilogram-moles per hour.

B.10

THE LUMMUS CO.
MATERIAL BALANCE

1200 t/d METHANOL FROM CO-RICH OFFGAS + PARTIAL OXIDATION OF OIL

BY _____

[illegible]

B.11

CASE 4

1200 t/d METHANOL VIA PARTIAL OXIDATION OF COAL

DATE _____

SHEET__ OF __

BY _____

[illegible]

B.12

TABLE 3.1-7

E. OR J. NO. _____
DATE _____
SHEET _____ OF _____
BY _____

THE LUMMUS CO.
MATERIAL BALANCE

CASE 5

650 t/d METHANOL VIA ELECTROLYSIS OF H_2O + SHIFT CONVERSION OF CO-RICH OFFGAS

[illegible]

NOTE: kg_m/h denotes kilogram-moles per hour.

THE LUMMUS CO.
MATERIAL BALANCE

1200 t/d METHANOL FROM CO-RICH OFFGAS + NATURAL GAS REFORMING - NO CO SHIFT

DATE _____

SHEET **OF**

BY _____

[illegible]

B.14

THE LUMMUS CO.
MATERIAL BALANCE

1200 t/d METHANOL VIA NATURAL GAS REFORMING - NO CO-RICH OFFGAS

DATE _____

SHEET ____ OF ____

BY _____

1	2	3
---	---	---

[illegible]

NOTE: kg_m/h denotes kilogram-moles per hour.

B.15

FIGURE 3.1-1

CASE 1: 200 METRIC TONS PER DAY METHANOL VIA SHIFT CONVERSION OF CO-RICH OFFGAS

FIGURE 3.1-2

CASE 2: 1200 METRIC TONS PER DAY METHANOL VIA STEAM REFORMING OF NATURAL GAS AND SHIFT CONVERSION OF CO-RICH OFFGAS

FIGURE 3.1-3

CASE 3: 1200 METRIC TONS PER DAY METHANOL VIA PARTIAL OXIDATION OF OIL

FIGURE 3.1-4

CASE 4: 1200 METRIC TONS PER DAY METHANOL VIA PARTIAL OXIDATION OF COAL

FIGURE 3.1-5

CASE 5: 650 METRIC TONS PER DAY METHANOL VIA ELECTROLYSIS OF WATER AND SHIFTING OF CO-RICH OFFGAS

FIGURE 3.1-6

CASE 6: 1200 METRIC TONS PER DAY METHANOL VIA STEAM REFORMING OF NATURAL GAS + CO-RICH OFFGAS

FIGURE 3.1-7

CASE 7: 1200 METRIC TONS PER DAY METHANOL VIA STEAM REFORMING OF NATURAL GAS (NO OFFGAS USAGE)

3.2 Basis for Evaluation

3.2.1 Technical

The basis for the development of the technical data for the preliminary screening study is as follows:

Feedstocks:

CO-Rich Offgas - The specifications for this gas are defined in Section 4.2.1 (Design Basis for the Methanol Plant Preliminary Basic Design).

Hydrocarbon - Typical compositions were assumed for the natural gas, oil and coal feedstocks. The compositions are as shown in the material balances (Figures 3.1-3 to 3.1-9).

Product:

For the purpose of the screening study, the plants were designed to produce Federal Grade A methanol.

Plant Capacity:

The plant capacities for each of the cases studied are as shown in Table 3.1-1.

When utilizing the CO-rich offgas with either no external source of hydrogen (Case 1) or with water as the hydrogen source (Case 5), the plant capacity is essentially fixed by the carbon available in the offgas.

When using a hydrocarbon feedstock as the source of supplementary hydrogen, the plant capacity has been set at 1200 metric tons per day. This 1200 t/d capacity is consistent with the use of a single train of methanol synthesis equipment.

3.2.2 Economic

Feedstock, fuel and utility costs for the preliminary study are based on the following data:

<u>Feedstocks and Fuels</u>	<u>\$/MM kcal⁽¹⁾</u>
Natural Gas	10.32
Oil	12.70
Coal	3.97
CO ⁽²⁾	5.95

3.2.2 Economic - cont'd

<u>Utilities</u>	<u>\$/Unit</u>
Electricity, kW ₃	0.03
Cooling Water, m ³	0.024

Notes:

(1) Based on higher heating value (HHV).

(2) This cost arrived at as follows:

\$4.37/MM kcal (LHV) for coal to replace CO
as a fuel.

\$1.58/MM kcal (LHV) for conversion to coal
firing equipment.

Total installed costs for equipment in each of the cases studied are based on "curve type" estimates of the process units from available in-house data.

4.0 PRELIMINARY BASIC DESIGN

4.1 Selection of CO Offgas Cleanup Scheme

4.1.1 General Requirements

The carbon monoxide gas to be utilized as a feedstock for methanol production is a phosphorus plant offgas. Phosphorus electric reduction furnace operation produces a phosphorus-containing gas which is subsequently cleaned of particulate impurities by electrostatic precipitation, and then cooled by water quenching to condense and recover the contained phosphorus. The CO feedstock to the methanol plant is the offgas exiting the phosphorus plant water scrubbers.

The CO-rich offgas, as available at the plant battery limits, contains gaseous impurities, volatile metallic compounds, and entrained particulates which must be removed prior to its utilization as a methanol plant feedstock. A detailed analysis of the offgas is given in Section 4.2.1. The major impurities to be removed in the cleanup system are phosphorus, phosphine, silicon fluorides and chlorides, metallic fluorides and chlorides, aluminum and boron compounds, metallic carbonyls, inorganic and organic sulfur compounds, and hydrogen cyanide.

With the exception of phosphorus, phosphine and the metallic carbonyls, the gaseous components can be absorbed in water. The primary cleanup scheme was therefore chosen to be an aqueous scrubbing system. As the absorption of the acidic compounds would produce a highly corrosive scrubbing solution, alkaline material is added to the scrubbing water. By maintaining a solution pH above 7, the need for costly materials of construction is eliminated. The use of an alkaline solution also tends to improve the absorption efficiency of the scrubbing system over that of a simple water wash.

Removal of phosphorus from the offgas may be accomplished either by cooling the gas so as to condense the phosphorus into a liquid effluent, or by chilling the gas such that the phosphorus will desublime onto metal surfaces for subsequent recovery. Section 4.1.2 discusses the various alternates examined for phosphorus removal and recovery. The selected cleanup scheme utilizes the elevated pressures obtained when compressing the CO for process use, thereby allowing condensation of phosphorus without cooling to desublimation temperatures.

The vapor pressures of phosphine and the metal carbonyls at near ambient temperatures do not allow these compounds to be removed by condensation. Removal of the metal carbonyls is proposed by chemical adsorption onto a copper catalyst. Using the heat supplied by the final stage of CO compression, the gas is fed over a copper catalyst bed wherein the carbonyls are decomposed and the elemental metal deposited onto the catalyst surface. Phosphine is removed from the gas by adsorption onto a bed of activated carbon (see Section 4.2.4.1).

A methanol wash, at elevated pressure, is included for final cleanup of any trace impurities remaining in the gas.

4.1.2 Alternate Cleanup Schemes

The market value of phosphorus, and the recoverable quantity contained in the offgas, makes the recovery of the contained phosphorus desirable. For this reason, several alternate cleanup schemes were examined, each centered on recovering phosphorus from the offgas.

The schemes investigated include:

Scheme 1 - Recovery Of Phosphorus Prior To Scrubbing:

- Blower.
- Desublimation of phosphorus by chilling in reversing heat exchangers.
- Slaked lime scrubbing.
- Caustic scrubbing/water wash.
- Compression.
- Final cleanup (copper catalyst, activated carbon, methanol wash).

Scheme 2 - Precipitation of Phosphorus During Scrubbing:

- Blower.
- Slaked lime scrubbing.
- Precipitation of phosphorus in a chilled caustic scrubber. Intermittent shutdown to melt phosphorus from surfaces for recovery.
- Final particulate removal in a Venturi scrubber..
- Compression.
- Final cleanup (copper catalyst, activated carbon, methanol wash).

Scheme 3 - Recovery Of Phosphorus After Scrubbing:

- Blower.
- Slaked lime scrubbing.
- Caustic scrubbing/water wash.
- Desublimation of phosphorus in reversing heat exchangers.
- Compression.
- Final cleanup (copper catalyst, activated carbon, methanol wash).

4.1.2 Alternate Cleanup Schemes - cont'd

Scheme 4 - Phosphorus Recovery By Compression After Scrubbing:

- Blower.
- Slaked lime scrubbing.
- Caustic scrubbing/water wash.
- Compression with phosphorus removal during interstage cooling.
- Final cleanup (copper catalyst, activated carbon, methanol wash).

Schematic flow diagrams for each of the alternate schemes are presented in Figures 4.1-1 to 4.1-4.

Recovery of phosphorus by compression, after offgas scrubbing (Scheme 4), is the selected scheme. Scheme 4 requires minimum additional capital investment beyond that required for cleaning the offgas. The phosphorus is removed in the liquid state with no thermal cycling required. A 90% phosphorus recovery efficiency could be realized by this method.

When compared to Scheme 4, the other alternates suffer the following disadvantages:

- All three remove phosphorus by chilling below the melting point. Desublimation onto the exchanger and tower surfaces requires thermal cycling to alternately melt the recovered phosphorus for removal. As a result, Schemes 1 and 3 require parallel heat exchanger trains for continuous operation, thereby increasing capital investment. Scheme 2 would require intermittent interruption of operation to melt phosphorus from the tower surfaces.
- Removal of phosphorus prior to offgas cleanup (Scheme 1) generates a highly acidic condensate, which may require costly construction materials.
- Removal of phosphorus during the scrubbing operation (Scheme 2) generates an impure phosphorus-containing effluent, which requires additional equipment for phosphorus recovery.
- All three schemes require refrigeration units to supply the chilling medium, thereby increasing both capital investment and operating costs.

The major disadvantage of Scheme 4 is the potential risk of phosphorus condensing in the compressor casing. However, available data indicates that this situation should not occur.

FIGURE 4.1-1

SCHEME 1: RECOVERY OF PHOSPHORUS PRIOR TO SCRUBBING

FIGURE 4.1-2

SCHEME 2: RECOVERY OF PHOSPHORUS DURING SCRUBBING

FIGURE 4.1-4

SCHEME 4: PHOSPHORUS RECOVERY BY COMPRESSION AFTER SCRUBBING

4.2 Plant Definition

4.2.1 Design Basis

4.2.1.1 Function

The plant is designed to produce U.S. Federal Grade AA Methanol from a CO-rich offgas feedstock. Supplementary hydrogen will be provided through the steam reforming of a natural gas feedstock.

4.2.1.2 Capacity

The plant is designed to produce 1200 metric tons per day (100 percent basis) of liquid methanol.

4.2.1.3 Product

The plant is designed to produce U.S. Federal Grade AA Methanol.

4.2.1.4 Feedstocks

The specification and composition of the CO-rich offgas, as supplied by Battelle, is given in Table 4.2-1.

In order to establish a design basis for the preliminary basic plant design, the average oxygen content of the offgas was converted to H₂O by combination with a stoichiometric quantity of hydrogen. The resultant offgas composition was then normalized to a 100% base.

The plant is designed to process CO-rich offgas and natural gas having the compositions shown in Tables 4.2-2, 4.2-3 and 4.2-4.

4.2.1.5 Battery Limit Conditions

The plant shall be designed to receive the design feedstocks from, and to deliver the products to, the battery limits at the temperatures, pressures and states specified in the following tabulation:

CO-Rich Gas:

State	Gas
Pressure	Atmospheric
Temperature	35-70°C (50°C Design)

4.2.1.5 Battery Limit Conditions - cont'd

Natural Gas:

State	Gas
Pressure	2.82 kg/cm ² (gauge)
Temperature	35°C

Product Methanol:

State	Liquid
Pressure	Atmospheric
Temperature	38°C

4.2.1.6 Utilities Specifications

The utilities, which are to be supplied to the plant or which are to be generated within the plant, and their specifications will be as follows:

Fuel:

Natural gas having the same composition and battery limit conditions as shown under natural gas feedstock is available as fuel.

Steam:

Pressure, kg/cm ² (gauge)	105.5	24.6	2.46	0.7
Temperature, °C	482	315	138	117

Makeup Water*:

Pressure, kg/cm ² (gauge)	Atmospheric
Temperature, °C	32

Cooling Water*:

Pressure, kg/cm ² (gauge)	Supply 5.3,	Return 3.5
Temperature, °C	Supply 27,	Return 46 (maximum)

Electric Power:

Motors 250 hp and over	4160 volts, 3-phase, 60-cycle
3/4 hp to 250 hp	460 volts, 3-phase, 60-cycle

Instrument & Plant Air:

Instrument Air	7.0 kg/cm ² (gauge), dry
Plant Air	10.5 kg/cm ² (gauge)

4.2.1.6 Utilities Specifications - cont'd

*The design of the water treatment facilities in this study is based upon an assumed raw water analysis as follows:

Calcium	as CaCO_3	150 mg/liter
Magnesium	as CaCO_3	50 mg/liter
Sodium	as CaCO_3	40 mg/liter
Bicarbonates	as CaCO_3	100 mg/liter
Sulfates	as SO_4	90 mg/liter
Chlorides	as Cl	50 mg/liter
Silica	as SiO_2	5 mg/liter
pH		7.3

TABLE 4.2-1

PHOSPHORUS PLANT OFFGAS SPECIFICATION

The specification and laboratory analysis of the phosphorus plant (CO-rich) offgas as supplied by PNL is as follows:

Pressure: 1.03 - 1.45 kg/cm², absolute
 Temperature: 35 - 70°C (50°C design)
 Flow Rate: 4536 - 31752 kg/hr of recoverable CO (24948 kg/hr design)
 Particulate loading: 13.1 - 20.8 mg/m³ (average 18.2) (80% below 0.3μ size) See Table 4.2-4 for the analysis of these compounds.

<u>Major Components</u>	<u>Mole % Dry</u>
	<u>Range</u> <u>Average</u>
CO	95.2 - 98.3 95.5
N ₂	1.5 - 4.0 2.6
O ₂	0.2 - 0.8 0.5
H ₂	1.2 - 1.5 1.33
CO ₂	0.13 - 0.17 0.15
H ₂ O	saturated @ P & T
Phosphorus	saturated @ P & T
<u>Minor Components</u>	<u>PPMV, Dry</u>
	<u>Range</u> <u>Average</u>
Ar	- 60
COS	70 - 78 74
H ₂ S	120 - 140 130
CS ₂	- 3
CH ₄	27 - 110 49
C ₆ H ₆	- 1
PH ₃	183 - 600 385
HCN	693 - 1100 880
Fluorides (as HF)	283 - 696 555
Chloride (as HCl)	77 - 129 103
NH ₃	4 - 38 14

Other Inorganic Volatile Compounds

The offgas is heavily loaded with volatile compounds. The metal₃ content (including Si and B) of these compounds can be as high as 4 gm/m³ of gas, or about 90 kg/hr. The actual chemical state of these compounds is not known. An analysis of these volatile compounds is given in Table 4.2-3.

TABLE 4.2-2

CO-RICH OFFGAS & NATURAL GAS COMPOSITIONS

<u>Component</u>	<u>Volume Percent (Dry)</u>	
	<u>CO-Rich Offgas*</u>	<u>Natural Gas</u>
Ar	60 ppm	-
H ₂	0.34	-
N ₂	2.62	-
CO	96.62	-
CO ₂	0.15	-
CH ₄	49 ppm	94.0
C ₂ H ₆	-	4.0
C ₃ H ₈	-	1.1
iC ₄ H ₁₀	-	0.3
nC ₄ H ₁₀	-	0.3
C ₅ H ₁₀	-	0.2
C ₆ H ₁₄	-	0.1
C ₆ H ₆	1 ppm	-
H ₂ S	130 ppm	1 ppm
COS	74 ppm	-
CS ₂	3 ppm	-
HCN	880 ppm	-
NH ₃	14 ppm	-
P ₄	400 ppm	-
PH ₃	385 ppm	-
Fluorides (as HF)	555 ppm	-
Chlorides (as HCl)	103 ppm	-
Total	100.0	100.0

Lower Heating Value (LHV) 2925 kcal/m³(normal) 9164 kcal/m³(normal)

*The above analysis is on a volatile compound and particulate matter free basis. The offgas is heavily loaded with volatile compounds and contains 18.2 mg/m³ of particulate matter (80% below 0.3μ size). An analysis of these compounds is given on Tables 4.2-2 and 4.2-3.

TABLE 4.2-3

VOLATILE COMPONENTS IN OFFGAS

<u>Elements ($\mu\text{g}/\text{m}^3$)</u>	<u>Range</u>	<u>Average</u>
Ag	21 - 91	61
Al	2300 - 130000	64000
As	6.3 - 18	13
B*	3000 - 300000	110000
Ba	0.5 - 15	4.4
Be	< 0.6 - 1	0.25
Ca	4300 - 11000	6400
Co	270 - 1900	800
Cr	28 - 11000	3700
Cs	< 1	
Cu	2 - 7	5.3
Fe	1500 - 39000	13000
Ge	0 - 140	45
Hg	< 0.3 - 0.9	0.2
K	30000 - 60000	48000
Li	18 - 461	160
Mg	8300 - 11000	9600
Mn	16 - 340	150
Mo	1 - 5	1.5
Na	13000 - 17000	14000
Ni	7 - 110000	47000
P	Proprietary Data - Assume Saturated	
Pb	1 - 2	1.3
Rb	1 - 15	4.5
S	1200 - 6400	3900
Se	640 - 1600	1100
Si*	9800 - 3,800,000	1,200,000
Sn	1 - 3	2
Sr	76 - 310	210
Ti	420 - 770	660
V	0.5 - 25	12
Y	< 1	
Zn	430 - 4200	1900
Zr	0 - 6900	4200

Based on elemental analysis of material passing through a heated (120°C+) filter and subsequently collected in a water-cooled condenser, ion exchange resin, and impinger solutions of a gas sampling train.

*High B and Si content may be due to fluoride attack on glassware.

TABLE 4.2-4

PARTICULATES

<u>Elements ($\mu\text{g}/\text{m}^3$)</u>	<u>Range</u>	<u>Average</u>
Ag	0 - 23	7
Al*	0 - 79	31
As	0.18 - 0.75	0.46
B	0 - 0.94	0.4
Ba	0 - 13	3
Cl	32 - 50	38
Co	0 - 1	0.25
Cr	0 - 0.85	0.21
F	87 - 253	160
Fe*	0 - 10	6
Ga	0.02 - 0.56	0.16
K	5 - 323	94
La	0.08 - 0.66	0.26
Li	0.3 - 5	2
Mg*	0 - 297	92
Mn	0 - 0.47	0.12
Na	24 - 2480	740
Ni	0 - 8	2
P	4865 - 9725	6300
Pb	0 - 3.3	0.9
Rb	0.04 - 1.5	0.4
Sb	0.3 - 3.3	2
Se	< 0.2 - 1.6	0.6
Si*	0 - 842	220
Sn	0.5 - 6.4	3
Ti	0 - 2	0.5
Zn	0 - 376	96

Elemental analysis of material collected on heated (120°C+) quartz filter.

Remaining elements below limits of detection or none detected in excess of blank filter.

*These elements are major impurities in filter medium.
Uncertainty greater for these components.

4.2.2 Plant Elements

The plant shall consist of processing and support facilities designed for the production of U.S. Federal Grade AA Methanol.

The Process Unit is sub-divided into the following areas:

- Area 100 Offgas Clean-Up and Compression
- Area 200 Synthesis Gas Generation and Compression
- Area 300 Methanol Synthesis
- Area 400 Methanol Purification

Major Utility Units included in the plant are as follows:

- Area 500 Steam and Condensate System
- Area 600 Water Treating and Potable Water System
- Area 700 Flare System
- Area 800 Product Storage Facilities
- Area 900 Cooling Water System
- Area 1000 Waste Disposal System

General Service Facilities included in the plant are as follows:

- Sludge Disposal Pond
- Fire Protection System
- Inert Gas Generation
- Instrument and Plant Air System
- Electrical Substation
- Truck Loading and Unloading
- Area Lighting
- Yard Piping
- Sewage System
- Buildings
- Roads, Parking Lots, Site Prep., Fence

4.2.3 Process Description

The general processing scheme shall be as shown on the Block Flow Diagram for the selected supplementary hydrogen source (Case 7) included in Section 3.1 of this report. Reference may also be made to the Process Flow Diagrams (E8852-00100, 00200, 00300, 00400), the Steam Balance Diagram, and the Cooling Water Balance Diagram.

A brief description of the process follows.

4.2.3.1 Offgas Cleanup and Compression

Carbon monoxide-rich offgas is available to the methanol plant from the overhead of the final water scrubber of an electric-reduction furnace phosphorus plant. The offgas contains gaseous impurities, volatile metallic compounds, and entrained particulates which must be removed prior to its utilization as a feedstock in methanol production.

Due to the multiplicity of impurities contained in the offgas, the cleanup system involves the following steps:

- Acidic component removal via alkaline water wash.
- Phosphorus removal via condensation at elevated pressures.
- Metal carbonyl removal via catalytic reduction.
- Phosphine removal via adsorption over activated carbon.
- Miscellaneous cleanup via absorption in methanol at elevated pressure.

The offgas, available at atmospheric pressure, is first boosted to 0.11 kg/cm² (gauge) by a centrifugal fan before entering an isothermal two-stage alkaline water scrubbing system. The gas flows through two towers, in series, counter-currently to a spray of slaked lime in the first tower and caustic in the second. Both towers are of open-area, spray-nozzle type to minimize the problem of scaling. Alkalinity (pH = 10) is maintained in the system by the addition of slaked lime and caustic to the first and second towers, respectively. An overall acid component removal efficiency of approximately 99% is attained in this system.

The CO-rich offgas is available to the clean-up system at temperatures ranging from 35°C to 70°C, saturated with phosphorus and water. In order to prevent phosphorus condensation within the scrubbing system, the circulating solutions are maintained at 70°C. In this manner, the offgas is kept at, or above, the phosphorus dewpoint during passage through the scrubbing system.

4.2.3.1 Offgas Cleanup and Compression - cont'd

The slaked lime scrubber tower bottom is designed as a large mixing sump to allow sufficient residence time for complete reaction between Ca(OH)_2 and the absorbed impurities. Removal of absorbed impurities from the caustic scrubber is accomplished by feeding a slip stream of circulating caustic solution to the mixing sump. The sump is provided with agitation to ensure adequate mixing and to maintain insoluble components in suspension.

Drawoff from the mixing sump is pumped back over the slaked lime scrubber. Impurities are removed via a slip stream taken out of the circulating solution and fed to a clarifier. The solids slurry is thickened in the clarifier from approximately 1 wgt % suspended solids to a 10 wgt % sludge. From the clarifier, the sludge is pumped to a lined disposal pond.

The disposal pond is designed to allow solar evaporation of all entering water. No liquid effluents are released from the pond. Continuous disposal of the clarifier sludge requires a total pond area of 13.5 acres. This area is divided into four individual ponds, each four feet deep. At any time, one pond is available for sludge disposal, while two are in various stages of water evaporation, and the fourth is undergoing solids removal.

Makeup calcium hydroxide solution is prepared in a lime slaking tank and pumped into the slaked lime scrubber mixing sump. Water for the slaking operation is provided by the clarifier overflow. Caustic solution concentration is maintained by makeup of NaOH to the caustic scrubbing tower.

Three water wash trays are provided above the spray nozzles of the caustic scrubbing tower. Wash water pumped over these trays removes traces of caustic in the gas, thereby protecting the CO compressor, and provides makeup water to the system.

The scrubbed offgas exiting the caustic tower, still containing metallic carbonyls, phosphorus, and phosphine, is cooled prior to being compressed in a turbine-driven, four-stage centrifugal compressor. Condensed water is removed from the gas in a knock-out drum at the compressor suction. This condensate is recycled to the clarifier. However, if the temperature of the CO-rich offgas feed to the plant is above 54°C , phosphorus will also be condensed and removed from the gas. Provision is made to recover this phosphorus by re-routing the condensate to the phosphorus collection tank. A portion of the offgas (approximately 43%) is removed after the second stage of compression (6.1 kg/cm^2 (gauge)) and sent to the fuel header. The remainder of the gas is further compressed to 34.5 kg/cm^2 (gauge) for process use as feedstock to the methanol synthesis loop.

Phosphorus is further removed from the gas by condensation during compressor interstage cooling. In order to ensure that desublimation of phosphorus does not occur during cooling, the gas outlet temperature from the intercoolers is maintained at 54°C . A suitable approach to the melting point of phosphorus (44°C) is thereby maintained, even allowing for increase due to the elevations in pressure. Cooling water for interstage cooling is supplied from the cooling water return header. In this manner, metal surface temperatures in the intercoolers are also maintained above the melting point of phosphorus. The condensed phosphorus and water mixture is fed to a heated collection tank and pumped back to the phosphorus plant. Approximately 90% of the phosphorus contained in the offgas is recovered.

4.2.3.1 Offgas Cleanup and Compression - cont'd

The gas exiting the compressor, raised in temperature by the heat of compression, is fed directly to a copper catalyst guard bed, wherein the metal carbonyls are decomposed and the elemental nickel, iron, and chromium are deposited on the catalyst surface. Following metal carbonyl removal, the gas is cooled to 54°C and passed through an activated carbon bed for removal of phosphine.

The final cleanup step is a methanol wash column which removes any traces of impurities remaining in the CO. Makeup methanol is supplied from the product storage tanks. The methanol purge stream is used as fuel in the auxiliary boiler. An overhead knock-out drum is supplied to remove traces of methanol carried over from the wash column by the offgas. Any liquid collected in this drum is burned as fuel in the auxiliary boiler.

The clean CO stream is now suitable for use as methanol feedstock. Exiting the methanol wash tower at 32.2 kg/cm² (gauge), the CO is fed into the interstage of the makeup syngas compressor.

4.2.3.2 Synthesis Gas Generation and Compression

The Synthesis Gas Generation and Compression Section of the plant comprises the following processing steps:

- Natural Gas Compression and Desulfurization
- Natural Gas Reforming
- Synthesis Gas Compression

Natural gas available at 2.8 kg/cm² (gauge) and 35°C is compressed by a centrifugal compressor and preheated in the convection section of the reformer. The trace amount of sulfur (less than 1 ppm H₂S) is removed by a ZnO bed.

The desulfurized feed is mixed with an appropriate amount of steam. The steam/natural gas mixture is preheated in the convection section of the reformer before it enters the vertical, nickel reforming catalyst-filled tubes in the radiant section of the reformer furnace.

The endothermic reforming reaction between methane and steam produces an effluent mixture of hydrogen, carbon monoxide, carbon dioxide, steam and residual methane. The heat required for the endothermic reaction is supplied externally to the catalyst tubes by the combustion of fuel gas.

The reformer furnace is a down-flow, top-fired design with provision for combustion air preheat. Additional heat recovery from the flue gases is attained by superheating 105.5 kg/cm²G steam.

Heat is recovered from the hot reformer effluent by generating high pressure steam in a transfer line exchanger, preheating boiler-feed water, generating two levels of low pressure steam, and preheating the feed water to the deaerator. The gas is further cooled against water prior to compression.

4.2.3.2 Synthesis Gas Generation and Compression - cont'd

The reformer effluent is now compressed from 14.1 kg/cm² (gauge) to approximately 32.8 kg/cm² (gauge) in the first stage of a two-stage steam-driven centrifugal compressor. Carbon monoxide, from the offgas clean-up area, is then mixed with the reformer effluent at the interstage pressure. The combined stream, which now comprises the makeup synthesis gas to the methanol unit, is compressed in the second stage of the compressor to approximately 72.8 kg/cm² (gauge).

4.2.3.3 Methanol Synthesis

The fresh makeup gas is mixed with a recirculating stream of methanol synthesis gas. The combined stream is then compressed to a suitable pressure for methanol synthesis.

The total feed gas from the discharge of the recirculator compressor is heated in a quench economizer to extract the last portion of the low level heat from the converter effluent. This total feed gas is then split into two streams. A portion is used for interbed quenching to limit the temperature rise of the synthesis gas in the methanol converter. The remaining fraction is passed to the converter feed/effluent exchanger, where it is preheated against part of the effluent stream and then fed to the first bed of the methanol converter.

The main reactions occurring over the ICI copper-based 51-2 catalyst are:

The overall effect of the above reactions is highly exothermic, and optimum conversion per pass is achieved by keeping a low temperature in the converter by using interbed quenching, as explained above.

Hot effluent gas from the converter is split into three streams for heat recovery. These streams, respectively, are used to preheat boiler feed water, generate low pressure steam, and to preheat the converter feed gas. The effluent gas is recombined to supply additional heat to the converter feed gas (in the quench economizer). Crude methanol is then condensed from the gas in a water-cooled exchanger.

Crude methanol is separated from the unconverted gases in a catchpot. A portion of the uncondensed gas is purged to maintain a reasonable level of inerts and reactants in the system. That purge is utilized as fuel in the reformer furnace. The balance of the uncondensed gas is combined with the makeup synthesis gas and recirculated, as described above.

The crude methanol from the catchpot is let down in pressure to flash off most of the dissolved gases. This flash gas is recovered as fuel to the reformer. Crude methanol, now at low pressure, flows to the crude storage tank.

4.2.3.4 Methanol Purification

During methanol synthesis, water and a small quantity of so called "light" and "heavy" ends are produced. The "light ends", which are primarily dimethyl ether, methyl formate, aldehydes, ketones, and other dissolved gases, are removed by fractionating the crude methanol in a topping column. Water and the "heavy" ends, which are predominantly alcohols (e.g., ethanol, propanol, isobutanol) known as fusel oil, are removed in the refining column.

Crude methanol is pumped from the crude storage to the topping column through a crude/waste water exchanger where it is heated by the refining column bottoms. A portion of the refining column bottoms is recirculated back to the topping column to increase the relative volatility of some of the light components with respect to methanol.

A small quantity of one percent caustic soda solution is injected into the crude feed in order to neutralize the small amount of organic acid present in the crude so that corrosion in the distillation section can be prevented. The rate of addition of caustic is controlled by monitoring the pH in the refining column bottoms.

The topping column overhead system consists of a primary condenser, which condenses most of the methanol water vapor and less volatile compounds from the overhead vapor, and a secondary condenser which further cools the uncondensed vapor to minimize methanol losses. Both condensates are combined and are returned to the top tray as reflux. The residual gas, consisting of the light ends and methanol vapor, is vented to a flare stack. As a safeguard, there is an allowance made to take a liquid purge if required.

The heat to the topping column is supplied by a low pressure steam reboiler. The "topped" methanol is withdrawn from the base of the column and pumped to the refining column, where fusel oil and water are removed.

Fusel oil is removed from the refining column by a small purge from the stripping section. It is cooled and sent to storage. This alcohol mixture, together with the secondary purge from the topping column, can be used as fuel. Water is removed from the base of the refining column. After being used to preheat the crude methanol feed, a portion of the water is recycled back to the topping column while the remainder goes to drain via an effluent tank. The refining column is reboiled by a low pressure steam reboiler.

The overhead vapor from the refining column is condensed and returned to the top tray. A small vapor bleed stream is taken if necessary. The refined product is withdrawn below a pasteurization section to a product cooler and then to the shift tank before final storage.

4.2.3.5 Steam and Condensate System

An overall steam balance for the plant is given in Section 4.2.5.3.

A nominal 160,000 kilograms per hour high pressure steam system is provided. High pressure (105.5 kg/cm^2 (gauge)) steam is generated in the transfer line exchanger by utilizing heat from the reformer effluent. It is superheated to 482°C in the convection section of the reformer. The process waste heat provides approximately 60% of the plant's high pressure steam requirement. The balance of the high pressure steam is supplied by an auxiliary boiler. One 91,000 kg/hr per hour auxiliary boiler (92% overall efficiency) is provided. This boiler will satisfy the normal operating plant steam requirements, as well as provide enough steam for start-up and shutdown of the plant.

Low pressure (2.46 kg/cm^2 (gauge) and 0.7 kg/cm^2 (gauge)) steam is generated by recovering heat from both the reformer effluent and the methanol converter effluent.

Process condensate is treated in a degassing tower which removes dissolved gases by contacting with air. The process condensate is then mixed with condensate from the turbine surface condensers, and the combined stream is then treated in a mixed bed polisher. Corrosive products and/or any ionic contaminants that may be present are removed via ion exchange.

The low pressure steam condensates (2.46 kg/cm^2 (gauge) and 0.7 kg/cm^2 (gauge)) are flashed at atmospheric pressure, and cooled by exchanging heat with a combined stream of cold, de-gassed process condensate, surface condenser condensate, and demineralized makeup water. The low pressure steam condensates are then treated in a carbon filter to remove any organic contaminants that may be present due to leakage in the low pressure steam generators.

The condensate streams and demineralized makeup water are then combined and preheated against the reformer effluent before being sent to the de-aerator.

4.2.3.6 Water Treating System

The demineralized water plant is defined based on an assumed water analysis which is typical of this general location (see Section 4.2.1.6). The plant is capable of supplying suitably treated water for a nominal 160,000 kilograms per hour, 105.5 kg/cm^2 (gauge), steam system as described above.

Raw water from storage is fed directly to two parallel ion exchange trains. One train is normally in service while the other is being regenerated. Each train consists of a cation exchanger, a CO_2 stripper, an anion exchanger, and finally a mixed-bed ion exchanger. Regeneration wastes are neutralized in a common pit and sent to the effluent pond prior to final discharge.

4.2.3.7 Flare System

A flare system is provided for safe disposal of combustible vapors released during start-up, shutdown and emergencies. These releases are collected in a closed header network and routed to a single, elevated flare stack. A knockout drum is provided to disengage any entrained liquids from the total vapor flow to the flare. Included in the flare design are both a gas seal and a liquid seal to prevent the ingress of air into the system.

4.2.3.8 Product Storage Facilities

Finished methanol product storage equivalent to one month's production is provided. Due to the product's vapor pressure at the storage temperature, floating roof tankage is specified to minimize product loss.

Product shipping pumps are specified for truck or tank car loading, assuming a frequency of four shipments per month and a 24-hour loading time.

4.2.3.9 Cooling Water System

An overall cooling water balance for the plant is given in Section 4.2.5.

An induced-draft cooling tower is provided to supply the cooling water requirements of the plant. The cooling water is circulated to the process users by two 50% pumps on steam turbine drives. One electric motor driven spare pump is also provided.

The cooling water system consists of two levels of distribution. The main process users will utilize the 32°C water exiting the cooling tower. Return water temperature from these users will be 44°C. A portion of the heated water will be further utilized as coolant in the CO-rich offgas cooler and CO compressor intercoolers (Area 100).

The temperature of the cooling water to the Area 100 users is controlled to between 44°C and 50°C. Maintaining a minimum temperature of 44°C to the offgas cooler and CO compressor intercoolers ensures that the exchanger metal temperatures will not drop below the melting point of phosphorus. The upper temperature limit is set to ensure adequate cooling of the gas prior to each stage of compression.

A steam-heated exchanger is provided to heat the cooling water should the temperature drop below 44°C. Provision is also made for direct injection of water exiting the cooling tower to maintain the upper temperature limit.

Chemical injection treatment systems are provided as follows:

- Chlorination
- Sulfuric Acid Injection
- Algaecide
- Corrosion Inhibition
- Scale Inhibition

4.2.3.10 Waste Disposal System

During normal operation, the plant will produce liquid waste streams as follows:

- Boiler Blowdown
- Cooling Tower Blowdown
- Demineralization System Waste
- Methanol Purification Waste Water
- Process Condensate (Natural Gas Compressor)

The liquid waste streams will be fed to a common holding pond, sized for a 48-hour holdup, and discharged to the river.

Of these waste streams, only the methanol purification waste water exhibits an appreciable Biological Oxygen Demand (BOD). This stream is not fed directly to the waste water holding pond. Instead, it is first mixed with the cooling tower makeup water. The BOD is reduced by approximately 80% through oxidation in the cooling tower. When diluted in the cooling tower blowdown and mixed with the other liquid wastes, the plant outfall will exhibit a BOD₅ of less than 10 ppm, corresponding to approximately 10 kg/day of BOD₅ material. This effluent stream is well within the limits set by the Federal Environmental Protection Agency of approximately 60 kg/day BOD₅ for a 1200 MT/D methanol plant.

4.2.4 Design Considerations

The methanol plant has been designed for a 1200 metric tons per day capacity based on the availability of the CO-rich offgas as a feedstock. Should the plant lose the carbon monoxide feedstock, a production rate of 815 metric tons per day can be maintained, based solely on natural gas reforming.

4.2.4.1 Offgas Cleanup System

The offgas cleanup system has been designed based on the definition of the phosphorus plant offgas as given in Section 4.2.1 (Design Basis). It should be noted that, due to the method of sampling the offgas samples, contamination by fluoride attack on 316 stainless steel and borosilicate glass components of the sampling train was likely. As a result, the Fe, Cr, Ni, Mo, Si, B, Na, K, Al and Ca contents of the offgas are questionable. Furthermore, as no commercial experience is presently available for cleanup of such a gas, much of the design is based on literature surveys of laboratory experimental data. In particular, the carbonyl and phosphine removal steps are based on information available from literature sources of laboratory experimentation only. Furthermore, little data is available concerning the reaction of elemental phosphorus with the circulating alkaline solutions in the scrubbing system. The formation of phosphine, phosphite, and hypophosphite is a potential problem in the clean-up system. Verification of the viability of the design by pilot plant testing will be required before investment toward a commercial unit could be made.

Recovery of phosphorus from the offgas by condensing in the CO compressor interstage coolers poses a potential danger to the compressor. Although available data indicates that condensation of phosphorus will not occur within the compressor casing, this approach should be verified by test. Deposits of solid phosphorus in the coolers and knock-out drums can be prevented by injection of a solvent, such as carbon disulfide, into the compression equipment.

4.2.4.2 Natural Gas Reforming

The reformer design parameters which play a significant role in determining the overall energy efficiency of the methanol plant are reformer temperature, steam/carbon ratio, and the reformer pressure.

High reformer temperature increases CO/CO₂ ratio of the synthesis gas and decreases its methane content. An increase in the CO/CO₂ ratio increases the carbon efficiency as methanol is made directly from CO and not from CO₂. The presence of larger quantities of CO₂ results in high equilibrium residual CO₂ levels resulting in greater CO₂ loss in the purge. The lower methane content of the reformed gas also increases carbon efficiency because of lower synthesis loop purge. Another important consideration in selecting the reformer temperature is that the methane leakage should be such that the synthesis loop purge gas does not exceed the overall plant fuel requirements. Based on these factors, a high reformer temperature consistent with the tube metallurgy was selected.

4.2.4.2 Natural Gas Reforming - cont'd

An increase in steam/carbon ratio decreases both the CO/CO₂ ratio and the methane content of the reformed gas, thereby affecting the carbon efficiency as explained above. A higher steam/carbon ratio generally lowers the overall thermal efficiency. This is because most of the unreacted steam in the reformed gas is recovered at low energy levels (low pressure steam generated).

The design steam/carbon ratio should be as close to a safe minimum as possible. A ratio within the limits of commercial experience was selected.

A high reformer pressure reduces the synthesis gas compression requirements but increases the natural gas compression and the methane content of the reformed gas. A reformer pressure of 16.9 kg/cm² (gauge) was selected for this design. This pressure in combination with the selected steam/carbon ratio and reformer exit temperature results in a high energy efficient design.

4.2.4.3 Methanol Synthesis

The methanol synthesis and purification sections utilize latest ICI technology.

A nominal synthesis pressure of 84.4 kg/cm² (gauge) is used in this design. This pressure level results in high carbon efficiency and falls in the optimum range for the ICI process. The use of a single synthesis reactor is also an important consideration in the selection of the synthesis pressure. We have determined that at the synthesis pressure used, a single reactor is satisfactory.

The reformer effluent comprises a synthesis gas with an excess of hydrogen over the stoichiometric quantity required for methanol production. In conventional methanol plants this results in a large hydrogen purge from the synthesis loop. However, the availability of CO in this plant allows the synthesis gas composition to be adjusted to a suitable stoichiometry, resulting in a minimum purge.

The synthesis loop purge, which is utilized as fuel, is available at a pressure suitable for energy recovery via an expansion turbine. This approach could be considered as an option in further study.

4.2.4.4 Steam System

Steam at a pressure of 105.5 kg/cm² (gauge) is generated in order to maximize recoverable energy. A part of this steam is used in the reformer after it is expanded in back pressure turbines to a pressure of 24.6 kg/cm² (gauge). The use of 105.5 kg/cm² (gauge) steam results in a higher thermodynamic efficiency when compared to a design utilizing lower steam pressures.

4.2.4.5 Methanol Storage

A product storage capacity equivalent to one month of methanol production has been provided. Two shift tanks, each having a capacity of eight hours production, have been provided to receive methanol from the refining column. The methanol in the shift tanks is analyzed and if all product specifications are met, it is sent to the product storage tanks. An eight-hour off-specification storage is provided to receive off-specification methanol from the shift tanks. A crude methanol storage tank, having an eight-hour capacity, is provided to receive crude methanol from the synthesis section. This tank avoids the need for shutting down the synthesis unit whenever there is a minor upset in the purification section and also provides capacity to receive crude methanol during start-up.

4.2.5 Process Details

Process details are presented in this section as follows:

- Process Flow Diagrams
- Material Balances
- Steam Balance
- Cooling Water Balance
- Fuel Balance

Detailed operating data (temperatures, pressures, flow rates, compositions) have been provided wherever possible. However, due to the confidential nature of the processes involved, certain restrictions have been imposed on the disclosure of information.

B.55

ISSUE
4-10-80

THE LUMMUS COMPANY
Bloomfield, N. J.

PROCESS FLOW DIAGRAM
SYN GAS GENERATION AND COMPRESSION
AREA 200

SCALE: 1" = 10' DRG. NO. E-8852-00200-

B.57

4-10-90

	THE LUMMUS COMPANY
	Bloomfield, N. J.
	PROCESS FLOW DIAGRAM METHANOL SYNTHESIS (AREA 300)
SCALE	DWG. NO. E-8852-00300

BY _____

AREA 100

OFFGAS CLEANUP AND COMPRESSION

[illegible]

(ABBREVIATION NOTE: kg_m/h denotes kilogram-moles per hour.)

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E. OR J. NO. _____
 DATE _____
 SHEET _____ OF _____
 BY _____

THE LUMMUS CO.
 MATERIAL BALANCE

AREA 100
 OFEGAS CLEANUP AND COMPRESSION

STREAM COMPONENT	101		102		103		104		105		106		107		108		109	
	SCRUBBED OFFGAS				CO TO				CO TO SYNGAS		SLUDGE		PHOSPHORUS		MAKEUP		MAKEUP	
	OFFGAS FEED		TO COMPRESSION		CO TO FUEL		METHANOL WASH		COMPRESSOR		TO POND		TO OSBI		LIME		NaOH	
	kg _m /h	Mole %	kg _m /h	Mole %	kg _m /h	Mole %	kg _m /h	Mole %	kg _m /h	Mole %	kg/h	Wgt %	kg _m /h	Mole %	kg/h	Wgt %	kg/h	Wgt %
H ₂	3.13	0.34	3.13	0.34	1.33	0.34	1.80	0.34	1.80	0.34								
N ₂	24.18	2.63	24.18	2.63	10.25	2.63	13.93	2.63	13.93	2.60								
CO	890.68	96.84	890.68	96.93	377.76	96.96	512.92	96.97	512.92	95.69								
CO ₂	1.38	0.15	0.55	0.06	0.23	0.06	0.32	0.06	-	-								
P ₄	0.38	0.04	0.38	0.04	0.03	0.01		12 ppm					0.342	100.00				
CH ₃ OH	-	-	-	-	-	-	-	-	7.36	1.37								
IMPURITIES	(Note 1)		(Note 1)								400	6.9						
TOTAL DRY	919.75	100.00	918.92	100.00	389.60	100.00	528.97	100.00	536.01	100.00			0.342	100.00				
H ₂ O	127.45		127.26		10.71		2.43				2475	93.1	114.12				40	50.0
CaO															215			
NaOH																	40	50.0
TOTAL WET	1047.20		1046.18		400.31		531.40		536.01		2875	(Note 2)	114.462		215		80	100.0
Molecular Weight	26.77		26.76		27.67		27.89		28.01				18.34					
Flow, kg/h	28035		27996		11078		14819		15011		2875		2100		215		80	
Temperature, °C	50		54.4		54.4		54.4		38		38		50		38		38	
Pressure, kg/cm ² (gauge) Atm.			0.02		4.80		34.11		33.76		-		-		-		-	

NOTE 1: See Attachment A for Impurities Content.
 NOTE 2: See Attachment B for Sludge Components.

(ABBREVIATION NOTE: kg_m/h denotes kilogram-moles per hour.)

MATERIAL BALANCE - AREA 100 - ATTACHMENT A

VOLATILE OFFGAS IMPURITIES

<u>Component</u>	<u>Concentration, ppmv</u>	
	<u>Offgas Feed</u>	<u>Exit Caustic Tower</u>
Ar	60	60
COS*	74	74
H ₂ S	130	30
CS ₂ *	3	3
CH ₄ *	49	49
C ₆ H ₆ *	1	1
PH ₃ *	385	385
HCN	880	10
NH ₃	14	12
Ag	Trace	Trace
Al	63	2
As	Trace	Trace
B	269	27
Ba	Trace	Trace
Be	Trace	Trace
Ca	4	< 1
Co	< 1	< 1
Cl	103	1
Cr*	2	2
Cs	Trace	Trace
Cu	Trace	Trace
F	555	555
Fe*	6	6
Ge	Trace	Trace
Hg	Trace	Trace
K	33	12
Li	< 1	< 1
Mg	10	4
Mn	Trace	Trace
Mo	Trace	Trace

MATERIAL BALANCE - AREA 100 - ATTACHMENT A

(cont'd)

VOLATILE OFFGAS IMPURITIES

<u>Component</u>	<u>Concentration, ppmv</u>	
	<u>Offgas Feed</u>	<u>Exit Caustic Tower</u>
Na	16	6
Ni*	21	21
Pb	Trace	Trace
Rb	Trace	Trace
S	3	< 1
Se	< 1	< 1
Si	1128	12
Sn	Trace	Trace
Sr	< 1	< 1
Ti	< 1	< 1
V	Trace	Trace
Y	Trace	Trace
Zn	< 1	< 1
Zr	1	< 1

*These components will not be removed in the scrubbing system. Cr, Fe and Ni, as the associated carbonyl compounds, will be removed in the copper catalyst guard bed. PH₃ removal is accomplished in the activated carbon guard bed. Miscellaneous components will be removed in the methanol wash.

MATERIAL BALANCE - AREA 100 - ATTACHMENT B

SLUDGE TO POND

The sludge stream to the disposal pond will contain the metal impurities as listed in Tables 4.2-2 and 4.2-3, calcium and sodium salts formed from the CO₂, fluorine, chlorine, and sulfur containing compounds in the feed gas, as well as silica formed by hydrolysis of incoming silicon.

The sludge will form a 10 wgt % solids slurry approximately as follows:

Suspended Solids	275 kg/h
Total Dissolved Solids	125 kg/h
Water	<u>2475 kg/h</u>
	2875 kg/h

BY _____

SYNGAS GENERATION

STREAM COMPONENT	201		202		203		204		205		206					
	NATURAL GAS		STEAM TO		FEED TO		REFORMER		CO FROM		MAKEUP GAS TO					
	FEED		REFORMER		REFORMER		EFFLUENT		METHANOL WASH		MeOH SYNTHESIS					
	kg _m /h	Mole %	kg _m /h	Mole %	kg _m /h	Mole %	kg _m /h	Mole %	kg _m /h	Mole %	kg _m /h	Mole %				
H ₂							3735.53	73.67	1.87	0.34	3737.33	66.66				
N ₂									13.93	2.60	13.93	0.25				
CO							858.01	16.92	512.92	95.69	1370.93	24.45				
CO ₂							318.95	6.29			318.95	5.69				
CH ₄	1148.25	94.0			1148.25	94.0	158.22	3.12			158.22	2.82				
C ₂ H ₆	48.81	4.0			48.81	4.0										
C ₃ H ₈	13.46	1.1			13.46	1.1										
i-C ₄ H ₁₀	3.67	0.3			3.67	0.3										
n-C ₄ H ₁₀	3.67	0.3			3.67	0.3										
C ₅ H ₁₂	2.46	0.2			2.46	0.2										
C ₆ +	1.26	0.1			1.26	0.1										
CH ₃ OH									7.36	1.37	7.36	0.13				
High Alcohols																
Light Ends																
TOTAL DRY	1221.58	100.0	*	*	1221.58	100.00	5070.71	100.0	536.01	100.00	5606.72	100.00				
Molecular Weight	17.35		18.02		17.35		9.50		27.98		11.26					
Flow, kg/h	21195		*		21195		48152		15011		63163					
Temperature, °C	35		316		*		*		38		38					
Pressure, kg/cm ² (gauge)	2.81		24.61		20.04		16.88		33.76		72.78					

(ABBREVIATION NOTE: kg_m/h denotes kilogram-moles per hour.)

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E. or J. NO. _____
DATE _____
SHEET ____ OF ____
BY _____

THE LUMMUS CO.
MATERIAL BALANCE

AREA 300

METHANOL SYNTHESIS

[illegible]

*Comprises proprietary information.

(ABBREVIATION NOTE: kg_m/h denotes kilogram-moles per hour.)

B.67

BY _____

METHANOL PURIFICATION

Molecular Weight	*	18.02	*	32.04	*
Flow, kg/h	56670	4440	1130	50600	530
Temperature, °C	38	49	38	38	15
Pressure, kg/cm ² (gauge)	6.3	0.70	Atm.	Atm.	0.14

(ABBREVIATION NOTE: $\text{kg}_{\text{m}}/\text{h}$ denotes kilogram-moles per hour.)

B.69

STEAM BALANCE DIAGRAM

Customer: .
Project: 1200 MT/D MeOH

4.2.6 Equipment List

Area 100 - Offgas Purification and Compression

DA-101	Slaked Lime Scrubber
DA-102	Caustic Scrubber
DA-103	Methanol Wash Column
DC-101	Copper Catalyst Guard Bed
DC-102	Activated Carbon Guard Bed
EA-101 & S	Slaked Lime Scrubber Start-Up Heater
EA-102 & S	Caustic Scrubber Start-Up Heater
EA-103	CO Compressor Intercooler #1
EA-104	CO Compressor Intercooler #2
EA-105	CO Compressor Intercooler #3
EA-106	CO Compressor Aftercooler
EA-107	Makeup Water Heater
EA-108	Offgas Cooler
FA-101	Slaked Lime Scrubber Mixing Sump
FA-102	CO Compressor Suction Knockout Drum
FA-103	CO Compressor Interstage Knockout Drum #1
FA-104	CO Compressor Interstage Knockout Drum #2
FA-105	CO Compressor Interstage Knockout Drum #3
FA-106	CO Compressor Final Knockout Drum
FA-107	Methanol Wash Column Knockout Drum
FA-108	Condensate and Phosphorus Collection Tank
FB-101	Lime Slaking Tank
FB-102	Caustic Mixing Tank
FC-101	Clarifier
FE-101	Lime Hopper
FH-101	Vibratory Feeder
GA-101 & S	Slaked Lime Circulation Pump
GA-102 & S	Caustic Circulation Pump
GA-103 & S	Wash Water Feed Pump
GA-104 & S	Slaked Lime Feed Pump
GA-105 & S	Clarifier Recycle Water Pump
GA-106 & S	Caustic Feed Pump
GA-107 & S	Sludge Pump
GA-108 & S	Phosphorus Pump
GA-109 & S	Methanol Circulation Pump
GA-110 & S	Makeup Methanol Feed Pump
GB-101 & S	Offgas Booster Fan
GB-102	CO Compressor (Turbine Driven)

4.2.6 Equipment List - cont'd

Area 100 - cont'd

GD-101 A/B	Slaked Lime Scrubber Sump Agitator
GD-102	Lime Slaking Tank Agitator
GD-103	Caustic Mixing Tank Agitator
JD-101	Bucket Elevator

4.2.6 Equipment List - cont'd

Area 200 - Synthesis Gas Generation & Compression

BA-201	Reformer
CA-201	Reformer Stack
DC-201	Sulfur Guard
EA-201	Natural Gas Bypass Cooler
EA-202	Natural Gas Compressor Intercooler
EA-203	Transfer Line Exchanger
EA-204	High Pressure BFW Preheater # 1
EA-205	Low Pressure WHB #1
EA-206	Low Pressure WHB #2
EA-207	Condensate Preheater
EA-208	Synthesis Gas Final Cooler
EA-209	Synthesis Gas Compressor Interstage Cooler
EA-210	Synthesis Gas Compressor Aftercooler
FA-201	Natural Gas Compressor Suction Drum
FA-202	Natural Gas Compressor Interstage Knockout Drum
FA-203	High Pressure Steam Drum
FA-204	Synthesis Gas Compressor Suction Drum
FA-205	Synthesis Gas Compressor Interstage Knockout Drum
FA-206	Synthesis Gas Compressor Final Knockout Drum
GB-201	Natural Gas Compressor (Turbine Driven)
GB-202 & S	Reformer Forced Draft Fan and Spare
GB-203 & S	Reformer Induced Draft Fan and Spare
GB-204	Makeup Synthesis Gas Compressor (Turbine Driven)

4.2.6 Equipment List - cont'd

Area 300 - Methanol Synthesis

BA-301	Synthesis Loop Start-Up Heater
DC-301	Methanol Converter
EA-301	Converter Feed/Effluent Exchanger
EA-302	High Pressure BFW Preheater #2
EA-303	Low Pressure Steam Generation #3
EA-304	Quench Economizer
EA-305	Methanol Condenser
FA-301	Crude Methanol Catch Pot
FA-302	Crude Methanol Letdown Drum
FB-301	Crude Methanol Storage Tank
GA-301 & S	Crude Methanol Pump and Spare
GB-301	Recirculator (Turbine Driven)

4.2.6 Equipment List - cont'd

Area 400 - Methanol Purification

DA-401	Methanol Topping Column
DA-402	Methanol Refining Column
EA-401	Topping Column Secondary Condenser
EA-402	Crude Methanol/Waste Water Exchanger
EA-403	Topping Column Reboiler
EA-404	Refining Column Reboiler
EA-405	High Alcohol Cooler
EA-406	Methanol Product Cooler
EA-407	Topping Column Primary Condenser
EA-408	Refining Column Condenser
FA-401	Concentrated Caustic Solution Tank
FA-402	Dilute Caustic Solution Tank
FA-403	Topping Column Reflux Drum
FA-404	Refining Column Reflux Drum
FB-401 A/B	Product Methanol Shift Tanks
FB-402	Liquid Purge Storage Tank
FB-403	Off-Spec Methanol Tank
GA-401 & S	Topping Column Reflux Pump and Spare
GA-402 & S	Topped Methanol Pump and Spare
GA-403 & S	Refining Column Reflux Pump and Spare
GA-404	Caustic Injection Pump
GA-405 & S	Product Methanol Transfer Pump and Spare
GA-406 & S	Liquid Fule Pump and Spare
GA-407 & S	Recycle Water Pump and Spare

4.2.6 Equipment List

Area 500 - Steam & Condensate System

BF-501	Auxiliary Boiler
BG-501	Phosphate Injection Unit
BG-502	Hydrazine Injection Unit
BG-503	Morpholine Injection Unit
BG-504 A/B	Condensate Carbon Filters
BG-505 A/B	Condensate Mixed Bed Polisher
CA-501	Boiler Stack
DA-501	Condensate Degasser
EA-501	CO Compressor Turbine Surface Condenser
EA-502	Natural Gas Compressor Turbine Surface Condenser
EA-503	Make-up Syngas Compressor Turbine Surface Condenser
EA-504	Flash Drum Vent Condenser, 35 psig
EA-505	Condensate Intercooler
EA-506	Dump Condenser
EA-507	Flash Drum Vent Condenser, 10 psig
EG-501	Deaerator
FA-501	High Pressure Boiler Continuous Blowdown Drum
FA-502	TLE Continuous Blowdown Drum
FA-503	Common High Pressure Boiler & TLE Blowdown Drum
FA-504	Low Pressure WHB #1 Blowdown Drum
FA-505	Low Pressure WHB #2 Blowdown Drum
FA-506	Low Pressure WHB #3 Blowdown Drum
FA-507	Condensate Accumulator, 35 psig
FA-508	Condensate Accumulator, 10 psig
GA-501 & S	CO Compressor Turbine Condensate Pumps
GA-502 & S	Natural Gas Compressor Turbine Condensate Pumps
GA-503 & S	Make-up Syngas Compressor Turbine Condensate Pumps
GA-504 & S	High Pressure BFW Pumps
GA-505 & S	Low Pressure WHB Feed Pumps
GA-506 & S	Condensate Pumps, 35 psig
GA-507 & S	Degasser Condensate Pumps
GA-508 & S	Condensate Pumps, 10 psig
GB-501	Degasser Air Blower
GB-502 A/B	Boiler Induced Draft Fans
GB-503 A/B	Boiler Forced Draft Fans

4.2.6 Equipment List - cont'd

Area 600 - Water Treating

AD-601	Neutralization Pit
BG-601 A/B	Cation Exchangers
BG-602 A/B	Anion Exchangers
BG-603 A/B	Mixed Bed Polishers
DA-601	CO ₂ Stripper
FB-601	Demineralized Water Storage Tank
FB-602	Sulfuric Acid Storage Tank
FB-603	Sulfuric Acid Day Tank
FB-604	Caustic Storage Tank
FB-605	Caustic Day Tank
GA-601 & S	Raw Water Feed Pump
GA-602 & S	Intermediate Booster Pump
GA-603	Cation Regeneration Pump
GA-604	Anion Regeneration Pump
GA-605	Anion Rinse Pump
GA-606 & S	Makeup BFW Pump
GA-607 & S	Neutralization Pit Circulation Pump
GA-608	Sulfuric Acid Transfer Pump
GA-609	Caustic Transfer Pump
GB-601	CO ₂ Stripper Fan

4.2.6 Equipment List - cont'd

Area 700 - Flare System

CB-701 Flare Stack
EA-701 Knockout Drum Vaporizer
FA-701 Flare Knockout Drum
GA-701 & S Knockout Drum Pumps

Area 800 - Product Storage Facilities

FB-801 A/B Methanol Product Storage Tanks
GA-801 & S Product Shipping Pumps

Area 900 - Cooling Water System

EA-901 Secondary Cooling Water Heater
EF-902 Cooling Tower
GA-901 A/B
 & S Cooling Water Circulation Pumps

Area 1000 - Waste Disposal System

AD-1001 Waste Disposal Pond
GA-1001 Waste Disposal Pump
GC-1001 A/B Surface Agitators

4.2.7 Equipment Specifications

The following section contains process equipment specifications for the Offgas Cleanup and Compression Area (Area 100) and Synthesis Gas Generation Area (Area 200). Due to the confidential nature of the ICI low pressure methanol process, details of the methanol processing equipment cannot be disclosed. Likewise, operating data considered to be proprietary in nature has been omitted from the synthesis gas generation equipment specifications.

Process support facilities have been estimated on an overall definition basis. No individual equipment specifications are included in the report. Descriptions and itemized equipment lists for these facilities are given in Section 4.2.3 and 4.2.5, respectively.

VESSEL OR TOWER NO.		DA-101	DA-102	DA-103		DC-101	DC-102							
SERVICE		SLAKED LIME SCRUBBER	CAUSTIC SCRUBBER	METHANOL WASH COLUMN		COPPER CATALYST GUARD BED	ACTIVATED CARBON GUARD BED							
POSITION		Vertical	Vertical	Vertical		Vertical	Vertical							
SIZE	DIAMETER, mm	2450	2450	920		3050	2300							
	LENGTH TANGENT TO TANGENT, mm	26520	21350	21350		9150	6900							
	SKIRT HEIGHT	N.A.	Minimum	Minimum		Minimum	Minimum							
TYPE HEADS		N.A.	Special Cone			2:1 Ellip.	2:1 Ellip.							
PRESS.	OPERATING, kg/cm ² (gauge)	0.5	0.5	32.4		34.5	33.1							
	DESIGN, kg/cm ² (gauge)	1.05	1.05	35.6		38.0	36.4							
TEMP.	OPERATING, °C	50	50	38		174	38							
	DESIGN, °C	65	65	190		190	190							
MAT'L	SHELL	C.S.	C.S.	C.S.		C.S.	C.S.							
	LINER	Rubber	Rubber											
DECKS OR BED SUPPORTS	NUMBER		3											
	TYPE		Bubblecap											
	SPACING													
	MATERIAL		316L SS											
PACKING	TYPE			Pall Rings										
	MATERIAL			S.S.										
		28 Ceramic Spray Nozzles	28 Ceramic Spray Nozzles			Contains 62.8 m ³ Catalyst	Contains 25.9 m ³ Carbon							
		Fully Insulated	Fully Insulated	Fully Insulated										
Corrosion Allowance				3 mm		3 mm	3 mm							

REMARKS:

THE LUMMUS COMPANY
Bloomfield

VESSEL AND TOWER LIST

CUSTOMER _____ PROJECT 1200 t/d MeOH

UNIT OFFGAS CLEAN-UP AREA 100

JOB NO. 8852

SHEET OF

ITEM NUMBER	SERVICE	SIDE	HEAT EXCHANGER MEDIUM								TEMPERATURE, °C				DUTY kcal/h (x 1000)	OVERALL HEAT TRANS. COEFF. kcal/m ² ·°C·h	FOUL FACTOR m ² ·°C/kcal	TOTAL SURFACE m ²	MAX ALLOWABLE PRESS. DROP. kg/cm ²	PRESSURE kg/cm ² Gauge		SIZE AND TYPE		MATERIALS	
			MATERIAL	FLOW kg/h	SPECIFIC GRAVITY	MOLECULAR WEIGHT	VISCOSITY AT AVG TEMP. cP	% VAPORIZED BY WEIGHT	% CONDENSED BY WEIGHT	IN	OUT	CORR. M.T.D.	DESIGN TEMP	OPERATING						DESIGN	NO. UNITS AND O.D. BY LENGTH	TYPE TEMA SYMBOLS	SHELL	TUBES	
EA-101 A/B	LIME SCRUBBER START-UP HEATER	SHELL	STEAM	5885					100	116	116		130	2589	732		50.6		1.8	3.9		FTS	CS	316SS	
	CAUSTIC SCRUBBER	TUBE	PROCESS H2O	84100						15	70	69.9	70					0.7	4.6	6.3					
EA-102 A/B	START-UP HEATER	SHELL	STEAM	2160					100	116	116		130	952	732		18.6		1.8	3.9		FTS	CS	316SS	
		TUBE	PROCESS H2O	28460						15	70	69.9	70					0.7	4.6	6.3					
EA-103	CO COMPRESSOR INTERCOOLER	SHELL	CW	171720						43	54	45.6	70	1908	244		171.5		5.3	7.0		FTS	CS	304SS	
		TUBE	OFFGAS	27725		27.0			6.2	174	54	45.6	190					0.2	1.6	38.0					
EA-104	CO COMPRESSOR INTERCOOLER	SHELL	CW	109980						43	54	45.6	70	1222	244		109.8		5.3	7.0		FTS	CS	304SS	
		TUBE	OFFGAS	26760		27.3			2.6	174	54	45.6	190					0.3	5.1	38.0					
EA-105	CO COMPRESSOR INTERCOOLER	SHELL	CW	48600						43	54	45.6	70	540	244		48.5		5.3	7.0		FTS	CS	304SS	
		TUBE	OFFGAS	15100		27.5			1.0	174	54	45.6	190					0.4	13.6	38.0					
EA-106	CO COMPRESSOR AFTERCOOLER	SHELL	CW	43245						43	54	45.6	70	480	244		43.1		5.3	7.0		FTS	CS	304SS	
		TUBE	OFFGAS	14755		27.8			0.4	174	54	45.6	190					0.7	34.5	38.0					
EA-107	MAKEUP WATER HEATER	SHELL	STEAM	177					100	116	116		130	93	732		2.1		1.8	3.9		FTS	CS	CS	
		TUBE	WATER	2431						32	70	63.1	87					0.7	4.6	6.3					
EA-108	OFFGAS COOLER	SHELL	CW	277000						43	54		70	3074	244		1010		5.3	7.0		FTS	CS	304SS	
		TUBE	OFFGAS	32851		25.0			14.8	70	50	12.9	87					0.01	.02	2.1					
		SHELL																							
		TUBE																							
		SHELL																							
		TUBE																							
		SHELL																							
		TUBE																							
		SHELL																							
		TUBE																							
		SHELL																							
		TUBE																							
		SHELL																							
		TUBE																							
		SHELL																							
		TUBE																							

ITEM NUMBER	COMPONENT	ENTERING				LEAVING				NOTES		
		kg/h		Bubble or Dew Pt. °C	SP GR	MOL. WT.	kg/h		Bubble or Dew Pt. °C		SP GR	MOL. WT.
		VAPOR	LIQUID				VAPOR	LIQUID				

REV.	DESCRIPTION	BY	APP	APP	DATE	JOB NO. 8852	SHEET 1 OF 1

THE LUMMUS COMPANY
Bloomfield

LUMMUS EXCHANGER SCHEDULE (MKS)
OFFGAS CLEAN-UP
UNIT AND COMPRESSION

VESSEL OR TOWER NO.		FA-101	FA-102	FA-103	FA-104	FA-105	FA-106	FA-107	FA-108		FB-101	FB-102	FC-101	FE-101
SERVICE		SLAKED LIME MIXING SUMP	CO COMP. SUCTION KO DRUM	CO COMP. KO DRUM #1	CO COMP. KO DRUM #2	CO COMP. KO DRUM #3	CO COMP. FINAL KO DRUM	METHANOL WASH COLUMN KO DRUM	PHOSPHORUS TANK		LIME SLAKING TANK	CAUSTIC MIXING TANK	CLARIFIER	LIME HOPPER
POSITION		Horizontal	Vertical	Vertical	Vertical	Vertical	Vertical	Vertical	Vertical			Vertical		Vertical
SIZE	DIAMETER, mm	6100	2290	1830	1450	915	765	765	1530		4880	1220	7620	3360
	LENGTH TANGENT TO TANGENT, mm	6250	2290	1830	2290	1830	1530	1530	3060		5490	1220	1980	110,880
	SKIRT HEIGHT		Minimum	Minimum	Minimum	Minimum	Minimum	Minimum	Minimum			Minimum		
TYPE HEADS			Dished	Dished	2:1 Ellip	2:1 Ellip	2:1 Ellip	2:1 Ellip	2:1 Ellip		Cone Roof	Dished	Cone Angle 150°	Cone Angle 50°
PRESS	OPERATING, kg/cm ² (gauge)	0.05	0.02	2.7	7.2	15.9	35.5	32.2	1.4		Atmosphere	0		Atmosphere
	DESIGN, kg/cm ² (gauge)	2.1	2.1	5.8	9.3	18.0	38.0	35.4	2.5			2.1		
TEMP.	OPERATING, °C	50	50	54	54	54	54	38	54		50	50		Ambient
	DESIGN, °C	65	65	190	190	190	190	190	70		67	67		
MAT'L	SHELL	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.		C.S.	C.S.	Concrete Tank	C.S.
	LINER	Rubber	304L SS	304L SS	304L SS	304L SS	304L SS		Rubber				W/316L Internals	
DECKS OR BED SUPPORTS	NUMBER													
	TYPE													
	SPACING													
	MATERIAL													
CORROSION ALLOWANCE, mm								3			3	3		
		Fully Insulated	Fully Insulated	Fully Insulated	Fully Insulated	Fully Insulated	Fully Insulated		Fully Insulated		Fully Insulated	Fully Insulated	Center Feed Pipe	
													Overflow Weir	
													Scraper W/Motor	

REMARKS:

THE LUMMUS COMPANY
Bloomfield

VESSEL AND TOWER LIST

CUSTOMER _____ PROJECT 1200 t/d MeOH

UNIT OFFGAS CLEAN-UP AREA 100

JOB NO. 8852 SHEET 1 OF 1

FH-101

VIBRATORY FEEDER

Capacity	215 kg/hr
Material Handled	Lime Powder
Density	800 kg/m ³
Material of Construction	Carbon Steel
Driver	Electric Motor
Power	0.746 kW

<u>Item No.</u>	<u>Service</u>	<u>Type</u>	<u>Liquid</u>	<u>Oper/Design Temp., °C</u>	<u>Differential Press., kg/cm²</u>	<u>Capacity m³/hr</u>	<u>BHP kW</u>	<u>Material</u>		<u>Driver Type</u>
								<u>Casing</u>	<u>Impeller</u>	
GA-101 & S	Slaked Lime Circ. Pump	Centrifugal	Lime H ₂ O Slurry ²	70/87	4.2	150	24.5	Rubber- Lined CS	316L	Electric
GA-102 & S	Caustic Circ. Pumps	Centrifugal	Caustic Slurry	70/87	4.2	117	19.1	Rubber- Lined CS	316L	Electric
GA-103 & S	Wash Water Feed Pump	Centrifugal	Water	32/49	4.2	3.6	0.64	CS	CS	Electric
GA-104 & S	Slaked Lime Feed Pump	Centrifugal	Slaked Lime	70/87	1.8	31	2.2	CS	CS	Electric
GA-105 & S	Clarifier Recycle Water Pump	Centrifugal	Water	70/87	1.8	33	2.4	Rubber- Lined CS	316	Electric
GA-106 & S	Caustic Feed Pump	Centrifugal	50% NaOH	70/87	1.8	2.3	0.2	CS	304L	Electric
GA-107 & S	Sludge Pump	Centrifugal	10% wt. Slurry	70/87	3.5	3.6	0.6	Rubber- Lined CS	304L	Electric
GA-108 & S	Phosphorus Pump	Centrifugal	Phossey Water	54/70	3.5	2.1	0.31	Rubber- Lined CS	304L	Electric
GA-109 & S	Methanol Circ. Pump	Centrifugal	Methanol	38/55	3.5	37	5.4	CS	CS	Electric
GA-110 & S	Make-Up Methanol	Centrifugal	Methanol	38/55	2.8	0.8	0.1	CS	CS	Electric

Pump ScheduleCustomer -Project - 1200 MTD MeOHUnit - Offgas Clean-UpArea - 100

GB-101 & S

OFFGAS BOOSTER FAN

Service	CO-Rich Offgas
Number Required	Two (2)
Type	Centrifugal
Stages	One (1)
Driver Type	Electric Motor
Estimated Power, kW	100

Process Conditions

Capacity, kg/hr	22725
Inlet m ³ /hr	27240
Inlet	
Pressure	Atmosphere
Temperature, °C	50
Differential Pressure	50 mm Hg
Gas Molecular Weight	27.1

GB-102

CO COMPRESSOR

Service	Clean Offgas
Number Required	One (1)
Type	Centrifugal
Stages	Four (4)
Driver Type	Steam Turbine
Estimated Power, kW	3600

Process Conditions

	<u>Stage</u>			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Capacity, kg/hr	27725	26760	15100	14755
Inlet m ³ /hr	27240	11155	2611	1040
Inlet				
Pressure, kg/cm ² (absolute)	1.05	2.66	6.89	15.47
Temperature, °C	54	54	54	54
Discharge				
Pressure, kg/cm ² (absolute)	2.87	7.17	15.87	35.51
Temperature, °C	198	204	171	181
Gas Molecular Weight	27.1	27.3	27.5	27.8

Utility Conditions

Steam	<u>Inlet</u>	<u>Exhaust</u>
Pressure	24.6 kg/cm ² (gauge)	115 mm Hg(abs.)
Temperature, °C	316	-
Cooling Water	<u>Supply</u>	<u>Return</u>
Temperature, °C	43.3	54.4

AGITATOR SUMMARY

<u>Item No.</u>	<u>GD-101 A/B</u>	<u>GD-102</u>	<u>GD-103</u>
<u>Location</u>	FA-101	FB-101	FB-102
<u>Position</u>	Vertical	Vertical	Vertical
<u>Impeller Dia. (mm)</u>	460	610	205
<u>Speed (rpm)</u>	100	100	100
<u>Material</u>	316L	304L	304L
<u>Driver</u>	Electric	Electric	Electric
<u>Power (kW)</u>	11.3	15	3.8

JD-101

BUCKET ELEVATOR

Height	23 m
Capacity	3.5 MT/hr
Material Handled	Lime Powder
Density	800 kg/m ³
Material of Construction	Carbon Steel
Driver	Electric
Power	3.8 kW

BA-201

NATURAL GAS REFORMER

Number Required	One
Type	Top-Fired/Down-Flow
Total Duty Absorbed	106.8 MM kcal/hour

HEAT ABSORPTION

Reforming Reaction	73.3 MM kcal/hour
Natural Gas & Steam Preheating	20.0 MM kcal/hour
Steam Superheating	13.5 MM kcal/hour

COMBUSTION DESIGN CONDITIONS

Type of Fuel	Purge Gas & Natural Gas
Excess Air	10%
Calculated Efficiency	94% (LHV)
Radiation Loss	1.5%, Of Heat Release (LHV)
Flue Gas Temperature	121°C, Leaving Convection Section

ITEM NO.	DESCRIPTION	LOCATION	MATERIAL	DESIGN TEMPERATURE (C°)	DESIGN PRESSURE (kg/cm ² , gauge)	DUTY (M kcal/hr)	TOTAL SURFACE (m ²)	TYPE (TEMA)	MATERIALS OF CONST.
EA-201	NAT GAS COMPRESSOR BYPASS COOLER	SHELL TUBE	COOLING WATER NATURAL GAS	60 160	7.0 4.9	838	110.5	FTS	C.S. C.S.
EA-202	NAT GAS COMPRESSOR INTERCOOLER	SHELL TUBE	COOLING WATER NATURAL GAS	60 160	7.0 30.0	1198	164.6	FTS	C.S. C.S.
EA-203	TRANSFER LINE EXCHANGER	SHELL TUBE	BFW & STEAM REF EFFLUENT	330 927	116.0 18.6	28485	209.2	*	C.S. C-1/2 Mo
EA-204	HIGH PRESSURE BFW PREHEATER NO. 1	SHELL TUBE	BFW REF EFFLUENT	330 510	123.0 18.6	8000	248.4	FTS	C.S. C.S.
EA-205	LOW PRESSURE WHB NO. 1	SHELL TUBE	BFW & STEAM REF EFFLUENT	160 285	4.9 18.6	6695	253.1	U-TUBE KETTLE	C.S. C.S.
EA-206	LOW PRESSURE WHB NO. 2	SHELL TUBE	BFW & STEAM REF EFFLUENT	140 170	3.2 18.6	7562	815.6	U-TUBE KETTLE	C.S. S.S.
EA-207	CONDENSATE PREHEATER	SHELL TUBE	COND & MAKEUP REF EFFLUENT	130 150	10.9 18.6	7888	510.7	FTS	C.S. S.S.
EA-208	SYNGAS FINAL COOLER	SHELL TUBE	COOLING WATER REF EFFLUENT	60 120	7.0 18.6	5918	721.4	FTS	C.S. S.S.
EA-209	SYNGAS COMPRESSOR INTERCOOLER	SHELL TUBE	COOLING WATER SYNGAS	60 170	7.0 81.6	3895	303.7	FTS	C.S. S.S.
EA-210	SYNGAS COMPRESSOR AFTERCOOLER	SHELL TUBE	COOLING WATER SYNGAS	60 170	7.0 81.6	4315	291.9	FTS	C.S. S.S.

*SPECIAL DESIGN FTS THERMOSIPHON.

EXCHANGER SCHEDULE

CUSTOMER _____ PROJECT 1200 t/d MeOH
UNIT SYNTHESIS GAS GENERATION AREA 200

ITEM NUMBER	DC-201	FA-201	FA-202	FA-203	FA-204	FA-205	FA-206
SERVICE	SULFUR GUARO	NATURAL GAS COMPRESSOR SUCTION DRUM	NATURAL GAS COMPRESSOR INTERSTAGE KNOCKOUT DRUM	HIGH PRESSURE STEAM DRUM	SYNGAS COMPRESSION SUCTION DRUM	SYNGAS COMPRESSOR INTERSTAGE KNOCKOUT DRUM	SYNGAS COMPRESSOR FINAL KNOCKOUT DRUM
POSITION	Vertical	Vertical	Vertical	Vertical	Vertical	Vertical	Vertical
SIZE							
DIAMETER, mm	1830	1600	1300	2135	1985	1830	1600
LENGTH, mm	4575	1600	1950	8540	2750	1830	1600
(Tangent to Tangent)							
SKIRT HEIGHT, mm	Minimum	Minimum	Minimum	-	Minimum	Minimum	-
DESIGN CONDITIONS							
TEMPERATURE, °C	399	158	158	334	165	165	165
PRESSURE, kg/cm ² (gauge)	23.5	4.9	11.5	111.1	16.5	36.7	80.2
MATERIAL							
SHELL	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.	C.S.
LINER	-	-	-	-	-	-	-
INTERNALS	-	-	-	-	-	-	-
CORROSION ALLOWANCE, mm	3	3	3	3	3	3	3

VESSEL SCHEDULE

CUSTOMER _____ PROJECT 1200 t/d MeOH

UNIT SYNTHESIS GAS GENERATION AREA 200

GB-201

NATURAL GAS COMPRESSOR

Service	Natural Gas
Number Required	One (1)
Type	Centrifugal
Stages	Two (2)
Driver Type	Steam Turbine
Estimated Power, kW	2950

Process Conditions

	<u>Stage</u>	
	<u>1</u>	<u>2</u>
Capacity, kg/hr	21050	21050
Inlet m ³ /hr	8225	3225
Inlet		
Pressure, kg/cm ² (absolute)	3.87	9.78
Temperature, °C	35	38
Discharge		
Pressure, kg/cm ² (absolute)	10.48	26.37
Temperature, °C	137	141
Gas Molecular Weight	17.3	17.3

Utility Conditions

Steam	<u>Inlet</u>	<u>Exhaust</u>
Pressure	24.6 kg/cm ² (gauge)	115 mm Hg(abs.)
Temperature, °C	316	-
Cooling Water	<u>Supply</u>	<u>Return</u>
Temperature, °C	32	43

GB-202 & S

REFORMER FORCED DRAFT FAN

Service	Air
Number Required	Two (2)
Type	Centrifugal
Stages	One (1)
Driver Type	Electric Motor
Estimated Power, kW	130

Process Conditions

Capacity, kg/hr	182,800
Inlet m ³ /hr	152,400 (Estimated)
Inlet	
Pressure, kg/cm ² (absolute)	Atmosphere
Temperature, °C	16
Differential Pressure	11 mm Hg
Gas Molecular Weight	28.4

GB-203 & S

REFORMER INDUCED DRAFT FAN

Service	Flue Gas
Number Required	Two (2)
Type	Centrifugal
Stages	One (1)
Driver Type	Electric Motor
Estimated Power, kW	200

Process Conditions

Capacity, kg/hr	194,140
Inlet m ³ /hr	232,000 (Estimated)
Inlet Temperature, °C	121
Differential Pressure	11 mm Hg
Gas Molecular Weight	27.1

GB-204

MAKEUP SYNGAS COMPRESSOR

Service	Synthetic Gas
Number Required	One (1)
Type	Centrifugal
Stages	Two (2)
Driver Type	Steam Turbine
Estimated Power, kW	9725

Process Conditions

	<u>Stage</u>	
	<u>1</u>	<u>2</u>
Capacity, kg/hr	48160	62900
Inlet m ³ /hr	8750	4335
Inlet		
Pressure, kg/cm ² (absolute)	15.1	34.1
Temperature, °C	38	38
Discharge		
Pressure, kg/cm ² (absolute)	34.5	74.9
Temperature, °C	149	149
Gas Molecular Weight	9.5	11.2

Utility Conditions

Steam	<u>Inlet</u>	<u>Extraction</u>	<u>Exhaust</u>
Pressure	105.5 kg/cm ² (gauge)	24.6 kg/cm ² (gauge)	115 mm Hg(abs.)
Temperature, °C	482	316	-
Cooling Water	<u>Supply</u>	<u>Return</u>	
Temperature, °C	32.2	43.3	

4.2.8 Utility Requirements

At design operating conditions, the estimated consumption of utilities is as follows:

<u>Commodity</u>	<u>Units</u>	<u>Quantity</u>
CO-Rich Offgas ⁽¹⁾		
Feed ⁽²⁾	normal m ³ /hr, dry kcal/hr	11855 34.67 MM
Fuel ⁽³⁾	normal m ³ /hr, dry kcal/hr	8730 25.52 MM
Natural Gas		
Feed	normal m ³ /hr, dry kcal/hr	27380 250.98 MM
Fuel	normal m ³ /hr, dry kcal/hr	6135 83.70 MM
Makeup Raw Water	kg/hr	200,000
Electric Power	kW	1200

NOTE:

- (1) The entire CO-rich offgas stream is processed in the Offgas Clean-up System (Area 100).
- (2) This stream is the portion of CO-rich offgas fed to the process.
- (3) This stream represents the portion of CO-rich offgas used as fuel. It is extracted from the CO compressor after clean-up (Area 100).

4.2.9 Catalyst & Chemical Requirements

At design operating conditions, the estimated consumption of catalysts and chemicals is as follows:

<u>Name of Catalyst or Chemical</u>	<u>Initial Charge</u>	<u>Estimated Life Or Consumption</u>
Zinc Oxide	11 m ³	3 years
Primary Reforming Catalyst	25 m ³	5 years
Methanol Synthesis Catalyst	130 m ³	5 years
Copper Catalyst	63m ³	1 year
Activated Carbon	26 m ³	1 year
Cation Resin	13.3 m ³	10 years
Anion Resin	9.3 m ³	3 years
CaO (100% Basis)	-	5160 kg/day
NaOH (100% Basis)	-	360 kg/day
Hydrazine (35% Commercial Grade)	-	635 kg/year
Morpholine (40% Commerical Grade)	-	115 kg/year
Disodium Phosphate (Na ₂ HPO ₄)	-	1815 kg/year
Sulfuric Acid (100% Basis)	-	435 kg/day
Chlorine	-	90 kg/day
Algaecide	-	1135 kg/year
Corrosion Inhibitor	-	4990 kg/year
Scale Inhibitor	-	3630 kg/year

4.2.9 Catalyst & Chemical Requirements

At design operating conditions, the estimated consumption of catalysts and chemicals is as follows:

<u>Name of Catalyst or Chemical</u>	<u>Initial Charge</u>	<u>Estimated Life Or Consumption</u>
Zinc Oxide	11 m ³	3 years
Primary Reforming Catalyst	25 m ³	5 years
Methanol Synthesis Catalyst	130 m ³	5 years
Copper Catalyst	63m ³	1 year
Activated Carbon	26 m ³	1 year
Cation Resin	13.3 m ³	10 years
Anion Resin	9.3 m ³	3 years
CaO (100% Basis)	-	5160 kg/day
NaOH (100% Basis)	-	360 kg/day
Hydrazine (35% Commercial Grade)	-	635 kg/year
Morpholine (40% Commerical Grade)	-	115 kg/year
Disodium Phosphate (Na ₂ HPO ₄)	-	1815 kg/year
Sulfuric Acid (100% Basis)	-	435 kg/day
Chlorine	-	90 kg/day
Algaecide	-	1135 kg/year
Corrosion Inhibitor	-	4990 kg/year
Scale Inhibitor	-	3630 kg/year

4.2.10 Preliminary Plot Plan

PLANT
NORTH

THE LUMMUS COMPANY Bloomfield, N. J.
PLOT PLAN METHANOL UNIT
Scale: 1" = 100' (approx.)

Scale: 1" = 100' (approx.)

Scale: 1" = 100' (approx.)

Scale: 1" = 100' (approx.)

Scale: 1" = 100' (approx.)

Scale: 1" = 100' (approx.)

B.101

4.3 Economic Data

4.3.1 Estimated Investment

The following sections comprise an equipment factor estimate for the battery limits Methanol Process Units and OSBL based on the equipment lists as given in Section 4.2.6.

Equipment costs were developed using in-house pricing data and vendor quotations for similar types of equipment purchased for other projects.

Commodity materials, subcontracts and direct construction labor costs were developed using statistical data based on Lummus' experience and modified to reflect current project application.

All costs of equipment, commodities, subcontracts and labor were estimated based on U.S. Gulf Coast December 1979 pricing level and do not include forward escalation.

A productivity factor has been included in the labor cost to adjust the total installed cost for a more typical, non-Gulf Coast location.

Testing, labor benefits and construction indirect costs were estimated on a statistical basis as a percent of total direct labor.

Home office costs were estimated using Lummus' experience and historical data applied on a manhour per piece method, excluding overtime premium and Lummus' fee.

4.3.1.1 Equipment Cost

The following is a breakdown of estimated equipment costs by equipment type.

<u>Equipment Account</u>	<u>\$M</u>			
	<u>Material</u>	<u>Labor</u>	<u>Sub-contractor</u>	<u>Total</u>
BA - Fired Heaters	4860.0	506.3	250.0	5616.3
BF - Steam Boilers	2000.0	7.5		2007.5
BG - Water Treating	417.5	13.6		431.1
CA - Stacks (Heater & Boiler)	40.0	10.4		50.4
CB - Stacks (Flare & Vent)	150.0	6.3		156.3
DA - Towers	638.2	18.7		656.9
DB - Tower Internals	121.4	3.8		125.2
DC - Reactors	1070.3	42.1		1112.1
EA - Exchangers	4301.1	102.3		4403.4
EF - Cooling Towers			600.0	600.0
EG - Deaerators	120.0	3.8		123.8
FA - Process Tanks	592.5	29.1	110.0	731.6
FB - Storage Tanks	19.5	1.3	1888.0	1908.8
FC - Clarifier	150.0	10.0		160.0

4.3.1.1 Equipment Cost - cont'd

<u>Equipment Account</u>	<u>\$M</u>			
	<u>Material</u>	<u>Labor</u>	<u>Sub- contractor</u>	<u>Total</u>
FE - Bins & Hoppers	26.0	1.3		27.3
GA - Pumps & Drivers	1312.5	57.3		1369.8
GB - Compressors & Drivers	6001.5	129.4		6130.9
GD - Mixers & Agitators	70.0	2.4		72.4
JD - Bucket Elevators	15.0	1.3		16.3
Totals	21905.5	946.9	2848.0	25700.4

4.3.1.2 Total Installed Cost

The total installed cost of the plant includes the equipment defined in the equipment lists (Section 4.2.6), as well as the General Service Facilities listed below:

- Sludge Disposal Pond
- Fire Protection System
- Inert Gas Generation
- Plant & Instrument Air System
- Electrical Substation
- Sewage System
- Buildings
- Truck Loading & Unloading Station
- Pipe Racks & Interconnecting Piping
- Lighting Network
- Roads, Parking Areas, Fence

The estimated TIC of the plant, as of December 1979, is \$100 MM. Details of the TIC components are shown on Table 4.3-1.

The TIC includes fee, state and local taxes, land and right of way, site preparation, initial charges of catalyst and chemicals, spare parts, insurance, and field labor overtime premium. Excluded from the TIC are forward escalation, working capital and risk allowance.

Table 4.3-2 shows a detailed breakdown of the total installed cost of the I.S.B.L. process and major utility units. The TIC shown is on a basis comparable to that used in the preliminary screening study. The total installed cost of the methanol plant, with the exclusions as noted in Table 4.3-2, is \$70 MM.

TABLE 4.3-1

ESTIMATED TOTAL INSTALLED COST SUMMARY

	<u>Cost (\$M)</u>
<u>Process and Major Utility Areas</u>	
Offgas Clean-up and Compression	9482
Synthesis Gas Generation and Compression	18535
Methanol Synthesis	10970
Methanol Purification	4478
Steam and Condensate System	9875
Water Treating and Potable Water System	1987
Flare System	677
Product Storage Facilities	4019
Cooling Water System	3256
Waste Disposal System	153
Sub-total	<u>63432</u>
<u>General Service Facilities</u>	
Sludge Disposal Pond	1818
Fire Protection System	1636
Inert Gas Generation	2273
Instrument and Plant Air	455
Electrical Substation	682
Area Lighting	282
Yard Piping	4091
Sewage System	182
Buildings	1910
Truck Loading and Unloading	136
Roads, Parking Lots, Site Prep., Fence	1182
Sub-total	<u>14647</u>
Initial Charge of Catalyst & Chemicals	2000
Spare Parts	650
Land & Right of Way (\$1000 per acre)	75
Fee	750
State & Local Taxes (3% of TIC)	3000
Insurance (3% of TIC)	3000
Productivity Adjustment	3200
Sub-total	<u>12675</u>
Contingency (10%)	<u>8895</u>
<u>Total Installed Cost</u>	99649
December, 1979	

4.3.2 Estimated Operating Costs

Table 4.3-3 contains a summary of the estimated cost of producing U.S. Federal Grade AA Methanol when utilizing the CO-rich offgas as a feedstock. The total estimated operating cost to produce 1200 MT/D of product methanol, excluding royalties, is \$120/t. The royalty charged for the ICI Methanol Process is a confidential item and cannot be included in the estimated operating cost.

TABLE 4.3-2

ESTIMATED TOTAL INSTALLED COST SUMMARY

Item	Cost (\$M)										Total
	Area 100	Area 200	Area 300	Area 400	Area 500	Area 600	Area 700	Area 800	Area 900	Area 1000	
Equipment - Material	3369.5	8822.6	4215.2	1118.0	3215.6	256.5	196.2	100.0	600.0	12.0	21905.6
- Subcontracts	141.0	250.0	45.0	225.0	-	187.0	-	1400.0	600.0	-	2848.0
Commodity - Material	1531.3	2847.6	2299.1	805.8	1929.4	266.1	117.7	900.0	720.0	7.2	11424.2
- Subcontracts	382.8	711.9	574.8	201.5	482.3	66.5	29.4	225.0	180.0	1.8	2856.0
Labor - Direct Equipment	99.6	605.1	108.4	32.8	62.1	13.9	9.6	2.9	11.3	1.1	946.8
- Commodities	1148.5	2135.7	1724.3	604.4	1447.1	199.6	88.3	675.0	540.0	5.4	8568.3
- Testing	37.4	82.2	55.0	19.1	45.3	6.4	2.9	20.3	16.5	0.2	285.3
- Field Benefits	411.9	904.2	605.0	210.1	498.3	70.4	31.9	223.3	181.5	2.2	3138.8
Construction Indirect Costs	649.5	1425.2	953.0	331.3	784.8	111.0	50.9	352.5	286.7	3.4	4948.3
Engineering Costs (Excl. Fee)	1710.0	750.0	390.0	930.0	1410.0	810.0	150.0	120.0	120.0	120.0	6510.0
Contingency Fee ($\pm 10\%$)	948.2	1853.5	1097.0	447.8	987.5	198.7	67.6	401.9	325.6	15.3	6343.1
Total Installed Cost (\$M) (December 1979, U.S. Gulf Coast)	10429.7	20388.0	12066.8	4925.8	10862.4	2186.1	744.5	4420.9	3581.6	168.6	69774.4

NOTE: Cost does not include forward escalation, fee, state and local taxes, working capital, field labor overtime premium, risk allowance, land and right of way, site preparation, initial charges of catalyst and chemicals, spare parts, or insurance.

TABLE 4.3-3
ESTIMATED OPERATING COST

	<u>Operating Cost (\$/t)</u>
<u>Raw Material</u> ⁽¹⁾	
Natural Gas	57.37
CO-Rich Offgas	4.15
Sub-total	<u>61.52</u>
<u>Utilities</u> ⁽¹⁾	
Fuel	
Natural Gas	19.13
CO-Rich Offgas	3.05
Make-up Water	0.09
Electricity	0.72
Sub-total	<u>22.99</u>
<u>Catalyst and Chemicals</u>	1.80
<u>Labor Related Costs</u>	
Operators ⁽²⁾	2.49
Supervision & Overhead ⁽³⁾	4.58
Sub-total	<u>7.07</u>
<u>Capital Related Costs</u>	
Maintenance (4% ISBL TIC)	4.83
Maintenance (2% OSBL TIC)	1.50
Property taxes, Insurance, etc. (2% ISBL & OSBL)	3.92
Depreciation (@ 10% ISBL, Cat. & Chem.) ⁽⁴⁾	12.26
Depreciation (@ 6.7% OSBL) ⁽⁵⁾	5.03
Sub-total	<u>27.54</u>
<u>By-product Credit (Phosphorous)</u>	<u>1.14</u>
<u>Total Operating Costs</u>	119.78

NOTES:

- (1) Cost data for raw materials and utilities is the same as used in the preliminary screening study (see Section 3.2.2).
- (2) Basis: 8 operators/shift
total 38 men
annual salary \$26,000
- (3) Basis: 200% of Operators
- (4) Basis: 10 years straight line
- (5) Basis: 15 years straight line

5.0 ALTERNATE USES OF CO FEEDSTOCK

The economic data generated during this study indicates that utilization of the CO-rich offgas as a feedstock for methanol production is sufficiently attractive to warrant commercial consideration. However, use of this offgas in the production of other chemical commodities may also be considered.

The CO can be entirely used for making acetic acid. With a supplemental source of methanol, a plant of world scale capacity can be designed. Monsanto offers the process and many plants of 150,000 metric tons per year capacity are under construction.

If chlorine is available nearby, it is feasible to react it into CO to make Phosgene which is further processed to Isocyanates, Pesticides and Polycarbonates. Stauffer Chemicals and Zimmer A.G. offer process licenses. However, capacities of these plants tend to be small.

There are a number of plants using the OXO Process of 50,000 metric tons per year capacity under construction. Propylene is hydroformulated with CO to make 3-Ethylhexanol. Ruhrchemie, BASF and Montedison offer the process know-how.

UNITS CONVERSION TABLE

UNITS CONVERSION TABLE

LENGTH

ft	x	.304 8	m/ft	→	m
in.	x	25.4	mm/in.	→	mm
	x	.025	m/in.	→	m

AREA

ft ²	x	.092 90	m ² /ft ²	→	m ²
in. ²	x	645.1	mm ² /in. ²	→	mm ²
	x	6.451	cm ² /in. ²	→	cm ²

VOLUME

ft ³	x	.028 31	m ³ /ft ³	→	m ³
in. ³	x	16 387	mm ³ /in. ³	→	mm ³
	x	16.38	cm ³ /in. ³	→	cm ³
	x	.016 38	l/in. ³	→	l(=dm ³)

VOLUME - cont'd

(US) gal	x	3.785	l/US gal	→	l(=dm ³)
----------	---	-------	----------	---	----------------------

UK (or Imperial gal)	x	4.545	l/UK gal	→	l(=dm ³)
-------------------------	---	-------	----------	---	----------------------

TIME

min	:	60	s/min	→	s
-----	---	----	-------	---	---

h	:	3600	s/h	→	s
---	---	------	-----	---	---

CONCENTRATION

Mass Concentration

PPM (parts per million)	x	1		→	mg/kg(=g/t)
----------------------------	---	---	--	---	-------------

ENERGY

Heat Content or Quantity, Internal Energy

Btu	x	1.055	kJ/Btu	→	kJ(=kW·s)
	:	3.412	Btu/Wh	→	W·h

cal	x	4.186	J/cal	→	J
-----	---	-------	-------	---	---

kcal, Cal	x	4.186	kJ/kcal	→	kJ
-----------	---	-------	---------	---	----

Energy, General

kW·h	x	3600	kJ/kWh	→	kJ
	x	3.6	MJ/kWh	→	MJ

W·h	x	3600	J/Wh	→	J(=W·s)
	x	3.6	kJ/Wh	→	kJ

 PRESSURE

Pressure

psi	x	.068 94	bar/psi	→	bar(=100 kPa =0.1 MPa)
	x	6.894	kPa/psi	→	kPa(=1000 Pa)
	x	68.94	mbar/psi	→	mbar(=100 Pa)

bar(=hectopieze)	x	100 000	Pa/bar	→	Pa(=N/m ²)
------------------	---	---------	--------	---	------------------------

lb/ft ²	x	.047 88	kPa/(lb/ft ²)	→	kPa(=0.01 bar)
--------------------	---	---------	---------------------------	---	----------------

kg/cm ² = kp/cm ²	x	.980 6	bar/(kg/cm ²)	→	bar
--	---	--------	---------------------------	---	-----

 VOLUME FLOW RATE

Air, Steam and Gas:

CFM ₃ (ft ³ /min)	x	1.699	(m ³ /h)/CFM	→	m ³ /h
	x	.471 9	(dm ³ /s)/CFM	→	dm ³ /s(=l/s)
1000 CFM	x	.471 9	(m ³ /s)/1000 CFM	→	m ³ /s

VOLUME FLOW RATE - cont'd

ft ³ /sec				→	m ³ /s
CFH				→	m ³ /h
1,000,000 CFD	x	.327 7	(m ³ /s)/(10 ⁶ CFD)	→	m ³ /s
SCFM _{60°F, 14.7psia}	x	1.607	(m ³ /h _{0°C})/CFM _{60°F}	→	m ³ /h _{0°C, 1.013 25 bar}
	x	1.695	(m ³ /h _{15°C})/CFM _{60°F}	→	m ³ /h _{15°C, 1.013 25 bar}
Liquid					
(US) GPM	x	.063 09	(l/s)/GPM	→	l/s(=dm ³ /s)
(gal/min)	x	.227 1	(m ³ /h)/GPM	→	m ³ /h
(UK, Imperial)	x	.075 76	(l/s)/UK GPM	→	l/s(=dm ³ /s)
(gal/min)	x	.272 7	(m ³ /h)/UK GPM	→	m ³ /h

MASS

lb	x	.453 5	kg/lb _m	→	kg
grain	x	.064 79	g/grain	→	g
	x	64.79	mg/grain	→	mg
(short or U.S.) ton	x	.907 1	t/short ton	→	t(=1000 kg)
(long or U.K.) ton	x	1.016	t/long ton	→	t(=1000 kg)

MASS FLOW RATE

lb/min	x	.007 559	(kg/s)/(lb/min)	→	kg/s
lb/h				→	kg/h
1000 lb/h	x	.125 9	(kg/s)(10 ³ lb/h)	→	kg/s
1,000,000 lb/yr	x	453.5	(t/10 ⁶ lb)	→	t/a
	x	.014 3	(kg/s)/(10 ⁶ lb/yr)	→	kg/s

 DENSITY

Mass per Volume

lb/ft ³	x	16.01	(kg/m ³)/(lb/ft ³)	→	kg/m ³
	x	.016 01	(kg/l)/(lb/ft ³)	→	kg/l(=kg/dm ³) =g/cm ³ =g/ml =t/m ³

lb/(US)gal	x	.119 8	(kg/l)/(lb/gal)	→	kg/l(=g/cm ³)
------------	---	--------	-----------------	---	---------------------------

lb/(UK)gal	x	.099 77	(kg/l)/(lb/UK gal)	→	kg/l
------------	---	---------	--------------------	---	------

 HEATING VALUE (PER UNIT VOLUME)

Btu/ft ³	x	.037 25	(MJ/m ³)/(B/ft ³)	→	MJ/m ³ (=kJ/dm ³)
---------------------	---	---------	---	---	---

kcal/m ³				→	kJ/m ³ (=0.001 MJ/m ³)
---------------------	--	--	--	---	--

POWER - HEAT FLOW - HEAT RATE

Power

HP	x	.745 6	kW/HP	→	kW
----	---	--------	-------	---	----

CV, PS, ch (obsolete metric horsepower)	x	.735 4	kW/CV	→	kW
---	---	--------	-------	---	----

ft-lb/sec	x	1.355	W/(ft-lb/sec)	→	W
-----------	---	-------	---------------	---	---

ft-lb/min	x	.022 59	w/(ft-lb/min)	→	W
-----------	---	---------	---------------	---	---

Heat Flow

Btu/h	x	.293 0	W/(B/h)	→	W(=J/s)
-------	---	--------	---------	---	---------

1000 Btu/h	x	.293 0	kW/(1000 B/h)	→	kW(=kJ/s)
------------	---	--------	---------------	---	-----------

Btu/min	x	.017 58	kW/(B/min)	→	kW
---------	---	---------	------------	---	----

kcal/h	x	1.162	W/(kcal/h)	→	W(=J/s)
--------	---	-------	------------	---	---------

boiler horsepower	x	9.180	kW/(boiler HP)	→	kW
-------------------	---	-------	----------------	---	----

POWER - HEAT FLOW - HEAT RATE - cont'd

Heat Rate

(1000 Btu/h)/HP x .393 0 → kW/kW

TEMPERATURE

Temperature Scale (Thermodynamic Temperature)

°F (t_F) ($t_F - 32^\circ\text{F}$):1.8 → °C

 ($t_F + 459.67^\circ\text{F}$):1.8 → K

°R (t_R) t_R :1.8 → K

°C (t_C) $t_C + 273.15^\circ\text{C}$ → K

K (t_K) $t_K - 273.15 \text{ K}$ → °C

Temperature Interval

°F : 1.8 °F/K → K(=°C)

POWER - HEAT FLOW - HEAT RATE

Power

HP	x	.745 6	kW/HP	→	kW
----	---	--------	-------	---	----

CV, PS, ch (obsolete metric horsepower)	x	.735 4	kW/CV	→	kW
---	---	--------	-------	---	----

ft-lb/sec	x	1.355	W/(ft-lb/sec)	→	W
-----------	---	-------	---------------	---	---

ft-lb/min	x	.022 59	w/(ft-lb/min)	→	W
-----------	---	---------	---------------	---	---

Heat Flow

Btu/h	x	.293 0	W/(B/h)	→	W(=J/s)
-------	---	--------	---------	---	---------

1000 Btu/h	x	.293 0	kW/(1000 B/h)	→	kW(=kJ/s)
------------	---	--------	---------------	---	-----------

Btu/min	x	.017 58	kW/(B/min)	→	kW
---------	---	---------	------------	---	----

kcal/h	x	1.162	W/(kcal/h)	→	W(=J/s)
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boiler horsepower	x	9.180	kW/(boiler HP)	→	kW
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HEAT TRANSFER COEFFICIENT - THERMAL CONDUCTANCE

Btu/(hr-ft ² -F)	x	5.678	(W/m ² K)/(B/ft ² hrF)	→	W/(m ² ·K)
	x	.005 678	(kW/m ² K)/(B/ft ² hrF)	→	kW/(m ² ·K)
kcal/(h·m ² ·°C)	x	1.162	W/(kcal/h)	→	W/(m ² ·K)

AMOUNT OF MATTER (SUBSTANCE)

lb mol	x	.453 5	kg/lb	→	kmol(=1000 mol)
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MOLAR FLOW RATE

lb mol/hr	x	.125 9	(mol/s)/(lbmol/h)	→	mol/s (=0.001 kmol/s)
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MOLECULAR MASS

(Relative) Molar Mass

Molecular Weight (Dimensionless)	x	1		→	g/mol(=kg/kmol) or dimensionless as relative molecular mass
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APPENDIX C

ADDENDUM TO METHANOL PLANT FEASIBILITY STUDY

Prepared for the
Pacific Northwest Laboratory
by the Lummus Company
Bloomfield, New Jersey

Lummus Job No. 8852
Special Agreement B-24827-A-E

SUMMARY

This addendum to the Methanol Plant Feasibility Study Report for the Pacific Northwest Laboratory comprises an estimate of the required investment for a 1200 MT/D methanol plant producing U. S. Federal Grade AA methanol when using natural gas as the only feedstock. This addendum supplements the estimate provided in the Feasibility Study Report for an equivalent methanol plant utilizing carbon monoxide rich off gas and natural gas as feedstocks.

The estimated total installed cost (TIC) of the methanol plant using only natural gas feedstock is \$103 MM. This represents approximately 3% increase in cost over the equivalent plant using CO-rich off gas as a feedstock.

The estimate presented in this addendum is based on equipment sizing obtained from recent proposals for similar methanol plants and adjusted accordingly. A contingency factor of 15% has been included to account for inaccuracies in proration.

Estimated Investment

The following sections comprise an equipment factor estimate for the battery limits Methanol Process Units and OSBL units required in a 1200 MT/D U. S. Federal Grade AA methanol plant utilizing natural gas as the feedstock.

Equipment costs were developed using in-house pricing data and vendor quotations for similar types of equipment purchased for other projects.

Commodity materials, subcontracts and direct construction labor costs were developed using statistical data based on Lummus' experience and modified to reflect current project application.

All costs of equipment, commodities, subcontracts and labor were estimated based on U. S. Gulf Cost December 1979 pricing level and do not include forward escalation.

A productivity factor for a non-Gulf Coast location has been included in the labor cost.

Testing, labor benefits and construction indirect costs were estimated on a statistical basis as a percent of total direct labor.

Home office costs were estimated using Lummus' experience and historical data applied on a manhour per piece method, excluding overtime premium and Lummus' fee.

Equipment Cost

The following is a breakdown of estimated equipment costs by equipment type.

<u>Equipment Account</u>	<u>\$M</u>			<u>Total</u>
	<u>Material</u>	<u>& Labor</u>	<u>Sub-contractor</u>	
BA-Fired Heaters	7965.0	747.0	380.0	9092.0
BF-Steam Boilers	800.0	3.0	---	803.0
BG-Water Treating	349.0	11.0	---	360.0
CB-Stacks (Flare & Vent)	187.0	8.0	---	195.0
DA-Towers	501.0	15.0	---	516.0
DB-Tower Internals	101.0	3.0	---	104.0
DC-Reactors	985.0	39.0	---	1024.0
EA-Exchangers	4888.0	116.0	---	5004.0
EF-Cooling Towers	---	---	620.0	620.0
EG-Deaerators	125.0	4.0	---	129.0
FA-Process Tanks	639.0	31.0	---	670.0
FB-Storage Tanks	67.0	4.0	1880.0	1951.0
GA-Pumps & Drivers	1231.0	54.0	---	1285.0
GB-Compressors & Drivers	5045.0	109.0	---	5154.0
GD-Mixers & Agitators	10.0	0.7	---	10.7
Totals	22893.0	1144.7	2880.0	26917.7

Total Installed Cost

The total installed cost of the plant includes the equipment required by the Process and major Utility Areas as well as the General Service Facilities listed below:

- Fire Protection System
- Inert Gas Generation
- Plant & Instrument Air System
- Electrical Substation
- Sewage System
- Buildings
- Truck Loading & Unloading Station
- Pipe Racks & Interconnecting Piping
- Lighting Network
- Roads, Parking Areas, Fence

The estimated TIC of the plant, as of December, 1979, is \$103 MM. Details of the TIC Components are shown on Table 1.0.

The TIC includes fee, state and local taxes, land and right of way, site preparation, initial charges of catalyst and chemicals, spare parts, insurance, and field labor overtime premium. Excluded from the TIC are forward escalation, working capital and risk allowance.

Table 2.0 shows a detailed breakdown of the total installed cost of the I.S.B.L. process and major utility units. The TIC shown is on a basis comparable to that used in the preliminary screening study. The total installed cost of the methanol plant, with the exclusions as noted in Table 4.3-2, is \$74 MM.

TABLE 1.0

ESTIMATED TOTAL INSTALLED COST SUMMARY

	<u>Cost (\$M)</u>
<u>Process and Major Utility Areas</u>	
Synthesis Gas Generation and Compression	26161
Methanol Synthesis	13720
Methanol Purification	5022
Steam and Condensate System	7226
Water Treating & Potable Water System	2714
Flare System	851
Product Storage Facilities	4463
Cooling Water System	3712
Waste Disposal System	<u>123</u>
Sub-total	63992
<u>General Service Facilities</u>	
Fire Protection System	1636
Inert Gas Generation	2273
Instrument and Plant Air	455
Electrical Substation	682
Area Lighting	282
Yard Piping	4091
Sewage System	182
Buildings	1910
Truck Loading and Unloading	136
Roads, Parking Lots, Site Prep., Fence	<u>1182</u>
Sub-total	12829
Initial Charge of Catalyst & Chemicals	1800
Spare Parts	650
Land & Right of Way (\$1000 per acre)	61
Fee	750
State and Local Taxes (3% of TIC)	3100
Insurance (3% of TIC)	3100
Productivity Adjustment	<u>3200</u>
Sub-total	12661
Contingency (15%)	13422
<u>Total Installed Cost</u>	102404
December, 1979	

Table 2.0
Estimated Total Installed Cost Summary

<u>Item</u>	<u>Area 200</u>	<u>Area 300</u>	<u>Area 400</u>	<u>Area 500</u>	<u>Area 600</u>	<u>Area 700</u>	<u>Area 800</u>	<u>Area 900</u>	<u>Area 1000</u>	<u>Total</u>
Equipment-Material	13050.0	5300.0	1170.0	2117.0	266.0	244.0				22893.0
-Subcontracts	380.0	—	230.0	—	194.0	—	104.0 1456.0	630.0 620.0	12.0 —	2880.0
Commodity-Material	3978.8	2761.0	914.5	1382.8	300.5	159.4				11339.7
-Subcontract	994.7	690.3	228.6	345.7	75.1	39.8	1019.0 254.7	816.5 204.1	7.2 1.8	2834.8
Labor-Direct Equipment	652.5	265.0	58.5	105.9	13.3	12.2				1144.7
-Commodities	2984.1	2070.8	685.9	1037.1	225.4	119.5	5.7	31.0	0.6	8504.8
-Testing	109.1	70.1	22.3	34.3	7.2	4.0	764.2	612.4	5.4	289.6
-Field Benefits	1200.1	770.8	245.7	377.2	78.8	43.5	23.1 254.1	19.3 212.3	0.2 2.0	3184.5
Construction Indirect Costs	2182.0	1401.5	446.6	685.8	143.2	79.0	461.9	386.0	3.6	5789.6
Engineering Costs (excl. fee)	630.0	390.0	1020.0	1140.0	1410.0	150.0	120.0	180.0	90.0	5130.0
Contingency Fee (+15%)	3924.2	2058.0	753.3	1083.9	407.1	127.7	669.5	556.8	18.5	9599.0
Total Installed Cost (\$M) (Dec., 1979, U.S. Gulf Coast)	30085.5	15777.5	5775.4	8309.7	3120.6	979.1	5132.2	4268.4	141.3	73589.7

NOTE: Cost does not include forward escalation, fee, state and local taxes, working capital, field labor overtime premium, risk allowance, land and right of way, site preparation, initial charges of catalyst and chemicals, spare parts, or insurance.

APPENDIX D

PHOSPHORUS REACTIONS IN ALKALI

PHOSPHORUS REACTIONS WITH ALKALI

The elemental phosphorus off gas cleanup system designed by the Lummus Company for the Battelle Process uses scrubbing with slaked lime (Ca(OH)_2) slurry followed by caustic (NaOH) solution in spray towers. A potential problem exists from reaction of these alkaline solutions with phosphorus present in the off gas as a saturated vapor.

An article by Strezhnev, Morgunova and Gabova (1963) reports experiments with slaked lime and elemental phosphorus-saturated slurries in which the effects of concentrations, temperature, and rate of agitation on reaction rate were studied in a reactor-emulsifier. The predominant reaction was considered to be:

A phosphorus balance at the end of a typical batch run was found to be 30% $\text{Ca(H}_2\text{PO}_2)_2$, 30% insoluble and 40% gas-phase (PH_3 and unreacted P_4). Rate of agitation was increased until it was believed that aqueous-phase kinetics were controlling the reaction rate.

Assuming that aqueous-phase kinetics were controlling in the experiments, a maximum reaction rate in the slaked lime tower can be calculated by assuming the same step controls. Onset of diffusion control in the tower would only lower the reaction rate. Volume fraction liquid in the tower can be calculated from the data in Appendix B by assuming an average droplet gas velocity of 5 ft/s. The volume of liquid in the heel of the tower need not be considered since the solubility of phosphorus is so low that the amount of dissolved phosphorus carried into the heel would be small. Using the above assumptions and the reported experimental data, phosphorus losses calculated by Equation (D.1) of 0.6% at 50°C and 4% at 93°C were determined. The amount of phosphine formed would be small in comparison with that in the entering gas. A later study by Morgunova and Averbukh (1967) reports similar experiments with the analogous reaction in caustic solutions.

Two reactions were supposed:

A typical phosphorus balance was 70% soluble phosphites and hypophosphites and 30% gas phase with no insolubles. Reaction rate was about twice as fast as with slaked lime but was still assumed to be controlled by liquid-phase kinetics. About twice as much reaction might therefore be expected in the caustic tower as in the slaked lime tower, except that kinetics in the caustic tower might be slowed by the build-up of the soluble reaction products in the circulating liquid.

It can be concluded from the above that kinetic limitations might prevent the subject reactions from posing significant problems through phosphorus losses. Accuracy of that conclusion, however, definitely should be checked by more representative experiments. In addition, the potential operating problems, such as slow reaction of any phosphorus condensed in the circulating liquors, need to be considered and checked in a pilot-scale system.

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