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**PRODUCTION OF OXYGENATES
FROM SYNTHESIS GAS:
A TECHNOLOGY REVIEW
FOR
U. S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER
FOR**

**DESIGN OF GENERIC
COAL CONVERSION FACILITIES**

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OXYGENATES

1.0 INTRODUCTION

In recent years a major change has occurred in gasoline composition due to the blending of oxygenates. The term oxygenates, as used here, refers to methanol, higher alcohols, and ethers. In addition to octane enhancement, blending of oxygenates such as alcohols and ethers into gasoline results in cleaner burning fuels. As gasoline additives, oxygenates have the potential of reducing carbon monoxide emission, indirectly reducing the ozone layer, improving the gasoline octane rating, acting as effective transportation fuel extenders, and improving fuel utilization (Srivastava, 1990). Such environmental benefits have been a major force in the continued growth of oxygenates in gasoline as an integral part of petroleum processing. Among these, methanol, ethanol, tertiary butyl alcohol (TBA), mixed alcohols, methyl tertiary butyl ether (MTBE), and ethyl tertiary butyl ether (ETBE) are receiving much legislative and administrative attention. Gradually stricter legislative regulations will increase the use of alcohols and ethers in gasoline, with the demand for the type of oxygenate being dictated on the basis of cost effectiveness.

In addition to the environmental benefits economic gains may also be derived by the use of oxygenates. Methanol, for example, has been shown to be an effective alternative to the use of petroleum fuels. Even if not used as a total substitute, oxygenates blended into gasoline replace a certain volume of petroleum fuel, extending the utility of this resource. The reduction of United States' dependence on imported crude oil by developing alternate fuels has been a principal objective of the U.S. Department of Energy. Advances in this area could produce major benefits for the country's economy. Balance of trade deficit, long-term energy pricing stability, energy and military security, as well as increased domestic employment, are among such benefits (LPMECH Program Report, May 1990).

The future economics of petroleum usage will boost the competition between methanol and synthesis gas as sources of liquid fuels. A major obstacle is problems (e.g. miscibility) associated with blending of methanol into gasoline. Such problems are virtually eliminated when oxygenates such as MTBE are used. However, present technologies for the production of such oxygenates rely, albeit partially, on petroleum-derived feedstocks (e.g. isobutylene). Therefore development of technologies and processes for complete utilization of synthesis gas as the raw material for the production of oxygenates is of great importance. Efforts by the DOE, industry, and academic institutions have been underway to bring advanced coal conversion technologies to commercial use.

A comprehensive review of oxygenates synthesis technology, including fixed and slurry bubble column reactors, was undertaken to develop an information base prior to the design of the Oxygenates Synthesis PDU. The unit is part of the Generic Coal Conversion Facilities to be built at the Pittsburgh Energy Technology Center (PETC). The pilot plant will include a fixed bed and a slurry bubble column reactor for the oxygenates synthesis mode.

This report concentrates on the production of oxygenates from coal via gasification and indirect liquefaction. At the present the majority of oxygenate synthesis programs are at laboratory scale. Exceptions include commercial and demonstration scale plants for methanol and higher alcohols production, and ethers such as MTBE. Research and development work has concentrated on elucidating the fundamental transport and kinetic limitations governing various reactor configurations. But of equal or greater importance has been investigations into the optimal catalyst composition and process conditions for the production of various oxygenates.

The report details established and emerging technologies for the synthesis of methanol, higher alcohols, and ethers, with emphasis on reactor types, catalysts, and operating ranges. An overview of existing technologies for the synthesis of

methanol from synthesis gas is given. Relevant reaction parameters, catalysts, and reactor types are discussed. This is followed by a discussion of several commercial scale methanol synthesis facilities employing established technologies, as well as recently demonstrated slurry bubble column reactor performance developed by Air Products & Chemicals, Chem Systems, and the DOE. Synthesis of higher alcohols and ethers, including reaction parameters and developments in catalysts and processing of these oxygenates, provides a comprehensive review of the present status and future directions for these technologies. The final section of the report presents issues related to the design of slurry reactors as pertains to oxygenates synthesis.

2.0 OVERVIEW OF METHANOL SYNTHESIS TECHNOLOGY

2.1 Reaction Conditions

The synthesis of methanol is accomplished through the catalytic process using synthesis gas containing mainly carbon monoxide (CO) and hydrogen (H₂).

The formation of methanol from gas mixtures of CO, H₂, and CO₂ proceeds via catalytic hydrogenation of CO, as shown by reaction (1). The conversion is thermodynamically limited, and high pressures and low temperatures favor the forward reaction (Ozturk et al., 1988).



The effect of pressure and temperature on equilibrium conversions and methanol concentration, for the case of synthesis gas typical of methane reforming units, is shown in Table 2.1 (Kine et al., 1988):

An important side reaction which also occurs under the synthesis conditions is the water-gas shift reaction, as shown by reaction (2). It provides H₂ to react with the feed CO to produce more methanol. By efficient removal of CO₂ from the system, the equilibrium can be shifted to remove water and produce H₂.



An undesirable reaction which may be significant in the synthesis is methanation. It proceeds according to reaction (3). Elevated temperatures aggravate this highly exothermic reaction.

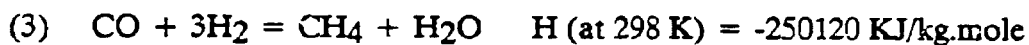


TABLE 2.1
 Equilibrium CO, CO₂ Conversion, and Exit CH₃OH Concentration vs. Pressure and Temperature^{a,b}
 [Kline et al., 1988]

Temperature C	CO Conversion, %			CO ₂ Conversion, %			Exit MeOH, VOL %		
	5 MPa	10 MPa	30 MPa	5 MPa	10 MPa	30 MPa	5 MPa	10 MPa	30 MPa
200	95.6	99.0	99.9	44.1	82.5	99.0	27.8	37.6	42.3
250	72.1	90.9	98.9	18.0	46.2	91.0	16.2	26.5	39.7
300	25.7	60.6	92.8	14.3	24.6	71.1	5.6	14.2	32.2
350	-2.3	16.9	73.0	19.8	23.6	52.1	1.3	4.8	21.7
400	-12.8	-7.2	38.1	27.9	30.1	44.2	0.3	1.4	11.4

^a Typical reformed natural gas composition (molar units) 15% CO, 8% CO₂, 74% H₂, 3% CH₄

^b H₂/(2 CO + 3 CO₂) = 1.30

Commercial production of methanol using high pressure synthesis began in the late 1920's in the United States. By 1965 a typical methanol production plant operated at 35 MPa (5100 psia) and had a capacity of 225 to 450 tons/day (Kine et al.). In the late 1960's low and medium pressure processes for the synthesis of methanol came into use, with ICI Ltd. operating a 400 tons/day plant at 5 MPa (725 psia). The new technology used copper-zinc oxide catalysts. Low and medium pressure processes have the advantage of good catalyst life, milder operating conditions, and hence reduced operating costs. Today essentially all new methanol plants are designed based on low pressure technology, and even older plants are being retrofitted to operate as such.

The low pressure process operates in the range of 200-300 C (392-572 F) and 5-25 MPa (700-3600 psia). Prior to this, the methanation side-reaction which is highly exothermic and leads to runaways, was a major problem in high pressure methanol plants. Methanation is worsened by the high temperatures (greater than 450 C) typical of the high pressure process. With the lower operating temperature range of the low pressure technology, methanation becomes insignificant.

For conventional methanol plants using the low pressure fixed-bed technology, there have been significant advances in feed gas preparation. Stoichiometric (balanced) feed gas can be prepared from natural gas, and several companies have designs for such process (Fox et al., 1990). Modern coal gasifiers can also be a source for the feed gas, but obtaining a stoichiometric gas from these units requires extensive shifting and CO₂ removal.

The feed synthesis gas can be categorized according to the it's source of generation. The following three cases have been identified as representative types for the development of processes to produce methanol from synthesis gas (LPMEOH PDU Report - Jan. 1991):

1. CO-Rich type: stoichiometrically unbalanced H₂/CO, typical for a modern Texaco coal gasifier

2. Balanced type: CO-rich gas which has undergone shift reaction and CO₂ rejection so that a stoichiometric ratio, i.e. H₂/CO = 2.0, is obtained
3. H₂-Rich type: stoichiometrically unbalanced H₂/CO, typical of synthesis gas from a steam methane reformer

2.2 Catalysts

An optimal catalyst for methanol synthesis is the copper oxide-zinc oxide-aluminum oxide system. The ratio of zinc to copper can be varied very substantially, with ratios in the range of 1:1 to 1:6 (on a molar basis) zinc to copper being favored (Stiles et al., 1991). The aluminum oxide forms 10 to 20% of the total mixed oxides. Reduction of the catalyst using a mixture of an inert gas with low hydrogen concentrations is necessary for activation.

High selectivity, in the range of 99.5% methanol, and high productivity can be achieved. In the laboratory, productivities in the range of 6 tons of MeOH/day-cu.ft. of catalyst bed have been observed (Stiles et al., 1991). A commercial scale methanol plant produces approximately 0.75 ton/day-cu.ft. Productivities in excess of 1.0 ton/day-cu.ft. cannot be achieved, since the exothermic heat of reaction is so large that heat dissipation becomes a major problem.

Catalyst properties for certain commercial methanol synthesis catalysts are available in the literature. For the the CuO/ZnO/Al₂O₃ catalyst manufactured by United Catalyst, Inc. a number of properties are available (Parameswaran et al., 1987). These are listed below:

Average BET surface area, m ² /g	80
Specific pore volume, cm ³ /g	0.43
Average pore diameter, A	200
Void fraction	0.58

The tortuosity factor for several commercial catalysts ranges between 3.3 and 7.5. Overall effectiveness factors of less than 0.5 (average of 0.29) have been reported for packed bed reactors. This means that pore diffusional limitations are significant factors in determining the methanol productivity when pellet sized catalysts are used.

2.3 Reactor Types

The traditional reactor design for methanol synthesis has been the fixed bed reactor. The single most important issue in the design of methanol reactors has been that of heat removal. This is due to the fact that as temperature increases, the conversion drops. The temperature control problem has been a major driving force for development of liquid-phase processes. The excellent mixing achieved in slurry-type reactors eliminates temperature gradients. In recent years this type of reactor has received considerable attention, as it holds the potential for improving the economics of methanol production (Srivastava, 1990). Operational plants using the two types of reactors are briefly discussed and pertinent operating conditions are reported below.

2.3.1 Commercial Fixed-Bed Process

Much of the effort in the design of fixed-bed reactors for methanol synthesis has concentrated on improved methods of heat removal, so that optimal conversion can be maintained. The ICI and Lurgi fixed bed reactor designs have been well tested, with many operating commercial-size plants around the world.

The fixed bed reactor is a two-phase system, in which the reacting feed gas flows through a bed of catalyst pellets. The exothermic heat of reaction is removed in either of two ways. In the ICI design, the reactor is divided into sections, with cold gas being fed in between; this design has been referred to as the multi-bed quench reactor. In the Lurgi design, small diameter tubes are filled with the catalyst. The tubes are assembled inside a shell, with pressurized boiling water on the shell-side

providing the heat removal medium. Pressures in the range of 5-10 MPa (700-1450 psia) and a temperature range of 220-280 C (428-536 F) are typical operating conditions for the fixed bed process. The ICI commercial process employs a Cu/ZnO/Al₂O₃ catalyst.

2.3.2 LaPorte Bubble-Column Slurry Reactor

- Process Development

The liquid-phase synthesis of methanol has been an area of active research. Chem Systems Inc. began development of the Liquid-phase Methanol (LPMEOH) technology in 1975. In 1981, Air Products and Chemicals, Inc. began a research and development program to prove the technical feasibility of the LPMEOH process. This liquid phase technology has several advantages over the gas-phase process. It provides easy temperature control, and diffusional resistances of the synthesis gas through the catalyst are eliminated or minimized. The LPMEOH technology is well suited to coal-derived synthesis gas, rich in CO. It is capable of processing feed gas containing high CO and H₂ concentrations and in variable proportions.

The process involves passing synthesis gas upward into a bubble-column slurry reactor, containing a catalyst. An inert hydrocarbon liquid serves to suspend the catalyst and to absorb the heat of reaction. As will be discussed in subsequent sections, early versions of the technology included an ebullating-bed reactor in which the catalyst pellets were fluidized by the upward flow of the liquid, and the liquid-entrained (slurry) reactor in which fine catalyst particles were suspended in the liquid within the reactor.

The LPMEOH Process Development Unit (PDU), located in LaPorte, Texas, has been a culmination of efforts by Air Products to demonstrate the commercial feasibility of the process. Through the 1984-1985 period of operation of the unit, the process performance and the catalyst activity over a wide range of operational conditions were investigated. An in-situ

reduction procedure in which the powdered catalyst is activated as it is circulating in slurry form through the reactor, was demonstrated successfully. Subsequent to material of construction change-outs in sections of the process to minimize metal carbonyl formation, excellent reactor performance was achieved. Efforts in process simplification and optimization, led to modifications which were implemented, and operation during the 1988 period demonstrated the improvements.

The simplified flow diagram for the PDU is shown in Figure 2.1. In the original process scheme for the PDU, makeup and recycle synthesis gas are compressed and heated through a feed/product exchanger. The gas stream is fed to the reactor bottom and is mixed with the incoming catalyst/oil slurry. Methanol and unconverted synthesis gas are separated from the slurry in a vapor-liquid separator. The slurry is pumped back to the reactor via a heat exchanger. The slurry can either be heated or cooled. The vapor from the separator is cooled against the incoming reactor feed to 150 C, condensing any vaporized liquid hydrocarbon. The uncondensed vapor is further cooled to 40 C using cooling water. Unconverted synthesis gas is recycled back to the reactor and a small purge stream is taken to prevent inerts buildup. The condensed methanol stream is flashed through a valve and the vapor stream is vented to flare. The liquid stream containing methanol and small amounts of hydrocarbons is phase-separated, and the methanol is sent to storage.

Initial process schemes for the PDU focused on two modes of operation for the reactor (LPMEOH PDU Report, Air Products, Jan. 1991). The first of these was the liquid-fluidized (or ebullating bed) mode in which the upward flow of hydrocarbon and synthesis gas resulted in catalyst (relatively large size pellets) fluidization. The second mode was the liquid-entrained (slurry) mode. In this mode of operation, fine catalyst particles are slurried in the inert liquid and circulated through the reactor. Two schemes for slurry circulation were investigated for the slurry mode. The external circulation

scheme involved pumping the slurry through an external exchanger and back into the reactor vessel. Optimization of the process led to the second scheme; internal circulation, in which the heat exchange and circulation occurred inside the reactor vessel. The slurry mode of operation, with internal circulation, was ultimately chosen due to its superior performance.

- Process Optimization

Subsequent to initial successful operation of the PDU, attention was turned to optimization of the process (LPMEOH PDU Report, Jan. 1991). It was determined that a process simplification which could eliminate the external slurry loop, would potentially improve the process economics through reduced capital costs and downtime caused by equipment failure.

Elimination of the slurry loop outside the reactor would require the vapor/slurry separation and heat exchange to be performed in the reactor vessel.

Several modifications were implemented to allow for the operation of the reactor in a non-circulating slurry mode with internal heat removal and vapor/slurry separation. A simplified sketch of the modified reactor system is shown in Figure 2.2. A longer reactor with a freeboard section and demister, and an optional cyclone, allowed for vapor/liquid disengagement. An internal heat exchanger with 1" diameter tubes manifolded by a 16" diameter heater ring at each end was installed. The exchanger occupied only 3.5% of the reactor cross-sectional area to minimize interference with the hydrodynamics. A newly designed circular gas sparger was used. The new sparger allowed suspension of high concentration slurries, while intimate gas/slurry mixing was maintained. It was estimated that the circulation due to the feed gas flow is an order of magnitude higher than that provided from the slurry pump, thus its elimination would not significantly affect the reactor hydrodynamics.

FIGURE 2.1
Simplified Process Flowsheet for LaPorte PDU
[LPMEOH PDU Report, Jan. 1991]

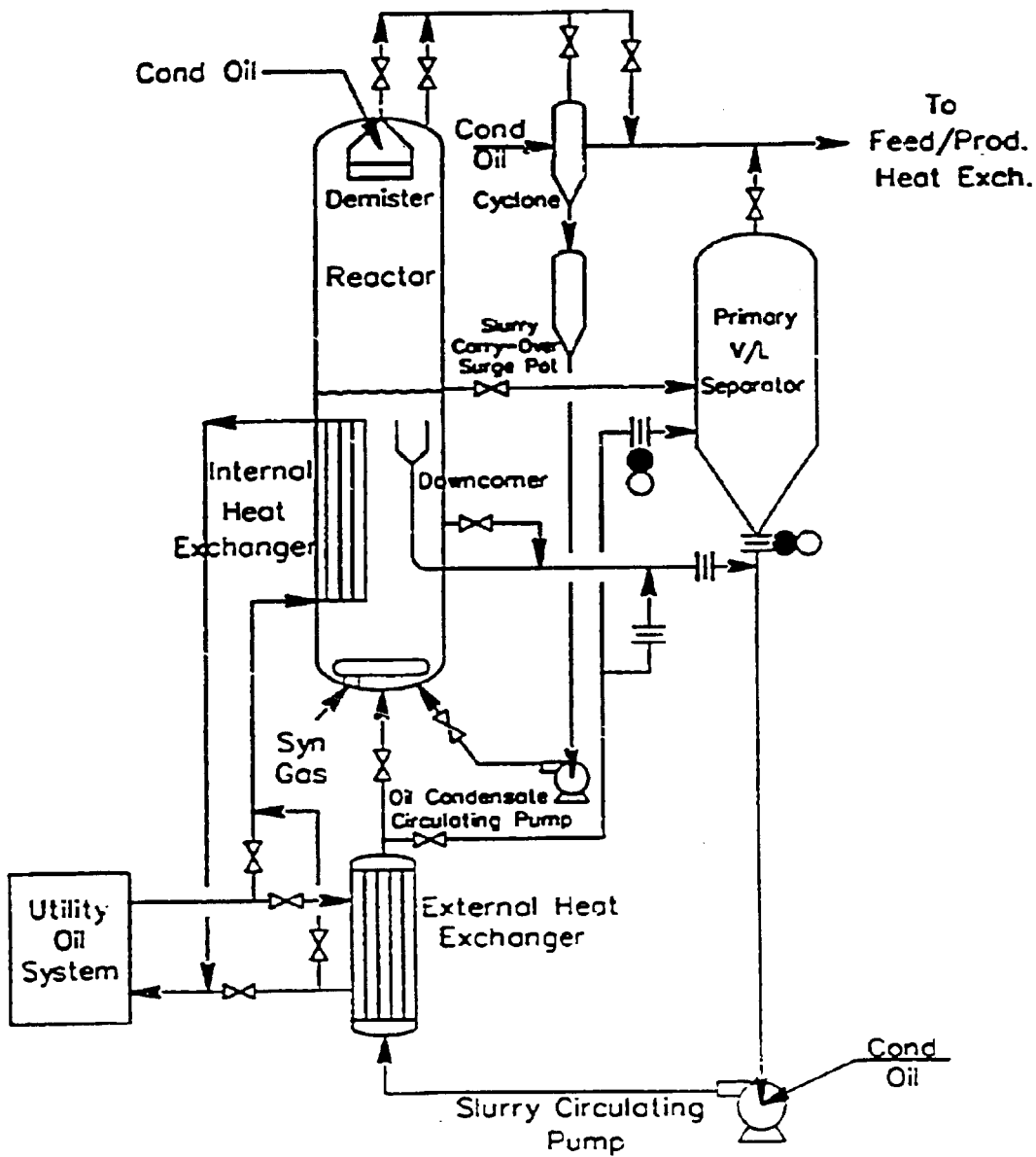
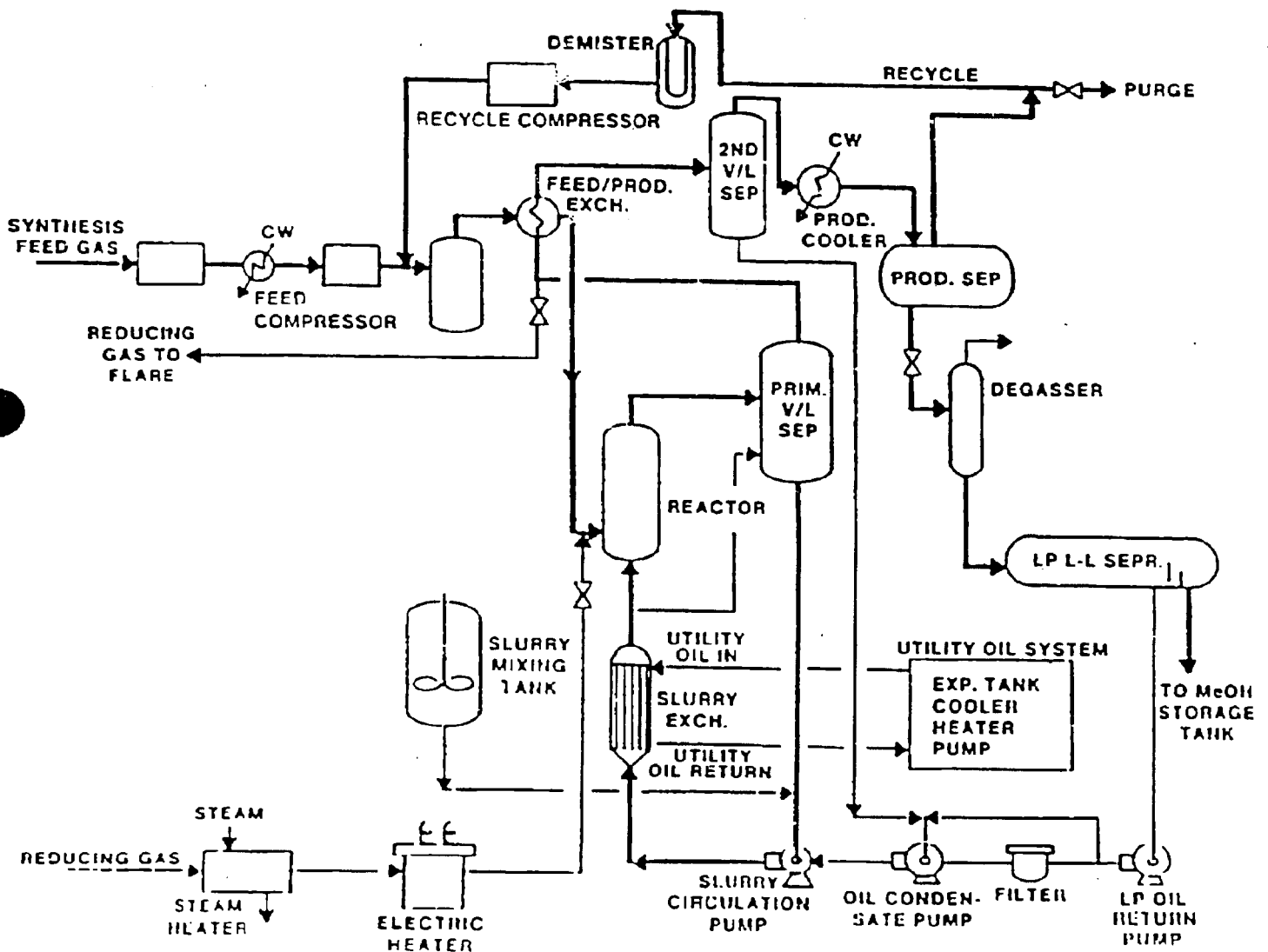


FIGURE 2.2
 Modified LPMEOH Reactor System
 [LPMEOH PDU Report, Jan. 1991]



Three feed gas compositions were investigated: 1) the balanced type, 2) the CO-rich type, and the H₂-rich type. The balanced type consists of 55% H₂ and 19% CO, the CO-rich type is 35% H₂ and 51% CO, and the H₂-rich type is 71% H₂ and 18% CO. Balanced type feed gas is suitable for total conversion to methanol via recycle, whereas the CO-rich type would be used for single-pass production with a resulting CO-rich fuel gas. The H₂-rich type represents synthesis gas from a steam methane reformer.

- Operating Conditions and Results

The ranges of operation for the LaPorte PDU follow:

	<u>Min</u>	<u>Normal</u>	<u>Max</u>
Reactor Pressure, MPa (psia)	3.55 (515)	5.27 (765)	6.31 (915)
Reactor Temperature, C (F)	235 (428)	250 (482)	270 (518)
Liquid-Entrained Space Velocity, l/hr-kg cat	2000	10000	17500
Liquid-Entrained Catalyst Loading, wt%	32.2	35.0	50.0
Superficial Gas Velocity cm/sec	3.0	15.5	22.0

The major achievements of the PDU as a result of the 1984-1985 operations were (LPMEOH PDU Report, Feb. 1987):

1. Demonstration of slurry preparation and handling capabilities at slurry concentrations above 40 wt% oxides.
 2. In-situ reduction procedure for catalyst activation.
 3. 0.28% per day decline in catalyst activity.
 4. Capability to maintain catalyst activity following extended down time.
 5. Methanol purities in the 96 wt% range for both balanced and CO-rich type synthesis gas.
- Catalyst Activity and Poisoning

It was also found that a nitrogen purge containing low H₂ content is suitable for maintaining the catalyst activity during extended downtime. Sampling and analysis of the catalyst indicated that sulphur, halogens, and trace metals such as iron and nickel are responsible for a rapid decline in activity. The excellent agreement between the PDU run and data gathered from an autoclave reactor, indicates that the efficient heat removal and uniformity of temperature experienced in stirred autoclave reactors are demonstrated equally in the LaPorte LPMEOH PDU. The selectivity to methanol was also high, averaging about 96 wt% methanol concentration throughout the run.

- Major Highlights of the Latest Operation

The major highlights of the 1988 operations, following the modifications which allowed the operation of the reactor in a non-circulating slurry mode with internal heat exchange and vapor/liquid separation, were (LPMEOH PDU Report, Jan. 1991):

1. Significant improvement in performance over the old reactor
2. Confirmation that high feed gas velocities are sufficient for slurry circulation
3. Sufficient heat transfer area can be installed internally without affecting the reactor hydrodynamics
4. Vapor/liquid separation can be achieved with a combination of a freeboard section in the reactor followed by a cyclone
5. Successful operation and in-situ activation of the catalyst at slurry loadings as high as 45%

At slurry loadings of 45%, the methanol production rate ranged between 8 to 9 tons/day. This exceeded the rate of 5 to 7 tons/day at 47% loading achieved with the old reactor operation. The higher methanol productivity without, compared to that with external recirculation, has been attributed to the lack of any significant contribution of the catalyst in the external loop to methanol production. The methanol productivity was greater than autoclave performance, which would indicate the elimination of mixing and mass transfer limitations with the new mode of operation.