Section 15

STATUS OF THE MOBIL METHANOL-TO-GASOLINE PROCESS

by

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ABSTRACT

The Methanol-to-Gasoline (MTG) Process is based on the ZSM-5 class of Mobil-discovered zeolite catalyst and offers a new and viable route for producing high quality gasoline from alternative energy resources such as coal, natural gas and biomass. These resources can be readily converted into methanol by using commercially available technologies. The MTG Process in turn converts the methanol into high octane gasoline which is directly marketable and totally compatible with petroleum derived gasoline. In addition, the MTG Process scheme is relatively simple and over 90% energy efficient.

Since the mid-1970's, Mobil has carried out extensive process development work on this process. Two modes of operation have been investigated - fixed-bed and fluidized-bed. The former is now ready for commercial application and has been selected for a commercial size plant in New Zealand which will produce 13,000 BPD of synthetic gasoline from natural gas. Startup is projected to be in 1984/1985. The latter is undergoing final stages of engineering development. A 100 BPD fluid-bed MTG pilot plant is under construction in Wesseling, W. Germany and will come on stream in mid-1982.

Introduction

The discovery of a new class of shape selective zeolite catalyst, namely the ZSM-5 class, has provided the basis for a new and efficient process for converting methanol to high octane gasoline.(1) Recognizing that methanol can be produced from coal and natural gas using well established commercial technology, Mobil undertook the development of the Methanol-to-Gasoline (MTG) Process to provide the first new route in 40 years for the production of premium transportation fuel from coal and other alternate energy resources. Two modes of operation have been developed - fixed-bed and fluidized-bed. This paper describes the development and current status of the MTG process.

Process Description

The production of gasoline from coal or natural gas using the MTG Process is shown conceptually in Figure 1. Synthesis gas (CO and H_2) derived from coal by gasification, or from natural gas by steam reforming, is readily synthesized into methanol, which is then converted to gasoline, LPG, and water by the MTG Process. It is significant to note that there are commercially proven processes available for the natural gas-to-methanol and coal-to-methanol paths. With the MTG Process now ready for commercial application, the final technological link is in place.

The basis for the MTG Process is a new class of zeolite catalyst (ZSM-5) with unique catalytic properties. A schematic drawing of the catalyst channel structure(2) is shown in Figure 2. There are two types of channels which intersect each other: elliptical 10-membered ring straight channels and sinusoidal, tortuous channels. The sizes of these channels permit only molecules of certain sizes to penetrate or exit. Consequently the reaction products exhibit a high selectivity. In the MTG reactions, the hydrocarbon products contain virtualy no molecules with a carbon number higher than ten and fall within the gasoline boiling range exclusively.

The MTG reaction chemistry is quite complex, with many competing and sequential reactions taking place at the same time. A simplified representation is given in Figure 3. The initial reaction is the dehydration of methanol to dimethyl ether. This reaction is reversible and the thermodynamic equilibrium is established rapidly. The methanol and dimethyl ether then undergo further dehydration to form light olefins. Subsequent reactions lead to the formation of heavier olefins, followed by naphthenes, paraffins, and aromatics. A more detailed discussion of the reaction chemistry is given by Chang and Silvestri (3). The paraffin fraction contains primarily branched (iso) species. This, together with the high yield of aromatics (25 to 45 wt % of the hydrocarbons), contribute to the high octane rating of the MTG gasoline.

The typical mass and energy balances for MTG are shown in Figure 4. Virtually complete methanol conversion is attained in normal MTG operations. For 100 mass units of methanol input, stoichiometric yields of 44 units of hydrocarbons and 56 units of water are obtained. Gasoline yield (including alkylate) is 85 to 90 wt % of the hydrocarbons. The energy balance, however, is extremely favorable; 95% of the thermal energy in the methanol feed is preserved in the hydrocarbon products. The remaining 5% is liberated as heat of reaction. After allowing for process utilities energy requirement, we estimate that the overall process energy efficiency will be in the range of 90 to 93%.

Process Development

In the development of the MTG Process, three major factors must be considered:

- Reaction heat removal
- Catalyst activity control
- Durene (1,2,4,5-tetramethylbenzene) selectivity

MTG reactions are highly exothermic. The heat of reaction is estimated to be about 740 Btu per pound of methanol converted. Unless this heat is promptly removed, the catalyst temperature could rise by as much as 1000°F and suffer thermal damage.

As the MTG reactions proceed, the catalyst undergoes two types of aging which contribute to a gradual loss of catalytic activity. A temporarily loss results from small amounts of "coke" formed as reaction byproducts and deposited on the catalyst surface. This loss can be reversed by oxidative regeneration of the catalyst, i.e.,by burning off the coke in an atmosphere containing a controlled amount of oxygen. A permanent loss of activity, however, also occurs gradually. The presence of significant amounts of steam in the reactor is believed to be primarily responsible for the permanent aging. Methanol conversion and product selectivity are affected by catalyst aging.

One notable difference between MTG gasoline and conventional petroleum derived gasoline is the presence of more durene in MTG gasoline. Durene is the largest molecule produced in the MTG process in any significant quantity. It boils in the gasoline range (386°F) and has a high octane rating (estimated 100 R+O). However, because of its high freezing point (175°F), it may cause drivability problems by "icing" in an engine carburator.

Durene formation is quite sensitive to process temperature and pressure as shown in Figures 5 and 6.(4) Increased temperature and reduced pressure would lower the durene content.

Two modes of operation have been developed for MTG - Fixed-Bed and Fluidized-Bed. Each mode of operation has its advantages and is significantly different from the other. The major distinguishing features are summarized in Figure 7 and are described in more detail in the following sections. Our experience indicates the advantages for the fixed bed are:

- Easy to scale up
- Commercial catalyst

For the fluid bed, the potential advantages are:

- Higher gasoline yield including alkylate from steady state operation
- Easy temperature control and heat removal

- Minimal recycle required and hence lower operating cost.

To fully exploit the merits of the fluid-bed, substantially more engineering development efforts are required than the fixed-bed. Based on these considerations, our strategy in the past few years has been to pursue both routes: conducting further R&D on the fluid-bed while at the same time proceeding with commercializtion of the fixed-bed process.

Status of Fixed-Bed MTG

The Fixed-Bed MTG Process is ready for commercial application. A commercial size plant capable of producing 13,000 BPD of gasoline is under design for construction in New Zealand. This venture is a joint effort by the New Zealand Government and Mobil. When completed, the plant will supply one-third of New Zealand's gasoline needs from its indigenous natural gas resource and lessen its demand for imported petroleum. The plant will be a grass-root, totally integrated facility. Natural gas from the offshore Maui Field will be converted to methanol using commercially proven technology. The MTG section completes the natural gas to gasoline conversion. The projected startup date is 1984-1985.

A typical schematic diagram of the Fixed-Bed MTG Process is given in Figure 8. The MTG conversion is carried out in two steps (using two different catalysts. In the first step, the dehydration of methanol to dimethylether (DME) is accomplished catalytically. About 20% of the total reaction heat is released in this step. The effluent is then sent, along with recycle light gas, to the MTG reactors where the conversion to gasoline is completed. The recycle gas, typically at a rate of 9 moles per mole of methanol, is used for reactor temperature control and reaction heat removal. Figure 9 shows normalized temperature rise profiles for the fixed-bed MTG reactor. For normal operations, the temperature rise in the bed is about 100 F. It will vary with changes in the recycle ratio.

As shown in Figure 9, the fixed-bed MTG operates in a cyclic mode. At the beginning of a cycle, the catalyst bed is highly active and only about 1/3 of the bed is needed for conversion. As the catalyst ages with time on stream the reaction zone gradually shifts towards the end of the bed, exhibiting the classical "band aging" phenomenon. When methanol breakthrough occurs, the reactor is shutdown and the bed is regenerated. A cycle lasts typically well over 20 days. Product selectivity varies within a cycle, with gasoline yield increasing from about 75 wt % of hydrocarbons produced to about 90 wt %. The average is about 85 wt %.(4) Typical properties of the fixed-bed MTG gasoline are shown in Table 1. The product is comparable to unleaded regular gasoline.

Initial development of the fixed-bed MTG process was carried out in bench-scale pilot plant.(4) Process conditions and the long-term aging behavior of both the dehydration and MTG catalyst were established. Recently, the fixed-bed Process has been scaled-up to a 4 BPD pilot plant to provide support for the design of commercial plants. This pilot plant has performed very well and is currently in operation at our Paulsboro Laboratory. As shown in Table 2, product selectivities and quality are practically identical in both units. In fact, longer cycle lengths were experienced in the 4 BPD unit than the bench-scale unit. Since the 4 BPD unit operates at the exactly same conditions as for the commercial plants, we do not expect any detrimental effect in scaling-up to commercial size reactors.

Status of Fluid-Bed MTG

The Fluid-Bed MTG Process is currently in its final stages of engineering development. A program is underway to design, construct, and operate a large-scale 100 BPD pilot plant. This $35 million, 5-1/2 year program is an international venture jointly supported by the Bundesminister fur Forschung und Technologie (BMFT) of the Federal Republic of Germany (FRG) and the U.S. Department of Energy (DOE). The cost-sharing industrial participants in this program include Union Rheinische Braunkohlen Kraftstoff AG (URBK), Uhde GmbH, both of FRG, and Mobil. The pilot plant will be located on a site provided by URBK in Wesseling, FRG. URBK is acting as the Operating Agent for the program. Uhde is responsible for engineering design. Mobil contributes the process technology, MTG catalyst, and guidance in all aspects of the program.

The major technical tasks of this program are:

- Cold Flow Model (CFM) Studies
- Pilot Plant Design and Construction
- Pilot Plant Operation
- Product Evaluation
- Conceptual Design of a Commercial Fluid-Bed MTG Plant

Figure 10 shows the program schedule. The CFM studies and the pilot plant design are well underway. Construction will begin in mid-1981 and startup is targeted for mid-1982. A 21-month operating period is planned. The product testing task will be carried out in Germany as well as in the U.S. The program will culminate in a conceptual design of a commercial size fluid-bed MTG plant.

The major objectives of the cold flow model studies are to:

- Charactrize the fluidized-bed quality at the design operating conditions.
- Develop internal baffle designs to assure high conversion performance.
- Optimize catalyst circulation strategy and control methodology.

Towards these ends, a full-size non-reacting model of the 100 BPD pilot plant reactor system has been built and put into operation in our Paulsboro Laboratory. A schematic diagram of the reactor system is shown in figure 11. There are three major process vessels - reactor, regenerator, and external catalyst cooler. The reactor consists of a dense bed section on top of a dilute phase riser section. Reaction heat removal can be carried out in two modes:

1) By circulating catalyst through the external cooler, or

2) By means of internal heat exchange pipes immersed in the dense bed.

Both modes will be tested in the pilot plant. To maintain a constant catalyst activity in the reactor, a small fraction of "coked" catalyst will be circulated continuously through the regenerator, where part of the coke is burnt off, and returned to the reactor. The reactor/regenerator circulation rate is low because of the very low coke make in the MTG reactions.

The design of the 100 BPD reactor system is a product of the orderly and evolutionary development of the fluid-bed MTG process. In early bench-scale unit studies (4), preferred operating conditions, product yields and selectivities, catalyst aging characteristics, and other process parameters were evaluated and determined. Subsequently the fluid-bed process was scaled-up to a 4 BPD pilot plant which performed highly successfully.(5) A simplified flow diagram of the 4 BPD pilot plant is shown in Figure 12. The reactor dimensions were 4" ID x 25' high. It was topped by a disengaging section where entrained catalyst was separated from the products and returned to the reactor base through an external recirculation line. By controlling the heat loss from this line, it also served as an external cooler. The thermal stability of this system was found to be excellent and, as shown in Figure 13, reactor was highly isothermal despite its high L/D ratio of 75. Detailed operating conditions and results have been reported previously.(6) The 4 BPD fluid-bed study also demonstrated successfully the concept of steady state operation at maximum gasoline (including alkylate) yield and repeated regenerability of the fluid-bed MTG catalyst.

Typical product yields and gasoline properties from the fluid-bed MTG process are shown in Tables 3 and 4, respectively. The raw hydrocarbon products contain about 60 wt % C_5+ hydrocarbons. However, by taking advantage of the stoichiometric amounts of i-C_4 butenes, and propene which can be easily converted to gasoline by conventional alkylation, total 9 RVP gasoline yield is increased to as high as 88 wt % of hydrocarbons. Octane quality of the fluid-bed MTG gasoline is very good, comparable to unleaded premium gasoline.

Concluding Remarks

The Mobil Methanol-to-Gasoline Process is the first new route in 40 years for synthesizing gasoline from coal, natural gas, and other alternate energy resources. The process is relatively simple, highly energy efficient, and produces a readily marketable, high-octane gasoline with good yields. In the last decade, the MTG process has grown from a laboratory discovery to a commercial process. Further advancement is expected from the current R&D efforts.

Acknowledgement

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(2) Kokotailo, G. T., Lawton, S. L., Olson, D. H., Meier, W. M., "Structure of Synthetic Zeolite ZSM-5," Nature, 272 (March 30, 1978).

(3) Chang, C. D., and Silvestri, A. J., J. Catalysis, 47, 249 (1977).

(4) Voltz, S. E., and Wise, J. J., "Development Studies on Conversion of Methanol and Related Oxygenates to Gasoline," Final Report, ERDA Contract No. E(49-18)-1773(1976).

(5) Kam, A. Y., and Lee, W., "Fluid-Bed Process Studies on Selective Conversion of Methanol to High Octane Gasoline," Final Report, DOE Contract No. EX-76-C-01-2490 (1978).

(6) Kam, A. Y., Yurchak, S., and Lee, W., "Fluid-Bed Process Scale-up and Development Studies on Selective Conversion of Methanol to High Octane Gasoline," paper presented at the 71st Annual AIChE Meeting, Miami, Florida (Nov. 1978).
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FIGURE 1

MOBIL METHANOL-TO-GASOLINE ROUTE

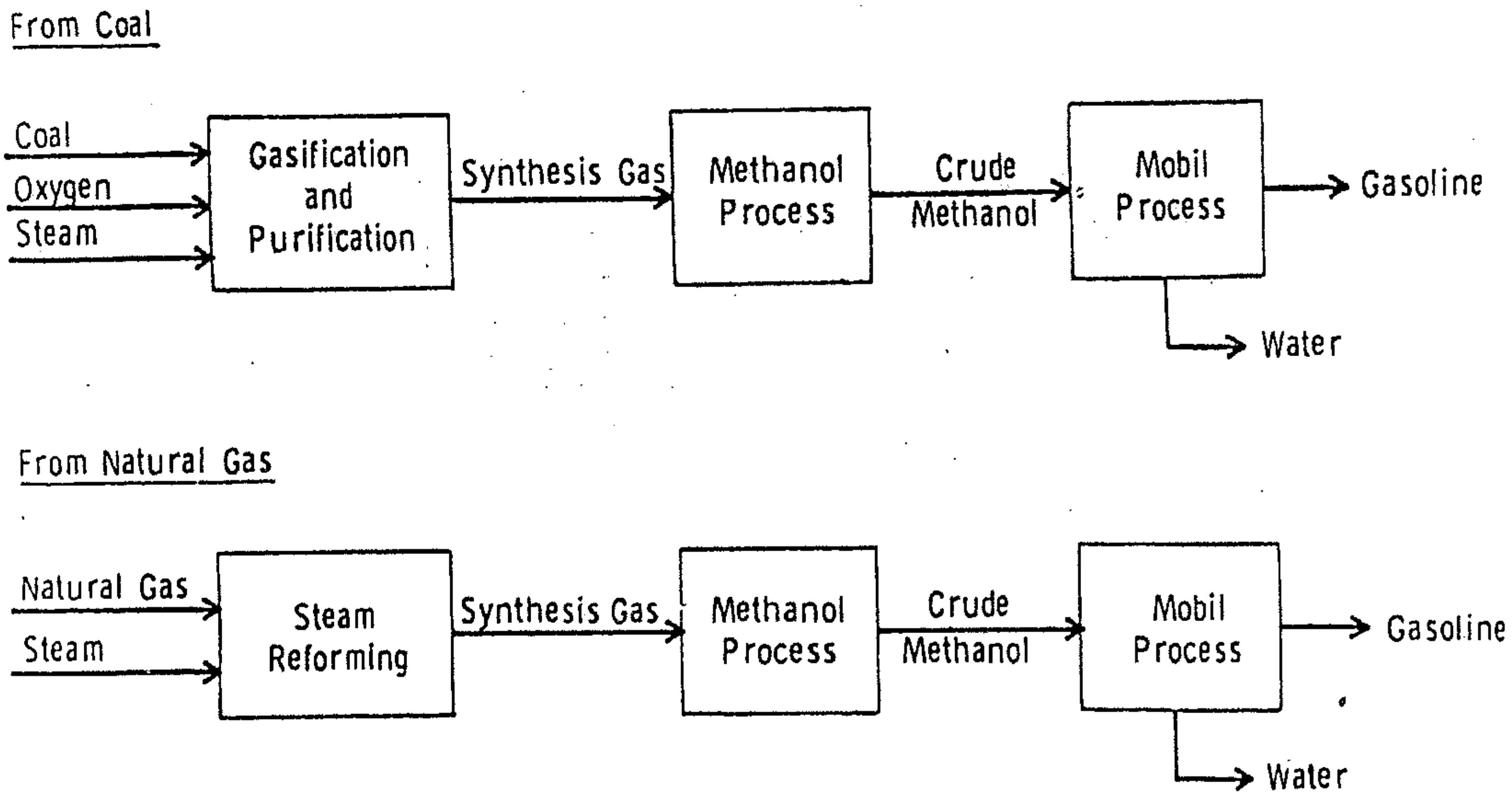

FIGURE 2

ZSM-5 STRUCTURE

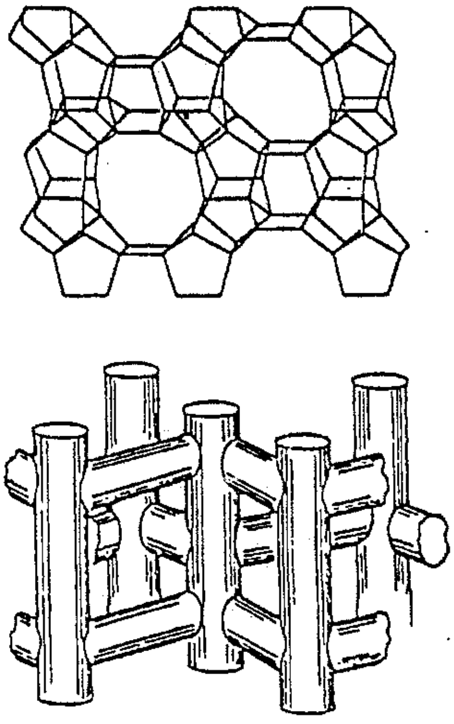

FIGURE 3

REACTION PATH

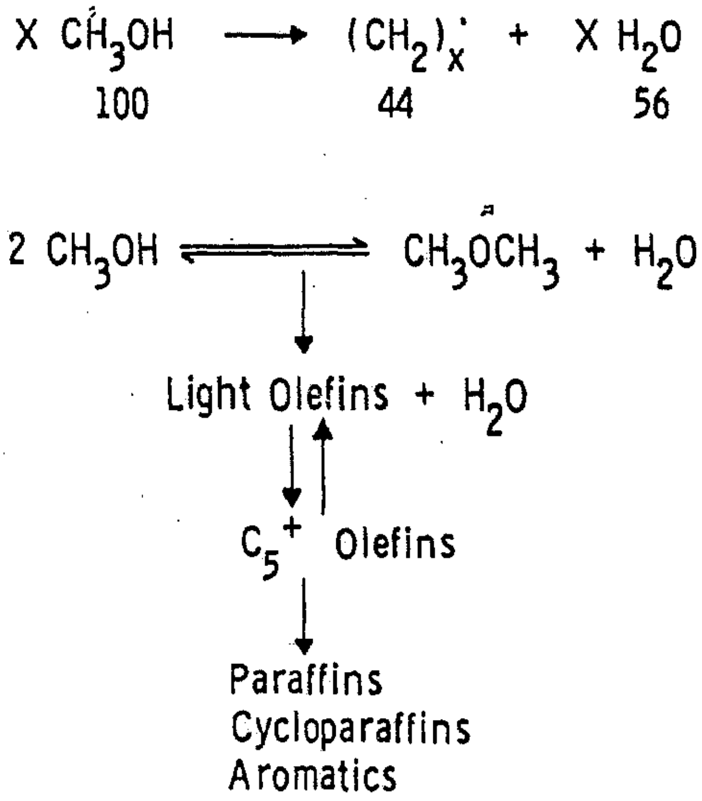

FIGURE 4

CHEMISTRY OF METHANOL CONVERSION TO GASOLINE

Feed **Product**

$$nCH_3OH \longrightarrow (CH_2)_n + nH_2O$$

$$\text{Methanol} \longrightarrow \begin{matrix}\text{Gasoline} \\ \text{Fuel Gas}\end{matrix} + \text{Water}$$

Material Balance: 100 Tons ⟶ 44 Tons + 56 Tons

Energy Balance: 100 Btu ⟶ 95 Btu + 0 Btu

FIGURE 5

FLUID BED TEMPERATURE EFFECT ON DURENE PRODUCTION

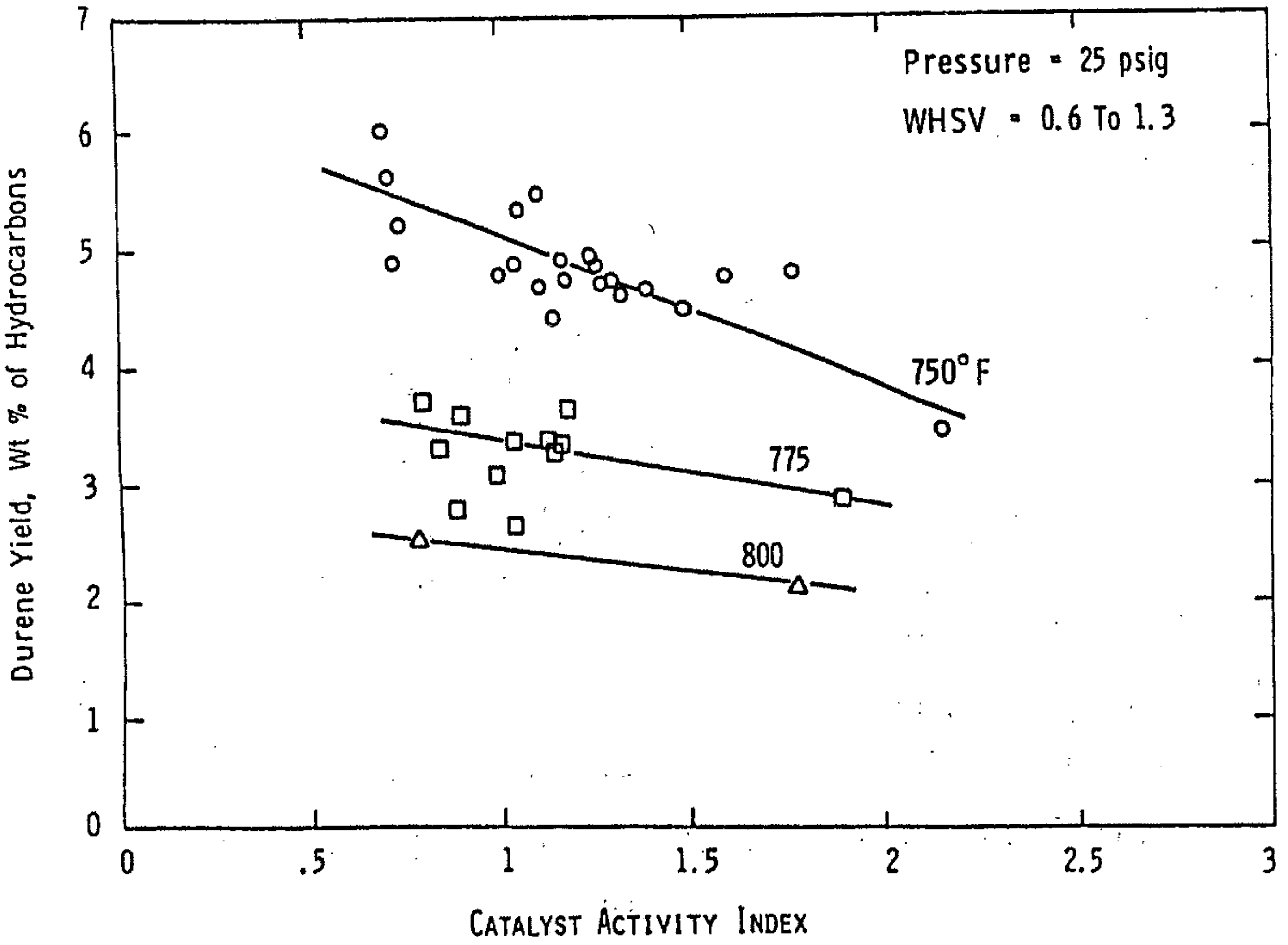

FIGURE 6

FLUID BED PRESSURE EFFECT ON DURENE PRODUCTION

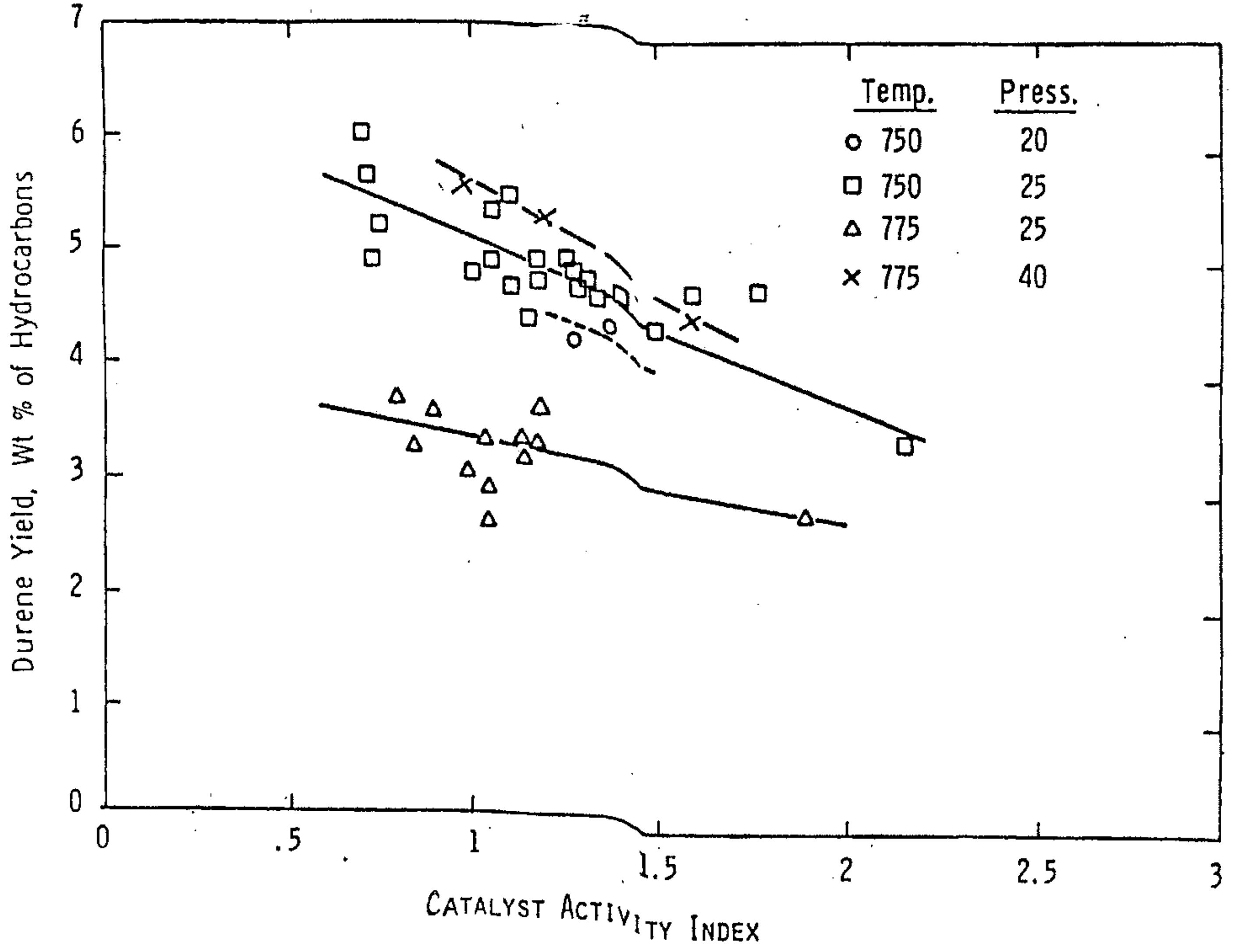

FIGURE 7

TWO MODES OF OPERATION FOR MTG PROCESS

	Fixed Bed	Fluid Bed
Methanol Conversion	2 Steps	1 Step
Heat Removal	Light Gas Recycle	Heat Exchanger Pipes
Operation	Cyclic	Steady State
Regeneration	Intermittent	Continuous

FIGURE 8

Fixed-Bed MTG Schematic Diagram

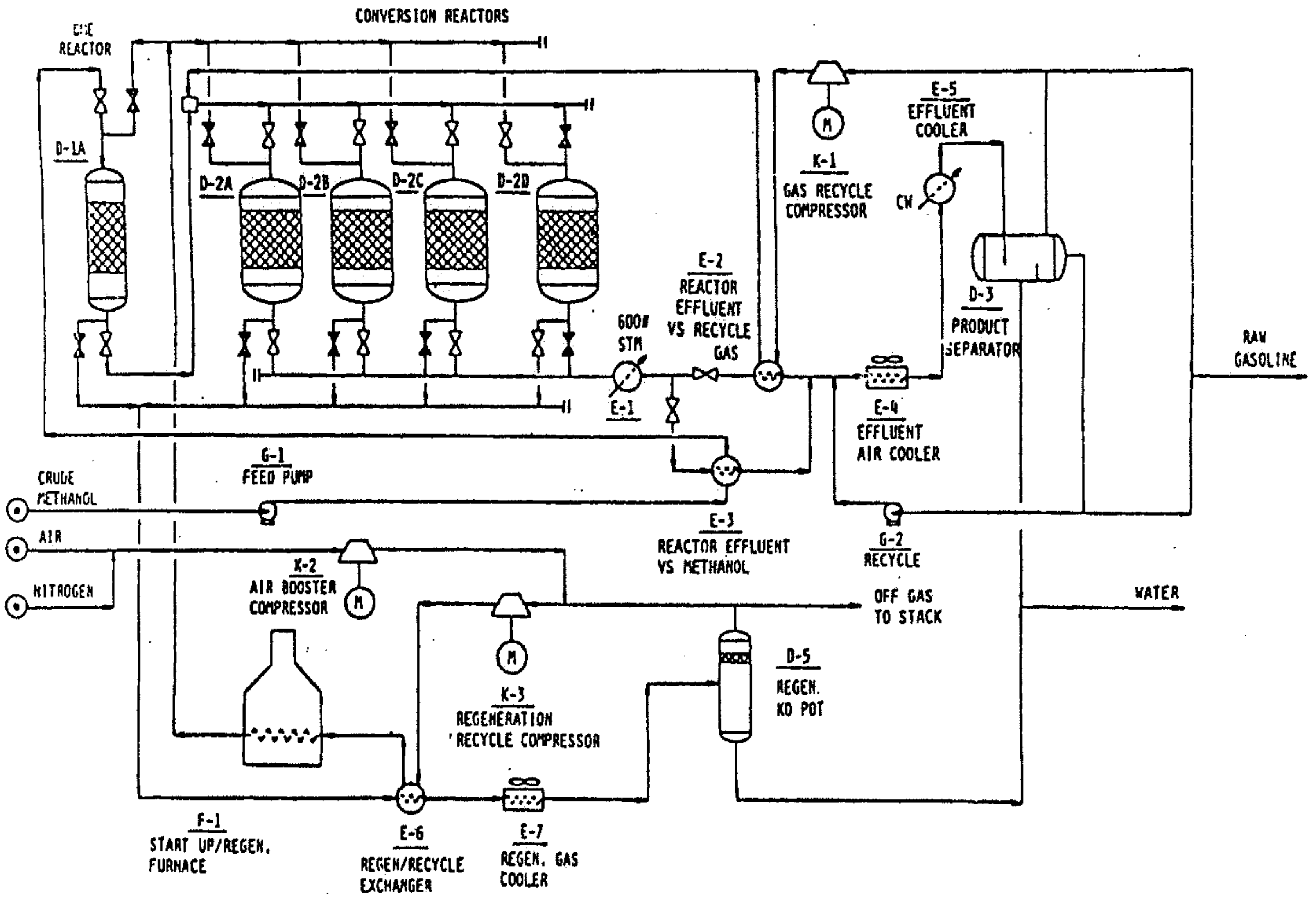

FIGURE 9

MOVEMENT OF NORMALIZED TEMPERATURE PROFILE THRU BED

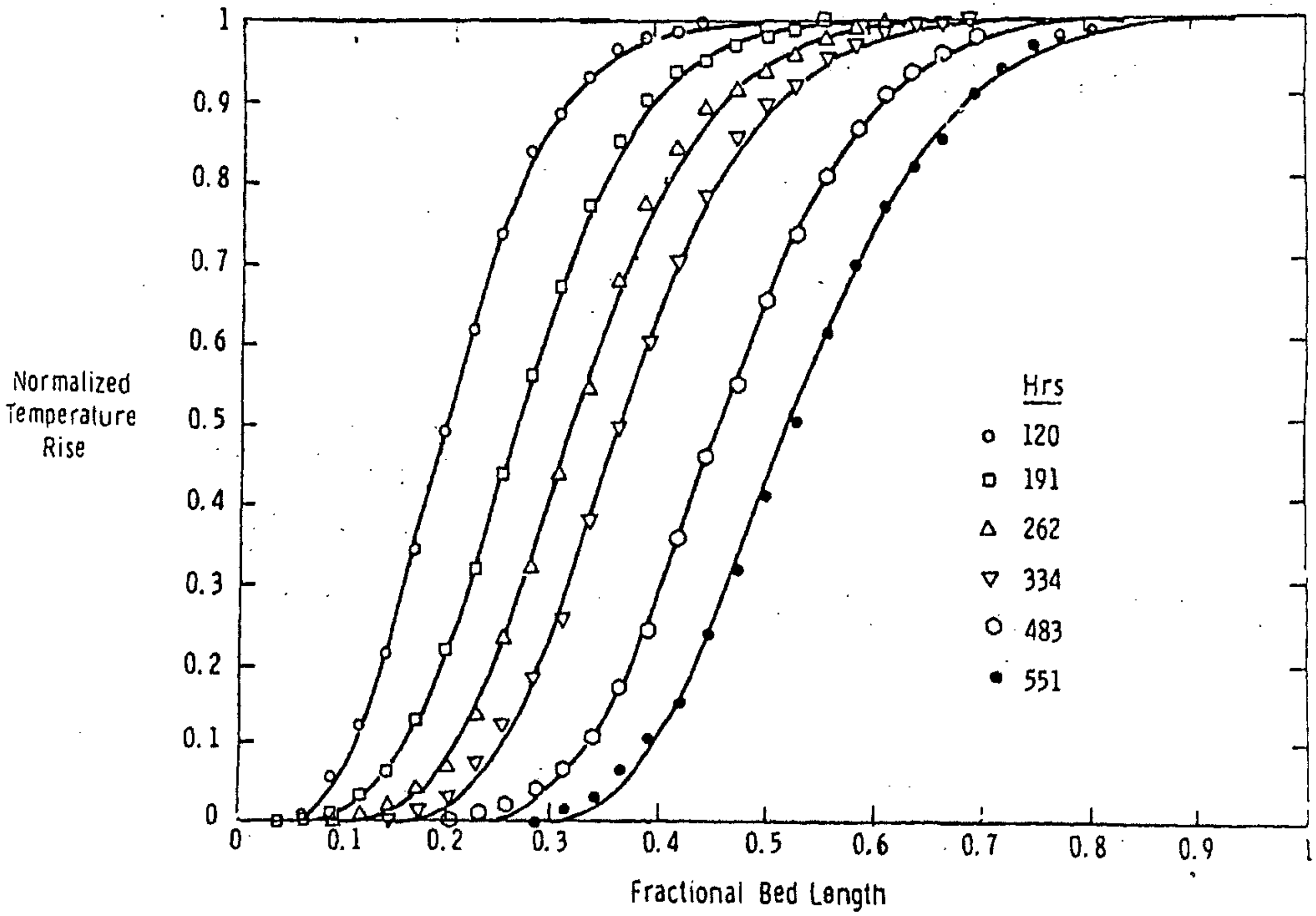

FIGURE 10

100 BPD FLUID-BED MTG PROGRAM SCHEDULE

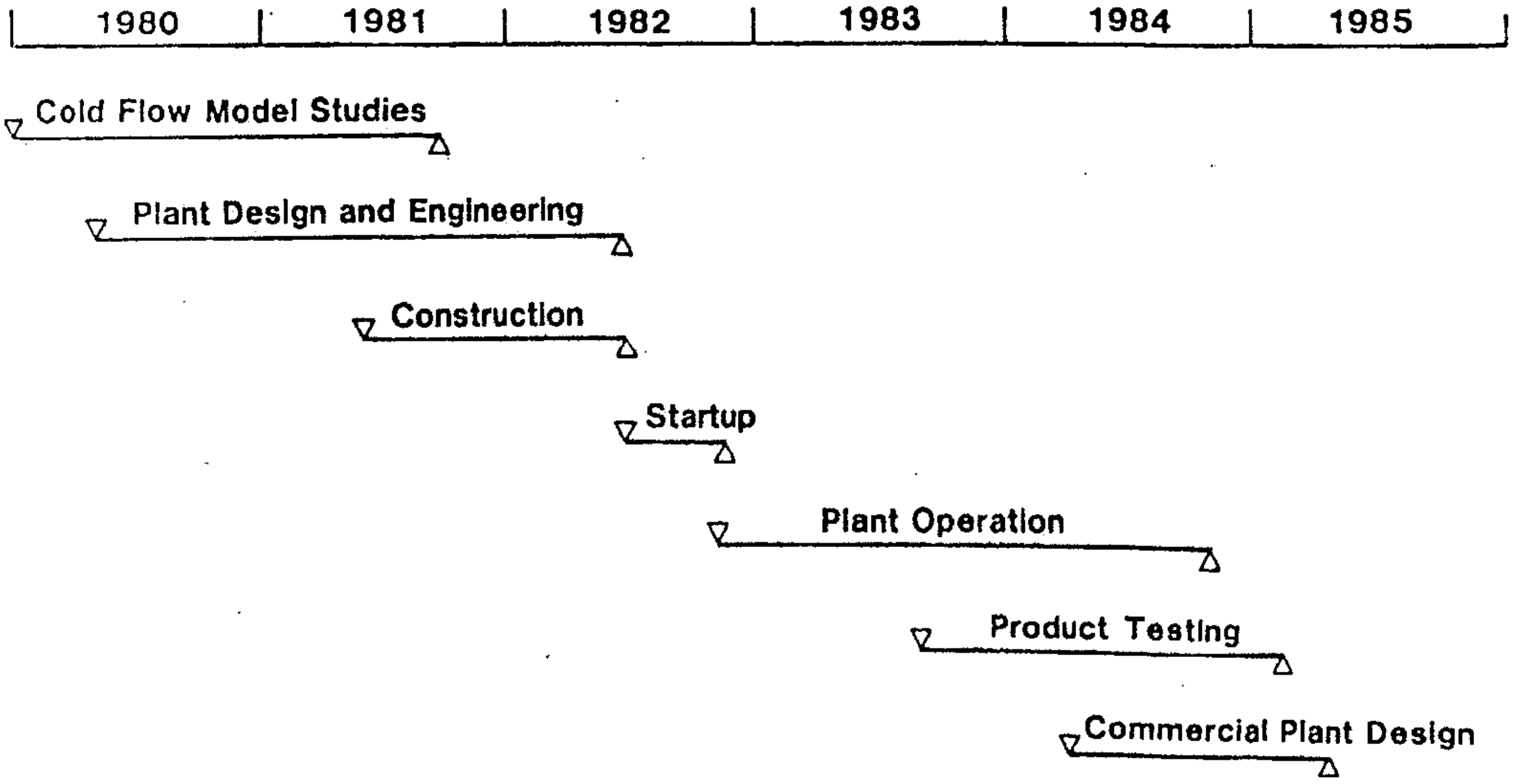

FIGURE 11

FLUID-BED MIG COLD FLOW MODEL

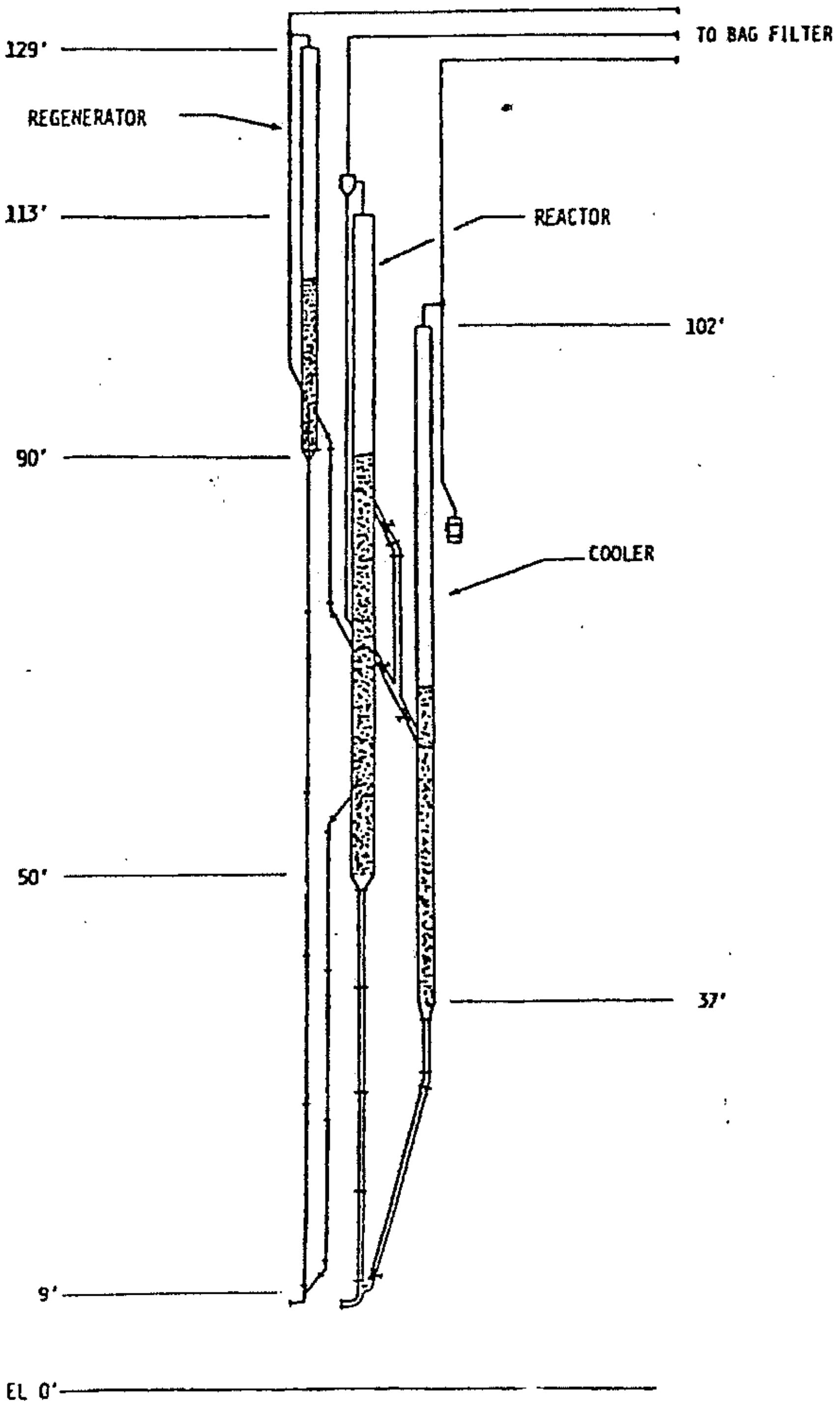

FIGURE 12

4 B/D FLUID BED PILOT PLANT

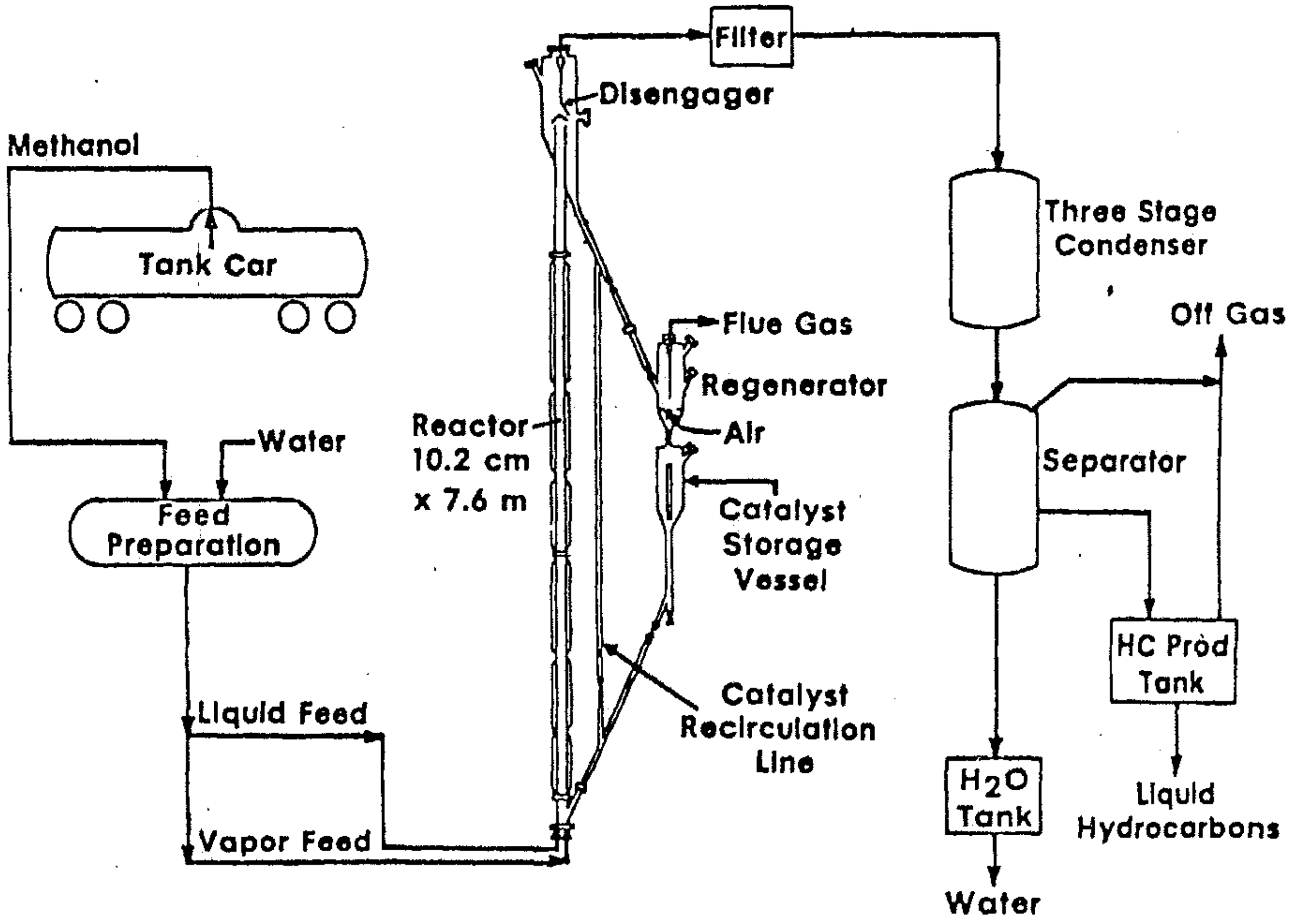

FIGURE 13

TYPICAL 4 B/D FLUID BED REACTOR TEMPERATURE PROFILE

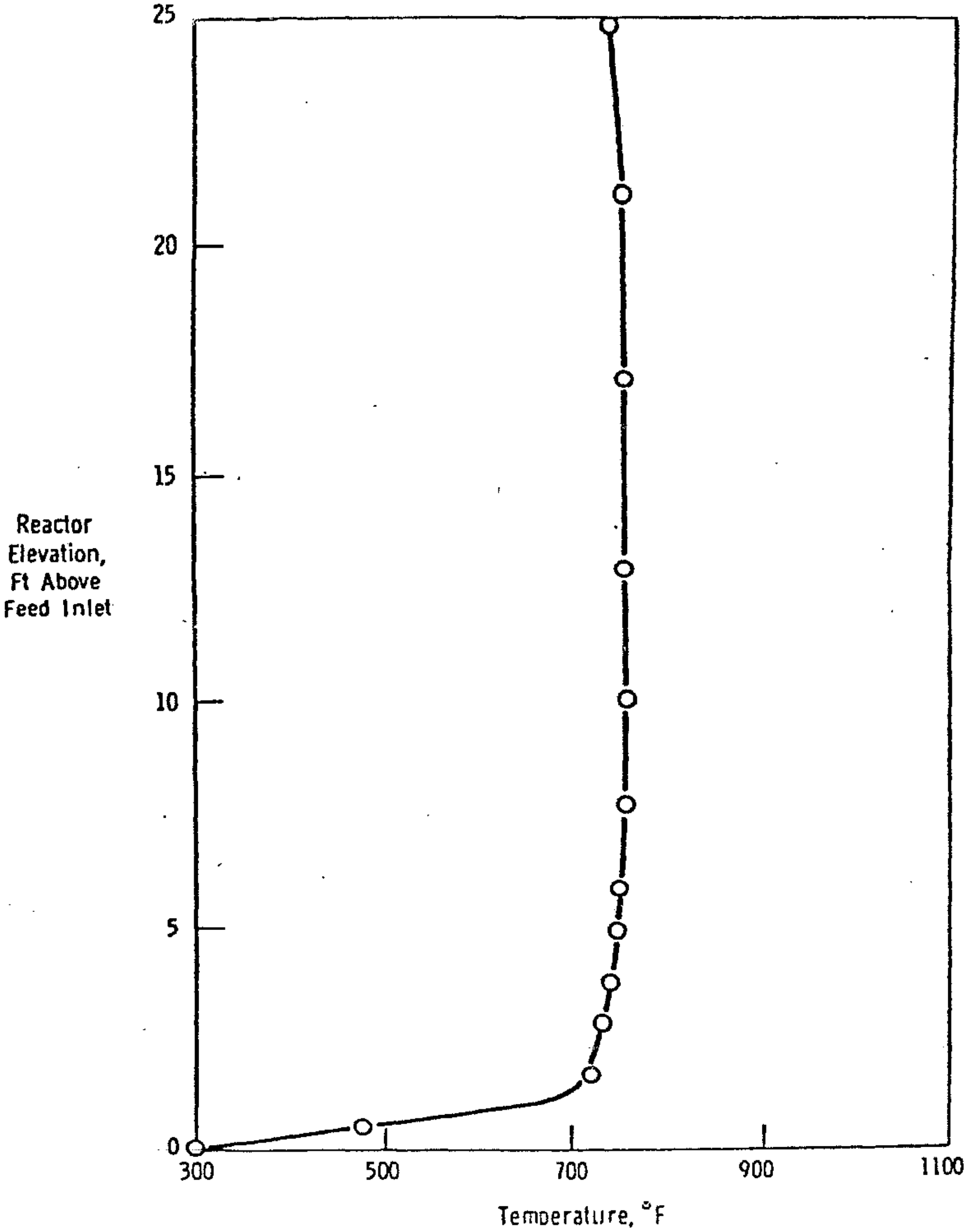

TABLE 1

TYPICAL PROPERTIES OF FINISHED FIXED-BED MTG GASOLINE

Components, % Wt	
Butanes	3.0
Alkylate	3.0
C_5^+ Gasoline	94.0
	100.0

Composition, % Vol	
Paraffins	53
Olefins	12
Naphthenes	7
Aromatics	28
	100

Physical Properties	
Research Octane	
Clear	93
Leaded, 3 cc TEL/USG	101
Reid Vapor Pressure, psig	9.0
Specific Gravity	0.728
Sulfur, % Wt	Nil
Nitrogen, % Wt	Nil
Corrosion, Copper Strip	1A
ASTM Distillation, °F	
10%	114
30%	145
50%	198
90%	330

Motor Octane	
Clear	83
Leaded, 3 cc TEL/USG	90

TABLE 2

FIXED-BED MTG SCALE-UP: YIELD COMPARISON AT SAME TEMPERATURE POSITION

Product, Wt % of Chg	4 B/D Unit	Bench Unit
Hydrocarbons	36.48	35.42
Water	63.49	64.51
CO, CO_2	0.03	0.07
Methanol	0.00	0.00
Dimethylether	0.00	0.00
	100.00	100.00
Hydrocarbon Product, Wt %		
Methane + Ethane	1.6	1.5
Ethylene	0.04	0.02
Propane	5.6	5.6
Propylene	0.2	0.2
n-Butane	2.9	2.9
i-Butane	8.7	8.8
Butenes	0.9	1.0
C_5^+ Gasoline	80.1	80.0
	100.0	100.0
Aromatics	29.6	33.4
9 RVP Gasoline		
Yield, Wt % of HC	85.2	85.3
R + O	93.7	94.3

TABLE 3

TYPICAL YIELDS FROM FLUID-BED MTG

Average Bed Temperature, °F	775°F
Pressure, psig	25
Space Velocity (WHSV)	1.0
Yields, Wt % of Methanol Charge	
Methanol + Ether	0.2
Hydrocarbons	43.5
Water	56.0
CO, CO_2	0.1
Coke, Other	0.2
	100.0
Hydrocarbon Product, Wt %	
Light Gas	5.6
Propane	5.9
Propylene	5.0
i-Butane	14.5
n-Butane	1.7
Butenes	7.3
C_5^+ Gasoline	60.0
	100.0
Gasoline (Including Alkylate) (96 R+0, 9 RVP)	88.0
LP Gas	6.4
Fuel Gas	5.6
	100.0

TABLE 4

TYPICAL PROPERTIES OF FINISHED FLUID-BED MTG GASOLINE

Components		
Butanes	2	
Alkylate	28	
C_5^+ Gasoline	70	
	100	
Composition, Wt %		
Saturates	67	
Olefins	6	
Aromatics	27	
	100	
Octane	**Research**	**Motor**
Clear	96.8	87.4
Leaded (3 cc TEL/US Gal)	102.8	95.1
Reid Vapor Pressure, kPa	76	
Specific Gravity	0.730	
Sulfur and Nitrogen	Nil	
Corrosion, Copper Strip	1A	
ASTM Distillation, °C		
10%	47	
30%	70	
50%	103	
90%	169	