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IMPROVED ECONOMICS IN CATALYTIC REFORMING[1]

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OUTLINE

INTRODUCTION	Industry Trends
OPERATING TECHNIQUES	Environmental Control, Catalyst Reactivation
CATALYSTS	New poly-metallics, Platinum-Rhenium
UNIT DESIGNS	Magnaforming, processing concepts Magnaforming with E-601 Catalyst Magnaforming optimization with E-601 Catalyst
TECHNIQUES	Early vs current techniques in reforming
SUMMARY	Conclusions

(1) The use of platinum catalysts to reform gasoline boiling range naphthas to produce high octane blending stock, aromatics and hydrogen quickly became a major refining tool following its introduction about 1950. A number of competitive process designs are presently operated on a variety of distillate fractions, generally boiling within the limits 65 to 200 °C, ASTM, derived from crude as well as from other refinery processes (thermal cracking, catalytic cracking and hydrocracking). The severity of operation, usually expressed as research octane clear of the C_5 plus reformate, varies quite widely from unit to unit depending upon individual unit objectives. The directional effects of changes in the principal process variables upon performance or economic factors are shown in Table I.

(2) The trend in use of catalytic reforming since its introduction has been a gradual increase in both severity and in the fraction of total refinery product processed for reasons of octane competition, increase in auto engine efficiency, and recently as a factor in arriving at lower auto exhaust emissions. This trend in process use would be expected to decrease yield selectivity and otherwise increase costs for a given catalyst and procedure of use. However, continued attention has been given to: (1) improving procedures of catalyst use, and (2) developing better catalysts. The positive results of these efforts have permitted improved unit design and operations to improve reforming economics, increase yield selectivity and reduce or minimize costs. In this paper we will discuss

items of procedure, new catalyst types and improved process design which our firm and associates have contributed.

(3) The great volumes of naphtha processed daily over platinum catalyst in World refineries is noted for the past years 1960 and 1970, and estimated for the years 1975 and 1980 in Table II. USSR and China reforming capacities are not included. The estimated severity ranges and catalyst loadings are approximations; however, the trends with time are believed to be realistic. For the overall severity range of 85 to 105 research octane clear reformates, the aromatics in reformates are correspondingly 45 to 88 volume percent. Of the estimates for future years, that for 1975 is most probable; that for 1980 could be considerably different, depending upon changes in automotive engines, clean air laws, etc. The increase in reforming severity over the years has been offset by an estimated decrease in catalyst loadings per unit of feed processed. The continued decrease in catalyst loading per unit of feed which we forecast, further reflects the improvements we are to discuss.

(4) The greatest volume of early industry capacity was run in semi-regenerative units (that is, units in which an operating cycle ran for several months, then were off line for 3 to 5 days for regeneration of the catalyst in situ). Other, more costly, cyclic units intended to process difficult feedstocks or to run at very high severity made up the balance of

the industry capacity. (Cyclic units have a spare or swing reactor which can be substituted on line for a reactor that requires regeneration; hence, the reactors on line can successively be taken out of service for regeneration and preparation to swing back on line).

(5) Operating techniques have greatly improved over the years, showing the greatest advances within the entire industry through the 1960's. Some of the most significant advances have been those relating to improved regeneration and reactivation procedures. Good catalyst performance is dependent upon having: (a) good metal activity, and (b) base or carrier activity which best accomplishes the principal desired reactions of (i) naphthane dehydrogenation to aromatics and hydrogen; (ii) paraffin dehydrocyclization to aromatics and hydrogen; and (iii) paraffin isomerization and hydrocracking. The deletarious reactions to be minimized are: (a) ring opening or cracking of naphthanes and (b) hydrocracking of terminal carbon atoms forming methane and ethane. The formation of propane and butane can be regulated to a certain extent by controlling the acidic function of the catalyst. In the U.S. their production is generally minimized due to the higher value received for reformate. The proper balance of metal and base activities can be maintained during the process cycle by use of proper operating procedures; and following catalyst regeneration these activities are re-established. An operating cycle in catalytic reforming is considered ended when sufficient coke accumulates on the catalyst to cause an excessive yield decline, or when the maximum unit operating temperature limit is reached. The catalyst is regenerated by treatment in place to remove the

coke and then to re-establish metal and acidic activities to their optimum levels.

(6) The activity of the catalyst support is largely dependent upon its degree of hydration and upon its acidic property which is mainly dependent upon chloride content. It follows that maintenance of good activity depends upon water and chloride partial pressures over the catalyst. A definite relationship has been determined for these two agents specific to the individual catalyst and the conditions of use. The benefit of environment control as related to moisture level in a <u>specific unit</u> is shown in Figure 1. The moisture content of circulating gas is shown for a period at the end of a cycle, next through the regeneration-reactivation period, and last through the start of cycle period when recycle gas moisture declines to a controlled level in equilibrium with moisture coming to the system. This controlled level is not difficult or costly to attain with a clean feed naphtha; it assures good reformate yield and good cycle life as shown by the two cross plots on the right side of Figure 1. Yield selectivities can very easily be reduced by several percent and cycle life to a small fraction of total potential if proper attention is not given to environment control. Quite obviously this environment factor must be near optimum for each catalyst used: this is also a very important factor in comparative testing of new catalysts.

(7) The RD-150 and RD-150C platinum catalyst (0.6 and 0.35 wt.% Pt respectively) produced by Engelhard, Newark, New Jersey, U.S.A. and Kali-Chemie Engelhard, Hannover, W. Germany, has been used by about one-quarter of the Western World reforming capacity. These catalysts have been shown to provide higher yields and to 2 to 3 times greater life with the proper procedures as compared to early, less effective operations. The new polymetallic catalysts or, specifically, the platinum-rhenium catalysts which we will discuss next require similar but specific procedures for their best performance.

(8) Catalysts have been greatly advanced in performance capabilities over the last few years by the introduction of supplemental metals along with platinum. These bi- or polymetallic catalysts are very responsive to careful environment and procedure control which closely parallels the best handling of the older platinum catalysts. Collectively, the more distinguished and best commercially proven of these new catalysts offer: (i) a greater range of activity; (ii) improved yield selectivity over total life; (iii) longer total life at higher operating severity, and (iv) reduced coke formation.

(9) Use of rhenium with platinum in commercial reforming catalyst was first announced by Chevron Research Company in early 1969. Following contractual arrangements with Chevron, Engelhard first introduced

a platinum-rhenium catalyst, E-501, in March, 1969. A following and improved Engelhard platinum-rhenium catalyst, E-601, was put into commercial use in mid 1971. Other platinum plus supplemental metal catalysts have been announced and introduced by others into commercial trials in the past two years.

(10) New catalysts are typically first evaluated in accelerated or high severity tests to determine their relative yield selectivities and cycle length capabilities. These bench scale, small unit tests provide selectivity and relative aging results which can be directly related to commercial performance.

(11) The comparative high severity test results for our platinum catalyst, RD-150C; our platinum-rhenium catalysts, E-501 and E-601, are shown in Figure 2. These tests are at constant space velocity and 100 research octane clear reformate on a Mid-Continent (USA) naphtha. The runs are made at low pressure and with low hydrogen to feed recycle ratio. Variation in reactor bed temperatures and in yields of C_5 plus reformate and hydrogen are shown against time. Yield selectivities with platinum-rhenium tend to be equal or better than with platinum at start of cycle, and hold essentially constant as the cycle progresses. As coke on terminal section catalyst reaches a value which is limiting, at 12 to 20 wt.% coke, the reformate yields over platinum-rhenium catalyst will

have declined by less than 2.0 volume percent. The reformate yields over platinum catalyst would have declined 2 to 4 volume percent or more at 10 to 15 wt.% coke on catalysts. The activities of platinum-rhenium catalysts are higher as shown by the 4 to 8 °C lower temperature requirement to make a given octane at start of cycle. Lastly, the greatly extended time of operation for the two platinum-rhenium catalysts as compared to RD-150 shows the promise of longer cycles even at lower pressures (for increased yields) and lower gas recycle ratios (for lower first costs and lower operating costs). Two in situ regenerations were made on this E-601 catalyst in this test run and the two following cycles gave equivalent or better performance than the first cycle which is shown in Figure 2.

(12) Commercial experience with the catalysts compared in Figure 2 is, of course, proportional to the time since they were introduced. RD-150C and RD-150 catalysts (of 0.35 and 0.6 wt.% platinum respectively) came into use in 1954-1955. With the use of the optimum procedures in reforming and in in situ regeneration-reactivation these catalysts run to very long ultimate lives, 5 to 10 years being reached frequently. Feed naphtha hydrotreating and stripping to prepare a clean reformer feed has been, and is, widely recognized as a requirement for longest reforming catalyst life. Earlier operations on these catalysts were characterized by successively shorter cycles following

the succession of in situ regenerations. As the significance of procedural steps were better understood and applied, cycles of catalyst use were not only lengthened but have come to be closely reproduced in successive cycles.

(13) The E-501 catalyst first used in commercial units in 1969 is operating in twenty-seven units amounting to about 32,000 MT/Day in capacity. These loadings have been made using from 100 to 65 wt.% as much catalyst as had previously been used. Depending upon forward operating circumstances with the individual units, these changes in operation, in different combination, have been the experience: (i) increase feed rate; (ii) increase severity and reduce octane additive (lead) use; (iii) reduce pressure to gain in yields; (iv) reduce recycle concurrent with reduced pressure and, in addition, to reduce recycle utilities. Thus, the more stable catalyst permits better reforming economics and/or quality improvement. In new units designed for use of a platinum catalyst, as little as 40% of design loading as E-501 catalyst is operating well.

(14) The longer or more severely used charges of E-501 catalyst are now in their sixth cycles. Instances of improper procedures or abnormalities resulting from upsets have caused a few short cycles. Proper regeneration-reactivation brings the following cycles back to their projected length or better. Overall, these cycles of operation on E-501 catalyst are running 2 1/2 to 3 1/2 times as long as estimated cycles for platinum catalyst.

(15) The new and more stable E-601 catalyst has been shown in laboratory testing to give significantly longer cycles than E-501 catalyst. This catalyst is presently in use in three commercial units and is scheduled as the next replacement catalyst in several other units. The first use cycles started six and seven months ago are still in progress.

(16) Unit designs require restudy from time to time to adapt to improvements in procedures and catalysts. Engelhard and Atlantic-Richfield Company collaborated on the Magnaformer design concept to get best reforming economics at higher severities with the RD-150C platinum catalyst. This concept is based on optimizing catalyst distributions, reactor-inlet temperature, and gas recycle ratio for a given feedstock, and operating pressure. The primary object of this optimization is improved yield selectivity and catalyst utilization. Recycle gas flow is split for maximum increase in cycle life relative to compression costs.

(17) As shown in the flow sheet, Figure 3, a typical Magnaforming design consists of a four-reactor system using a highly skewed catalyst distribution and gas recycle introduced ahead of the first and third reactors. The reactor-inlet temperature pattern is ascending with inlet temperatures of the first two reactors held constant throughout the process cycle.

(18) Due to the initial rapid rate of naphthene dehydrogenation and associated temperature drop, the aromatic/naphthene equilibrium is closely approached at high space velocities. As temperature decreases and equilibrium is approached, additional catalyst is ineffective and may actually contribute to overall loss of selectivity. It is, therefore, most advantageous to utilize catalyst in the terminal reactors where it can be used at higher temperatures. Use of low reactor-inlet temperatures minimizes paraffin and naphthene cracking and contributes to the improved selectivity. Low reactor-inlet temperature also makes it possible to operate these reactors at very low hydrogen-recycle ratios without significant catalyst deactivation. The use of low temperature in the lead reactors results in a slightly lower conversion. However, the use of an additional reactor, relative to conventional design, and the catalyst which has been shifted to the terminal reactors when operated at a slightly higher temperature provides the necessary compensation.

(19) Pilot-plant and commercial-unit operation show that reformate yields up to 3% over those from conventional designs are possible with Magnaformer designs. The greatest yield advantages are obtained on paraffinic stocks, with the least improvement shown by heavy hydrocrackates.

(20) The gas-recycle split is provided by use of two compressors, or more typically, a single side-takeoff centrifugal machine. Since the quantity of gas which must accompany the fresh feed through exchange and preheat is significantly reduced, the savings in compression cost can be applied to supply

additional gas recycle to the terminal reactors. As a result, higher recycle in the terminal reactors and thus better catalyst life is obtained at no increase in utility cost over a lower overall recycle ratio in a conventional single-recycle-loop design. Since reactor-inlet temperatures to the lead reactors are not raised over the cycle, the additional heat, obtained from exchange as terminal-reactor temperatures are raised, can be diverted by use of valves V_1 and V_2 to supplement the No. 2 interheat requirement.

(21) Seventeen Magnaformer design units are operating or in stages of construction or design. They total about 31,000 MT/Day reforming capacity and include four expansion revamp units.

(22) The Magnaforming operation with E-601 catalyst was evaluated in a multiple reactor adiabatic pilot unit with the results shown in Figure 4. Initial operation was at equal reactor inlet temperatures and a single recycle gas flow. After a period of conventional operation, the inlet temperatures and recycle flows were adjusted to Magnaforming conditions. The yield selectivities showed an immediate increase. A cycle of conventional operation on RD-150 catalyst is shown for reference. This illustrates that improved yield selectivity derived from the Magnaforming operation and from improved catalysts are compatible, the two being complementary.

(23) Should it be necessary to maintain continuous on-stream operation or if the feedstock or severity be such that semi-regenerative operation is not practical because of short cycle length or poor stream efficiency, a swing-reactor design may be employed. Since the lead reactors operate at very low average catalyst temperature over the entire process cycle, their deactivation rate is extremely low. Cycle lives much greater than one year have been established. Thus, in a swing-reactor design, the lead reactors would be regenerated after about 24 months operation when the unit is brought down for maintenance.

(24) An external regeneration loop and additional reactor can be provided to allow continuous operation while a portion of the catalyst in the terminal reactors is being regenerated. Should the swing-reactor operation not be required for initial operation of the unit, provisions can be made to add the regeneration loop and additional reactor when required.

(25) An optimization study of Magnaforming design for most economic use of E-601 catalyst has been carried through a multiplicity of cases based on a specific feed reformed to 103 clear research octane number. An exemplary case using anticipated 1975 U.S. product values is shown in Table III. The recycle loop pressure drop shown is a safe minimum practical for low pressure circuits as demonstrated by experience to date.

(26) In developing the conditions for optimum economics in this case, the incremental total dollar values varied with the interrelated process conditions as shown in Figure 5. Total dollar value increased but slowly with change in cycle length, WHSV, and pressure at a constant gas recycle ratio.

(27) For a constant cycle length, say five months, the maximum dollar values can be determined with change in recycle gas ratio, in space velocity, and in system pressure. A plot of incremental total dollar values vs system pressure for the different optimum cases is shown in Figure 6.

(28) Definitive design and pricing of a Magnaformer as described previously in Table III shows capital requirements to be lower by about 20% for a 2,600 MT/Day unit than for other current unit designs requiring continuous catalyst regeneration. An intermittent terminal reactor regeneration system to permit a Magnaformer to supply hydrogen continuously for up to 24 month periods is estimated to increase the capital requirement by about 15% for this size unit.

(29) The present state of catalytic reforming (improved catalysts, procedures and unit designs) prompt a comparison of reforming results using earlier technology as compared to that going into use in new units today. Such a comparison, covering the change in industry severity approximated in Table II, 1960 to 1975, is shown in Tables III-A

and III-B. The pre-1960 design operation on the feedstock shown produces 92.0 research octane clear with an 82.5 volume % yield of C_5 plus reformate. The current design is shown to produce the same reformate yield, 82.5 volume %, but these supplementary advantages are obtained:

i) reformate research clear octane is up by 7 numbers, 99.0 compared to 92.0

ii) aromatics yields are greater by 1.3 times

iii) hydrogen yields are greater by close to 2.0 times.

(30) In summary, catalytic reforming has progressed with these significant attainments:

i) Semi-regenerative, lower cost unit designs can produce the probable maximum quality products required with acceptable operating cycle lengths of 6 to 12 months;

ii) Operating pressures for these units will be increasingly in the 7.0 to 15.0 Kg/cm^2 gage range with correspondingly high yields of reformate and hydrogen;

iii) While catalyst costs per unit weight will trend upward, due to increasing complexity in preparation and reduced volume of sales, costs to refiners per unit of product will be reduced due to use of less catalyst and its greater useful life.

APPENDIX

TABLE I

PRINCIPLE PROCESS VARIABLE EFFECTS

CHANGE OF PROCESS VARIABLE	YIELDS	CYCLE LENGTH	ECONOMICS CAPITAL	ECONOMICS OPERATING COSTS
Decrease pressure	Increase	Decrease	Increase below ~17.5 Kg/cm2	Increase
Decrease recycle gas to feed mol ratio	(1)	Decrease	Decrease	Decrease
Increase feed boiling range	(2)	Decrease	(1)	(1)
Increase severity of operation	Decrease	Decrease	Increase	Increase

(1) Little or no effect

(2) Dependent on feedstock properties

TABLE II

INDUSTRY TRENDS

WORLD CAPACITY, SEVERITY, CATALYST LOADING ESTIMATES

YEAR	METRIC TONS/DAY	SEVERITY RANGE RON CLEAR OF REFORMATES	CATALYST LOADINGS KG/MT DAILY CAPACITY
1950	INITIAL	-	-
1960	313,000	85 - 100	26
1970	722,000	90 - 102	21
1975	1,000,000	95 - 103	19
1980	1,200,000	95 - 105	15 - 17

TABLE III

SEMI-REGENERATIVE MAGNAFORMER - OPTIMUM ECONOMICS

BASIS:

MID-CONTINENT (U.S.) NAPHTHA FEED	2,600 MT/DAY
C_5 PLUS REFORMATE, RON, CLEAR	103
CYCLE LENGTH, MONTHS	5
CATALYST	E-601

CONDITIONS FOR BEST 10-YEAR ECONOMICS, ALL COSTS INCLUDED:

AVERAGE REACTOR PRESSURE, KG/CM^2 GAGE	11.0
WEIGHT HOURLY SPACE VELOCITY	2.2
TERMINAL REACTOR RECYCLE GAS/FEED MOL RATIO	9
RECYCLE LOOP PRESSURE DROP, KG/CM^2	4.5

TABLE III-A

COMPARATIVE REFORMING

CURRENT AND PRE-1960 DESIGNS

FEEDSTOCK:

API	53.8 (.7636)
ASTM DISTILLATION, °C	
IBP	101
10	119
50	142
90	169
EP	185
PARAFFINS, VOL.%	47
NAPHTHENES	45
AROMATICS	8

TABLE III-B

COMPARATIVE REFORMING

CURRENT AND PRE-1960 DESIGNS

OPERATING CONDITIONS & YIELDS:

	A Current Design E-601 Catalyst Magnaforming at Low Pressure		A Design Pre-1960 RD-150C Catalyst Conventional Reforming At Intermediate Press.	
C5-EP, RES ON CLEAR	99.0		92.0	
" " " +3CC TEL	103.0		98.5	
YIELDS, %	**Wt.**	**Vol.**	**Wt.**	**Vol.**
H_2	3.1		1.6	
C_1	1.1		1.9	
C_2	1.6		2.8	
C_3	2.3		3.8	
iC_4	1.0	1.4	1.7	2.2
nC_4	1.5	2.0	2.6	3.3
C_5+	89.4	82.5	85.6	82.5
C5-EP REFORMATE:				
API	39.5 (.8275)		47.5 (.7905)	
Paraffins, Vol.%	21.5		35.5	
Naphthenes, "	2.5		5.5	
Aromatics, "	76.0		59.0	

FIGURE-1
ENVIRONMENT EFFECT ON YIELD & LIFE

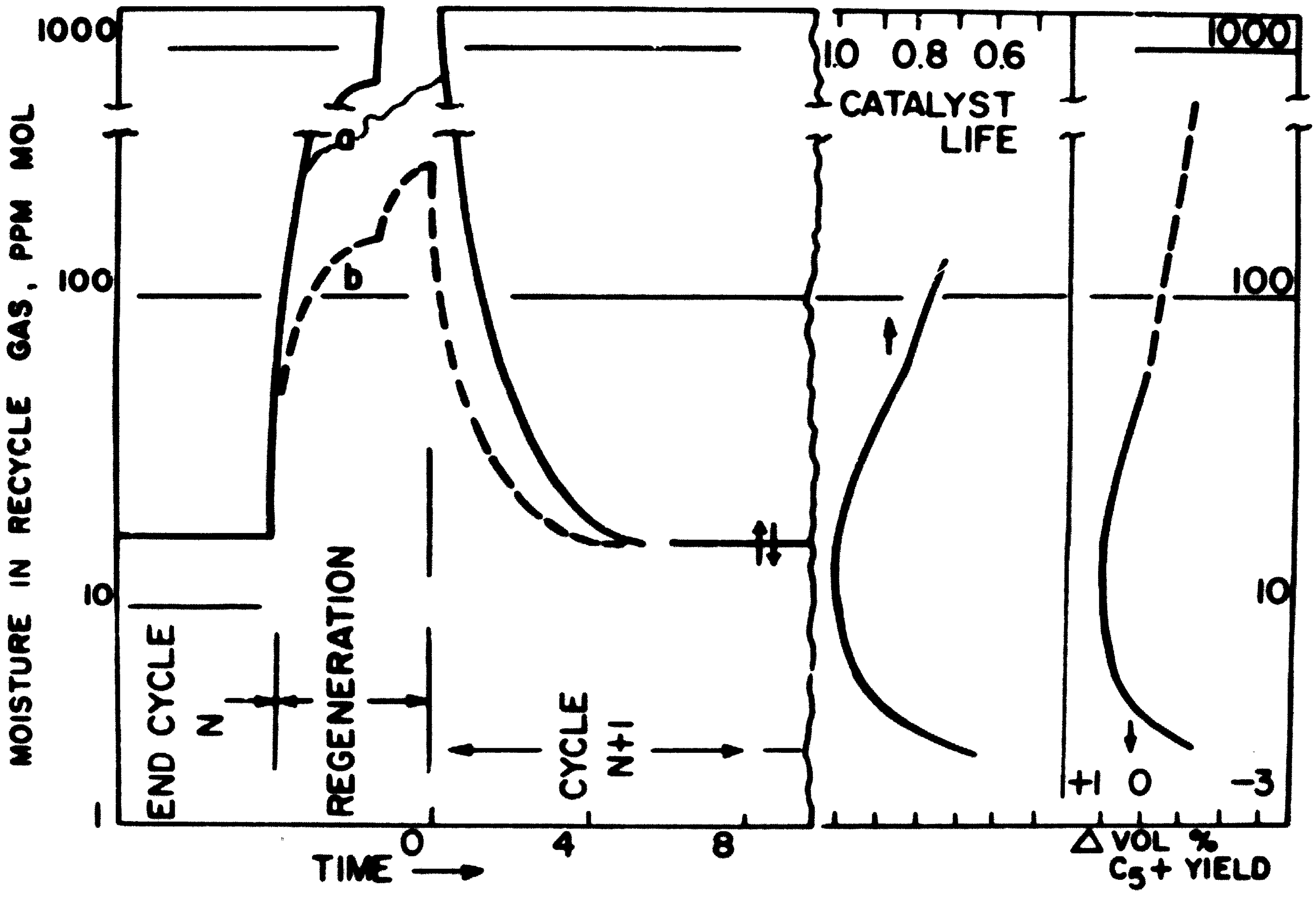


FIGURE-2 COMPARATIVE CATALYST PERFORMANCE TESTING

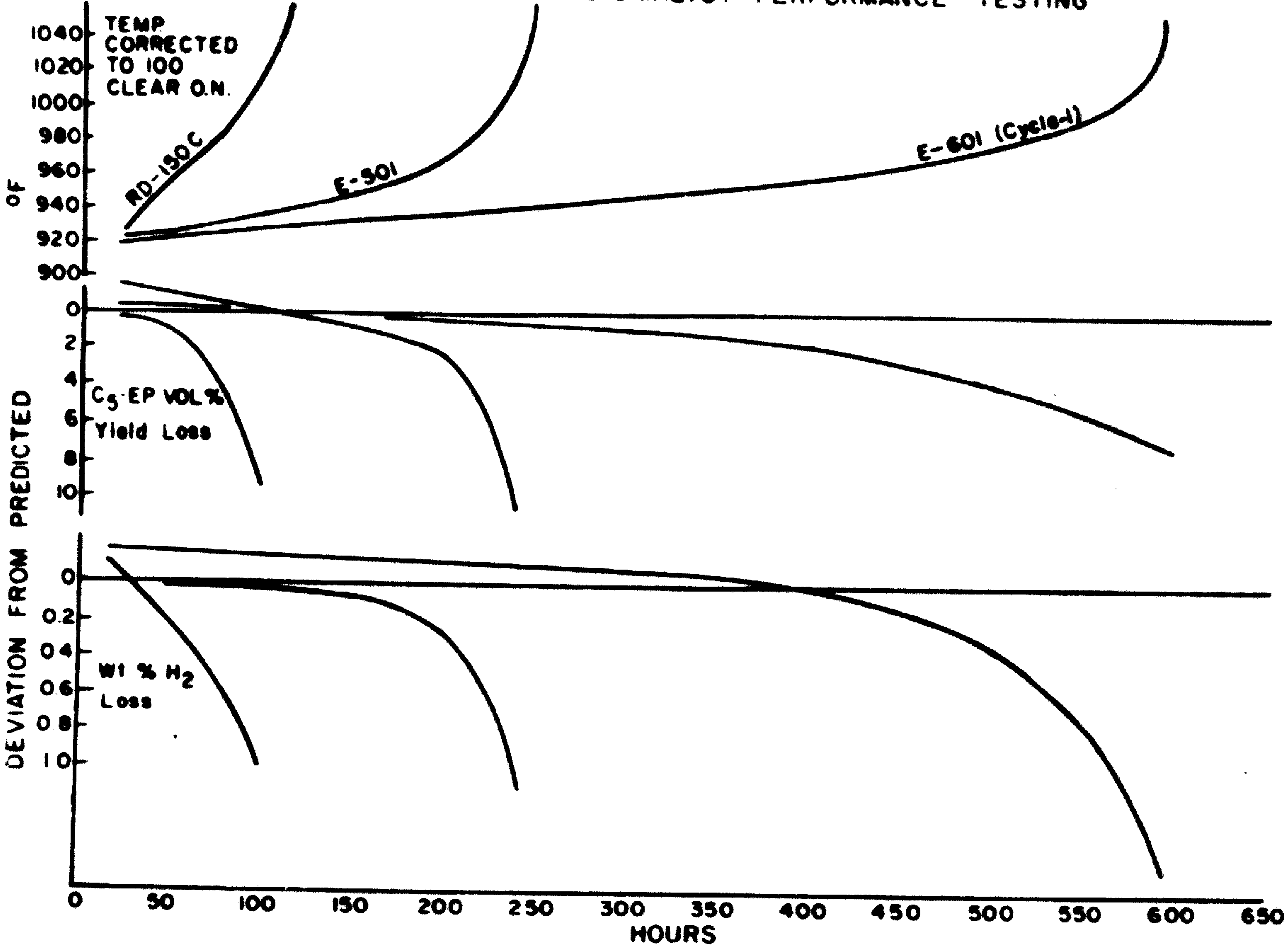


FIGURE-3

MAGNAFORMING FLOW DIAGRAM

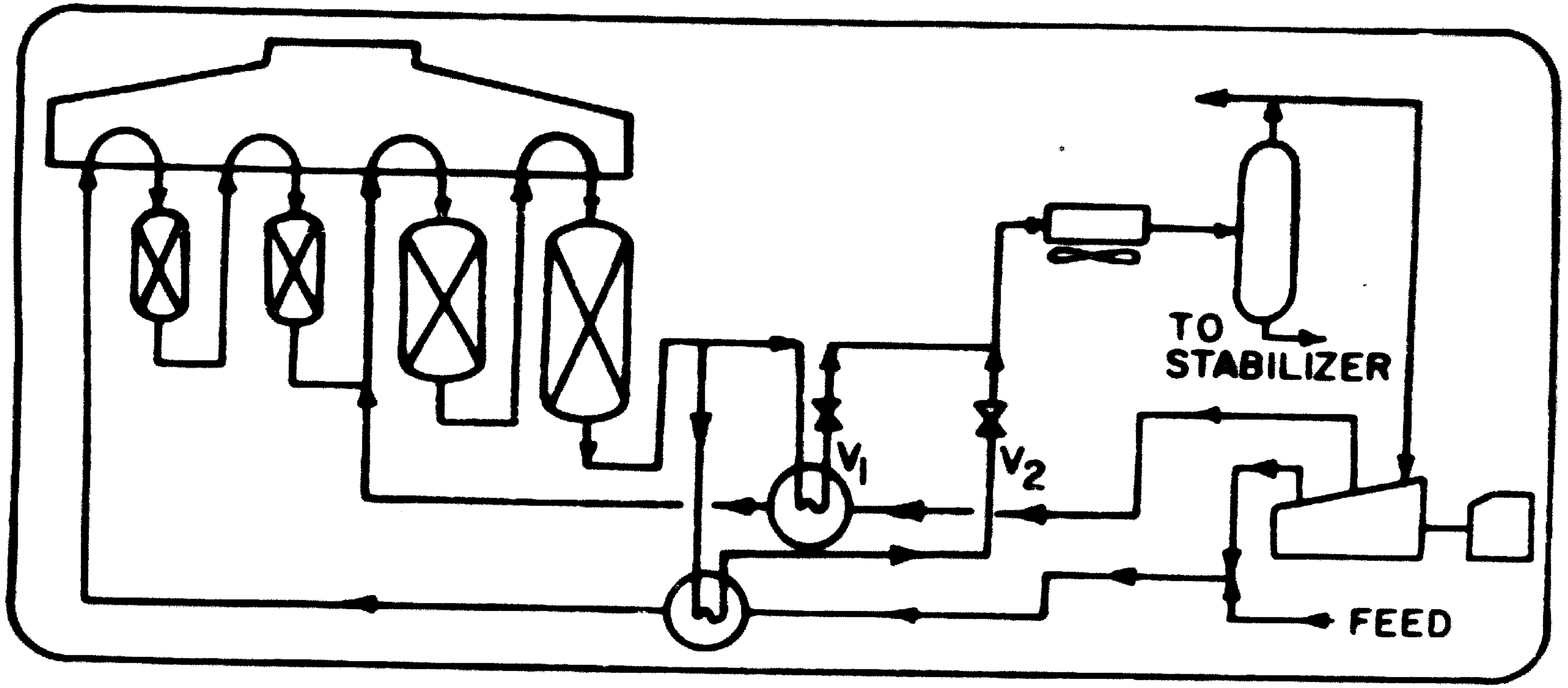


FIGURE-4 MAGNAFORMING WITH E-601 CATALST

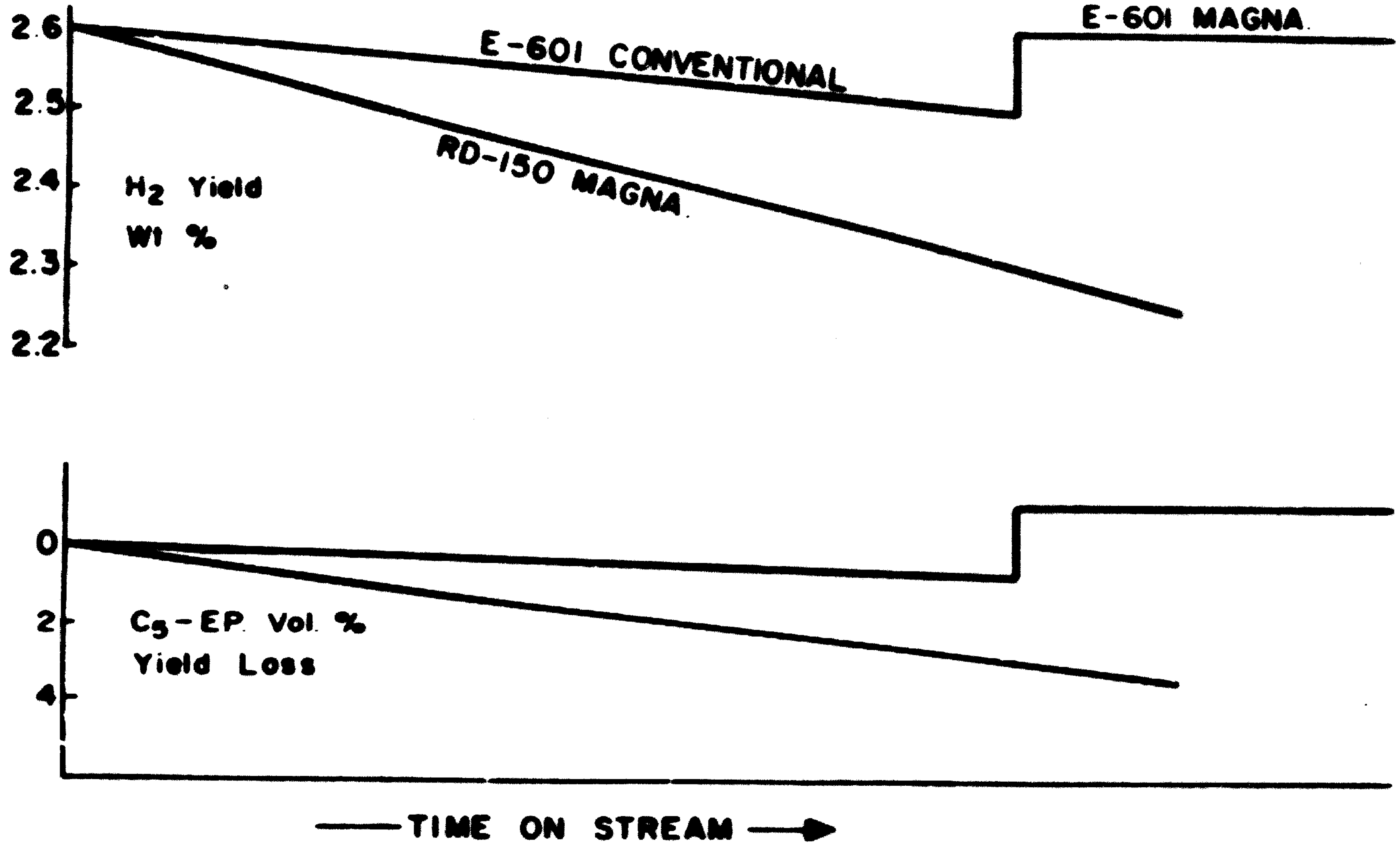
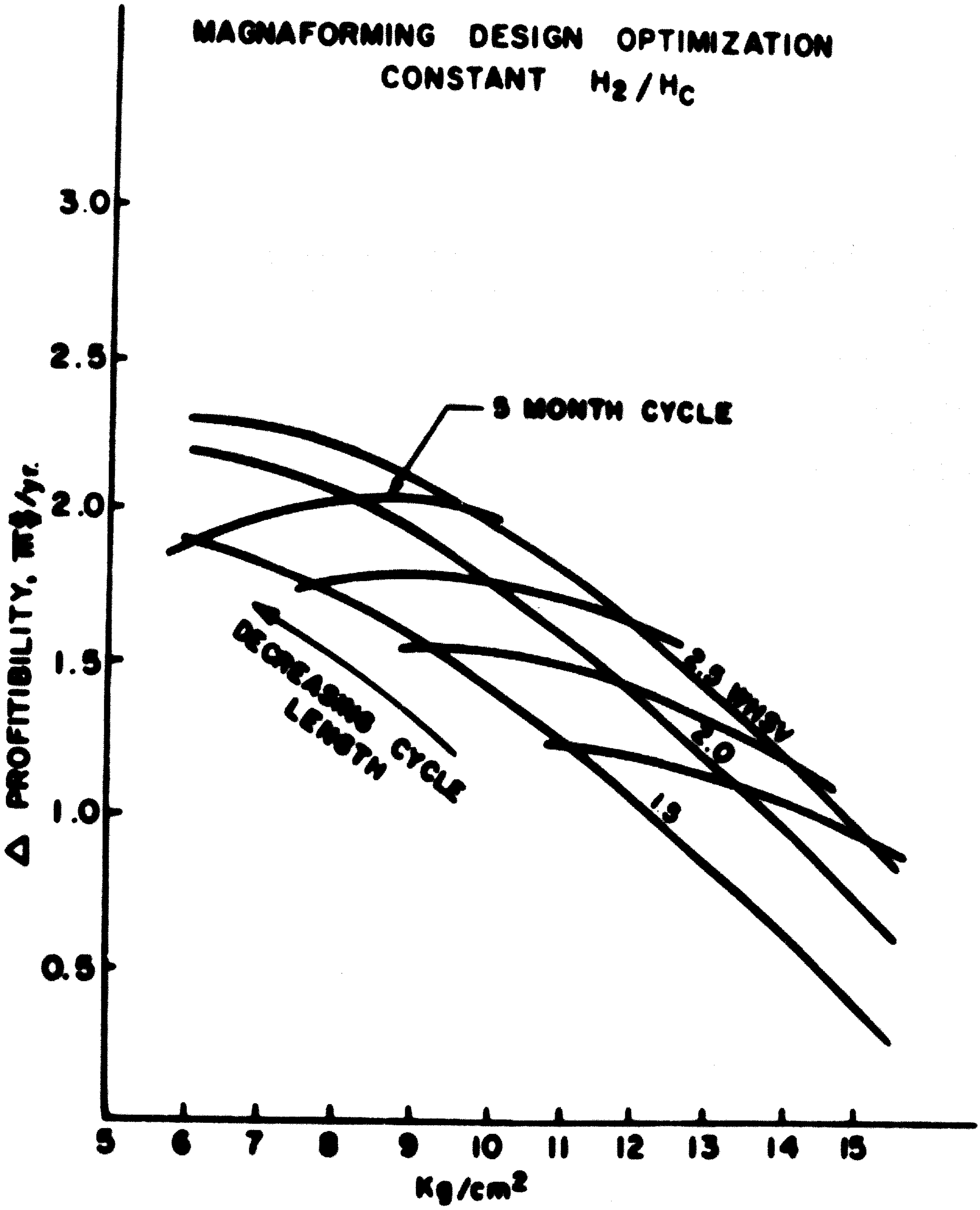


FIGURE - 5



MAGNAFORMING DESIGN OPTIMIZATION
CONSTANT H_2/H_C

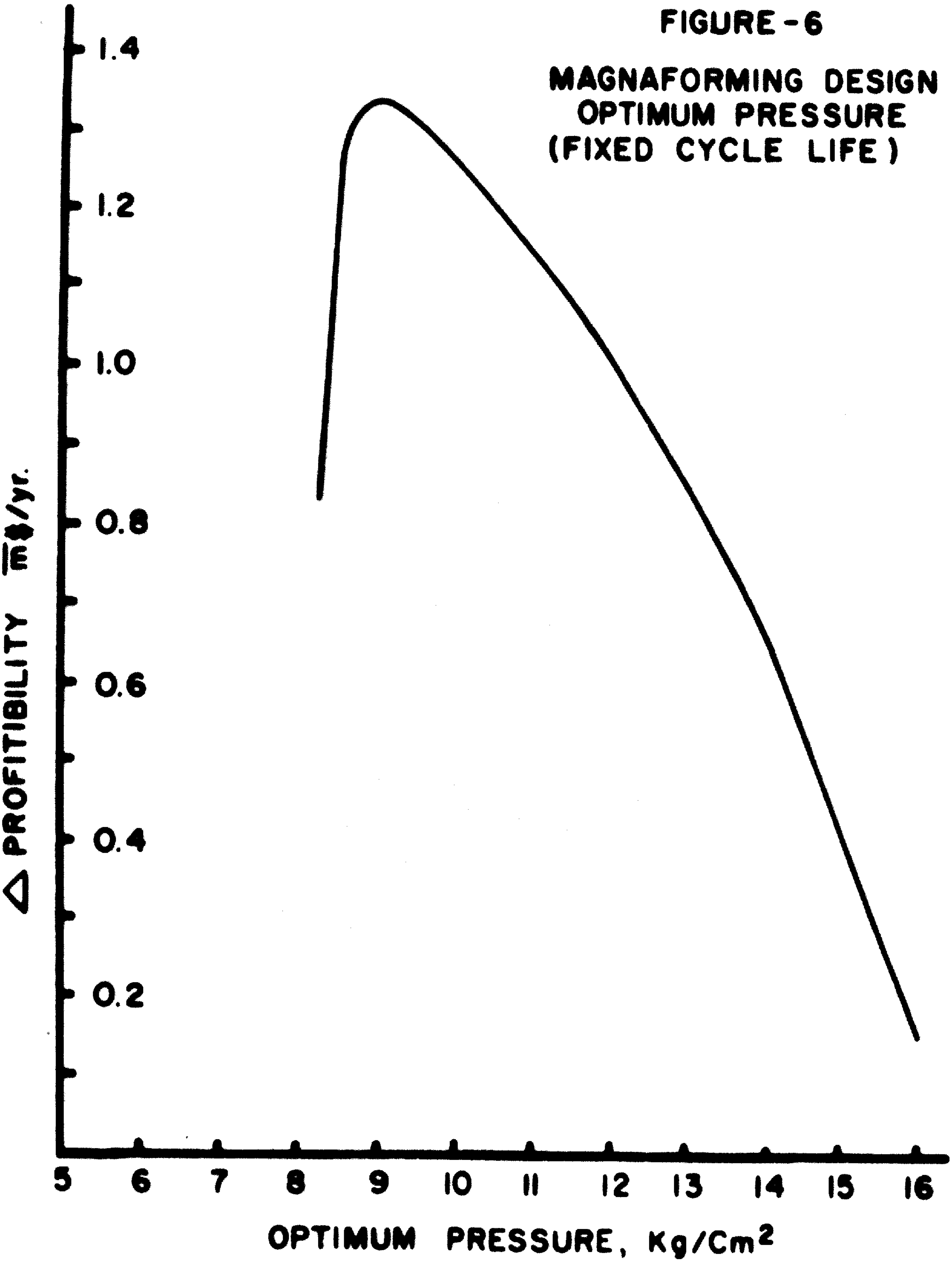
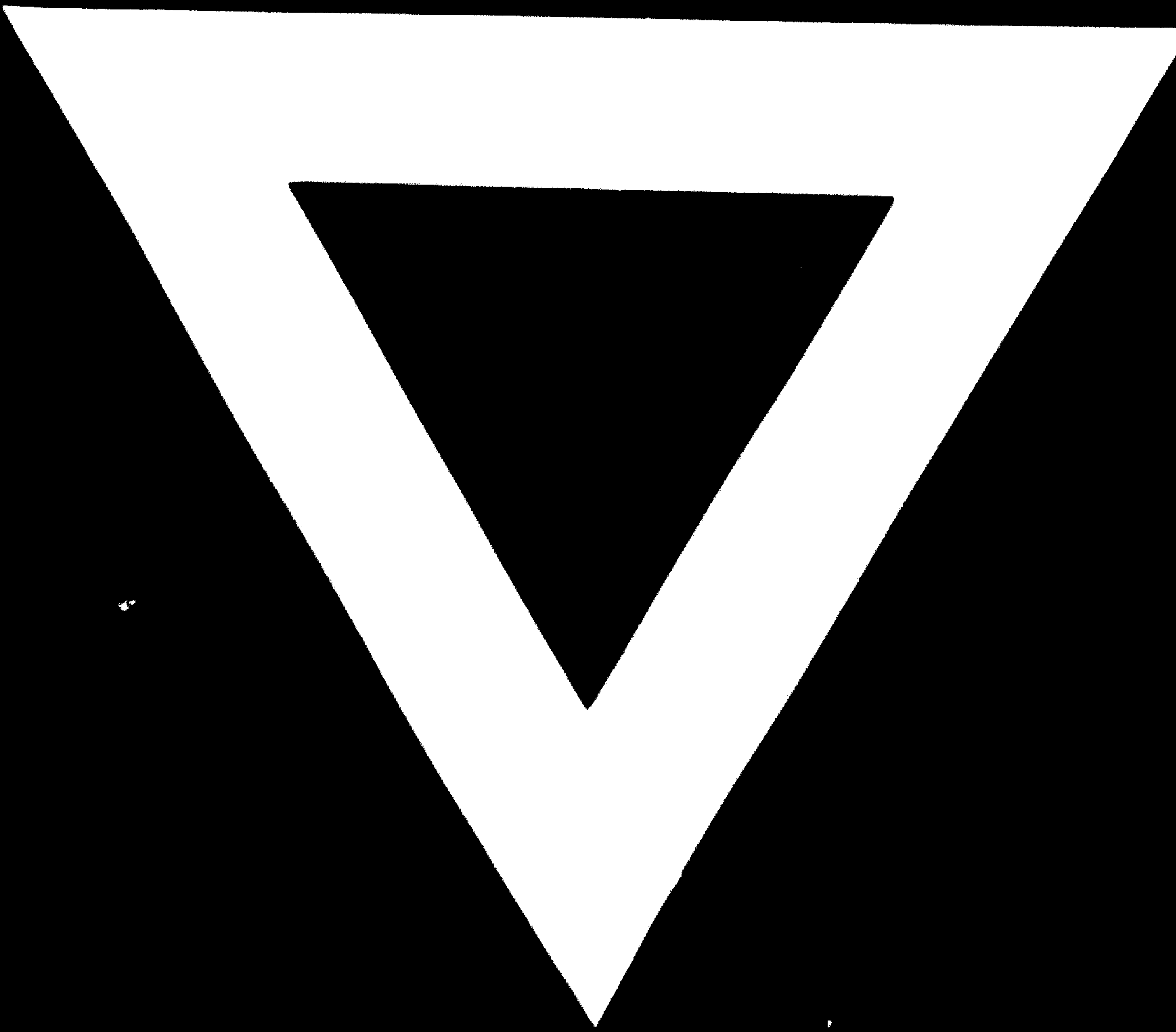


FIGURE-6

MAGNAFORMING DESIGN
OPTIMUM PRESSURE
(FIXED CYCLE LIFE)



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