Case 2 - LPMAS/Petroleum Refinery

3.1 Background

The scenario for Case 2, petroleum refinery, was chosen for four reasons:

- Coke gasification produces a low H_2/CO ratio syngas which has been shown to be favorable to higher alcohol production.
- In many instances, the feedstock for syngas production, petroleum coke, has a zero or negative value.
- The refinery consumes ethers for oxygenated or reformulated gasolines.
- The refinery can consume a limited amount of unconverted syngas.

3.2 Study Basis

Figure 3-1 shows how the LPMAS plant was integrated into an existing petroleum refinery. The shaded blocks represent the new plants that are required. Syngas from the coke gasification plant is sent to acid gas removal where H_2S and CO_2 are removed. The clean syngas is sent to the LPMAS plant. The mixed alcohols from the LPMAS plant are separated and the C_{4+} alcohols are dehydrated. The primary products from the new plants are methanol, C_{4+} olefins and unconverted syngas. These products are consumed by the refinery to produce additional ethers and reduce the amount of purchased MTBE.

3.2.1 Gasification

The petroleum coke composition and the gasification syngas yield and composition are based on an article by Mahagaokar and Hauser.[1] The analysis of the coke is shown in Table 3-1. The syngas composition is shown in Table 3-2. The coke feed rate, 1800 stpd, is determined by the coke production from the refinery.

3.2.2 Syngas Conversion

One of the key differences between Case 2 and Case 1 is that instead of examining a range of syngas conversion levels, only a single conversion level, 95%, was studied. This level was chosen so that the refinery fuel system would not be diluted with large volumes of low-btu unconverted syngas.

To achieve the 95% conversion:

- A recycle LPMAS system is required.
- Steam is added to the LPMAS feed to provide hydrogen via internal water gas shift (WGS).
- CO_2 (generated by the WGS) is removed from the LPMAS recycle loop.

A block flow diagram of the LPMAS plant is shown in Figure 3-2. The plant is similar to Case 1 except that the recycle portion of plant is required to achieve the high overall conversion and stay within the limits of methanol equilibrium. CO_2 is removed from the recycle loop to reduce the volume of recycle gas and to minimize reverse water gas shifting.

3.2.3 LPMAS Recycling

A recycle LPMAS system is required to achieve the high conversion level since a single pass system is limited by methanol equilibrium. The minimum recycle ratio needed to avoid methanol equlibrium constraints is 2.1. The effect of recycling was examined by varying the recycle ratio between 2.1 and 4.7.

At the higher ratios, the methanol equilibrium is not restricting. Figure 3-3 shows that the per pass syngas conversion decreases as the recycle ratio increases.

3.3 Linear Programming Analysis

To estimate the value of the LPMAS products to a petroleum refiner, the Bechtel proprietary Process Industry Modeling System (PIMS) was used for linear programming (LP) analysis. LP analysis is used by the process industry to determine optimum processing configurations and conditions.

A refinery LP model developed for another project was used for the analysis. The model, shown in Figure 3-4, simulates a 285,000 bpd refinery running at capacity. The feedstock is a generic crude which is expected to be typical of feedstock in the Midwest in the year 2000. The product slate consists of reformulated and conventional gasolines, jet fuel, and three grades of diesel. Product specifications are based on EPA regulations for the year 2000.

3.3.1 Objective Function

In linear programming, objective function is defined as:

Objective function = Revenue - purchases - utilities - capital charges

The revenue, purchases, and utilities components are on a daily basis. Capital charges are the daily charges for the capital costs of increasing the capacity of one or more process units. The PIMS linear program maximizes the objective function term by changing the flow configuration and process unit yields throughout the refinery.

3.3.2 Base Case – Petroleum Refinery

The base case consists of the aforementioned 285,000 bpd refinery without the addition of the coke gasifier and LPMAS plant. Fuel-grade coke from the refinery is assigned a zero value. The product slate and product volumes are fixed at estimated demand levels. The objective function for the base case, 1482.1 M$/day, is broken down as follows:

	M$/day
▪ Revenue	7574.5
▪ Purchases	5814.3
▪ Utilities	278.1
▪ Capital charges	0.0
Objective function	1,482.1

Capital charges are zero because no expansion is required for any of the process units.

The purchases are as shown in Table 3-3. The utilities are as shown in Table 3-4.

3.3.3 Modification for Coke Gasification/LPMAS

As shown in Figure 3-1, a new submodel, SMAS, was developed which simulates the following plants as a single block:

- Gasification
- Acid gas removal (AGR)
- LPMAS
- Alcohol separation
- Alcohol dehydration

The spreadsheet estimates the flows and properties for the following streams, which are products from this block of plants:

- C_{4+} olefins
- Unconverted syngas
- Methanol

The isobutylene and isoamylene content of the C_{4+} olefins is used by PIMS to determine the amount of MTBE and TAME production. As this amount increases, the volume of purchased MTBE decreases. Unconverted C_4-C_5 olefins are routed to the alkylation plant. The small amount of C_6 olefin is sent to gasoline blending.

Unconverted syngas is used in the model as fuel, primarily for steam production. Methanol is used for ether production.

The high-pressure steam generated by the coke gasification plant is used to drive the air separation plant compressors. Medium-pressure steam from the LPMAS plant that is not consumed by the AGR plant is used for process heating within the refinery. Hydrogen sulfide from the AGR plant is converted into sulfur and sold.

3.4 Case Studies

The sequence for evaluating different recycle ratios as outlined in Section 3.2.3 was as follows:

1. For each case, the spreadsheet was used to calculate the flows and properties of the three primary products from the SMAS block of units. Utilities for this block were also estimated.

2. The data from Step 1 were entered into the PIMS refinery model.

3. The PIMS model was run to determine how best to utilize the products from the SMAS block.

4. The objective function was calculated for each case.

Table 3-5 provides the cash flow and the objective function for each case. Capital charges are for expansion costs of the base refinery process units. In these case studies, the only process units that require expansion are the MTBE/TAME and alkylation units. The capital costs for the units in the SMAS block are not included, but are considered outside of the linear programming analysis (see Section 3.5).

Table 3-5 also shows that the objective function for all of the cases are higher than the objective function for the base case. The primary reason for the higher objective functions is that the purchase and utility components of the objective functions are lower.

Table 3-6 summarizes the refinery purchasing and utility requirements for the different cases. This shows that adding a gasification/LPMAS system reduces the amount of purchased MTBE. Table 3-6 also summarizes the key operating conditions and production rates for each of the four different recycle ratio cases.

3.5 Economic Analysis

Capital costs were estimated for the units in the SMAS submodel (gasification, AGR, LPMAS, alcohol separation and alcohol dehydration) per the basis outlined in Section 3.2. Since the coke feed rate is the same for all cases (1800 stpd), the total costs for the gasification and AGR do not change. The costs of the LPMAS, alcohol separation and dehydration units change, but these costs do not represent a significant portion of the overall capital costs.

For each case, the change in the objective function from the base case represents the increase in cash flow due to adding the SMAS units. For example, the objective function for Case 2-1 is 1700.3 M$/day. The change in objective function from the base case is 218.2 M$/day (1700.3 - 1482.1).

A discounted cash flow spreadsheet was then used to calculate the internal rate of return (IRR) for the coke gasification/LPMAS expansion. The two key inputs were the change in objective function from the base case and the capital costs for the process units in the SMAS submodel. Operating and maintenance costs were also estimated and used in the IRR calculation.

The following basis was used for the economic analysis:

- $0/short ton coke
- 2-year construction period
- 100% equity
- 85 cent/gallon MTBE
- 25-year plant life

Table 3-7 summarizes the economics for each of the four recycle ratio cases.

3.6 Results

Figure 3-5 shows the rate of return as a function of per pass conversion. The highest rate of return, 13.9%, is at the methanol equilibrium limit (highest per pass conversion/lowest recycle ratio).

Figure 3-6 shows that the required catalyst productivity declines as the recycle ratio increases. At the minimum recycle ratio, the required productivity is 265 g isobutanol/Kg-hr.

3.7 Conclusions

- Within the study basis parameters, a LPMAS plant could be economically integrated into an existing refinery.
- A catalyst productivity of 265 g isobutanol/Kg-hr is required to achieve a 13.9% rate of return (1.03 mole methanol / mole isobutanol, 5000 sl/Kg-hr SV).
- Recycling of unconverted syngas, steam addition and CO_2 removal are all required.

3.8 References

1. Mahagaokar, U. and Hauser N., "Gasification of Petroleum Coke in the Shell Coal Gasification Process," unknown publication.

3.9 Tables and Figures

Table 3-1
Petroleum Coke Analysis

Item	Value
Proximate analysis, wt%	
Moisture	9.31
Volatile matter	9.62
Fixed carbon	80.62
Ash	0.45
Total	100.00
Heating value, Btu/lb MF	15,342
Ultimate analysis, wt%	
Carbon	89.23
Hydrogen	3.59
Sulfur	5.22
Oxygen	0.10
Nitrogen	1.35
Ash	0.50
Chlorine	0.03
Total	100.02

Table 3-2
Coke Gasification Raw Syngas Composition

Constituent	Vol%
H_2	25.4
CO	63.9
CO_2	2.1
CH_4	0.018
N_2	5.0
H_2O	2.1
H_2S + COS	1.5
Total	100.00

Table 3-3
Feedstock Purchases for Base Case

Item	Bpd	$/Barrel	M$/day
Crude	285,966	18.00	5,147.4
Methanol	1,360	14.70	20.0
MTBE	10,626	35.7	379.3
n-Butane	2,112	13.66	28.8
i-Butane	12,787	17.22	220.2
Natural gas, FOE	1,534	$2/10^6$ Btu	18.6
Total			5,814.3

FOE - Fuel oil equivalent barrel (6.05 x 10^6 Btu/bbl)

Table 3-4
Utilities for Base Case

Item	Daily Consumption	M$/day
Power	2,926 MWh	146.3
Fuel gas	32,285 x 10^6 Btu	64.6
Catalyst/chemicals		35.4
Sulfuric acid	732 x 10^3 lb	31.1
Water	6,709 x 10^3 gal	0.7
Total		278.1

Table 3-5
Case 2 - Refinery/LPMAS
Cash Flows/Objective Function

Case	Base Case - no LPMAS	2-1	2-2	2-3	2-4
Revenues	7574.5	7582.4	7582.4	7582.4	7582.4
Purchases	5814.3	5553.3	5534.8	5553.3	5534.8
Utilities	278.1	300.2	319.2	301.1	320.5
Capital charges	0.0	28.6	28.6	28.6	28.6
Objective function, M$/day	1482.1	1700.3	1699.9	1699.4	1698.6

Table 3-6
Case 2 - Refinery/LPMAS
Operating Summary

	Base Case No LPMAS	2-1	2-2	2-3	2-4
Case Conditions					
Coke gasification capacity, stpd		1800	1800	1800	1800
No. of LPMAS Trains		1.0	1.0	1.0	1.0
LPMAS fresh feed, MMSCFD		166	166	166	166
LPMAS reactor feed, MMSCFD		459	524	647	893
LPMAS recycle ratio, recycle mol/feed mol		2.04	2.43	3.17	4.65
No. of LPMAS reactors per train		2.00	2.00	2.00	2.00
Overall syngas conversion		95%	95%	95%	95%
Overall CO conversion		95%	95%	95%	95%
Overall H2 conversion		93%	93%	93%	93%
Per pass syngas conversion		46%	42%	35%	26%
Per pass CO conversion		50%	45%	38%	29%
Per pass H2 conversion		39%	34%	28%	21%
LPMAS reactor inlet molar composition					
CO		40.15%	38.96%	37.36%	35.39%
H2		19.81%	19.61%	19.34%	19.12%
CO2		0.53%	0.47%	0.39%	0.28%
H2O		5.49%	4.82%	3.91%	2.85%
Methanol		0.27%	0.28%	0.29%	0.31%
Isobutanol		0.01%	0.02%	0.02%	0.02%
N2, Ar, H2S		33.68%	35.79%	38.64%	41.97%
CH4		0.05%	0.05%	0.06%	0.06%
LPMAS reactor outlet molar composition					
CO		24.83%	25.67%	26.73%	27.78%
H2		14.85%	15.35%	15.97%	16.76%
CO2		13.76%	11.74%	9.17%	6.39%
H2O		0.51%	0.44%	0.35%	0.26%
Methanol		2.46%	2.15%	1.76%	1.34%
Isobutanol		2.10%	1.79%	1.40%	0.98%
Other alcohols		0.16%	0.13%	0.11%	0.07%
N2, Ar, H2S		41.27%	42.66%	44.43%	46.35%
CH4		0.06%	0.06%	0.07%	0.07%
Total alcohol production, stpd		1169	1169	1169	1169
Catalyst activity, g MeOH/kg cat		118	103	84	61
Catalyst activity, g iBOH/kg cat		266	233	189	137
Methanol to ether production, bbl/day		2415	2415	2415	2415
Additional potential ether production, bbl/day		7134	7134	7134	7134
Refinery Requirements					
Purchased gas, MMBtu/hr	1345	847	1234	847	1234
Purchased power, MW	122	153	154	154	155
Purchased methanol, bbl/day	1360	1361	1361	1361	1361
Purchased MTBE, bbl/day	10626	3178	3178	3178	3178
MTBE capacity, bbl/day	3996	11133	11133	11133	11133
MTBE expansion capacity, bbl/day		7138	7138	7138	7138

Table 3-7
Case 2 - Refinery/LPMAS
Economic Summary

Case	Base Case	2-1	2-2	2-3	2-4
Objective function, M$/day	1482.1	1700.3	1699.9	1699.4	1698.6
Objective function change from Base Case		218.2	217.8	217.4	216.6
Operating Cost Summary, MM$/yr (lst year)					
Operations and maintenance labor		3.1	3.1	3.1	3.1
Maintenance, taxes, and insurance		3.8	3.9	4.0	4.5
Catalyst and chemical costs		2.5	2.5	2.5	2.5
Capital Cost Summary, MM$					
Gasification		98.7	98.7	98.7	98.7
Air separation		39.3	39.3	39.3	39.3
Acid gas removal		11.5	11.5	11.5	11.5
Mixed alcohol synthesis		60.1	64.5	72.6	102.4
Alcohol separation		2.2	2.2	2.2	2.2
Alcohol dehydration		1.7	1.7	1.7	1.7
Offsites		39.8	39.8	39.8	39.8
Total		253.4	257.9	266.0	295.8
Field indirect costs and HO eng. costs		38.0	38.7	39.9	44.4
Contingency		58.3	59.3	61.2	68.0
Total plant costs , MM$		349.7	355.8	367.0	408.1
Discounted internal rate of return		13.9	13.7	13.3	12.0

1. Objective Function = Revenues - purchases - utilities - daily capital charge (for MTBE/alkylation expansion only)

Figure 3-1
Case 2 - Petroleum Refinery/LPMAS
Block Flow Diagram

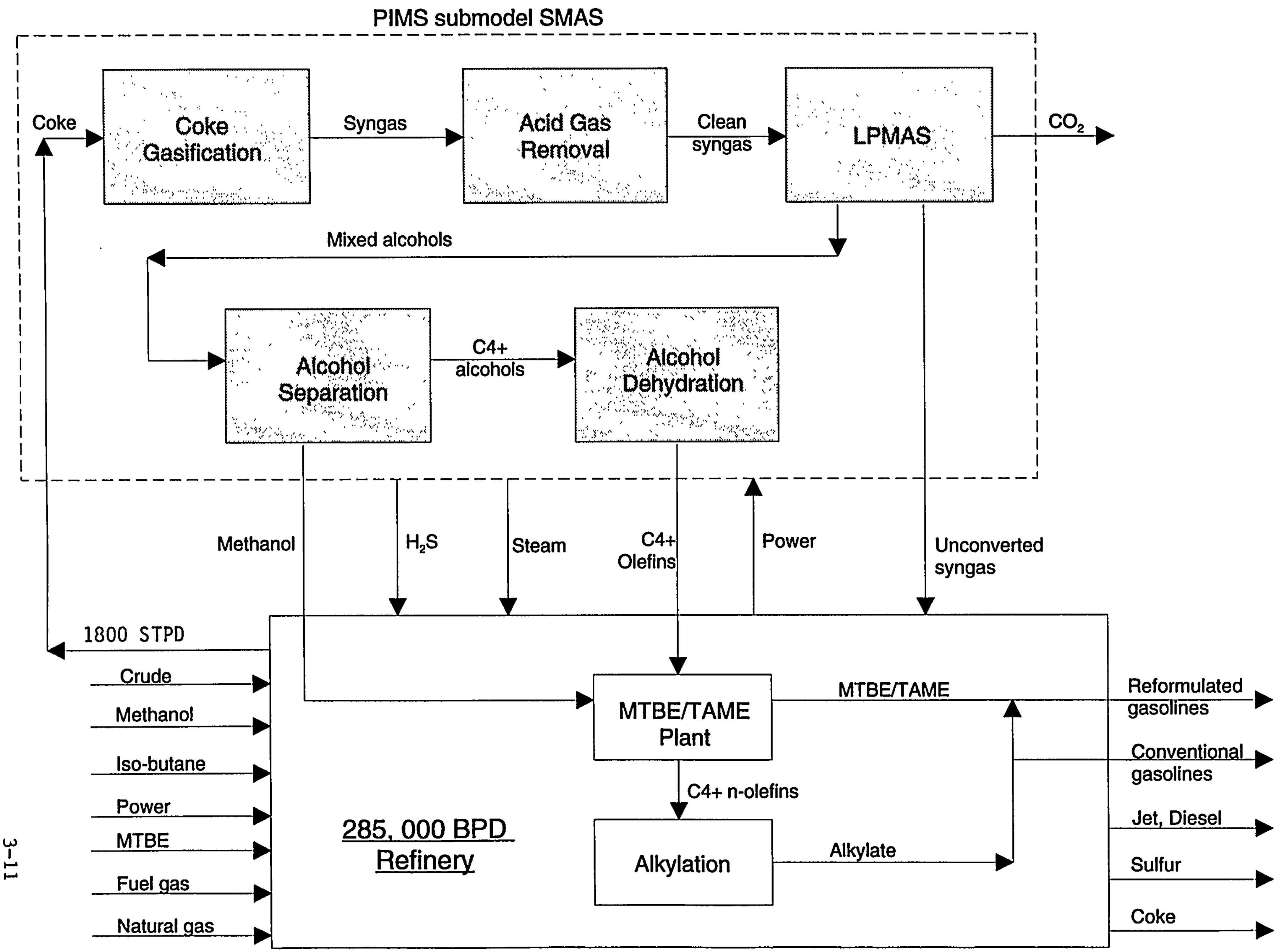


Figure 3-2
Case 2 LPMAS
Block Flow Diagram

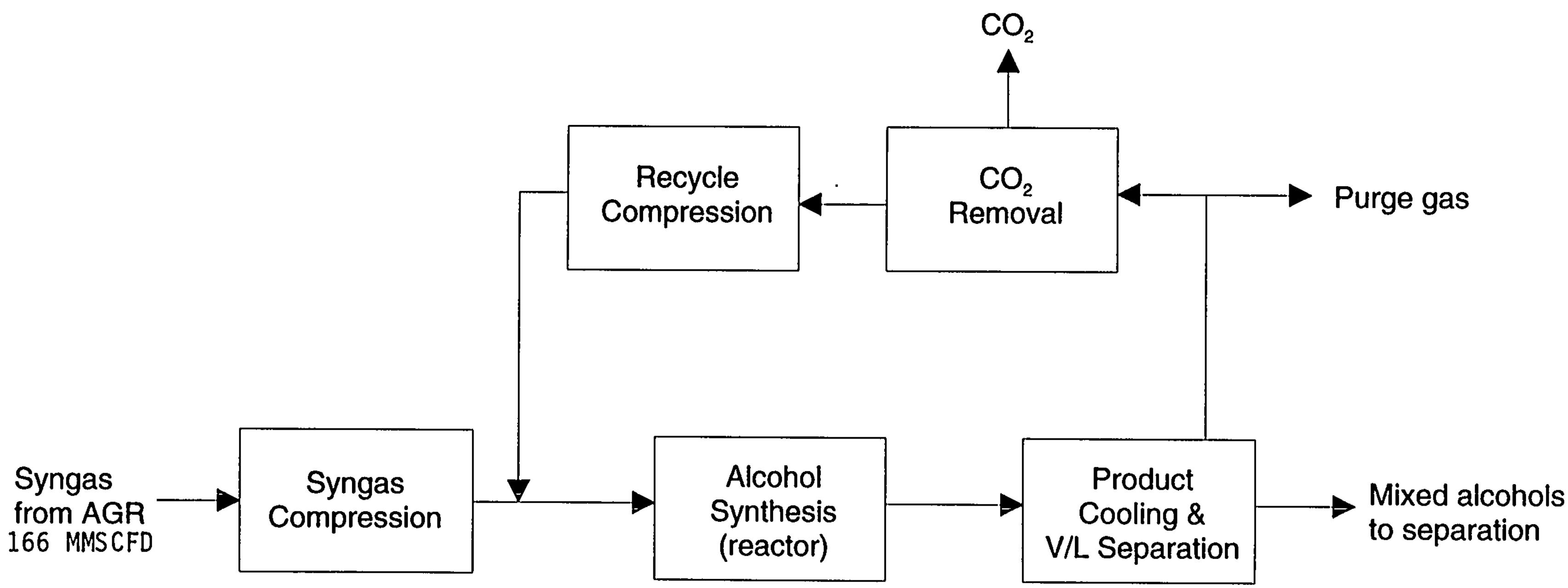
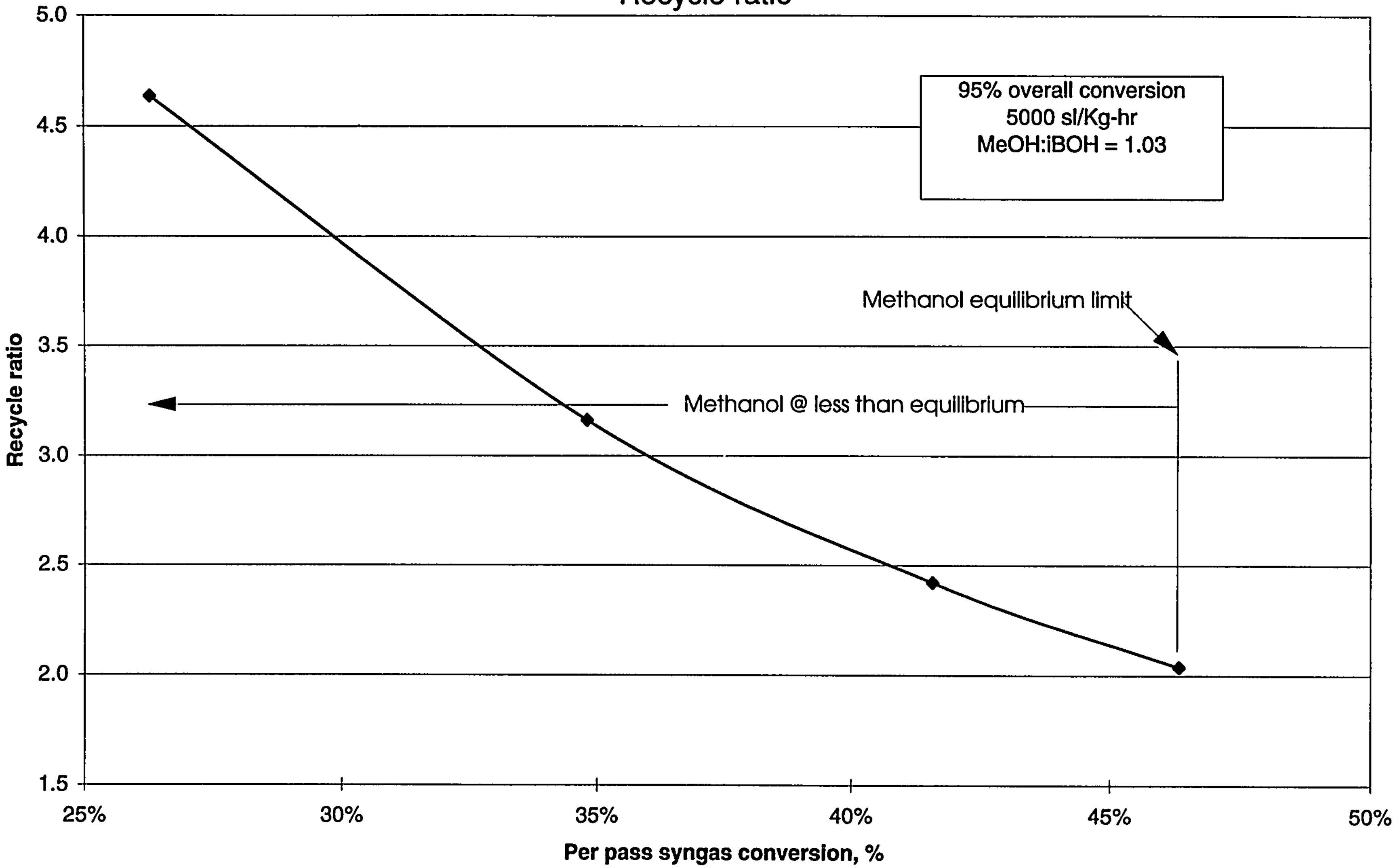
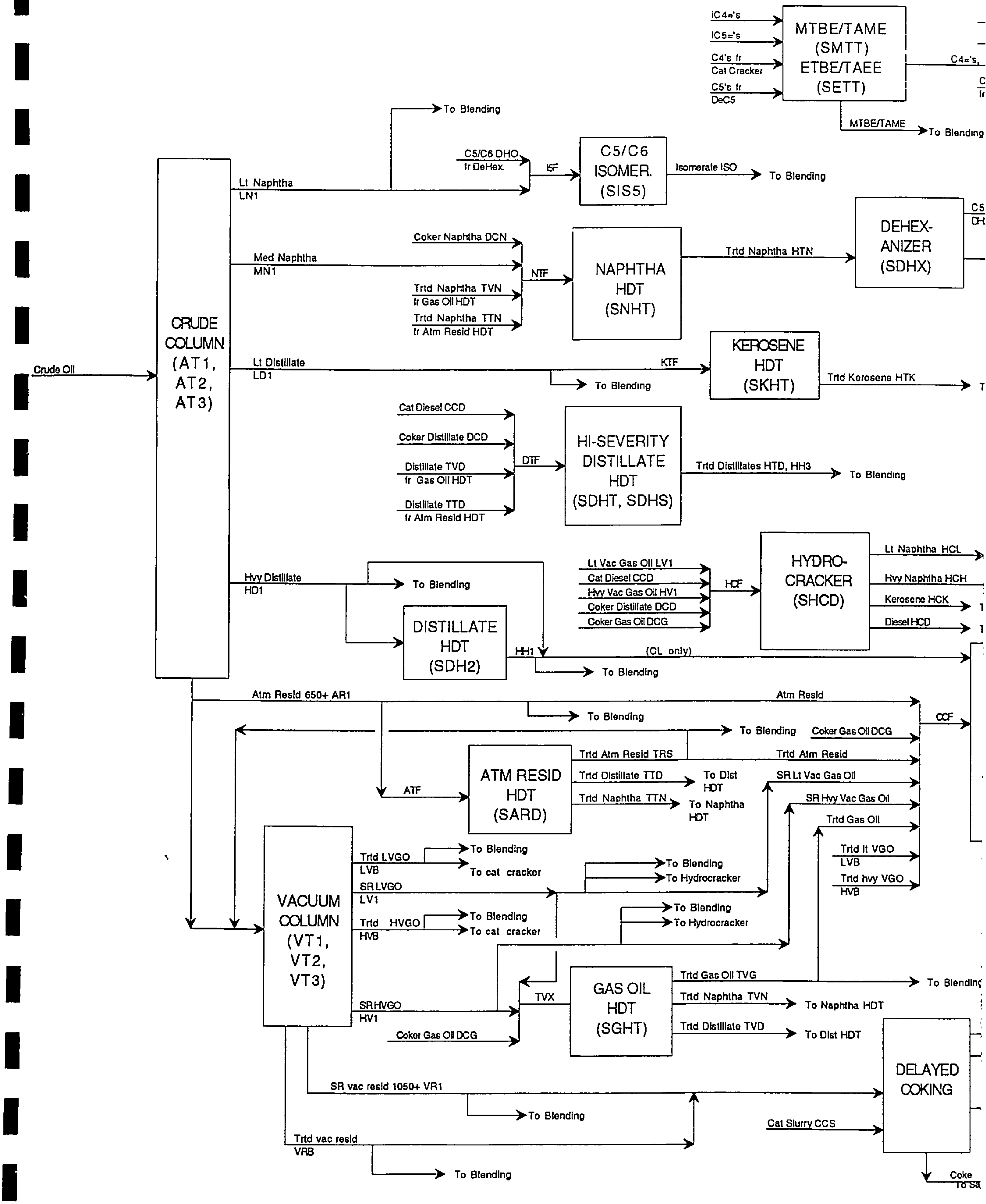


Figure 3-3
Case 2 - Refinery/LPMAS
Recycle ratio





iC4='s
IC5='s
C4's fr Cat Cracker
C5's fr DeC5
MTBE/TAME (SMTT) ETBE/TAME (SETT)
MTBE/TAME
To Blending
C4='s,
To Blending
C5/C6 DHO fr DeHex.
ISF
C5/C6 ISOMER. (SIS5)
Isomerate ISO
To Blending
CRUDE COLUMN (AT1, AT2, AT3)
Crude Oil
Lt Naphtha LN1
Coker Naphtha DCN
Med Naphtha MN1
Trtd Naphtha TVN fr Gas Oil HDT
Trtd Naphtha TTN fr Atm Resid HDT
NTF
NAPHTHA HDT (SNHT)
Trtd Naphtha HTN
DEHEX-ANIZER (SDHX)
Lt Distillate LD1
KTF
To Blending
KEROSENE HDT (SKHT)
Trtd Kerosene HTK
Cat Diesel CCD
Coker Distillate DCD
Distillate TVD fr Gas Oil HDT
Distillate TTD fr Atm Resid HDT
DTF
HI-SEVERITY DISTILLATE HDT (SDHT, SDHS)
Trtd Distillates HTD, HH3
To Blending
Hvy Distillate HD1
To Blending
DISTILLATE HDT (SDH2)
HH1
(CL only)
To Blending
Lt Vac Gas Oil LV1
Cat Diesel CCD
Hvy Vac Gas Oil HV1
Coker Distillate DCD
Coker Gas Oil DCG
HCF
HYDRO-CRACKER (SHCD)
Lt Naphtha HCL
Hvy Naphtha HCH
Kerosene HCK
Diesel HCD
Atm Resid 650+ AR1
Atm Resid
To Blending
To Blending
Coker Gas Oil DCG
CCF
ATF
ATM RESID HDT (SARD)
Trtd Atm Resid TRS
Trtd Atm Resid
Trtd Distillate TTD
To Dist HDT
Trtd Naphtha TTN
To Naphtha HDT
SR Lt Vac Gas Oil
SR Hvy Vac Gas Oil
Trtd Gas Oil
VACUUM COLUMN (VT1, VT2, VT3)
Trtd LVGO LVB
To Blending
To cat cracker
SR LVGO LV1
To Blending
To Hydrocracker
Trtd lt VGO LVB
Trtd hvy VGO HVB
Trtd HVGO HVB
To Blending
To cat cracker
To Blending
To Hydrocracker
SR HVGO HV1
Coker Gas Oil DCG
TVX
GAS OIL HDT (SGHT)
Trtd Gas Oil TVG
To Blending
Trtd Naphtha TVN
To Naphtha HDT
Trtd Distillate TVD
To Dist HDT
SR vac resid 1050+ VR1
To Blending
Cat Slurry CCS
DELAYED COKING
Trtd vac resid VRB
To Blending
Coke

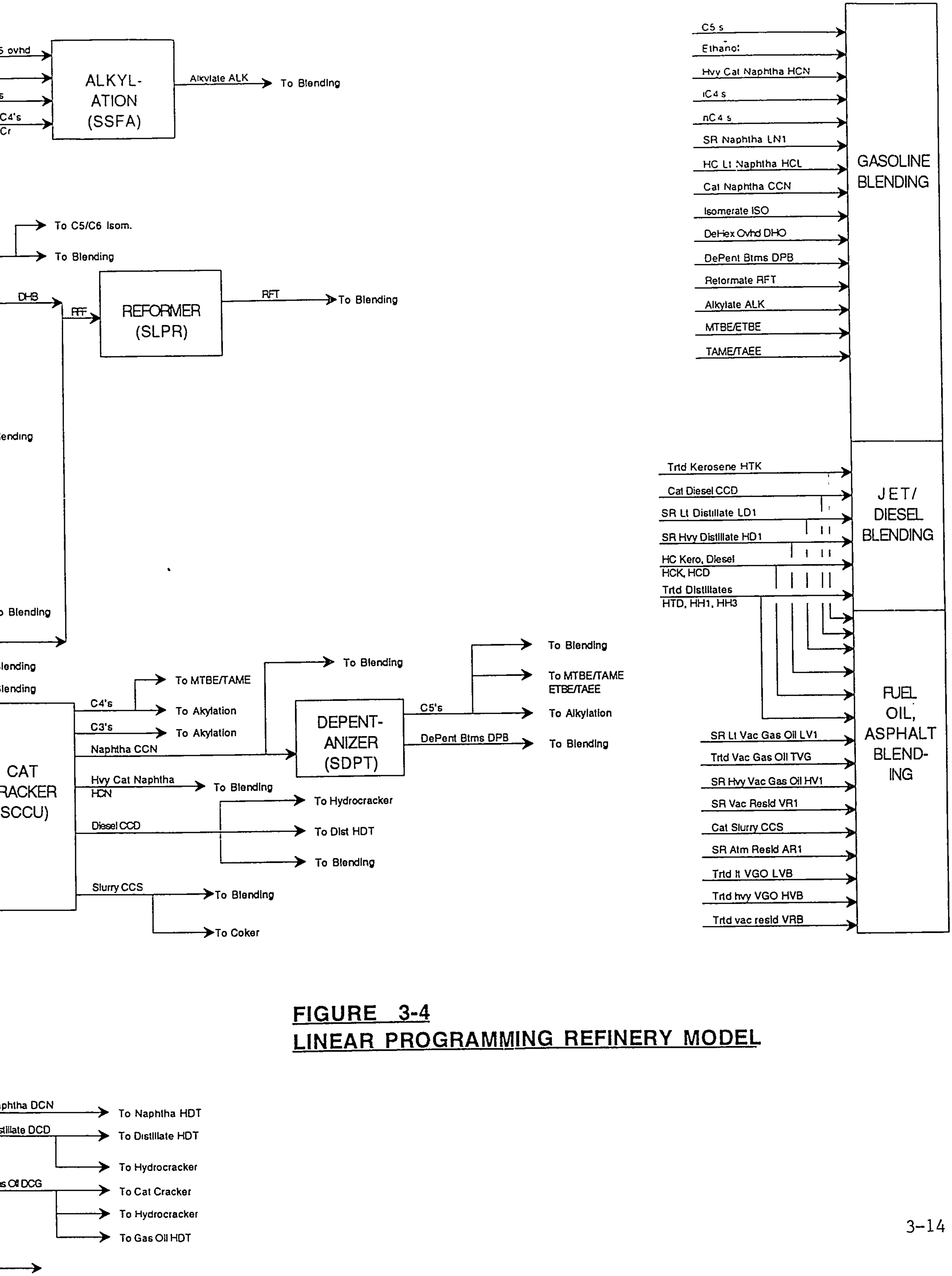


FIGURE 3-4
LINEAR PROGRAMMING REFINERY MODEL

Figure 3-5
Case 2 - Refinery/LPMAS
Rate of return

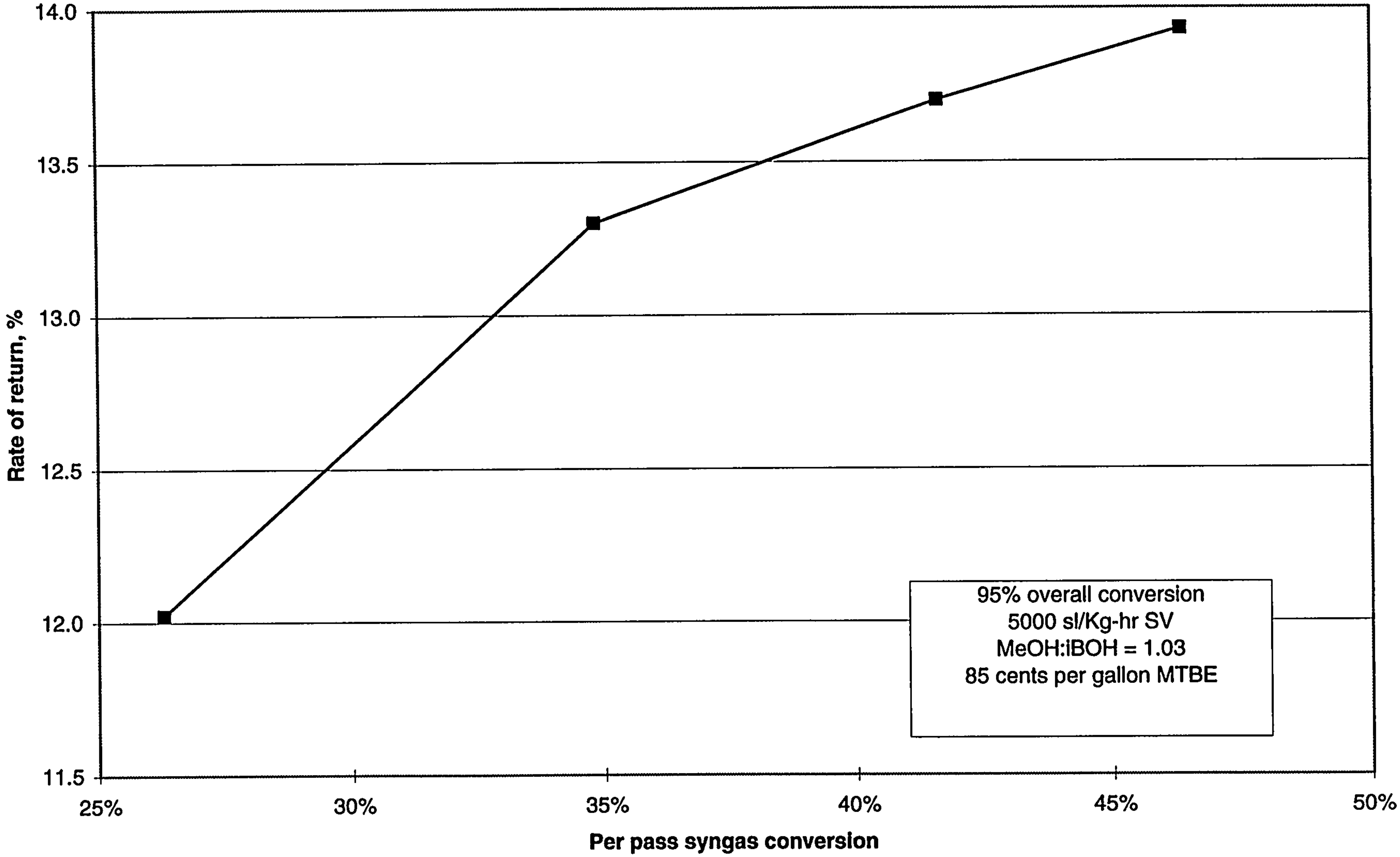


Figure 3-6
Case 2 - Refinery/LPMAS
Catalyst Productivity