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Options for Reducing Benzene in the Refinery Gasoline Pool

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Options for Reducing Benzene in the Refinery Gasoline Pool

Introduction

US refiners are in the process of planning and executing capital projects to comply with the new MSAT (Mobile Source Air Toxics) II regulations that become effective January 1, 2011. These new rules will restrict the annual average benzene level in the gasoline sold in U.S. except California to 0.62 vol%. California has similar restrictions on gasoline benzene content.

Of the various refinery streams that are blended into gasoline 70 – 85% of the benzene is contributed by reformate from catalytic reforming and 10-25% by FCC gasoline. Most MSAT II compliance strategies focus on reducing benzene in reformate. The benzene content in reformate can be changed by either removing compounds in the reformer feed that form benzene in the reforming reaction or by removing benzene from reformate by hydrotreating or solvent extraction. Removal of benzene from FCC gasoline is less straight forward. The relationship of feed properties and reaction process conditions to the production of various compounds in a FCC unit is complex and thus does not present a straight forward solution for benzene control. Further, FCC gasoline contains olefins and heavier aromatics that are the major contributors to the octane of this stream. Any hydroprocessing route focused on benzene reduction would also saturate a significant portion of these compounds.

There are several options for reducing the benzene content in gasoline:

- Reduce benzene precursors in catalytic reformer feed via fractionation.
- Saturate benzene contained in light straight run and/or light hydrocrackate.
- Install a reformate splitter to produce a benzene rich stream followed by hydroprocessing to remove benzene.
- Remove benzene from reformate with solvent extraction.
- Purchase benzene credits from other refineries. The maximum average benzene content must still be below 1.3 vol%.

The magnitude of the benzene reduction achievable with the above options is presented in a refinery case study that follows. An optimization study to establish the design parameters for a new naphtha fractionator is also presented. This study considers the sensitivity of the column design to reflux ratio and light and heavy naphtha qualities. The tower size is then optimized based on capital and operating costs.

MSAT II Regulations:

Currently the benzene content of reformulated gasoline, which represents about one third of all US gasoline, is limited to 1.0 vol% . The benzene in the balance of the US pool (conventional gasoline) is regulated relative to historical base line levels. The new regulations will reduce the average benzene concentration in gasoline to 0.62 vol%. Since this is a corporate average, standard individual facilities in a refiners system can have higher benzene levels but are limited to a 1.3 vol% maximum average. Refiners who meet the corporate average standard by purchasing credits must meet the maximum average standard (1.3 vol%) by July 1, 2012. The new regulations also provide controls for portable gasoline containers in 2009 and phased in controls for cold temperature exhaust starting in 2010.

Benefits of Benzene Removal (1):

The 1999 National Air Toxics Assessment addressed 177 air toxics and identified benzene as one of the worst. The study concluded that Mobile Source Air Toxics are responsible for 44% of outdoor toxic emissions and 50% of cancer risks. Benzene was identified as the most significant contributor to cancer risk. People who live or work near major roads or live in houses with attached garages are at the highest risk. By 2030 it is estimated that the MSAT II regulations will be responsible for reductions of air toxics by 330,000 tons and benzene emissions by 61,000 tons. Further, passenger vehicles will emit 45% less benzene and portable containers 80% less benzene. Cancer risks from all MSATS will be reduced by 30% and cancer risk from benzene is estimated to be reduced by 37%.

Benzene in Gasoline:

Benzene is present in virgin materials such as crude oil and condensate that is a by product of natural gas processing. Benzene is also formed in a number of catalytic and thermal processes in the refinery. Table 1 shows a typical range of benzene concentrations for various refinery streams (2).

Table 1

Benzene Content and Typical Gasoline Fraction of Gasoline Blendstocks

	Benzene Level Vol%	Typical Volume in Gasoline Vol%	Typical Contribution to Gasoline Benzene Content %
Reformate	1 - 6	30	70 - 85
FCC Gasoline	0.5 - 1.2	35 - 40	10 - 25
Alkylate	0	10 - 15	-
Isomerate	0	5 - 10	-
Light Hydrocrackate	1 - 3	0 - 4	4
Light Straight Run (LSR)	0.3 - 4	5 - 10	2
Light Coker Naphtha	1 - 3	0 - 2	1
Natural Gasoline	0.3 - 3	0 - 5	1
Butane	0	3 - 5	-

Figure 1 shows a block flow diagram of a notional 150,000 BPSD refinery. Major process conversion units include isomerization, catalytic reforming, FCC, alkylation and delayed coking. Hydroprocessing facilities for naphtha, kerosene, diesel, FCC feed and FCC gasoline are also included. The gasoline pool benzene concentration is 1.68 vol %.

Figure 2 shows the Base Case naphtha processing configuration. Full range virgin naphtha from crude distillation is combined with coker naphtha and naphtha from the diesel and gas oil hydrotreaters and processed in a naphtha hydrotreater for sulfur and nitrogen removal. The hydrotreated naphtha is fractionated in a 30 tray splitter with a reflux to distillate ratio of 1.2. The light naphtha overhead contains 2.6 vol % C_7+ and is processed in an isomerization unit. The splitter bottoms flows to the reformer. In the reformer, benzene is formed via several pathways:

- Dehydrogenation of cyclohexane to benzene
- Isomerization of methylcyclopentane to cyclohexane then dehydrogenation to benzene
- Conversion of C_6 paraffins to cyclohexane followed by dehydrogenation to benzene
- Hydrocracking (de alkylation) of heavier aromatics to benzene

In the Reformer, benzene precursors in the feed (C6 paraffins, cyclohexane and methylcyclopentane) are partially converted to benzene. Cyclohexane conversion to benzene is essentially 100%. About half of the methyl cyclopentane and 20% of the C_6 paraffins are converted to benzene. Additional benzene is formed in the reformer by hydrocracking heavier aromatics. This route to benzene formation is a function of the reformer operating pressure and reformer severity. In the base case example with the 30 tray naphtha splitter the combined benzene, cyclohexane and methylcyclopentane in the reformer feed is 4.05 vol%. The benzene content of the reformate product is 4.5 LV% benzene.

Benzene Reduction Options:

Figures 3 and 4 show two benzene removal options (Case 1 and 2) where a new naphtha splitter with 60 trays is installed to reduce the concentration of benzene, cyclohexane and methylcyclopentane in the reformer feed to less than 0.5 vol%. The splitter overhead C_7 + content is held at 2.5 vol% to limit liquid yield loss in the isomerization unit. The number of trays selected for this application was based on an optimization of equipment and operating costs. More details of this evaluation are given later.

Since much of the C_6 material that was included in the base case reformer feed is now removed in the new splitter overhead, the feed to the isomerization unit is increased by about 15%. For Case 1 (Figure 3) it is assumed that the existing Isomerization Unit is operating at capacity, thus the excess volume of light straight run produced is bypassed directly to the gasoline pool. This results in a reduction in the reformate benzene content from 4.5 to 1.0 vol%. The gasoline pool benzene concentration is reduced to 0.63 vol% which is very close to the new gasoline pool average limit. Typically the naphtha fractionation approach can come very close to meeting the new benzene limit, and in some cases, will be sufficient. Obviously for this approach the benzene content of the FCC gasoline is very important.

Based on the recent revision to the renewable fuels standard (RFS) the US gasoline pool will average about 10 vol% ethanol in the future thus the naphtha fractionation approach could be an acceptable strategy for many refineries. The only uncertainty is the relative timing of the revised RFS and the MSAT II regulations.

Since about 15% of the light straight run bypasses the isomerization unit the overall pool R+M/2 is estimated to be reduced by 0.24 numbers. The pool octane reduction can be off set by increasing the reformer severity by about 1.0 RONC, however this increases the reformate benzene content to 1.1 vol% and the gasoline pool benzene content to 0.66 vol%. Higher reformer severity may require a reformer revamp. Other options to offset the reduction in pool octane are:

- Produce less premium gasoline.
- Offset the octane loss by blending ethanol in the finished product. This would also allow a proportionally higher benzene level in the refinery gasoline pool.

Case 2 (Figure 4) is similar to Case 1, but it is assumed that the existing isomerization unit is revamped to handle the increased feed. The gasoline pool benzene content is 0.61 vol%. The benzene in the reformate is 1.0 vol % and pool octane is reduced by 0.14 R+M/2.

Another consideration for the naphtha fractionation approach is that individual refineries can have an average gasoline pool benzene content up to 1.3 vol% as long as the average for the corporation is no greater than 0.62 vol%. This could allow a refiner to use a combination of naphtha fractionation in some sites to get the plant pool average below 1.3 vol % and benzene conversion or extraction technology (which can achieve pool benzene concentrations well below the limit) at other sites to satisfy the corporate average gasoline pool benzene limit.

In Case 3 (Figure 5) a configuration for removing benzene from reformate is employed. A reformate splitter is installed to yield a light reformate stream that contains essentially all of the benzene. The light reformate may then be processed in one of several proprietary schemes involving benzene saturation, benzene alkylation or solvent extraction. For Case 3 a benzene saturation approach is assumed. A pool average benzene content of 0.6 vol % is achieved by feeding about 80% of the whole reformate to the splitter and benzene saturation unit. The gasoline pool R+M/2 is reduced by 0.2. The reformate benzene content is identical to the base case of 4.5 vol %. The octane loss could be off set by increasing the reformer severity. Another option to recover the lost octane would be to utilize a combination benzene saturation /isomerization unit.

Table 2 shows a summary of the results of the cases evaluated.

Table 2

	Base Case	Case 1 New Naphtha Splitter Excess LSR Bypass Isom Unit	Case 1A New Naphtha Splitter Excess LSR Bypass Isom Unit Increase Reformate Severity	Case 2 New Naphtha Splitter No Excess LSR Bypass Isom Unit	Case 3 New Reformate Splitter & Benzene Saturation Unit
Benzene in Total Gasoline, LV%	1.68	0.63	0.66	0.61	0.60
LSR Production	Base	Base x 1.15	Base x 1.15	Base x 1.15	Base
(R+M)/2	Base	Base - 0.24	Base	Base - 0.14	Base - 0.20
Benzene in Reformate, LV%	4.5	1.0	1.1	1.0	4.5
Reformate RON Clear	Base	Base	Base + 1.0	Base	Base
% of Benzene in Reformate Saturated	0	0	0	0	80%

Fractionator Optimization:

The benzene removal strategies that have been addressed here employ a new fractionator for either reformer feed or reformer product. Either of these applications require distillation columns with a large number of trays and significant energy input to achieve the separation desired. The size of the naphtha splitter for the naphtha fractionation case was based on an optimization exercise that considered the variation of capital and operating costs relative to the number of trays in the column. The splitter system (Figure 6) consisted of a feed/bottoms exchanger, the splitter column, overhead condenser, overhead receiver, combined reflux/product pump, overhead trim cooler, steam reboiler and bottoms pumps.

The bottoms fractionation specification was set at 0.5 vol% combined benzene, cyclohexane and methyl cyclopentane. Figure 7 shows the sensitivity of this specification to the reflux ratio for columns with 40, 50, 60 and 70 trays. The full range naphtha feed temperature was set at 200^{o}F. The C_7+ content of the overhead was set at 2.5 vol% based on the sensitivity of this specification to the reflux ratio (Figure 8). The feed tray location was established in a similar fashion (Figure 9). The overhead receiver temperature and pressure were set at 115^0F and 5 psig.

Sized equipment lists and utilities were developed for the four tower tray options noted above. The price of the equipment was obtained and a factored cost estimate prepared for each case based on US Gulf Coast labor.

Less energy input is required to meet the overhead and bottoms product specifications as the number of trays is increased. For each case the annual operating cost was calculated based on a steam cost of $9.22 per MLBs. Table 3 shows the capital and yearly operating cost for each case. The evaluated cost was then calculated as the capital cost plus three years of operating cost and plotted as a function of the number of trays (Figure 10). Based on this evaluation method a 60 tray tower has the lowest evaluated cost, however, the variation of this parameter is only 1 – 2 % for 50 and 70 tray towers respectively. From a practical stand point one would want to have a suitable design margin for the reboiler, condenser and reflux pumps to handle feed flow and composition variations.

Table 3

40,000 BPD Naphtha Splitter				
Number of Trays	40	50	60	70
Steam, 1000 lb/hr	83.6	71.0	66.6	64.7
Electricity, kW	316	279	260	245
Cooling Water, gpm	96	96	96	96
Total Utility Cost, $ MM/yr	7.11	6.05	5.67	5.51
Total Installed Cost, $ MM	21.4	21.1	21.4	22.7
Steam = $9.92 /1000 lb Electricity = $0.077/kW				

Figure 10 also shows the impact of energy costs 25% lower and higher than the base values from above. This does not materially alter the previous conclusions; although there is a slight shift to more trays for the higher energy cost.

Table 4 shows the equipment sizes and estimated delivery times for the 60 tray tower and auxiliary equipment.

Table 4

Size equipment List for 60 Trays Design
40,000 BPSD Naphtha Splitter

Service	Size	Estimate Delivery Schedule Weeks
Naphtha Splitter	12'-0" I.D. x 150'-0" T/T, 60 trays	~ 50
Overhead Receiver	8'-0" x 24'-0"	~ 30
Reboiler	Two 3465 ft2 Exchangers in Parallel	~ 45
Feed/Bottoms Exchanger	Two 1920 ft2 shells in Series	~ 45
Overhead Condenser	Air Cooler, 29,000 ft2 Bare Tube Area	~ 45
Overhead Product Trim Cooler	One 760 ft2 Shell	~ 45
Overhead Reflux Pumps	Two 1325 gpm pumps (one as spare) Include 20% design Margin	~ 45
Bottoms Product Pumps	Two 1040 gpm pumps (one as spare) Include 10% design Margin	~ 45

Conclusions:

The MSAT II regulation will become effective on Jan. 1, 2011 and will require that the corporate average gasoline pool benzene content not exceed 0.62 vol %. There are several strategies that are being considered by refiners to comply with this regulation but most approaches involve some modification to the naphtha reforming area of the refinery. The installation of a naphtha splitter designed to limit benzene, cyclohexane and methyl cyclopentane in the reformer to around 0.5 vol % can reduce the benzene in reformate by about 80% which results in a gasoline pool benzene content very close to the MSAT II limit of 0.62 vol %. The revised renewable fuels standard will require that the US gasoline pool contain about 10 vol % ethanol in the future, thus the naphtha fractionation approach would be an acceptable strategy for many refineries.

An alternate, more robust compliance approach is to fractionate the reformer product to produce a light reformate stream containing essentially all of the benzene. This stream is then processed in a conversion facility where the benzene is converted to cyclohexane. In the study case presented, 80% of the benzene produced by the reformer had to be converted in order to attain a gasoline pool benzene content of 0.6 vol %.

All of the benzene removal options addressed resulted in some overall refinery gasoline pool octane reduction. This octane loss can be offset by increasing reforming severity or reducing the volume of premium gasoline. The future inclusion of increased volumes of ethanol in gasoline as noted above would more than offset the octane penalties identified in the examples above.

A naphtha splitter system design to limit benzene plus benzene precursors to 0.5 vol % was prepared for the refinery example presented in this paper. Based on an evaluation of capital and operating costs a tower with 60 trays was selected. The variation of the selection parameter, evaluated cost, only changed marginally between 50 and 70 trays. A variation in energy costs of 25% above and below the base value did not impact the selection of the optimum number of trays.

References:

1. Control of Hazardous Air Pollutants from Mobile Sources; Summary for EPA 40 CFR 59,80,85 and 86.
2. Regulatory Impact Analysis, Control of Hazardous Air Pollutants from Mobile Sources: Table 6-3-1, p. 6-17. US EPA 420-R-07-002, February 2007

FIGURE 1

BASE CASE 150,000 BPSD REFINERY

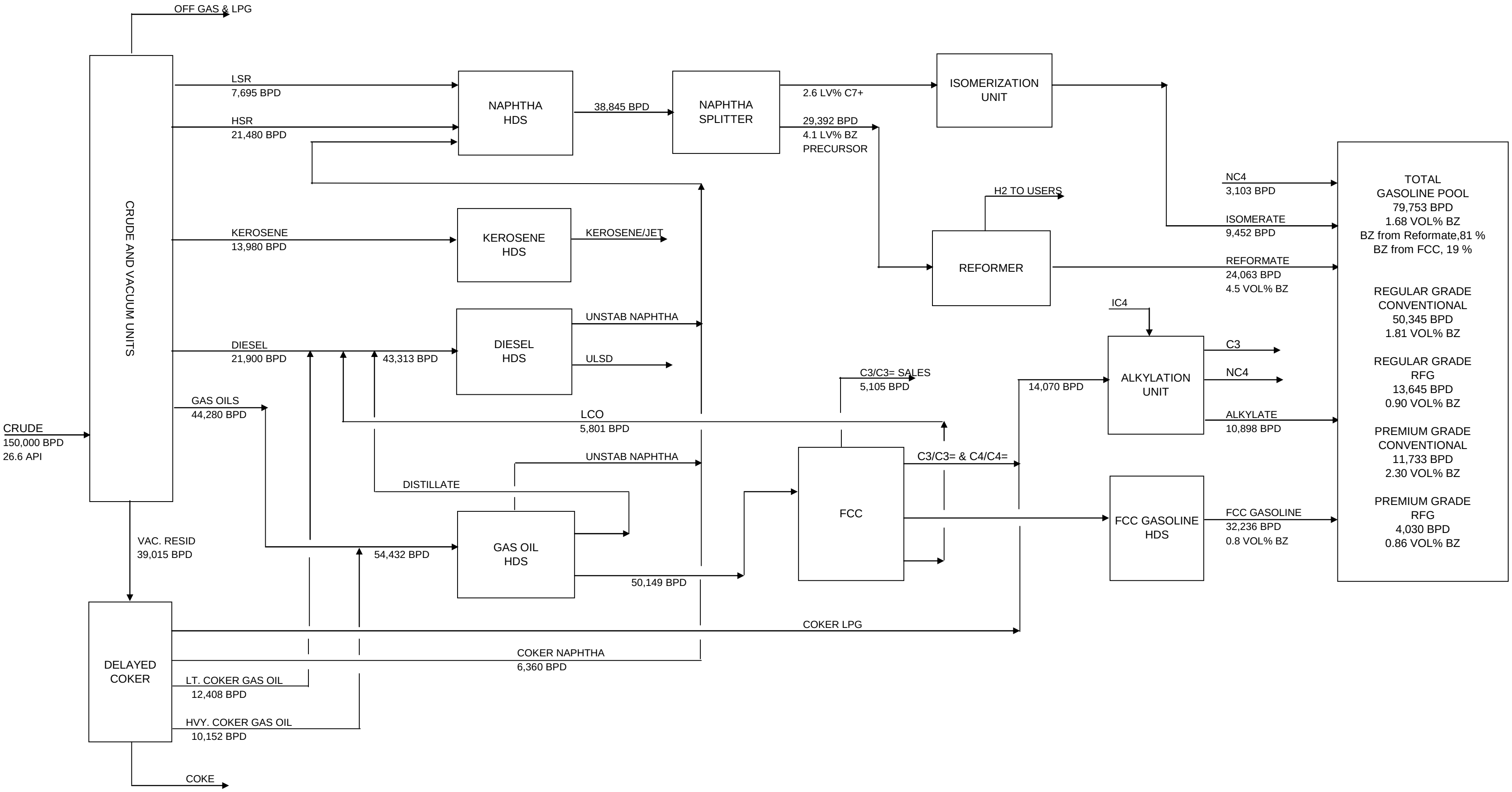
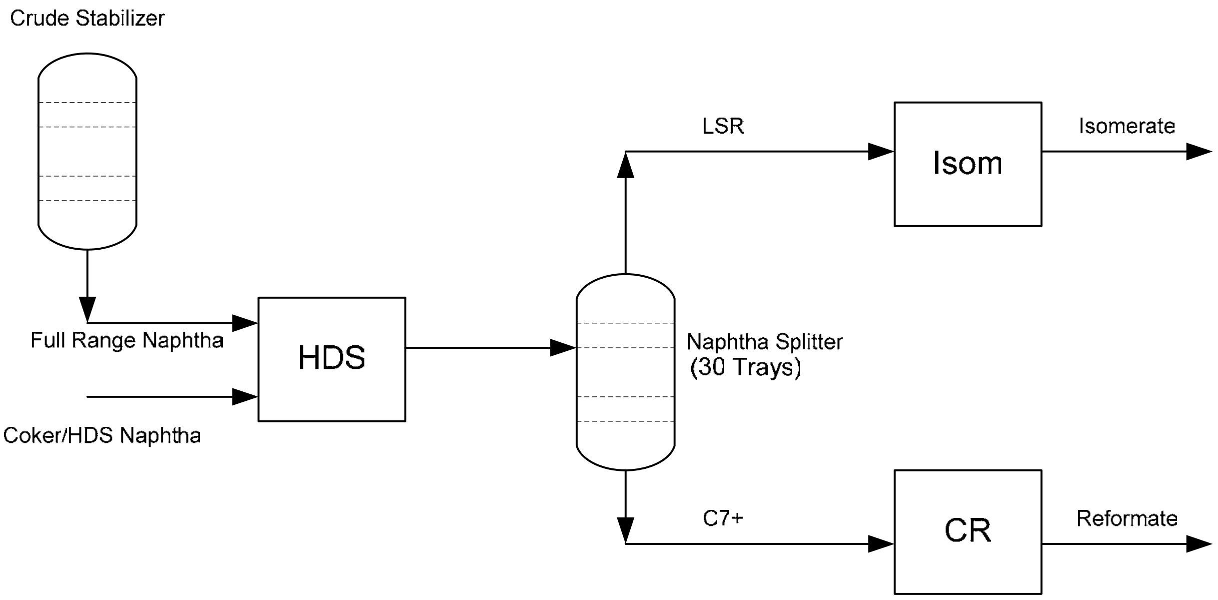


FIGURE 2

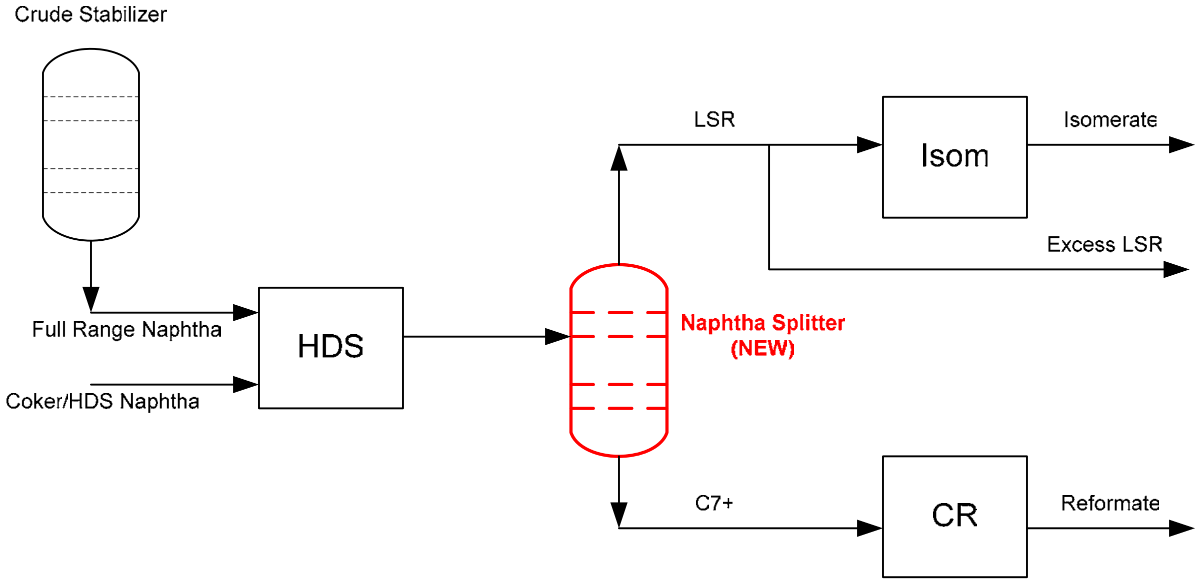
Base Case



LSR Production	Base
Benzene in Pool	1.68 LV%
Pool (R+M)/2	Base
Benzene in Reformate	4.5 LV%
Reformer Severity, RONC	Base

FIGURE 3

Case 1
New Naphtha Splitter By Pass Isom



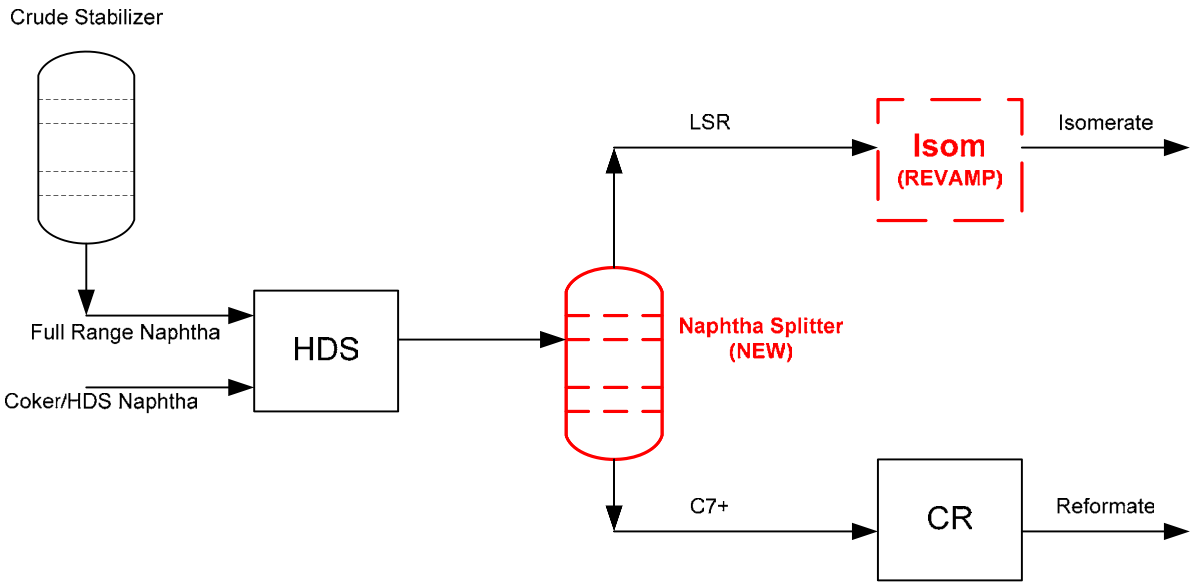
LSR Production	Base x 1.15
Benzene in Pool	0.63 LV%
Pool (R+M)/2	Base – 0.24
Benzene in Reformate	1.0 LV%
Reformer Severity, RONC	Base

* To maintain pool base (R+M)/2, Reformer severity
Would have to increase by about 1.0 RONC.

FIGURE 4

Case 2

New Naphtha Splitter Revamp Isom

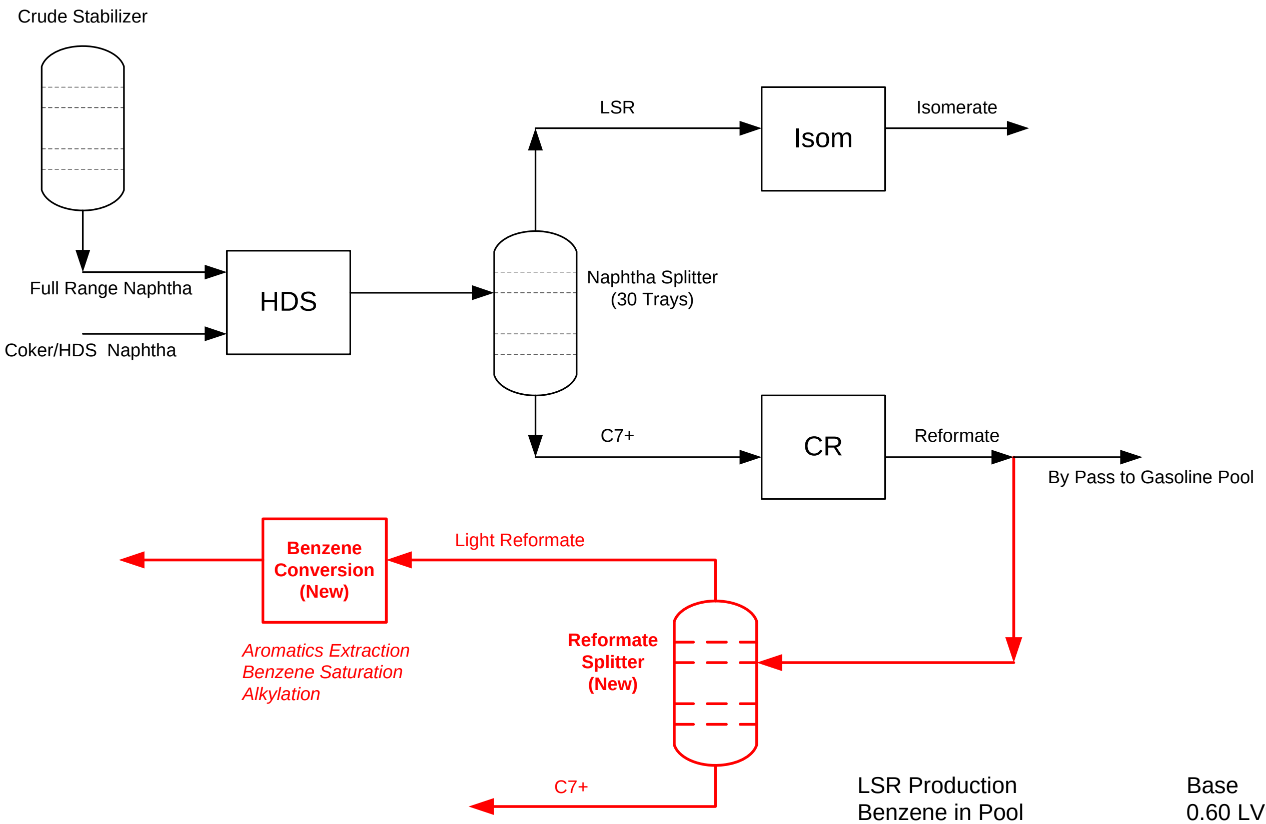


LSR Production	Base x 1.15
Benzene in Pool	0.61 LV%
Pool (R+M)/2	Base – 0.14
Benzene in Reformate	1.0 LV%
Reformer Severity, RONC	Base

Options for Reducing Benzene in the Refinery Gasoline Pool

FIGURE 5

Case 3
Benzene Conversion



LSR Production	Base
Benzene in Pool	0.60 LV%
Pool (R+M)/2	Base – 0.2
Benzene in Reformate	4.5 LV%
Reformer Severity, RONC	Base
% Benzene in Reformate Saturated	80%

FIGURE 6

New Naphtha Splitter

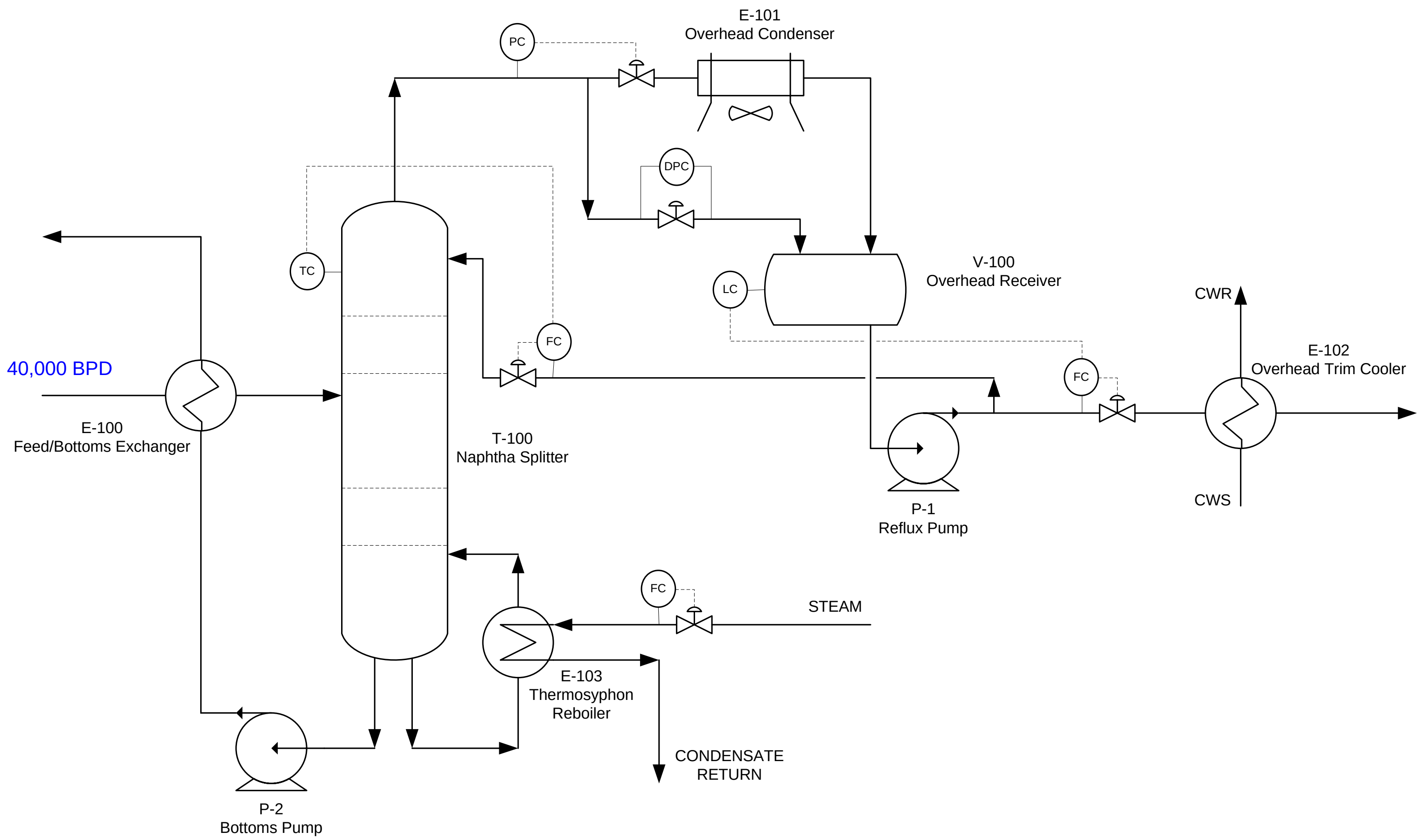


FIGURE 7

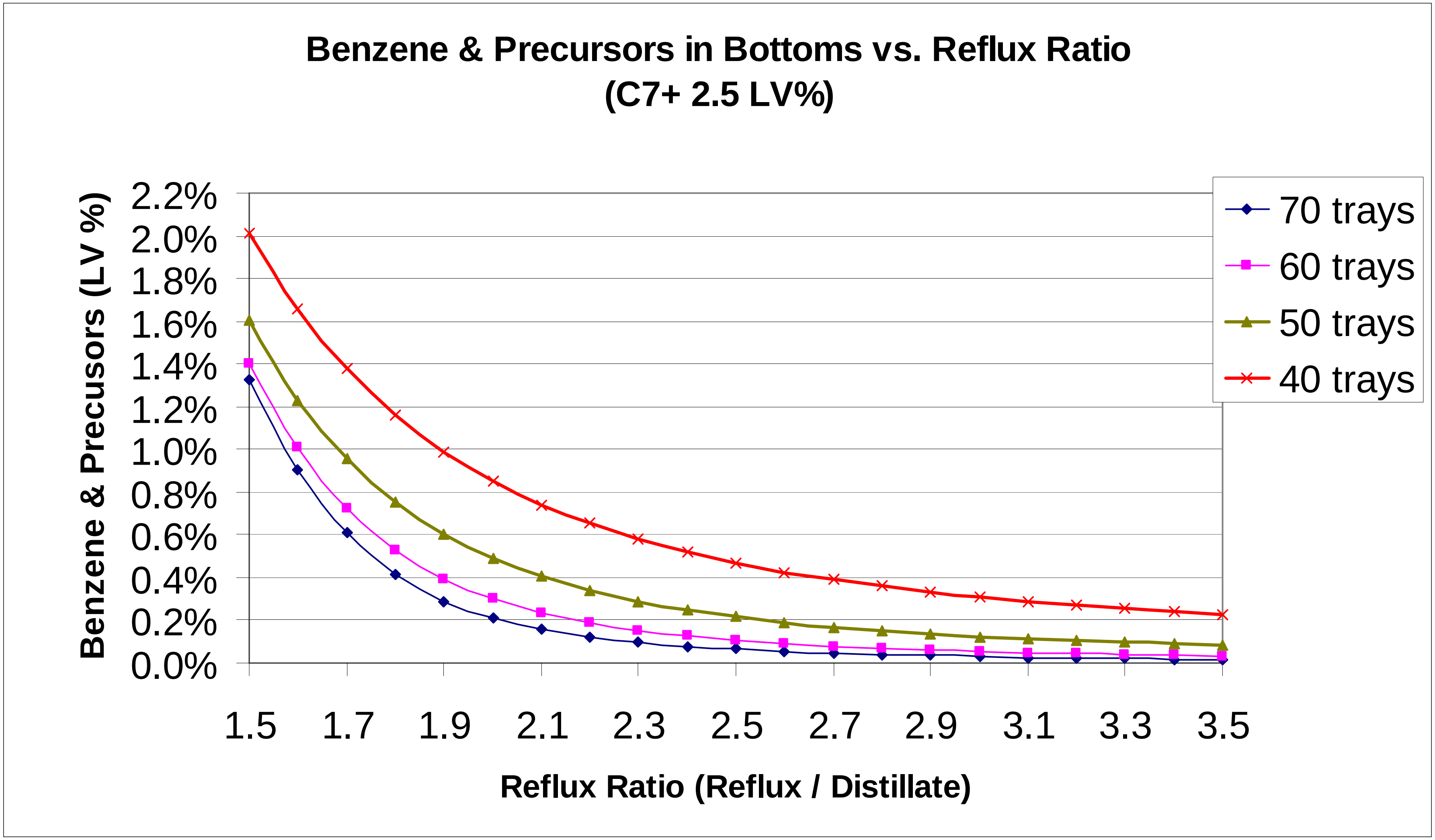

Benzene & Precursors in Bottoms vs. Reflux Ratio
(C7+ 2.5 LV%)
Benzene & Precusors (LV %)
2.2%
2.0%
1.8%
1.6%
1.4%
1.2%
1.0%
0.8%
0.6%
0.4%
0.2%
0.0%
1.5
1.7
1.9
2.1
2.3
2.5
2.7
2.9
3.1
3.3
3.5
Reflux Ratio (Reflux / Distillate)
70 trays
60 trays
50 trays
40 trays

FIGURE 8

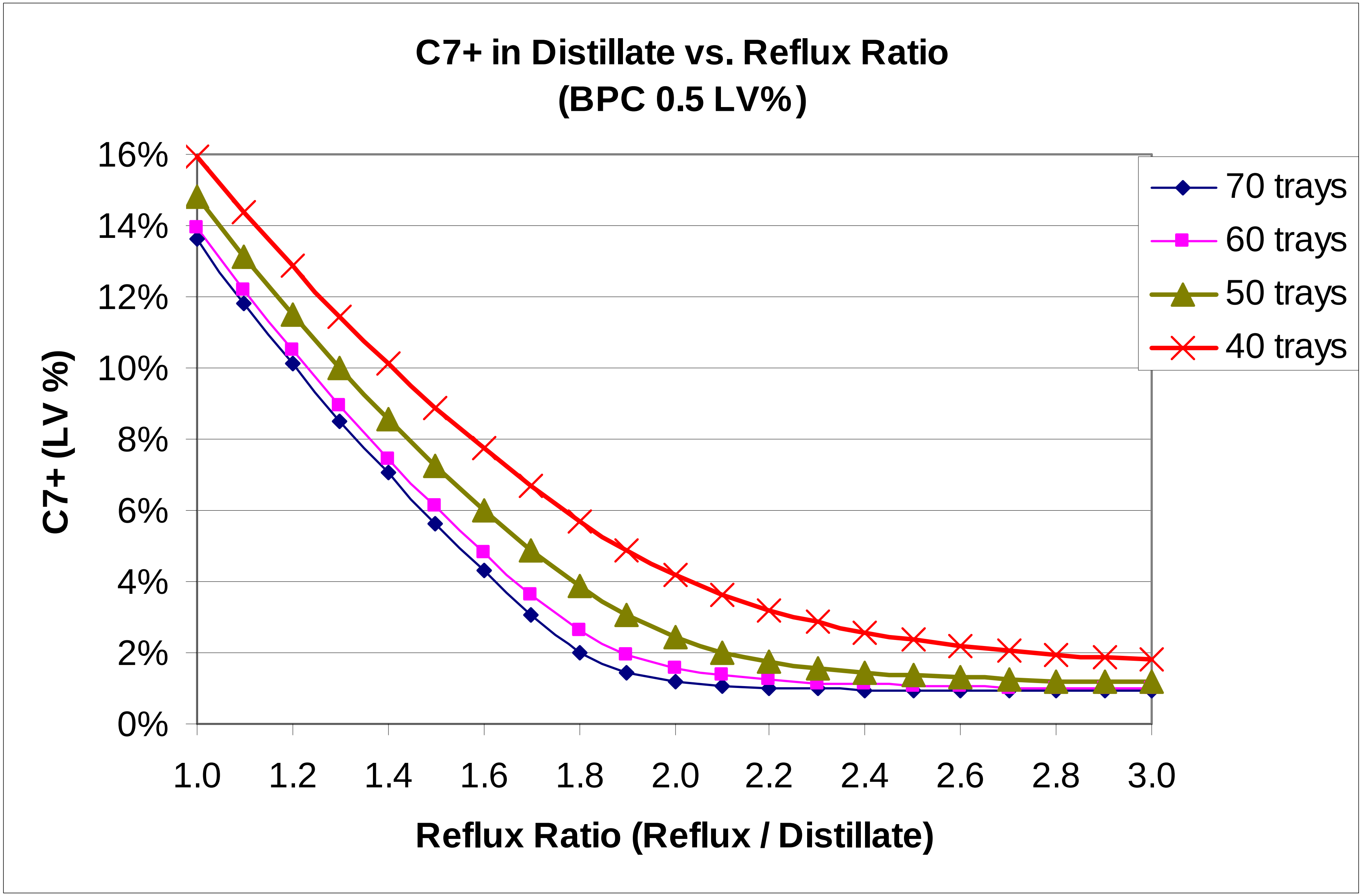

C7+ in Distillate vs. Reflux Ratio
(BPC 0.5 LV%)
C7+ (LV %)
16%
14%
12%
10%
8%
6%
4%
2%
0%
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
Reflux Ratio (Reflux / Distillate)
70 trays
60 trays
50 trays
40 trays

FIGURE 9

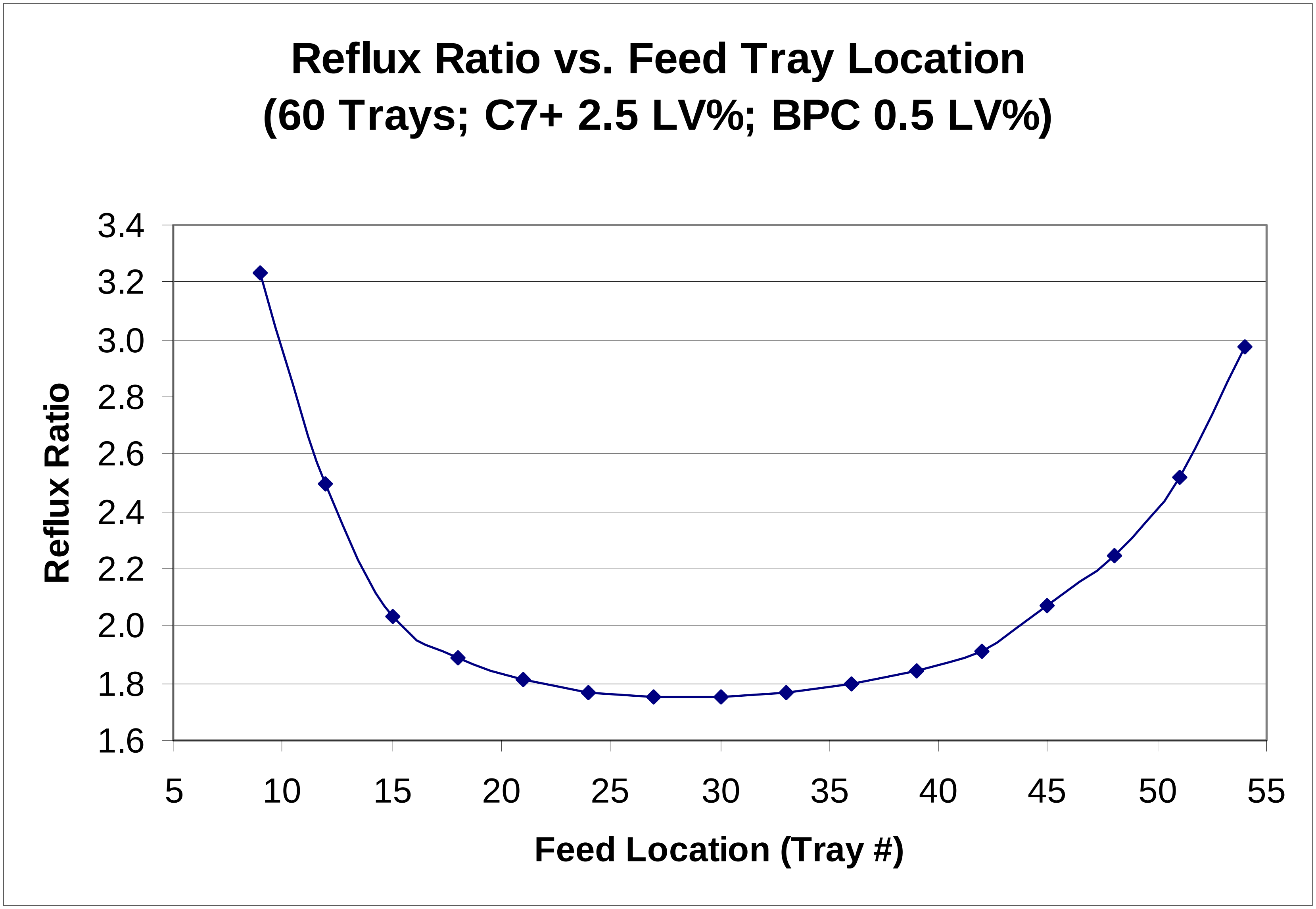
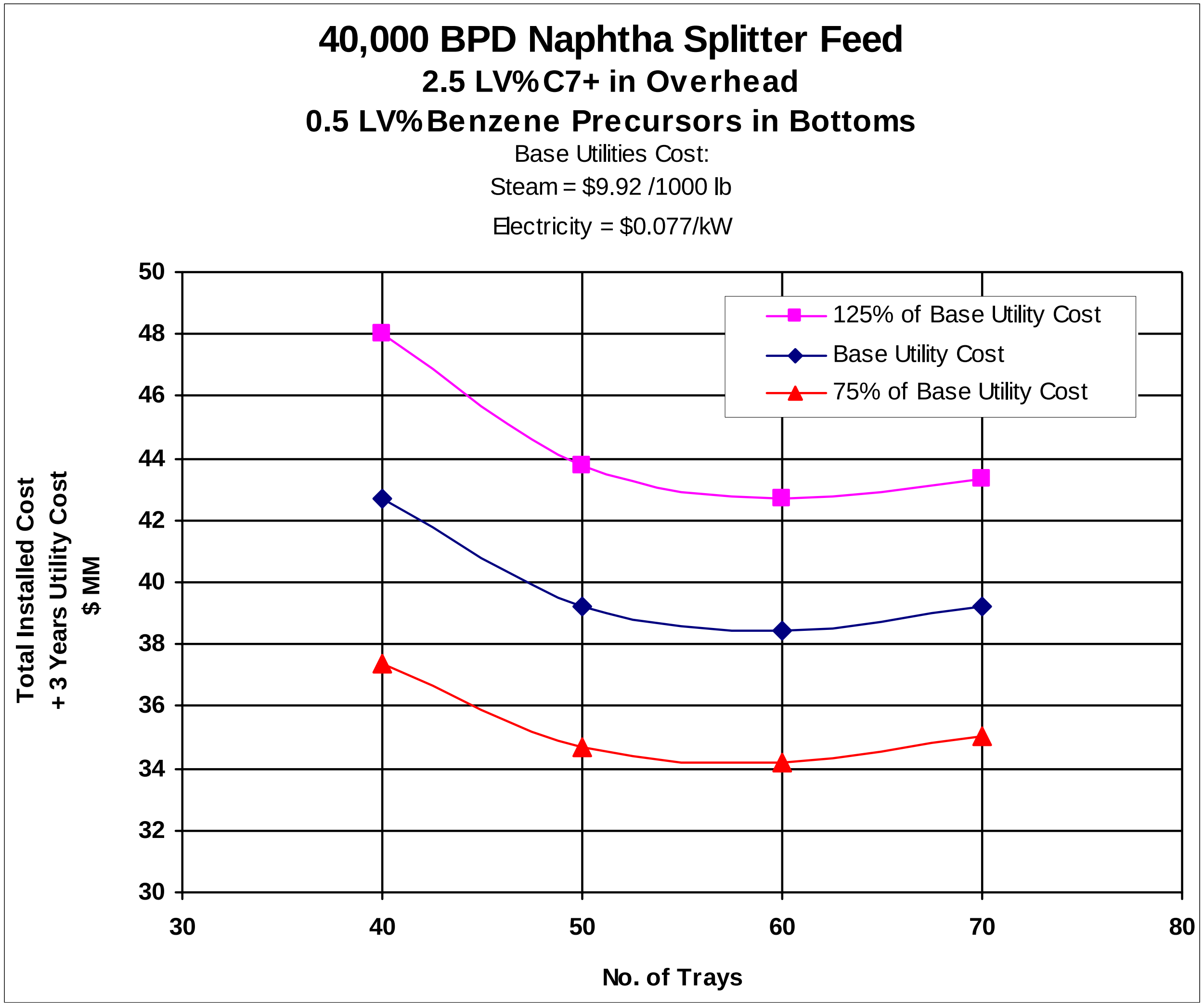

Reflux Ratio vs. Feed Tray Location
(60 Trays; C7+ 2.5 LV%; BPC 0.5 LV%)
Reflux Ratio
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
5
10
15
20
25
30
35
40
45
50
55
Feed Location (Tray #)

FIGURE 10


40,000 BPD Naphtha Splitter Feed
2.5 LV% C7+ in Overhead
0.5 LV% Benzene Precursors in Bottoms
Base Utilities Cost:
Steam = $9.92 /1000 lb
Electricity = $0.077/kW
125% of Base Utility Cost
Base Utility Cost
75% of Base Utility Cost
Total Installed Cost
+ 3 Years Utility Cost
$ MM
50
48
46
44
42
40
38
36
34
32
30
30
40
50
60
70
80
No. of Trays