

# **IMPACT ON FUTURE REFINERY OF PRODUCING ULTRA LOW SULFUR GASOLINE**

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## **INTRODUCTION**

On December 21, 1999, the EPA issued regulatory announcements for “Tier 2” emission standards for vehicles and gasoline sulfur standards for refineries and flexibility in meeting “Tier 2” standards. These regulations apply to vehicles that weigh up to 10,000 lbs. and will reduce ultimately the sulfur content of fuel from a United States present average of 340 ppm to 30 ppm (peak of 80 ppm) phased in from 2004 to 2008. Based on review of proceedings for the public hearings of the proposed “Tier 2” standards, it is apparent that there is a very strong lobby by the Alliance of Auto Manufacturers, automobile companies, health organizations, and environmental organizations to do even more, i.e., ultra low sulfur fuels (5 to 10 ppm of sulfur). This drive for lower sulfur fuels is the result of anticipated enhanced performance of existing vehicles’ catalytic pollution control systems using higher quality fuel and a move towards introduction of more efficient, direct fuel injection engines that may use NOx catalyst traps that are sensitive to fuel sulfur. Based on the strong lobby strength with government regulators of many of these companies and organizations, we believe ultra low sulfur gasoline and diesel will be the fuels of the future and the timing for introduction fuels could overlap the phase-in of 30 ppm average sulfur gasoline. It should be noted that present requirement for California’s CARB gasoline is 30 ppm sulfur and a number of states with areas of severe pollution are considering opting into a CARB program. California has recently announced their intention of further reducing the sulfur specification of CARB gasoline to 15 ppm.

Two excellent reports have been prepared by MathPro, Inc. (References 1 and 2) for The American Petroleum Institute and The Alliance of Automobile Manufacturers for estimating the cost of producing 40 ppm and 10 ppm sulfur content gasoline. These studies utilized pseudo linear programming models that were representative of an average refinery for PAD’s 1 through 3. The goal of this paper is not to duplicate this previous work but to analyze the impact of producing ultra low sulfur gasoline using a specific refinery configuration.

Case studies were developed for two hypothetical U.S. Gulf Coast conversion refineries processing sweet (Brent type) and medium high sulfur (Light Arabian type) crudes. A base case model for each refinery was developed based on an assumed conventional/RFG gasoline pool split with a fixed premium/regular ratio for conventional and reformulated grade gasolines. The incremental capital investment, operating costs, and white products balances were then determined for reducing the gasoline pool average sulfur content to 30, 10, and 5 wppm. Stancil and Co. of Dallas, Texas assisted us by using LP modeling to optimize the gasoline pool for each case based on maximizing the production of premium gasoline while meeting all product specifications and tailpipe emission limits per EPA complex model. Based on these results, the incremental per gallon cost, including investment related charges of reducing the average sulfur content of the gasoline to the above targets was estimated.

## Base Case Refineries

Simplified block flow diagrams for the two different crude oil feed types are presented in Figures 1 and 2. Key features of the base case refineries assumed to be operated for maximum gasoline production are summarized below:

<u>Crude Oil Type</u>	<u>Brent</u>	<u>Light Arabian</u>
Feed Sulfur, wt. %	0.44	1.78
Feed Rate, BPCD	150,000	150,000
<u>Crude Fractionation</u>		
Crude Unit	Yes	Yes
Vacuum Unit	Yes	Yes
<u>Conversion Units</u>		
FCCU	Yes	Yes
Conversion, LV %	80	80
Delayed Coker	Yes	Yes
H <sub>2</sub> SO <sub>4</sub> Alkylation	C <sub>4</sub> 's	C <sub>4</sub> 's
CCR Reformer	Yes	Yes
Severity, RON	100	100
MTBE	Yes	Yes
<u>Treating Units</u>		
LPG Caustic Extraction	No	Yes
LSR Caustic Extraction	No	Yes
Lt. Coker Gasoline		
Caustic Treating	Yes	Yes
Reformer Feed HDS	Yes	Yes
Kerosene HDS	No	Yes
Kerosene Caustic Treating	Yes	No
Diesel HDS	Yes	Yes
FCCU Feed HDS	No	Yes
% HDS	--	87.9
FCCU C <sub>3</sub> 's, Caustic Trt.	Yes	Yes
FCCU C <sub>4</sub> 's, Caustic Trt.	Yes	Yes
FCCU Gasoline		
Caustic Treating	Yes	Yes

Both base case facilities are considered advantaged refineries for gasoline sulfur reduction because the pool sulfur content for Brent and Light Arabian are 227 ppm and 81 ppm, respectively, which is significantly less than the United States' average sulfur content of approximately 340 ppm. It is anticipated that a severely disadvantaged refinery may produce a gasoline with an average sulfur content of 600 ppm or higher and would be more severely impacted when producing ultra low sulfur gasoline. As expected, most of the sulfur is concentrated in the FCC gasoline. The gasoline pool sulfur distributions are presented below:

### **% of Pool Sulfur**

<u>Gasoline Component</u>	<u>Brent Case</u>	<u>Light Arabian Case</u>
LSR	1.37	3.59
Light Coker Gasoline	1.38	9.79
Reformate	0.18	0.45
Alkylate	0.35	1.09
MTBE	0.21	0.56
FCC Gasoline	<u>96.51</u>	<u>84.52</u>
	100.00	100.00
Gasoline Pool Sulfur, ppm	227	81

It should be noted that based on the sulfur distributions for the Brent and Light Arabian gasoline pools, even if the sulfur in FCC gasoline could be completely eliminated, the respective sulfur content of the gasolines would still be 8 ppm and 12 ppm. Since it is not economically viable to completely desulfurize FCC gasoline, it is apparent from this analysis that production of ultra low sulfur gasoline requires a multi-faceted desulfurization approach rather than only desulfurization of FCC gasoline.

#### **Basis for the Study**

1. No consideration was given for operation of the FCCU without the FCCU Feed HDS and FCC Gasoline HDS. It was assumed that sufficient intermediate storage capacity for FCCU feed and high sulfur FCC gasoline is available. No added investment cost is included in the FCC gasoline desulfurizer for significant rerun capacity.
2. The overall desulfurization requirements were established on the basis of having the actual gasoline sulfur content equal to approximately 87% of the nominal average gasoline sulfur specification, i.e., for production of 30 ppm sulfur gasoline, the actual gasoline pool sulfur content would be 25 ppm.
3. It was not considered practical to only use more severe FCCU Feed HDS for desulfurization of the FCC gasoline although this may be economically viable for selective refineries for production of 30 ppm sulfur gasoline. The basis for this study is to only use gasoline desulfurization.
4. No considerations are included for required changes to the marketing and products' supply and distribution systems.
5. All cost estimates are of scoping quality and are based on installation at the start of 2000 in a U.S. Gulf Coast location.
6. Gasoline blending was performed on the basis of using a maximum sulfur content of an individual gasoline grade blend to average sulfur content of the pool of 80 ppm to 30 ppm (present EPA regulation).
7. The base cases include the use of ethers for production of RFG. Sulfur reduction cases assume a ban on the use of ethers and there is no oxygen mandate.

8. The operating cost basis is:

- High Pressure Steam, \$/1,000 lbs.	4.7
- Low Pressure Steam, \$/1,000 lbs.	2.5
- Refinery Fuel, \$/MMBTU	2.5
- Power, ¢/KWH	6.0
- Operating Man Shift, \$/Year	250,000
- Cooling Water, \$/1,000 gal.	0.012
- Maintenance, % of TIC	3.0

9. The value of capital employed is based on a discounted cash flow rate of return of 15.0% with: tax rate of 37.0% , ad valorem tax of 1.75%, ten year double declining depreciation, and a twenty year project life.

10. Feed and product prices are based on United States averages for the first eight months of 1999 and are:

- Propane, \$/gal.	0.300
- Butane, \$/gal.	0.387
- Conventional Regular Gasoline, \$/gal.	0.535
- Premium Conventional Gasoline, \$/gal.	0.623
- Regular RFG, \$/gal.	0.568
- Premium RFG, \$/gal.	0.674
- Purchased MTBE, \$/gal.	0.615
- Methanol, \$/gal.	0.271
- Purchased Hydrogen, \$/MM SCF	1,500

11. The impact to the refineries for producing essentially zero sulfur gasoline suitable for future fuel cell vehicles was not evaluated. Since these fuels do not have an octane requirement, severely hydrotreated naphtha could be used for this application.

### **Desulfurization Case Descriptions**

#### **Production of 30 ppm Sulfur Gasoline**

Production of 30 ppm sulfur gasoline requires an overall desulfurization level of 89% and 69% for the Brent and Light Arabian cases, respectively, with an ether ban. Since the FCC gasoline contains 97% and 85% of the total sulfur in the gasoline pool for Brent and Light Arabian cases, respectively, the nominal 30 ppm sulfur specification can be achieved by only treating the FCC gasoline stream.

Treating FCC gasoline to reduce sulfur can be accomplished primarily by hydrotreating or by other non-hydrotreating processes and the merits of each method has been presented in the literature by UOP, Exxon, CDTech, Mobil, IFP, etc., for hydrotreating, and Phillips and Black & Veatch/Pritchard for other technologies. Performing an evaluation for determining the best technology for removing sulfur from FCC gasoline is outside of the scope of this paper, thus the treating approach was fairly arbitrary but may nearly be optimum for some refinery applications. This approach, which is presented in Figure 3, uses a combination of caustic extraction of mercaptan sulfur (caustic treating) for the light FCC gasoline (C<sub>5</sub>'s and C<sub>6</sub>'s) and hydrotreating of the heavy FCC gasoline using licensed hydrotreating technology. In both refinery cases, FCC gasoline is produced as a full range distillation product and it is necessary to add an FCC gasoline fractionator to produce the different FCC distillation range streams for further treatment.

The characteristics of the light FCC gasoline include a high concentration of high octane olefins and the lowest concentration of sulfur which is mostly mercaptan sulfur that is extractable by caustic. Although a detail analysis of the sulfur components for these two crude types was not available, it was assumed that the sulfur content of the C<sub>5</sub>'s and C<sub>6</sub>'s can be reduced to less than 10 ppm while preserving the concentration of high octane olefins. CDTech also has a selective hydrotreating process, which can be used for similar results.

The heavy FCC gasoline, which has a substantially higher concentration of sulfur and aromatics, and lower concentration of olefins, is hydrotreated using licensed technology. This report is based on hydrotreating results presented in the literature that were adjusted for the feed quality and required severity. These results which are hydrotreating technology neutral should be considered results that are the average of those presented by UOP, Exxon, Mobil, and CDTech.

The same basic type of FCC gasoline treating scheme was used for all levels of desulfurization. We believe the merits of this type of processing scheme where light olefins are separated from the primary hydrotreating step is to allow the refinery an opportunity to better optimize the hydrotreater technology selection thus potentially decreasing the total investment cost and improving the overall refinery profitability. Because the overall desulfurization requirements are relatively modest for production of 30 ppm sulfur gasoline, a heart cut FCC gasoline stream is produced from the FCC fractionator. This stream, which has an intermediate level of sulfur and olefins is bypassed around the hydrotreater to further decrease the olefins in the hydrotreater feed and associated hydrotreater costs. Required operating conditions for the FCC gasoline treater block are summarized below:

**FCC Gasoline Treating Block  
30 ppm Sulfur Gasoline**

<u>Case</u>	<u>Brent</u>	<u>Arabian</u>
Overall Desulfurization, wt %	92.5	81.5
Overall Yield, LV %	99.5	99.7
Overall Road Octane Loss	0.4	0.25
FCC Gasoline S, ppm	49	34
Fractionator Fd., BPCD	27,030	27,670
Caustic Treater Fd., BPCD	8,640	8,850
Light FCC Gasoline S, ppm	10	10
FCC Gasoline Heart Cut, BPCD	4,240	8,410
FCC Hvy. Gasoline, BPCD	14,150	10,410
% HDS	97.7	95.1
Product Sulfur	24	18

The gasoline pool sulfur distributions for the two nominal 30 ppm sulfur crude oil cases are summarized below:

**% of Pool Sulfur**

<u>Gasoline Component</u>	<u>Brent Case</u>	<u>Light Arabian Case</u>
LSR	12.95	11.60
Light Coker Gasoline	13.04	31.77
Reformate	1.68	1.52
Alkylate	4.49	4.75
FCC Gasoline	<u>67.84</u>	<u>50.36</u>
	100.00	100.00
Gasoline Pool Sulfur, ppm	25	25

From the summary of the gasoline sulfur distributions for these two cases, it becomes clear that LSR, Light Coker Gasoline, and FCC Gasoline blending components are all targets for further desulfurization to produce ultra low sulfur gasoline.

Additional changes to the base cases refineries for production of 30 ppm sulfur gasoline are expanding the existing sulfuric alkylation units by 34% and 35% for the Brent and Light Arabian cases, respectively, to alkylate the isobutylene because of the assumed ether ban.

- Production of 10 ppm Sulfur Gasoline

Compared to the 30 ppm sulfur case, this option required:

- More severe treating of FCC gasoline;
- The hydrodesulfurization of light straight run and light coker gasoline by expanding the naphtha splitters in the crude units and reformer feeds HDS units. These modifications are presented in Figure 4.

The revised operating conditions for the FCC gasoline treating are summarized below:

**FCC Gasoline Treating Block  
10 ppm Sulfur Gasoline**

<u>Case</u>	<u>Brent</u>	<u>Light Arabian</u>
Overall HDS, wt %	96.9	90.8
Overall Yield, LV %	98.5	99.3
Overall Road Octane Loss	0.80	0.85
FCC Gasoline S, ppm	20	17
Splitter Tower Fd., BPCD	27,030	27,670
Caustic Treater Fd., BPCD	8,640	8,850
Light FCC Gasoline S, ppm	10	10
FCC Gasoline Heart Cut, BPCD	0	0
FCC Hvy. Gasoline, BPCD	18,390	18,820
% HDS	97.3	92.0
PPM S	24	20

Desulfurization of the light straight run and light coker gasoline is accomplished by changing the service of the naphtha splitters to desulfurized naphtha splitters and revamping of the naphtha HDS units to process the additional light naphthas. To accommodate these changes, it is necessary to expand the crude unit naphtha splitters by approximately 12 percent and 14 percent, respectively, for the Brent and Light Arabian cases. The naphtha HDS units are expanding by 28 percent and 27 percent, respectively, for the Brent and Light Arabian cases.

The gasoline pool sulfur distributions for the two nominal 10 ppm sulfur crude oil cases are summarized below:

**% of Pool Sulfur**

<u>Gasoline Component</u>	<u>Brent Case</u>	<u>Light Arabian Case</u>
Light Gasoline	1.38	1.39
Reformate	4.96	4.78
Alkylate	13.22	14.97
FCC Gasoline	<u>80.44</u>	<u>78.86</u>
	100.00	100.00
Gasoline Pool Sulfur, ppm	8	8

- Production of 5 ppm Sulfur Gasoline

In addition to the modifications required for the 10 ppm sulfur gasoline cases, these cases assume improved operation of the naphtha HDS unit to consistently reduce the treated naphtha sulfur content from 1 ppm to 0.5 ppm and replacement of the deisobutanizer caustic feed treatment in the alkylation units with modern sulfuric acid wash systems to reduce the sulfur content of the alkylates from 10 ppm to 2 ppm. In addition to these modifications, it is necessary to increase the severity of operations for the FCC gasoline treating blocks. The revised operating conditions for the FCC gasoline treating block are summarized below:

**FCC Gasoline Treating Block  
5 ppm Sulfur Gasoline**

<u>Case</u>	<u>Brent</u>	<u>Light Arabian</u>
Overall HDS, wt %	98.4	94.6
Overall Yield, LV %	98.0	99.1
Overall Road Octane Loss	1.0	0.95
FCC Gasoline S, ppm	11	10
Splitter Tower Fd., BPCD	27,030	27,670
Caustic Treater Fd., BPCD	8,640	8,850
Light FCC Gasoline S, ppm	10	10
FCC Gasoline Heart Cut, BPCD	0	0
FCC Hvy. Gasoline, BPCD	18,390	18,820
% HDS	98.5	96.0
PPM S	11	10

The sulfur content of alkylate can be as high as 10 to 15 ppm and can be a result of:

- Poor performance of the deisobutanizer tower caustic wash system;
- Adverse reactor operating conditions; and
- Outside feed streams to the deisobutanizer with high sulfur contents.

Although each refiner would have to determine the cause of the high sulfur content alkylate by using a sound, systematic troubleshooting procedure, this study assumes that sulfur content of the alkylates can be reduced from 10 to 2 ppm by installation of modern acid wash systems for treating the deisobutanizer feed. For this analysis, it is assumed that the sulfur content of the desulfurized light gasoline and reformate can be reduced from 1 to 0.5 ppm by improved operation of the naphtha HDS units. To this end, the cost of an additional operator man shift is included for better testing and control of gasoline sulfur reduction facilities. Better control of the sulfur content of the desulfurized naphtha could also be accomplished by using sulfur adsorption technology on the naphtha HDS stripper tower bottoms. No provisions are included for sulfur adsorption in this study.

The gasoline pool sulfur distribution for the two nominal 5 ppm sulfur crude oil cases are summarized below:

<u>Gasoline Component</u>	<u>Brent</u>	<u>Light Arabian</u>
Light Gasoline	1.42	1.14
Reformate	5.10	8.81
Alkylate	5.38	5.40
FCC Gasoline	<u>88.10</u>	<u>84.65</u>
	100.00	100.00
Gasoline Pool Sulfur, ppm	4	4

### **Gasoline Blending**

Gasoline blending calculations were performed by Stancil & Co. using their “PIMS” based linear programming gasoline blending model. In addition to the cases presented in this paper, results are also presented for modified base cases using no oxygenates in gasoline blending to enable distinguishing between the effect of oxygen elimination and sulfur reduction. The general basis for blending calculations is: production of a maximum amount of reformulated gasoline (RFG) and to maximize premium gasoline production with approximately an equal percentage of premium gasoline in the RFG and conventional gasoline pools. All blending calculations were for a winter operation producing an RVP of 11.2 psi.

The calculated distribution of grades of gasoline produced for the different cases is summarized below. It should be noted that there appears to be an anomaly in the calculated results for the Brent base case when using no oxygenates since the amount of reformulated and premium gasoline production are limited by the maximum toxic specifications. This anomaly disappears in the Brent cases with reduced gasoline sulfur content.

The amount of premium gasoline that could be produced was evaluated on the basis of operating the reformer at a maximum severity of 100 RONC for all cases. This resulted in an abnormally high refinery yield of premium gasoline in the Brent base case with MTBE and Light Arabian base case with MTBE of 50 LV% and 47 LV%, respectively. Although the premium gasoline production for these two cases are

considered higher than what would be typically marketed, the relative changes between cases provides a good indication of how the desulfurization of gasoline and elimination of oxygenates adversely affects the capability of a typical refinery to produce premium gasoline.

**Table 1  
Brent Cases Gasoline Distribution**

	Base Case <u>W/MTBE</u>	Base Case <u>No MTBE</u>	30 ppm <u>Sulfur</u>	10 ppm <u>Sulfur</u>	5 ppm <u>Sulfur</u>
Reformulated Gasoline, %	35.0	25.2	35.0	35.0	35.0
Premium Gasoline, %	50.0	16.8	25.0	24.0	22.8
Total Gasoline Production, % of B.C.	--	98.2	98.0	97.7	97.5

**Table 2  
Light Arabian Cases Gasoline Distribution**

	Base Case <u>w/MTBE</u>	Base Case <u>No MTBE</u>	30 ppm <u>Sulfur</u>	10 ppm <u>Sulfur</u>	5 ppm <u>Sulfur</u>
Reformulated Gasoline, %	37.0	37.0	37.0	37.0	37.0
Premium Gasoline, %	46.8	27.9	25.0	18.8	18.0
Total Gasoline Production, % of B.C.	--	98.9	98.8	98.6	98.5

**Cost of Sulfur Reduction**

The offsite estimates were based on our judgment for similar projects and ranged from 10% to 20% of total for modified facilities and 25% to 40% of total for grass-roots additions. The estimated total installed cost estimates for the different sulfur reduction cases are summarized below:

**TIC, MM\$**

<u>Case</u>	<u>30 ppm S</u>	<u>10 ppm S</u>	<u>5 ppm S</u>
<u>Brent Cases</u>			
Onsites	41.0	52.0	55.6
Offsites	<u>11.2</u>	<u>13.6</u>	<u>14.5</u>
Total	52.2	65.6	70.1
<u>Light Arabian Cases</u>			
Onsites	37.9	52.4	56.1
Offsites	<u>10.3</u>	<u>13.8</u>	<u>14.6</u>
Total	48.2	66.2	70.7

To recover the costs for production of low sulfur gasoline, including a ban on the use of ethers, the price of the gasoline pools would have to increase by the following amounts:

<u>Gasoline Pool Price Increase, ¢/gal.</u>			
<u>Case</u>	<u>30 ppm S</u>	<u>10 ppm S</u>	<u>5 ppm S</u>
<u>Brent Cases</u>			
Adjusted Gross Revenues	1.19	1.39	1.59
Incremental Operating Cost	0.58	0.76	0.77
Capital Charge	<u>0.83</u>	<u>1.07</u>	<u>1.15</u>
Total	2.60	3.22	3.51
<u>Light Arabian Cases</u>			
Adjusted Gross Revenues	1.50	1.83	2.02
Incremental Operating Cost	0.56	0.80	0.82
Capital Charge	<u>0.83</u>	<u>1.14</u>	<u>1.22</u>
Total	2.89	3.77	4.06

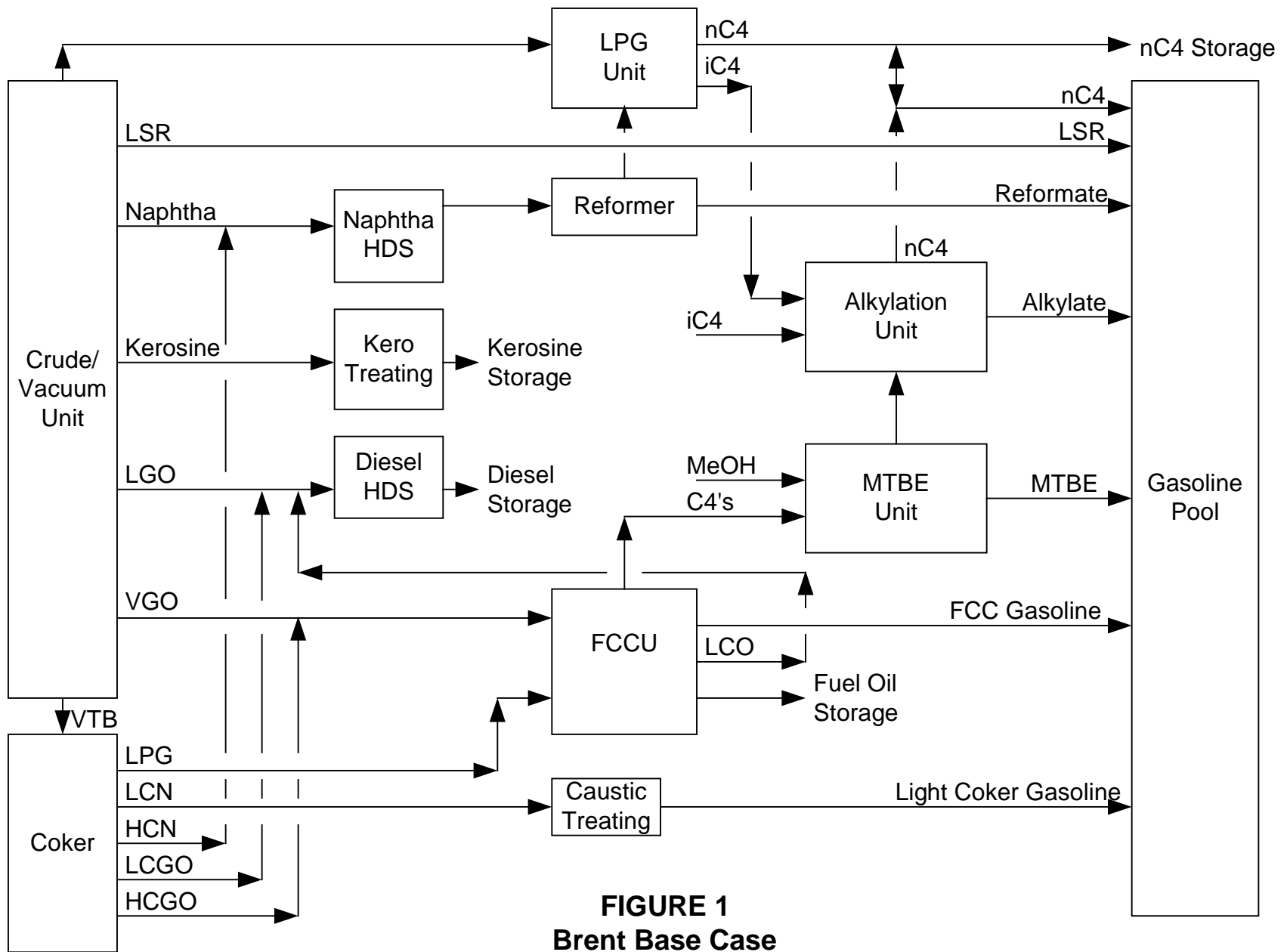
Based on these projections, the increased cost for producing ultra low sulfur gasoline instead of 30 ppm sulfur gasoline is in the range 0.9 to 1.2¢/gal. All investment/operating cost calculations are based on the total sulfur reduction modifications being made in one step. If ultra low sulfur gasoline is produced in two steps, i.e., 30 ppm sulfur in first step and ultra low sulfur in the latter step, which is the most realistic scenario, the increased cost for producing ultra low sulfur gasoline could be significantly greater. As noted earlier, these analyses are considered representative of advantaged refineries for sulfur reduction. If the sulfur content of the refineries' existing gasoline pool is much higher, the costs for production of ultra low sulfur gasoline could be adversely impacted.

### **Outlook and Summing Up**

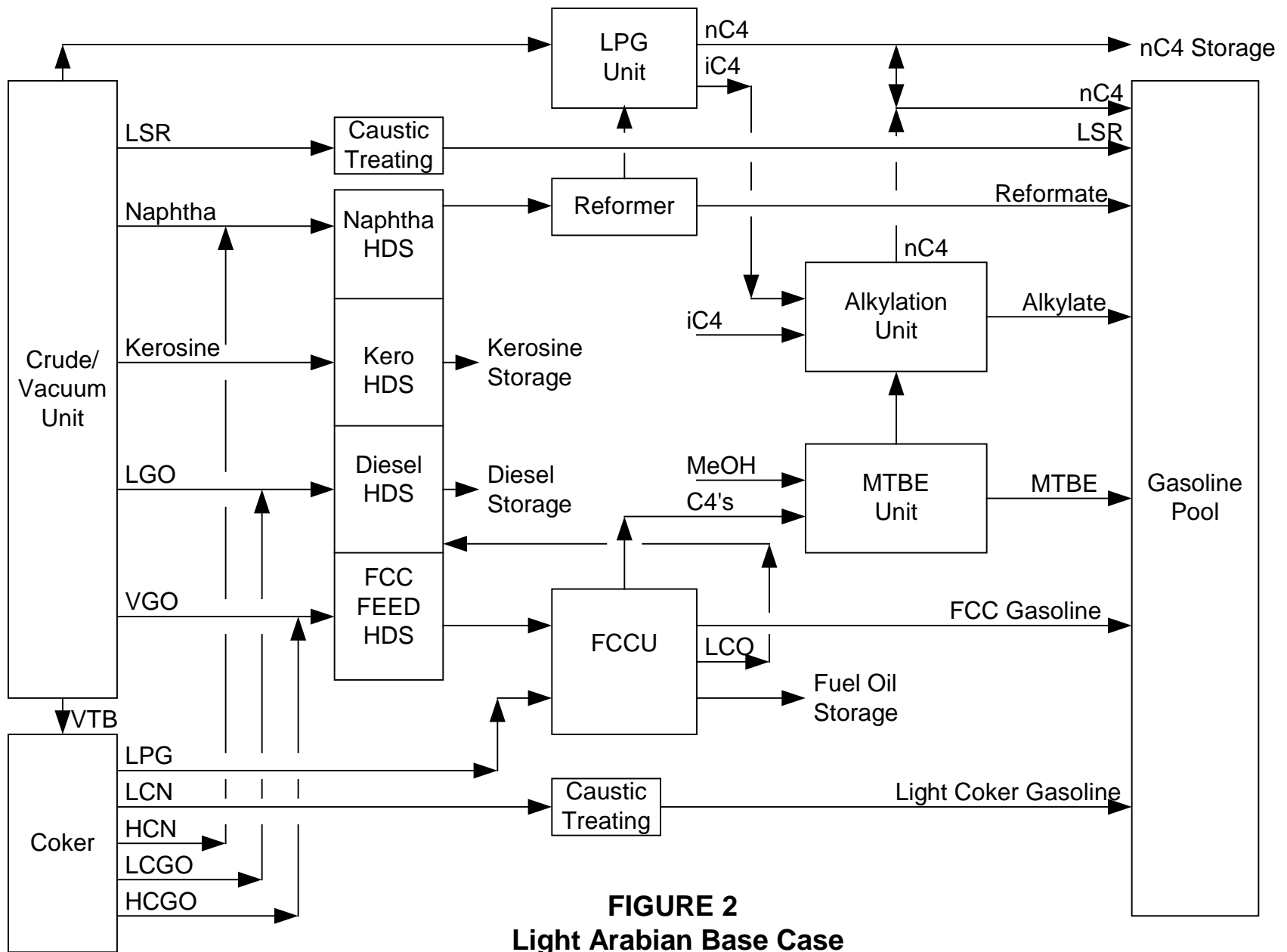
Key impacts to the future refinery for producing ultra low sulfur gasoline and other considerations are summarized below:

- We believe that there is a high likelihood of a future regulation requiring the production of ultra low sulfur gasoline. Based on feedback on EPA's regulation for "Tier 2" fuel, it appears that initially the average sulfur content will be reduced to 30 ppm and production of ultra low sulfur gasoline will be a second regulatory step in the future.
- Most likely the production of ultra low sulfur gasoline will proceed in two different steps, therefore the projected additional cost of 0.9 to 1.2¢/gal. presented in this paper is considered optimistic.
- Essentially all refinery processing units that yield a gasoline blending component containing modest amounts of sulfur will be impacted when producing ultra low sulfur gasoline.
- It is projected that the future ultra low sulfur gasoline regulation should include a significant peak to average sulfur content provision to allow for gasoline blending flexibility.
- Consideration should be given to developing an overall refinery strategy for production of ultra low sulfur gasoline that is compatible for the initial plan for production of 30 ppm sulfur gasoline. This will enable optimization of the initial expenditures consistent with maintaining a viable option(s) for producing lower sulfur gasoline in the future.

- Does pre-investment for future ultra low sulfur gasoline make sense?
- Should the design operating cycle time of the FCC Gasoline HDS unit be compatible with the FCCU or is extra storage for high sulfur FCC gasoline going to be available?
- The technology selection for the FCC gasoline HDS should be consistent with the needs for production of ultra low sulfur gasoline in the future.
- Will extra tankage be required for gasoline reblends and pool component reprocessing?
- What additional operational control measures will be needed to minimize the production of blending components with extreme sulfur levels?
- Refineries with higher gasoline sulfur contents, multiple similar gasoline production units, or difficulty in segregating similar gasoline component streams for treating could be more significantly impacted for production of ultra low sulfur gasoline.

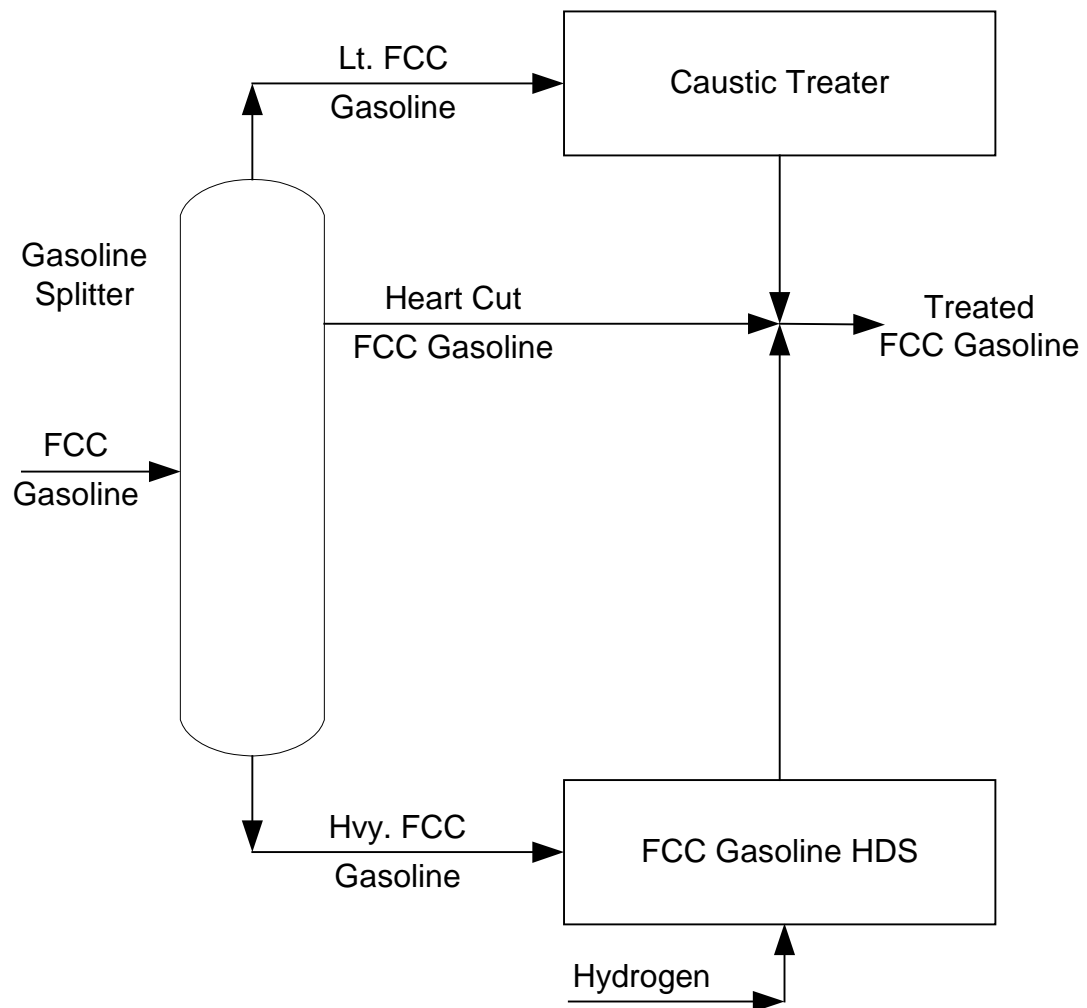


**FIGURE 1**  
**Brent Base Case**

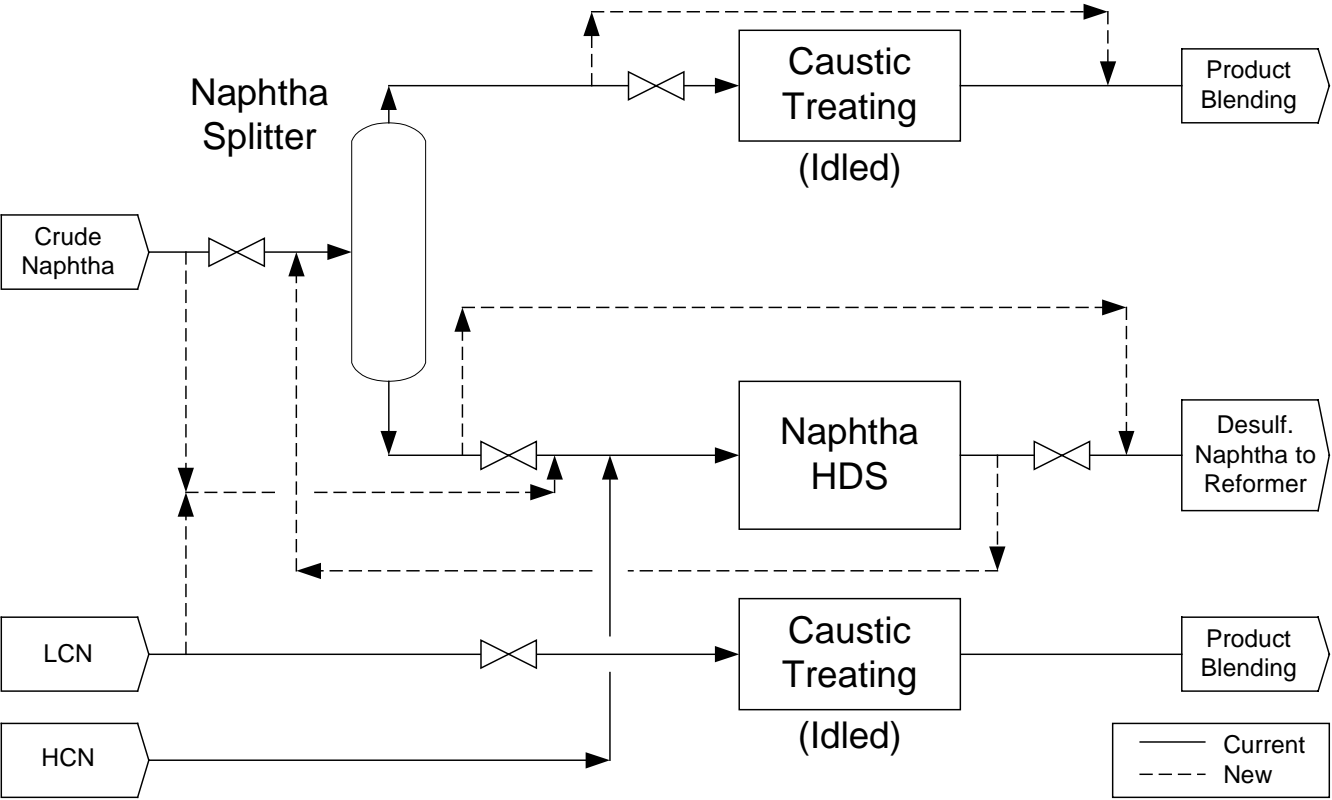


**FIGURE 2**  
**Light Arabian Base Case**

**FIGURE 3**  
**FCC Gasoline Treating**  
**Block**



**Figure 4**  
**HDS of LSR and LCN**



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## **ACKNOWLEDGEMENTS**

Jeffrey Nichols and Joseph Ceurvorst at Stancil & Co. for their assistance in gasoline blending calculations.