

Producing ethylbenzene

David Netzer, Consulting Chemical Engineer, USA, explores how the production of ethylbenzene can be very synergistic with reducing the benzene content of gasoline, increasing the octane number and co-producing olefins.³

The combination of a reduced benzene content of gasoline, an increased octane number and the co-production of olefins, during the production of ethylbenzene, illustrate a payback of 10 months on a proposed revamp project of a major refinery and steam cracking complex in the US Gulf Coast. The concept could be even more attractive in Europe where major refineries are low on octane, have an excess of gasoline and facing investments associated with benzene reduction.^{1, 2, 6, 7}

The original name plate capacity of the cracker for 100% gas oil feed, was 680 000 tpy of ethylene. However, over the years, the plant was debottlenecked to produce 930 000 tpy of ethylene with over 55 wt% SG=0.857 hydrotreated gas oil feed from several OSBL sources. The balance is full range naphtha from multiple OSBL sources. The plant has been modified to accept dilute ethylene from adjacent FCC offgas USGC No. 1 for olefins recovery. Fully hydrotreated, pyrolysis gasoline is exported for BTX recovery at OSBL.

The new feed to the steam cracker would comprise a total 205 tpy (45 000 bpd) of dilute benzene (13.4 vol%) streams from four USGC refineries, one North Eastern US refinery and one West European refinery.

The dilute benzene feed is produced by reformat splitting between light cut containing benzene and C₅ - C₇ at approximately 95 °C and heavy cut comprising toluene and C₈⁺. The dilute benzene cut, average RON=68, is a less desired portion, approximately 8 vol% of the gasoline pool in USA, 6.5% in Western Europe, and could present an environmental obstacle in meeting European, Japanese and US gasoline specifications for benzene. The heavy cut represents average RON of approximately 111, lower RVP and is a superior blending component to the gasoline pool.

In addition to 205 tpy dilute benzene (45 000 bpd, SG=0.69), the steam cracker will receive 193 tpy (34 000 bpd, SG=0.857) hydrotreated gas oil which is considered an advantageous feed in this particular instance.

Design basis

The 930 000 tpy olefin plant receives the following feedstock sources:

- FCC gas from USGC No. 1, at 35 kg/cm²-g after ISBL compression.
- Naphtha, strategic global mix, 40 -190 °C, 9 wt% aromatics SG=0.714.
- Hydrotreated gas oil from USGC refineries, 13.85 wt% hydrogen, SG=0.857.

The basis of the yield estimate is: P/E=0.53 in the furnace outlet, C₂ recycle cracking at 65% conversion per pass and C₃ recycle at 93% conversion per pass. Hydrotreated atmospheric gas oil 232 - 400 °C, 5 - 95vol% TBP boiling range and M.W=255.

Hydrotreated pyrolysis gasoline from a nearby olefin plant is available as a benzene source for ethylbenzene production. The production rate is 8.40 tpy, approximately 1460 bpd, with 56 wt% benzene, 28 wt% toluene/C₈ aromatics and balance 13 wt% C₆ - C₈ non aromatics.

The total combined pyrolysis gasoline from steam cracker and adjacent steam cracker exported to OSBL is 8800 bpd (49 tpy) containing 21.1 tpy benzene.

New mode of production

Operation of the adjacent olefin plant is not 'interrupted'. Excess C₃⁺ fractionation capacity available in the adjacent cracker is used to debottleneck the added 14.5 tpy of the C₃= produced at the revamped steam cracker.

Ethane, propane and C₃/C₆/C₇ from benzene fractionation recycle to cracking.

The naphtha feed is replaced with dilute benzene feed, 205 tpy (45 000 bpd) containing 35.0 tpy of benzene and 0.5 tpy toluene and combined SG=0.69.

The possible dilute benzene feeds are as follows:

- 14 000 bpd from USGC refinery No. 1 with 13.0 vol% benzene.
- 7000 bpd from USGC refinery No. 2 with 10.0 vol% benzene.
- 8000 bpd from USGC refinery No. 3 with 12.5 vol% benzene.
- 3500 bpd from USGC refinery No. 4 with 14.0 vol% benzene.



Figure 1. Continuous catalytic reformer (CCR).

- 5500 bpd from US North East No. 1 with 16.0 vol% benzene.
- 8000 bpd from Western European refinery with 14.5 vol% benzene.

The non-aromatics are estimated to have 0.5 wt% C₄, 25 wt% C₅, 40 wt% C₆ and balance 35.0 wt% of C₇, approximately 70% iso paraffins, 2% cyclo-paraffins, and 0.5% olefins.

Maximum production rate of dilute ethylene is achieved by increasing cracked gas flow rate by 21%, while maintaining a single compression and fractionation trains. This added production of ethylene will represent the chosen capacity of the

Propylene from FCC	2.26
Ethane from FCC	7.45
Ethylene from FCC	6.32
Methane from FCC	10.90
Hydrogen from FCC	0.90
Naphtha	120.00
	(25 250 bpd, SG=0.714, 9 wt% aromatics)
Atmospheric gas oil	193.00
	(34 000 bpd, SG=0.857)
Total	340.83

Hydrogen	3.90
Methane	53.80
Ethylene yield BL	110.70
Propylene yield BL	52.00
C ₄ mix yield BL	35.80
Benzene	16.40
Toluene	10.80
Xylene/styrene	8.70
C ₆ - C ₈ NA	4.70
C ₉ + fuel oil	44.00
	(6150 bpd)
Total	340.80

ethylbenzene plant. The benzene captive to pyrolysis gasoline amounts to approximately 87% of the required benzene.

- Cracking pressure will be increased by 0.30 kg/cm², reducing olefins production per pass by approximately 1.6% (0.6% yield), but increasing benzene yield.
- Benzene depleted pyrolysis gasoline will be blended to gasoline pool as high, approximately 125 RON additive.

In addition to hydrotreated C₅ recycle to cracking (approximately 20 tph):

- Recycle of C₆/C₇: 4.30 tph.
- Benzene recycles from fractionation: 1.20 tph.

Total benzene depleted, pyrolysis gasoline approximately 16.7 tph plus 2.40 tph originated from adjacent cracker total 19.1 tph, comprising 62 wt% toluene, 38 wt% C₈ aromatics approximately 3300 bpd of RON 125.

- Ethane recycle from C₂ fractionation.
- Propane recycle from C₃ fractionation.
- C₅/C₆ recycle from benzene recovery with 2% of the benzene.
- Purge of C₆/C₇ from ethylbenzene plant containing 20 wt% benzene.

The integrated mode as proposed, increasing the feed rate by 21% will increase cracked gas compression power by 4%, from 43 000kW to 44 500 kW, it will increase propylene refrigeration load from 27 000 kW to 31 500 kW and it will reduce ethylene refrigeration from 11 250 kW to 6750 kW. Cooling water circulation power will remain approximately 4500 kW, 33 000 m³/hr. Approximately 4500 kW will shift from the low pressure stage to the high pressure stage of the propylene compressor. It is assumed that the casing of the propylene machine is adequately sized for the new internal reconfiguration of the load.

The added feed will shift the steam balance, and an additional 78 tph of steam, above present production level at 42 barg 370 °C will be available for export to USGC No. 1 refinery. It is estimated that the TLE (transfer line exchangers) at the crackers will produce steam at 115 barg and 510 °C, and the extraction header will operate at 42 barg 370 °C.

In order to reduce the load on the cracked gas compressor, cracking pressure is increased by 0.30 bar, from an

Atmospheric gas oil	193.00
	(34 000 bpd)
Dilute benzene feed	205.00
	(45 000 bpd)
Propylene from FCC	2.26
Ethane from FCC	7.46
	(recycle to cracker)
Ethylene from FCC	6.32
Methane from FCC	10.9
Hydrogen from FCC	0.90
C ₆ - C ₇ from adjacent cracker	1.36
	(After benzene recovery)
Total	427.20

Hydrogen	4.40
Methane	67.5
Ethylene, polymer grade	110.7
Dilute ethylene	24.00
	(contained as 11.8 vol%, 2 ppm propylene)
Propylene	66.50
C ₄ mix	43.00
Benzene	52.50
Toluene	10.20
Xylene/Styrene	6.50
C ₉ + fuel oil	41.90
	(6580 bpd)
Total	427.20



Courtesy of Stone & Webster, a Shaw-Group Company.

Figure 2. Typical liquid cracker.

assumed 0.83 to 1.13 barg at the end of coils.

Cracked gas from TLEs in a single header proceeds at approximately 455 °C to quench oil, generating dilution steam at an estimated 9 barg. The C₉⁺ pyrolysis fuel oil, C₉⁺ 6700 bpd, is mostly condensed and bled from quench oil. This fuel oil, high in aromatics is sent to USGC No. 1 refinery.

Cracked gas from quench oil at an estimated 120 °C is sent to quench water, generating warm water at approximately 75 °C. This water is used for reboiling duty for downstream users.

The top of the quench water system, for the EB integration case, is modified with chilled water section. Chilled water at 7 °C reduces the suction temperature of the first stage compression to 9 °C.

In the cracked gas compression, each interstage drum is modified to act as a 'sloppy' chilling tower with 7 °C water, thus cooling the suctions to 9 °C. The combined effect of raising the suction pressure by 0.30 kg/cm² and chilling the suctions is expected to increase output by approximately 17%. After fourth stage compression, cracked gas at approximately 20 barg undergoes amine scrubbing for bulk H₂S/CO₂ removal followed by caustic scrubbing for residual H₂S/CO₂ removal.

During five stages of compression to an estimated 36 barg residual water, almost all the C₆⁺, including benzene, most of the C₅ and much of the C₄ are condensed along with some of

the C₃ and C₂. All this is separated in interstage drums and undergoes C₂/C₃ stripping back to compressor suction. The gasoline is debutanised and proceeds to pyrolysis gasoline hydrotreating. Two stages of hydrotreating are assumed to exist: stage one for di-olefins and stage two for olefins and sulfur. The hydrotreated pyrolysis gasoline is blended with hydrotreated pyrolysis gasoline from the adjacent

Table 5. Benzene to ethylbenzene 57.0 tph (after adding 4.5 tph from adjacent plant)

Benzene converted to EB	56
Dilute contained ethylene to EB	24
Dilute ethylene to residue	0.40
Dilute ethylene to vent gas	0.50
Pure benzene from OSBL	8.50

Table 6. Dilute ethylene converted to EB 23.1 tph

Ethylbenzene produced	87.50 (735 000 tpy)
Residue fuel oil produced	0.80 (130 bpd)
Benzene requirement	64.50 (11 080 bpd)
Benzene available from py-gas sources	56.00 (9620 bpd)
Benzene import from OBL	8.50 (1460 bpd)

Table 7. Capital cost estimate USGC 2003 (million US\$)

Steam cracking expansion	32
2x100 000 tpy crackers	
Quench oil system/dilution steam revamp	3.5
Quench water system-revamp	3.0
Cracked gas compression revamp	4.0
Gas chilling/propylene wash	1.0
Dilute ethylene acetylene reactor	3.0
Re-pipe demethaniser/turbo expander	1.0
Chilled water system	3.0
Revamp pyrolysis gasoline hydrotreating	3.0
Reweel last stage of propylene compressor	2.0
Subtotal ethylene plant	55.5
Single, 800 000 tpy EB plant, two 50% reactors	37.0
A purge alkylation reactor	2.0
PSA 26 000 Nm ³ /hr Hydrogen recovery, 6 beds 53% recovery	6.5
Dehexaniser (60 trays, 3700 mm ID)	3.0
Benzene col (40 trays, 3500 mm ID)	2.0
Subtotal benzene EB production	50.5
Reformate fractionation (62 000 bpd USGC No. 1)	4.0
Reformate fractionation revamp (36 000 bpd, USGC No. 2)	1.0
Reformate fractionation (45 000 bpd, USGC No. 3)	3.0
Reformate fractionation (21 000 bpd, USGC No. 4)	2.0
Reformate fractionation (39 000 bpd, US North East)	3.0
Reformate fractionation (42 000 bpd, West Europe)	3.0
Subtotal refineries investment	16
Total battery limits	122.0
General offsite allowance	48.0
Total project	170.0

olefin plant and proceeds to newly added benzene recovery unit. The depentaniser of the existing pyrolysis gasoline hydrotreating is replaced by dehexaniser, 60 actual trays 3700 mm internal diameter (ID) where key components are benzene and methyl-cyclo-pentane. In order to operate on the 'right' side of the azeotrope, approximately 2% of the benzene is allowed overhead along with 80% of the methylcyclo-pentane. This along with all the C₅ and light C₆ recycles to the crackers and increasing ethylene yield. Bottom stream from the dehexaniser proceeds to the debenzeniser, 40 actual trays 3500 mm ID. The overhead product is estimated at 98.0 wt% benzene and 2.0 wt% C₆/C₇ mostly methyl-cyclo pentane, cyclo hexane and di-methyl-pentanes, and less than 100 ppm

100 ppm methane, 82% of the ethylene in the chilling train, 98% of the ethane and all the C₃⁺ go to the deethaniser column. The ethylene feed to the deethaniser operating at approximately 26 barg is unchanged. The C₃ + bottom product proceeds to depropaniser.

The deethaniser overhead proceeds to a two-stage acetylene conversion reactor using some excess of hydrogen. Acetylene-free product with traces of methane and hydrogen proceeds to ethylene fractionation at approximately 16.5 barg. Ethylene product is made as a near top side draw and ethane bottom product is recycled to cracking after cold recovery.. The depropaniser overhead, comprising an estimated 93 mol% propylene and 6% propane and 1% of methyl-acetylene

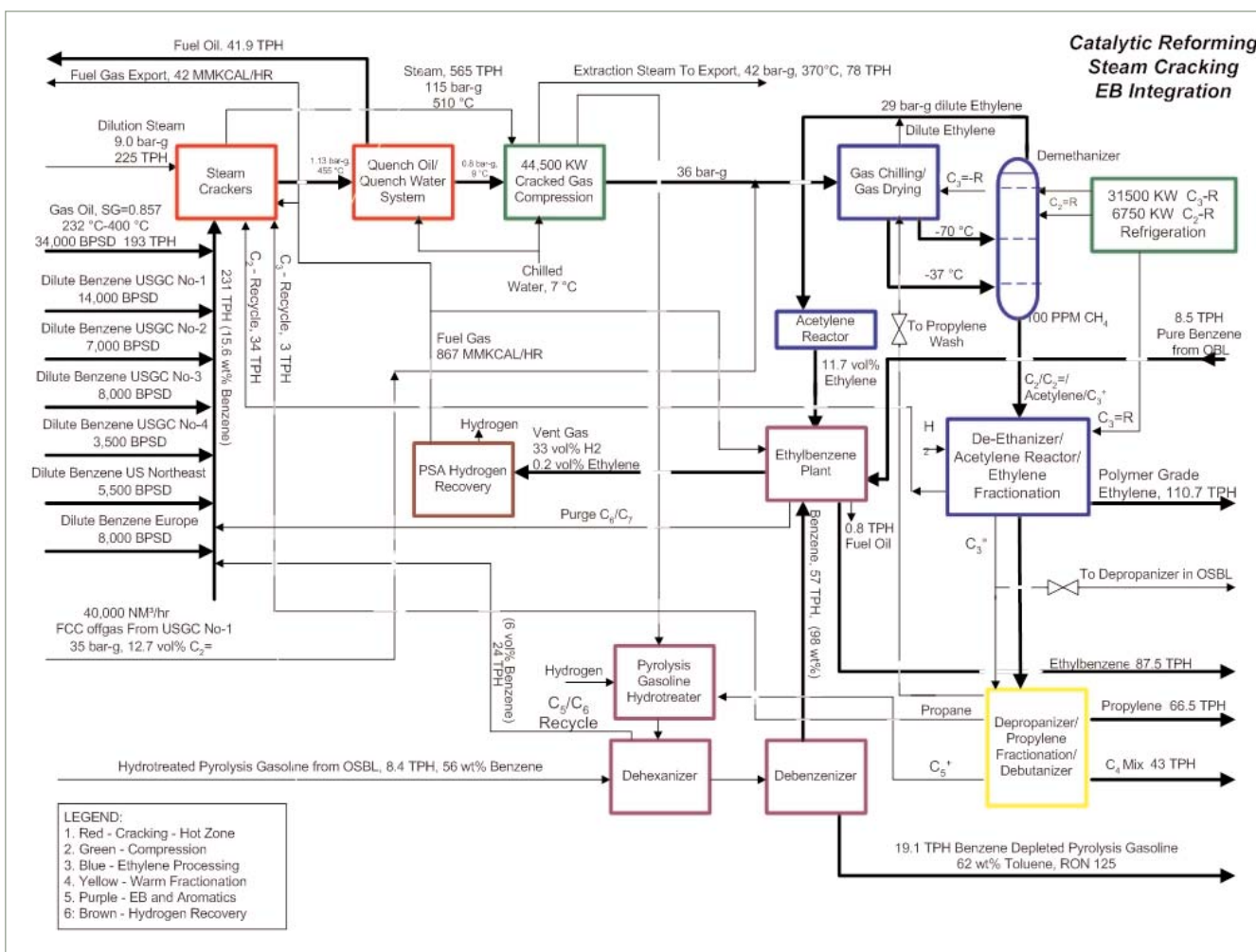


Figure 3. Process flow diagram.

toluene.

Compressed cracked gas at 36 barg is chilled to 15 °C prior to molecular sieve drying where essentially all water is removed. Dry gas is further chilled and proceeds to the first K.O drum at an estimated -37 °C. Liquids are separated and routed to the lower section of the demethaniser column. Vapour overhead is chilled to -70 °C. Essentially all C₃⁺, 96% of the ethane, approximately 90% of the ethylene, 50% of the methane and approximately 4% of the hydrogen are condensed and fed to the demethaniser column. Overhead gas with 2000 vol ppm propylene undergoes propylene wash, down to 2 ppm, with a small slipstream of C₄⁺ from the bottom of the depropaniser. The reflux of the demethaniser, is turned down by 65% allowing 7% of the ethylene to be overhead yet avoiding any propylene breakthrough.

The bottom of the demethaniser contains approximately

and propadiene (MAPD), undergoes MAPD saturation reaction with hydrogen for bulk conversion to propylene. This proceeds to propylene fractionation producing polymer grade 99.6 wt% propylene. Propane with residual MAPD recycles to cracking.

Dilute ethylene from the demethaniser overhead and dilute ethylene from the -70 °C drum proceeds after cold recovery to an added single-stage acetylene reactor. All the acetylene, approximately 1200 vol ppm, is converted at approximately 57 °C mostly to ethylene.

The ethylbenzene is a mixed phase alkylation type⁴ at 180 °C, 26.0 barg. Two alkylation reactors are used in a single train. The alkylation is assumed at space velocity of 0.30 kg of ethylene per hr per kg of catalyst such as zeolite beta and bulk density of 0.550. On this basis 160 m³ of total catalyst is required, using two alkylation reactors of 4 m ID x 8 m T-T. A

catalyst such as ExxonMobil⁵ EBMaX or Zeolite beta is proven to operate with impure benzene with ethylene conversion of 98% at the start of run. Approximately 6 - 7% of the ethylbenzene is further converted to di-ethyl benzene and tri-ethylbenzene and 0.8% is converted to heavy residue of polyalkylated benzene and di-phenyl. Internal stoichiometric excess of 400% benzene is used. The crude EB containing C₆/C₇ impurities and excess benzene undergoes stripping for benzene, C₆/C₇ and traces of toluene removal. EB with di-ethylbenzene, tri-ethylbenzene and heavies undergo fractionation for EB recovery.

The di-ethylbenzene and tri-ethylbenzene are further fractionated in a vacuum, and proceed to transalkylation using a zeolite beta catalyst. In this liquid phase reaction, at approximately 250 °C, approximately 75% of the di-ethylbenzene

Table 8. Products and feedstocks, tph

Product/feedstock	Current operation	Integrated EB production
Ethylbenzene	Not produced	87.5
Polymer grade ethylene	110.7	110.7
Polymer grade propylene	52.0	66.5
C4 mix to BL	35.8	43.0
Benzene from OSBL	None	-8.5
Fuel gas in steam Crackers	-633 million Kcal/hr LHV	-793 million Kcal/hr LHV
H ₂ recovery by PSA	3.0 (76% recovery)	2.32 (53% recovery)
Net fuel/H ₂ produced	670 million Kal/hr	-867 million Kcal/hr
Fuel Export to cracker OSBL	37 million Kcal/hr	74 million Kcal/hr
H ₂ for pyrolysis gasoline	-0.920	-1.15
H ₂ for acetylene/MAPD	-0.50	-0.50
Net H ₂	-1.42	-1.65
Hydrogen export to OSBL	1.58	0.67
Pyrolysis gasoline	49.0	Not exported
Toluene/xylene rich gasoline	Not produced	19.1
Pyrolysis fuel oil, C ₉ +	44.0	41.9
Residue aromatic fuel	Not produced	0.80
Steam export 42 barg 370 °C	In balance	78
Steam 8.0 bar-g dilute benzene recovery in reforming	Not applicable	-200
Steam for cracker's benzene fractionation 3.5 bar-g	Not applicable	-85
Steam for EB plant	Not applicable	120
Steam for EB 42 barg	Not applicable	-16
Fuel gas for EB	Not applicable	-32 million Kcal/hr
Utilities and feed import	Current operation	Integrated EB production
Electric power cracker	2200 kW	2400 kW
Electric power for EB	Not Applicable	1000 kW
Make up water	1000 m ³ /hr	1100 m ³ /hr
Low aromatic naphtha	-120	Not consumed
Gas oil (SG=0.857)	-193	-193
Dilute benzene (17 wt%)	Not consumed	-205
Pure benzene	Not consumed	-8.5

reacts with benzene to form ethylbenzene. Pure benzene from OSBL is used for production control, approximately 15%, it would be advantageous to use the pure benzene make up for the transalkylation.

The vent gas from the alkylation reactor and after benzene recovery⁴ contains 2% of the ethylene in the feed, 0.3% of the benzene in the feed and a balance of hydrogen, methane and ethane. This vent gas at 25.0 barg proceeds to PSA hydrogen recovery. The combined hydrogen content is in the order of 33 vol% and recovery of hydrogen 99.9 vol% at 24 barg and fuel gas at 4.0 barg without recompression is the process objective. This will call for hydrogen recovery in the order of 53%, 2.3 tph, and 26 000 Nm³/hr, depending on PSA optimisation. Approximately 91% of the fuel gas after PSA hydrogen recovery will be used as a fuel for steam cracking, approximately 4% will be used for the EB plant and a small amount (approximately 5%) will be routed to OSBL.

The dilute benzene produced by a simple fractionation of

reformate at each refinery source. Approximately 75 actual trays are needed for this low pressure fractionation using 8 barg steam. The C₅ - C₇ and benzene cut would be the light cut, and to be used as a feed to the cracker. The toluene and heavy cut is high RON gasoline blending component.

Cost estimate and project economics

Calculating the value of dilute benzene

Assuming a 'conventional' US\$ 0.30/octane-bbl and a 2.0 octane boost will increase the value of the remaining gasoline, approximately 92 vol% of the original gasoline pool, from US\$ 37.4/bbl (US\$ 315/t) to US\$ 38/bbl (US\$ 320/t). The credit for RVP reduction is estimated at US\$ 0.15/bbl depending on alternative outlet for excess C₅ and C₄. Thus, the value of gasoline product will increase to US\$ 38.15/bbl. Selling the dilute benzene, approximately

Table 9. Differential Cash Flow, USGC Q2 2003 (million US\$/yr)

Polymer grade ethylene production	0.0
Ethylbenzene production	361.1
Polymer grade propylene	52.4
C4 mix	11.3
Pyrolysis gasoline	-88.5
Rich toluene gasoline RON 125	40.1
C ₉ + fuel oil	-2.4
Heavy residue from EB	0.80
Steam export (42 barg)	7.0
Steam export 3.5 barg	2.0
Steam 8.0 barg at refineries	-16.8
Fuel gas, 5 million Kcal/hr	1.7
Hydrogen 0.91 tph	-6.3
Power (1200 kW)	-0.6
AGO feed	0.0
Naphtha feed 120 tph	221.8
Dilute benzene feed 205 tph	-359.0
Benzene feed 8.5 tph	-19.6
Total cash flow	205.9
The payback period is:	
US\$ 170 million investment	= 0.825 years
US\$ 205.9 million cash flow	= 10 months

8 vol% of gasoline pool, at US\$ 28.75/bbl (US\$ 257/t) as a feed to the steam cracker will create a break-even situation for the refiner after the cost of fractionation is carried by the petrochemical operation.

In January 2003 the average Gulf Coast average regular gasoline blend at the refinery gate was US\$ 37.4/bbl. The estimated equivalent value of pre-cut hydrotreated naphtha feed to catalytic reforming, SG= 0.715, is approximately US\$ 35.4/bbl. On this basis, the value of full range naphtha, is estimated at US\$ 34.0/bbl (US\$ 292/t). Based on all the above, the value of dilute benzene is 11.6% (US\$ 35 per t) lower than the alternative full range naphtha feed.

Average products and feeds values for five years cycle: 1997 - 2002 are as follows:

- Atmospheric gas oil feeds are 'internal' advantageous streams in both the current operation and revamp case, thus these huge cost items cancelled out.
- FCC offgas feeds are internal advantageous streams with unknown values however in both the current operation and



Figure 4. CosMar EB/SM facility, Carville, USA.

revamp case these cost items cancelled out.

- For economic analysis, use styrene at US\$ 550/t and derate it by 11% to US\$ 490/t as a value of EB.
- The value of propylene, polymer grade is US\$ 430/t.
- The value of C₄ mix, is estimated at US\$187/t.
- The value of 60 RON petrochemical naphtha, 9 wt% aromatics is US\$ 220/t at ISBL.
- For naphtha, US\$ 220/t ISBL, hydrotreated pyrolysis gasoline is rated at US\$ 222/t FOB and delivered by barges to OSBL at US\$ 215/t.
- The value of 125 RON toluene rich gasoline is US\$ 250/t.
- The value of dilute benzene, is derated by 8.5% over naphtha to US\$ 201/t, and 3.1% margin is becoming the incentive to the refineries. Use an average shipping cost of US\$ 7.5/t, US\$ 208.5/t at ISBL.
- The value of pure benzene is US\$ 275/t.
- The value of C₉⁺ fuel oil is US\$ 140/t.
- The value of residue aromatic fuel is US\$ 120/t.
- The value of fuel gas is US\$ 16/million Kcal LHV.

- The estimated value of hydrogen is US\$ 850/t.
- The value of electric power is US\$ 0.06/kW.
- The value of steam, 42 barg 370 °C 95% condensate return, is US\$ 13/t.
- The value of steam, at 8.0 barg 95% condensate return, is US\$ 10/t.
- The value of steam at 3.5 barg 95% condensate return, is US\$ 7.0/t.

Bibliography

1. 'Benzene production from refinery sources', *NPRA Presentation*, March 2003, Paper AM-03-10.
2. A patent on this subject has been allowed in the USA.
3. 'Integrate Ethylbenzene Production with an Olefins Plant', *Hydrocarbon Processing*, May 99.
4. 'Method for producing ethylbenzene', *U.S. 6,252,126*, 'Mixed phase Alkylation', *U.S. 5,977,423*.
5. GROOTJAN ET AL., ATOFINA, *U.S. Patent 5,750,814 and HENDRIKSEN ET AL., EXXONMOBIL, U.S. Patent 6,002,057*.
6. 'Combination Process for Manufacturing Ethylene Ethylbenzene and Styrene', *U.S. Patent 5,880,320, European Patent 1,017.651*, Chinese Patent allowed, Indian patent pending.
7. 'Combination Process for Manufacturing Ethylene Benzene and Alkylated Benzene', *U.S. Patent 6,177,600*.

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