BENZENE SUPPLY TRENDS AND PROPOSED METHOD FOR ENHANCED RECOVERY

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ABSTRACT

This paper focuses on the two traditional sources for petrochemical benzene, which are catalytic naphtha reforming from petroleum refining and steam cracking of petroleum liquids. These sources yield 27,300 KT/Y (560,000 bpsd) or 75% of the global benzene supply for the petrochemical industry. An additional 6,000 KT/Y (123,000 bpsd) of benzene is produced by toluene conversion processing, and most of this toluene is captive to reforming and steam cracking sources.

In the U.S., catalytic reforming of naphtha accounts for about 38% of benzene production. Benzene is an incidental product from reforming during the manufacture of high-octane blending components (HOBC) used in gasoline blending. A further 28% of benzene is attributed to pyrolysis gasoline from steam cracking sources where the benzene is an incidental product during the production of ethylene and propylene. In Europe, the ratio is about reversed where steam cracking accounts for nearly 52% of benzene while catalytic reforming accounts for about 30%.

Benzene costs rose to about 2.9 times the cost of crude oil in 2004 as compared to an average of 1.9 times crude oil from 2000-2003, despite the dramatic increase in price of crude oil. This 50% increase in cost ratio, and nearly 200% increase in total cost has caused the petrochemical industry to review market factors causing the supply/demand imbalance and look for more cost effective ways of buying and using benzene in their processes.

This presentation tries to identify the root cause of market supply trend, review alternate approaches and to propose at least a partial solution that will alleviate the imbalance in the market. The fall out of this approach would be; improving the environmental impact by removing benzene from the gasoline pool and also substantially elevating the octane of the gasoline pool and reducing vapor pressure. Future anticipated regulations for benzene reduction in the gasoline pool would be extremely synergistic with the proposed concept.

One concept that could further benefit the industry is use of lower purity benzene (97-98 wt%) instead of the traditional high purity stock (99.5-99.9 wt%). The concept has previously been discussed in the NPRA paper AM-03-10 presentation on March 2003, Hydrocarbon Processing April 2002, Hydrocarbon Engineering Nov. 2003 and U.S. Patent 6,677,496, (www.petrochemicals.dnetzer.net) showing **a typical economic advantage of 30-40%.** The concept involves fractionation of dilute benzene streams (8-25 vol% benzene) from catalytic reforming in petroleum refining. This dilute benzene is used as feed or partial feed to steam cracking producing olefins and shifting the benzene recovery from the refining operation to the petrochemical operation.

Benzene Supply Sources and Market Trend

On a global basis, catalytic reforming accounts for some 55% of benzene production including associated toluene conversion. Steam cracking and associated toluene conversion accounts for nearly 40% of benzene production.

A typical benzene yield from steam cracking could be as follows.

- Cracking naphtha, 4.5-6.5 wt%, depending on feedstock and cracking severity.
- Cracking of gas oil, 4.5-6.5 wt%, depending on feedstock and cracking severity.
- Cracking of propane and butane, 2.5-3.0 wt% benzene depending on severity.
- Cracking of ethane 0.6-1.0 wt% depending on pressure and ethane conversion.

On a global basis, about 50% of ethylene is produced via naphtha cracking at an average yield of about 31-35%. About 6% of ethylene is produced via cracking of gas oil at an average cracking yield of 25-28%. The balance of the ethylene, about 44%, is produced via gas cracking: about 14% by cracking C3/C4 at about 38-44% cracking yield and 30% from cracking ethane at about 76-81% average cracking yield.

Production of ethylene from ethane, aside from low benzene yield has very limited co-production of propylene. Since the recent trend in the olefin market is focused on propylene, the propylene production brings new issues affecting benzene production. Traditionally, about 60-65% of propylene has been attributed to steam cracking while nearly all the balance is attributed to FCC (fluid catalytic cracking) gasoline production in petroleum refining. About 2% of propylene production is attributed to dehydrogenation of propane.

The Benzene Attributed to Steam Cracking is Captive to the Following Sources:

• 75.0% to cracking of naphtha	0.175 ton benzene per ton of ethylene
• 13.5 % to cracking of gas oil	0.220 ton benzene per ton of ethylene
• 9.0 % to cracking of C3/C4	0.070 ton benzene per ton of ethylene.
• 2.5 % to ethane cracking.	0.010 ton benzene per ton of ethylene.

The average global benzene production from steam cracking sources is 0.12 ton benzene per ton of ethylene produced at B/L and associated toluene conversion by hydrodealkylation could account for additional 0.01 ton of benzene per ton of ethylene, thus resulting in a total of 0.130 ton benzene per ton of ethylene on a total global basis.

Recent trends in steam cracking have been to increase propylene market share in relationship to ethylene, as high as 0.65 ton of propylene per ton of ethylene at OBL of liquid crackers as opposed to higher severity P/E=0.50 as the more traditional average. The low severity operation, driven by propylene market results in reduction of benzene make for most full range naphtha feeds by about 15-20% or more, thus further disturbing the benzene supply situation. As discussed later, the emergence of high severity FCC as driven by the propylene market, co-produces substantially higher benzene yield, thus potentially creating a niche market opportunity for additional benzene production in situations where VGO (vacuum gas oil) is attractively priced; however, at this point it represents a very minor share of the benzene market and is exclusive to China.

The following twenty olefin projects are officially in advanced planning or invitation to bid to major contractors, or are under construction, and scheduled for operation by year 2009. About 17,520 KT/Y ethylene will be produced if all these projects are materialized, and as shown 9,115 KT/Y (52%) in the Middle East and 6,240 KT/Y in China(36%). It would be a reasonable assumption that not all these projects materialize for typical business reasons; however, it is reasonable also to assume that some additional projects in FSU, Mexico, India, Venezuela, and perhaps even the U.S., Canada and Europe are yet to be announced.

Based on the data in the table below, the estimated benzene to be co-produced will be 1,600 KT/Y, 340 KT/Y (21%) in the Middle East and 1080 KT/Y (68%) in China. The total benzene production is estimated at 1,730 KT/Y after assumed hydrodealkylation of toluene, 0.098 ton benzene per ton of ethylene about 75% of current global average.

MAJOR ETHYLENE EXPANSIONS (2005 - 2009)

LOCATION	FEEDSTOCK	CAPACITY	TIMING
Brazil	Ethane/Propane	540	2005
Iran	EPB/Naphtha	520	2005
Iran	Ethane	1,000	2005/06
Iran	Ethane	1,100	2006
Iran	EPB/Naphtha	1,320	2006/07
Iran	Ethane	500	2008
Kuwait	Ethane	850	2008
Saudi Arabia	Ethane,Propane,Butane	1,325	2008/09
Saudi Arabia	Ethane/Propane	1,300	2008/09
Saudi Arabia	Ethane/Propane	1,200	2009
India	Naphtha	900	2009
China	Naphtha	700	2005
China	Naphtha	900	2005
China	Naphtha/Gas Oil/Residues	800	2006
China	Naphtha/Gas Oil/Residues	640	2007
China	EPB/Naphtha/Gas Oil/Residues	1,000	2008/09
China	Naphtha	1,000	2008/09
China	Naphtha	1,200	2006/07
Thailand	Ethane	315	2005
Thailand	Ethane	410	2007

On this basis for an ethylene growth rate of 4.0% per year, including ethylene conversion to propylene, the growth in benzene from steam cracking sources would be only 3.0% per year.

Industry search for alternate feedstock for steam cracking is well underway. For example, it was recently announced that Dow's joint venture in China and others are studying the option of methanol to ethylene, producing methanol via coal gasification. (http://www.dow.com/dow_news/corporate/2004/20041220a.htm) The methanol product will be used for MTO (methanol to olefins) producing olefins. Regardless of the final results of the studies, based on a currently known technology, see SRI report PEP 111-A, no appreciable co-production of benzene is anticipated. The same is the case converting methanol to propylene; see SRI report PEP Review 98-13 and methanol to gasoline, (MTG) see SRI report PEP-191.

The growth of new refining capacity in the U.S., Europe and Japan has been nearly stagnant over the past two decades. As a matter of fact, according to ExxonMobil, (see Hydrocarbon Processing Jan. 2005) gasoline consumption in Europe is expected to decline by about 0.9% per year through 2020 while motor fuel demand is shifting toward diesel. The growth of refining capacity in China, India, and the Middle East has involved adding relatively smaller reforming capacity compared to the U.S. because the domestic fuel product slate in these regions of the world is geared more toward diesel and fuel oil rather than high octane gasoline. For example, the published reforming capacity in China is under 7% and India 5% of crude oil fractionation capacity, as opposed to 21% in the U.S., 17% in Mexico, and about 15% in the European Union and Japan and about 11% in the Middle East. Needless to say, this lack of growth further contributes to the imbalance in supply/demand of benzene.

Traditionally, as a rule of thumb, the sale price of benzene (SG=0.88/ 30 API gravity) has been 1.75-1.90 times the cost on weight basis of crude oil. Recent market trend has brought the cost of benzene to a historic high of 3.6 times crude oil, and a recent decline has stabilized the cost at 2.5-2.9 times the cost of crude oil. Given the new processing trend of steam cracking it appears a reasonable assumption as any, that the near future cost ratio of benzene to crude oil price could remain at this level. The key to these issues is the growth rate in benzene consumption in China.

The growth of benzene derivatives has been on the order of 4.0% per year, mostly into styrene, cumene and cyclohexane, which has created a supply demand imbalance that is the current focus issue of the petrochemical industry.

Potential Added Benzene Recovery

In some twenty one (21) known refineries, including twelve (12) refineries in California, one (1) in the state of Washington, two (2) in Eastern Canada and the balance in Europe and Australia, where benzene is being produced in reforming that potentially could be recovered, it is being hydrotreated to meet environmental specifications of benzene in the gasoline pool. The current benzene specifications are limited to 1.0 vol% in much of the U.S., European and Japanese markets, and further reductions can be anticipated in the future.

The currently practiced hydrotreating (http://www.uop.com/objects/Bensat.pdf) of benzene, aside of significant hydrogen consumption, approximately 40-60 Scf/bbl (0.5 kg/ton) on the total average gasoline pool, amounts to about \$0.1/bbl (\$0.85 per ton) gasoline depending on the value of hydrogen. Benzene saturation also reduces the octane of the typical gasoline pool by 0.20-0.25 RON. This octane penalty by itself accounts for about \$0.10-0.15/bbl (\$0.85-1.30/ton) gasoline. Eliminating MTBE from California gasoline blend has even further aggravated the octane issue, and blending of ethanol has its own limitations especially higher RVP (Reid Vapor Pressure).

In the state of California, or gasoline dedicated for marketing in the state of California, the hydrotreated benzene concentrate is very good molecular composition in terms of meeting the T-50 (mid boiling point) and olefins of CARB gasoline. The added value of CARB gasoline, probably \$0.06-0.08/gallon over a conventional regular gasoline could provide an incentive to the current hydrotreating practice of benzene. A major project recently completed in a refinery in the U.S. northwest was focused on avoiding export of benzene concentrate to the Gulf Coast and hydrotreating and isomerization of C5/C6 cuts, thus producing a good blend for CARB gasoline for the California market. Nevertheless, this practice should be assessed against the changing market values of benzene vs. the market for CARB gasoline. Further, unlike isomerization of pre-fractionated C5/C6 from reformer feed, the isomerization of C5/C6 from unconverted naphtha results in very marginal boost in octane.

In this context it should be noted that the gasoline's end point, which is one of the key attributes of CARB gasoline, is not affected by the proposed removal of the dilute benzene cut and the effect on average olefin content, another attribute to CARB gasoline, is very small, (see CARB model http://www.arb.ca.gov/fuels/gasoline/premodel/premodel.htm).

The assumed legal obstacles or perceptions of legal obstacles in liability of handling dilute benzene could be a factor as well. It is assessed that the estimated increase in octane of about 1.8-2.0 RON resulting from removal of dilute benzene and reduction in RVP, probably by far will out weigh the issues of olefins, T-50 and **perceptions** of liability. At the end, based on regulatory development in other states and Europe, it is assessed that the probability of adopting some of the CARB gasoline specifications like the T-50 is very small.

The Following Sources of Benzene Could Be Considered

- Benzene recovery from reformers which are not practicing benzene recovery.
- Benzene recovery from High Severity FCC gasoline, 570-600 C reaction. .
- Benzene recovery from tar sand processing, mostly in western Canada.
- Benzene production from LPG such as Cyclar process in Saudi Arabia.

High Severity FCC (http://www.uop.com/objects/PetroFCC.pdf)

The high severity FCC projects are driven mostly by the increase in demand for propylene. A typical propylene yield of 17-20 wt% and about 3 wt% ethylene was reported from severely hydrotreated VGO (vacuum gas oils) using 0.015-0.020 ton of hydrogen per ton of VGO, as opposed to 4-5 wt % propylene and 0.8-1.0 wt% ethylene yields in conventional FCC. The benzene production in HS FCC is 3.0 to 3.5 higher than "normal" FCC, and the assumed benzene recovery would become economically more viable after disproportionation of toluene to additional benzene and xylene, probably for downstream production of paraxylene. Therefore, benzene recovery is almost incidental to paraxylene production, and the overall economics of HS- FCC is governed by the assumed values of VGO as well as values of propylene and paraxylene. Nevertheless, at the end, the key to the relative economics of high severity FCC as a route for aromatics and propylene is **the value assigned to VGO,** vacuum gas oil. It is speculated that for projects of high severity FCC, mostly in China and a recent project in the Middle East, the assigned values of VGO are considerably lower than the known market rates as posted. Once advantageous pricing for VGO is achieved, the option of conventional steam cracking of hydrotreated VGO also deserves a consideration.

Benzene From Oil Sand

Not much has been reported on benzene recovery from tar sand or shale oil. Alberta Energy Research, the province of Alberta, Canada, has sponsored with interested parties a number of studies related to the added value of petrochemicals production from synthetic crude oil. The estimated investment in an assumed typical complex could be on the order of $5,000 MM U.S. producing clean fuels, olefins and co-producing paraxylene and some 500 KT/Y of benzene. High severity FCC is likely to be a core unit in the petrochemical operation along with delayed coking, coke gasification for hydrogen production and hydrocracking for producing premium products, including CARB gasoline.

The overall added economic value of the assumed petrochemical operation will likely be indexed to two major factors:

- Cost of synthetic crude, mostly capital charges
- Relative competition of natural gas, as indexed to the U.S. market.

At the moment, all olefins production in western Canada is based on ethane which of course is derived from natural gas, mostly exported to the U.S. Massive imports of LNG to the U.S., particularly to California or Baja California, Mexico, could indirectly reduce the overall incentive of petrochemicals from oil sand. On the other hand, these tar sand upgrading units are expected to utilize very significant hydrocracking capacity and hydrocracked gasoline, low in olefins and sulfur is more compatible with CARB gasoline and exporting this gasoline blend to California could result in higher margin. Nevertheless, regardless of the final economic case, given the order of capital investment and the location, it seems that for benzene production, this oil sand option presents a niche market at best.

LPG to Benzene

A single commercial Cyclar plant, benzene from LPG was built in 1991 in Saudi Arabia. No additional second plant was ever built, while benzene has been imported to Saudi Arabia. This leads one to speculate that alternate methods of producing benzene have proven more economical than Cyclar.

Benzene From Catalytic Reforming

Reforming Overview

Most reformers built in the past generation, about 35% of global reforming capacity, are of CCR type. Reformate comprises about 30% of U.S. gasoline and about 43% of European gasoline pools. On a global basis, reformates are being produced in 450 refineries, including 120 refineries in the U.S., twenty (20) in Canada and six (6) large refineries in Mexico. A typical reforming capacity could range in volumetric capacity between 10-30% of the input to the crude oil distillation unit and its volumetric yield between 75-82 vol%. The octane of reformates typically ranges from 94 RON to 102 RON, where 97-100 RON would be a reasonable range for a modern CCR.

A good measure for naphtha reforming quality is N+2A, which is volumetric percentage of naphthene content + twice the percentage of aromatics content. An N+2A of over 50 would represent a good reforming feedstock and N+2A=70 would represent an excellent feedstock. Highly paraffinic naphtha, typically from the Middle East, may have N+2A content around 40, and is thus good for olefins via steam cracking but traditionally less advantageous for reforming as compared with naphtha from crude oils such as Brent North Sea, N+2A=72, light Louisiana crude and Alaska North Slope N+2A=60, Isthmus (Mexico) N+2A=52, Dura (Indonesia) and West African N+2A=78-80 .

In any of the above methods, additional benzene could be produced by hydrodealkylation of toluene, HDA. Since most toluene is produced in catalytic reforming, most of the benzene production by conversion of toluene is accounted as a portion of global benzene share as captive to catalytic reforming and amounts to 6% of global benzene production. The economics of converting toluene and in rare cases xylene to benzene by HDA, is a function of relative values of benzene to toluene as well as cost of hydrogen and value of fuel gas. The basic benzene yield of HDA is about 80% and in today's market this operation is justified, however, the relative merit of HDA is very cyclic. The conversion of toluene to benzene and xylene by disproportionation would be driven by the economics of paraxylene.

Based on all the above, the presentation will focus on an improved method of benzene recovery from HOBC which is in most cases more economical than the alternate methods. In this context it should be noted that higher yield of benzene by CCR (continuous catalytic reforming) could be achieved as compared with the older semi-regenerative reforming technology.

Reverting reformer operations to pre 1990 Clean Air Act, standards could significantly increase the benzene yield, and in most cases with relatively small capital investment. However, in some cases, the added isomerization capacity is so integrated with reforming operation that reverting to pre 1990 Clean Air Act standards could become a complex issue, complex but not impossible. Needless to say, the installation of new reforming capacity would be more ideally suited for the proposed production of dilute benzene.

As said, it is anticipated that future regulations will call for further benzene reduction as opposed to the current 1.0 vol%. All present methods of reconfiguring the reformers for minimum benzene production have nearly reached their practical limits, thus the only known methods of eliminating benzene are by either hydrogenation of benzene concentrate heart cut, as currently being practiced, or alkylation with light olefins. In either case, fractionation of benzene concentrate heart cut will be required thus diversion of dilute benzene to OBL steam cracking could be a fall out. In about four (4) U.S. refineries, two in the Gulf Coast and two in the North East, two (2) Canadian refineries and probably several European refineries, C6/C7 heart cut benzene concentrate from reforming is being recovered. However, rather than being hydrotreated such as in California it is sold for benzene extraction, and in case of eastern Canada and one U.S. North East refinery, the benzene concentrate is shipped to the U.S. Gulf Coast.

On average, at least in the U.S. and Europe, benzene attributed to reforming represents 70-80% of total benzene in gasoline, while the balance 20-30% of the benzene is essentially in the FCC gasoline. Therefore, eliminating this benzene from reformate streams as discussed later, would present the most viable approach for meeting future environmental regulations, while simultaneously recovering valuable petrochemical product. Further, removing benzene from FCC gasoline, typically 0.5 vol%, would present a very uneconomical operation.

Illustrative Refinery Configuration With Typical Catalytic Reforming

The following diagram, Generic Refinery Configuration, represents a conventional high conversion 200,000 bpsd 31.5 API crude input refinery, including 50 vol% Mid East paraffinic crude. The refinery configuration includes 34,000 bpsd, continuous catalytic reforming CCR of naphtha, N+2A=50 to produce 28,000 bpsd HOBC (high octane blending component) RON=98.5 and 50 MM scfd of hydrogen at 87 mol% purity. The atmospheric fractionation in a crude unit is producing:

- LPG fuel gas cut about 2,000 bpsd
- Naphtha cut 350 F end point 38,000 bpsd
- Kerosene cut 550 F end point 20,000 bpsd
- Diesel cut 700 F end point 25,000 bpsd
- Atmospheric gas oil, AGO, 750 F cut point 15,000 bpsd
- Atmospheric residue 100,000 bpsd

The atmospheric residue proceeds to vacuum distillation and produces the following cuts:

- Vacuum gas oil, VGO, 650-950 F boiling range 60,000 bpsd
- Vacuum bottom 40,000 bpsd

The vacuum bottom proceeds to delayed coking to produce:

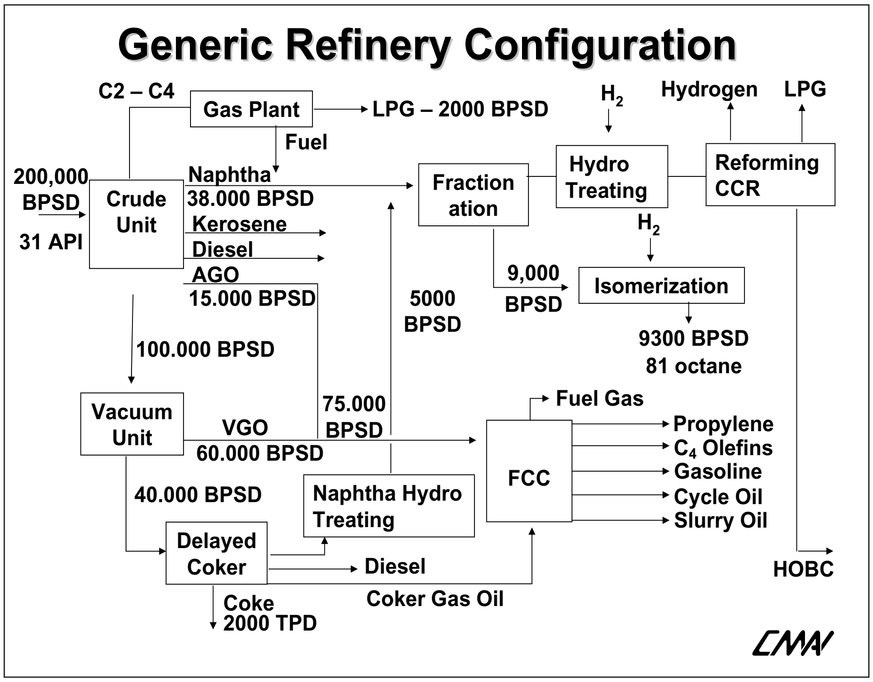
- 2,000 stpd petroleum coke, 4.0 wt% sulfur, 15.000 btu/lb
- 5,000 bpsd coker naphtha, relatively high in sulfur olefins and benzene.
- 2,000 bpsd LPG- to Merox (Mercaptan oxidation)
- 10,000 bpsd coker diesel - to hydrotreating
- 11,000 bpsd coker gas oil- to FCC.
- Coker off gas- to fuel.

The combined atmospheric, vacuum and coker gas oils 86,000 bpsd is feeding a conventional FCC unit and producing:

- 49,000 bpsd gasoline, end point 430 F, benzene content 0.6 vol%.
- Light cycle oil, aromatic diesel material, 15,000 bpsd
- Slurry oil , heavy fuel oil 3,000 bpsd
- C4 mix 8,500 bpsd to alkylation
- Propylene 6,500 bpsd (185 KT/Y) for petrochemical recovery
- Fuel gas CH4 /C2/H2, containing about 13 mol% ethylene.

The C4 mix along with some 4,000 bpsd imported isobutane is feeding a 9,000 bpsd alkylation unit. The alkylate RON=95 MON=92 is blended to the gasoline pool.

The coker naphtha rich in olefins and di-olefins and sulfur is hydrotreated. The atmospheric naphtha and coker naphtha are pre-fractionated to 9,000 bpsd light naphtha C5-C6 and 34,000 bpsd heavy cut 96 C cut point. The combined hydrotreated heavy naphtha, feeds to the catalytic reforming producing 27,500 bpsd reformate RON=98.5 containing 3.6 vol%, (4 wt%) 1,000 bpsd benzene and 23.5 vol%, 6500 bpsd C5-C7 non-aromatics.



A light reformate dilute benzene cut, 7,500 bpsd RON=70, MON=58 is fractionated and sent as a feed to steam cracking. An optional fractionation of 3,300 bpsd C5-i C6 is possible along with sending this stream to isomerization for further octane enhancement.

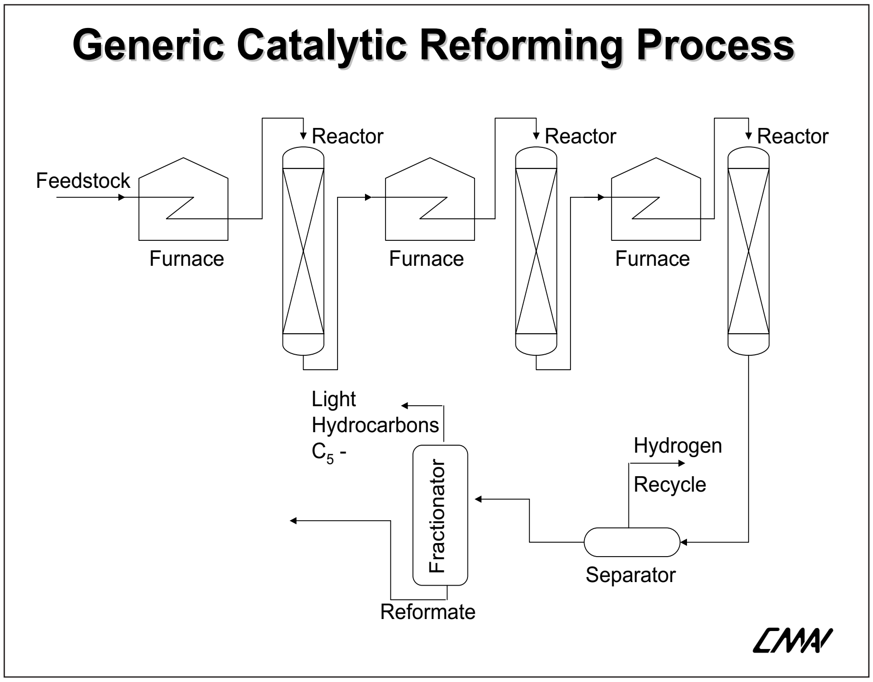
Under the first scenario the net gasoline make is 87,000 bpsd and 7,500 bpsd of steam cracking feedstock containing 13.3 vol% benzene. In the alternate case 90,300 bpsd gasoline is produced and 4,200 bpsd C6/C7 petrochemical feedstock containing 24 vol% benzene is feeding the steam cracking.

In the first case the RON of the gasoline is elevated from 92.0 to 93.9. The impact on the MON (Motor Octane), is even higher, thus the actual octane revenue could increase by about $70,000-80,000 per day ($25 MM per year) and let alone the 0.4 psi reduction in RVP. This reduction in RVP will allow blending of some 400 bpsd of N-butane.

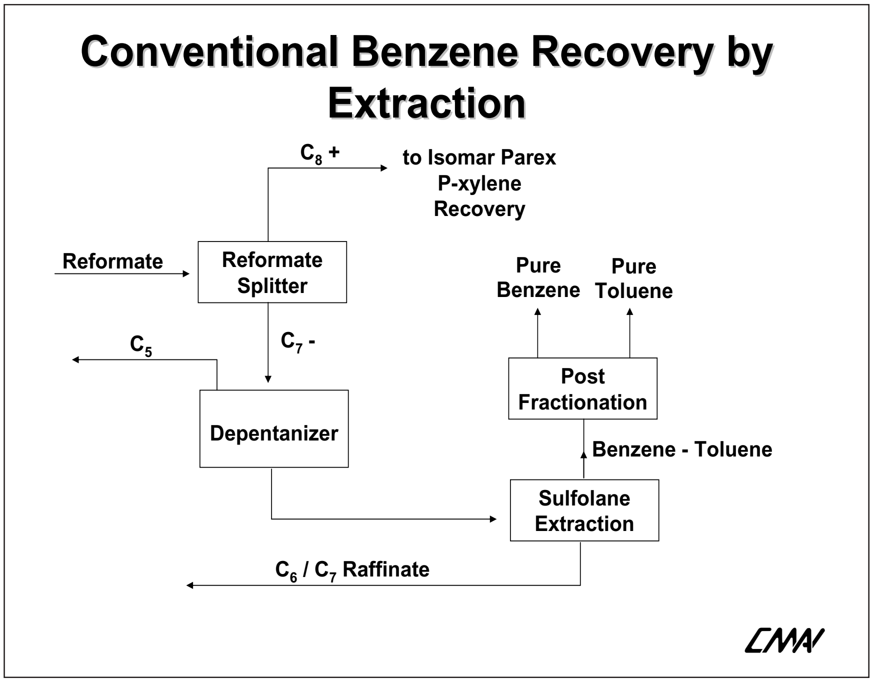
If as discussed later, if 20% added reforming capacity can be made available, about 7,000 bpsd of naphtha dedicated to steam cracking or an alternate source can be partially swapped with 9,000 bpsd dilute benzene to be fractionated while co-producing an additional 10 MM scfd of hydrogen and an additional 500 bpsd (15 KT/Y) of LPG. The total gasoline make under this scenario will be 92,600 bpsd and RON= 94.2.

Once dilute benzene recovery is in place, or for that matter even conventional recovery by extraction, more precursors of benzene could be introduced to the reformer thus increasing benzene make by some 25-50% depending on particular naphtha analysis and process limitations of the reformer. Adding precursors of benzene to reformer feed may increase the firing duty of the first heater by some 10%.

Inexpensive ceramic coating, say an investment of $500,000, could alleviate this potential bottleneck if existing in the first place.


Generic Catalytic Reforming Process

The diagram to the right represents a simplified scheme of continuous catalytic reforming. Naphtha feed is being prefractionated of majority of benzene precursors as light depleted naphtha. The heavy C7-360 F naphtha is being hydrotreated, primarily for organic sulfur, less than 1 ppm, and nitrogen. Hydrotreated naphtha is entering a three to four stage reformer operating at nominal 5 bars-g and 450-500 C reforming initial temperatures and pressure. Reformer hydrogen rich product gas is being recycled at a ratio of 5-6 to 1 to the feed on a molar basis. Heat is recovered from the flue gas of interheaters producing steam at 40 bar-g and 400 C. This steam is used as motive power source in the refinery and a steam turbine for the reformer recycle compressor would be an ideal user. The reformate is under going stabilization by separating C3/C4 LPG product and hydrogen rich by-product 50 MM scfd of contained hydrogen as 87-90 vol% is proceeding to OBL, probably 38 MM Scfd to diesel hydrotreating and about 12 MM scfd for naphtha hydrotreating. The hydrotreater off-gas, mostly H2S, is routed to a sulfur recovery unit.


Conventional Benzene Recovery by Extraction

The diagram to the right represents a "typical" benzene recovery from reforming sources 4-9 wt% (3.5.-8 vol%) benzene in reformate streams using extraction such as the Sulfolane process.

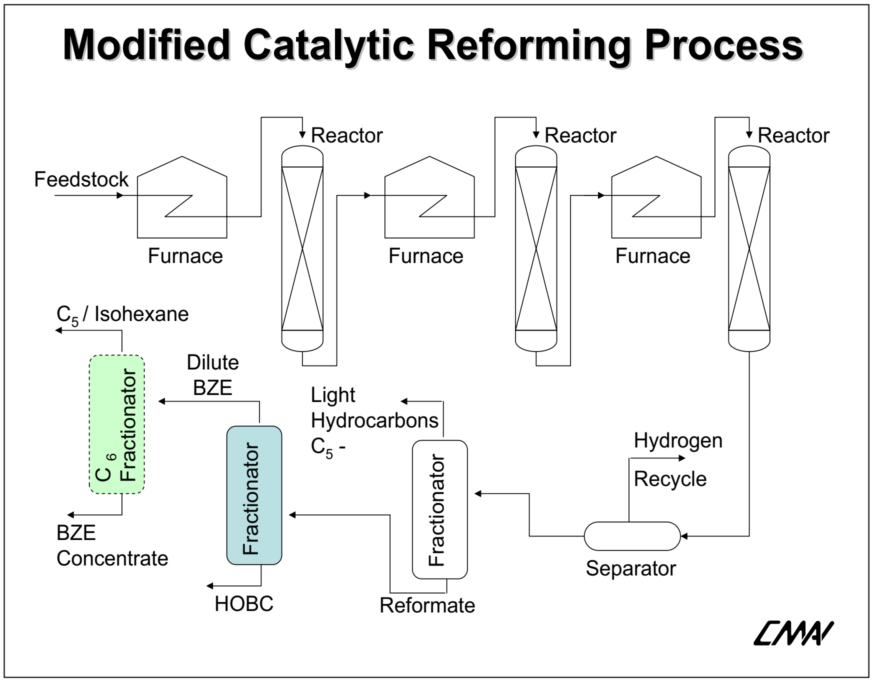
About 65% of reformers do not practice benzene or BTX recovery from HOBC reformate streams. **To the contrary**, in order to minimize benzene in the gasoline pool, at least in the U.S., Canada, Australia, West Europe and Japan, benzene and precursors of benzene such as cyclohexane and methylcyclopentane are pre-fractionated prior to reforming thus meeting benzene specification in the gasoline pool and not necessarily presenting an optimal gasoline production scheme had the benzene limitation not been an issue like pre-1990 Clean Air Act. Thus, the refinery operation is driven not by gasoline economy as prior to the Clean Air Act, but rather environmental considerations. Recovery of dilute benzene for steam cracking as would be suggested, will allow many U.S. and West European refineries to revert to the old operation while increasing benzene production by some 30% and possibly 50% in some cases and yet meet all environmental limitations. Refineries in Mexico, East Europe and Asia **could avoid all together** this benzene control modification as already being practiced in the U.S., Canada, Australia, Europe and Japan.

As shown, in the **conventional** scheme reformate is under going reformate splitting C8+ as heavy reformate and C5-C7 **including toluene** is light cut, and this fractionation uses about 70 trays. The light cut proceeds to a depentanizer, followed by aromatic extraction. Benzene and toluene is being extracted as a BT mix and undergoing post fractionation for benzene recovery and incidental pure toluene recovery. The C6/C7 raffinate RON=55-60 could be reblended in the gasoline pool, or it could more likely go as a feed to steam cracking.

Recovery of benzene from pyrolisis gasoline sources in steam cracking, say 35-50 wt %, lent it self more in favor of extractive distillation such as Uhde's Morphylane, Lurgi's Distapex or GTC Technology, rather than conventional typical Solfulane extraction.

New Method of Benzene Recovery From HOBC Catalytic Reforming Sources

Reformate, RON=94-102 is being fractionated in a simple 75 tray low pressure column to produce light cut unconverted naphtha mostly C5-C7 paraffin containing all the produced benzene 200 F cut point. This low octane, about 20-25 vol% of the reformate containing 10-20 vol% benzene and essentially **no toluene** has a typical octane RON=68-72 thus representing a bad blend to a gasoline pool with RON=92. This material is used as a feed, or more likely a partial feed to steam cracking. The heavy cut with RON=105-115 is used as very high octane low RVP (Reid Vapor pressure) gasoline blending component. Another variation of this scheme is to further concentrate the benzene by



fractionation of C5 and light C6 and returning it to the gasoline pool. The assumed benzene cut to the steam cracker would represent 5-9 vol% of the typical gasoline pool in the U.S. and 7-11 vol% in Europe depending on specific refinery configuration.

It should be noted that by removing benzene from gasoline, aside from the removal of a known toxic material from the gasoline pool, the benzene as a gasoline blend represents the highest relative contributor to greenhouse gas emission because of the higher ratio of carbon to hydrogen. Steam cracking of dilute benzene tends to increase propylene yield, which is well synchronized with current market trends.

Naphtha Dilute Benzene Swap to Improve the Above Method.

It has been discovered by my own personal survey with 35 U.S. and Canadian refineries that in about 65-70% of reformers in the U.S., 15-20% additional reforming capacity could be achieved with relatively small capital investment and in some cases no investment at all. As a good rule of thumb, it could be said that in 65-70% of U.S. reformers, an additional 15-20% capacity could be achieved with an investment of 3-5% of the cost of a new reformer at the same capacity. For example the investment in a 35,000 bpsd reformer including OBL could be on the order of $150 MM U.S., while for $6.0 MM it may be debottlnecked to 42,000 bpsd and preserving the original octane. A typical debottlenecking may involve replacing the feed effluent exchanger with a plate type exchanger such as Packinox, ceramic coating of the tubes in the heaters and other mechanical revamps as applicable on a case-by-base basis.

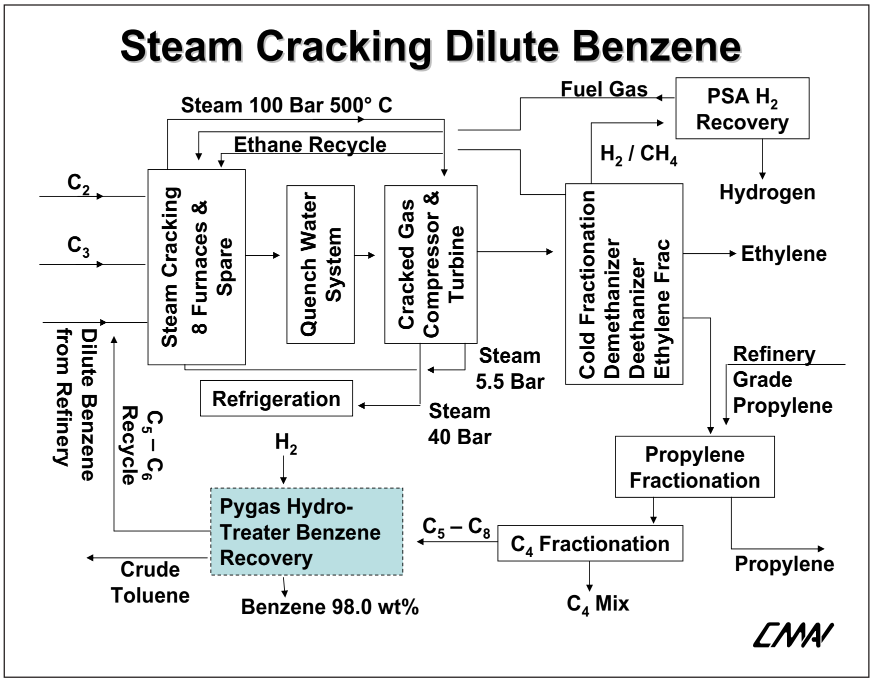
Under the above scenario, naphtha from OBL dedicated to steam cracking is swapped with unconverted naphtha dilute benzene cut. Application of this concept is likely to elevate the RON of the gasoline pool by 1.8-2.5, will increase hydrogen and LPG production, eliminate benzene in the gasoline pool and will reduce RVP by 0.3-0.5 psi. For California refineries or refineries dedicating their product to the state of California, it would be a prudent idea to run the CARB model for T-50 (mid boiling point) driveability index etc. These issues could affect some of the design considerations. It should be noted that typical naphtha dedicated to steam cracking tends to be paraffinic, in order to achieve maximum olefin yield, while reformer naphtha is on the naphthenic/aromatic side in order to achieve high octane. Therefore, this issue of feed swap should be viewed with caution and on a case-by-base basis.

Steam Cracking of Dilute Benzene

Dilute benzene stream C5-C7 cut or in an alternate case C6-C7 cut can be introduced as an exclusive feed to a cracking furnace, and in most cases as a partial feed after being mixed with naphtha. It has been determined that the impact of benzene on the cracker in terms of operability or process limitations is rather small, and actually in most cases, likely to be negligible. The resulting pyrolysis gasoline instead of being comprised of 35-50 wt% benzene would comprise 70-85 wt% benzene. Thus downstream recovery of benzene from 35-85 wt% benzene concentration would be far more economical than benzene recovery from a reformate stream comprising 4-9 wt% benzene. Further, producing pyrolysis gasoline with 70-85 wt% benzene will allow conventional fractionation of benzene to 97-98 wt% or more at much lower capital cost and utilities than the common extractive distillation, and let alone conventional extraction from reformate streams. To a degree the benzene concentration would be a function of cracking severity, and higher severity will minimize C6/C7 production, thus improving the benzene concentration. Nevertheless, the cracking severity at the most is a very secondary issue.

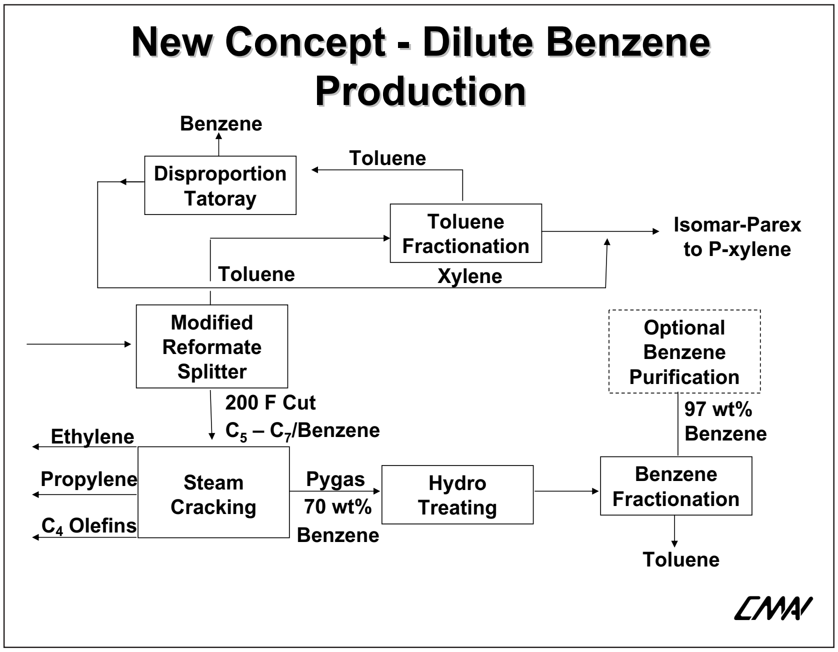
Lower Purity Benzene

It has been discovered that for liquid phase or mixed phase alkylation operating at 150-260 C for producing ethylbenzene and cumene, **benzene purity has no impact** on the alkylation or transalkylation catalysts.



As for alkylation, catalyst issues have been fully resolved by ExxonMobil and Atofina. The non-aromatics in the benzene feed with some residual benzene would be purged to steam cracking, thus all the benzene is ultimately recovered and the impurities are converted to additional olefins. Lower purity benzene will not affect the purity of ethylbenzene or downstream production of styrene monomer.

The initial research by UOP, ExxonMobil, Chevron and Atofina, U.S. 6,002,057, U.S. 5,750,814, U.S. 5,273,644, U.S. 5,083,990, U.S. 4,209,383 on alkylating dilute benzene streams was motivated originally by the desire to alkylate benzene concentrate from gasoline, say 30 wt% benzene heart cut from reformate with ethylene from FCC off-gases. This was intended to reduce the benzene content of the gasoline pool and be an alternative to the benzene hydrogenation as discussed before. The catalyst as developed for the gasoline application, by Chevron, known as Zeolite Beta has an excellent application for petrochemical usage and the patent on the formulation of the catalyst, U.S. 4,891,458 issued in 1990, is currently owned by ExxonMobil.



Further, it was also discovered that for cyclohexane oxidation to adipic acid as a precursor to nylon 6,6, benzene purity of 97-98 wt%, where the balance is C6/C7 non-aromatics containing methylcyclopentane, that resulted in lower purity cyclohexane is more than adequate. A recent evaluation in pilot plant operation by a nylon 6,6 producer has demonstrated that lower purity cyclohexane containing some 3,000 ppm methylcyclopentane is not an issue. For adipic acid nylon 6,6, some minor process modifications are needed to solve new issues associated with the downstream cyclohexane oxidation process. The common industry specifications of cyclohexane are 99.85% purity and not to exceed 200 ppm methylcyclopentane and 50 ppm aromatics, but these were driven by caprolactam producers. However, new testing for adipic acid nylon 6,6 which is about 33% of global and 60% of the U.S. nylon market, have shown that common specifications for cyclohexane with the exception of aromatics may have run their "useful life" and new specifications could be adopted.

The following benzene concentrations could be achieved by conventional double column fractionations;

• Benzene from reforming sources-	30-40 wt% benzene
• Benzene from typical pygas-	86-96 wt% benzene
• Benzene from pygas of dilute benzene feed-	96-99 wt% benzene

Recovery of toluene, 92-95 wt% and 5-8 wt% C7-C8 non aromatics will require an additional column. This toluene would be suitable for HDA with higher hydrogen consumption.

The final concentration of benzene is simply a function of the ratio of benzene to C6/C7 co-boilers, which needs to be determined on a case-by-case basis and related to feed composition and severity of cracking.

For the very conservative operator producing ethylbenzene by liquid phase or mixed phase, and concerned by benzene purity, the 97-98 wt% benzene produced by conventional fractionation of pyrolysis gasoline, could be further purified to 99.9 wt% at a capital cost of about 50% of "normal" extractive distillation of pyrolysis gasoline and considerable less utilities, mostly 17 bar steam. Nevertheless, the "conservative" operators can also **easily test the benzene purity** concept by injecting 2-3 wt% impurities, cyclohexane, methylcyclopentane, N-hexane dimethylpentane methylcyclohexane into the benzene stream and reaching their own conclusions. As said, conventional fractionation of benzene from reformate stream HOBC may reach a limit of 20-40 wt%, thus benzene extraction or extractive distillation of reformate is the only way for benzene recovery from reformate streams.

Total Global Opportunity

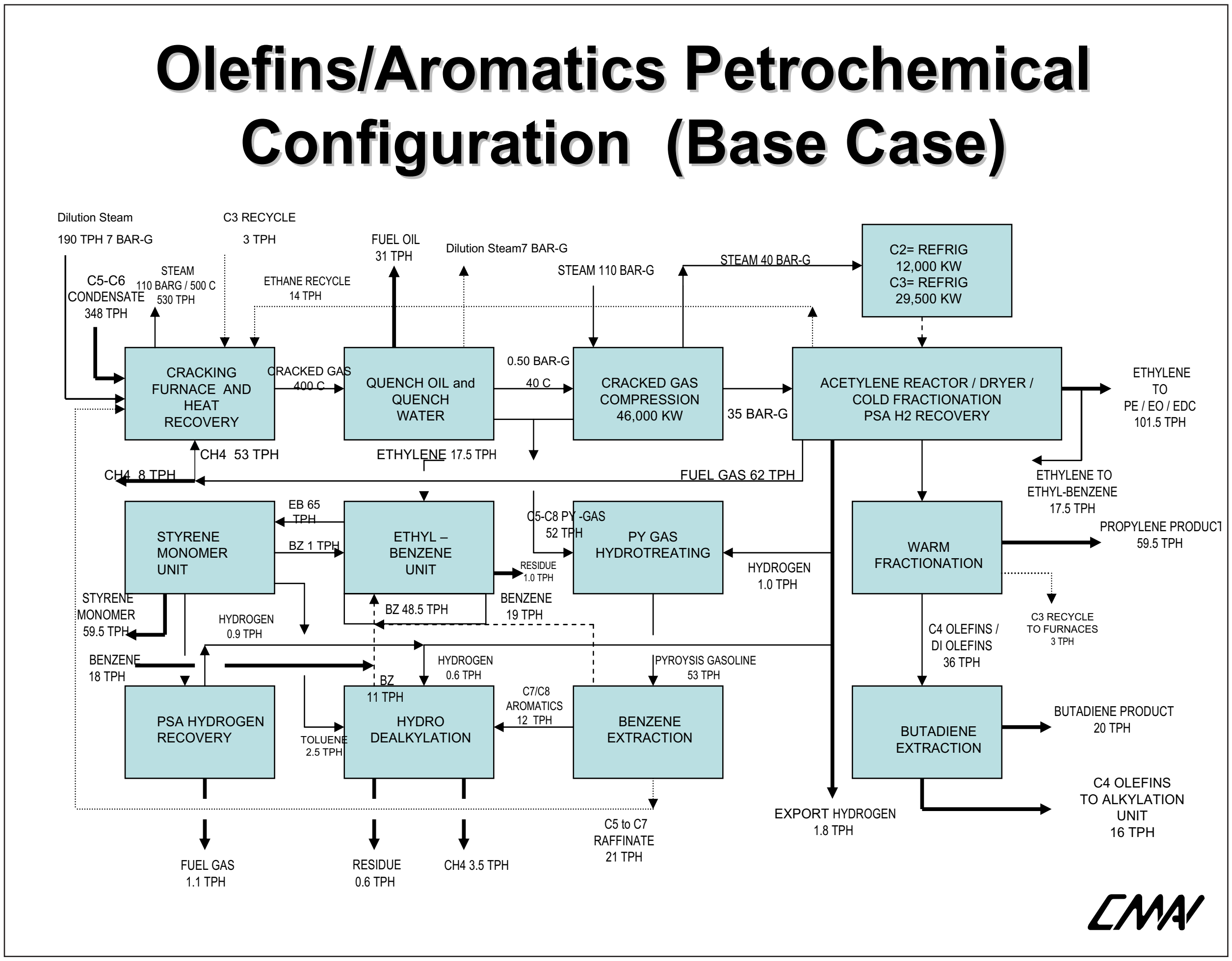
The bottom line is very simple: a technical survey of some 35 best candidate refineries in the U.S. and Canada alone, show that about **1,700 KT/Y of benzene** that could be easily recovered as dilute benzene and logistically located near waterways or in close proximity to the market, is left unconverted in the gasoline pool or hydrotreated. An additional 400 KT/Y could be recovered from reformer gasoline in Mexico, and probably some 1,500 KT/Y in the European Union, with additional substantial recovery in the FSU, Japan, Venezuela, Algeria, Australia and India.

Business Cases

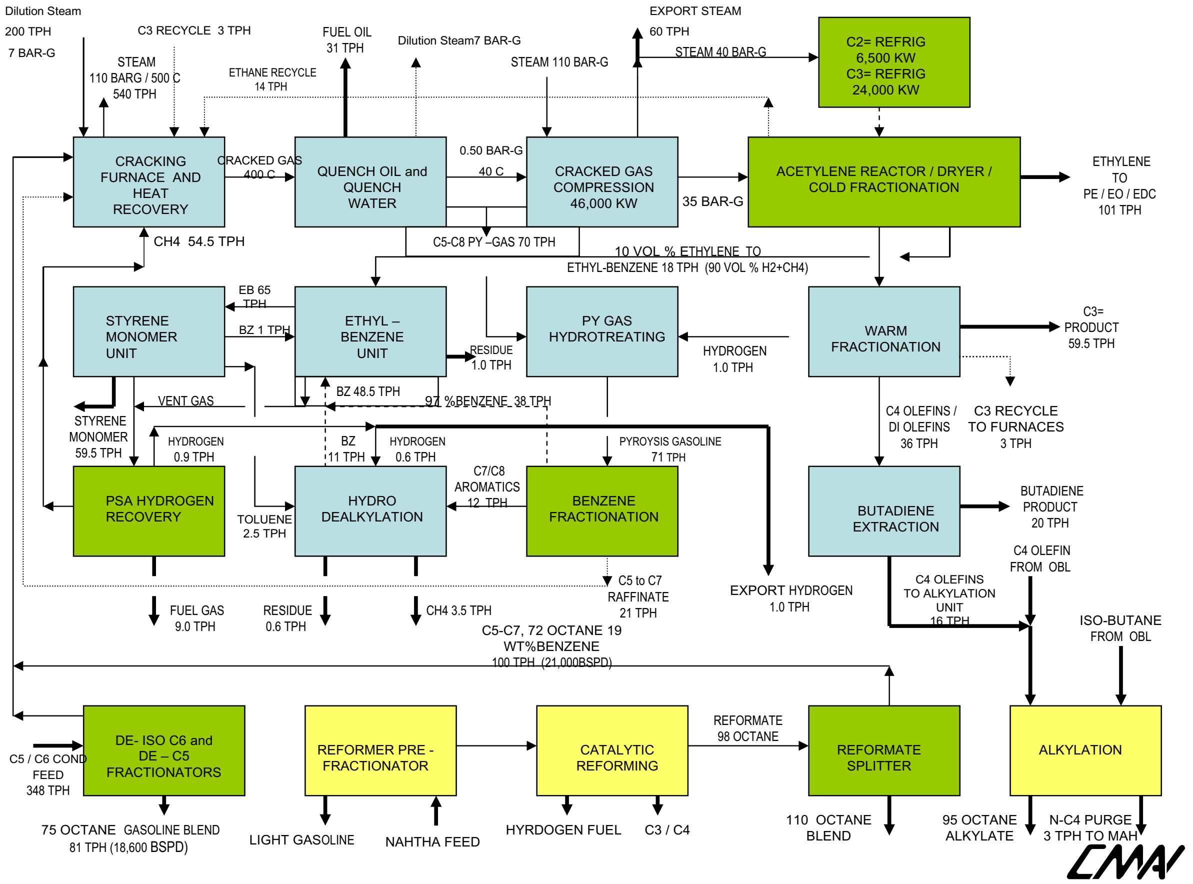
Two business cases are analyzed; producing styrene monomer in a generic emerging market and producing low purity cyclohexane in the U.S. Gulf Coast. The modified oxidation process of cyclohexane is third party confidential information.

Ethylbenzene Styrene production

1. The Base Case represents a conventional steam cracking of light naphtha, mostly C5/C6 from natural gas condensate. The assumed project produces 1,000 KT/Y ethylene, 500 KT/Y propylene and 500 KT/Y styrene monomer. Ethylene and propylene are polymerized in down stream operation. About 160 KT/Y benzene is produced by extractive distillation of hydrotreated pyrolysis gasoline and an additional 70 KT/Y benzene is produced by hydrodealkylation of toluene and xylene. The balance of the benzene, 160 KT/Y, is imported from OBL.
2. In the alternate Case, about 19,000 bpsd iso-C6 Octane =75 RON is being fractionated from the 80,000 bpsd condensate. The iso-C6 and 3,000 bpsd of C4 olefin mix is being exchanged with 21,000 bpsd dilute benzene stream from two refineries and 1,000 bpsd n-butane purge from alkylation. Based on this scheme the gasoline production rate, the octane and the Reid

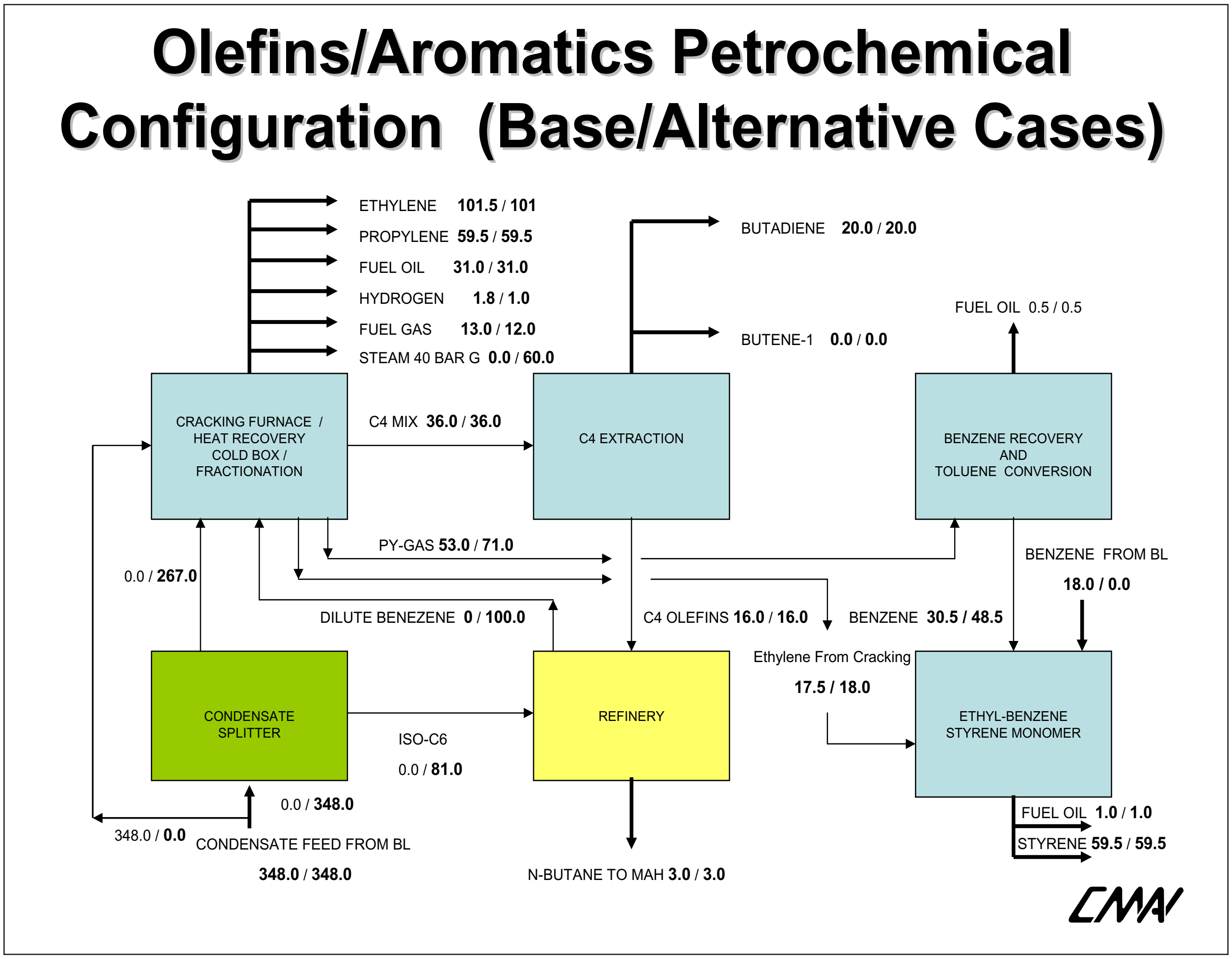

Olefins/Aromatics Petrochemical Configuration (Base Case)

Olefins/Aromatics Petrochemical Configuration (Alternate Case)



Vapor Pressure (RVP) and all other gasoline qualities remain the same or slightly improved. About 160 KT/Y benzene is removed from the gasoline pool, and the petrochemical complex becomes self sufficient in benzene. Additional advantages are obtained by using dilute ethylene alkylation using 10 vol% ethylene from the demethanization zone operating at about 30 bars. Benzene at 97 wt% purity is produced thus avoiding aromatic extraction.

3. The economic diagram as shown in the slides represent the two cases. Product and feedsock values of October 2004 show the net benefit of the Alternate Case is $130 MM U.S. per year. The total cost of feedstock was estimated at $1,200 MM per year. The total value of products was estimated at $2,000 MM U.S. per year. Thus the added benefit represents 11% of the feedstock and 27% of the margin.

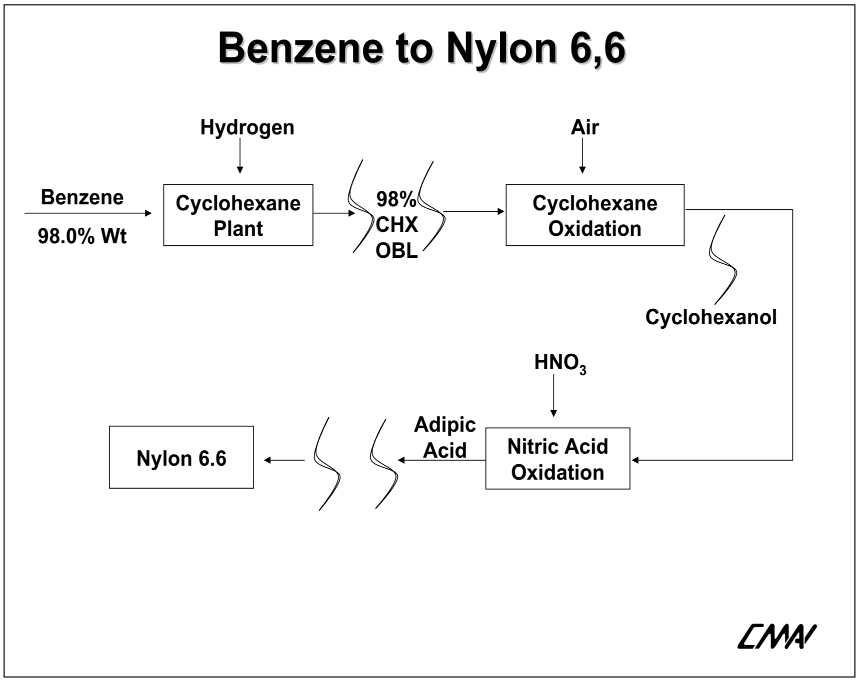


Olefins/Aromatics Petrochemical Configuration (Base/Alternative Cases)

Cyclohexane Case

A gas cracker in U.S. Gulf Coast cracking ethane and propane has the capability to accept up to 24,000 bpsd of liquids, in this case about 22,000 bpsd of dilute benzene and 2,000 bpsd of hydrotreated pyrolysis gasoline recycle. The dilute benzene will probably come from three (3) refineries and will be cracked with 35-40% of furnace capacity. Benzene is recovered from hydrotreated pygas by conventional fractionation as 97-98 wt% benzene and balance of C6/C7 non- aromatics including some 3,000 ppm methylcyclopentane. The benzene would be dedicated for on-site conversion to cyclohexane using hydrogen as produced by the cracker. The lower purity cyclohexane is moved off-site for air oxidation followed by oxidation with nitric acid to adipic acid. The oxidation was recently tested in a pilot plant and all necessary modifications to the existing system have been identified. As said, the nature of the modification remains a third party confidential.

1. The diagram above represents the configuration of the steam cracker prior to the revamp. This operation calls for five (5) furnaces operating on propane net feed of 29 tons per hour each plus 6.5 tons per hour propane recycle. Also three (3) furnaces on ethane 16 ton per hour net



feed on each in addition to 7.0 tons per hour ethane recycle. Dilution steam at 5 bar-g, about 0.35 ton per ton of total feed is extracted from the main steam turbine driver. Untreated C4 and pygas are moved to OBL for hydrotreating and olefins saturation.

2. The shaded portion of the diagram on the previous page represents the revamped operation. Two stages pygas C5-C8 hydrotreating have been added. The first stage converts di-olefins to olefins while the second stage saturates the olefins and removes sulfur compounds which could be critical to the cyclohexane oxidation process. A new cyclohexane 220 KT/Y is added that is exporting 26 tons per hour steam at 5.5 bar-g to the steam cracker dilution steam system thus reducing dilution steam make by about one-third. The hydrotreated pygas, 2,000 bpsd 9.0 tons per hour mostly C5 is recycled to 3 cracking furnaces along with the dilute benzene feed 22,000 bpsd, 110 tons per hour.

3. As said the lower purity cyclohexane is moved to the OBL oxidation facility using proprietary process as well as proprietary modification to handle the impurities.

The reduction in cost of cyclohexane would be very much a site specific analysis. Early analysis of lower purity benzene production NPRA 2003 AM-10 has shown 30% cost advantage for producing ethylbenzene styrene. Nevertheless, the introduction of dilute benzene feed changes the product slate. For example, it increases propylene yield, very substantially increasing benzene yield and C4 mix yield. Cost of dilute benzene feedstock, value of by-products, and the overall business model will greatly affect the value of cyclohexane.

<u>Summary</u>

It is our opinion that with the exception of niche market situations and advantageous pricing of feedstock, benzene production via the conventional route as co-product to gasoline production is the more economical route. Further, the production of new molecules of benzene at least on the short term is not necessary. The molecules of benzene, as said over **3,500 KT/Y are here now** and being blended to gasoline while the refining industry is facing investments to reduce this carcinogenic material in gasoline. It is estimated that close to 50,000 b/d of benzene have disappeared from the U.S gasoline pool since 1990.

It is thought by reverting to pre 1990 Clean Air Act and the appropriate European and Japanese regulation could further alleviate the shortage of benzene for petrochemical industries by increasing the availability **of benzene to 5,000 KT/Y**.

Recovery of benzene as dilute benzene feedstock to steam cracking and downstream benzene recovery from pyrolysis gasoline is by far more economical than conventional extraction of benzene from reformate streams.

Recovery of benzene as impure material, 97-98 wt% will fit to over 60% of market need. Once vapor phase alkylation for production of EB-styrene is replaced by liquid phase or mixed phase, which is industry trend, well over 80% of the market for benzene derivatives will fit to the lower purity mode. The mixed phase alkylation, is attributed to dilute ethylene alkylation and well described in NPRA paper AM-03-10.

Based on all the above, and given the fact the relative reforming capacity in the Middle East is limited, the naphtha is paraffinic (lean), and all steam crackers are gas crackers, mostly ethane crackers, the production of benzene and derivatives in Middle East locations does not offer an advantage over other global locations such as the U.S. and Europe with high reforming capacity using rich naphtha feeds and steam cracking capacity of liquid feedstock. Low cost dilute ethylene or lower purity propylene, from steam cracking sources could further enhance the relative economics of benzene derivatives of non Middle East locations. (ECN, Dec. 6th 2004)

The final cost of benzene and derivatives should be analyzed on a case-by-case situation, subject to cost of feedstock, by-products and business model. Prior case analysis in NPRA -03-10 suggested **savings of over 30%** and no new information suggests the reversal of this prior assessment.