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Reduce Benzene While Elevating Octane And Co- Producing Petrochemicals

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REDUCE BENZENE WHILE ELEVATING OCTANE AND CO-PRODUCING PETROCHEMICALS

David Netzer, March 20th 2007

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Abstract

New challenges and opportunities will result from newly imposed regulations of the United States Environmental Protection Agency (U.S. EPA) that control benzene in the U.S. gasoline pool [1]. The new rules are already in the preliminary stages of implementation and will become fully effective in 2011.

The current benzene limitation is 1.0 vol% in reformulated gasoline, which comprises about 35% of U.S. market and much of the western European market. Benzene content of regular gasoline averages 1.5 vol% in the U.S. and probably ranges from 2.0 vol% to as high as 5% in other countries outside the U.S., Western Europe and Japan. The majority of the benzene in gasoline, about 60% in the U.S. and about 75% in Europe, results from blending reformat, a high Octane Blending Component (HOBC), obtained by catalytic reforming of C₇-360°F naphtha. Reformate accounts for about 28% of the U.S. gasoline pool and about 44% of the European gasoline pool. The balance of the benzene in the gasoline pool, about 40% in US and 25% in Europe is attributed mostly to FCC gasoline. Small percentages of the benzene are attributed to coker naphtha, hydrocracker naphtha and light straight run gasoline.

As the industry is aware, the new U.S. EPA benzene limit in gasoline of 0.62 vol% became a rule on February 9, 2007. In effect this rule will require benzene saturation, removal or recovery by all U.S. refineries and will likely be followed by Canadian, European and Japanese refineries. This 0.62 vol% benzene limit is already being achieved in California and several other locations by hydrotreating a benzene containing heart cut from catalytic reformate. About 75% of U.S. and worldwide refineries having an estimated 50% of the world's catalytic reforming capacity are not currently practicing benzene recovery from reformate and will now fall under this category [2].

Where benzene is removed from reformate to meet environmental goals, mostly for CARB gasoline, the benzene concentrate is about 20-25 vol% benzene and balance is C₆-C₇ non aromatics. This benzene cut, typically 5% of the gasoline pool is hydrotreated, while converting benzene to cyclohexane and methyl-cyclopentane. The hydrotreated concentrate is returned to the gasoline pool but at an octane loss.

The proposed concept of this presentation was initially discussed at 2003 spring meeting of NPRA, [2]. Benzene concentrate or dilute benzene is used as a feedstock for steam cracking to produce ethylene, propylene and benzene rich streams for petrochemical operations. This feedstock is very economically competitive with conventional naphtha or condensate feedstocks for steam cracking. The largest benzene derivatives are styrene, about 50-52%, cumene, about 21-23% and cyclohexane about 14-15%. The proposed

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removal of benzene concentrate tends to increase the overall octane of the gasoline pool by about 1.5-2.5 points while reducing the Reid vapor pressure (RVP). Steam cracking of benzene concentrate has already been commercially demonstrated and is winning acceptance in the petrochemical industry.

Furthermore, the benzene product at 98 wt% purity containing 2 wt % C₆/C₇ non aromatics, as opposed to the traditional 99.5-99.9 wt% purity, is suitable for over 60% and potentially 80% of aromatic derivatives while substantially reducing the cost of recovering the benzene from traditional sources.

The reduction in gasoline production of a given refinery, resulting from diverting benzene concentrate to petrochemicals, can be mitigated by substituting ethanol or naphtha from outside battery limits (OBL) sources while preserving gasoline characteristics such as T-50 (mid point boiling) and end point.

General Overview

This paper focuses on the two traditional sources of petrochemical benzene, which are catalytic naphtha reforming from petroleum refining and steam cracking of mostly petroleum liquids. These sources yield 35,000 KT/Y (720,000 bpsd) or 95% of the global benzene supply for the petrochemical industry.

In the U.S., catalytic reforming of naphtha accounts for about 65% of benzene production. Benzene is a by-product from catalytic reforming during the manufacture of high octane blending components (HOBC) used in gasoline blending or co-product from production of p-xylene via disproportionation of toluene. About 33% 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 reversed: steam cracking accounts for nearly 65% of benzene and derivatives while catalytic reforming accounts for about 30%. This is because over 85% of olefins in Europe are attributable to steam cracking of liquids, which as shown later, are relatively high producers of benzene compared with gas cracking, which is commonly practiced in the U.S., Canada, Mexico and the Middle East.

Benzene (SG=0.88, 30°API), costs recently rose to about 2.2-2.5 times the cost of crude oil on volume basis compared to the traditional average of 1.70-1.90 times crude oil. Furthermore, the cost of crude oil dramatic increased, doubling in price since 2003. This 30% increase in the benzene-to-crude cost ratio and nearly 160% total increase in total cost of benzene have caused the petrochemical industry to review market factors causing this supply/demand imbalance and to look for more cost effective ways to buy and use benzene in their processes. Compounding the complexity of the benzene issue is the new EPA ruling on the benzene content of gasoline [1]. The EPA rules have created new challenges and opportunities to bring the imbalance in benzene supply for petrochemicals into a good equilibrium while simultaneously reducing benzene emissions and as discussed later, also increasing the octane of the gasoline.

Application of the proposed concept could lead to a reduction in benzene content in the average U.S. gasoline pool to about 0.35 vol% and further benzene reduction will require benzene removal from FCC gasoline. This FCC benzene issue would present some very different challenges and are beyond the scope of this presentation.

One concept that could further benefit the petrochemical industry, aside of availability of benzene, is the proposed use of lower purity benzene, about 97-98 wt% instead of the traditional high purity stock, 99.5-99.9 wt%. The concept of lower purity benzene has previously been discussed [2-6] showing a typical economic advantage of 30% compared to high purity benzene. The proposed concept involves fractionation of dilute benzene streams (8-25 vol% benzene) from catalytic reforming sources in petroleum refining. This dilute benzene or benzene concentrate is used as feed or partial feed to steam cracking to produce olefins while co-producing benzene. This proposed method shifts benzene recovery from the refining operation to the petrochemical operation.

The cost of transporting benzene concentrate or dilute benzene from a given refinery in U.S. Mid-West, West Coast, East Coast or off shore to the U.S. Gulf Coast (or in Europe to Western European steam crackers), by barges, rail cars, or ocean tankers is not prohibitive and not measurably higher, if higher at all, than the cost of transporting ethanol from Mid Continent US corn producing states, or naphtha, especially on a naphtha dilute benzene trade swap basis.

Benzene supply sources and market trend

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

The benzene production attributed to catalytic reforming is a function of:

- Naphtha feed composition (PONA)
- Cut point separation of heavy naphtha from light naphtha
- Reformer operation, such as pressure, hydrogen recycle etc.

For petrochemical refinery geared toward producing aromatics, naphthenic/aromatic rich naphtha feeds, such as North Sea, many US continent and Alaska North Slope naphtha would represent advantageous reforming feedstocks. For exclusively fuel producing refineries, as well as refineries providing feedstock to steam cracking, Mid East paraffinic lean naphtha, could be a good fit.

As far as steam cracking, a typical benzene yield from steam cracking is as follows:

- Cracking lean naphtha, 4.5-6.5 wt%, depending upon feedstock PONA and cracking severity.
- Cracking of gas oil, 4.5-6.5%, depending upon 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.

A good measure of cracking severity is the ratio of propylene to ethylene, and higher the ratio, which is the trend today, the lower the severity and also the lower is the co-production of benzene during steam cracking.

On a global basis, about 50% of ethylene is produced via steam cracking of naphtha at an average ethylene yield of about 30-36% depending on assay of the naphtha, severity of cracking and disposition of C₄ product. About 6% of ethylene is produced via cracking of gas oil at an average ethylene yield of 20-30%, and very sensitive to hydrogen content. Hydrotreated gas oil would yield 26-30 % ethylene. The balance of the ethylene, about 44 %, is produced via gas cracking: about 14% by cracking C₃/C₄ at about 38-44% ethylene yield and 30% from cracking ethane at about 76-81 % average ethylene yield.

Production of ethylene from ethane, which in recent years increased its global market share, besides low benzene yield, has very limited co-production of propylene. Since the recent trend in the olefin market is focused on propylene mostly from liquids cracking, this 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 during petroleum refining. About 2% of propylene production is attributed to dehydrogenation of propane.

Benzene attributed to steam cracking is captive to the following sources:

- 75.0% from cracking naphtha (0.165 ton benzene per ton of ethylene)
- 13.5 % from cracking gas oil (0.220 ton benzene per ton of ethylene)
- 9.0 % from cracking of C₃/C₄ (0.070 ton benzene per ton of ethylene)
- 2.5 % from ethane cracking (0.010 ton benzene per ton of ethylene).

The average global benzene production from steam cracking sources is 0.115 ton benzene per ton of ethylene produced at B/L of the steam cracking facilities. Associated toluene conversion as produced by steam cracking, by hydrodealkylation could account for an additional 0.01 ton of benzene per ton of ethylene. Thus the total is estimated 0.125 ton benzene per ton of ethylene on a total global basis.

The recent trend of steam cracking has been increasing propylene market share in relationship to ethylene by reducing severity. Propylene production from liquids cracking

has reached a ratio as high as 0.60-0.65 ton of propylene to ton of ethylene at OBL compared to 0.47-0.50 ratio in the traditional higher severity cracking. The low severity operation results in a reduction of benzene production from most full range naphtha feeds by about 15-20% or more, which further disturbs the benzene supply

The growth of new refining capacity in U.S., Europe and Japan was nearly stagnant the last two decades along with consequent stagnation of benzene production. The growth of steam cracking and consequent benzene production has been marginal. New refining projects have been announced in past years and substantial studies and some engineering work are well under way. Regardless of the location of the new refining projects, dilute benzene or benzene concentrate recovery for steam cracking feed even a long distance away from the refineries is likely to be a viable option.

As for the European market, according to ExxonMobil [7], the 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 with 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 and India is under 7% and 5%, respectively, of crude oil fractionation capacity compared to 21% in U.S., 17% in Mexico, about 15% in the European Union, 15% in Japan and about 11% in the Middle East.

Potential sources for added benzene recovery

In some twenty-one known refineries, including twelve in California, one in Washington State and two each in Eastern Canada, Europe and Australia, where potentially recoverable benzene is produced during reforming, benzene is hydrotreated to meet environmental gasoline specifications of 1.0 vol% and as said reaching 0.62 vol% in California. The new benzene specification of 0.62 vol% in U.S, and probably soon in Europe and Japan, will further, along with the challenges, increase the opportunity for benzene recovery for petrochemical users. The future trend [1] is pointing toward benzene reduction from FCC gasoline, but on a practical level, some technical issues are yet to be resolved.

Research of benzene transportation issues from refineries in California, the U.S. Mid-West and East Coast as well as from most European refineries to petrochemicals users in US Gulf Coast, Western Europe or Far East by ocean tankers, barges and rail cars have shown, especially in today's market, to be very economical. As shown later, swapping of dilute benzene for ethanol or naphtha will provide a further advantage to the proposed concept.

The currently practiced hydrotreating [8 or 9] of benzene, besides significant hydrogen consumption (approximately 40-60 Scf/bbl (0.5 kg/ton) for the total average gasoline pool) amounts to about \$0.15/bbl (\$1.25 per ton) gasoline depending on 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 \$0.12-0.17/bbl (\$1.00-1.50/ton of gasoline).

In the state of California, or gasoline dedicated for marketing in the state of California, the hydrotreated benzene concentrate has a very good molecular composition for meeting the T-50 (mid boiling point) and olefins specifications of California Air Resource Board (CARB) gasoline. The added value of CARB gasoline, probably \$0.07-0.09/gallon over a conventional reformulated gasoline, could provide an incentive to the current hydrotreating practice of benzene. Nevertheless, this practice of benzene saturation should be assessed against the changing market values of benzene compared to the market for CARB gasoline let alone octane and RVP issues. Further, unlike isomerization of pre-fractionated C₅/C₆ from reformer feed attributed to straight run naphtha, the isomerization of C₅-C₇ of hydrotreated benzene cut from catalytic reforming 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 dilute benzene cut and the effect on average olefin content, another attribute to CARB gasoline is very small, see CARB model [10].

The assumed legal obstacles or perceptions of legal obstacles regarding liability of handling dilute benzene could be a factor as well. It is assessed that the estimated increase in octane of about 1.5-2.5 RON resulting from the removal of dilute benzene or benzene concentrate and reduction in RVP, probably will far out weigh the issues of olefins, the T-50 and perceptions of liability. At the end, based on regulatory developments 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.

As said, the removal of the non-aromatic, mostly paraffinic C₆/C₇ from gasoline will boost the octane; especially the motor octane thus will avoid investments in expensive alkylation units and will further improve environmental impact.

The following sources of additional benzene should be considered:

- Benzene recovery from reformers that are not practicing benzene recovery.
- Benzene recovery from High Severity FCC gasoline, 1060-1110°F (570-600°C) reaction temperature, probably via co-production of p-xylene.
- Benzene recovery from tar sands processing, mostly in Western Canada by any known methods, such as catalytic reforming or via production of p-xylene.
- Benzene production from LPG such as via the Cyclar process in Saudi Arabia or equivalent processes.
- Benzene production by AROMAX or equivalent process, cyclizing C₆ paraffins to benzene.
- Benzene recovery via membrane technology from highly aromatic streams like coker naphtha.

High Severity FCC

High severity FCC (HS FCC) projects are driven mostly by an increase in demand for propylene [11] and not gasoline. A typical propylene yield of 17-22 wt% along with about 3-4 wt% ethylene was reported from severely hydrotreated VGO, consuming 0.015-0.020 ton of hydrogen per ton of VGO, compared to conventional FCC yields of 4-5 wt % propylene and 0.8-1.0 wt% ethylene. Benzene production in HS FCC is 3.0 to 3.5 higher than in “normal” FCC while the yield of gasoline could be about 40 vol% lower than conventional FCC of hydrotreated VGO. Because of its highly aromatic content, HS FCC gasoline octane is higher compared with conventional FCC gasoline. Due to newly imposed benzene environmental rules, benzene removal from HS FCC gasoline, typically in the order of 3.5vol %, will become mandatory for the U.S. and probably several other major global locations. However, some technical challenges may be faced because of the trace sulfur, say 30 ppm, and high olefin content of the FCC gasoline, about 15% as opposed to about 0.2% olefins in reformer gasoline. The chances are that hydrotreating of the HS FCC gasoline say 300 scf/bbl will be required at the very least for sulfur removal, and most likely for traces of nitrogen as well. Otherwise sulfur and nitrogen species could end up in the benzene and prevent achieving the required benzene specifications, especially for alkylation processing.

The assumed benzene recovery from HS FCC gasoline would become economically more viable after disproportionation of toluene in the FCC gasoline to additional benzene and xylene, probably for downstream production of p-xylene. Therefore, benzene recovery would become almost incidental to p-xylene production, and the overall economics of HS- FCC would be governed by the assumed values of VGO as well as values of propylene and marketing issues regarding p-xylene. 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 the VGO. It is speculated that for HS FCC projects, mostly in China and recent projects in the Middle East, the assigned values of VGO are considerably lower than the known posted market rates. However, once advantageous pricing for VGO is obtained, the option of conventional steam cracking of hydrotreated VGO also deserves consideration. The selection between conventional steam cracking of VGO and HS FCC would be greatly affected by marketing consideration of p-xylene. The issue of basic nitrogen, if it exists to a significant degree in VGO, deserves serious attention due to potential deactivation of the assumed ZSM-5 zeolite catalysts normally used in HS FCC. Many heavy crude oils such as Maya crude in Mexico, Canadian heavy and bitumen are known for high content of basic nitrogen and perhaps other catalysts, not known to public domain would be required.

To illustrate the above “marketing issues” of p-xylene, the following is the estimated global production of products that could be partially attributed to HS FCC:

	<u>KT/Y</u>
Gasoline	900,000
Ethylene	115,000
Propylene	70,000
Benzene	37,000
p-Xylene	23,000

The xylene yield, say 20-25% after toluene conversion, in a typical HS- FCC, could be about 1.25 times the propylene yield. The global production ratio of p-xylene to propylene as shown above is about 0.33. Aromatic control in gasoline, especially in Europe, by co-production of p-xylene would face the above marketing constraints.

Finally, it should be noted that molecules of xylene, including a portion of p-xylene and let alone benzene, already exist in any reformat that is being blended to gasoline. Thus the proposed production of p-xylene from HS FCC could be a classic syndrome of the “tail wagging the dog” and be a niche market at best.

We recognize that the market demands propylene, which is decoupled from the production of ethylene, thus bringing the propylene to ethylene to the correct market ratio. However the proposed method of producing propylene via HS FCC will decouple the propylene from ethylene but will re couple it to p-xylene.

Given all the above we should be aware that production of propylene via dimerization of ethylene to C₄ olefins and subsequent reaction of C₄ olefins with ethylene to produce propylene are commercially proven and very economical processes that deserve a serious consideration. We are aware that toluene from HS FCC gasoline could be converted to benzene by hydrodealkylation. However as discussed the economics of this process are very cyclic and for most part can not compete with molecules of benzene that already exist in reformer gasoline.

Benzene from oil sand

Alberta Energy Research, the province of Alberta, and the Hydrocarbon upgrading task force (HUTF) have sponsored, along with interested parties, a number of studies related to the added value of petrochemicals production from bitumen produced in the Fort McMurray area of Northern Alberta. Initial studies, 200,000 bpsd bitumen, using HS FCC and p-xylene co-production have shown relatively high benzene production, about - 4.5 wt% of the bitumen, but altogether, on a global project basis, not sufficiently attractive economics. In a more recent bitumen study of a 300,000 bpsd bitumen upgrading refinery with petrochemical integration, mostly ethylene, the ultimate benzene production of the proposed design configuration is under 200 KT/Y, about 1.1%, but altogether attractive economics on global project basis. This benzene contained as 72 wt% in enriched pyrolysis gasoline, although a nice revenue stream, still represents a niche market situation for benzene.

LPG to benzene

A single commercial Cyclar plant, benzene from LPG at about 18 wt% benzene yield and production of other aromatics, was built in 1998 in Saudi Arabia. No additional second plant was built or known to be in planning stage. This and the fact that other equivalent processes did not impact the global benzene production leads one to speculate that alternate methods of producing benzene have proven more economical than Cyclar.

Benzene by AROMAX

Not much has been published about this process in the public domain. From the patents assigned to Chevron-Phillips we learn that the AROMAX process involves cyclizing C₆ molecules in high temperature catalytic environment similar to catalytic reforming, but probably using a different catalyst, and for the sole purpose of producing benzene as a key product along with hydrogen and incidental light fuels. No doubt, the benzene yield is much higher than benzene yield of conventional catalytic reforming of heavy naphtha, but the overall economics is a function of many factors. As a matter of general interest, in the 1970's IFP has developed a process focusing on benzene production by cyclizing C₆ but this process has been abandoned in favor of conventional catalytic reforming.

As of now, about five Aromax units are known to exist, most if not all owned or partially owned by Chevron-Phillips. A new and probably the largest unit is approaching completion in Saudi Arabia and is probably based on feedstock of NGL rich in C₆. Based on prior known practices in Saudi Arabia, we believe that a dual pricing system could have been used for NGL fuel gas and power for this AROMAX as well as other petrochemical projects in Kingdom of Saudi Arabia, especially the one based on feedstock derived from natural gas. It is not clear what would be the future feedstock pricing practice in Saudi Arabia after joining the world trade organization WTO.

Benzene via membranes.

We are aware that removal of benzene via membranes from coker naphtha has been proposed by others. As for straight run naphtha, we are proposing fractionating the coker naphtha and for that matter hydrocracker naphtha, with lower than normal cut point. This fractionation will shift the benzene to the heavy naphtha fraction and consequently to the reformer feed. Ultimately the benzene will be captured in the reformate and the membrane processing would be avoided with added benzene recovery.

Benzene from catalytic reforming

Reforming Overview

Most reformers built in past generation, about 35% of global reforming capacity, are of the continuous catalyst regeneration (CCR) type. U.S. gasoline comprises about 28% reformate and 12% alkylate as key octane boosters. European gasoline pools comprise 44% reformate and 3% alkylate. Essentially all the balance comprises FCC gasoline and light naphtha, mostly isomerized. On global basis, reformates are produced in 450 refineries including in 120 refineries out of 140 in the U.S., twenty in Canada and six

large refineries in Mexico. A typical reforming capacity ranges in volumetric capacity between 10-30% of the input to the crude oil distillation unit and its volumetric yield between 75-82 vol% of high octane reformat. The majority of feeds to reformers and associated isomerization units comprises straight run naphtha while a portion, say 15-20%, is from hydrocracking naphtha and cokers naphtha that are relatively rich in benzene, about 2-3 vol%. The octane of reformates typically ranges from 94 RON to 102 RON and up to 106 RON in petrochemical refineries. Octane of about 97-101 RON would be a reasonable range for a modern reformers producing high octane blending components (HOBC) [12].

A good measure for naphtha reforming quality is N+2A, which is the volumetric percentage of naphthene content plus twice the percentage of aromatics content. An N+2A over 50 would represent a good reforming feedstock and N+2A of 70 would represent an excellent feedstock. Highly paraffinic naphthas, typically from the Middle East may have a N+2A contents around 35-40 and thus are good for olefin via steam cracking but traditionally less advantageous for reforming as compared with naphtha from crude oils such as Brent North Sea (N+2A of 72), light Louisiana crude and Alaska North Slope (N+2A of 60), Mexican Isthmus (N+2A of 52), Dura (Indonesia) and West African (N+2A of 78-80). In this context, it is worth mentioning that naphtha produced by gas to liquids (GTL), is expected to be of low octane, very paraffinic and essentially non-reformable. However, it would be a good feedstock for steam cracking, which normally is economically driven by the high olefins yield. Based on recently published capital investment data for GTL, the GTL derived naphtha is expected to be by far more expensive than the dilute benzene feed proposed for steam cracking.

In any of the above methods, additional benzene could be produced by hydrodealkylation (HDA) of toluene. 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's share captive to catalytic reforming and amounts to about 6% of global benzene production. The economics of converting toluene, and in rare cases xylene, to benzene by HDA is a function of the relative values of benzene to toluene as well as the cost of hydrogen and the value of fuel gas. The basic benzene yield of HDA is about 80 vol % and, in today market, this operation could be 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 p-xylene. About 12-13% of global benzene production is attributed to production of p-xylene.

Case study: benzene recovery from refinery sources

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

Reverting reformers operations to those before the 1990 Clean Air Act could significantly increase the benzene yield as well as hydrogen yield and, in most cases, with a relatively

small capital investment if any. However, in some cases, especially in California, the added isomerization capacity is so integrated with the reforming operation that reverting to pre-1990 Clean Air Act operation could become a more complex, but not impossible, issue. Needless to say, installation of new reforming capacity would be more ideally suited for the proposed production of dilute benzene. As a general point of interest, it is estimated that since the 1990 Clean Air Act, close to 30,000 bpsd (1,440 KT/Y) of benzene have disappeared from the U.S. gasoline pool alone. The real question is how much of it could be economically reverted and be used for petrochemical applications and also co-production of hydrogen.

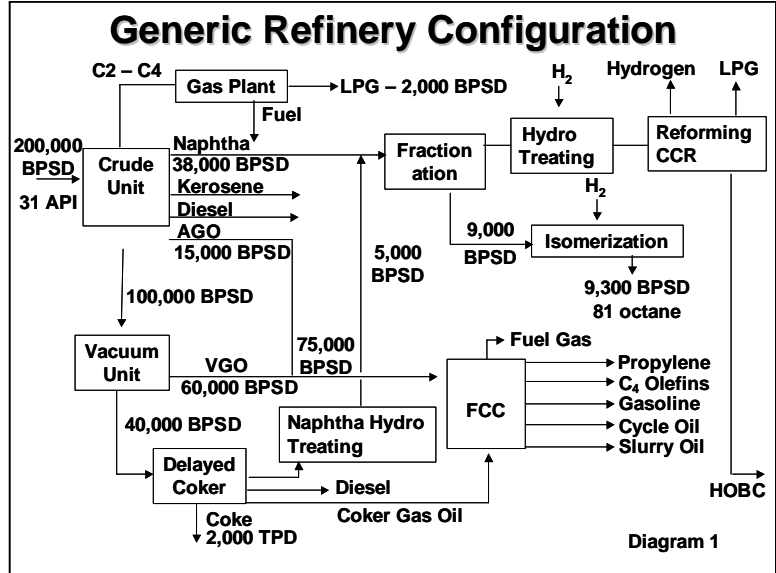
All present methods of reconfiguring reformers for minimum benzene production have nearly reached their practical limits. Thus the only practiced methods of eliminating benzene for meeting the new regulations is by either hydrogenation of a benzene heart cut concentrate and potentially as suggested in number of patents [16-21] for alkylation with light olefins, probably FCC off gases. In either case, fractionation of benzene heart cut concentrate will be required. Thus diversion of dilute benzene to OBL, either adjacent or in remote location steam cracking could present a good synergism. In about four U.S. (two Gulf Coast and two in North East), two Canadian refineries and probably several European and Japanese refineries, C₆/C₇ heart cut benzene concentrate, about 20-25 vol% benzene, from catalytic 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 US North East, the benzene concentrate is shipped to the U.S. Gulf Coast and possibly other locations.

As said, gasoline consumption in Europe is on the decline, about 0.9 % per year. On this basis, removal of dilute benzene from the gasoline pool in Europe for petrochemical usage will be the most economical way to achieve supply/demand balance while upgrading the environmental quality of the gasoline and raising the octane.

At least in U.S. and European refineries, benzene attributed to reforming represents 50-80% of the total benzene in gasoline for a given refinery, while the balance is mostly in the FCC gasoline. Therefore, eliminating this benzene from reformat streams as discussed later, would present the most viable approach for meeting the new environmental regulations while simultaneously elevating the octane and recovering a valuable petrochemical product. Reducing benzene from FCC gasoline, average about 0.65-0.70 vol% and typically 0.5-1.2 vol%, depending on severity would present a very uneconomical operation using known conventional methods of extraction or hydrotreating. The high olefin content of FCC gasoline is a significant contributor to this difficulty.

Illustrative refinery configuration with typical catalytic reforming (Diagram [1])

Diagram [1] represents a conventional high conversion 200,000 bpsd (31.5 API) crude input refinery, comprising of 50 vol% Mid-Eastern paraffinic crude and balance of crude oil from Western Hemisphere. The refinery configuration includes a 35,000 bpsd continuous catalytic reforming of naphtha, (N+2A of 50) to produce 28,000 bpsd high octane blending component (HOBC) of 98.5 RON and contained 50 MM scfd hydrogen as 87 mol% purity. The atmospheric fractionation 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 producing 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 producing:

- 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 highly olefinic LPG (to Merox for mercaptan oxidation)
- 10,000 bpsd coker diesel (to hydrotreating)
- 11,000 bpsd heavy coker gas oil (to FCC)
- Coker off gas to fuel.

The combined atmospheric, vacuum and coker gas oils (86,000 bpsd) is fed to a conventional FCC unit producing:

- 49,000 bpsd gasoline (end point 430°F, benzene content 0.65 vol%)
- Light cycle oil, an aromatic diesel material (15,000 bpsd)
- Slurry oil, a 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 of imported isobutane is feed to a 9,000 bpsd alkylation unit. The alkylate (95 RON, 92 MON) is blended into gasoline.

The coker naphtha, rich in olefins, (say 30 wt% olefins, 3 wt% diolefins 1 wt% sulfur and 2% benzene) is hydrotreated in two stages for olefins, diolefins and bulk sulfur and nitrogen removal. The atmospheric naphtha and hydrotreated coker naphtha are pre-fractionated to produce 9,000 bpsd light naphtha (C₅-C₆) and 34,000 bpsd heavy cut (205°F, 96°C cut point). The combined heavy naphtha is hydrotreated for trace sulfur removal and fed to the catalytic reformer to produce 27,500 bpsd reformat (98.5 RON, containing 3.6 vol%), 1,000 bpsd benzene (4 wt%) and 6,500 bpsd C₅-C₇ non-aromatics (23.5 vol%).

A light reformat dilute benzene cut (7,500 bpsd, 70 RON, 58 MON) is fractionated and sent as a feed to steam cracking. An optional fractionation of 3,300 bpsd C₅ and Iso-C₆ is possible and in many cases economical. Sending this stream to isomerization would enhance the octane of this fraction by 4-5 points and about 0.12-0.15 RON for the entire gasoline pool.

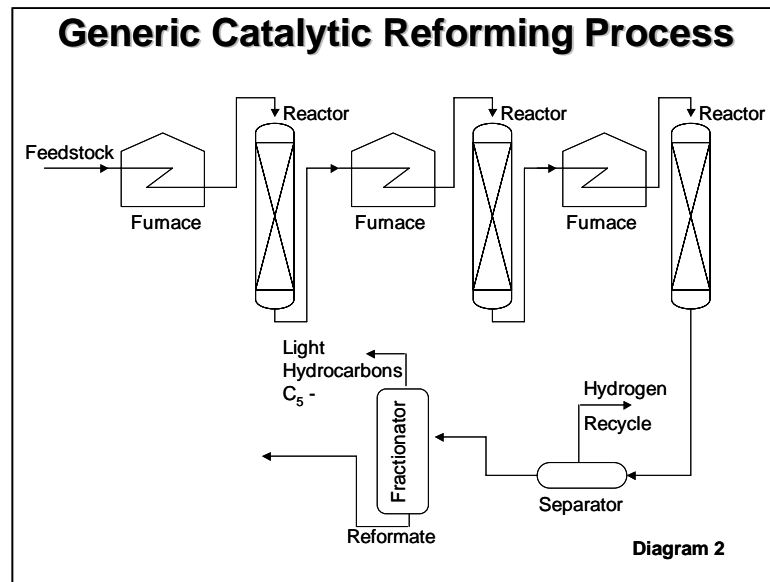
Under the first scenario, the net gasoline make is 87,000 bpsd and 7,500 bpsd of steam cracking feedstock containing 13.3 vol% benzene. In the alternate case, more likely in remote integration of the refinery and steam cracker, 90,300 bpsd of gasoline is produced and 4,200 bpsd C₆/C₇ petrochemical feedstock (containing 24 vol% benzene) is feed to the steam cracker.

In the first case the RON of the gasoline is raised 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 \$80,000-100,000 per day and at this point, no revenue consideration is given to reduction in RVP. The reduction in RVP may allow blending of N-butane into the gasoline pool.

If, as discussed later, 20% added reforming capacity can be made available, about 7,000 bpsd of naphtha dedicated to steam cracking (or from an alternate source) could be partially swapped against dilute benzene. Reforming of this OBL naphtha will produce an additional 10 MM scfd of hydrogen and additional 15 KT/Y of LPG. The total gasoline make under this scenario will be 92,600 bpsd and 94.2 RON.

Once dilute benzene recovery is in place, or for that matter even the 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. This operation, upon reverting to pre-1990 Clean Air Act operation, will also result in substantially higher co-production of hydrogen, which is very synergistic with future trend of refining industry using increasingly lower API, higher sulfur and hydrogen deficient crude oils. Adding precursors of benzene to reformer feed may increase the firing duty of the first heater by some 10% and perhaps some other minor debottlenecking would be required. Adding an inexpensive ceramic coating, say a \$500,000 investment, could alleviate this potential bottleneck.

Diagram [2] reference [12] represents a simplified scheme for continuous catalytic reforming. Naphtha feed is pre-fractionated of a majority of benzene precursors as light depleted naphtha. The heavy C_7 -360°F naphtha is being hydrotreated, primarily for organic sulfur, to less than 1 ppm, and nitrogen. Hydrotreated naphtha enters a three- or four-

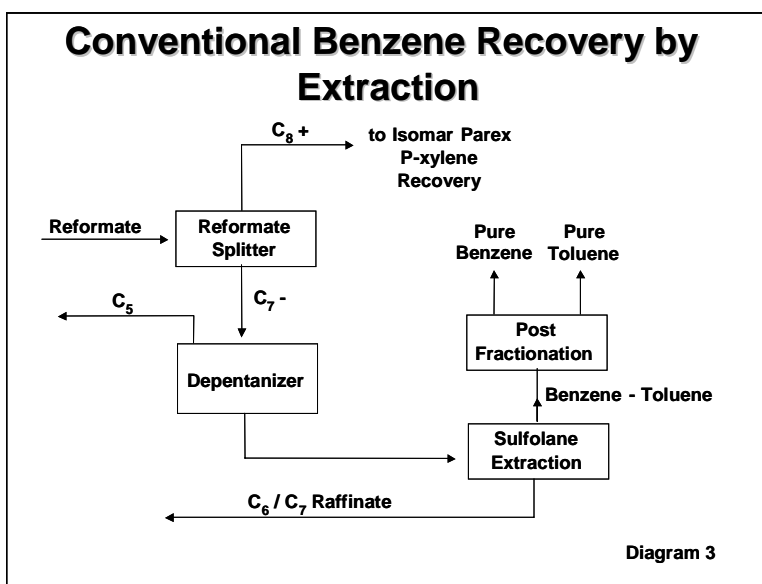


stage reformer operating at a nominal 5 bars-g and 840-930°F (450-500°C) reforming initial pressure and temperatures. Reformer hydrogen rich product gas is recycled at ratio of 6.0 to 1.0 to the feed on molar basis. Heat is recovered from the flue gas interheaters, producing steam at 40 bar-g and 750°F (400°C). This steam is used as motive power in the refinery, and steam turbine for the reformer recycle compressor would be an ideal user. The reformat undergoes stabilization by separating a C_3/C_4 LPG product and a hydrogen rich by product, about 50 MM scfd of contained hydrogen as 87-90 vol% and balance $C_1 - C_4$ proceeds to 40-43 MM scfd hydrogen recovery, probably via PSA. Most of the hydrogen goes to diesel hydrotreating and the balance goes to naphtha hydrotreating. The hydrotreater off gas, mostly H_2S , is routed to a sulfur recovery unit. In most cases, the light depleted naphtha is isomerized for octane boosting and blended to gasoline pool. However, this light naphtha and more so after isomerization is a significant contributor to RVP of the gasoline pool, and still relatively low in octane. Therefore, exporting this naphtha as feed to steam cracking may be worth consideration.

Diagram [3] represents a “typical” benzene recovery from catalytic reforming sources (4-9 wt%, 3.5-8 vol% benzene in reformat streams) using extraction such as the Sulfolane process [15].

As said, about 75% of reformers and probably about 50% of reforming capacity do not practice benzene or BTX recovery from HOBC reformat streams. To the contrary, in order to minimize benzene in gasoline pool, at least in U.S., Canada, Australia, West Europe and Japan, benzene and precursors of benzene such as cyclohexane and methylcyclopentane are pre-fractionated prior to reforming to meet gasoline pool benzene specifications and not necessarily optimal gasoline production. Thus, the refinery operation is driven not by gasoline economy as prior to Clean Air Act of 1990, but rather governed by environmental considerations aiming at benzene reduction. Recovery of dilute benzene or benzene concentrate for steam cracking, as 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 and actually exceed all new environmental limitations related to benzene.

As shown in the conventional scheme, reformat is split with C₈+ produced as heavy reformat and C₅-C₇ (including toluene) as a light cut. This fractionation uses about 70 trays. The light cut is depentanized and then the aromatics are extracted. Benzene and toluene are extracted as a BT mixture and undergo post fractionation for benzene recovery and incidental pure toluene recovery.



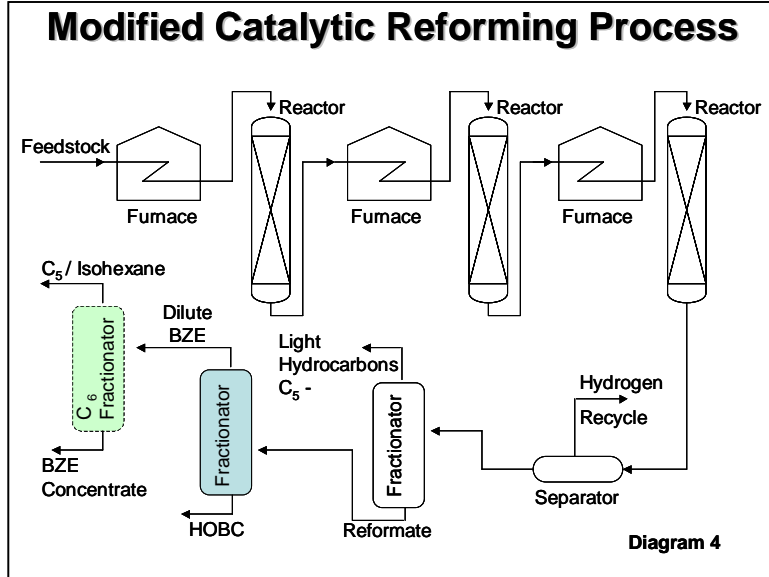
The C₆/C₇ raffinate (55-60 RON) could be reblended into the gasoline pool but more likely will go OBL as a feed to steam cracking.

Recovery of benzene from pyrolysis gasoline from steam cracking, say 35-50 wt %, lends itself more in favor to extractive distillation, such as Uhde's Morphylane, Lurgi's Distapex or GTC Technology, rather than to conventional, typically Sulfolane extraction.

New method of benzene recovery from HOBC catalytic reforming sources

Referring to Diagram [4], reformat (94-102 RON) is fractionated in a simple 75 tray, low pressure column to produce a light cut of unconverted naphtha (mostly C₅-C₇ paraffins) containing essentially all the produced benzene (200°F cut point). This low octane stream, typically 68-72 RON, about 20-25 vol% of the reformat, contains 10-17 vol% benzene and essentially no toluene. This is a bad stream to blend into a gasoline pool (92 RON). This material is used as a feed, or more likely a partial feed, to a steam cracker. The heavy cut is a very high octane (105-115 RON), low RVP (Reid Vapor pressure) gasoline blending component. In another variation of this scheme especially preferred for remote integration and minimizing transportation cost, the benzene is

further concentrated by fractionation of the C₅s and light C₆s, which are returned to the gasoline pool. The assumed dilute benzene/ benzene concentrate cuts as fed to the steam cracking would represent 4-6% of the typical U.S. gasoline pool and 6-8 % of a typical European pool for benzene concentrate and 6-10% and 9-12% for dilute benzene respectively, depending on specific refinery configuration.



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

The recovery of benzene from reformate will call for pre-fractionation of the reformate feed, including coker naphtha and hydrocracker naphtha, in such a way that benzene and its pre-cursors such as cyclohexane (boiling point 180°F) will be routed to the reformer rather than to light gasoline. By this process, all the benzene bearing streams except FCC gasoline will be accounted in the proposed benzene recovery schemes.

Naphtha/ ethanol dilute benzene swap to improve the above method

It has been discovered that in about 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, in 70 % of U.S. reformers, an additional 15-20 % capacity could be achieved with an investment of only 3-5% of cost of a new reformer of the same capacity. For example, the investment in a 35,000 bpsd reformer (including OBL) could be in the order of \$180 MM US while for \$8.0 MM it may be debottlenecked to 42,000 bpsd while preserving the original octane rating. A typical debottlenecking may involve replacing the feed effluent exchanger with a plate type exchanger such as manufactured by Packinox, ceramic coating of the tubes in the heaters and other mechanical modifications as would be applied on case by case basis.

Under the above scenario, naphtha from OBL and dedicated to steam cracking is swapped for an unconverted dilute benzene naphtha cut. Application of this concept is likely to elevate the RON of the gasoline pool by 1.8-2.5 numbers and will increase hydrogen and LPG production, reduce benzene in the gasoline pool and will reduce RVP.

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) drivability index and other properties, since these issues could affect some of the design considerations. As said, it should be noted that typical naphtha dedicated to steam cracking tends to be paraffinic, in order to achieve the 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 case basis. It is probably a good assumption that the recent shortage of benzene could have shifted the optimal feed to a steam cracker towards a more aromatic rich feedstock. Stripping of dissolved oxygen from naphtha from OBL storage sources may be a prudent idea and this could be achieved by a 10 tray stripper using nitrogen.

If the added reforming capacity can't be achieved, as is the case in 30% of the refineries, the dilute benzene could be swapped for light C₅ /C₆ naphtha from OBL. This naphtha with a probable RON of 60-63 could be isomerized to RON 80-83 or be blended directly to gasoline, depending on specific refinery considerations.

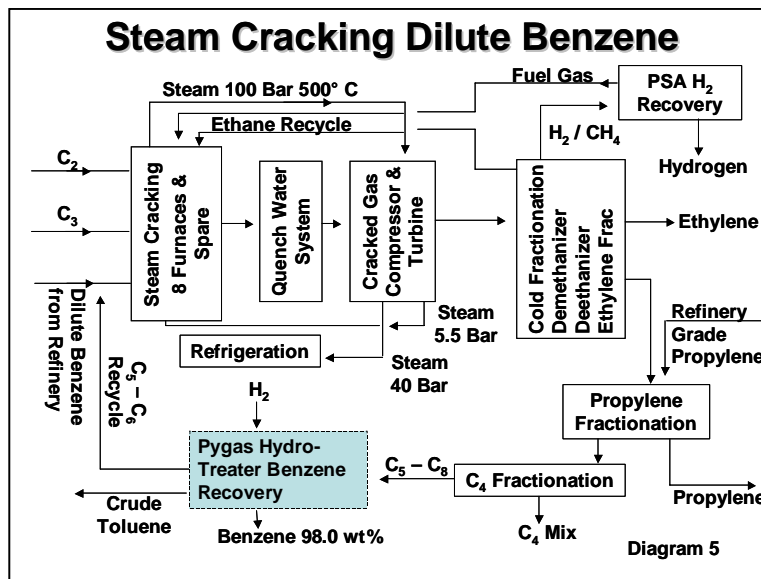
An alternate swap could be swapping dilute benzene or benzene concentrate for ethanol. This could be very synergistic with the recent phase out of MTBE in order to maintain the oxygen content, preserve the T-50 and further elevate the octane. However blending ethanol will increase RVP. This issue needs to be addressed on a case by case basis, considering the 1.0 psi waiver for gasoline/methanol blends.

The naphtha/ethanol swap method could have an additional potential advantage when a total limit is imposed on total aromatics, such as 35 wt%, as well as on olefins such as 18 wt%. Under this scenario, benzene concentrate, say 30 wt% benzene, will be drawn rather than dilute (say 15 wt%) benzene. The impact on the aromatic content of the gasoline pool will be minimal. Once the benzene concentrate is swapped for light naphtha or ethanol, the total gasoline aromatic content is reduced and the total olefin content remains unchanged.

Since the great majority of olefins are attributed to the FCC gasoline, controlling olefins is beyond the scope of this paper. Nevertheless, the following could be a point of interest. Hydrotreating FCC gasoline for sulfur removal involves non desirable side reaction of olefins saturation. This olefins saturation, besides the hydrogen consumption, results in about a 1.0 RON loss in the gasoline pool. The proposed increase of the octane rating by the elimination of the benzene as a concentrate would be very synergistic with the hydrotreating of FCC gasoline.

Steam cracking of dilute benzene or benzene concentrate (Diagrams [5] [6])

Dilute C₅-C₇ cut benzene stream or in an alternate case a C₆-C₇ cut benzene concentrate can be introduced as an exclusive feed to cracking furnace or in most cases as a partial feed after being mixed with naphtha or condensate. It has been determined by major petrochemical producers that the impact of benzene on the cracker in terms of operability or process limitations is rather small,



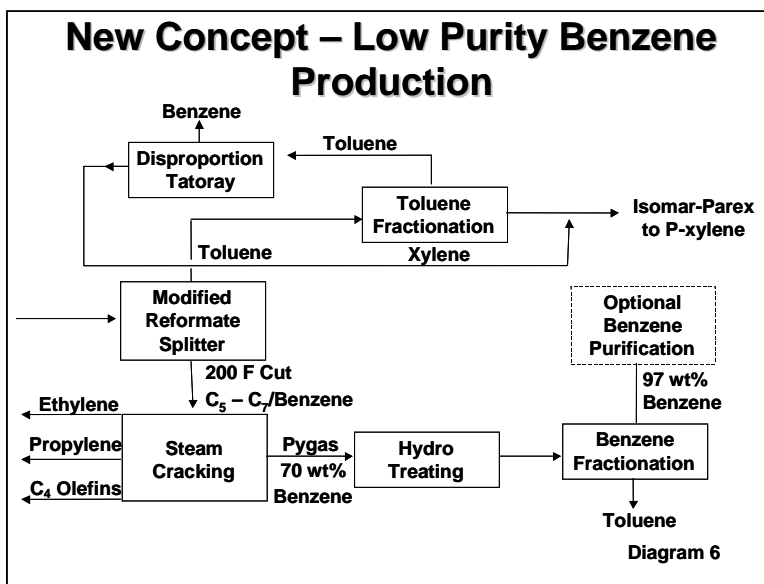
and actually in most cases, is likely to be negligible. Steam cracking of benzene rich streams was inadvertently proven in a US Gulf Coast refinery. A Sulfolane benzene extraction unit was forced to shut down, however the reformer had to continue operation due to hydrogen balance considerations in the refinery. Reformate with over 60% aromatics including 7.0 vol% benzene was sold at distress sale to two steam crackers with available cracking and fractionation capacity at the time. As expected, the olefin yield was low and the firing duty per unit olefin production in the furnaces was higher, however, no particular operational problems like coking, were observed and as expected much of the added firing duty was recovered as high pressure steam. The concept of cracking benzene concentrate is accepted now by most major petrochemical producers operating steam crackers. More detailed discussion of these issues could be found in reference [2]

By using benzene concentrate or dilute benzene feeds, the resulting pyrolysis gasoline, instead of being comprised of 35-50 wt% benzene in conventional crackers, would comprise of 70-85 wt% benzene, depending on the relative share of dilute benzene feed. Thus downstream recovery of benzene from a 35-85 wt% benzene concentrate would be by far more economical than benzene recovery from reformate stream comprising of 4-9 wt% benzene. Furthermore, 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 or conventional extraction from reformate streams. To a degree the benzene concentration would be a function of cracking severity. Higher severity will minimize the C₆/C₇ non aromatic production, which will improve the benzene concentration. Nevertheless, the cracking severity at the most is very secondary issue.

Value of dilute benzene and benzene concentrate

An attempt to calculate the fair market value of dilute benzene is shown in references 2 and 4. No published market information is available for dilute benzene or benzene concentrate. The calculation is based upon market conditions of years 2002-2003 with octane and RVP adjustment and no credit was given to environmental impact of benzene removal. The value of dilute benzene was estimated on weight basis to be 10% lower than the value of naphtha. Nevertheless, it is recognized that the real value is subject to negotiation between the refiner and the petrochemical producer and should be established on a case by case basis.

Imposing benzene limits on gasoline producers will create a new situation where a base case would be as practiced in California and Eastern Canada. This base case will have to be evaluated against the proposed concept. For refiners, the value of the dilute benzene will equal the value of the relatively low octane, high RVP light gasoline after derating for capital investment in benzene



fractionation and isomerization and making allowances for hydrogen and steam consumption and including losses of about 0.25 RON from the gasoline pool. This value to the refinery and cost of transporting the benzene will vary on a case by case basis.

For the petrochemical facility, the value of the dilute benzene will be determined from the cracking yield and the values of the subsequent products compared to conventional naphtha feed after adjustment for the cost of transportation of the dilute benzene feed. As a point of general reference, pyrolysis-gasoline containing about 40-50 wt% benzene is being transported in one known instance via rail cars for distances of over 2,000 miles.

Lower purity benzene (Diagram [6])

It has been demonstrated that for a liquid phase or mixed phase aromatic alkylation unit operating at 300-500°F (150-260°C) to produce ethylbenzene and cumene, benzene purity has no impact on the alkylation or transalkylation catalysts.

As for aromatic alkylation, catalyst issues have been fully resolved by ExxonMobil and Atofina. The non aromatics in the benzene feed with some residual benzene are purged to steam cracking (see reference 4), thus all the benzene is ultimately recovered and the

impurities are converted to additional olefins and aromatics. Lower purity benzene will not affect the purity of ethylbenzene or the downstream production of styrene monomer.

Further, pure benzene resulting from most extractive distillation processes, may contain 1-5 ppm of organic nitrogen. This nitrogen, unless removed by a special adsorber, could have a negative impact on alkylation catalysts. The impurities of C_6/C_7 non aromatics as in the proposed method, are totally benign to alkylation catalysts under 260 C.

The initial research by UOP, ExxonMobil, Chevron and Atofina, [16-21] on alkylating dilute benzene streams was motivated by the desire to alkylate benzene concentrate from gasoline, say a 30 wt% benzene heart cut from reformat, with ethylene from FCC off gas. The intent was to reduce the benzene content of the gasoline pool and provide an alternate to benzene hydrogenation. The catalyst, developed for the gasoline application by Chevron, is Zeolite Beta, which also is an excellent application for petrochemical usage. The patent on the formulation of the catalyst [21] has recently expired.

Furthermore, it was also discovered that for cyclohexane oxidation to adipic acid (a precursor to nylon 6,6), benzene purity of 97-98 wt%, where the balance is C_6/C_7 non-aromatics containing methylcyclopentane, the lower purity cyclohexane is more than adequate. A recent pilot plant evaluation, by a nylon 6,6 producer, demonstrated that lower purity cyclohexane and containing about 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 wt% purity, not to exceed 200 ppm methylcyclopentane and 50 ppm aromatics. However, new testing for adipic acid nylon 6,6, about 40% of the global and 60% of 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, 25-40 wt% benzene
- Benzene from typical pyrolysis-gasoline, 85-96 wt% benzene
- Benzene from pyrolysis-gasoline from dilute benzene feed, 96-99 wt% benzene.

Recovery of toluene (92-95 wt%, with 5-8 wt% C_7-C_8 non aromatics) will require an additional column. This raw toluene would be suitable for hydrodealkylation, for producing additional benzene, but with higher hydrogen consumption along with higher fuel gas production.

The final concentration of benzene is simply a function of the ratio of benzene to C_6/C_7 co-boilers in the pyrolysis gasoline resulting from steam cracking and needs to be determined on a case by case basis. This ratio would be related to the feed composition to the cracker and severity of cracking.

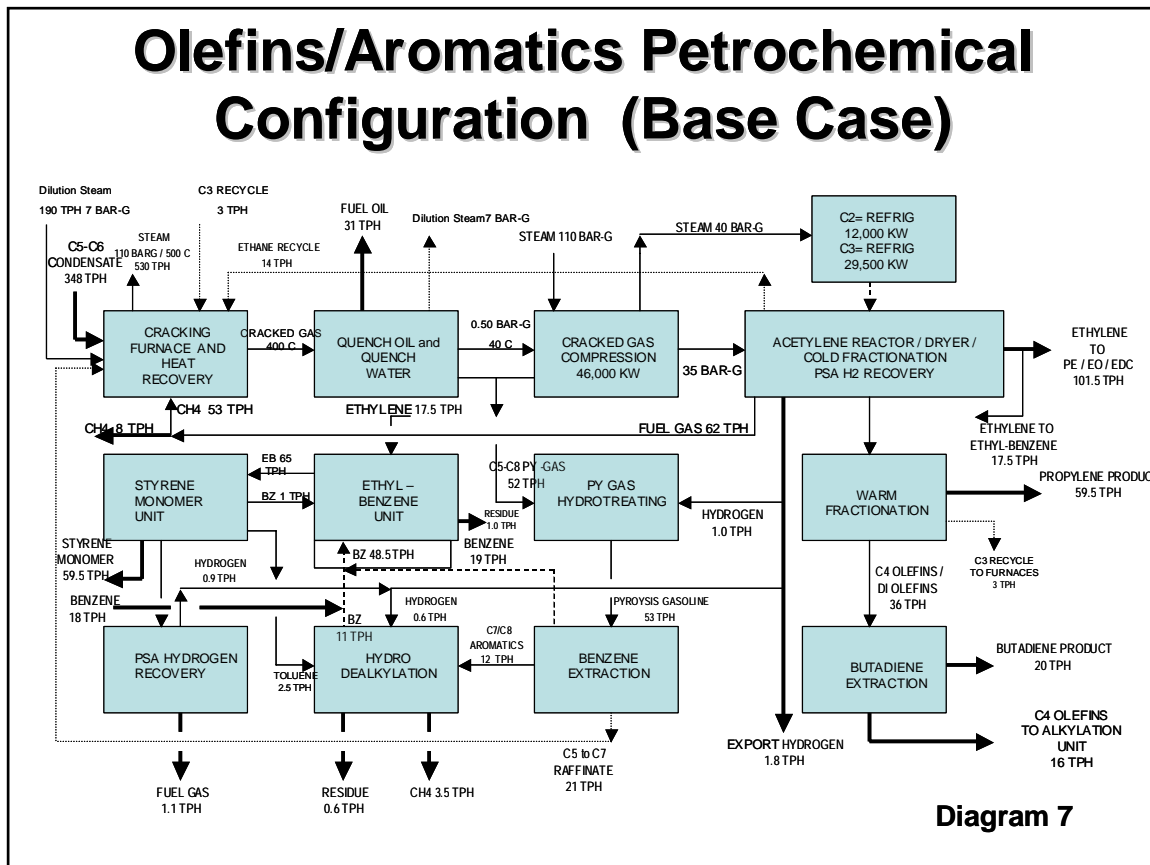
For the very conservative operator producing ethylbenzene by liquid phase or mixed phase, who is concerned about benzene purity, the 97-98 wt% benzene produced by conventional fractionation of pyrolysis gasoline could be further purified to 99.9 wt%. The cost is about 50% of a “normal” extractive distillation of pyrolysis gasoline but uses considerable less utilities, mostly shown as 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 reach their own conclusions. As said, conventional fractionation of benzene from reformat stream HOBC may reach a limit of 25-40 wt%, thus benzene extraction or extractive distillation of reformat is the only way for benzene recovery from reformat streams.

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 cyclohexane oxidation process is based on third party confidential information.

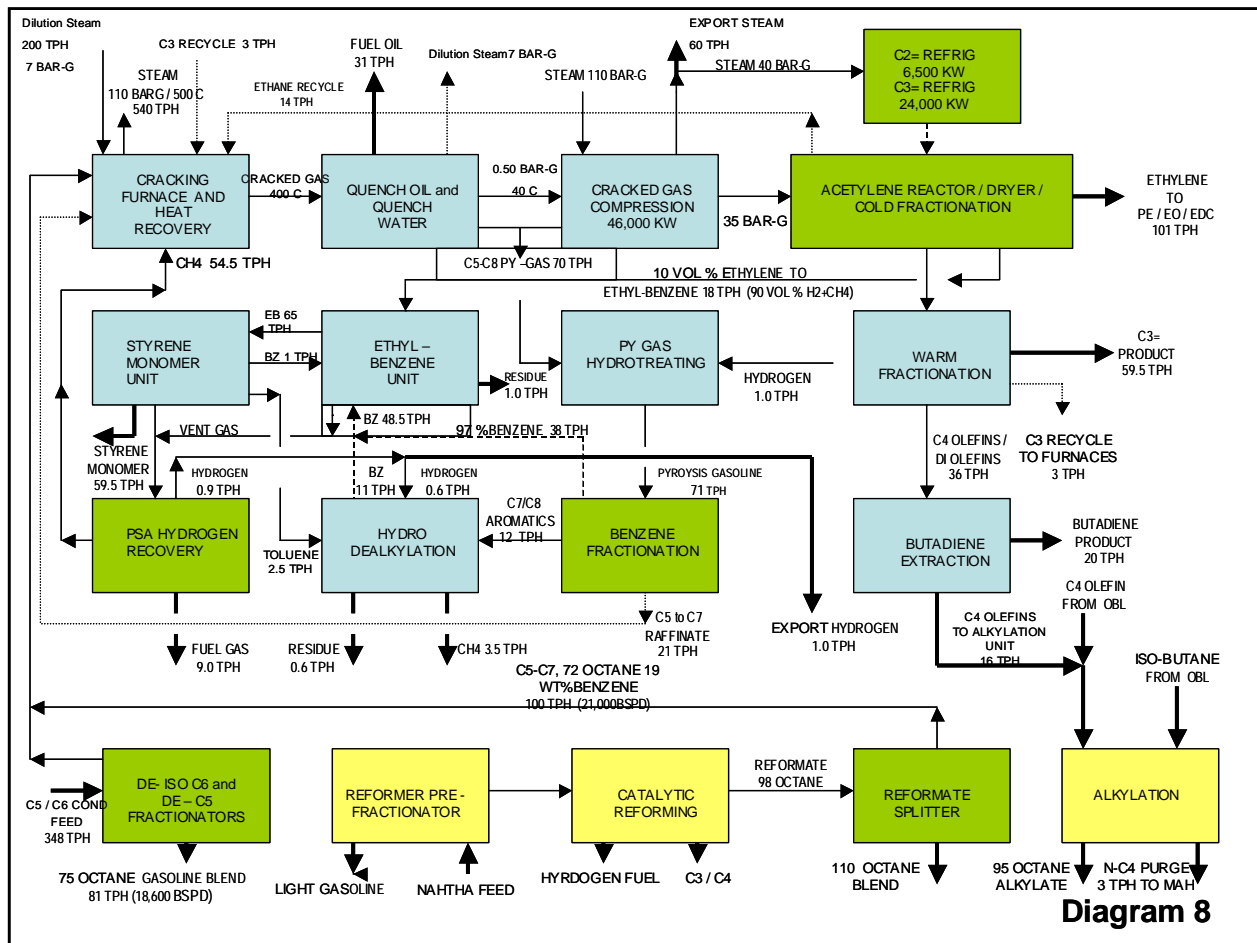
Ethylbenzene-Styrene production

1. **Base Case:**(diagram [7]) A major petrochemical complex that was considered in 2004 is based upon generic and published data. The Base Case represents a conventional steam cracking of light naphtha, mostly C₅/C₆ from natural gas

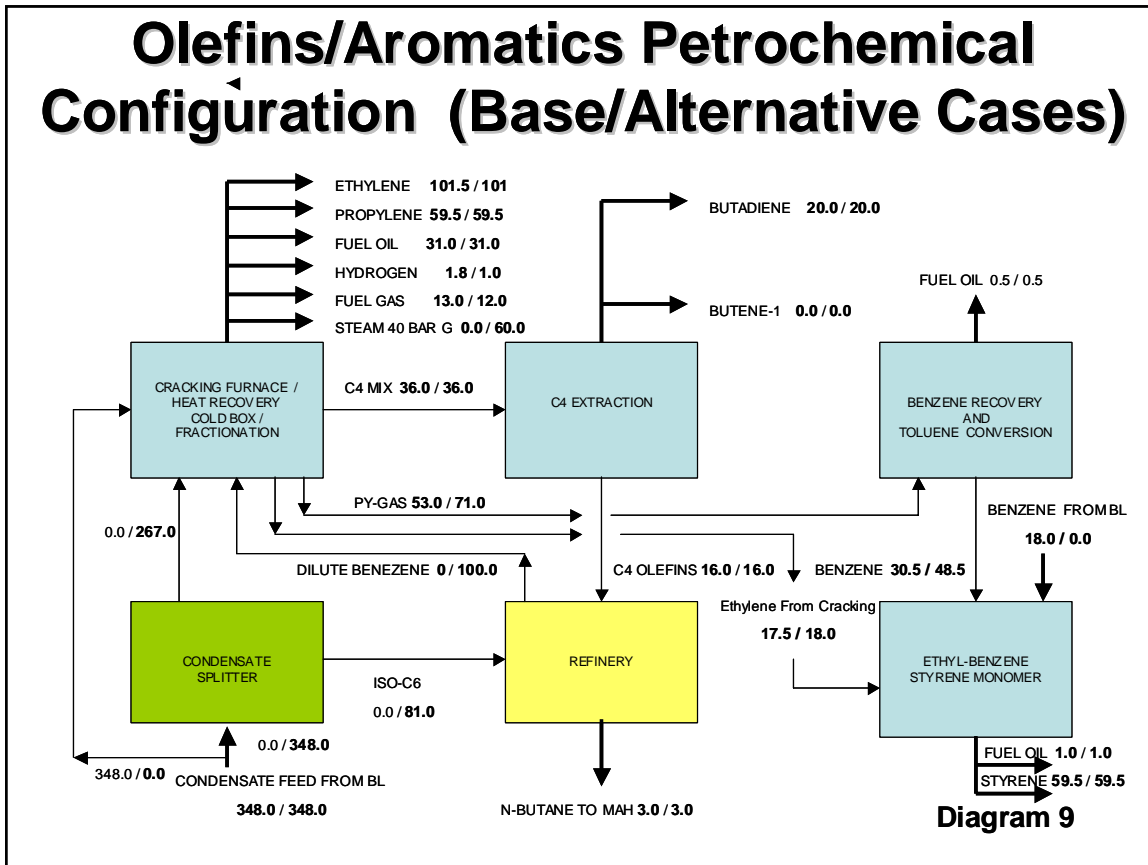


condensate. The assumed project produces 1,000 KT/Y ethylene, 500 KT/Y propylene and 500 KT/Y styrene monomer. Ethylene and propylene are polymerized in a down stream operation. Benzene (about 160 KT/Y) is produced by extractive distillation of hydrotreated pyrolysis gasoline. An additional 70 KT/Y benzene is produced by hydrodealkylation of toluene and xylene. The balance of the benzene, 160 KT/Y, is imported from OBL.

2. **Alternate Case:** (diagram [8]) About 19,000 bpsd of Iso-C₆ (75 RON) is fractionated from 80,000 bpsd of condensate. The I-C₆ and 3,000 bpsd of mixed C₄ olefins is exchanged for 21,000 bpsd of a dilute benzene stream from two refineries and 1,000 bpsd of n-butane purge stream from alkylation. Based on this scheme, the gasoline production rate, the octane and the Reid vapor pressure (RVP) and all other gasoline qualities remain the same or slightly improved. About 160 KT/Y of benzene is removed from the gasoline pool and the petrochemical complex becomes self sufficient in benzene. Additional advantages are obtained from dilute ethylene alkylation using 10 vol% ethylene obtained from a demethanization zone operating at about 30 bars. Benzene at 97 wt% purity is produced, which avoids aromatic extraction



3. **Economic Diagram (diagram [9])** shows the two cases: Using product and feedstock values of October 2004 show the net benefit of the Alternate Case is \$130 MM US per year and giving no credit for the benzene removal from the gasoline. The total cost of feedstock is estimated to be \$1,200 MM per year. The total value of products is estimated to be \$2,000 MM US per year. Thus the added benefit represents 11% of the feedstock and 27% of the margin.

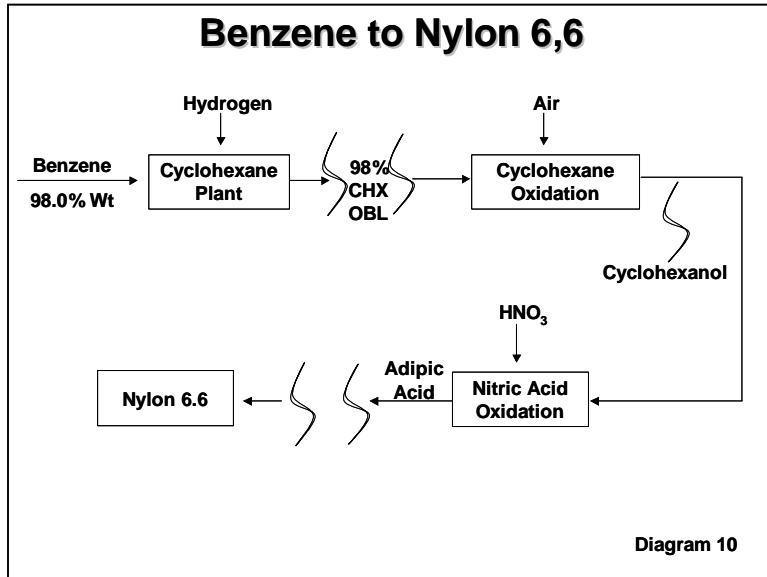


Integrated--Ethylbenzene with steam cracking and catalytic reforming

This case is described in reference [4]. The cost estimates and products pricing data are based on year 2003 and need to be adjusted. Nevertheless as shown for 2003, the payback is compelling and no environmental credit is given for the benzene removal in the refineries. It is a safe assumption that based on today's marketing the concept is even more compelling.

Cyclohexane case (Diagram [10])

A gas cracker in the U.S. Gulf Coast cracking ethane and propane in 8 furnaces (plus one spare) 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 refineries and will be cracked in three cracking furnaces. Benzene is recovered from hydrotreated



pyrolysis gasoline by conventional fractionation as 97-98 wt% benzene with the balance of C₆/C₇ non aromatics including about 3,000 ppm of methylcyclopentane. The benzene would be dedicated for on site conversion to cyclohexane using hydrogen produced by the cracker. The lower purity cyclohexane is sent OBL for air oxidation followed by oxidation with nitric acid to adipic acid. The oxidation has been tested in a pilot plant of a major nylon 6,6 producer and all necessary modifications to the existing system have been identified. As said, the nature of the modification remains third party confidential.

1. Diagram 5 represents the configuration of a steam cracker prior to revamp. This operation calls for five furnaces operating on propane net feed of 29 ton per hour each plus 6.5 tph propane recycle. Also three furnaces on ethane (16 ton per hour net feed on each) in addition to 7.0 tph 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 pyrolysis-gasoline are sent OBL for hydrotreating and olefins saturation.
2. Diagram 5 blue shaded block represents the revamped operation. Two stages of C₅-C₈ Pyrolysis-gasoline hydrotreating are added. The first stage converts diolefins to olefins while the second stage saturates the olefins and removes sulfur compounds that could be critical to the cyclohexane oxidation process. A new cyclohexane unit (220 KT/Y) is added that exports 26 tph of steam (5.5 bar-g) to the steam cracker dilution steam system, which reduces the dilution steam make by about 33%. The mostly C₅ hydrotreated pyrolysis-gasoline (2,000 bpsd, 9.0 tph) is recycled to three cracking furnaces along with the dilute benzene feed (22,000 bpsd, 110 tph).
3. As said, the lower purity cyclohexane is sent OBL to an oxidation facility that uses a proprietary process as well as a proprietary modification to handle the impurities.

This concept of lower purity cyclohexane has been accepted by a second major nylon 6,6 producer as a viable route for nylon 6,6. The reduction in cost of cyclohexane would be

very much site specific. Early analysis of lower purity benzene production shows a 30% cost advantage in producing ethylbenzene-styrene [2]. Nevertheless, the introduction of dilute benzene feed changes the product slate, for example, increasing propylene yield, very substantially increasing benzene yield and the C₄ mix yield. The cost of dilute benzene feedstock, the value of by products, and the overall business model will greatly affect the value of the cyclohexane.

Total global opportunity

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

Summary

It is our opinion that, with the exception of niche market situations and advantageous feedstock pricing, benzene production via the conventional route as a co-product of 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 (over 3,500 KT/Y) are here and now are being blended into gasoline while the refining industry is facing investments to reduce this material in gasoline.

Reverting to pre-1990 Clean Air Act and the appropriate European and Japanese regulations could further alleviate the shortage of benzene for petrochemical industries by increasing the availability of benzene up to 5,000 KT/Y.

The recovery of benzene for use as a dilute benzene feedstock in steam cracking and downstream benzene recovery from pyrolysis gasoline is by far more economical than conventional extraction of benzene from reformat streams.

Recovery of benzene as an impure material (97-98 wt%) could fill over 60% of the market's need. Once vapor phase alkylation for the production of ethylbenzene-styrene is replaced by liquid phase or mixed phase processes, which is the industry trend, well over 80% of the market for benzene derivatives will fit the lower purity mode. Mixed phase alkylation is applicable for dilute ethylene alkylation and is well described in reference [4].

Based on all the above and given the following facts:

1. the relative reforming capacity in the Middle East is limited,
2. the naphtha is paraffinic and lean,
3. all steam crackers are gas crackers (mostly ethane crackers),

Production of benzene and derivatives at Middle Eastern locations does not offer an advantage over other global locations, such as the U.S. and Europe, having high reforming capacity for rich naphtha feeds and liquid feedstock steam cracking capacity. Nevertheless it is worth noting that an announced joint venture between Aramco and Dow in Ras Tanura, Saudi Arabia, will focus on ethane and naphtha steam cracking. This project will affect, to a small degree, the benzene balance in the Middle East.

Low cost dilute ethylene or lower purity propylene from steam cracking sources could further enhance the relative economics of benzene derivatives of non Mid East locations [22].

The added advantage of dilute ethylene alkylation (discussed in reference [4]) increases the total savings when producing styrene to a strategic magnitude. Further, it should be noted that dilute ethylene from steam cracking sources as described in reference 4 is totally free of organic nitrogen and other non desirable compounds as would exist in dilute ethylene from FCC off gas.

The final cost of benzene and derivatives should be analyzed on a case by case basis, subject to the cost of feedstock, the value of by-products and the business model. A prior case analysis presented in reference [2] suggests savings of over 30% and no new information suggests the reversal of this assessment.

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