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Here is a new concept for the production of purified benzene, about 98 wt% pure, while co-producing ethylene via steam cracking. The purified benzene is of adequate purity to meet the growing market demand for aromatic alkylates and cyclohexane. This method could be used for disposal of dilute benzene (10-20 vol%) obtained from refinery sources while reducing the Reid Vapor Pressure (RVP) of the gasoline pool and increasing the pool's octane numbers.

For decades benzene at a purity level of 99.9 wt% has been used in the petrochemical industry. This high purity was achieved by aromatic extraction. Improvements in alkylation technology and new data on cyclohexane oxidative processing suggest lower purity benzene can find its way to 90% of the market place, particularly for manufacturing styrene monomer, cumene, cyclohexane, linear alkylated benzene and derivatives, at a benzene cost savings of approximately 30%.

Introduction

Benzene is produced primarily from three sources: catalytic reforming, pyrolysis gasoline and coke oven gas. Benzene from refinery catalytic reforming accounts for about 55% of global production⁽⁶⁾, including associated toluene conversion. Benzene produced from pyrolysis gasoline obtained as a by-product of ethylene manufacturing accounts for about 40% of global benzene production. About 5% of worldwide benzene production is generated from coal sources such as coke oven gas while less than 1% is from C₃-C₄ conversion. It is worth noting that about 19% of benzene is produced via toluene conversion processes⁽⁶⁾; however, the vast majority of toluene originates at catalytic reforming sources. In the USA, which accounts for 30% of the global benzene market⁽⁶⁾, catalytic reforming sources represent 70% of benzene production⁽⁶⁾, including associated toluene conversion processes. Pyrolysis gasoline accounts for 28% and coal sources for 2%.

The most common method of benzene recovery and purification is aromatic extraction. Reformate from catalytic reforming of naphtha, typically composed of 65-82 wt% aromatics and

18-35 wt% non-aromatics, consists essentially of C₅ to C₇ paraffins, mostly isoparaffins. Separation of benzene from C₇ isoparaffins by conventional distillation is rather difficult due to the azeotrope forming characteristics of C₇ isoparaffins as well as of cyclohexane and methylcyclopentane.

About 52% of global benzene production (normally 99.9 wt% purity) is consumed by alkylation with ethylene to produce ethylbenzene, a precursor to styrene. An additional 20% of global benzene production is consumed by alkylation with propylene to produce cumene, which is a precursor to phenol. Furthermore, about 14% of benzene is used to manufacture cyclohexane, a precursor to cyclohexanol, which is in turn a precursor to adipic acid and nylon 6,6. Only about 4% of benzene is used for linear alkylated benzene.

Recent technological advances in alkylation catalysis have created an opportunity to alkylate benzene in the range of 90-99 wt% purity while meeting downstream products' specifications⁽²⁾. Our case study shows that the price of purified benzene (98 wt%) is reduced by US \$90 per ton compared with nitration grade benzene (99.9 wt%).

Existing Benzene Production

Most large scale, high conversion refineries are equipped with catalytic reforming units that are sources of aromatic-rich streams. In most cases, reformers are operated for octane enhancement and the co-production of hydrogen. On a global basis comprising 732 refineries, 420 refineries have a total of 550 catalytic reforming units totaling 11,000,000 BPSD⁽⁴²⁾ capacity. About 115⁽⁴²⁾ of the global reforming facilities are reported to have benzene and other aromatic recovery facilities for downstream petrochemical production. In the U.S., of a total of 143 refineries, 120 have catalytic reforming facilities. Reformer capacity totals 3,500,000 BPSD in 130 reforming units. Only about 34⁽⁴²⁾ of the U.S. refineries are equipped with benzene recovery units. On the U.S. Gulf Coast, 21 out of 35 catalytic reforming facilities are reported to have benzene recovery facilities including ExxonMobil in Baytown, Baton Rouge and Beaumont and Shell in Deer Park where benzene is recovered from the integrated refineries' olefins complexes. No benzene recovery is reported for the 36 U.S. catalytic reforming facilities west of the Rocky Mountains.

Overview of Process Technologies

Continuous Catalytic Reforming

Since 1980, the conventional continuous catalytic reforming process (CCR) is the most widely used method for reforming naphtha to produce reformate and feed for downstream aromatics extraction units. In a conventional CCR process, a C₇₊ naphtha cut is converted into aromatics (65-82 wt%) and non-aromatics (18-35 wt%). The non-aromatics are mostly isoparaffins with only 0.1-1.0 wt% olefins. The reformate is generally routed to an aromatic extraction unit that recovers over 99% of the benzene at high purity while meeting all other product specifications. Full range naphtha is pre-fractionated at about 95°C cut point to C₅/C₆ and a C₇₊ cut. The C₇₊ cut is hydrotreated to less than 0.5 ppm sulfur, which also removes the organic nitrogen and oxygen. The hydrotreated C₇₊ stream proceeds to a multi-stage reformer operating at about 500°C and 5 kg/cm²-g. The CCR unit produces reformate, hydrogen rich gas, and light ends. In the business case we discuss below, 37,200 BPSD (1,670 KT/Y) of reformate that contains 9.0 wt% benzene is generated from common Middle East naphtha. This naphtha is produced from a 12 vol% atmospheric cut of 31°API crude oil⁽²⁰⁾.

AROMAX

The most recent Aromax⁽²²⁾ unit, designed to process 28,000 BPSD, was brought on stream in 1999 for Saudi Chevron Phillips Chemicals in Al-Jubail, Saudi Arabia⁽³⁾. Previously smaller AROMAX units were installed at the Chevron Refinery in Pascagoula, Mississippi and at a petrochemical complex in Puerto Rico. The Al Jubail and Puerto Rico AROMAX units are followed by large production capacities of cyclohexane.

In the AROMAX process, naphtha is hydrotreated and then fractionated^(3,4). To maximize benzene yield, the C₆-C₇ naphtha cut is further processed through an adsorber bed to reduce the sulfur to less than 20 ppb before it is sent to the first stage of the AROMAX reformer. The fractionator's heavy C₈+ naphtha cut proceeds to the second stage of reforming to produce xylenes. The benzene-rich product, containing toluene and C₆-C₇, is routed to an extractive distillation unit for recovery of pure benzene.

CYCLAR

The concept of CCR has been applied to the conversion of C₃-C₄ to BTX in the Cyclar process⁽⁵⁾. A single commercial plant was built for SABIC at Yanbu, Saudi Arabia. The reported benzene yield for 50 wt% C₃ and 50 wt% C₄ LPG (0.54 specific gravity) feedstock is in the range of 18 wt% of high purity benzene product. The total aromatic yield is in the order of 65 wt%; the balance is hydrogen, about 5 wt%; and fuel gas, about 30 wt%⁽⁵⁾.

AROMATIC EXTRACTION

There are several licensed technologies marketed for benzene recovery and purification by extraction or extractive distillation. The Sulfolane extraction process⁽²³⁾, is the most widely used process in terms of market share. Morpholine⁽²⁴⁾, Distapex and GTC⁽²⁵⁾ extractive distillation technologies have a significant market share for single aromatics or either benzene-toluene or toluene-xylene extraction. It is estimated that extractive distillation processes represent about 25% of benzene production while conventional aromatic extraction processes represent the remaining 75% of the benzene market.

Depending on downstream considerations, reformat from a catalytic reforming unit, is fed to a reformat splitter. Two streams are produced: a benzene-toluene cut containing C₅-C₇ non-aromatics and a C₈+ aromatic cut having traces of C₈ non-aromatics. The benzene-toluene cut is normally sent to a depentanizer and then to an aromatic extraction process. This results in recovery of a pure benzene-toluene mixture plus a raffinate that is mostly C₆-C₇ non-aromatics containing about 0.5-0.75% of the benzene and 1.0-1.5% of the toluene. The C₈+ cut is then routed to an aromatic plant, probably for p-xylene production. The preferred outlet for the raffinate and the C₅ stream is steam cracker feedstock. To remove trace olefins and to comply with color specifications, the aromatics extract stream is treated in a clay tower followed by benzene/toluene fractionation.

Global Benzene Production and Specifications

In 2002, the estimated global benzene production is on the order of 33,000 KT/Y⁽⁶⁾ with approximately 30% of this production in the USA. About 52% of the global benzene supply is dedicated to ethylbenzene production, a precursor to styrene.

Benzene specifications are based on ASTM test methods; the key tests are:

- Solidification temperature
- Relative density
- Color
- Boiling range
- Acidity and residual sulfur
- Non-aromatics content

The solidification test is an important specification. The freezing temperature of pure benzene is +5.5°C. Contamination of benzene with C₆-C₇ or toluene will depress the freezing temperature. The freezing point specification of nitration grade benzene, which is the most commonly available grade in the marketplace today, is above 4.85°C. This implies the level of impurities is equivalent to 0.5 wt% of C₆-C₇. Specification of a boiling range test allowing 1.0°C difference between the initial and final boiling points around 80.1°C, or specification of a density test at 15°C where density of the benzene is allowed to be between 0.8820-0.8860, is less sensitive to impurities than the solidification test. In reality, nitration grade benzene is available at over 99.9 wt% with the impurities being toluene, under 500 ppm, and C₆-C₇. It is worth noting that specifications for organic nitrogen, sulfur, olefins, acetylene, moisture, ... are highly dependent on the particular downstream users.

Table 1 shows the historical spot market prices⁽⁷⁾ of nitration grade benzene as well as naphtha in U.S. dollars based on U.S. Gulf Coast delivery. The global price averages for the same period were about the same as these average prices.

Table 1
Average U.S. Gulf Coast Spot Market Price, US \$/MT, for Benzene and Naphtha as Registered in the Month of December

	1990	1991	1992	1993	1994	1995	1996	1997	1998
Benzene	473	361	289	248	351	257	323	326	219
Naphtha	310	186	194	129	167	157	220	171	106
Differential	163	175	95	119	184	100	103	155	113

Due to environmental restrictions already in effect for reformulated gasoline RFG in the U.S., Canada and parts of Europe that effectively limit benzene in the gasoline pool to about 1.0 vol% (0.55-0.8 vol% in California), it was predicted the benzene market would be depressed. However the recent market trend has shown a strong recovery in the price of benzene while maintaining a good margin for toluene as a high octane blending component. In January 2003 the contract price of benzene has reached historically high value of \$1.57/gallon⁽⁴⁵⁾, \$472 per ton, and \$1.95/gallon⁽⁴⁵⁾ spot market price. One proposed method for reducing benzene in the gasoline pool is to alkylate the reformate heart cut's dilute⁽³¹⁾ benzene with ethylene obtained from FCC off gases to form benzene-alkylated fuel. The portion of the marketed pyrolysis gasoline, which is partially hydrotreated and contains about 35-40 wt% benzene, may no longer be acceptable as a blending stock in the gasoline pool and would be diverted for benzene recovery. Reducing the portion that is toluene hydrodealkylated could offset this additional benzene supply. In the year 2000, toluene hydrodealkylation accounted for 6% of global benzene market. The net result is changes in regulations will have a minimal impact on the potential market for the proposed purified benzene concept discussed in this paper.

Since the global production of styrene monomer (approximately 22,000 KT/Y) represents by far the largest share of benzene consumption (about 17,000 KT/Y of benzene), the issues of impure benzene are focused on ethylbenzene. However, the same logic is applicable to the production of cumene, cyclohexane and linear alkylated benzene.

Ethylation of Benzene

Catalytic systems for ethylation of benzene may be grouped into four categories:

1. *Liquid phase alkylation using $AlCl_3$ catalyst.* This method represents about 25% of global market share and is declining. The most recent $AlCl_3$ alkylation system was licensed in 1986⁽²⁶⁾. Industrial grade benzene, in the range of 98-99 wt% purity, has been used in a number of these alkylation systems.
2. *Vapor phase alkylation using zeolite catalyst such as ZSM-5.* This method represents about 50 % of global ethyl benzene (EB) market share and is also declining. The most recent vapor-phase plant was licensed in 1995⁽²⁷⁾. Pure benzene is required for vapor-phase alkylation. The vapor-phase process is known to produce over 1,000 ppm of xylene in the product, which is economically undesirable.
3. *Mixed phase alkylation using zeolite catalyst.* This method^(9, 28) represents about 2%^(8,9,10,11) of global market share and is rapidly increasing. It is capable of using dilute ethylene feed in lieu of polymer grade ethylene and seems very adaptable for accepting purified benzene at purity levels of over 90 wt%. In this case no xylene in the product is produced.
4. *Liquid phase alkylation such as zeolite beta catalyst.* This method represents about 23% of global market share and is increasing⁽²⁸⁾. This alkylation method is the prevailing one since 1995 and is adaptable for accepting 90 wt% purity benzene if the operating temperature is under 260°C.

The zeolite catalyst liquid-phase and mixed-phase systems are very sensitive to organic nitrogen, organic sulfur and to a lesser degree to acetylene and moisture. Additional clay treating or other processes would be required to remove traces of organic nitrogen. The most common sources of organic nitrogen contamination during alkylation are:

- Residual organic nitrogen from certain benzene extraction processes^(24, 25), and
- Traces of dimethylformamide (DMF)⁽¹²⁾ from acetylene extraction in ethylene plants. It has been reported that ethylene delivered via pipeline in the U.S. Gulf Coast is contaminated with traces of DMF.

Key Technical Issues

The source of benzene is a light deheptanized reformat cut consisting of about 12-30 wt% benzene and 70-88 wt% C_5 - C_7 non-aromatics, mostly isoparaffins. Because of the azeotrope forming characteristics of C_6 - C_7 with benzene, conventional fractionation to produce over 80 wt% benzene is essentially impossible. Table-2 is a summary of the azeotropic characteristics of binary benzene and C_6 - C_7 paraffins at atmospheric pressure. The data in Table 2 illustrates conventional fractionation issues. Note that the boiling point of pure benzene is 80.1°C.

Table-2
Binary Benzene and C₆-C₇ Paraffins Azeotropic Characteristics

	Benzene, Wt. %	Boiling Point, °C	Azeotropic B. P., °C
Component			
Cyclohexene	85	82.1	79.5
Cyclohexane	55	81.0	77.5
Methylcyclopentane	10	72.0	71.5
n-Hexane	5	68.5	69.0
2,4 Di-methyl-pentane	48.5	80.5	75.0
2,3 Di-methyl-pentane	79.5	86.0	79.0
2,2 Di-methyl-pentane	46.5	79.0	76.0
n-Heptane	99.3	98.5	80.0
Tri-methyl-butane	50.5		76.5

As an alternate to benzene extraction, our new concept is based on routing benzene-rich light reformat to steam cracking where essentially all non-aromatics are converted to olefins along with some co-production of aromatics. The concept assumes that in a steam cracking environment (815-840°C, residence time of 0.20-0.5 seconds and added dilution steam) benzene is essentially unaffected. Thus the operation and decoking cycle of the cracking furnace is expected to be about identical to the “normal operation” of naphtha cracking.

The purified benzene product, about 98 wt% pure, which is produced by this method contains C₆-C₇ but has no organic nitrogen, no olefins and no sulfur. This benzene is suitable for mixed phase or liquid phase alkylation and liquid phase transalkylation below 260°C using zeolite catalysts without cracking^(13,14) of the non-aromatics. The non-aromatics would be purged from the alkylation loop to the proposed deheptanizer, slightly increasing the fractionation load.

In a conventional ethylene plant designed to process naphtha, the feed typically contains less than 2 wt% benzene and less than 10 wt% total aromatics. Mitsubishi Chemical in Japan and Reliance Industries in India⁽¹⁶⁾ demonstrated one known exception to this practice. In these cases, naphtha derived from Bombay High crude (offshore India) containing up to 25.0 wt% aromatics was cracked. These successful demonstrations strongly suggest that cracking of benzene-rich feed is feasible from an operational viewpoint. In this case the ethylene battery limit (BL) yield for the 29.3 wt% aromatics feed case (Business Case) is about 27.3 wt% ethylene as compared to 37.5 wt% BL yield obtained from the alternate raffinate feed containing 3 wt% aromatics. However, the overall plant economics remain favorable as shown in Tables 3 and 5 below. The yield estimate of the steam cracker is based on the assumption that essentially all of the benzene entering the crackers is unaffected by the cracking environment. The benzene yield calculated for the liquid crackers could be somewhat different from yield obtained by common cracking programs. The database of these programs is limited to about 10.0 wt% benzene and is outside the range of the 28.6 wt% given benzene content in the feed to the cracker as shown in Table 3-A, stream 2.

For disposing of dilute benzene from fuel oriented refineries producing reformat with 3.5 wt% (3.2 vol%) benzene, the benzene-aromatics concentration is expected to be on the order of 17 wt% as opposed to 29 wt% in the illustrated case. This concentration of aromatics is close to the range of commercially available naphtha, thus further minimizing any perception of technical risk associated with steam cracking.

In the final analysis, the predicted yield and overall performance could be confirmed in a pilot test. Several pilot units are available⁽¹⁵⁾ and the estimated cost of conducting relevant tests is less than US \$100,000.

The alkylation of dilute benzene is documented in ExxonMobil^(13, 14) and Atofina patents as well as unpublished data. These references suggest that the same is true for alkylation with propylene for the production of cumene. Since alkylation of benzene with propylene in the liquid phase occurs at about 150°C all issues relating to cracking of impurities would be further minimized.

Cyclohexane Issues

As stated earlier, about 14% of benzene on the market is converted to cyclohexane by hydrogenation in either the liquid or vapor phase⁽²⁹⁾. Over 90% of cyclohexane is converted by air oxidation processes at low conversion per pass, but with an ultimate yield of 75-90% depending upon the technology. The product of air oxidation⁽⁴¹⁾ is a mixture of 60-95 wt% cyclohexanol and 5-40 wt% of cyclohexanone, known as KA Oil. Of the balance, about 10-25% of the cyclohexane, a portion is oxidized to over-oxidized products, including a portion which is oxidized to CO₂ and H₂O. On a global basis, 65% of KA Oil is used to make adipic acid via oxidation by nitric acid. Adipic acid is a precursor to nylon 6,6. The balance of the KA Oil, 35% (and 25% in U.S.) is converted to caprolactam, which is a precursor to nylon 6. Purified benzene of about 98 wt% purity as shown in Table 3-E, Stream -22, will probably meet all specifications for manufacturing adipic acid⁽³⁶⁾ and subsequently nylon 6,6. It has been reported by several industry sources that DuPont⁽³⁶⁾ in the U.S. used up to 100 KT/Y of cyclohexane of 97.5 wt% purity. This lower purity cyclohexane, which included about 3,000 ppm methylcyclopentane, was supplied by the Phillips refinery at Borger, Texas⁽³⁷⁾.

Solutia⁽³⁸⁾ in Pensacola, Florida, which use a different cyclohexane oxidation technology than DuPont uses in the U.S., agrees that cyclohexane resulting from the purified benzene concept, as shown in Table 3-E, will probably meet their downstream adipic acid and nylon 6,6 specifications without the need for an added purification step. Prior to a major capital expenditure, actual pilot testing on a specific project case is a prudent idea.

It is thought that methylcyclopentane, 3,000 ppm shown in Table 3-E, stream -22, and after stream 22 conversion to impure cyclohexane, will be oxidized to α -methylcyclopentanol (BP 135°C). On that basis, fractionation of α -methylcyclopentanol from KA oil (BP 157-161°C) could be achieved by a simple 45 tray fractionator. Therefore even for caprolactam and subsequent nylon 6 applications, the purity issue could be economically resolved for the purified benzene. However, at this point, no independent confirmation from BASF or DSM was obtained for this theory.

Under the above scenario, all the impurities will be oxidized to organic acids and will be disposed during downstream processing. The adjacent production of ethylene could be a good source of low cost, high purity hydrogen needed for converting benzene to cyclohexane.

In summary, it appears that normal specifications for cyclohexane, 99.85 wt% purity, 200 ppm methyl-cyclopentane and 50 ppm aromatics are of minimal, if any, consequence for the adipic acid nylon 6,6 production route, with the exception of the aromatic specifications. However, the aromatic specifications are not related to the benzene purity issue, but simply are a function of the benzene saturation processing. Further investigation is needed for the caprolactam issue.

Linear Alkylated Benzene

Linear Alkylated Benzene (LAB) is a common precursor for detergents where heavy olefins like C₁₂ – C₁₆ are reacted with benzene. Benzene purity is not a key issue; however the non-aromatics need to be purged from the alkylation loop. This purge, containing 20 wt% benzene could be recycled to the steam cracker for benzene recovery.

Benzene Disposal from Fuel Oriented Refineries

Unlike petrochemical refinery applications that represent on purpose benzene production, in the fuel oriented refineries the benzene content of reformat in the U.S. has typically been reduced to 2.2-4.5 wt% (2.0-4.0 vol%) as opposed to the 9.0 wt% in the demonstrated petrochemical refinery case. This reduction in benzene content is driven by the benzene content limitations on the gasoline pool. This reduction is achieved by sharp pre-fractionation of precursors of benzene such as methylcyclopentane and cyclohexane as well as a reduction in reforming pressure. Removal of dilute benzene using the described deheptanizer method will result in dilute benzene of 12-20 wt% (9.1-15.8 vol%) purity as opposed to the 29 wt% (23.5 vol%) obtained in petrochemical refinery case as shown in Figure 2 and Table 3-A, Stream-2.

For an average regular gasoline pool RON of 92.0, it is estimated that the proposed dilute benzene cut, which is about 8% of the gasoline pool and contains 13.0 vol% (16.6 wt%) benzene, the average RON is about 67- 70. Reformat resulting from a significant portion of cracked naphtha feed, more common in Europe, will show above average content of benzene. This dilute benzene stream could serve as an excellent feedstock for steam crackers. Removing this 8% cut of dilute benzene will increase the octane number of the remaining 92% of the gasoline pool by approximately 2.0-2.2 points to a RON of 94.0-94.2 for a highly paraffinic (lean) naphtha. For a rich naphtha (higher in aromatics and naphthenes), the impact on octane number would be somewhat lower, approximately 1.5-1.7 numbers. Removal of the dilute benzene cut will reduce the RVP by approximately 0.3-0.4 psi.

Assuming a “conventional” \$0.30/octane-bbl⁽⁴³⁾ and a 2.0 octane boost will increase the value of the remaining gasoline, say 92 vol% of the original gasoline pool, from \$37.4/bbl (\$315/ton, \$0.89/gal)⁽⁴⁴⁾ to \$38.00/bbl (\$320/ton). The credit for RVP reduction is estimated at \$0.15/bbl depending on alternative outlet for excess C₅ and C₄. On this basis the value of gasoline product will increase to \$38.15/bbl. Selling the dilute benzene, say 8.0 vol% of gasoline pool, at \$28.75/bbl (\$257/ton) as a feed to the steam cracker will create a break-even situation for the refiner. After the assumed MTBE phase out by 2005, the value of an octane-barrel is expected to rise to \$0.35-0.40/octane-bbl and this could further improve the merit of the proposed concept.

Using Nov. 2002⁽⁴⁴⁾ as crude oil data base 24.34/bbl Brent 34° API mix and WTI Cushing \$26.35/bbl, about \$27.5/bbl or \$200/ton is the estimated average refinery acquisition cost. In Jan 2003 the average Gulf Coast average regular gasoline blend at refinery gate is \$37.4/bbl (\$315/ton, \$0.89/gal)⁽⁴⁴⁾. The estimated equivalent value of pre-cut hydrotreated naphtha feed to catalytic reforming, (specific gravity of 0.715) 66.5 °API, is about \$35.4/bbl (\$312/ton). On this basis, the value of full range naphtha, for example 9.0 wt% aromatics and (SG of 0.73 or 62.5 °API), is estimated at \$34.0/bbl (\$292/ton). Based on all the above, the value of dilute benzene is 11.6% (\$35 per ton) lower than the alternative full range naphtha feed. At this point no monetary credit is given for reducing the benzene content in the gasoline pool. The ethylene yield resulting from cracking dilute benzene is expected to be about 31.5 % vs. 33.5% for full range naphtha feed. However, the extra BTX production will make up for much of the olefin

yield losses. The olefin produced after allowing a \$35/ton discount on the feed to the cracker over full range naphtha could gain a net profit of about \$42 per ton of olefins and liquid products.

All the above assumptions and calculations need to be confirmed on a very site specific basis. However, the bottom line is most integrated steam crackers-petroleum refining-aromatic complexes, which have a business choice of blending raffinate (resulting from benzene extraction) to the gasoline pool or of using the raffinate as a feed to the steam crackers, have elected the second option. Furthermore, in many cases refiners are exporting their raffinate to OSBL olefin plants, depending upon the relative economics of gasoline versus olefins, which may be dictated by the appropriate business cycles.

The elimination of the dilute benzene could amount to 8 vol% of gasoline pool and could affect the gasoline boiling curve and increase the T_{50} (mid point boiling point) from about 212°F (100°C) to about 219°F (104°C). This could become an imminent issue in meeting California's CARB II specifications where T_{50} is close to the maximum limit. Since the boiling point of ethanol (79°C) is close to the estimated mid boiling point of dilute benzene (about 77°C), replacing dilute benzene with ethanol will maintain the T_{50} . However, due to nonlinear mixing properties, the RVP increases by 1.0-1.3 psi. Ethanol has a research octane number (RON) of 99 versus an estimated 67-70 RON for the dilute benzene cut (RON of 99 for pure benzene) and will further increase the octane number of the gasoline blend. Ethanol as an oxygen carrier, could provide an excellent replacement for MTBE and TAME, which are facing the prospect of being phased out in much of the market, however the octane (RON) of MTBE is about 117. As said above, the reduction in C_5 content of the gasoline will allow an additional blending of 0.5 vol% of n-butane, into the gasoline while maintaining the original RVP and increasing octane. This is particularly true during the summer gasoline season when the alternate outlet of n-butane as LPG product is facing a weak market. The sources of n-butane could be atmospheric distillation as well as purge streams from alkylation units. The cost of ethanol or C_6 additive from NGL or perhaps raffinate sources and all issues related to MTBE and TAME phase-out are beyond the scope of this presentation and would be very highly dependent upon the given refinery configuration, location and seasonal climate considerations.

A case study was made for a major U.S. liquid cracker integrated with 6 refineries as a source of 48,000 BPSD of dilute benzene feed. The average combined composition was 13.6 vol% (17.3 wt%) benzene and 86.4 vol% (82.7 wt%) C_5 - C_7 . This dilute benzene, along with 35,000 BPSD of another existing advantageous heavy liquid feed (0.86 specific gravity, 13.85 wt% hydrogen), was integrated to produce 720 KT/Y of ethylbenzene via dilute ethylene (at about 11.0 vol%) from a cracker source and purified benzene, 98 wt%, which is nearly identical to stream -22 in Table 3-A. A total economic analysis points towards an investment of \$160 MM with a savings of \$120-160 MM per year or \$167-221 per ton of ethylbenzene, depending upon the assumed values of various factors. Factors include the assumed values of the dilute benzene streams, of ethylbenzene, and the credit for by-products such as propylene and C_4 mix. Since the market value of ethylbenzene is not reported, it is assumed to equal the value obtained by de-rating the market value of styrene by 13%. As said, relative values of dilute benzene to the alternate naphtha feed were estimated on a very generic basis. The relative values are very site specific and will be affected by the following considerations:

- Need of the refiner to control the benzene content of the gasoline pool,
- Pre-fractionation of feed to catalytic reforming,
- The availability of existing C₅ and C₆ isomerization units,
- Gasoline boiling curve issues especially in California,
- Replacement of dilute benzene by ethanol or C₆ and ethanol tax credit.
- RVP and oxygen issues related to addition of ethanol,
- Incentive to reduce RVP,
- Incentive to increase the gasoline octane number,
- Transportation of dilute benzene including environmental permits, and
- Pipelining issues of the gasoline-ethanol blend, such as the absorption of moisture.

Optimized Conventional Extraction Method (Base Case, see Figure 1)

To illustrate the merits and advantages of the new process arrangement for the production of purified benzene, a conventional benzene extraction method will be used as a benchmark and basis for comparison. Referring to the simplified block diagram shown in Figure 1, reformate is fed to the reformate splitter (4.75 meter ID, 70 trays, 28 MM Kcal/hr reboiler using 40 kg/cm²-g steam). The mixed benzene-toluene-C₅-C₇ product is charged to a depentanizer (2.5 meter ID, 32 trays, 5.5 MM Kcal/hr reboiler using 3.5 kg/cm²-g steam). Depentanizer bottoms consisting of benzene, toluene and C₆-C₇ proceeds to an aromatic extraction unit (that uses 52 tph of steam at 40 kg/cm²-g). Aromatic extract, benzene-toluene product, is clay treated and routed to a benzene-toluene fractionator (2.75 meter ID, 65 trays and 9.6 MM Kcal/hr reboiler using 8.0 kg/cm²-g steam). Reformate splitter bottoms composed of C₈+ with traces of C₈ non-aromatics proceeds to an aromatics plant. The research octane number (RON) of the C₆-C₇ raffinate is about 50-60, thus its value as a feed to steam cracking is at least \$20-24 per ton higher than its value as a gasoline blending stock.

The cost of transporting raffinate from the Middle East to European or Japanese steam crackers is also in the range of \$20-24 per ton. This price differential represents a credit advantage of approximately \$7.0-8.4 million per year for the business case. This would easily justify the added investment in the steam cracker for the mixed feed design, particularly when considering the incremental propylene and BTX production. The raffinate, C₆-C₇ product, about 7,450 BPSD along with 2,750 BPSD C₅ mix, provide additional feed to the steam cracker, resulting in production of 144 KT/Y of ethylene, 67 KT/Y of propylene, 34 KT/Y of C₄ mix and 18 KT/Y of benzene.

Figure 1

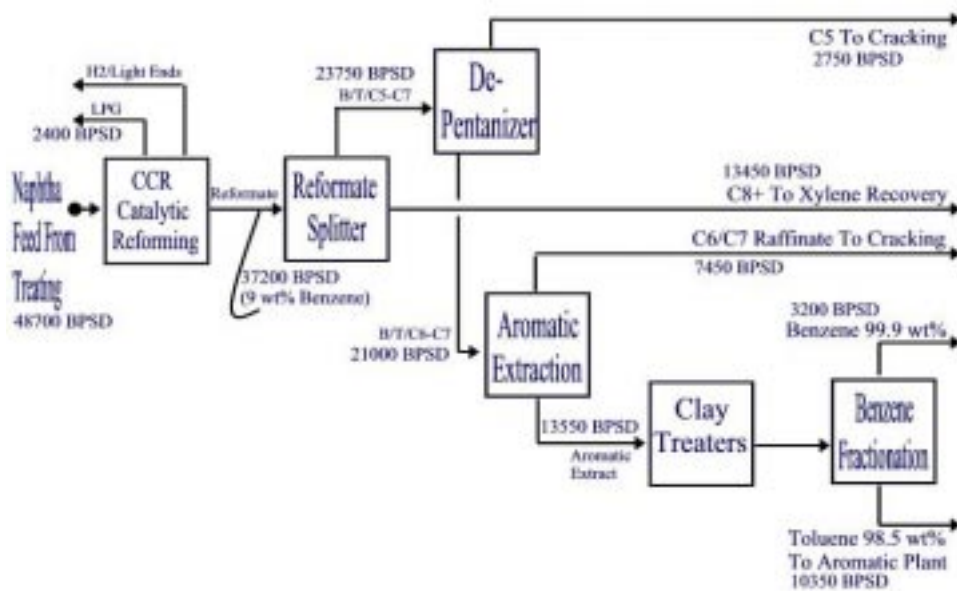
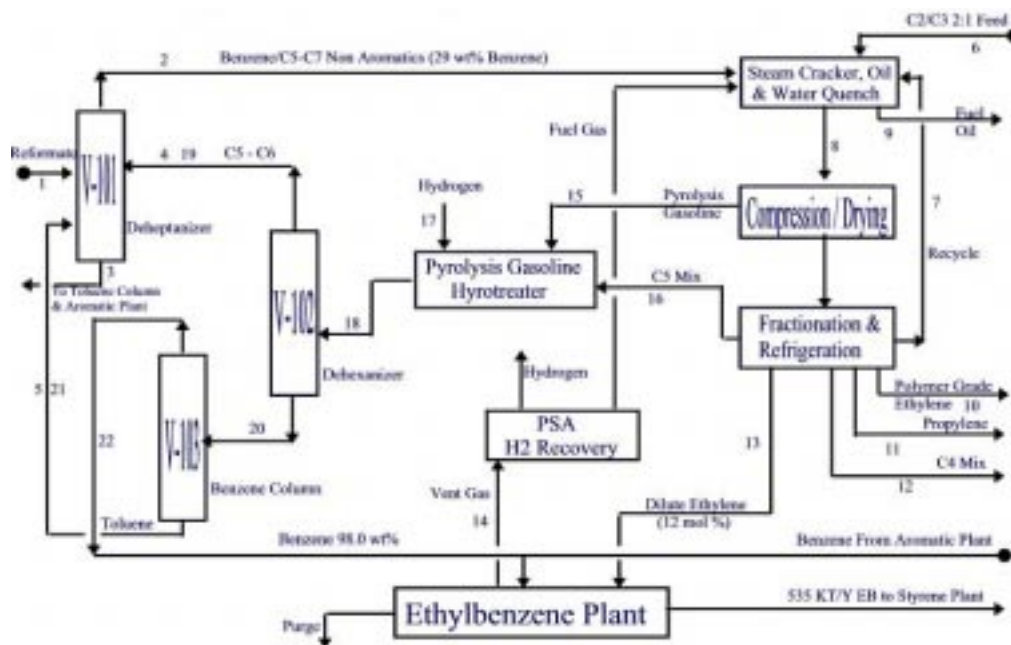


Figure 2



Business Case (see Figure 2)

A likely business case based on gas feed to a steam cracker in the Arabian Gulf is developed. It is assumed that the contemplated ethylene plant is adjacent to a large petroleum-refining complex that includes a catalytic reforming unit. For illustration purposes, CCR catalytic reforming technology is assumed as the source of the benzene⁽²⁰⁾.

The concept as shown in the business case **is also very applicable to liquid crackers** including those cracking heavy liquid feedstocks. Benzene of 98 wt% range purity could be obtained by cracking liquid feeds at medium severity (propylene/ethylene, P/E, of 0.53 per pass). If needed, lower purity benzene would be acceptable; the issue of benzene purity is a subject of process optimization and not a catalyst performance issue.

Plant Definition

The primary feed to the steam cracker is an ethane-propane mix with 2.0 weight ratio of C₂ to C₃ however, additional olefins, about 17% of the total ethylene, are produced by cracking C₅-C₇ produced from light reformat. The design capacity of the ethylene plant is 850 KT/Y based on 350 days per year on stream operation. C₄ mix product is exported outside the battery limits. About 147 KT/Y of contained ethylene is diverted to the production of 535 KT/Y of ethylbenzene, which is converted to 500 KT/Y of styrene monomer. The balance of the ethylene, 703 KT/Y, is directed to the production of polymer grade ethylene. Pyrolysis gasoline containing about 80 wt% benzene is hydrotreated and fractionated to form 189 KT/Y benzene of 98 wt% purity that meets specifications for organic nitrogen, sulfur, moisture and olefins. The toluene could be fed to a disproportionation unit to produce 195 KT/Y of pure benzene and 290 KT/Y of xylenes in addition to the pre-existing 395 KT/Y of xylenes, 85 KT/Y ethylbenzene and 215 KT/Y of C₉+ aromatics. An additional 20 KT/Y of toluene and 5 KT/Y of benzene by-products from styrene production will make the complex self sufficient in benzene totaling about 400 KT/Y.

The business case as described herein is based upon using 12.0 mol% dilute ethylene (88 mol% hydrogen and methane) from the demethanization section^(18,19) of a front-end de-ethanizer ethylene plant at 27.5 kg/cm²-g as a feed to the alkylation unit. The plant design includes a front-end acetylene hydrogenation unit. Feasibility studies show for alkylation applications that this dilute ethylene scheme is **by far more economical** when compared with either of two alternatives. The first alternative is the 72 mol% ethylene feed that could be recovered from the C₂ fractionator. The second alternative is the 38 mol% ethylene, 15 mol% ethane, 16 mol% methane and 31 mol% hydrogen that could be diverted from the output of the acetylene reactor. The advantage of the 12 mol% ethylene over conventional pure ethylene alkylation is estimated to be **over \$50 per ton of styrene**. In this case, this advantage is worth over \$25 MM per year.

Process Description

Figure 2 is a simplified block diagram that illustrates the technical concept of the business case. An overall material balance corresponding to Figure 2, based on 8,400 hours per year operation is shown in Tables 3A to E.

About 2,000 KT/Y (48,700 BPSD) of pre-cut naphtha⁽²¹⁾ feeds the CCR unit to produce 1,670 KT/Y (37,200 BPSD) of reformat (Stream -1) along with 75 KT/Y (2,400 BPSD) of C₃-C₄⁽²¹⁾ and a hydrogen rich gas, about 87 mol%. The reformat along with 1,200 BPSD from benzene purification (V-103) is charged to deheptanizer V-101. This is a 75 tray, 4.0 meter ID column

operating at a top pressure of 1.5 kg/cm²-a. The deheptanizer bottoms are reboiled (duty of 19.5 MM Kcal/hr) by steam at 8.0 kg/cm²-g. The toluene-xylene rich bottom product proceeds to a toluene column (4.0 meter ID, 55 trays and a reboiling duty of 17.5 MM Kcal/hr using steam at 40 kg/cm²-g) and aromatic plant that are not shown in Figure 2. Circulating tempered water, loading the heat on seawater at 33°C and releasing at 38°C, provides condensing duty up to 65°C. Overhead flow (Stream -2) is directed to a steam cracker for ethylene and propylene production.

The bottom flow of toluene and heavy aromatic (Stream -3) is directed to an aromatic plant for xylene and additional benzene production. The benzene rich light reformat feed along with the C₂-C₃ feed produce the desired nominal 850 KT/Y ethylene, 126 KT/Y propylene and 70 KT/Y C₄ mix products, containing 50 wt% butadiene. The contemplated ethylene plant will require eight or nine steam cracker furnaces including a spare, consisting of two liquid crackers and 6-7 gas crackers. All of these furnaces include steam generation at 120 kg/cm²-g and 510°C. The liquid crackers require 15.0 MM Kcal/hr (18%) more firing duty than the raffinate crackers due to the high benzene feed produce approximately 11 tph of additional steam at 120 kg/cm²-g and 510°C and about 9.0 tph steam at 8.0 Kg/cm²-g. However, cracking may require some 9.0 tph of additional dilution steam at 8.0 Kg/cm²-g over the conventional raffinate and also a slight increase in 120 kg/cm²-g 510°C motive steam to drive the cracked gas compressor.

The liquid crackers are equipped with a quench oil system. Cracked gas from quench oil merges with cracked gas from the gas crackers and enters the quench water system. Cracked gas from the quench water system is cooled to 42°C, water and heavy liquids are separated prior to entering a 5-stage cracked gas compressor driven by a 38,000 KW steam turbine. The suction pressure is about 0.4 kg/cm²-g and the discharge pressure at the after-cooler knock out (K.O.) drum, is 32 kg/cm²-g. Traces of H₂S and CO₂ are removed by an inter-stage caustic wash. The bulk of the benzene and C₅+ liquids are condensed in the inter-stage, after-stage and pre dryer coolers, separated in the drums and routed to olefins saturation. Cracked gas is chilled with further liquid separation prior to drying. The dry gas is reheated to 60 °C prior to entering acetylene reactor. The acetylene-free dry cracked gas is then chilled before proceeding to de-ethanizer. The de-ethanizer overhead (at about 29.5 kg/cm²-g) consists of CH₄, C₂H₄, C₂H₆ and traces of propylene. The overhead is chilled and proceeds to a "sloppy cut" demethanizer. The demethanizer overhead (at 27.5 kg/cm²-g) consists of all the produced hydrogen and methane along with about 17.5 % of the ethylene, about 2% of the ethane and less than 1 ppm of propylene. After cold recovery, this stream becomes the dilute ethylene feed at 26.0 kg/cm²-g and 35 °C to the ethylbenzene plant, Stream -13.

The bottoms of the de-ethanizer proceed to a depropanizer. Overhead from depropanizer proceeds to propylene fractionation and the bottoms are sent for C₄ mix recovery. The C₅ pyrolysis gasoline from C₄ mix recovery is combined with pyrolysis gasoline from the compressor drums and sent to a 2-stage hydrotreating unit. The first stage saturates di-olefins and the second stage saturates olefins and reduces sulfur content to below 0.5 ppm. Hydrotreated pyrolysis gasoline, containing about 80 wt% benzene, is routed to a benzene purification unit consisting of two columns. The first column, V-102, is a 60 tray, 2.0 meter ID dehexanizer having a 6.5 MM Kcal reboiler using 3.5 kg/cm²-g steam. The dehexanizer overhead containing the bulk of C₆s and some residual benzene is recycled to deheptanizer V-101. The bottom product proceeds to a benzene column, V-103. The benzene column has 40 trays, is 2.0 meter ID and has a 5.0 MM Kcal reboiler using 3.5 kg/cm²-g steam. The overhead product is 98 wt% benzene. The bottoms are a toluene-rich stream that is recycled to deheptanizer V-101. The purified benzene (Stream 22) along with supplemental benzene from an aromatic plant, reacts with dilute ethylene to form ethylbenzene. Vent gas from the dilute

ethylene unit is sent to a PSA unit for hydrogen recovery and fuel gas separation. The ethylbenzene is then routed to a conventional dehydrogenation or to a propylene oxide styrene monomer (POSM) styrene plant.

Material Balance

The following is a material balance for the case described above expressed in units of Kg/hr. The simulations of reformat and benzene fractionation use SRK thermodynamic package. The streams as listed below correspond to the numbers indicated in Figure 2. The feed (Stream -1 and consequently Stream -2) as shown in Table 3-A may include 0.5 wt% olefins that are not listed in the table.

**Table 3-A
Deheptanizer Section**

	Stream -1	Stream -2	Stream-3	Stream-4	Stream-5
i-C ₄ H ₁₀	25	25	0	0	0
n-C ₄ H ₁₀	595	665	0	70	0
C ₅ mix	10,865	12,980	0	2,115	0
n-C ₆ H ₁₄	5,780	5,980	10	210	0
i-C ₆ H ₁₄	10,750	10,920	10	180	0
M-Cyclo C ₅	335	562	3	230	0
Cyclo C ₆	45	58	2	15	0
n-C ₇ H ₁₆	5,330	4,835	535	5	35
i-C ₇ H ₁₆	9,890	9,910	10	10	20
M-Cyclo C ₆	100	30	110	5	35
Benzene	18,060	18,595	10	495	50
Toluene	58,420	305	59,660	5	1,540
P-Xylene	10,310	2	10,383	0	75
O-xylene	13,785	2	13,878	0	95
M-xylene	22,420	5	22,570	0	155
EB	9,730	10	10,245 0	533	
C ₈ Non-Arom	0	0	35	5	30
C ₉ + Aromatics	22,510	0	22,510	0	0
Total	198,950	64,884	139,971	3,345	2,568

**Table 3-B
Ethylene Cracking Plant Section**

	Stream 6	Stream 7	Stream 8	Stream -9
Hydrogen	0	0	6,260	0
CO	0	0	155	0
Methane	455	0	25,040	0
Acetylene	0	0	2,140	0
Ethylene	0	0	98,560	0
Ethane	83,335	42,005	42,720	0
MAPD	0	0	595	0
Propylene	0	55	15,055	0
Propane	41,270	3,040	3,095	0
C ₄ mix	455	0	8,790	0
C ₅ mix	0	0	2,035	0
C ₆ NA	0	0	835	0
C ₇ NA	0	0	250	0
C ₈ NA	0	0	30	0
Benzene	0	0	22,620	0
Toluene	0	0	1,550	0
Xylene +EB+Sty	0	0	850	0
Heavy Fuel oil	0	0	0	4,690
Total	125,515	45,100	230,580	4,690

**Table 3-C
Product Fractionation Section**

	Stream -10	Stream-11	Stream-12	Stream-13	Stream -14
Hydrogen	0	0	0	6,260	6,260
CO	0	0	0	155	155
Methane	5	0	0	25,040	25,040
Ethylene	83,500	0	0	17,530	500
Ethane	115	5	0	850	850
Propylene	15	15,015	25	0	0
Propane	0	55	0	0	0
C ₄ mix	0	5	8,790	0	0
C ₅ mix	0	0	90	0	0
Benzene	0	0	0	0	50
C ₆ -C ₇	0	0	0	0	15
Total	83,630	15,070	8,905	49,835	32,870

**Table 3-D
Product Hydrotreating Section**

	Stream -15	Stream-16	Stream 17	Stream-18
Hydrogen	0	0	142	0
C ₄ mix	15	51	0	70
C ₅ mix	910	1,130	0	2,115
C ₆ mix NA	623	210	0	870
C ₇ mix NA	232	15	0	260
C ₈ mix NA	29.7	0.3	0	30
Benzene	20,230	2,390	0	22,620
Toluene	1,530	20	0	1,550
Xy/EB/Styrene	849.3	0.7	0	858
Total	24,419	3,817	142	28,373

**Table 3-E
Benzene Fractionation**

	Stream -19/4	Stream-20	Stream-21/5	Stream 22
n-C ₄ H ₁₀	70	0	0	0
C ₅ saturated	2,115	0	0	0
M-Cyclo C ₅	230	65	0	65
Cyclo C ₆	15	125	0	125
i-C ₆	180	5	0	5
n-C ₆	210	45	0	45
i-C ₇	10	155	20	135
n-C ₇	5	100	35	65
C ₇ Napht	5	45	35	10
C ₈ NA	0	30	30	0
Benzene	495	22,125	50	22,075
Toluene	5	1,545	1,540	5
C ₈ aromatic	0	858	858	0
Total	3,340	25,098	2,568	22,530

Capital Investment Considerations

Table 4 represents the relative capital investments for the optimized conventional design (Base Case) compared to the purified benzene production design (Business/ New Case). The average OSBL in this comparison is 40% of ISBL. All figures are based on 2001, U.S. Gulf Coast location, curve type⁽³⁵⁾ estimate in million US dollars⁽³⁰⁾.

Table 4
Relative Capital Investment for Conventional Benzene Extraction vs. Purified Benzene Method, Total Installed Cost (TIC) Basis

Description	Base Case (Conventional Extraction Method) in US\$ MM	Business Case (Purified Benzene Method) in US\$ MM
Catalytic Reforming 50,000 BPSD, about \$130 MM investment	Base	Base
Depentanizer	\$2.5	----
Reformate Splitter	\$4.5	----
Deheptanizer	----	\$4.0
Aromatic extraction 93 KT/Y (21,000 BPSD,) 71 wt% (64 vol%) benzene/toluene <ul style="list-style-type: none"> • Extraction solvent initial charge / inventory 	\$42	----
	\$2.0	----
Clay Treating, 67 KT/Y, (2x50% units)	\$3.0	----
Dehexanizer	----	\$2.5
Benzene Column	\$3.5	\$2.0
Toluene Column	----	\$3.5
Six or seven gas crackers (Capital investment of about \$140 MM)	Base	Base
Two liquid crackers with steam generation 8.5 tph ethylene each at BL ⁽³⁴⁾	\$30	\$34.5
Quench oil /quench water /dilution Steam	Base	\$1.0
Cracked gas compressor	Base	\$0.5
Pyrolysis gasoline stripper & hydrotreating (High benzene adjustment)	Base	\$1.0
Ethylbenzene Plant (Capital investment about \$32 MM)	Base	Base
Total	\$87.5	\$49.0

Table-4 shows the capital investment requirements for the Business (New) Case, based on the purified benzene production method, are US \$38.5 million less than the capital required for a conventional benzene extraction method.

Utilities

Table-5 represents approximate utilities consumption figures for Base Case and Business (New) Case. Plant water, instrument air and other minor utility consumption figures are considered negligible and are not accounted for.

**Table 5
Utilities Consumption Figures (Estimated)**

Description	Base Case	Business (New) Case
Depentanizer <ul style="list-style-type: none"> • Steam @ 3.5 kg/ cm² - g 	11 tph	----
Reformat Splitter <ul style="list-style-type: none"> • Steam @ 40 kg/ cm² - g 	65 tph	----
Deheptanizer <ul style="list-style-type: none"> • Steam @ 8.0 kg/ cm² - g 	----	40 tph
Aromatic Extraction <ul style="list-style-type: none"> • Steam @ 40 kg/ cm² – g • Power 	52 tph 700 kw	---- ----
Clay Treating <ul style="list-style-type: none"> • Steam @ 8.0 kg/ cm² – g 	2.5 tph (based on 5% of aromatic extraction unit steam consumption)	----
Dehexanizer <ul style="list-style-type: none"> • Steam @ 3.5 kg/ cm² – g 	----	12.5 tph
Benzene Column <ul style="list-style-type: none"> • Steam @ 8.0 kg/ cm² – g 	20 tph	9.5 tph
Toluene Column <ul style="list-style-type: none"> • Steam @ 40 kg/ cm² – g 	----	43 tph
Liquid Crackers (2) ⁽³⁴⁾ <ul style="list-style-type: none"> • Steam @ 120 kg/ cm² – g / 510°C • Fuel Gas LHV 	---- 83.0 MM Kcal/hr	-11 tph (export) 98.0 MM Kcal/hr
Quench Oil / Quench Water / Dilution Steam <ul style="list-style-type: none"> • Steam @ 8.0 kg/ cm² – g 	----	9 tph - 9 tph (export)
Cracked Gas Compressor <ul style="list-style-type: none"> • Steam @ 120 kg/cm²-g/510 C 	Base	1.8 tph (500 kw)
Heat Rejection (Air Coolers / Tempered Water / Sea Water) <ul style="list-style-type: none"> • Power 	1,450 kw	-----

Economic Analysis

The following Table-6 depicts the economic comparison between the Base Case (Conventional Extraction Method) and the Business (New) Case (Purified Benzene Method) for 185 KT/Y contained benzene.

Table 6
Economic Comparison between Base Case and Business Case

Item	Description	Base Case (Conventional Extraction Method)	Business Case (Purified Benzene Method)
1	Capital charges @ 28% <ul style="list-style-type: none"> Extraction solvent initial inventory @ 20% 	\$23.94 MM \$0.40MM	13.72 MM 0.0
2	Electric power @ \$0.050/kwh	\$1.070 MM	Base
3	Fuel gas LHV @ \$5.0/MMKcal	\$3.49 MM	\$4.16 MM
4	Steam, 90% condensate recovery <ul style="list-style-type: none"> 120 Kg/cm²g 510°C @ 14/ton 40 Kg/cm²g sat. @ 10.5/ton 8.0 Kg/cm²g sat. @ 8.0/ton 3.5 Kg/cm²g sat. @ 6.0/ton 	Base \$10.05 MM \$1.52 MM \$0.53MM	-\$1.082 MM \$3.8 MM \$3.33 MM \$0.63 MM
5	Extraction solvent make up	\$0.21 MM	0.0
6	Total	\$41.21 MM	\$24.56 MM

Table-6 shows that the Business Case based on the Purified Benzene Method has a cost advantage of approximately US **\$17 million per year** over the Conventional Extraction Method. This is equivalent to a cost savings of more than \$90 per ton of contained benzene. Adjusting the economic analysis for a Middle Eastern location may increase the savings to over \$100 per ton of benzene. As said, additional savings, \$25 MM per year are obtained by alkylating with dilute ethylene.

Global Synergism –Dilute Benzene Supply and Demand

As said, benzene limits on the gasoline pool are imposed in U.S., Canada, Western Europe and Japan. It is assumed that dilute benzene recovery could be economical for unit sizes of over 10,000 BPSD and on this basis the following are the estimated capacities of catalytic reforming units without benzene recovery:

U.S.	1,350,000	BPSD, Includes U.S. West Coast
Canada	120,000	
Western Europe	1,400,000	
Japan	250,000	
Total	3,120,000	

Assuming a 80% volumetric yield from catalytic reforming, this can produce 2,500,000 BPSD of reformate with 3.1 vol% benzene based on an average benzene content in HOBC (high octane

blending component). Potential dilute benzene recovery is 550,000 BPSD with assumed average of 13.0 vol% benzene, 71,500 BPSD of contained benzene.

The naphtha consumption for olefin production in these zones of the world, producing 32,000 KT/Y of ethylene is shown below. The ethylene yield is estimated at an average of 33.5% and based on naphtha density of 250 lb/bbl (SG=0.71):

U.S.	600,000	BPSD
Canada	30,000	
Western Europe	1,400,000	
Japan	500,000	
Total	2,530,000	

The total of 2,530,000 BPSD includes about 10% of C₆/C₇ raffinate from benzene extraction.

On the other extreme, the relative potential for benzene production from catalytic reforming in China, is very limited. Only four reforming units with capacity of over 10,000 BPSD are reported,⁽⁴²⁾ with a total capacity of 72,000 BPSD.

Assuming 31.5% ethylene yield from the dilute benzene feed, the above 550,000 BPSD of dilute benzene could replace 19% of naphtha feed in these zones or alternately based on 2.5% growth per year, will provide ethylene market growth for 7 years. The assumed 19% growth in ethylene production will yield additional 14,000 BPSD of benzene via cracking of hydrocarbons.

The additional benzene production resulting from the above concept is 85,500 BPSD which is about 18.5% of the 460,000 BPSD (22,500 KT/Y) estimated benzene consumption in the U.S., Canada, Western Europe and Japan. Thus the growth in ethylene, 19%, is very synergistic with the 18.5% growth in benzene.

The trend to limit the benzene content in gasoline is getting global acceptance including Mexico, East Europe and refineries in the Middle East where the gasoline product is dedicated to export to the U.S. and Europe. In most of these refineries, the benzene content of the reformate is on the order of 4-7 vol% and overall benzene in the gasoline pool is over 2 vol%. Thus refiners are facing investments to reconfigure the reformers and to add isomerization capacity. The dilute benzene concept as presented here could provide an interesting alternative solution.

Based on the above, the imbalance in dilute benzene production in Japan and China could be reduced by potentially importing 115,000 BPSD dilute benzene from the U.S. West Coast. The Kingdom of Saudi Arabia is known to be short of benzene and perhaps dilute benzene from Europe or the Western U.S. could be swapped with Saudi NGL thus achieving a mutually beneficial situation.

A maximum of about 160,000 BPSD of ethanol will supply the equivalent energy value of the dilute benzene removed from the U.S. West Coast gasoline pool. This ethanol replacement will represent about 11.5 vol% of the gasoline pool and will provide about 4.3 wt% oxygen to gasoline pool. This is nearly in range with the 10 vol% maximum ethanol limit as recently proposed by API⁽⁴⁰⁾ and significantly less than the 20-22 vol% ethanol blend being used in many locations in Brazil. As said above, blending of ethanol and gasoline is not ideal and tends to increase the RVP well above the molar linear contribution of ethanol, about 18 psi proportional RVP for 10 vol% ethanol. A 1.0 psi exemption is proposed on RVP resulting from ethanol blending, however reformulated gasoline is not qualified for the exemption⁽⁴⁰⁾. A more realistic

blend, using a maximum of 5.5-7.5 vol% ethanol (2.0-2.8 wt% oxygen) and 3.0-4.5 vol% isomerized C₆s could present a more optimal market blend.

The cost of transporting dilute benzene from the U.S. West Coast to Japanese crackers could be in the order of \$2.30/bbl, and slightly more for Chinese crackers. This cost includes \$0.80/bbl port fees and based on 240,000 bbl tankers capacity, as opposed to \$4.0-6.0/bbl cost of moving the material to U.S. Gulf Coast via rail cars or domestic tankers via Panama Canal⁽³⁹⁾. Therefore, if the T₅₀ specification could be met in U.S. West Coast refineries by adding ethanol or C₆s, movement of dilute benzene from U.S. West Coast to Japanese crackers, Chinese crackers and possibly to Saudi crackers, could be very synergistic with the global supply demand balance.

Summary and Conclusions

Process improvements in alkylation indicate that use of purified benzene in the range of about 90-98 vol% in lieu of nitration grade benzene is technologically feasible and economically advantageous. The overall cost savings derived from producing benzene from refinery sources by co-production of olefins are substantial, calculated at over \$90 per ton of 98 wt% benzene in the case study presented here (Tables 7 and 8).

The potential consumption of purified benzene could account for up to 90% of the benzene market. Production of benzene from toluene conversion, or C₃-C₄ conversion, about 20%, would result by default in pure benzene without a need for aromatic extraction. The US Gulf Coast is a home to 92% of U.S. ethylene production (about 23,000 KT/Y) along with 100% of styrene, and about 70% of cumene and cyclohexane. This production independently “coexists” with 1,500,000 BPSD catalytic reforming capacity⁽³²⁾. This include about 450,000 BPSD of reforming capacity without benzene recovery which could produce 120,000 BPSD of dilute benzene. In the rest of the world, the vast majority of steam crackers, alkylation facilities and catalytic reforming units are all located in the same proximity within the confines of industrial complexes. Nevertheless, in most cases the cost of moving dilute benzene by ocean tankers even for a distant user would not significantly reduce the synergism between dilute benzene disposal and steam cracking.

Slide No-1 Benzene marketing data

- Total global benzene production: 33,000 KT/Y, 675,000 bpsd.
- About 30% of global benzene production, 10,000 KT/Y is in U.S
- EB-styrene has 52% of market share; cumene, 20%; cyclohexane, 14%.
- About 55% of global benzene production is captive to catalytic reforming.
- About 40 % of global benzene is captive to pyrolysis gasoline in olefin plants.
- About 70% of benzene in US is captive reforming and 28% to pyrolysis gasoline.

Slide No-2 Catalytic reforming /benzene specifications data

- Common benzene purity is 99.9 wt% produced by from aromatic extraction.
- Non-aromatic, C₆/C₇ raffinate from BTX extraction could feed steam cracking.
- Global catalytic reforming capacity is 11,000,000 BPSD in 420 refineries.
- U.S. reforming capacity is 3,500,000 BPSD in 120 refineries.
- About 33 vol % of U.S. gasoline pool is captive to catalytic reforming.
- About 70% of reformers are dedicated for octane enhancing , 95-102 RON.
- About 30% of reformers are dedicated for BTX petrochemical production.

Slide No-3, benzene production issues.

- Production of pure benzene by conventional fractionation is not possible because of azeotrope forming C₆-C₇ components.
- Benzene content in a typical reformate stream dedicated for aromatics production is in the order of 7-9 vol%.
- C₅-C₇ non-aromatics in reformate streams account for about 20-30 vol%.
- Benzene content in a typical reformate stream dedicated for fuel production and facing environmental limitations on benzene content, is in the order of 2-4 vol%.
- Limiting benzene in U.S. under 1.0 vol%, is imposed on reformulated gasoline. Limitations are imposed in much of Europe and are getting global acceptance.

Slide No-4, new technological and market approaches

- New mixed or liquid phase alkylation technology was developed by ExxonMobil.
- The non-aromatics impurities are no longer a catalyst or product purity issue for liquid and mixed phase alkylation of lower purity benzene under 500°F.
- For the case of ethylbenzene, alkylation of lower purity benzene is very synergistic with dilute ethylene because of lower temperature alkylation, 340-370 F.
- The above technology is suitable for alkylation of lower purity benzene with refinery grade propylene (90-95 wt%) to form cumene.
- New data suggest cyclohexane at lower purity, 97.5 wt%, for production of adipic acid and nylon 6,6, is acceptable. Applications for nylon 6 needs further investigation.
- Nylon 6,6 accounts for about 65% of global nylon market and 75% of US nylon market.
- Dilute benzene from Europe or the U.S. West Coast could be a viable feedstock for steam crackers in China and Saudi Arabia, and could be swapped with NGL.

Slide No-5 gasoline issues

- Dilute benzene can be removed from the gasoline pool by splitting the reformat of benzene and C₅-C₇ non-aromatics, 200 F cut, from toluene and heavy aromatics.
- The average RON of a dilute benzene cut is estimated to be 67-70, comprising 8% of average US gasoline pool.
- Removal of dilute benzene will increase the octane of the gasoline pool by 1.5-2.5 points and will reduce the RVP by 0.3-0.4 psi. T₅₀ can be maintained by adding ethanol or C₆.
- Cost of dilute benzene could be 10-15% lower than cost of full range naphtha.
- Dilute benzene, could serve as feed to steam crackers and cracking will produce olefins and pyrolysis gasoline with about 80 wt% benzene.
- Pyrolysis gasoline will be hydrotreated for olefins and di olefins and will be conventionally fractionated to produce purified benzene at 98 wt% purity.

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Mr. Chris Wallsgrove, Manager, Ethylene Technology at Selas Fluid Processing Corp., a US subsidiary of Linde AG. Mr. Wallsgrove has reviewed the draft material as well as reviewing the concept during early stages of development. Mr. Wallsgrove made very valuable contribution to the issues related to cracking of dilute benzene feed and general issues related to co-production of olefins.

Russell Heinen, Assistant Director Process Economics Program, and Dr. Richard Nielsen, Senior Consultant, both of the Process Economics Program of SRI Consulting, Houston, TX provided valuable market data on benzene and derivatives.

Ernie Leuenberger, former FCC specialist at ARCO Products, Anaheim Technical Center in California, who provided valuable gasoline blending data.

Notes

(1) Patent application on this subject has been filed with the U.S. Patent Office. Patent issuance is expected in 2003.

(2) Integrate Ethylbenzene Production with an Olefins Plant, May 99 issue, Hydrocarbon Processing.

(3) Private communication with Steven Horlacher, Aromatic Team Leader at Chevron Phillips Chemicals, Kingwood, TX.

(4) U.S. Patent 6,143,166 Nacamuli, Process for Production of Aromatics in Parallel Reforming with Improved Catalyst Life and Reduced Complexity.

(5) BP-UOP process, LPG to BTX Products. C. D. Gosling, F. P. Wilcher and L. Sullivan of UOP, Des Plaines, IL and R. A. Mountford of BP International. Hydrocarbon Processing, Dec. 91 issue.

(6) Interpolation of several data sources including SRI 2,000 benzene report.

(7) Data from Bonner & Moore Associates, Houston TX.

(8) Nova Chem in Sarnia, Ontario 400 KT/Y styrene and Dow BSL, Germany, and PASA in Argentina.

(9) CDTech EB Technology. A breakthrough in Ethylbenzene Technology. Gautam Phanse and Stephen Pohl ABB Lummus. ARTC Petrochemical Conference, Feb 12-14 2001, Kuala Lumpur.

(10) U.S. 6,252,126, Method for producing ethylbenzene; U.S. 5,977,423

(11) Website: www.ExxonMobil.com/chemical/licensing/petro_chem/index.html

(12) Union Carbide at Texas City, TX and Chevron at Cedar Bayou, TX have operated DMF acetylene recovery units.

- (13) U.S. Patent 5, 750,814 Grootjan et al., Atofina
- (14) U.S. Patent 6,002,057 Hendriksen et al. ExxonMobil.
- (15) University of Gent in Belgium, Kellogg Brown & Root, Houston, TX, Linde AG Munich Germany and ABB Lummus.
- (16) Communication with ABB Lummus.
- (17) By interpolation of Data from SRI Styrene report 1999.
- (18) U.S. Patent 5,880,320, Allowed European Patent: Combination Process for Manufacturing Ethylene Ethylbenzene and Styrene. D. Netzer. Patent applications are pending in India, and China.
- (19) U.S. Patent 6,177,600. Combination Process for Manufacturing Ethylene Benzene and Alkylated Benzene. D. Netzer.
- (20) Such as UOP platforming and IFP CCR.
- (21) The depleted naphtha 200°F cut point is about 460 KT/Y and the C₃-C₄ 75 KT/Y could be used as a feed to the cracker to produce 200 KT/Y ethylene.
- (22) Chevron Phillips Chemical, formerly Chevron Chemical
- (23) By Shell-UOP
- (24) Morpholine solvent is licensed By Uhde
- (25) Arosolvan BTX extraction and Distapex extractive distillation are licensed By Lurgi. GTC Technology www.GTChouston.com
- (26) Most of past units were licensed by ABB Lummus.
- (27) Most of it was licensed by Raytheon-Badger Technology Center
- (28) Offered for licensing by Washington Group-Badger Technology Center and ExxonMobil catalyst. Also by ABB Lummus and UOP catalyst.
- (29) Chevron-Phillips Chemical is one of the largest producers of cyclohexane.
- (30) Based on communication with Stone & Webster.
- (31) U.S. Patent 6,002,057 Hendriksen; U.S. Patent 5,273,644 DA Wgerer; U.S. Patent 5,083,990 Hsieh; U.S. Patent 4,209,383; U.S. Patent 4,140,622 Herout
- (32) This is based on the Corpus Christi, TX to Pascaguola, FL section of the U.S. Gulf Coast. Total U.S. reforming capacity is 3,500,000 BPSD and global capacity 11,000,000 BPSD.
- (34) Cost ratio of 0.85 power of firing duty OSBL is 30% of ISBL

- (35) Accuracy of +25%, -15%
- (36) Data from several private industry sources, general information and communications with DuPont and CMAI in Houston.
- (37) By practicing Phillips U.S. Patent 3,009,002 by Carl Kron
- (38) Communication with Solutia R&D in Pensacola, FL and business center of Solutia in St. Louis, MO.
- (39) Private communication with Kinder Morgan, Houston, TX.
- (40) <http://books.nap.edu/books/039067790/html/46.html#pagetop>
- (41) Attempts to increase conversion per pass and yield by using pure oxygen were facing reluctance by industry due to safety perceptions^(36,38). See U.S. Patent 5,780,683 Cyclohexane Oxidation, by ABB Lummus.
- (42) Oil & Gas Journal Dec 24 2001.
- (43) Communications with IFP, Houston Texas. This value can vary widely depending on refinery configuration and octane boosting options.
- (44) Energy Information Agency <http://www.eia.doe.gov/price.html>. Table 13 for the period of Nov-2002 crude oil benchmark prices and Jan 2003 US Gulf Coast regular gasoline mix.
- (45) Chemical Week January 29 2003.