

PROCESS TECHNOLOGY

Integrate ethylbenzene production with an olefins plant

An innovative ethylene processing route uses lower priced feedstocks to incorporate side petrochemical production

D. Netzer, Consultant, Los Angeles, California

Why not combine ethylbenzene (EB) production with an ethylene facility? A new olefins processing scheme can offer economic benefits from integrating side petrochemicals, such as EB within the olefins process.¹ This tech-

nology can be applied to existing and new liquid crackers.

Lesser value feedstocks. To co-manufacture EB, a naphtha feedstock with a high-aromatic content replaces the traditional petrochemical-grade naphtha, which is low in aromatics and more expensive. Instead of cryogenically purifying and recovering 100% of the ethylene, a dilute ethylene stream is separated and used as feed for the EB unit.

In the integrated process, about 10% to 25% of the ethylene is recovered in dilute form. Crude benzene is recovered from the aromatic naphtha. The dilute ethylene, at concentrations of 8–15 mole% and crude benzene (90–96 wt%) are reacted to EB in a novel alkylation system. The EB is converted to styrene by dehy-

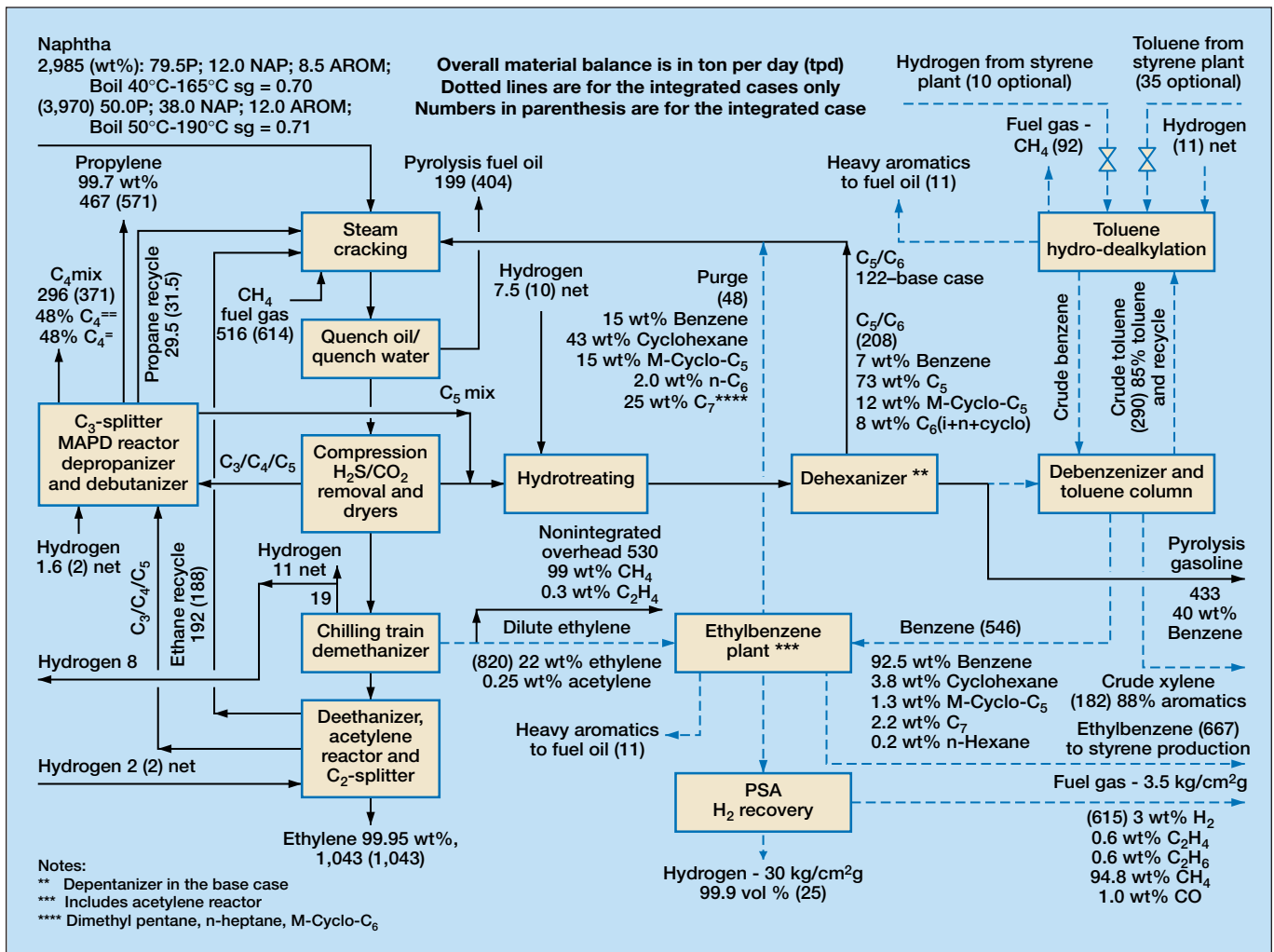


Fig. 1. Process flow diagram for an integrated ethylene and ethylbenzene facility.

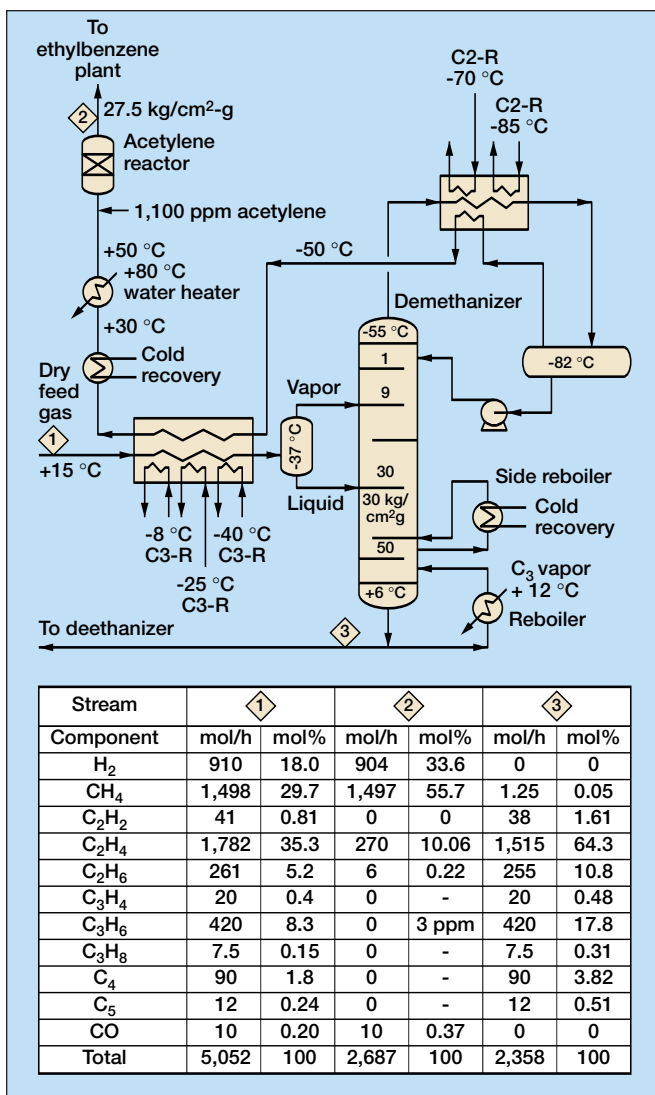


Fig. 2. Chilldown demethanizer with the dilute ethylene process.

drogenation or as a byproduct from propylene oxide.

A detailed debottlenecking case analysis shows economic incentives for an existing ethylene unit to add coproduction of EB. If the integration benefits are attributed toward EB manufacturing, about 30%–40% cost reduction can be achieved, thus saving \$160 to \$200 per ton of styrene. If the total benefits are credited toward the pure ethylene product, the savings would amount to \$100 to \$110 per ton of ethylene.

A separate analysis, was done for a grass roots integrated facility, 500,000 tpy net ethylene production coproducing 330,000 tpy of EB. This resulted in a capital reduction of about \$30–35 MM and overall annual saving of \$50–65MM.

The incentive for this processing method is nearly independent of the ethylene and the styrene market cycle, and the pay-out time, over the nonintegrated approaches is 1.25 to 1.40 years.

General background. At most manufacturing locations, olefins production and EB/styrene production are separate business entities. Thus, process integration of olefins and EB/styrene manufacturing is very infrequent.² Olefins are produced by thermal steam cracking of hydrocarbon feeds with subsequent recovery of key products—ethylene and propylene—along with pyrolysis gasoline, pyrolysis fuel oil, hydrogen and methane. Depending on specific economics, a C₄ mix containing over 95% of C₄ diolefins and olefins is recovered to produce butylene and butadi-

ene. In most cases, methane is internally consumed as a fuel in the thermal cracking. Much of the hydrogen, after satisfying internal usage, is available for export or can be consumed as fuel. Crude pyrolysis gasoline consists of C₅ to C₈ hydrocarbons, with majority of aromatics.

Worldwide ethylene production capacity is 90 million tpy (90 MMtpy); about 50%–52% is based from naphtha, 6%–8% from gas oils, 26%–28% from ethane³ and the balance, about 11%–13% from propane and butane. Pyrolysis gasoline, after di-olefins and olefins hydrotreating, is sent to an offsite aromatic unit.

Liquid-feed olefin plants, typically use highly paraffinic naphtha with low aromatics content (5–10 wt %) to maximize olefins yield. Yet, the resultant pyrolysis gasoline product accounts for 30% of the world's benzene production. About 50%–55% of the world's benzene output, at 99.9 wt % purity, along with 8%–9% of the world's ethylene output are used as raw materials for EB. Nearly all the chemical-grade EB is instantly converted to styrene monomer (SM).

A new processing concept. As shown in Fig. 1, high-aromatic naphtha feed is fed to an integrated ethylene and EB production facility. The key design elements are:

- About 10%–25% of the ethylene from cracking, at concentration of 8–15 mole% and containing hydrogen and methane, is diverted to EB production. Vent gas from EB, depleted of ethylene, proceeds to hydrogen recovery via pressure swing adsorption (PSA).
- Naphtha feed for the thermal cracking will contain 10–20 wt% aromatics rather than the common 5–10 wt% aromatics. The aromatic content serves as a major source for onsite benzene production, followed by EB processing.
- Benzene, containing impurities of co-boilers and close boilers such as cyclohexane and methyl-cyclopentane, will be produced onsite by simple fractionation.
- Benzene, 90–96 wt%, along with dilute ethylene, is fed to the EB unit using a concept of mixed-phase alkylation with a zeolite catalyst at low temperatures, about 180° C. A purge alkylation reactor is used for high benzene utilization.

Analysis. Several competing technologies exist for ethylene production; they use thermal cracking of hydrocarbons to generate crude ethylene. The sequence of product fractionation and recovery depends on the given technology.

In thermal cracking of naphtha, a mixture of steam and hydrocarbon, at pressures of about 0.7–1.0 kg/cm²-g, is undergoing thermal cracking at about 850°C. The cracked-products mix are cooled while generating steam at 480°C–525°C and 100–130 kg/cm²-g. The cracked product proceeds to quench oil, followed by a quench-water system. Essentially, all of the C₉⁺ is condensed in the quench-oil system. In the quench-water system, much of the C₆⁺ is condensed. After further cooling to about 27°C–40°C, the cracked gas proceeds to four to five stages of compression to about 35–40 kg/cm²-g, prior to product separation and recovery. After final compression, essentially all the C₆⁺, and much of the C₃⁺ are condensed.⁴ The condensate is stripped of C₂ and proceeds to downstream recovery. The compressed cracked gas proceeds to drying, followed by cryogenic product fractionation by several competing technologies:

- Front-end demethanizer,⁵ back-end acetylene reactor. This sequence accounts for about 75%–80% of the world's present ethylene production capacity.
- Front-end deethanizer, front-end acetylene reactor.⁶ Nearly 15%–18% of the world's ethylene production capacity uses this method.

Table 1. Debottleneck analysis

Add 70,000 mtpy cracker, for higher feed throughput
Revamp other crackers for 15% higher feed throughput
Increase cracking pressure by 0.3 kg/cm ² -g (results in 0.5% yield reduction) ¹⁹
Debottleneck quench oil system, add a dilution steam generator and drum
Debottleneck quench water system, add a pump and cooler
Add five chillers to charge gas compressor, chill suctions from 38°C to 15°C
Reduce discharge pressure from 38.0 kg/cm ² -g to 35.0 kg/cm ² -g
Shorten cycle time on cracked-gas dryers and increase pressure drop
Bypass the chill-down train below -37°C and bypass turbo expander
Add heater and single-stage acetylene reactor to dilute ethylene (no spare)
Revamp PSA for 57% hydrogen recovery at the tail end of EB plant
Discharge purge gas from PSA will be 3.5 kg/cm ² -g to be routed to fuel system
Add dehexanizer, debenzenizer, 77°C cut and add toluene column, 110°C cut
Add toluene hydrodealkylation (THDA) reactor loop and fired heater
Revamp existing depentanizer for benzene toluene fractionation from THDA
Debottleneck depropanizer, debutanizer, MAPD reactor and C ₃ -splitter
Debottleneck pyrolysis gasoline hydrotreating

product, 99.5–99.8-wt%, and bottom propane-rich stream that is recycled to cracking. Bottom product from the depropanizer proceeds to debutanizer. The C₅⁺ from the debutanizer is recycled to olefins hydrotreating of the crude pyrolysis gasoline.

New concept—dilute ethylene production. In an alternate route (See Fig. 2), the demethanizer section operates at “a sloppy mode.” Instead of 0.2 mole% ethylene at the overhead, the ethylene content is increased to about 10 mole-%. Because of the high ethylene content at the overhead, the demethanizer can be refluxed at -80°C. Again, in the conventional systems, bulk hydrogen separation as vapor occurs in the -130°C drum and external to the demethanizer. In the new concept, all of the hydrogen can be separated within the demethanizer column and reflux system, and yet, the refrigeration power associated with the reflux is reduced by about 50%.

A key design consideration is avoiding propylene breakthrough in the dilute ethylene stream. If allowed, propylene could form cumene (iso-propylbenzene) in the downstream EB unit. The dilute ethylene will include acetylene, about 1,000–1,300 ppmv¹² and some ethane.

Chilldown demethanizer—dilute ethylene production. After chilldown, by -40°C propylene refrigeration and cold recovery (Fig. 2), vapor liquid separation occurs at -37°C. Vapor and liquid products feed the demethanizer. Demethanizer overhead is refluxed by -85°C and -70°C ethylene refrigeration. Overhead product—dilute ethylene—proceeds to cold recovery and acetylene reactor, before feeding the EB unit. Vent gas from EB processing is sent to PSA for hydrogen recovery at 26.0 kg/cm²-g and fuel gas separation at about 3.5 kg/cm²-g.

Crude benzene production. As shown in Fig. 1, pyrolysis gasoline (C₅ to C₉) is hydrotreated. This is done in two stages for di-olefins and olefins and the sulfur content is reduced to below 1 wt ppm. The hydrotreated pyrolysis gasoline is fractionated in three columns:

► Dehexanizer column forms an overhead cut, consisting of all the C₅, about 60% of the nonaromatic C₆ and about 5% of the benzene in the feed. This overhead is recycled to cracking. Bottom product is benzene, cyclohexane, some of the methyl-cyclopentane and C₇⁺ and is sent to benzene recovery.

► De-benzenizer column produces a 78°C atmospheric cut that is mostly of benzene, 90–96 wt%, along with cyclohexane, methyl-cyclopentane and about 25% of the non-aromatic C₇, which is mostly methyl-cyclohexane and n-heptane, along with traces of toluene.

► Toluene column generates 110°C atmospheric cut, of 85 wt% toluene and a balance of C₇/C₈ nonaromatic. The bottom C₈⁺ cut, which is mostly xylenes/EB mix, is exported.

The toluene product is sent to a conventional hydro-dealkylation unit where toluene is hydrocracked to benzene, at about 95% yield, and methane. Nonaromatics are cracked to methane, thus doubling the hydrogen consumption. This unit can accept toluene by-product that is generated in styrene production by dehydrogenation of EB.

The conventional EB route. EB is formed by catalytic reaction between ethylene and benzene. About 5%–15% of the EB further reacts with ethylene to form DEB (di-ethylbenzene). About 10%–20% of the DEB continues to react and forms triethylbenzene (TEB). Some of the TEB reacts with ethylene to produce heavier aromatics. These products are referred to as PEB (polyethylated benzene). Having a stoichiometric excess of benzene in the alkylation loop minimizes the formation of PEB. The DEB and TEB after recovery by fractionation react with benzene in a transalkylation reactor to form EB. The heavy PEB, rejected as fuel, would represent a yield loss of 0.5%–2.0%.

Side reactions, such as formation of xylenes at about 200–2,000 wt ppm, depend on the design fundamentals and runlength. The xylenes are considered an undesirable element to downstream styrene processing. Any propylene, present as a contaminant of the ethylene feed stream or formed by cracking nonaromatic impurities, can further react to cumene, (iso-propylbenzene). Over the last 15 years, zeolite catalysts were introduced to improve yields, reduce maintenance and improve environmental impact. These catalysts gradually replaced the traditional AlCl₃ catalyst.

The two basic EB processing systems with zeolite catalysts are: vapor-phase alkylation and transalkylation process, at 400°C to 440°C, and liquid-phase processes at about 240°C to 270°C. In recent years, product demand for low-xylenes content has shifted the market and now favors liquid-phase zeolite catalyst alkylation and transalkylation.

Conventional EB production from dilute ethylene source.¹⁴ In the past, dilute ethylene, 10–14 vol%, from refinery FCC offgases were used as a feedstock for EB production in vapor-phase reaction. This could be a viable approach for using the dilute ethylene, however, pure benzene feed would be required. Due to 400°C alkylation, any nonaromatics impurities, if present, would crack.

New EB system. A novel mixed-phase EB processing technology has been developed that uses impure benzene and dilute ethylene.¹⁵ The proposed concept operates under the dew point temperature of the mixture. The diluents of the ethylene and a portion of the benzene remain in the vapor phase, while the balance of the benzene and essentially all of the EB product remain in the liquid phase. Zeolite catalysts such as Zeolite Y¹⁶, Zeolite Beta and other catalysts can be used. The Zeolite Beta¹⁷ was proven

Table 2. Capital cost estimate

	\$U.S., million (MM)
Add pyrolysis furnace, 70,000 mtpy (1,000 m ³ /d naphtha)	10.0
Revamp existing crackers for higher feed throughput	1.5
Debottleneck quench oil and quench water system	2.0
Add five chillers to cracked gas compressor (4,000 m ² total)	3.5
Allowance for piping reconstructions	1.0
By-pass part of chilling train and turbo-expander	0.5
Add heater and acetylene reactor, 2,700 kg-mole/hr	2.0
Revamp PSA unit for 2,500 kg-mole/hr, 37% hydrogen	2.3
Readjust utilities systems, DCS and general offsites	0.5
Additional infrastructure and offsites for furnace	3.0
Add naphtha storage, 10 days, 16,000 m ³ (floating roof)	2.3
Add 1,600 m ³ pyrolysis fuel oil storage (floating roof)	0.5
Debottleneck depropanizer and debutanizer	1.0
Debottleneck C ₃ -splitter, 5,000 mm ID, 260 trays	2.4
Subtotal, IBL and OBL olefins capacity increase	32.5
Benzene production	
Add dehexanizer column (60 trays 2,300 mm ID)	1.8
Add debenzenizer (45 trays 2,200 mm ID)	1.5
Add toluene column (35 trays 2,000 mm ID)	1.2
Debottleneck the pyrolysis gasoline hydrotreating	1.5
Add 250 tpd toluene hydro dealkylation catalytic reactor ²⁰	6.0
Add benzene storage, 10 days, two 3,000 m ³ (floating roof)	1.5
Add toluene storage, 10 days, two 1,500 m ³ (floating roof)	1.0
Subtotal, onsite benzene production	14.5
Total revamp olefins and benzene plant	
Ethylbenzene plant from dilute ethylene (670 tpd)	20.0
Add purge alkylation reactor (50 wt% benzene feed)	4.0
Add infrastructure and offsite to ethylbenzene	7.5
Total investment for integrated facility	78.5
Investment in nonintegrated styrene plant ²	55.0
Additional offsite allowance for styrene production	20.0

recently for benzene, containing 70 wt% of C₆/C₇ nonaromatic and 20 mole% ethylene in laboratory scale. For this illustrated case, alkylation will occur at about 180°C and transalkylation at about 250°C. The lower reaction temperature allows introducing nonaromatics with the benzene feed, and its subsequent build-up in the reactor loop, without the risk of cracking.¹⁸ Several accidental operations of liquid-phase alkylation systems, with a buildup of about 5–20 wt% of C₆/C₇ nonaromatic have shown no cracking, thus substantiate the above.

The cost reduction for EB by using the “cheap” impure benzene and “cheap” dilute ethylene is about 30%–40%. Typical past improvements in catalyst technology, system designs, or yields improvements have lowered processing expenses by 1%–2%. Due to the lower alkylation temperature in the new processing scheme, the xylenes content is expected to be under 50 wt ppm. Impurities in the benzene feed, such as cyclohexane, are allowed to concentrate, but will not affect product purity. Nonaromatics could be purged to the pyrolysis gasoline export, or be routed to a purge reactor, for high benzene utilization.

Mixed-phase ethylation system. Fig. 3 depicts the general concept of the mixed-phase alkylation. The process uses: ethylation reactor, transalkylation reactor, benzene stripper and overhead rectifier and are in a single vessel. For 670-tpd EB process, the vessel size would be about 3,500 mm ID and 52,000 mm T-T. The benzene stripping creates a localized excess of benzene and increases the temperature in the catalytic, isothermal ethylation section. Thermal energy for benzene stripping is provided by a fired heater. Steam generation in the isothermal reactor absorbs the stripping heat input and the heat of reaction. The nonaromatics are allowed to build up to about 50 wt% in the overhead section and are

purged to a purge ethylation reactor, which includes a benzene and nonaromatics stripper. The purge-reactor product, rich in PEB, is recycled to transalkylation in the main ethylation system. The transalkylation catalytic section, with very little thermal effect, reverses the formation of PEB by 50%–85% per pass, depending on runlength. Residue from the purge reactor and product recovery, about 85 wt% nonaromatic with about 15 wt% unreacted benzene is routed to cracking.

The vent gas—depleted of ethylene and containing methane, hydrogen, traces of CO and ethane—is rich in benzene and cyclohexane. The eutectic effect of the cyclohexane and other nonaromatic C₆ suppresses the solid-formation temperature of the vent gas to well below +5.5°C, which is the normal freezing temperature of pure benzene. Thus, benzene recovery from the vent gas is achieved by using +12°C and –8°C refrigeration, (60 kW) obtained from the integrated ethylene plant, and subsequent cold recovery from the chilled vent gas. The benzene content of the vent gas after chilling is 400 mole-ppm, which is about 0.3% of the benzene in the feed. The crude EB product, with 3–7 wt% PEB is fractionated to separate the PEB and to form EB product. By further fractionation of PEB under vacuum, DEB and TEB are fractionated from heavier aromatics and recycled to the transalkylation. The heavy aromatic represents 1.0 % yield loss and is rejected to the fuel oil product. EB product with about 1,700 wt-ppm benzene and 330 wt-ppm of nonaromatics, cyclohexane and other light C₆ and C₇ is routed to the styrene plant. In the styrene plant, the above impurities are ultimately recycled to the EB plant and should not affect the purity of the styrene.

Debottleneck case analysis. To illustrate the new processing concept, a generic facility will be revamped. This example will consider operating criteria at two locations—Japan and Western Europe. In this analysis, annual onstream time is 345 days; naphtha is imported from Singapore or Rotterdam refineries, respectively. Other design criteria are:

- ▶ Current feed is straight-run naphtha—IBP= 40°C, EP=165°C, sg = 0.70. PONA analysis: paraffin 79.5 wt %, naphthenes 12.0 wt%, and aromatic 8.5 wt%, iso/normal=0.95. Operation: medium severity, propylene/ethylene weight ratio is 0.5, coil-outlet pressure is 0.75 kg/cm²-g. All C₄ mix is exported to OBL.

- ▶ Original design capacity is 300,000 tpy of ethylene in 1978. Single-cold train and eight cracking furnaces with no onsite EB production.

- ▶ Debottlenecked capacity was 360,000 tpy ethylene in 1988. Re-rotor cracked-gas and refrigeration compressors, added turbo-expander with generator and cracking furnace.

- ▶ Design mode: 33 kg/cm²-g front-end demethanizer and back-end acetylene reactor.

- ▶ Existing pyrolysis section has nine furnaces including a spare and recycle gas furnace.

The new expansion considerations are:

- ▶ Styrene production of 210,000 tpy, nominal, which depends on aromatic content of naphtha and toluene byproduct recycle to hydrodealkylation

- ▶ Styrene production is preceded by EB production of 230,000 tpy

- ▶ Produce 62,000 tpy ethylene, in dilute form, and impure benzene for EB.

- ▶ Pure ethylene production 360,000 tpy, thus total ethylene make is 422,000 tpy

- ▶ New feed is straight-run naphtha: IBP = 50°C, EP = 190°C, sg = 0.71. PONA analysis: paraffin 50.0 wt%, naphthenes 38.0

Table 3. Pricing data for key petrochemicals for Rotterdam and Singapore locations²³

Rotterdam fob	3Q95	4Q95	1Q96	2Q96	3Q96	4Q96	1Q97	2Q97	3Q97	4Q97	Avg
Petrochemical naphtha	153	152	168	193	199	217	194	169	172	184	180.1
Reformer naphtha	144	140	165	183	177	205	195	173	179	163	172.4
Ethylene	636	562	503	552	548	582	615	608	603	554	576.1
Propylene	499	370	273	429	331	389	440	480	462	406	407.9
Benzene	243	253	270	260	282	303	319	333	280	313	285.6
Pyrol. fuel oil	154	157	172	180	192	218	208	145	182	185	179.3
Styrene		632	568	644	550	576	633	660	588	517	596.3
Singapore fob	3Q95	4Q95	1Q96	2Q96	3Q96	4Q96	1Q97	2Q97	3Q97	4Q97	Avg
Petrochemical naphtha	156	152	166	182	194	222	165	172	229	212	185.0
Reformer naphtha	145	140	165	183	177	205	195	173	179	163	172.5
Ethylene	315	295	367	476	491	527	403	465	590	546	437.3
Propylene	249	338	390	432	440	475	517	571	564	516	449.2
Benzene	281	240	215	257	281	301	239	278	249	297	268.1
Pyrol. fuel oil	154	162	168	160	169	195	178	164	165	167	168.2
Styrene	555	481	506	488	497	445	415	408	494	475	476.4

Source: Bonner & Moore Associates, Houston, Texas

Table 4. Utilities expenses for Japan and Western Europe installation

Electric power	\$0.065/kwh
Hydrogen at 30kg/cm ² -g	\$0.075/Nm ³
Fuel gas, LHV	\$15.0/MM Kcal
Steam, 40kg/cm ² -g, saturated ²⁵	\$12.0 per ton
Steam, 7kg/cm ² -g, saturated ²⁵	\$8.0 per ton
Saturated steam 3.5 kg/cm ² -g ²⁵	\$6.5 per ton
Deaerated boiler feed water at 50 kg/cm ² -g	\$2.5 per ton
Water cooling, 5.0 kg/cm ² -g, 15°C rise	\$0.025 per ton

wt%, and aromatic 12.0 wt%, iso/normal=1.0. Operation: medium severity, propylene/ethylene = 0.5 wt, coil-outlet pressure = 1.05 kg/cm²-g. All C₄ mix is exported to OBL

► Facility to be nominally self-sufficient in benzene from naphtha feed source.

Table 1 lists the required revisions to enable EB production at the this existing olefins facility. For the revamp, the cracked-gas compression load has increased from 18,700 kW to 20,500 kW, while refrigeration load decreased from 16,700 kW to 14,900 kW. This loading change would require adjusting the steam distribution, however, no changes are needed in the cracked-gas compression and refrigeration. Calculations were based on using the Dresser Rand compressor, two casings D-24A8 and D-20R9.

Using a conservative yield analysis, this debottlenecking project will result in no excess of hydrogen. Hydrogen byproduct from an adjacent styrene production, or higher hydrogen recovery from PSA, will provide the hydrogen supply margin for safe design.

Cost estimate. Table 2 lists the estimated capital investment. U.S. Gulf Coast 4th quarter 1998 is used as a basis for capital expenditures. It is reasonable to assume that capital expenditure for Japan and Europe will be higher. For the nonintegrated case, the battery limits capital investment, for a liquid-phase EB plant using pure benzene and pure ethylene feed at 35 kg/cm²-g, is estimated at \$18.5 MM, including catalyst, and the assumed dedicated off-site \$8.5 MM.

Basis for economic analysis. All the assumed raw materials and product are going through significant world market cycles.

Key items in this economic analysis are the relative values of highly paraffinic/low aromatic, "petrochemical" naphtha and highly aromatic, "reformer" naphtha. This is a complex issue. The cost of the "petrochemical" naphtha follows the price cycle of ethylene, and the cost of the "reformer" naphtha follows the price cycle of gasoline. Commonly²² known sources for high aromatic naphtha are: Ardjuna Indonesia, Alaska North Slope, Brent North Sea, U.S. Gulf and many Chinese crude oil sources.

The cost data (Table 3) used is for Western Europe and Asia Pacific and is reported in U.S. dollars.²³ The U.S. Gulf Coast is omitted, because naphtha feeds account for less than 20% of U.S. ethylene³ production capacity as opposed to 85%–90% in Europe and the Asia Pacific. The "reformer" naphtha as shown, is referred to feeds of catalytic reforming. All prices are average contract prices for the given time frame, with the exception of pyrolysis fuel oil, which would represent spot market prices. Prices of 4Q98 are reported lower for most products and naphtha feeds.

For the economic analysis, the following adjustments are made: Add \$17/ton for transporting of naphtha feeds. For the nonintegrated case, use \$17/ton for transporting benzene from Singapore or Rotterdam to the assumed users in Japan or Europe. The propylene values as given are for chemical grade, and will assume a \$33/ton premium for polymer grade. All products are assumed to be distributed to Japanese or European users. For this analysis, the Singapore or Rotterdam fob values are used respectively.

On this basis, for Japanese and European locations, use \$202.0 and \$197.1 per ton respectively, for "petrochemical" naphtha for the nonintegrated case. For the integrated case use \$189.5 and \$189.4 per ton for the highly-aromatic naphtha feed.

The second pricing issue is the relative value of pyrolysis gasoline depleted of benzene and toluene, but rich in xylenes mix, in the integrated case, against the conventional pyrolysis gasoline with 40 wt% benzene in the nonintegrated case. The xylenes mix could be very valuable, particularly in Asia Pacific. However, at this point, both types of pyrolysis gasoline are assumed as blended to the gasoline pool. The value of the xylenes-rich pyrolysis gasoline and the value of hydrotreated pyrolysis gasoline are assumed as equal in values to the "reformer" naphtha feed, \$172.5 and \$172.4 per ton respectively.

The C₄ mix for the above cases consists of about 48–50 wt% butadiene, 48–50 wt% butylenes and the balance, 2–4 wt% of butanes. The value of butadiene in Japan, from 1994–1996, was reported as ranging from \$1,000 to \$1,200 per ton, while in Western Europe, it was reported as \$400 to 450 per ton. The prices of butylenes depends on the isomers and is mostly related to the fuel market. From 1990 to 1993, the reported U.S. price for butene-1 was \$500–600 per ton, and of high purity iso-butylene was \$600–700 per ton. On the above basis, a credit of \$250 per ton for the mixed C₄ is conservatively realistic for both locations. However, the Japanese market for C₄ mix favors the integration concept.

Very little EB is traded on the world market, since almost all of it is instantly converted to styrene by dehydrogenation²⁴ or propylene oxide styrene monomer. Thus, no significant price pattern could be identified for EB. For this analysis, the base cost of EB was derived by derating the cost of styrene for capital charges, 6%

yield loses to toluene, 4% royalties and utilities. Thus, the fob values for Singapore and Rotterdam are estimated at \$420 and \$526 per ton respectively.

A blank capital charge of 28% is assumed. This would cover depreciation, return on investment (ROI), operating and maintenance labor, insurance and taxes (3.5 years payback). The following constant values were assumed for utilities, for both Japan and Europe and are shown in Table 4. The economic advantage of the proposed processing concept was chosen to reflect the differential production cost between the integrated and the nonintegrated. This analysis considers only utilities products and raw materials relevant to the comparison.

Economic analysis. Table 5 lists a detailed economic comparison for two existing olefin locations—Japan and Western Europe. The presented criteria examine the benefits of constructing an EB unit in an integrated facility vs. a nonintegrated site. Differential annual cost in favor of integrated system is \$35.7 MM and \$40.6 MM respectively. This amounts to \$153.9 and \$174.8 per ton of EB in Japan and Western Europe respectively.

If these benefits were applied toward the ethylene products, the cost reductions will be \$98.3 and \$111.7 per ton in Asia Pacific and Western Europe respectively. Analysis on the same basis, for 4Q98, shows about equal savings as above. Reduction in market value of benzene, ethylene, propylene, etc., is nearly balanced by the reduced cost of naphtha feed.

As shown, the incentive for the new process is *essentially independent of the ethylene and styrene business cycle*. Application of products, benzene and naphtha pricing data for the period 1990–1995 would show an even a stronger incentive for the integrated concept.

Integration of grassroots facilities. Integration of 600,000 tpy of ethylene, 510,000 tpy net production, and 330,000 tpy EB was analyzed. While the more immediate potential is for revamp and debottleneck as discussed, the merits for integrating a new facility are even stronger. The front-end deethanizer may have some slight additional synergism in adopting the integration scheme.

The key unique elements for the integrated scheme:

- ▶ Cracked-gas compression by four stages to 27–29 kg/cm²-g rather than five stages to 35–40 kg/cm²-g in the conventional design. Saving of compressor casing is possible.

- ▶ Combined ethylene and propylene refrigeration load power will be reduced from 27,000 kW²⁸ in the conventional case vs.

Table 5. Economic analysis for Japan and Western Europe locations, in U.S. \$MM/yr

	Nonintegrated Ethylene and EB plants		Integrated ethylene and EB plants	
	Singapore	Rotterdam	Singapore	Rotterdam
Petrochemical naphtha feed 360,000 tpy ethylene production	1,030,000 tpy		NA	
	-208.1	-203.0		
High-aromatic Naphtha feed 422,000 tpy ethylene	NA		1,369,000 tpy	
			-259.5	-259.3
Pyrolysis gasoline export xylenes rich, 88 wt% aromatic	NA		63,000 tpy	
			10.9	10.8
Pyrolysis gasoline export benzene rich	146,000 tpy		NA	
	25.2	25.1		
Pyrolysis fuel oil export	68,500 tpy		147,500 tpy	
	11.5	12.3	24.7	26.3
Pure ethylene export	360,000 tpy		360,000 tpy	
	157.4	207.4	157.4	207.4
Propylene export	161,000 tpy		197,000 tpy	
	77.6	65.7	95.0	80.4
C ₄ mix export	102,000 tpy		128,000 tpy	
	25.5	25.5	32.0	32.0
Excess fuel gas ²⁶ over cracking heat	8.0 MM Kcal/hr		44.0 MM Kcal/hr	
	1.0	1.0	5.6	5.6
Dilution steam correction for integrated case, 7.0 kg/cm ² -g with total condensate loss	Base		8,000 kg/hr	
			-0.60	-0.60
Additional hot water for reboiling in C ₃ /C ₄ recovery	Base		No value	
Hydrogen export at 30 kg/cm ² -g	3,700 Nm ³ /hr		Zero	
	2.30	2.30		
Turbo expander power at demethanizer section	350 kW		Zero	
	0.20	0.20		
Steam export 3.5 kg/cm ² -g from EB plant	47,000 kg/hr		5,000 kg/hr	
	2.50	2.50	0.50	0.50
Steam export 7.0 kg/cm ² -g from EB plant	Zero		33,000 kg/hr	
			2.2	2.2
Steam import 40 kg/cm ² -g to EB plant	37,000 kg/hr		5,000 kg/hr	
	-3.70	-3.70	-0.50	-0.50
Power for EB plant	350 kWh		250 kWh ²⁷	
	-0.20	-0.20	-0.15	-0.15
Fuel gas for EB plant 90% combustion efficiency	2.0 MM Kcal/hr		10.0 MM Kcal/hr	
	-0.30	-0.30	-1.50	-1.50
Fuel for toluene hydrodealkylation 70,000 mty benzene production	NA		1.15 MM Kcal/hr	
			-0.15	-0.15
Power for toluene hydrodealkylation	NA		90 kW	
			-0.05	-0.05
Steam 3.5 kg/cm ² -g for dehexanizer	2,500 kg/hr		10,000 kg/hr	
	-0.15	-0.15	-0.55	-0.55
Steam 3.5 kg/cm ² -g for debenzenizer	NA		9,000 kg/hr	
			-0.50	-0.50
Steam 7.0 kg/cm ² -g for toluene column	NA		8,000 kg/hr	
			-0.50	-0.50
Pure benzene import to EB plant	173,000 tpy		NA	
	-49.3	-52.3		
Pure ethylene import to EB plant	62,000 tpy		NA	
	-27.1	-35.7		
Total	14.35	46.65	64.3	101.4
Economic summary	Nonintegrated ethylene EB		Integrated ethylene EB	
Capital charges	-7.45	-7.45	-22.0	-22.0
Base number materials and utilities	14.35	46.65	64.3	101.4
Subtotal	6.90	39.2	42.3	79.4

18,500 kW in an integrated case where 15% of the ethylene is recovered as dilute ethylene

► About 60% reduction in the capital cost for the chill-down and demethanizer section

► Reduce the capital cost of the C₂-splitter by 10%, regardless of pressure

► For front-end deethanizer, use a single column at 25–27 kg/cm²-g, as opposed to dual columns at 35 kg/cm²-g and 17 kg/cm²-g

► Increase by about 2.0%–2.5% the capital cost of the cracking and 5.0%–6.0% of the quench oil and quench water system. This is due to the 8%–12% higher feedrate.

► Added cost for impure benzene recovery, as discussed for the revamp case.

Key integration issues. A reasonable concern for integration would be the forced outage of the EB plant. A forced outage scenario, of 10 days per year, where dilute ethylene, was released to fuel, was analyzed against the overall benefits. For the revamped case, the operator can move back to the old mode of operation. For new facility, the benefit of the integration was found to be higher by a factor of 25–30 over the assumed ethylene losses to fuel.

Other integration issues. Essentially 100% of EB and styrene plants in Asia Pacific and 85% in Europe²⁹ are adjacent to ethylene production units. In Europe, essentially all the EB producers are the ethylene producers as well. Integration of inside business units, or alliance of producers can achieve the above combined savings.

New opportunities. In the conventional way of producing EB, raw materials account for over 90% of the cost. In the present example, the cost of producing EB on average in Japan and Europe has dropped by 35% and 33.5 % respectively, simply by reducing the cost of raw materials. If the cost saving is credited toward the 360,000 tpy ethylene product, savings of 22.5% and 19.5% can be achieved respectively. *Thus, a strong incentive exists to replace existing EB plants, even with sunken capital, and regardless of the given styrene business cycle.* EB plants, which are using zeolite catalyst in the vapor phase, are producing product with 500–2,000 ppm of xylenes. The incentive to replace these along with old plants with AlCl₃ catalyst is even stronger.

ACKNOWLEDGMENTS

Mr. Chris Wallsgrove, Olefins Marketing Manager, Stone & Webster, Houston, Texas, has reviewed the content and made valuable comments to the section dealing with the debottlenecking of the ethylene plant. Dr. Andrew Swanson, Director Commodity Chemicals Practice, Chem Systems, an IMB Company, Tarrytown, New York, has provided valuable marketing information pertinent to the process integration. Dr. Sidney Stern of BOC Process Plants, and formerly with ARCO Chemical, reviewed the draft material and made valuable comments. Bill Lo of BOC Process Plants and formerly with Raytheon-The Badger Technology Center, assessed the ethylbenzene technology.

NOTES

¹See U.S. Patent No 5,880,320 Netzer, D. A patent is pending in India and PCT International priority was applied for Europe, Russia, China, Japan, Korea, Indonesia, Brazil and Mexico.

²Dow in Terneuzen, Holland, Dow BSL Germany, Huntsman in Odessa, Texas. In these debottleneck cases, ethylene at 65–85-mol% is used as feed to EB along with pure benzene.

³In North America, ethane/propane/butane mix amounts to about 70% of ethylene feedstock and produces relatively small amounts of aromatics. In Mexico and Arabian Peninsula nearly all are C₂ feed.

⁴With the exception of design for front-end depropanizer. The H₂S and CO₂ are removed by caustic scrubbing prior to C₂-stripping and final compression.

⁵Old CE Lummus, old Stone & Webster and M. W. Kellogg. For naphtha feeds, some designs are using a pre-cut demethanizer where the C₃⁺ and some C₂ are separated.

⁶By Stone & Webster in past 10 years and also by Linde AG and C F Braun.

⁷C F Braun, which has merged with M. W. Kellogg and is known as Kellogg Brown & Root, and also Stone & Webster

⁸Technip accounts for 1.5%–2% of the capacity, about 1% by olefin recovery from refinery, FCC offgases. The alkylation system as described is also suitable for FCC offgases.

⁹In the last 20 years, ABB Lummus has changed their design from high-pressure to low-pressure demethanizer. This design amounts to some 10 % of the total capacities. Using a pre-cut, high-pressure demethanizer could produce dilute ethylene.

¹⁰This would represent the practical minimum temperature for ethylene refrigerant while keeping pressure above atmospheric.

¹¹Turbo expanders are common in recent 20 years, older technology used J.T valves.

¹²Acetylene reactor, as described, would not be needed for a front-end deethanizer or front-end depropanizer technologies.

¹³About 110–120 trays for 24–28 kg/cm²-g and 75–95 trays for 3–7 kg/cm²-g.

¹⁴Raytheon-Badger/Mobil technology for Shell UK and Chevron in Pascagoula, Mississippi. Sinopec Technology in China.

¹⁵ABB Lummus/CDTech has developed mixed-phase technology. Netzer, D., "Olefins Recovery from FCC Gas," *Hydrocarbon Processing*, April 97.

¹⁶U.S. Patent No. 4,891,458, Innes, R., Liquid Phase Alkylation Using Zeolite Beta.

¹⁷Hendriksen, D., "Alkylation Process Using Zeolite Beta," International WO98/09928 Exxon.

¹⁸Based on catalyst data, no measurable cracking of nonaromatics is expected below 275°C.

¹⁹Additional 1.5% feed would be required because of the lower olefins yield. The aromatic and fuel oil production will increase by 5%.

²⁰Much of the benzene product recovery can be integrated within the existing facility.

²¹Additional advantages by (a) Using the convection section of the cracking furnaces as a low-pressure steam superheater for the styrene plant. (b) Using the integrated product fractionation and route the toluene byproduct, to existing hydro-dealkylation.

²²Arjuna, Indonesia 19 wt% aromatic, Alaska North Slope 17 wt%, Brent North Sea 14 wt%.

²³Conversation with R. Harvan, Director of Petrochemicals, Bonner & Moore Associates, Inc., Houston, Texas.

²⁴It is instantly converted to styrene in an integrated operation using dehydrogenation. About 20% of EB is used for propylene oxide production with coproduction of styrene.

²⁵Assume 85% condensate return to the steam generation cycle.

²⁶Firing duties in cracker for the base and integrated case are 257 and 306 MM Kcal/hr respectively, the firing duty was adjusted for equal HP steam production per ton of ethylene. The integrated case will use steam to H/C=0.5 for the added feed, but no credit was given to the additional 80°C water produced.

²⁷The power includes 60 kW refrigeration load as provided from ethylene plant.

²⁸For low-pressure, front-end demethanizer scheme, the net refrigeration load is lower, but also uses methane refrigeration. The refrigeration load is also affected by ethylene recovery.

²⁹In the U.S., about 50%–60% of the EB production capacity is remote to ethylene production and adjacent to ethylene pipeline along the U.S. Gulf Coast. In Japan, 100% of EB plants are adjacent to ethylene plants but only 60% of EB is produced by ethylene manufacturers.



David Netzer, PE, (netzerd@worldnet.att.net), is a consulting chemical engineer, in the field of petroleum, petrochemicals and synthesis gas. Mr. Netzer is currently on a consulting contract with BOC Process Plants, Murray Hill, New Jersey. He has 32 years of experience in petrochemicals, synthetic fuels refining and gas processing for major U.S. engineering and technology organizations. While working in a capacity of business development for Lotepro Corp., subsidiary of Linde AG, Mr. Netzer originated the concept (1995) that led to the project of olefins recovery from FCC offgases and subsequent polypropylene production for ARCO Products the Los Angeles, Carson refinery. This is the first petrochemical project in California in over 20 years. While working for Fluor in 1978, Mr. Netzer was a key member of the team that developed the concept of the Tennessee Eastman, coal to synthesis gas. This project in Kingsport, Tennessee, was the first commercial demonstration of the Texaco coal gasification process. Mr. Netzer holds six U.S. patents and has written eight articles for major publications in the field of petrochemicals, synthetic fuels and enhanced oil recovery.