The petroleum industry's answers to the benzene and naphthalene supply problem—stable domestic sources for primary consumers

HYDRODEALKYLATION PROCESSES

A noteworthy transition is occurring in this country in aromatic production potential, as evidenced by a phenomenal growth rate, aromatic product quality improvement, and a broadening of raw material sources. Development and rapid commercial acceptance of processes for the manufacture of benzene and naphthalene from their alkylated homologs is one of the more recent consequences of the emergence of petroleum as the prime source of aromatic hydrocarbons in the United States.

When aromatics were produced solely as by-products of the coke and coal gas industries, production and demand for benzene, toluene, and xylene were roughly balanced, the higher yield of benzene from coking being matched by the bigger benzene market. There was little need then for dealkylation processes.

At the high temperatures and low pressures used in coke ovens, dealkylation increased benzene production at the expense of toluene and xylenes. These same conditions produced high yields of naphthalene relative to methylnaphthalenes. Any imbalance could be corrected through imports, available at low cost.

It was fortunate that the larger chemical market for benzene over toluene or xylene, and for naphthalene over methylnaphthalenes coincided with the greater supply of the simpler compounds. However, no such economic windfall has come to the aid of petroleum chemists.

Petroleum became an established source of aromatics about 10 years ago as consequence of:

—*Development of catalytic reforming processes*
—*Inadequate supply of coal tar by-products*
—*Development of improved separation processes for isolating high purity aromatics*

For years the shortage of aromatics was met adequately by installing appropriate facilities for producing and recovering aromatics. Unlike that in coal tar, however the distribution of aromatics in catalytic reformates runs quite the reverse of market demands. For example, volume percentages of aromatics obtained from typical coal-coking and naphtha-reforming operations compare with the 1960 chemical end-use market as:

	Coal Tar	*Reformate*	*Market*
Benzene	80	10	65
Toluene	15	40	20
Xylenes	5	50	15
	100	100	100

In recent years, during restricted coke and steel production, the market for benzene exceeded the capacity of refineries with aromatics facilities to produce benzene without increasing crude runs and suffering the effects of overproduction of fuel products. In this

LICENSORS CLAIM THESE ADVANTAGES...

Thermal Processes

No catalyst to purchase, charge, or regenerate
Less down time due to catalyst handling
Clean reactions
Good selectivity
Simplicity of operation
Wide feedstock variability

Catalytic Process

Higher reaction efficiencies
Lower hydrogen consumption
Higher conversions
Lower operating temperatures
Naphthalenes from stocks other than alkylnaphthalenes
Higher liquid yield
Open to advances in catalysis
Clean operations
Good selectivity

same period the market for naphthalene exceeded its production from coal tar. Another undesirable result of reduced coke-oven production is the effect of longer coking periods at reduced temperature, giving reduced yields of benzene and naphthalene relative to the methylalkylated compounds. The expanding chemicals industry in Europe now consumes surpluses which were available for export to the United States. These factors explain Tariff Commission data which show the U. S. a net exporter of aromatics, a condition which will probably persist until foreign refiners install additional aromatics capacity.

Under these circumstances any process which would efficiently dealkylate toluene to benzene or methylnaphthalene to naphthalene would appear attractive. Over half the toluene and xylene currently produced finds its market in aviation and motor gasoline at a price of less than 2 cents per pound. Conversion of petroleum toluene to competitively priced benzene is profitable, where the weight loss is just 20%, operating costs are low, and difficulties from impure feeds can be avoided. Xylene is somewhat more costly to recover than toluene. It is a less desirable feed, perhaps an uneconomic one at current prices. In dealkylation it suffers a 30 to 35% weight loss and consumes more hydrogen than does toluene. Because extremely pure feed stocks are available in quantity, there appears little doubt that these processes will help to solve the imbalance between the supply and demand for benzene, and will be economic, provided an adequate differential in price exists between benzene and toluene.

Production of naphthalene from petroleum feed stocks has been studied for many years. Processes were developed and tentative plans to install petroleum naphthalene plants were made by several of the major oil companies. Until recently, cheap imported naphthalene or satisfactory markets for the petroleum feed stocks proposed have rendered these plans unattractive. Now, however, the world naphthalene consumption is increasing beyond the coal tar industry's capacity to produce. A permanent demand is developing for the petroleum-derived product. It can be demonstrated that methylnaphthalene fractions worth 1$^1/_2$ to 2 cents per pound can profitably be converted to naphthalene selling at 6 cents per pound. Although suitable feeds may be prepared either as bottoms distilled from catalytic reformate, or as a narrow cut distilled and concentrated from refractory cycle oils, problems in preparing feed for naphthalene can be more troublesome than those for the manufacture of benzene.

Rerun bottoms (400° F. end point) from catalytic reformate are satisfactory feeds for dealkylation to naphthalene. Typically these fractions contain over 95% aromatic, 20 to 30% alkylbenzenes, 10 to 15% naphthalene, 50 to 60% methylnaphthalenes, and small percentages of other compounds. These feeds, however, would be available only from refiners who reform high end-point (400° F. and over) naphtha or produce large volumes of reformate. Operating cost of reforming high boiling naphthas and of rerunning the reformate must be borne either by the gasoline from which they are derived or by the naphthalene product to be produced. The reformate route appears to have the least pitfalls and has been chosen for the majority of the new plants. However, the supply of adequate quantities of reformate bottoms may become a problem.

U. S. AROMATICS PRODUCTION AND CAPACITY

(Millions of gallons/year)

	1960		*1961–62*
	Production	*Capacity*	*Capacity*
Benzene			
Petroleum based	310	369	750
Coke ovens	136	187	187
Tar distillers	13	16	16
	459	572	953
Toluene			
Petroleum based	250	326	424
Coke ovens	31	39	39
Tar distillers	3	4	4
	284	369	467
Xylenes			
Petroleum based	318[a]	308	418
Coke ovens	8	11	11
Tar distillers		1	1
	326	320	430

[a] Includes tar distillers.

BENZENE END-USE PATTERN

	Consumption, Millions of Gallons			
	1959	*1960*	*1961*	*1965*
End use				
Styrene monomer	180	219	232	270
Phenol	87	102	99	140
Nylon	29	37	42	80
Synthetic detergents	35	34	34	37
Aniline	14	13	12	15
DDT	15	16	16	17
Benzenehexachloride	2	2	2	2
Maleic anhydride	9	10	18	30
Mono- and dichlorobenzene	10	11	12	15
Nitrobenzene	2	2	2	2
Miscellaneous	20	22	23	25
Exports	7	23	50	150
Total	410	491	542	783

Aromatic cycle stocks from cracking operations contain methylnaphthalenes but little naphthalene. A 450°–550° F. cut of FCC (fluid catalytic cracking) light cycle oil might contain 50% of aromatics, largely mono-, di-, and trimethylnaphthalenes. Because of the

CRUDE NAPHTHALENE

(Millions of pounds)

Year	*Production*	*Imports*	*Domestic Supply*	*Domestic Sales*
1950	288.5	110.8	399.3	206.7
1952	355.7	73.6	429.3	255.3
1954	295.1	66.9	362.0	224.2
1956	491.4	78.9	570.3	299.0
1958	345.1	81.1	426.2	212.6
1959	425.3	65.0	490.3	235.0
1960	510.0	41.4	551.4	310.3
1961[a]	490.0	105.0	595.0	320.0
1965[a]	650.0	25.0	675.0	305.0

[a] Estimated.

availability of light catalytic cycle stock and its relatively low price, it has been considered by many as a feed for naphthalene manufacture. Preparation of a suitable dealkylation feed from this material is even more costly *than from reformate.* Requirements are:

Concentrate the aromatics and preferably the naphthalenes to minimize hydrogen consumption and losses of feed to fuel gas. Distillation and solvent extraction have been proposed for this purpose.

Pretreat for sulfur, nitrogen, and olefin removal either before or after concentration to the low level required by the particular dealkylation process, or by the purity specifications for the product.

Several hydrogen-treating processes have been considered. But at high severities these processes risk saturation of the aromatic rings. This undesirable side reaction is wasteful of hydrogen and would be expected to promote subsequent destruction of the rings in hydrocracking.

Preliminary estimates of feed stock costs, considering raw materials plus processing, indicate that reformate bottoms and cycle stock concentrate are roughly equal in cost.

Any other aromatic fraction rich in methylnaphthalenes could be considered. In general the higher the severity of the cracking process from which these materials are derived the greater will be the concentration of the lower members of the aromatics series and the lower the paraffin content. Extraction processes such as sulfur dioxide, furfural, and phenol are reported to be suitable for concentration of aromatics for naphthalene manufacture.

With this background one may consider the accompanying descriptions of available hydrodealkylation processes accompanying this article *which have been* developed over the years but which have been commercialized only recently.

AUTHOR *This staff feature was prebared with the generous assistance of the seven major licensors noted here and the Badger Manufacturing Co.*

THD: GULF OIL CORP.

Application: A thermal process for producing benzene and naphthalene

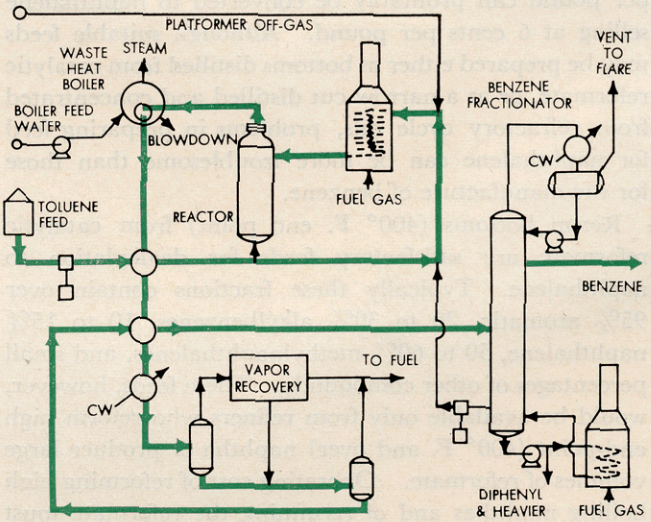
Charge: Benzene—toluene, xylenes, other alkyl benzenes, and reformate fractions. Naphthalene—heavy reformate bottoms, catalytic gas oil fractions and extracts, coal tar oils, selected fractions of virgin kerosines

Description: When producing benzene, nitration grade toluene is charged to a furnace with hydrogen from naphtha or gas reforming. The combined stream goes to a specially designed reactor at an elevated temperature and pressure. Reactor effluent goes to a boiler where high pressure steam is generated. Product is then exchanged with fresh toluene, cooled, and gas and liquid is separated. Liquid product is separated in a fractionator for benzene recovery. *Unreacted toluene is recycled to the furnace.* Heavy bottoms fraction, diphenyl, and other high boiling hydrocarbons, amounting to about 1%, is drawn off. Benzene is produced in greater than 95% of theoretical yield. Three commercial plants are now being designed for this process.

Quality of feed stock is generally dictated by the specifications of the benzene product. If extremely pure benzene is required, toluene and other alkyl benzenes should be severely pretreated to remove substantially all sulfur and nitrogen contaminants. If the aromatic charge is an extract from reforming, sulfur and nitrogen are probably low enough *without further treatment.* Olefins and diolefins are potential coke formers, and pre-treatment is desirable if they are present in the charge stock. Pretreatment of naphthalene charges is also desirable in certain instances *for sulfur, nitrogen, and olefin removal. Yield of naphthalene* depends primarily on concentration of naphthalene rings in the charge stock.

Hydrogen: As low as 25% has been used in toluene hydrodealkylation without noticeable effect on yields or selectivity. Enrichment and recycle are not normally used, but can be if required by one of several processes.

Investment: Benzene from toluene—$1.2 million for 1000 barrels per stream day charged.



SUN OIL CO.

Application: A process for producing benzene and naphthalene

Charge: Catalytic cycle stock, heavy reformate, and nitration toluene

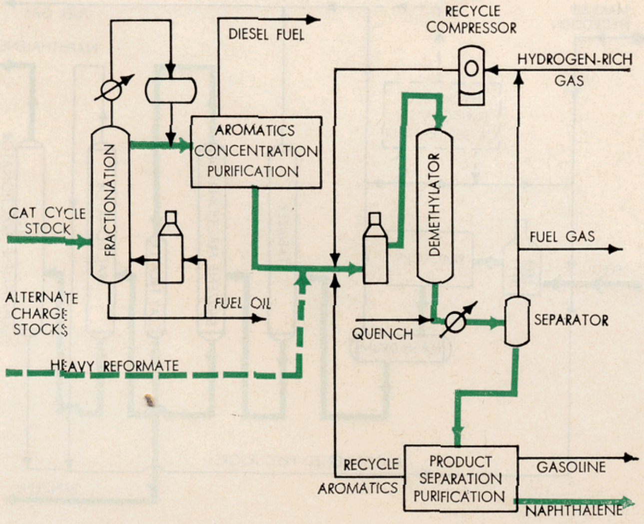
Description: Process for aromatic hydrodealkylation is considered unique in that it can handle catalytic cycle stock as raw material for naphthalene production. A highly purified aromatic fraction containing mono- and dimethylnaphthalenes is concentrated in the feed preparation with high aromatic recovery. Demethylation step of the process is equally adaptable to this aromatic concentrate, to heavy reformate, or to toluene demethylation. Aromatic concentrating step produces high cetane Diesel fuel as a by-product when catalytic cycle stock is used as the feed. Process does not necessarily require use of catalyst. Presence of sulfur, nitrogen, olefins, and diolefins in heavy reformate and catalytic cycle stock feeds is not considered to be a problem. In heavy reformate feed, an aromatic content of 98% is desirable. No range is available for catalytic cycle stock but the higher the aromatic concentration, the better. In example cited, feed was 14.6% by weight of dicyclic aromatics and 49.0% by volume of total unsaturates.

Investment and Costs: Benzene from toluene—1000 barrels per stream day charged

Investment, million $	1.2
Utilities	
Electric power, kw.	255
Fuel, million B.t.u./hr.	10
Steam, lb./hr.	21,000
Circulating water, gal./min.	1700
Chemicals, $/mo.	350

Naphthalene—50 million pounds per year

Feed	Heavy Reformate	Cat. Cycle Stock
Investment, million $	2.0	4.2
Utilities		
Electric power, kw.	420	630
Fuel, million B.t.u./hr.	40	90
Steam, lb./hr.	4000	0
Circulating water, gal./min.	900	1500
Chemicals, $/mo.	1000	2100



HDA: ATLANTIC REFINING CO., HYDROCARBON RESEARCH, INC.

Application: *A thermal process producing benzene,* naphthalene, and selected aromatics

Charge: Heavy reformate light cycle oil products, catalytic or thermal cracking gas oils, from coke oven by-products, or from thermal pyrolysis operations

Description: Hydrogen-rich make-up gas from catalytic reforming and recycle gas are compressed and mixed with liquid aromatic feed. Feed is preheated by exchange then by fired preheater going to reactor. Reactor operates between 1100° and 1400° F. and 500 to 1000 p.s.i.g. Reactor product is cooled by generating steam, by heat exchange with reactor feed, and by cooling water. Cooled reaction product is separated into gas and liquid fractions. A portion of the gas is recycled to reaction system, remainder is removed as fuel gas product. Separator liquid is preheated by stabilizer bottoms and then goes to stabilizer tower. Fuel gas is recovered overhead. Bottoms product containing aromatics is passed to recovery unit.

Hydrogen: Hydrogen-rich gas obtained from catalytic reforming operations may be employed. Minimum purity is set by availability and concentration. Enrichment can be obtained by using oil adsorption, low temperature purification, or solid absorption. Hydrogen-rich recycle is used if availability of gas is low or if feed stock contains high percentage of paraffinics. Hydrogen utilization in toluene hydrodealkylation can be as high as 88% when making benzene.

Investment and Costs: *Benzene from toluene*—1000 barrels per stream day charged

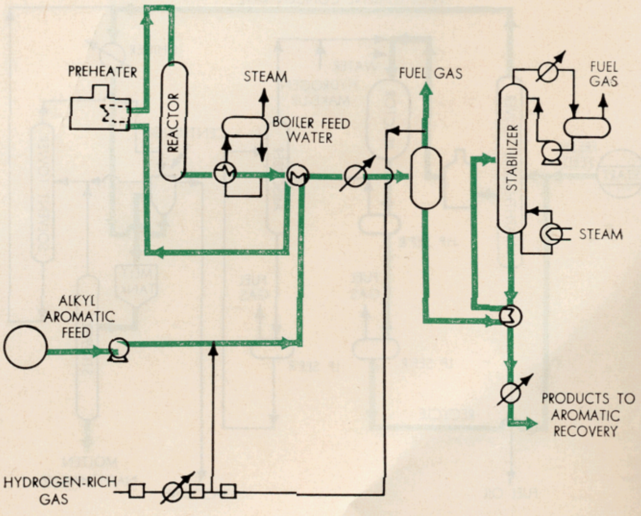
Investment, million $	1.0
Operating costs, ¢/gal. benzene	3.2

Hydrogen enrichment reduces total gas make-up from 4.5 million standard cubic feet per day to 2.0 million but increases investment costs by about $300,000 and operating cost about 1 cent per gallon of benzene.

Naphthalene—50 million pounds per year

Investment, million $	1.5
Operating costs, ¢/lb. naphthalene,	1.5

Note: Process includes certain technical information and rights under patents of Esso Research and Engineering Co.



UNIDAK: UNION OIL CO. OF CALIFORNIA

Application: Fixed-bed catalytic process commercialized for production of naphthalene. Benzene production being developed

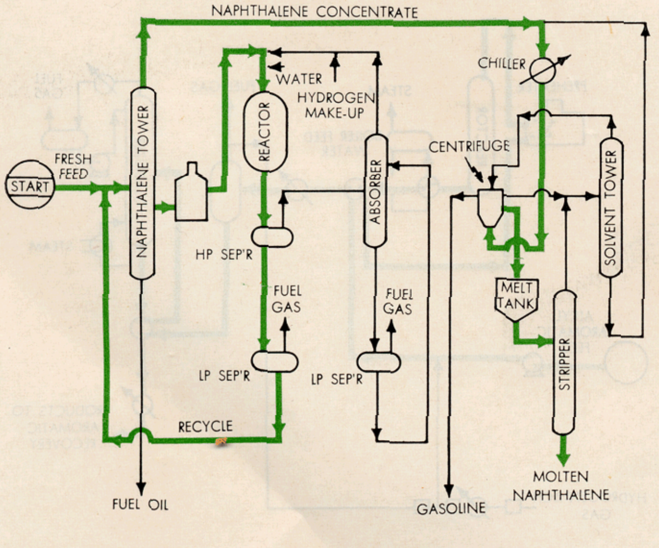
Charge: Catalytic reformate bottoms, catalytic cycle stocks, and aromatic fractions from severe thermal cracking liquid feedstocks

Description: Fresh feed and recycle reactor product are fed to a fractionator to produce a naphthalene concentrate, an alkylnaphthalene concentrate as reactor charge, and a small fuel oil cut as a by-product. Reactor charge is mixed with hydrogen-rich gas and water and passed through fixed bed reactor. Reactor effluent is heat-exchanged with inlet stream and sent to gas separation to produce hydrogen-rich make gas and small fuel gas stream. Water, used to moderate reaction, is also separated. Portions of make-gas and water streams are recycled to reactor inlet. Reactor product is fractionated. Naphthalene is separated from concentrate and nonnaphthalene material is produced as a gasoline by-product. Naphthalene may be finished to 100% purity.

Hydrogen: Hydrogen-rich gas may be used on a once-through or recycle basis, depending on the need for conservation. Hydrogen consumption is less than 7 standard cubic feet per pound of naphthalene produced by reaction. For the case shown here hydrogen, available at 95 mole % purity and 500 p.s.i.g., is fed to reactor section at 3.22 million standard cubic feet per day. An 80 mole % hydrogen make gas is produced at 3.06 million standard cubic feet per day along with a fuel gas at 0.02 million cubic feet. Net hydrogen consumption is 653 standard cubic feet per barrel of fresh feed.

Investment and Costs: Naphthalene—50 million pounds per year

Investment, million $	2.195
Costs	
Utilities, ¢/lb.	0.150
Labor, maintenance, etc.	1.386
Total, ¢/lb.	1.536



DETOL: HOUDRY PROCESS CORP.

Application: A commercial catalytic process for the production of benzene and naphthalene

Charge: Toluene and/or xylene, heavy catalytic reformates, catalytic cycle oils, high severity thermal cracking residue distillates, aromatics from petroleum coking steam cracking. Charge need not be desulfurized

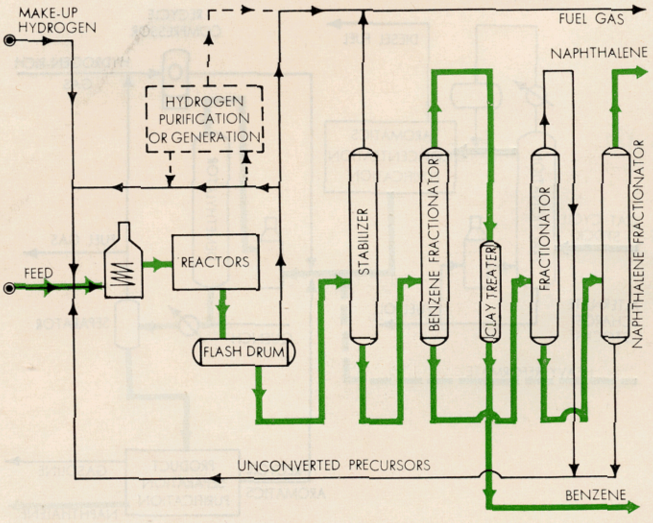
Yields: Selectivity to benzene and naphthalene from alkylbenzenes and alkylnaphthalenes, respectively, is 96 to 98 mole %. Added naphthalene and benzene is produced when feed also contains cyclics such as decalin, indane, etc.

Description: Distillation equipment depends on composition of the charge material and products desired. Feed stock at elevated pressure with recycle aromatic precursors, make-up and recycle hydrogen is heated by exchange and a fired furnace to 1000° to 1200° F. reaction temperature. In the reactors precursors are dealkylated and, in some cases, dehydrogenated. Materials not producing aromatics are converted to light hydrocarbons. Reactor effluent is cooled, flashed, and the hydrogen-rich vapor recycled with excess sent to fuel. Liquid is stabilized to remove dissolved hydrocarbons boiling below benzene. Products of desired purity are fractionated from stabilizer bottoms and unconverted precursors are recycled. Clay treating is recommended when producing high purity benzene or naphthalene.

Hydrogen: With no hydrogen upgrading, streams containing about 60 mole % hydrogen can be used. This requires larger quantities of make-up gas than using typically available make-up hydrogen of 75 to 85 mole % purity. Make-up gas quantity can be further reduced by a hydrogen purification step. Acceptable purity depends on the economics of each specific plant. Availability and purity of make-up hydrogen usually dictates use of internal hydrogen recycle. Typical hydrogen consumption is a little more than theoretical—1 mole per mole of benzene produced from toluene plus an amount for physical loss.

Investment: Benzene from toluene—1000 barrels per stream day charged, $1.1 million

Use of a hydrogen enrichment unit will decrease make-up hydrogen requirement by about 40 to 50%. It reduces size of catalytic equipment, furnaces, and exchangers. Cost should then be considered incremental, about $50,000 to $150,000, depending on enrichment system used.



STANDARD OIL CO. (INDIANA)

Application: Thermal process developed specifically for naphthalene production. Could be adapted to toluene dealkylation but no information available at present.

Charge: Heavy catalytic reformate

Description: High purity naphthalene is produced by selective dealkylation of alkylnaphthalenes which occur in the heavier fractions of catalytic reformate. Typically, a reformate stream boiling between 430° and 650° F. (true boiling point) is fractionated at the dealkylation unit to produce an 80% heart cut, rich in alkylnaphthalenes, and boiling between 450° and 600° F. (true boiling point). Feed to dealkylating unit is joined with hydrogen and passed to the reaction section. Product is separated in recovery section to produce a vent gas rich in hydrogen, a light aromatic stream rich in benzene, a heavy-ends stream, and a high purity naphthalene. Although the process has not been commercialized, it has been extensively developed and tested on a pilot plant scale and potential commercial applications have been studied from design and engineering viewpoints.

Investment and Costs: About $2.0 million for on-site making of naphthalene at a rate of 50 million pounds per year. Annual maintenance costs would be about 4% of investment cost.

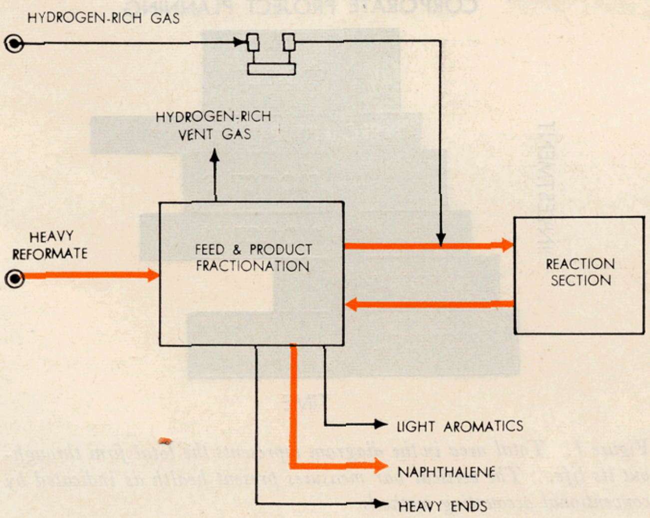
Utilities:

Steam, 125 p.s.i.g., million lb./yr.	2.79
Fuel fired, million B.t.u./yr.	237,000
Electricity, million kw./yr.	6.70
Cooling water, million gal./yr.	650
Labor, man hr./day	72
Raw materials	
Heavy reformate, million lb./yr.	97.7
Hydrogen-rich gas (85% H_2),[a] moles/hr.	750
By-products	
Light aromatic-rich naphtha,[b] million lb./yr.	8.48
Heavy ends, million lb./yr.	23.4
Hydrogen-rich off gas (67.5% H_2),[c] moles/hr.	750

[a] Stream rate. Reformer hydrogen assumed available at 200 p.s.i.g.

[b] Composition, vol. %: pentanes, 4; benzene, 60; toluene, 9; xylene + aromatics, 27

[c] Discharged at higher pressure than input hydrogen



HYDEAL: UNIVERSAL OIL PRODUCTS CO.

Application: A catalytic process for making benzene and naphthalene

Charge: Toluene, xylene, and other alkyl benzenes heavy reformate from rerun catalytic reformates, light cycle oil from catalytic cracking

Description: Predominant reaction is removal of alkyl groups from aromatic nuclei in a hydrogen atmosphere. Liquid charge is mixed with hydrogen, heated by an exchanger and a heater, and introduced into the reactor. Reactor effluent is cooled and introduced into liquid-gas separation and hydrogen enrichment section. Methane and heavier constituents from the recycle gas are removed. Liquid products from phase-separation are sent to recovery system. Product from the reaction are clay treated to remove color bodies. Clay-treated product is introduced into benzene column and specification benzene is recovered overhead. Bottoms go to toluene column. Toluene column can be operated to produce specification toluene overhead or to make a stream for recycle to the Hydeal reactor. Bottoms from the toluene column can be either xylene or heavier or the column can be operated to reject high boiling components from the system. Essentially the same system is used for naphthalene production.

Hydrogen: Make-up gas from catalytic reformer off-gas about 90% hydrogen by volume, mixes with the feed in the ratio of 5 parts hydrogen to 1 part feed. High utilization efficiencies of the available hydrogen in the make-up gas are obtained. Equipment requirements are modest and operation is economical in cost.

Investment and Costs: Benzene from toluene—1000 barrels per stream day charged

Investment, million $ 1.25

Yield, barrels per stream day: 800 benzene; 15 xylene and heavier. off-gas, 1.8 million standard cubic feet per day

Costs, direct operating equal to 2.32 cents per gallon

Naphthalene from heavy reformate—75 million pounds per year

Investment, $2.8 million

Costs, direct operating equal to $1953 per stream day