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Petrochemical Industry—Feed Stocks

1.0.0. Petrochemical Industry in India

Petrochemical industry in India is still in incipient stage. Born much later than Petroleum Industry, around 1966, the topical growth it made during the last few years in the midst of technological upheavels, is really encouraging. Realising the importance of petrochemicals in national development the Government initiated, encouraged and supported the industry in both private and public sectors to grow with full vigour.

The modest beginning of petrochemical industry started with commissioning of an ethylene plant (20,000 tpa of naphtha cracker) by Union Carbide in 1968, (1.a) National Organic Chemicals Ltd. (NOCIL) soon followed the trend and established another 60,000 tpa naphtha cracker at Thane, Maharashtra in 1968. The Govt. of India harping over the industrial development entered the venture, since then a gigantic transformation took place in the prodigious form of Indian Petrochemicals Ltd. (IPCL) at Baroda in 1971, with a capital investment of 3,000 crores of rupees. Infact, it may not be possible to forget the role of ONGC which was meant for exploration and production of oil and gas in India, took an active pivotal role in starting an Aromatics Extraction Plant and olefin complex. Later on the Aromatics plant joined the Gujarat Refinery, while the olefins complex was christened as IPCL.

The development of IPCL into full fledged petrochemical complex is gradual and has shown its vigorous commitant growth by manufacturing 32 chemicals of which 15 different chemicals and intermediates were indigenously developed from the earlier six products at birth.

IPCL has a programme of Rs. 4875 crores in 8th plan to run on-going projects and start a grass root cracker at Gandhar. In joint venture with general Engineering plastics, Netherlands; IPCL has the plans for the production of alloys, blends, polycarbonate and poly phenyline oxide, carbon filaments.

The various petrochemicals produced by IPCL are shown in Table 1.1 (*a*) and detailed plant flow sheet of products is shown in Fig. 1.1 (*a*).

Table 1.1 (*a*)

IPCL PRODUCTS
AROMATICS

A	**Xylenes**	
	Process Licensor : KRUPP KOPPERS, FRG.	
	Products	Licensed capacity (MTA)
	Ortho and mixed xylenes	23,500
	Paraxylene	17,000

	Solvent CIX	10,000
	Hepton	20,000
B.	**DMT**	
	Process Licensor : DYNAMIT NOBEL, FRG	
	Products	Licensed capacity (MTA)
	Dimethyl terephthalate	40,000
	Methyl benzoate	300
	Dimethyl isophthalate (impure)	200
	OLEFINS	
A.	**NAPHTHA CRACKER**	
	Process Licenser : LUMMUS CO., UK	
	Products	Licensed capacity (MTA) Present capacity 3 lakh ton
	Ethylene	1,30,000
	Propylene (polymer grade)	38,000
	Propylene (chemical grade)	43,300
	Carbon black feed stock	17,900
B.	**BUTADIENE EXTRACTION**	
	Process Licensor : UNIVERSAL OIL PRODUCTS, U.S.A.	
	Products	Licensed capacity (MTA)
	Butadiene	22,000
	C_4 Raffinate	8,200
C.	**AROMATICS EXTRACTION**	
	Process Licensor : UNIVERSAL OIL PRODUCTS, U.S.A.	
	Products	Licensed capacity (MTA)
	Benzene	23,600
	Cixon	12,000
D.	**PYROLYSIS GASOLINE HYDROGENATION**	
	Process Licensor : INDIAN INSTITUTE OF PETROLEUM, DEHRADUN, INDIA; IFP, FRANCE,	
	Products	Licensed capacity (MTA)
	Light pyrolysis gasoline	29,300
	Heavy pyrolysis gasoline	34,600
	ACRYLONITRILE	
	Process Licensor : SOHIO, U.S.A.	
	Products	Licensed capacity (MTA)
	Acrylonitrile	24,000

	Acetonitrile	900
	Hydrocyanic acid	3,600
	POLYBUTADIENE RUBBER	
	Process Licensor : POLYAR INTERNATIONAL S.A., SWITZERLAND	
	Product	Licensed capacity (MTA)
	Polybutadiene rubber (Cisamer)	20,000
	LINEAR ALKYL BENZENE	
	Process Licensor : UNIVERSAL OIL PRODUCTS, U.S.A.	
	Products	Licensed capacity (MTA)
	Linear alkyl benzene	43,500
	Poly alkyl benzene	3,500
	Heavy n-paraffins	25,000
	Ceton	16,000
	L.R. 2030	15,000
	POLYPROPYLENE HOMOPOLYMER	
	Process Licensor : MONTEDISON, ITALY	
	Products	Licensed capacity (MTA)
	Polypropylene homopolymer	
	(Koylene)	30,000
	Atactic Polymer	3,000
	ETHYLENE GLYCOL	
	Process Licensor : SCIENTIFIC DESIGN CO., U.S.A.	
	Products	Licensed capacity (MTA)
	Ethylene glycol	20,000
	Polyethylene glycol	2,400
	Ethylene oxide	5,000
	Diethylene glycol	2,500
	Triethylene glycol	250
	LOW DENSITY POLYETHYLENE	
	Process Licensor : AQUITAINE TOTAL ORGANIC CHIMIE (ATO CHIMIE), FRANCE	
	Product	Licensed capacity (MTA)
	Low density polyethylene (Indothene)	80,000
	MONOCOMPONENT ACRYLIC FIBRE ACN	30,000
	Process Licensor : ASAHI CHEMICAL CO., JAPAN	
	Product	Licensed capacity (MTA)
	Monocomponent acrylic fiber	
	(Indacrylon)	12,000

	VINYL CHLORIDE / POLYVINYL CHLORIDE	
A.	**EDC/VCM**	
	Process Licensor : STAUFFER CHEMICAL CO. U.S.A.	
	Products	Licensed capacity (MTA)
	Ethylene dichloride	1,00,000
	Vinyl chloride	57,300
B.	**PVC**	
	Process Licensor : B.F.GOODRICH, U.S.A.	
	Product	Licensed capacity (MTA)
	Polyvinyl chloride (Indovin)	55,000
	ACRYLATES	
	Process Licensor : NATIONAL CHEMICAL LABORATORY, PUNE, INDIA	
	Products	Licensed capacity (MTA)
	Methyl acrylate	2,000
	Ethyl acrylate	3,000
	Butyl acrylate	4,000
	2-Ethyhexyl acrylate	1,000
	Ammonium sulphate	12,000
	PETROLEUM RESIN	
	Process Licensor : CdF CHIMIE, FRANCE	
	Product	Licensed capacity (MTA)
	Aromatic hydrocarbon resin (Petrez)	5,000

1.1. Play of Trans National Corporations (TNC)

Biggest boost to the petrochemical industry given by IPCL is equally supplemented by the Trans National Corporations with active collaborations and new ventures. India's march in the last two decades in different fields has been justified due to the permeation of petrochemicals into all walks of life. The large necessities of imports to face the race in petrochemical field has generated an urgent wave of establishing various petrochemical industries.

The Sixth Plan period has barged to establish a firm footing in oil and petrochemical industries. The Seventh Plan witnessed a huge leap in petrochemicals displacing the oil industry to second place. The most important industry in this plan is the gas industry. The biggest gas cracker complex in Maharashtra (11,670 million rupees) (see Fig. 1.1 (*b*)) is a right beginning in this direction, under the surveillance of IPCL. Ten major gas based fertilizer units along with the self supporting energy schemes and transportation of Bombay High-Bassein gas to Jagdishpur (HBJ-gas line) are some of the major ventures in this Plan.

1.1.0.1. HBJ Gas-Grid (Fig. 1.1.c)

Associated gas comes out along with oil. The quantity of gas dissolved depends upon the saturated pressure of the reservoir. Commonly about 500 SCF dissolves in a barrel of oil under a pressure of 2500 psi. when the production of oil has to be stepped up naturally the associated gas quantum also increases. During the initial stages of Bombay High development there were no infrastructure facilities to consume the gas hence it was flared. During 80-90 the quantum of gas flared was enormous. About two decades back gas was ranked second to oil, but today the thinking has changed. Right from a boiler fuel to petrochemical feed stock and a clean fuel for automobiles; the utility and serviceability of gas has brought increase its creditability to No. 1 fuel. Today GAS Refinery is a reality. The enhanced gas consumption during last decade and ever increasing demand is a real meter to show how it is being regarded as most important material in daily life. GOI has started looking for Hydrocarbon deposits throughout the country. The results of which were significant. Rajasthan, Gujarat, Tripura, Palk straits etc. are some of the examples. KG basin discovery in the late 80s brought significant change in the hydrocarbon activity in this region.

To successfully utilise the enormous amount of associated gas from Bombay High, a gas processing plant at Hazira was commissioned and this sweetened gas is transported through a pipe line known as Hazira-Bijapur-Jagdishpur Pipe line (HBJ). The length of this pipe line initially was 1700km, (presently it is 2300km long) and in the second phase was able to transport 20MMCMD gas. The gas is supplied to ten fertiliser plants, and power house for generation of 4000MW besides to a gas cracker plant at Gandhar and to IPCL. With branch line drawn up to Kanpur, Faridabad and Salimpur Petrochemical complex (originally planned) if works in full capacity; the line can transport 33 MMMD of gas.

KG basin is the next biggest Off-Shore activity in India, approximate reserves are 7 trillion CM, With the entrance of Relaince Industries with the partnership of Niko Resources of Canada into this basin remarkable achievements were attained. With the success in Gas discovery in M-1 and H-1 wells it has plans to produce 45MMCMD of gas from its structure D6 (The reserves of which are 1.45 trillion cubic meters gas). Presently 60,000 to one lakh cu.meters of gas is being supplied to Power house in Kovvur 80Km away from KG basin and other gas consumers. The future of gas is secure in KG basin and will provide gas to Nagarjuna Fertilisers and other gas based power houses when the production reaches one million cu. meters.

In a remarkable turnaround, Hazia Gas Processing Complex of Oil and Natural Gas Corporation Ltd. (ONGC) has reached a throughput level of 28 million metric standard cubic metres a day (mmscmd) of Gas to the HVJ Pipeline, 70 per cent of its pre-shut-down level. Domestic gas supplies may be available from the KG basin from D-6 blocks of RIL in 2008-09. On the other hand the supply projected by ONGC in the XIth plan period is likely to witness fall from 47.28 MMSCMD in 2007-08 to 41.08 MMSCMD in 2011-12., which is a concern for fertilizer units. However the supply from private players/JVs is expected to increase from 23.26 MMSCMD to about 57.22 MMSCMD in 2011-12. DGH has projected additional supply of 20, 30 MMSCMD and 40 MMSCMD from RIL fields in 2009-10, 2010-11 and 2011-12, respectively, and 54 MMSCMD from GSPC in each of the above years. This shows that the gas supply will be 70.54 MMSCMD in 2007-08, and is expected to grow to 192.30 MMSCMD in 2011-12. The demand-supply gap projected in the XIth Five-Year Plan period clearly indicates the need for imports. —LNG supply will reach a level of 23.75 MMTPA by the year 2011-12. Though there is a possibility of availability of gas from Iran through Pakisthan and Myanmar-India pipeline another 30-40 MMSCMD in 2010-11 may be available.

HBJ pipeline project was conceived in year ’82. This pipeline of 1758 km long at a cost of 1760 crores of rupees is capable of transporting 30 million Cu. meters of gas at peak demands. Presently, the gas production of Bombay High South Bassein and satellite platforms amount to 26 M_2 Cu meters a day, the present processing capacity of Hazira terminal; which in two or three years will touch a new high mark of 50 M^2 CMD.

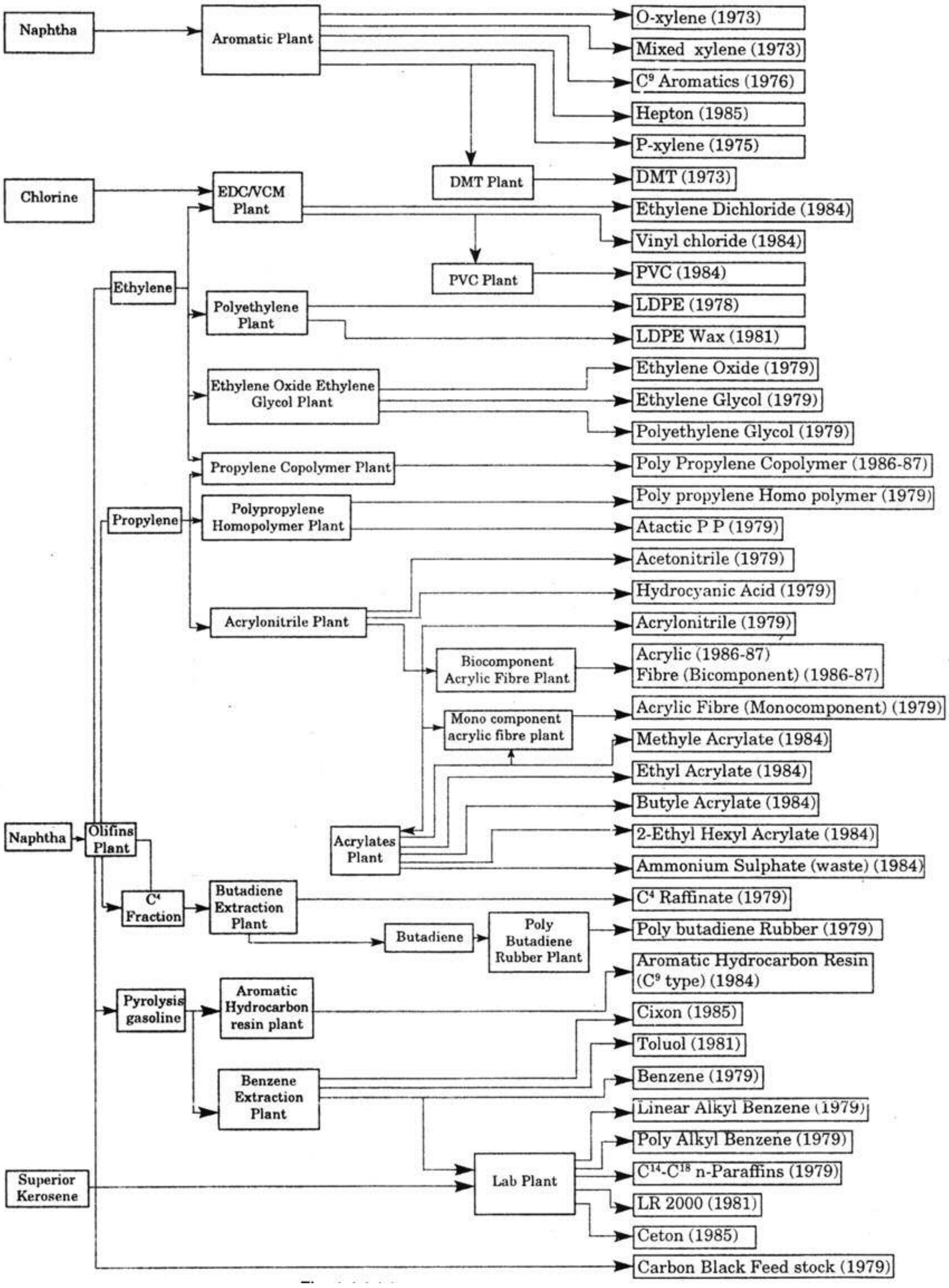


Fig. 1.1 (*a*) Flow Sheet of IPCL-Products.

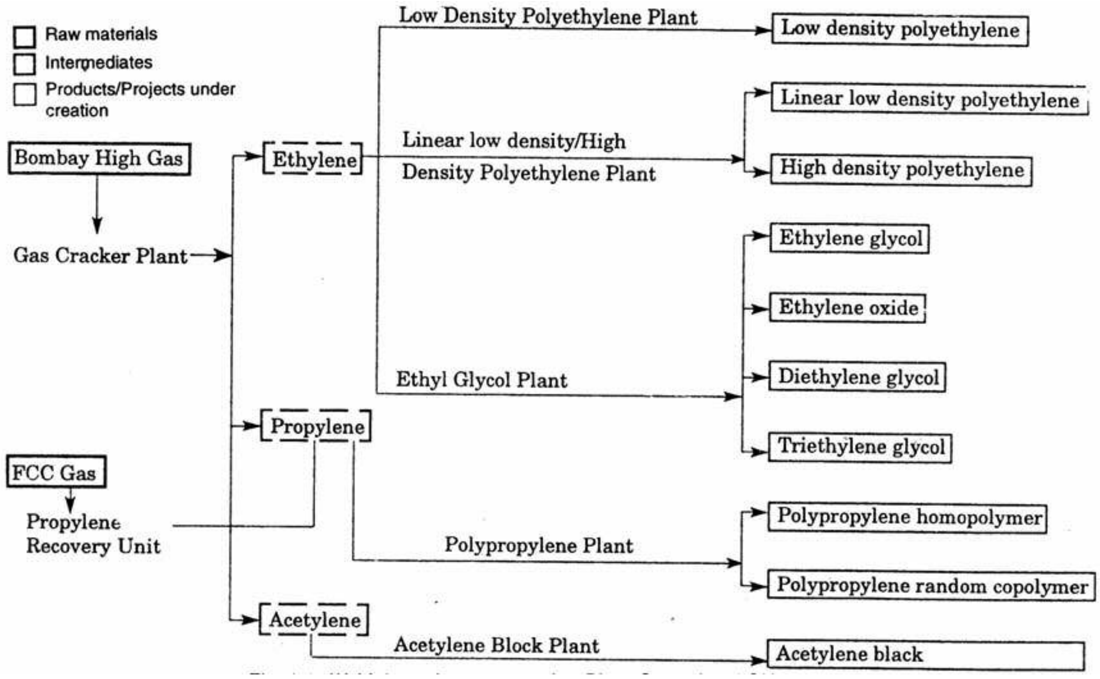


Fig. 1.1. (*b*) Maharashtra gas cracker Plant-Operational Schemes.

The consumption of gas by 6 fertilizer plants, petrochemical units, power and other industries will roughly need a 30-36 M^2 CMD of gas which may thus permit about 20 M^2 CMD gas to south zone, if pipeline connections are laid. Thus the total needs of south India amounting to 20 M^2 CMD for fertilizer, thermal power plants and other units can be safely met. K.G. and Caveri basins are likely to yield about 6.5 and 3.5 M^2 CuM gas respectively per day by 1994-95. Fig. 1.1(*c*) shows HBJ pipeline.

This is in congruence with new alignment policy of the government with respect to increasing gas and oil strikes. Presently, the production of gas on all the fronts is around 60 M^2. Cu. M per day (1995) and 30% of the gas is still flared. Government had set up a working group on petrochemicals for the Seventh Plan to work out demand projections for various petrochemicals and their indigenous production (shown in Table 1.1*b*). Consumption of petrochemicals were 3.28 lakh tonnes in 1982-83 and increased at an average annual rate of 5% till 1990, it is likely to increase further. The anticipated demands for olefins would be met by Maharashtra Gas Cracker Complex and another one in Gujarat. Three aromatic recovery units one each in Kerala, Maharashtra and U.P. during Sixth Plan would supply the BTX streams. Salempur Petrochemical Complex has been already initiated and it is based on naphtha from Mathura Refinery.

Salempur project likely to produce (Investment Rs. 625×10^7).

Benzene	1.6×10^5 tonnes
O-xylene	53×10^3 tonnes
p-xylene	1.53×10^5 tonnes
Alkyl-benzene	17.5×10^3 tonnes
Dimethyl tere phthalate	1.5×10^3 tonnes
Cyclohexane	90×10^3 tonnes

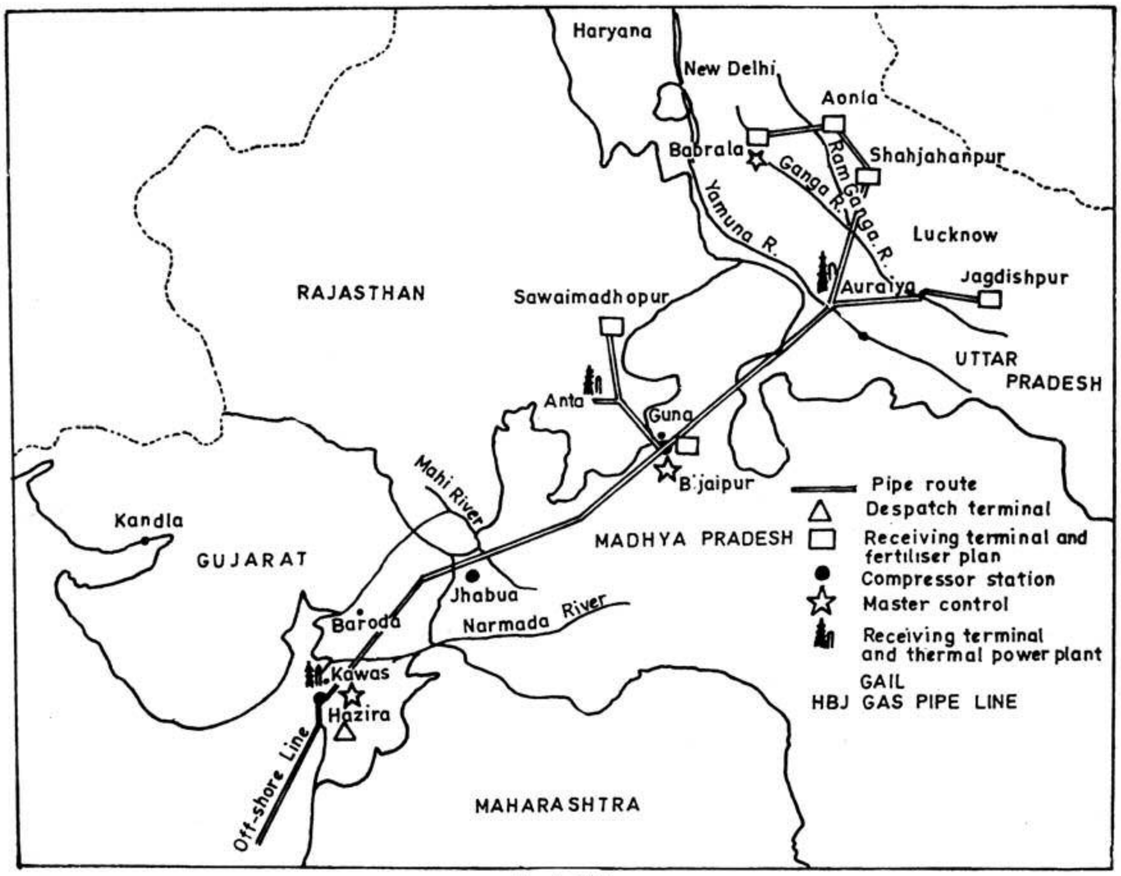


Fig. 1.1 (*c*).

The picture is not the same always; for instance the utilisation of full capacity in some cases for PVC, LDPE is remote. Hence the production, demand and consumption has to be linked always.

Fast advances elsewhere would cause dismay at the technology and the uneconomical methods adopted in our country. These developments indicate formidable odds, which India has to reckon with while continuing the production on the basis of imported technology. Thus, keeping track of advances on the subject and concerned technology is essential to relegantly face the march. Revamping, retrofitting of the existing complexes by jettisoning old technology and or by adopting assured technology on the basis of feed-stocks availability are some of the prime essentialities of the pollution free industrial future.

The major industries have been surveyed in depth and can be divided into four broad groups such (2) as :

(*a*) Basic bulk chemicals
(*b*) First generation intermediates
(*c*) Second generation intermediates, and
(*d*) End products.

Table 1.1 (*b*) Physical Targets in Seventh Plan

Plastics (thousand tons)	*1984-85*	*1989-90*
LDPE	110	211
HDPE	39	113
Poly-propylene	26	103
PTFE	0.5	—
PVC	80	197
Ethylene Oxide	30000	50000
Acetone	40000	125000
Caprolactum	60000	130000
Butadiene	50000	65000
LAB	80000	120000
Poly Styrene	19.6	331.6
SBR	41	71.5
PBR		
NBR	5	—
ABS	10	—
Synthetic Fibres		
Nylon filament yarn	30	70
Polyester staple and filament	95	191
Moulding powders		
PF	4.6	
MF	3.5	
UF	3.5	
CA	0.55	

Petrochemical industry is dominated by two dozen TNCS some of them being petroleum companies. The design and construction are strict monopoly of these TNCS and developing countries are at the mercy of such companies for know-how.

1.1.1. Plastics and Synthetic Fibre Industry

Plastics as well as synthetic fibres development is a post war activity. In case of plastics, the real starting commenced with establishing a synthetic rubber plant at Bareilley (1962, product SBR 30,000 tonnes). The raw material used was alcohol and the same old technology is continued till now. Soon ICI started manufacturing polyethylene; again based on alcohol; a polystyrene plant was also commissioned by Hindustan Polymers now known as LG Polymers at Vizag using alcohol as feed material. This shows the early plastic industry was based upon the then available alcohol raw material. Even today, India is one of the largest producers of alcohol (1300 million litres). The new industries like NOCIL, Hindustan Organics, Poly Olefins, etc. were based on the petroleum feed stocks. Some of the earlier plastics, like Urea-phenol/formaldehyde combinations, are even today operating on the same technology. However, the new industries are clearly shifting towards petroleum feed stocks. Establishment of other petrochemical industry has been a great fillip to the growth of plastic industry. Initially, two petrochemical industries, Union Carbide and NOCIL were set up with a limited capacity based upon naphtha. IPCL was the real institution to bring about a transformation in the country by familiarising the plastics, like LDPE, Polypropylene, PVC, Methacrylates. Though engineering plastics and speciality polymers have not been developed in par with the progress, the diffusion of plastics into all walks of life, has made them essential ingredients of the modern industry. Presently, consumption of plastic raw materials is a meagre 4.5 lakh tonnes virgin and 75,000 tonnes reprocessed; the target for 1990 is fixed at one million tonnes. Poly Urethane-foams (present production 5000 tpa) a leading plastic has not been fully given importance till now. Production of isocynates has not been given any importance at all. In 1987-88, about 66,000 tonnes of SBR was produced for which 210 million litres of alcohol was required.

1.1.2. Synthetic Fibres

Except cellulose fibres, all the synthetic fibres are based upon the petroleum feed stocks and these industries are relatively new. In fact the activity of these would be touching all time high at the end of Seventh Plan. Even today, the consumption of cellulosic fibres tops as shown here.

Consumption of fibres	*1983*	*1984*	*1985*
Total (10^3) (tonnes)	1,518	1,547	1,672
Cotton	1,341	1,371	1,500
Viscose Rayons	151	116	105
Polyester	39	40	45
Acrylic	12	15	17
Miscellaneous	5	5	5

Synthetic Fibres (Production) 1989-1990

Cotton	2.8 lakh tons
PSF (Filament)	1.6 lakh tons
Fibre	1.1 lakh tons
Acrylic	32,000 tons
Nylon	37,726 tons
Polypropylene	911 tons
Viscose (filament yarn)	46,000 tons
Cellulosic fibre	1,92,435 tons
Total man made fibres/yarns	4,40,000 tons

Production of Fibres (*in TMT*)

Group	*2002-03*	*2003-04*	*2004-05*	*2005-06*	*2006-07*
Synthetic Fibres	1669	1755	1868	1875	1906
Fibre intermediates	2417	2648	2691	2851	2963

Thus, India has a distinction of being one of the countries with the lowest per capita consumption of fabrics (14.8 metres/head).

The growth of polyester staple fibre in India has not been in a significant manner, because of the policy of government *i.e.* classifying these fibres meant for affluents only and raising the cost. However, the folly has gradually disappeared and it is ultimately realised that synthetic fibre industry has to go along with natural fibres and cannot be dispensed with. Presently, there are 7 nylon plants, and 5 polyester plants. One acrylic fibre plant would soon be joining the national stream. The capacity in 1985, was 54,200 tonnes of polyester. In 1996, installed capacity polyester fibre is 4.95 lakh tonnes.

Existing Units	*Capacity production (Thousand tonnes)*		
	1985	*1987*	*1990*
IEL (CAFI Division)	10	16	30
Indian Organic	12	18	30
Swadeshi Poletex	12.62	12.2	15
Calico	7.6	15	15
J.K. Synthetics	12.2	18	30
New Units			
Bongaigon		30	30
India Polyfibres		15	25
Orissa Synthetics		15	25
Madhya Pradesh Fibres		15	25
Punjab Polyfibres		15	25
Reliance Industries		45	45

1.1.3. Rubbers

Though Indian Natural Rubber Industry is century old, synthetic rubbers industry has not yet come out of ages. Synthetic rubbers based on butadiene, which is mostly derived from alcohol till now are the only rubbers produced. However, the butyl rubber, though the potentiality of the stock is about 89,000 tpa as shown below; is yet only 25,000 tpa produced.

	i-Butylene available
IPCL	9,000 tonnes
Koyali	11,000
HP-Bombay	9,000
Cochin Refinery	12,000
Mathura Refinery	11,000
Madras Refinery	7,400
BPCL	12,000
Panipat	10,000
NOCIL	4,000
WBIDC, Haldia (not yet begun)	7,000
Vizag Refinery	7,400
Total	89,800 tpa

Natural rubber production in the country is about 1.86 lakh tonnes in 1985 and there is no hope of further increase. However, the expansion of refineries specially by instituting FCC-units, the production of butylenes has increased, that would solve the production of butyl rubber.

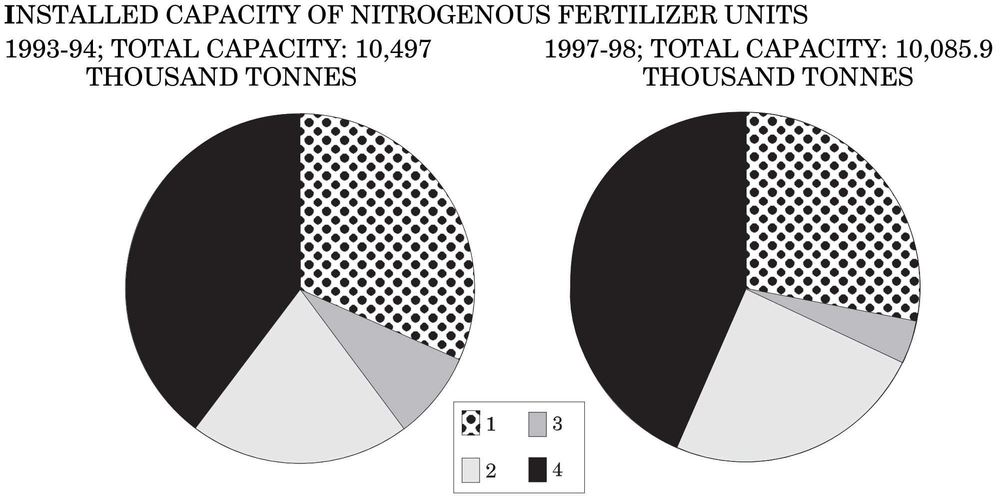
1.1.4. Nitrogen Industries

With reference to the present context, nitrogen industries are mainly regarded as ammonia and urea industries *i.e.* fertiliser, being large tonnage product. The first fertiliser unit (ammonia was built by Maharaja of Mysore, as an essential step of industrialisation of Mysore), soon Maharaja of Travancore followed by establishing a unit based on wood gasification. This continued till the post independence period, and the industrial activity started from 1950 and continued with rapid strides. Started at 60,000 tonnes in 1951-52 the production of nitrogenous fertilisers rose to 5.235×10^6 tonnes in 1984-85 and expected to cross ten million tonnes shortly. The first coke based fertiliser plant at Sindri became the center of activity of R and D plans under Fertiliser Corporation of India Ltd. Initial capacity of the ammonia and urea plants were of 600 tonnes each. These gradually expanded to 900 tonnes and 1350 tonnes per day of ammonia and urea, but today 1350 tonnes ammonia and 1500 tpa urea plants are under construction. Presently, there are 41 units producing 5.235 million tonnes of nitrogen (NPK) fertiliser. R and D wing of FCI and Projects and Development (India) Ltd., (which was a part of FCI till 1978) are actually involved in the creation of fertiliser producing capacity ; other R and D wing of FCI being FACT. The requirement of food grains by 2000 AD when the population reaches around a billion is about 236 M^2 tpa (food grains production in 1997-98 was about 199.3 M^2T ; in 1998-99 it was about 200 M^2T, 231 M^2T in 2007-08.

The development of the industry systematically scanned for various raw materials and still continuing. Coal gas, coal-coke, lignite, are the chosen raw materials in early sixties, afterwards naphtha reforming and fuel oil partial oxidation technologies have been introduced. Presently, natural gas is envisaged for the production of fertilisers. Dearth of oil shortage and abundant low grade coals have forced to go for coal gasification units, the results of which took the shape of Ramagundam and Talcher fertiliser units. The success of gas strikes in different parts of the country, not to speak of existing Bombay High-Bassein and Cambay sites, have prompted to go for gas based fertiliser units, the result of which is Hazira-Bijapur-Jagdispur (HBJ) pipe line to transport the natural gas form Bassein to Thal Vaishet plants in Maharashtra and Hazira in South Gujarat. This pipe line would link 10 gas based fertiliser units with the supporting electric power units. Gujarat Narmada Valley Fertiliser (GNFC)[5.8] unit at Baruch is the biggest (1800 tpd) single train urea plant in India based on gasification of fuel oil. Similarly, Hazira plant is the biggest urea producing plant in the world. The plans, if successful would utilise only 80% of the gas and probably 20% of the gas would be flared.

The planning of these fertiliser units is based upon the available raw materials and the prominence has been shifted from one feed stock to the other in due course of time, Naphtha gas as well as LSHS are equitable but from 1990 onwards gas was major feed-stock for nitrogenous as well as petrochemical industries. Upgrading the older plants and integrating with the modern technology and advanced instrumentation to save energy and increase efficiency and production have been also given highest priority. Presently, several fertiliser plants are producing about 80% of the capacity, though a few plants warrant substantial improvement in working.

In 1998-99, 78 million cubic meters of gas per day has been produced. The demand for nitrogen fertilizer will be crossing 10 million ton by 2000 AD. The capacity installed till 1997 was 9.8 million tons and the production was about 9.6 million tons. The fertiliser units working on various feed stocks and the trend in share of feed stocks can be seen from Table 1.1(*d*). By the end of the Eighth Plan, plants working are shown in the Table 1.1(*e*). The utilisation of installed capacity in public sector and other sectors is shown in the following Table 1.1.



1 : Viable units ; 2 : Loss making units; 3 : Co-operatives ; 4:Private sector

Table 1.1(c)

Installed Capacity of Nitrogen Fertilisers in thousand tonnes

	1993-94	1997-98
Public Sector		
Viable	3306	3041.6
Loss making	1011	299.3
Co-operative	2268	2310.7
Private	3910	4434.3
Total	10,497	10,085.90

Similarly the Ministry of Fertilisers and Chemicals has outlined the necessary targets of production and consumption of fertilisers during Ninth Plan and projected outlay at 11,448 crores of rupees. This would enhance the nitrogen fertiliser capacity installed from the 9.77 MMTPA to 14 million tons. This all depends upon the availability of gas in, Western and KG Basin and regular supply to fertiliser units. Thus in Western sector Aonla, Bijapur and Jagdishpur could not run to full capacity. With the KG basin now able to produce 3 MMCUMPD the two fertiliser units at Kakinada may touch full capacity. The main objective of Ninth Plan will be to ensure regular feed stock availability at steady prices and locating the producing units in deficit areas. Thus new projects to be implemented are :

FACT's replacement of ammonia plant at Udyogamandal with a capacity of 2.97 lakh tons, GSFC's ammonia plant at Baroda with a capacity of 4.45 lakh tons, IFFCO's Kandla expansion project 3.7 lakh tons of NPK and 2.27 lakh tons of di-ammonium phosphate, Chambal Fertiliser and Chemicals unit at Gadepan with an expansion to 7.75 lakh tons of urea, Oswal Chemicals and Fertilisers Paradeep project of 15 lakh ton of diammonium phosphate are almost ready and are likely to work by the end of 1999. Again KRIBHCO's proposal for third ammonium plant to produce 7.26 lakh tons of ammonia based fertilisers and another new plant at Gorakhpur with identical capacity Rastriya Chemicals and Fertiliser expansion project at Thal Vaishet for another 7.26 lakh tons urea. SPIC and Jordan Phosphatic Mines company have already set-up a phosphatic unit in Jordan. Similar joint ventures with Oman Oil Company; SPIC's interest in setting up a gas based plant in Iran has been approved. Thus the fertiliser industry had been licensed with the proven technologies from the four proprietary licensors Halder Topse, Uhde, Kellog and Brown and Roots of USA for ammonia synthesis and Snam Progetti, Stamicarbon and Toyo of Japan for urea; which claim superior technologies with energy economy.

The performance of fertiliser units is shown in Table 1.1(*d*). The stiff competition from liberal imports was partially responsible to cut short the indigenous production. Further some of the public sector units like Durgapur, Namrup, Barauni (HFC) showed deterioration in performance. Gorakhpur unit was shut down, while Talcher and Ramagundum (FCI) were working under below capacity.

Table 1.1 (*d*) Percentage Installed Capacity[8] of Nitrogen According to Source of Feedstock

Period	*Naphtha*	*Natural gas*	*Electric Power*	*Coke-oven gas*	*Lignite*	*Coal*	*Fuel oil*
1960	-	-	0.8	99.2	—	—	—
1970	65.3	10.2	6.0	13.3	5.2	—	—
1980	51.7	13.0	1.7	1.7	—	9.9	19.6
1984	48.0	14.2	1.5	1.3	—	8.8	22.6
1990	27.4	45.8	0.9	0.8	—	4.9	14.2

Table 1.1 (*e*) Capacity of N and P Plants Factory–wise[8] and the Expected Date of Commissioning (7th Plan Period)

(*Thousand tons*)

	Plant		*Capacity N*	*P_2O_5*	*Date of Commissioning*
1.	RCF, Thal, Vaishet (2 Plants)	Plant I	341.5	—	April '85
	(Maharashtra)	Plant II	341.5	—	July '85
2.	MCFL, Mangalore Expn. Karnataka		25.0	63.0	April '87
3.	KRIBHCO, Hazira, Gujarat	Plant I	334.0	—	Dec. '85
		Plant II	334.0	—	April '86
4.	Hindustan Lever, Haldia (West Bengal)		29.0	73.0	Dec. '85
5.	HFCL, Namrup III, Assam		152.0	—	Oct. '86
6.	HFCL, Haldia, West Bengal		152.0	75.0	April '86
7.	Paradeep Phosphates,	Phase I	58.5	150.0	April '86
	Paradeep (Orissa)	Phase II	58.5	150.0	Jan. '98
8.	Godavari Fertilisers and Chemicals, Kakinada (A.P.)		54.0	138	Jan. '88
9.	GSFC, Sikka (Gujarat)		59.0	150.0	Oct. '87
10.	SPIC, Tuticorin (Retrofitting)		19.0	48.0	Jan. '87
11.	NFL, Vijaypur (Dist. Guna), MP		334.0	—	Dec. '87

Contd...

	Plant		*Capacity N*	*P_2O_5*	*Date of Commissioning*
12.	Indo-Gulf Fertilisers and Chemicals, Jagdishpur (Dist. Sultanpur), UP		334.0	—	June '88
13.	IFFCO, Anola (Dist. Bareilly), UP		334.0	—	April '88
14.	Aravali Fertilisers, (Dist. Sawai Madhopur), Rajasthan		334.0	—	Jan. '89
15.	Tata, Babrala (Dist. Bedaun), UP		334.0	—	July '89
16.	Caparo Group (VIth gas based Plant), Shahjahanpur, UP		334.0	—	Oct. '89
17.	Nagarjuna Fertilisers, Kakindada (A.P.)	Ammonia Urea	1900 tpd 3000 tpd	—	1998 1998

1.1.4.1. Technology-TNCS

There are at present eight major technologies available on gas based fertiliser units. They are Halder Topsoe, ICI, Kinetic Technology International, Humphreys and Glasgow, Kellog Lummus, C.F. Braun, Snam Progetti. All these technologies are directed at maximising[9] energy saving and elimination of pollution. Energy saving may be an outcome of choosing active catalysts enabling the operation at low temperatures and less pressures, or the reactor modification etc. and successful utilisation of energy saved. In nitrogen fertilisers urea will account for 84% and the share of production in different sectors is as shown below :

	%	*N_2 share in total capacity*
	1984-85	*1989-90*
Public Sector	57	49
Private Sector	34	35
Cooperative Sector	9	16

The consumption of fertilisers and the feed stock distribution and the addition of plants, technology, that took place during these years are shown in Table 1.2. Some of the major fertiliser units capacities feed stocks etc. are presented.

Table 1.2. Fertiliser Plants Based on Different Feed Stocks

Hindustan Steels	Coke oven gas	
Gorakhpur, Durgapur (FCI)	900 TPD	
IFFCO's Three plants	1.9 M^2 Tonnes	(Urea fertilisers (6) annually)
Pulphur (UP) 27×10^3	1300 TPD	Naphtha Reforming (Ammonia urea).
Kandla Gujarat		Gas
Kalol Gujarat		
Aonla	50×10^3	Urea (gas based)
Varanasi (UP)	24×10^3	Urea (Naphtha)
Maharashtra, Cooperative (Thane)	62×10^3	Urea

Contd...

Trombay, RCF	98×10^3	Gas from Uran.
	(152×10^3)	
Gorakhpur, FCI	55×10^3	Partial oxidation
Ennore, Parry	9×10^3	Partial oxidation
Alwaye, FACT	100×10^3	Naphtha Reforming
Mangalore		
Deepak Fertilisers, Taloja	50×10^3	Associated gas from Uran
Coromandal Fertilisers	91×10^3	Urea (Naphtha) GSFC, Baroda 2nd phase
	(550×10^3)	
Durgapur (FCI)	85×10^3	Naphtha
MFL Madras	199×10^3	Naphtha
Kotari SCI	185×10^3	Naphtha
Kanpur IEL	243×10^3	Naphtha
Cochin FACT	185×10^3	Naphtha
Goa ZAC	190×10^3	Naphtha
Mysore MCFL	194×10^3	Naphtha
Nellore (A.P.)	7.2×10^5	Naphtha (Urea)
Tuicorn (SPIC)	236×10^3	
	(1100×10^3)	First phase-Naphtha
Barauni, HFC (FCI)	600×10^3	Refinery gas
Namrup Extension (FCI)	185×10^3	Natural gas
Sindri FCI	600 TPD	Coal & Coke (P.O.)
Nangal-Original (Electrolysis) (LSHS)/fuel oil	92×10^3	Low sulphur heavy stock
Nangal Extension	135×10^3	
Ramagundam/Talcheru FCI	900 Epd.	Coal gasification
Korba, FCI	267×10^3	Coal
Kota, FCI	185×10^3	Fuel oil
Mithapur	152×10^3	Fuel oil
Mathura	285×10^3	LSHS, 1
Panipat (Liquid Fertiliser plant)	285×10^3	Fuel oil partial oxidation
Bhatinda	46×10^3	Gas
Nagarjuna	46×10^3	Gas
Paradip	55×10^3	Imported ammonia
	295×10^3	F/O
Babrala (UP) Tata Chemicals Ltd.	1350 tpd	Gas
Kota Ex-FCI	185×10^3	Gas
GNFC (Bharuch)	295×10^3	Fuel oil/LSHS

(*Contd...*)

RCF (Rashtriya Chemical Fertiliser) Thal Vishet (Two units)	1350 tpd	(Gas) Pollution free-7 fertiliser plants & 1500 tpd 3 units have been of ammonia
Kanpur (IEL)		600 tpd Naphtha
Hazira KRIBCO Gujarat,	1350 NH_3 1300 Urea	(Two Units-gas)
Sawai Madhopur Rajasthan	1350	Urea/Gas
Luri Agro Chemical Ltd.	1800	Ammonia
Godavari Fertilisers, Kakinada	57×10^3	Naphtha Guna gas
Paradeep Fertilisers	60×10^3	Fuel oil
M.P. Agro Morarji, Jabalpur	10×10^3	
West Coast NP/NPK Project	50×10^3	Fuel oil
Bombay High gas based plants ; Guna		
V Ratlam (MP)	345×10^3	Urea
VI Ratlam (MP) Rajasthan	245×10^3	Urea
VII Ratlam Badhnan (UP)	245×10^3	Urea
VIII Ratlam (MP) Bareilly (UP)	245×10^3	Urea
IX Ratlam Shajahanpur (UP)	345×10^3	Urea
X (MP) Sultanpur (UP)	345×10^3	Urea

Fertiliser[8] plants to be commissioned in 7th plan are shown in Table 1.1 (*e*). The change of feed stock for fertilisers during last two decades is shown in Table 1.1(*d*).

1.1.4.2. Fertilisers

The consumption of fertilisers (NPK) has been stagnant around 12 million tonnes between 1990-91 and 1993-94. Subsequently, it increased to reach the level of 14.3 million tonnes in 1996-97. There were changes in the policy on fertilisers in the 1990s. Phosphatic and potassic fertilisers were decontrolled in August 1992. Only urea (nitrogenous fertiliser) continued to be under the price control system and involves a heavy subsidy for keeping the farm gate prices low. Consequent to decontrol in 1992, prices of phosphatic and potassic fertilisers rose sharply. The gap between the controlled price of urea and the decontrolled prices of phosphatic and potassic fertilizers increased leading to an imbalance in their use. Against the optimum N, P and K ratio of 4 : 2 : 1 and an actual ratio of 5.9 : 2.4 : 1 just before the decontrol, the ratio during the end of the Eighth Plan worked out to 10 : 2.9 : 1. It may be, however, noted that this ratio differs from area to area.

The consumption of fertilizers (NPK) during 1996-97 was 14.31 million tonnes. The total nutrient requirement in the terminal year of the Ninth Plan is projected at 20.0 million tonnes. During the Ninth Plan greater use of biofertilisers and bio-technological research in this direction will be encouraged. To support the programme for achievement of a target of 234 million tonnes of foodgrains, in the terminal year of the Ninth Plan, a very strong network of all associated activities would be required to be created in the country. This would include, inter-alia, the Integrated Plant Nutrient Management system, use of organic sources and bio-fertilisers, use of legumes by farmers for generating and sustaining the inherent nutrient potentiality of soils, followed by application of chemical fertilisers. Programmes of campaigning for making the farming community aware of micro-nutrient deficiencies and their use would be launched.

1.1.4.3. Some Important Fertiliser Units

As of February 2000, the installed capacity is around 11.07 mtpa of nitrogen and 3.6 mtpa of phosphate nutrients, making India the third largest fertilizer producer in the world. The country has 64 large size fertilizer plants besides 79 medium and small single superphosphate units. The country is self-sufficient to the extent of 92% in nitrogen nutrients. However, in the case of phosphates, the availability of domestic raw material is a major hurdle. Roughly 66% of the phosphatic fertilizer requirement is met through domestic production based on either indigenous/imported rock phosphate and imported sulphur or by imports of intermediates, viz., ammonia and phosphatic acid. Since indigenous rock phosphate supplies meet only 5-10% of total requirement there are usually imported. Chambal Fertilizers and Chemicals Limited (CFCL), has the capacity to manufacture 4500 tonnes of urea per day. The company is ideally located close to the fertile belt of Uttar Pradesh, Punjab and Haryana. Though urea is the mainstay of the company, it has diversified into many related/unrelated businesses such as trading in phosphatic fertilizers, manufacturing of potato seeds, software, housing finance and textiles.

Gujarat Narmada Valley Fertilizers Co Ltd

Urea, ANP and CAN are leading players as the prices boost the profit due to decontrolling by the Government. However the other organic chemicals manufactured are acetic, nitric acids and methanol.

Gujarat State Fertilizers and Chemicals Ltd

Gujarat State Fertilizer & Chemicals Limited, (GSFC) has varied business interests ranging from fertilizers to industrial chemicals to polymers and LPG bottling. Of the business mix DAP accounts for 52% of the revenue.

DAP was decontrolled in 1992, which resulted into immediate price hike thereby effecting volume off takes. The NPK ratio continues to be skewed in favor of urea however adhoc subsidies provided by government for phosphatic and complex fertilizers has eased the situation for DAP manufacturers. The DAP market is expected to grow at 12% yoy.

Caprolactam, a part of the petrochemical sector is subject to cyclical fluctuations. Initially GSFC reaped rich benefits due to increase in demand from the user industries. However excess capacities both in the domestic and international markets has effected business. Caprolactam is expected to grow at 4% yoy.

Executive summary

Indo Gulf Corporation Ltd, is one of the largest private sector fertilizer company. Urea was the mainstay of the company until its foray into copper. The company has the fertilizer unit at Jagdishpur in Uttar Pradesh. The unit comprises single stream 1350 mtpd ammonia and 2250 mtpd urea plant. The company's 0.1mtpa copper plant located at Dahej in Gujarat, commenced operations in March '99. For the first full year of operations (FY00) the smelter operated at 115% capacity. The company's DAP plant is expected to commence operations in September'00 and the Precious Metal refinery by mid April'00. The company's fertilizer business is expected to provide steady returns while the copper business is expected to perform well, backed on higher prices on the LME.

Domestic fertilizer industry earnings are regulated, with the Government controlling selling prices and providing subsidies to meet excess costs. In case of urea (the popular fertilizer), Government assures a 12% post tax ROE, based on 90% normative capacity utilisation. This allows companies to earn above normal returns by utilising more than 100%

capacity. In case of DAP and other complexes, which were freed from price control in 92, government provides adhoc subsidy. Subsidy is also extended to imported fertilizers. Future prospects of fertilizer companies are therefore closely dependent cumulative Average Growth Rate on Government policies.

Domestic fertilizer consumption is growing at a CAGR of 12% since last 25 years. Usage pattern of N:P:K is skewed to a ratio of 8.5 : 3.1 : 1 as against the ideal 4:2:1, due to the lopsided and half hearted government policies. The industry continues to face problems such as shortage of natural gas, the key raw materials and delays in receipt of subsidy payments.

Rashtriya Chemicals and Fertilizers Ltd

Rashtriya Chemicals & Fertilizers Ltd (RCF) is one of the largest fertilizer and chemical company in Asia. The company has its manufacturing facilities at Trombay and Thal respectively. These units produce Nitrogenous, Phosphatic and Potash Fertilizers along with wide range of Industrial Chemicals. The company has good marketing network spread all over the country, which is a prerequisite in a decontrol scenario. The company has earmarked about Rs. 25Bn towards expansion and modernization, for the next five years. The company is currently at the threshold of privatization. Of the equity base of Rs. 5.10Bn government holding is about 92%. The cabinet committee for disinvestment has decided to offload 51% stake to a strategic partner. The partner would be finalized via a bidding process carried out by a global advisor. RCF has depreciated plants and the cost of manufacturing urea is as low as Rs. 4600 per ton while the international prices are about Rs. 6500/ton. In a decontrolled scenario this would translate into profits of about Rs. 2000/ton.

Executive Summary

Zuari Industries Ltd. (ZUAR) is a K.K. Birla group company, engaged in manufacturing of fertilizers, pesticides and cement. The company has plans to hive off its cement division and concentrate on its core business. The cement division would have reduced ZUAR's exposure in the regulated fertiliser business. In fertilizer business, government controls the prices while in cement business prices an of demand-supply and since the company's plant is situated in a product deficit area (South), ZUARI could demand a premium.

Nagarjuna Fertilisers & Chemicals Ltd.

Nagarjuna Fertilizers & Chemicals Limited (NFCL), is the largest urea manufacturer in South parts (an installed capacity of 3000/mt per day). The plant operates at 135-140% capacity but the efficiency is not reflected on to the earnings because of government policies. The company also trades in DAP manufactured by Godavari Fertilizers, Coromandel Fertilizers etc. but in the long run NFCL proposes to be a complete Solution Provider to the agriculture industry. The company believes in enhancing farmer's productivity and to do so it provides a wide range of products from seeds to agro-chems to specially fertilizer and others. Further to widen its reach the company has decided to start a portal dedicated to agriculture.

The company has also ventured into the Oil sector. NFCL is the lead company in the 6mtpa refinery coming up at Cuddalore in Tamil Nadu. The company decided to enter into this field since growth in fertilizer business has nearly plateaued as it is impossible to increase capacity utilization beyond the current operating levels. The company foresees huge unmet demand for petro products especially in south.

The Department of Fertilizers in consulation with Ministry of Petroleum & Natural Gs has drawn up a concrete action plan for supply of gas to the fertilizer sector till the year 2011-12, considering the fact that the growing production of food grains :

Of the 37 urea units including existing, closed, green-field and brown-field expansion projects, as many as 13 urea units are already based on HBJ pipeline and have adequate supply of gas. For the other 9 gas based units, though the supply of gas is deficient, assurance from. Petroleum ministry for the adequate gas supply by 2008-09.

For the three FO/LSHS based plants of National Fertilizers Ltd in North India also the pipeline connectivity and availability of gas is expected by 2008-09.

For the 7 closed units of the public sector Hindustan Fertilizer Ltd and Fertilizer Corporation of India, connectivity and gas supply may be available by 2009-10.

For the unit of Fertilizer and Chemicals Travancore (Cochin) and Madras Fertiliers Ltd (Chennai), gas is likely to be available by 2008-09.

The problem seems to be with the Goa unit of Zuari Industries Ltd, the Tuticorin unit of SPIC and the Mangalore unit of Mangalore Chemicals and Fertilizers Ltd as there is no provision for gas supply. The installed capacity as on 2005 has reached a level 120.6 MMT of Nitrogen and urea capacity is 205 MMT while 56 MTPA phosphorus of India is the third bigges producer of fertilizers while GNFC is the World's largest urea producer. There are 57 large sized fertilisers while 29 are for urea remaining DAP, Phosphorus. There are small and medium size single super phosphate units.

1.1.5. Petro Chemical Industries and Products

Haldia petrochemical complex shall be the second biggest downstream industry in the country. The complex commenced production from April 2001.

Haldia Petrochemicals Ltd. is Rs. 5170 crores, with Rs. 1979 crores Equity and Rs. 3191 crores Debt. Production Started Aug 2001 Haldia Petrochemicals Ltd, a resurgence of industrial development is targeted in the region, around a range of downstream plastic processing industries which will be supported by ancillary and service industries.

Plant	*LSTK Contractor*	*Technology / Licensor*	*Capacity*
Naphtha Cracker Unit	Toyo, Japan	ABB Lummus, USA	420 KTPA
Butadiene Extraction Unit	Lurgi, Germany	BASF, Germany	74.5 KTPA
Pyrolysis Gasoline Hydro Unit	Lurgi, Germany	IFP, France	300 KTPA
Benzene Extraction Unit	Lurgi, Germany	Lurgi, Germany	75.5 KTPA
C4 Hydrogenation Unit (EPCM)	IDEA, India	IFP, France	110 KTPA
Polypropylene Plant	Daelim, S. Korea	Montell, Italy	210 KTPA
High Density Polyethylene Plant	Daelim, S. Korea	Mitsui, Japan	200 KTPA
Lin. Low Density Polyethylene Plant	Tecnimont, Italy	Montell, Italy	225 KTPA
Captive Power Plant (BOO)	Larsen & Toubro, India		116 MW
Nitrogen Plant (BOO)	Praxair, India		9,000 NM3

1.1.5.1. Gandhar Gas Cracker

IPCL's Gandhar Gas Cracker complex at Dahej will have large gas separation facilities. It can crack 3 lakh ton gas to produce 1.6 lakh ton of HDPE and one lakh ton of ethylene oxide/glycol, PVC and is expected to put on full stream by 2000. Thus the investment by IPCL alone accounts for more than 30,000 crores by the end of this century. The production achieved by IPCL alone is amounting to 9.65 lakh ton in 1997-98. The Gas Authority of India Ltd (GAIL) plant at Auriya is to produce ethylene of 9.3 lakh tons by cracking gas.

A recent study reveals that by 2000-2002 India will be surplus in polyolefins and the capacity of ethylene is shown below :

Reliance	1.6 MMTPA
IPCL	1.0 MMTPA
HPCL	0.43 MMTPA
GAIL	0.30 MMTPA
NOCIL	0.3 MMTPA
Others	0.31 MMTPA

In fact most of the South-East Asian countries due to financial crunch desperately sold the polymer stocks resulting in drop in the prices of polymers. Because of Reliance (Hazira) cracker plant of 7.5 lakh ton of ethylene, almost 50% increase in production of polymers and a fall of 30% imports was noticed. Indian polymer scene is better described by the Table 1.1(*f*).

Table 1.1 (*f*)

Polymer scene in 1997-98

	Production	*Imports*	*Exports*	*Consumption (Tons)*
LD/LLDPE	3,43,600	1,20,000	5,000	4,58,600
HDPE	3,63,000	1,35,000	8,700	4,89,300
PP	4,94,600	1,10,000	8,000	5,96,000
PVC	6,81,300	40,000	30,000	6,91,300
PS	1,20,700	20,000	12,000	1,28,700
ABS	27,500	5,000	—	32,500

Polypropylene demand and supply scene is given below :

Year	*1995-96*	*1996-97*	*1997-98*	*1998-99*	*1999-2000 (Thousand tons)*
Demand	320	415	510	620	750
Capacity	115	540	540	890	890
IPCL	115	190	190	190	190
Reliance	-	350	350	700	700

Besides IPCL and Reliance, NOCIL, Haldia, Square-D, and Krishna Chemicals have entered into polymer industry.

The global over-supply position in polymers, the consequent squeeze on margins for producers, the high debt burden of the Company and a difficult liquidity position are real issues, which are being addressed by the management. It is compounded due to economic recession.

High density (HDPE) polyethylene	80,000 tpa
Polyethylene glycol	50,000 tpa
Acrylonitrile	50,000 tpa
Butadiene	20,000 tpa
Styrene	30,000 tpa
Naphtha Cracker capacity	6,00,000 tpa

Additional products like : Vinylchloride/PVC/Propylene glycol will be also available.

Next important complex is being installed at Salempur (UP) to produce

Benzene	1,60,000 tpa
O-xylene	53,000 tpa
p-xylene	1,53,000 tpa
Alkyl benzene	17,000 tpa
Cyclohexane	90,000 tpa

Bongaigon Petrochemical Complex is the second complex under public sector industries occupying immediate place after IPCL. Separation of aromatics is the priority.

Xylene	35,000	tpa (O-xylene 10,550 tpa; p-xylene 23,700 tpa)
DMT	45,000	tpa ....
Polyester	30,000	tpa ....

Petrofoils Cooperative Ltd. (IPCL) was setup in 1974 under joint venture. It is to produce polyester yarn at Baroda - 7,000 tpa.

Hindustan Petroleum Corporation Ltd., Vizag (Former Caltex Refinery, after take over by the Govt. has joined the wing of Hindustan Petroleum Corporation Ltd.). The capacity of the refinery is raised to process 7.5 M^2 TA, this has given a fillip to go for petrochemical venture. And the products likely to be obtained are :

Acrylonitrile	6,000 tpa
Butyl rubber	25,000 tpa
Styrene	10,000 tpa
Linear Alkyl Benzene (LAB)	33,000 tpa
Vinyl acetate	10,000 tpa
Butadiene	18,000 tpa
Ethyl hexanol	30,000 tpa
Maleic acid	3,000 tpa

(Also supplies Naphtha to Fertiliser Plant at Kakinada)

Union Carbide. Union Carbide commissioned 60,000 tonnes naphtha cracker in early 1966, which heralded the birth of petrochemical industry in India. Beyond its activities as a petrochemical producer, it produces batteries, electrodes and agricultural chemicals. Its major products include 20,000 tpa LDPE, 10,890 tpa of benzene and carbon black.

Gujarat State Fertilisers Company. Setup in 1960 as the first joint sector complex in India. Besides, fertiliser plant at Baroda it produces caprolactum, Nylon-6, melamine.

Caprolactum	20,000 tpa
Nylon-6	4,000 tpa
Melamine	4,000 tpa
Polyester Staple fibre	45,000 tpa
MEG	40,000 at Patalganga
LAB	50,000 tpa
Poly olefins plant at Thane produces HDPE	70,000 tpa
Poly propylene (Reinforced)	4,000 tpa

Nagothane complex (Maharashtra Gas Cracking Complex)

LDPE	80,000 tpa
LLDPE and HDPE	1,35,000 tpa
Polypropylene	60,000 tpa
Ethylene glycol	50,000 tpa
Ethylene oxide	5,000 tpa
Acetylene black	1,740 tpa

Hindustan Organic Chemicals Ltd, Rasayani (Maharashtra) incorporated in 1960, comprises over 20 plants to manufacture several chemicals. Its extension plant at Cochin is producing Nonyl-phenol, Dodecyl phenol, Bis-phenol, Polycarbonates, Diphenyl methoane, iso cynates, phenol, acetone, propylene, PTFE.

Formaldehyde	30,000 tpa
H_2SO_4/Oleum	30,000 tpa
BHC	3,000 tpa
Chlorobenzene	4,400
Nitrobenzene	11,000
Nitro toluene	1,200
Nitro chlorobenzene	4,800
Aniline	6,000
Nitrophenols	1,350
Phenol	40,000
Acetone	24,640
Propylene	29,900

IOCL : Bombay incorporated in 1960

Acetic anhydride	600 tpa
Ethyl acetate	1,880 tpa
Ethyl acetoacetate	300 tpa

Butyl acetate	2,000
Amyl acetate	250
Propyl acetate	4,000
Ethyl chloride	1,000
Benzyl chloride	300
Plasticisers	10,000
Polyester fibres	6,100

ABS Plastics Ltd., 1973, Ahmedabad

Additives for PVC	3,250 tpa
Leather mix items	1,000 tpa
Polyester-polymeric type Plasticisers	3,250 tpa

Adarsh Chemicals and Fertilisers Ltd. (1957) Gujarat

Maleic Anhydride	3,000 tpa
Beirad Chemicals	
A B S Plastics	2,000 tpa

PVC Producers

IPCL (Baroda)	55,000 tpa
NOCIL (Bombay)	21,500 tpa
Chemplast (Mettur)	20,000 tpa
Shriram Chemicals (Kota)	26,400
Plastic Resin and Chemicals	12,000 tpa
C and P India Madras	16,000 tpa
Calico	6,000 tpa

Southern Hydrocarbons Ltd. 1977, Lakshmanapatti

Aldehydes, Acetic anhydride, H_2 and other petrochemicals

Thirumali Chemicals Ltd. 1972, Bombay : (Phthalic Anhydride, 6000 tpa)

Gujarat Petro Synthesis proposes to produce : Polybutene (Raw material will be supplied by IPCL)

Continental Chemicals Syntec Detergents UP and Haryana

FICOM-organics; Dodecyl phenol—2500 tpa.

Coming up petrochemical industrial and the productions are enlisted here.

J.K. Synthetics Ltd. (1993)

Nylon, Polyester	3,000 tpa
DMT	600 tpa
Methylene glycol	1000 tpa

Imperial Chemical Complex

PVC	52,000 tpa
Polyester	13,000 tpa
HDPE	28,000 tpa
LDPE	28,000 tpa
CA Moulding Powder	1,300 tpa
MF Moulding Powder	275 tpa

Indian Organic Chemicals Ltd. (Tamil Nadu) (with the assistance of MRC) : PTA; Polyester fibre 30,000 tpa. (MRL expansion to 5.6 M^2 ta has a FCC unit to handle 6 lakh tonne feed stock to produce cycle oils, LPG and petrochemicals include LAB 50,000 tpa and PP 17,000 tpa). Also, it incorporates an Aromatic extraction plant based on Bombay High Naphtha to produce

BTX	21,500 tpa
Butylene	25,000 tpa
i-Butylene	
-OXO alcohols	16,000 tpa

1.1.6.1. Synthetic Detergents

One of the important industries of modern society and industrial development, is the detergent industry. Tendency is to produce cheap and effective cleaning agents. Textile industry is the largest consumer; industries other than household, are leather, paper, food industries. During 2nd Five Year Plan the synthetic detergent industry started in our country. Major producers of synthetic detergents are :

Hindustan Levers	Bombay, Calcutta, Haldia (LAB)-	40,000 tpa
Tata Oils	Bombay	10,000 tps
Swastik Oils	Bombay	20,000 tpa
Godrej Soaps		20,000 tpa
Indo Burma Petroleum Co. Ltd., Bombay		
I.P.C.L. Detergent alkylate and about 20 units more		30,000 tpa

Non Soapy-Detergents (NSD) powder market has grown upto the tune of 1.7 million tons and is likely to reach 3 million tons by the end of 2000. Hindustan Levers Ltd. the pioneer in the synthetic detergents industry launched Surf, in 1959, followed by Rin and Wheel powder and Bars. Proctor and Gramble's Ariel and another competitive market item Nirma were introduced in Eighties. The industry by the turn of century will grow up to more than 4500 crore-rupees worth. Major innovations have taken place in detergent manufacturing—like enzyme incorporations to eliminate different stains and even tough dirt and oily residues. Further traditional spray drying technology has also been discarded and concentrate powders of these detergents have been significantly left their presence in the market.

1.1.6.2. Out Look of Olefins

Impact of olefins in the modern world is multifacet. Ethylene and propylene are well known and butene is another important olefin the use of which has not been upto the mark. Plastics and synthetics have carved special place on modern life and the effect is enormous and unparalleled, the day begins and ends with plastics. World wide share of polymer consumption (14 polymers) is shown below and the growth rate of polymers in developed countries is 3%.

N. America	26.6%
Asia Pacific	36.6%
West Europe	23.3%
East Europe	5.3%
Africa/ME	3.6%
S/Central America	4.7%

In 1977 World Ethylene supply was 79 million tons (US ethylene production 29 Million tons). By 2010 ethylene consumption will be 140 million tons demanding a capacity growth of 60 million ton. Asia Pacific and Africa are sighted to be fastest growing regions. Ethylene capacity in India in 1997 was 1.41 million tons which was excess by 4 lakh tons, however by 2005 it will be deficit by 1.2 million ton. Ethylene supply, production, consumption are always complex problems. Economic competitiveness is the main reason, for which mega mergers, improvement in design and effective methods of naphtha cracking are some complements or remedies to the industry. This is a big threat to the SSI and MSI industries, which are the main producers of commercial articles. Large distribution net works, focus on business management are the helpful criteria.

Polystyrene PVC, PET, are some prospering plastics. Even timely pioneering of one product is sufficient to establish the industry as seen in the case of GSFC for caprolactum. Propylene ranks next to ethylene and is being consumed in several ways, propylene consumption never dwindles but may be more expensive because of gasoline manufacturers, if win back from gasoline industry, it gives a considerable relief to petrochemical industry. This may not be true with India as the gasoline industry is irrelevant to propylene production. 46 million tons of propylene was consumed in 1998 through out the world. While US and E Europe are the largest markets, Asia market growth rate is highest. Perhaps manufacturers of propylene chemicals are guilty of building over capacity, as can be seen in 1999 itself about 16 producers added 3.2 million tons and the trend is not checked. Propylene growth rate is expected to be 5.3% while ethylene may be hovering around 4.8%. Because of FCCs in Refinery operations more availability of propylene leading to more investments in industry are justified Global production of plastics in 1998 was 128 million tons and is expected to touch 160 million ton in 2003. Some times unexpected down turns happen too. In 1977 ASEAN economic crisis lashing out, perhaps India remained unaffected, while PE capacity of 2.2 million tons has been delayed or cancelled. In our country demands of these two polymers are projected to increase in next three years as polyethylene 23%, Polypropylene 34% Butylene production has shot up because of institution of FCCs (presently 9) in refineries.

1.1.6.3. Out look of Fibers and Filaments

During a three year period of 1995-98 Global polyester demands grew by 44%, even then ASEAN crisis has not affected the production of TPA which grew at the rate of 6 to 8%. Polytrimethylene terephthalate a competitor for PET has not been introduced yet. 20 million tons of synthetic fiber produced round the world, against this India's performance is not bad. Synthetic fibers production in last two decades showed a big jump in production. In 1980-81 polyester was only 35 million kgs and nylon was 20 million kgs by 1997 polyester was 6.85 lakh tons and nylons touched 65,000 tons. Not much change in acrylic filament production was noticed (Max. 45,000 tons). Of late the commencement of Reliance would increase the production of PTA, DMT, Ethylene oxide by 40-50%.

The plastic industry is geared more to take up newer packaging materials which may require 52% of the plastics leaving 15% for consumer goods, perhaps rest shared by Automobile and Electrical industries. PVC is another strong competitor for PP and PE and has many advantages due to selective and versatile applications.

Further the new Millenium will witness a revolution in materials science.

Indian polymer industry was only 2.7 million ton in 1999. Ninth Plan demands of olefins are shown below :

Olefins Demand

	1998	*2001-02*
	(‘000 tons)	
Ethylene	2002	3419
Propylene	886	1581
Butadiene	140	246
Aromatics	1450	2366

Polypropylene demand in 1995-96 was 320,000 against a capacity of 115,000 tons which was entirely supplied by IPCL; by 2000 the demand will rise up to 750,000 tons while the capacity may be 890,000 tons of which 700,000 tons will be from Reliance itself. Reliance is the largest producer of PE 4,00,000 tpa, the tenth largest in the World, with production capabilities of one million ton polypropylene it is again the biggest in the World and also the highest producer of PTA (350,000) and p-xylene of 1.4 million tons etc. Polymers form 50% of the petrochemical industry while 40% is shared by fibers, the remaining goes for other uses.

Demands of Unsaturates (India)

(*in ’000 tons*)

	1999	*2001-02*
Ethylene	2000	3419
Propylene	888	1582
Butadiene	140	246
Aromatics	1450	2366
World Ethylene	79 mmt (1997)	110 mmt by 2003
USA Alone	30 mmt	World growth rate 4.8%
India	1.4 mmt	World Growth rate 23%
Propylene	46 mmt (1998)	55 mmta 2003
World growth rate %	5.3%	
India	0.32 mmt	Growth rate 34%
HDPE (World)	19 mmt	26 mmt (2003)
PET (World growth rate)	15%	India 30%
PP (India)	320,000 (95-96)	750,000 (99-00)
CAPACITY	115,000	890,000
IPCL	115,000	190,000
RELIANCE		700,000
PVC	693,000 (‘98)	

Synthetic Fibres ('97) (million kgs) (Filament Yarn)

Nylon	63
Polyester	395
(Staple Fibre)	
Polyester	270
Acrylic	55

Thermosettings : (Demand : Tons : 2000)

UF	28,000
PF	89,000
MELAMINE-F	2,700

Engineering Plastics

ABS	38,000
Polyamides	20,000
Polyacetals	4,500
Polycarbonates	15,000

1.2. Feed Stocks for Petrochemicals

Our petrochemical industry started much later than the oil industry; hence there was no coordination between these too. Lately integrated complexes have been installed and are becoming successful. Our country with meager resources in hydrocarbons has to utilize and conserve the hydrocarbons to a great extent. Thus implementing a petrochemical complex project virtually depends upon the feed stock availability and an assured supply for at least 20 years. The feed stocks for an integrated complex will thus be naturally different from an independent installation.

Generally the feed stocks are classified on the basis of the existing from *i.e.* solid, liquid and gas. These are :

1. Gases : Associated gas (obtained with crude oil), Lean gas (Gas stripped of the condensable; mostly methane), Refinery off gas (gases from crackers, cokers, stabilizers and other units) Natural gas, LPG etc.
2. Light Liquids : Natural gas liquids, Naphthas, wild gasolines, Kerosene, gas oils Reformates, coker fractions, FCC lights etc.
3. Heavy Liquids : Vacuum gas oils, fuel oils, waxy distillates, heavy crudes etc.
4. Solids : waxes, Deasphalter bottoms, bottoms of distillation columns and storage tanks, Residuum.

In fact there is no bar in using any hydrocarbon, however the economy, purification, availability of the raw material in abundance and technology for the particular fraction are the only impediments. It is traditional to use some fractions for certain intermediates or

Table 1.3. Approximate Composition of Different Gases

Component	*Natural gas*						*Process gas*		
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Hydrogen	-	-	-	-	0.2	0.1	6	1	0.5 to 1.0
Methane	80.3	71.4	19.26	78.44	16	1	6	4.1	9.3
Ethane	7.9	5.3	0.43	7.24	17	16.9	6	3.4	4.5
Ethylene	-	-	-	2.6	20.8	-	-	31.3	27
Propane	3	3.8	0.1	4.59	21.4	25.1	17	0.6	0.35
Propylene	-	-	-	-	9	17.4	-	13.1	16.4 + 0.64 + others
Butane (*i* & *n*)	1	1.8	0.05	1.95	20.5	10.2	33	-	0.14
Butenes	-	-	-	-	13.1	8.1	-	7	6.2 + 5.05 dienes
C5+	0.3	0.6	0.02 C6 = 0.01	0.5 C6 = 0.26	-	-	Balance C5+	Saturates 6	4.5
Nitrogen+ Oxygen	3.1	10.9	71.66 + 1.94	0.01	0.01	traces		Balance heavy liquids	C6 + 7.43 BTX 7.9
Carbon dioxide	4.4	6.1	6.14	6.49	0.1	0.2			Feed oil 9.7
H_2S+Mercaptans	1185 ppm	-	He 0.09-0.12	-	-	-	-	-	-

Legend:

1. South Basein gas
2. Cambay
3. Ghotaru (Rajasthan)
4. Bombay High
5. Thermal Cracker (under pressure)
6. Coker
7. Reformer
8. Naphtha
9. Hydrocracker gas

products, like naphtha for olefins or for synthesis gas or hydrogen. One can see the production of hydrogen through different processes using different feeds, however the available raw material has to be utilized for pecuniary gains and conservation of the petroleum stocks. When a raw material is used for producing a chemical, the purification of the stock is foremost important and the purification is devised on the state and condition of the feed stock. Each fraction or each destination requiring a special type of purification perhaps in addition to common purification procedures. The complications of purification and cost of purification usually increase with the molecular weight of the feed stock. Though a maximum purification is anticipated in gaseous feed stocks, the cost may not be that much compared to the purification of heavy stocks, because the gas, either field or process, can be easily purified.

Usually the field gases will be rich in saturates though the composition of each is different and the processed gases will be rich in unsaturates. Hence the purification procedure and the degree of purification varies from gas to gas. Table 1.3 shows the composition of different gases.

1.2.1. Purification of Gases

All the gases above listed are used as feed stocks for petrochemicals. However, if facilities for petrochemical industries are not available, then the gases of high heating value are diverted to industrial heating systems or to domestic necessities. All the gases, irrespective of origin, contain some unwanted extraneous constituents named impurities. Most common of the impurities are listed below :

1. Water vapour
2. Mechanical (suspended) impurities
3. Chemical impurities
4. Other than above mentioned impurities

1.2.1.1. Exploration and Development of Gas and Oil Fields

Most of the Country's NG comes from Western Off-Shore area. South Basein gas fields Tapati and onland gas fields in Tripura, Rajasthan, Gujarat are famous. Presently KG Basin has major significance. Next to Bombay High this basin is the leading producer of oil and gas. The ONGC & the OIL have together planned to add 865 million tonnes of oil equivalent in-place hydrocarbon reserves during Ninth Plan. These efforts will be supplemented by addition of some reserves in the exploration blocks awarded to the private parties. An accretion of up to 200 million tonnes oil and oil equivalent of gas (O+OEG) is envisaged in deep water areas where a breakthrough is expected in the Ninth Plan. The estimated recoverable reserves will be in the range of 245.84 to 342.72 million tonnes of oil equivalent. The cumulative oil and gas production during the Ninth Plan is projected at 335.16 million tonnes of oil equivalent (Oil production is about 180.8MMT) It may be mentioned that considering the reserve accretion and the production of oil and gas during the Ninth Plan, the Reserve Replacement Ratio (RRR) will be in the range of 0.73 to 1.0. All efforts would be made to bring the RRR above the unity level. Although a New Exploration Licensing Policy (NELP) has already been formulated, certain fiscal and financial incentives would be required under this Policy to attract investment for exploration. Exploratory activity should be given infrastructure status to attract necessary investments from both public and private sector companies. According to The Petroleum Ministry projection oil production during the XIth Plan Period (2007/8-11/12) is about 207.756MMT, of which ONGC would be responsible for 141.06MMT OIL will produce 18.99MMT others would produce the balance. Similarly NG production will be stepped upto 229 BCM 45% higher than the XI th Plan achievment of 159BCM. Similar is the case with LPG with the current consumption rate of 11MMTPA by the end of XI th Plan 17 MMTPA will be required to meet the domestic and transport sector needs.

OIL AND GAS PRODUCTION (Ninth Plan)

Oragnisations	97-98	98-99	99-00	00-01	01-02	05-06	Total
OIL PRODUCTION (Million Tonnes)							
(*i*) ONGC	27.73	28.09	29.18	29.87	30.02		144.89
(*ii*) OIL	3.10	3.20	3.29	3.38	3.50		16.47
(*iii*) JVC PRODN.	3.59	4.40	4.08	3.93	3.46		19.46
TOTAL	34.42	4.40	4.08	3.93	3.46		180.82

GAS PRODUCTION (MMSCMD)							BCM
(*i*) ONGC	62.75	63.81	65.49	65.29	69.04	51.0	119.04
(*ii*) OIL	5.60	6.33	7.19	7.81	8.28	4.0	12.86
(*iii*) JVC PROD.	6.73	7.26	6.98	6.82	6.79	20.0	12.63
TOTAL	75.08	77.40	79.66	79.92	84.11	95.0 @	144.53

MMSCMD: Million Metric Standard Cubic Metre per Day @ inclusive of 20 LNG
BCM: Billion Cubic Metre

Refining Capacity Addition During 9th Plan (Million Tonnes)

Refineries	97-98	98-99	99-00	00-01	01-02	04-06
Capacity as on 1. 4.97	61.55	61.55	61.55	61.55	61.55	61.55
1. Gujarat, IOC	—	—	—	3.00	3.00	13.70
2. Panipat, IOC	0.00	6.00	6.00	6.00	6.00	6.0
3. Haldia						6.0
4. Barauni						3.3
5. Guwahati						1.0
6. Mathura						8.0
7. Digboi						0.65
8. Numaligarh, NRL			3.00	3.00	3.00	3.0
9. Visakh, HPCL	—		3.00	3.00	3.00	7.5 (8.4)
10. Mumbai						5.5 (7.9)
11. Bina, BPC						9.0 (15)
10. BPCL, Mumbai						6.90
11. Bina, BPC	—	—				6.00
12. MRPL Expn			6.00	6.00	6.00	9.50
13. Kochi						7.5
13. Bongaigon						2.35
14. ESSAR, Pvt				9.00	9.00	9.00
15. Reliance				15.00		22.00
16. Paradip						15.00
17. Ennore Petrochemical Complex, CPCL+IOC						15.00
18. Bhatinda IOC						15.00
19. ONGC TAIPAKA						3000BPSD
20. Bina						3.0
Sub-total: Cap.Addition	0.00	6.00	43-40	46-40		66-69
Total	61.55	67.55	104.95	107.95		>137MMTPA*

*By the end of 10th Plan

Eighth Plan To 2005 Petroleum Products-consumption

Component	97-98	98-99	99-2K	00-01	01-02	04-05
(*i*) Light Distillate	16.87	18.25	19.62	21.03	22.15	36.83
(*ii*) Middle Distillate	50.45	53.43	56.62	60.24	64.38	60.96
(*iii*) Heavy Ends	16.41	16.88	17.43	17.80	18.27	15.51
Total	83.63	88.56	93.67	99.07	104.80	127.00*

*inclusive of boiler fuels

Draft Report of the Working Group on Petroleum and Natural Gas for the XIth Five Year Plan (2007-08) is to be believed; India will transform into a gas surplus country by the year 2011-12. A supply of 40 MMSCMD of gas from the KG Basin (Reliance Industries Ltd (RIL)) and 54 MMSCMD from GSPC's discovery, in the KG Basin will be the first stage. The other scenario takes into account the unlikely possibility of no gas supplies at all from the two KG Basin blocks. Under scenario-I, the domestic gas supply position goes up from 80.54 MMSCMD in 2007-08 to only 108.30 MMSCMD in 2011-12 whereas under the other scenario, the supply touches 202.30 MMSCMD. In this period the imported LNG supply to move up from 30.45 MMSCMD to 83.12 MMSCMD. Thus, the total supply under the two scenarios could be either 285.42 MMSCMD or 191.42 MMSCMD. Also the report has projected total countrywide gas demand at 178.97 MMSCMD in 2007-08 and at 282.55 MMSCMD in 2011-12. So under the scenario where gas is available from the KG basin, the country will have a surplus of 2.87 MMSCMD of gas whereas under the worse case scenario, the deficit will be 91.13 MMSCMD. If the demand projections are right, India may actually end up with a larger surplus than has been projected under one of the scenarios by the Working Group. RIL is planning to produce not 40 MMSCMD, but 80 MMSCMD of gas from its D-6 discovery within the XIth Five-Year Plan. In fact, the company is informally talking of taking output up to as much as 110 MMSCMD. Similarly, the GSPC's find in the KG Basin is likely to be equally big and gas output could swell well above the 50 MMSCMD. If gas output from the KG Basin goes up, there may, in fact, be no requirement for additional imports of LNG beyond what is brought in by 2007-08 or gas through transnational pipelines.

Total hydrocarbon resources, inclusive of deep waters, are estimated at around 28 billion tonnes oil and oil-equivalent of gas (O+OEG). As on 01.04.2004. initial in-place oil of 7.89 billion tonnes and ultimate reserves of 2.94 billion tonnes have been established. The resources estimated by DGH for its 'internal use'. for the country, are 32 billion tonnes (O+OEG). India's sedimentary area (up to economic zone 200 miles) is 3.14 million square kilometers, of which 0.42 million sq.km area is offshore area, spread over 6000 km coastal line and 0.4 million sq.km area is available in the form of continental slope, while the remaining area is land based. India's offshore basins are divided into 8 regions out of total 26 basins, as shown in Fig. 1.1.b. The hydrocarbon potentiality of the entire region is 23 billion tons. The biggest offshore activity started with discovery of Bombay High in 1973. Oil and oil equivalent (OEG) gas available in the country as per survey's of April 2004 is 1650 MMT. According to estimates the reserves of gas are 763 billion cu. Meters while the production has not gone up beyond 90 MMSCD. While the demand goes well over the production schedule.

1.2.1.2. Some Projects Under Implimentation

Petronet LNG Limited company was incorporated in April, 1998 and is setting up LNG Terminals at Dahej (5 MMTPA) and at Kochi (2.5 MMTPA), have recently signed the sale purchase agreement for LNG supplies with M/S Rasgas-Mobil of Qatar and work on setting up of the terminals is progressing.

Kandla-Loni LPG Pipeline

GAIL is in the process of laying a 1246 km LPG pipeline network from the Western region (Kandla, Jamnagar in Gujarat) to the Northern Region (Loni in U.P. via Delhi) at an estimated capital cost of Rs. 1229.45 crores including a foreign exchange component of Rs. 386.73 crores. The line pipe diameter ranges between 8" and 16". LPG will be collected at the import location at Kandla and Jamnagar (refineries of M/s. Reliance and M/s. ESSAR). The initial capacity of the pipeline system would be 1.7 MMTPA. The capacity of the pipeline will be increased to 2.5

MMTPA by augmenting the pumping capacities to match the LPG demand in the Northern Region.

Gas Processing Complex at Gandhar

GAIL is setting up an LPG plant at Gandhar in Gujarat. The plant shall process 5 MMSCMD feed gas will have a capacity of producing 207 TMT of LPG.

1.2.2.1. Water Vapour

This is exceptionally present in all the fractions. Gases from atmospheric column or other refinery units, condensate gases and natural gas do have variable amounts of water vapour. This can be removed by passing through drying agents like silica gel, bauxite, dehydrated salts or even by absorbing with glycols. It is observed that some hydrocarbons have the capacity to form crystalline hydrates, such examples are CH_4 $7H_2O$, C_2H_6 $7H_2O$, etc. These gases exhibit the crystalline forms even above the freezing point of water. These hydrates not only clogg the delivery lines but facilitate other abnormalities like corrosion, malign catalyst, cause hydrolysis in chemical reactions.

In modern literature, hundreds of dehydrating agents are mentioned, of late, the tendency of using polyhydric alcohols[9] or glycols has been on increase.

Liquid absorbents are not as efficient as solid desiccants for absorbing water vapour. Ethylene glycol is a conventional absorbent used to remove the moisture from gasoline as well as gases. However, the amount of glycol required for circulation is very high, *i.e.* 20-40 times of water vapour removed. Usually 35-40°C drop in dew point is obtained with glycols.

Addition of toluene to glycol helps in reducing the water content to less than 1000 ppm and is used in DRIZO process[10]. Solid desiccants, synthetic gels, calcium chloride can decrease the dew point even by 80°C. Presently, molecular seives of type 4A, 5A have shown a commendable performance. They can lower the dew point even by 100°C. These sieves are vastly used in N.G. and air liquefaction plants.

Obviously drying by means of solid adsorbents is more economical and simple. When bentonite clays are used as adsorbents, regeneration may not be attempted. But, when synthetic adsorbents are used the regeneration is done simply by heating the bed to 200ºC to 300°C. The moisture capacity of the clays is usually small-of the order 2.5 to 4%, while that of synthetic alumina gels is 5 to 8%. Similarly, synthetic alumina gels voraciously adsorb moisture up to 22%, when they are fresh, but due to fatigue in long duration of operation the capacity drops to 10%. Each adsorbent has got its own moisture removal capacity and regeneration temperature. The best dehydrating agent, of course, is lithium chloride, but its use is curtailed due to its cost.

1.2.2. Mechanical (Suspended) Impurities

The sources for mechanical impurities are many. Mining operations invariably bring clay, dust etc. Catalytic cracker gases are abound in catalyst dust. Process gases like coker, cracker gases, if not contain any solid particles, likely to bring condensed droplets of tars. Relatively, Atmospheric Distillation Unit (ADU) and stabiliser gases are free from such impurities. Usually all types of mechanical impurities can be removed by washing with water. Suitable solvent is preferred if tar and heavy hydrocarbon oils are present, sometimes, the removal of suspended particles is resorted to by simple settling but it does consume a good deal of time. When a solvent wash is decided to eliminate chemical impurities naturally water washing may be skipped off. The washed solvent is filtered before recycling, this will ensure the continuous removal of suspended impurities too.

1.2.3. Chemical Impurities

Sulphur and its compounds are the foremost of the chemical impurities. Sulphur can exist right in gaseous form to liquid form. The elimination of sulphurous compounds will not only reduce the corrosion problem but indirectly helps quality of fractions too. Such cases are plenty; sulphur free gasoline requires less lead to boost the octane number. Further sulphur defies the activity of catalyst. In some reactions sulphur is very detrimental too.

Sulphur exists in the form of hydrogen sulfide, mercaptans, thiophanes, thiophenes, sulphides, polysulphides etc. These impurities are present in all the gaseous fractions and light petroleum fractions (full range naphtha). Sulphides, polysulphides are present in high boiling stocks. Even natural gas that forms the feed for ammonia has to be desulphurised. This is carried out using activated carbon fortified by zinc oxide and other metallic[11] additives. At a temperature of 400°C, these catalyst preparations are good for removal of H_2S, mercaptans and small percentage of COS.

Cat cracker or coker gases invariably contain carbon dioxide to a small amount, *i.e.* 1000 ppm. Other impurities like ammonia, oxides of nitrogen mark their presence to an extent of a few ppm.

Many processes are listed for the selective removal of these impurities. The most famous process of all these is ethanolamine[12] (Girbotol). This employs a 20 to 30% aqueous solution of ethanol amine (mono, di, tri). Ethanol amines being basic can absorb all the acidic gases freely as per the reactions cited :

$$(CH_2\,CH_2\,OH)\,NH_2 + H_2S \rightarrow (NH_3\,CH_2\,CH_2\,OH)_2\,S$$

$$\rightarrow (NH_3\,CH_2\,CH_2\,OH)HS$$

$$(CH_2\,CH_2\,OH)\,NH_2 + H_2O + CO_2 \rightarrow (NH_3\,CH_2\,CH_2\,OH)_2\,CO_3$$

$$\rightarrow (NH_3\,CH_2\,CH_2\,OH)\,H\,CO_3$$

All the absorption reactions are favoured by low temperatures (25 – 30°C), while temperatures above 100°C favour the desorption reactions.

Other solvents based on amine compositions are diglycol amine (DGA), disopropylamine (DIPA), methyl diethanol amine (MDEA). Some new solvents[13] are credited with taking very heavy loads *i.e.*, about 2 to 3 cubic meters of gas can be absorbed per equal amount of circulation (mole to mole). Further sulphur (mercaptan) removal is upto 55% (C_1-fractions).

The recent innovations suggest methyl diethanol[14] amine (MDEA) is a better solvent when high concentration of CO_2 is present in the feed gas. When concentration of acid gases exceeds 0.45 Mol/Mol amine solution; MEA, DEA, TEA are not suitable. The first plant in the world Dome's North Caroline Amine[15] Plant has been converted to MDEA solvent system and is found to operate convincingly at a higher efficiency.

In fact, there are many processes which are currently under operation to scrubb the off gases, a gist of which is presented in Table 1.4. When a high amount of carbondioxide (65%) and fairly a good amount of H_2S are present, the mixture can be handled by Selexol process which uses dimethyl ether of propylene glycol[2].

All the gas treating processes may be classified into three classes depending upon the operational pressure.

(*a*) Low pressure operation (Below 10 bars) Girbotol, Economiser, Flex sorb-PS, Thiolex, Selexol, Sulferex, Sulfolin.

(*b*) Medium pressure (upto 100 bars). MDEA, Adip Benfield, Catacarb, Flexsorb-HP, Giammarco-Vetrocoke, Stretford, Sulfinol.

(*c*) High pressure (above 100 bars) Rectisol, Selexol, Benfield.

When sulfur removal alone is to be judged, Amine/Claus process is economical for large installations, because of the capital-intensive nature. Such installations are good for recovering more than 25 tpd of sulfur. Locate iron-redox process is suitable for recovering less than 1 tpd of sulfur, however operating costs are much. Sulferox of DOW, employs improved iron chealates, that can work under higher concentrations without much dilution thus decreasing operating and equipment cost. Bender Sweetening is generally useful for NGLs, gasolines, however LPG can also be processed. These plants are considered to be cheap as the mercaptans are converted to disulfides only.

Beavon sulfur recovery (BSR) MDEA process is a purification process for the tail gas from different units. The process works in two steps, initially all sulfur is converted to H_2S by hydrogenation. In second stage H_2 S is absorbed by amine. Merox process is another new one; it can treat gases, LPG, light naphtha and kerosenes. This extracts mercaptans from gases and low volatiles, while heavy stocks respond to oxidising mercaptans to disulfides.

ADIP Process uses Di isopropanol amine or teritiary amine, methyl diethynol amine in 50% aqueous solution and is capable of handling gases of 100 ppm sulfur 10 ppm sulfur in liquids COS is generally oxidised. Similarly Thiolex employing caustic solution extracts Hydrogen sulfide, carbon dioxide and mercaptans. Beavon-others process is peculiar in one respect it alters the composition of Claus tail gas and by first catalytic oxidation of all sulfur compounds over a CuO bed and then hydrogenated to convert the gases into H_2S or NH_3. MDEA extracts sulfur compounds to separate clean gas from acid gas stream and Seleoxl separates clean gas from elemental sulfur[30].

Modop is a process for removal of sulfur from tail gas to meet the pollution regulations. Tail gas is first heated with fresh air and fuel to oxidise all the components of sulfur and then hydrogenated to yield H_2S which is later selectively oxidised to sulfur. Shell Claus off-gas treating (Scot) process also works on the same principle. Selexol is another process for recovering sulfur from H_2S streams, while sulferex is suitable for removing SO_2 from off gases. Stretford process is suitable for operation on H_2S gas streams.

The operation is simple and illustrated in Fig 1.2*a*. Mixture of gases enters at the bottom of absorber, through a gas distributor. The gas goes into the absorber and mixes freely with the down coming liquid, and the purified gas leaves the absorber at the top. The fat liquid is filtered and desorbed in a similar column by steam heating. When DEA solutions are used for gas treating plants filters are required to remove fine particles, which are trapped during contact with liquid. This is to remove foams and inimical deposits. This is however absent with MEA[16] solution. Absorbed CO_2, H_2S are liberated by steam stripping as shown in the figure. The solution is then made to the required concentration and cooled; after which it is fed into the absorber from the top. The absorption, desorption temperatures are kept around 25°C, 110°C respectively. To facilitate easy absorption, the absorber is superimposed with a pressure of 0.5 to 1.0 MPa. It may be thus mentioned the merits of a process is more or less connected with the amount of impurities and nature of these[17]. Beavon-otter process is shown in Fig. 1.2 (*b*). The selector X separates sulfur from gas.

Membrane separators[18] along with amine treatment have been tried for efficient and economic operations. Sulphur removal[19] by adsorption or solvent absorption is followed in the same operations where CO_2 or H_2S romoval is effected. Molecular sieves are also employed to desulphurise certain stocks, specially gases. In most of the cases, solvents are regenerated by expelling the absorbed gases. Except in certain cases, (the regeneration is done by air-blowing (Merox)) when solutions are employed for removing impurities, the gases are again dried.

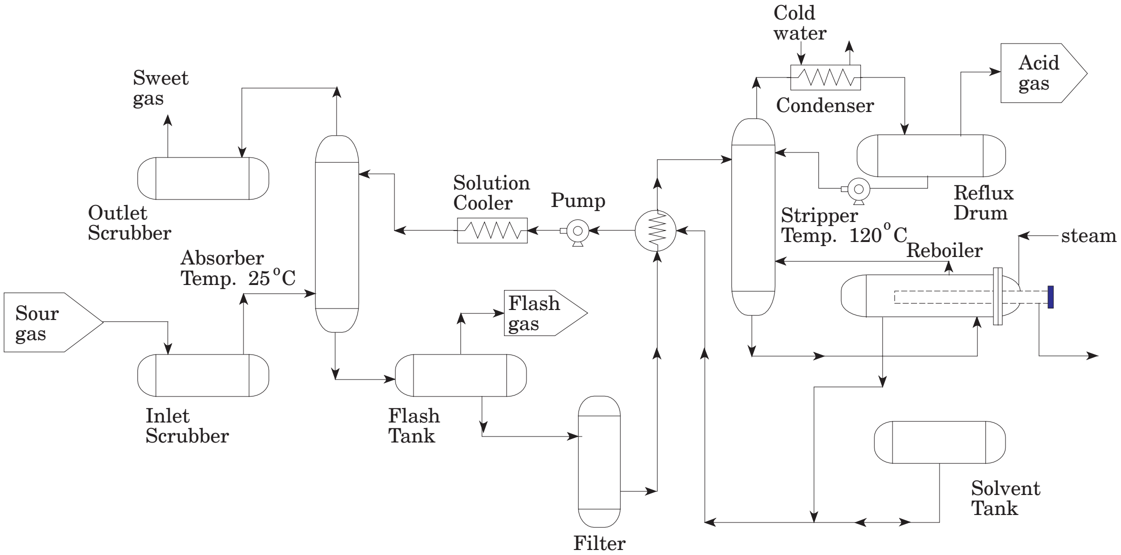


Fig.1.2. (*a*) Process Flow for Typical Ethanolamine Sweetening Unit.

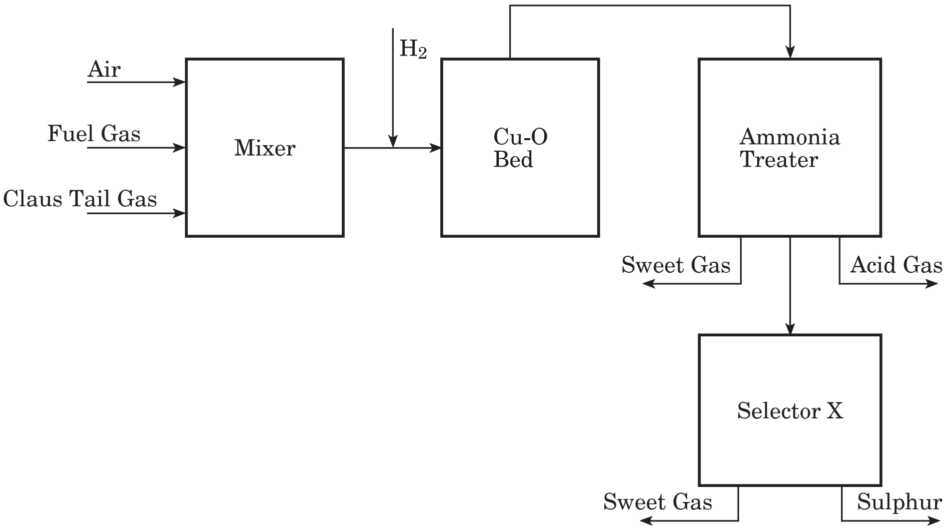


Fig. 1.2 (*b*) Beavon-otter process.

1.3.1. Separation of Gases into Individual Constituents

Gases ranging from $C_1 - C_4$ are freely available either in cracked, ADU, or stabiliser streams. Further, permanent gases like air, N_2, CO, CO_2, and H_2 are also present in varying extents. The separation of the gases into individual constituents is a costly process, but has to be.

Industrially the separation techniques consist of

1. Absorption-Desorption
2. Compression-Liquefaction
3. Low-temperature fractionation
4. Adsorption
5. Special techniques.

Table 1.4. Survey of Different Processes for Treatment

Sl. No.	*Name of the process*	*Chemicals involved*	*Constituents removed*	*Operating conditions*	*Regeneration*
1.	Girbotol	Ethanol amines Mono-di	H_2S, CO_2 from natural, cracked gases	Reaction temp. 25°C 20% concentration	Backward reaction 105°C
2.	Shell solutiser	Tripotassium phosphate	H_2S, from NG	35°C	105-110°C air blowing
3.	Alkazid BASF	Sodium, potassium salts of diethyl/methyl amino propionic acids/amino acetic acids	H_2S,CO_2 from NG, liquid hydro carbons	Ordinary conditions	
4.	Benfield Corporation	Hot potassium carbonates containing Benefield reagents	CO_2, H_2S, COS NG, synthesis gas	High pressures, above 3kg /cm^2. Any convenient temperature	
5.	Cat Carb	Potassium salts	CO_2 (NG, H_2, NH_3 or sour gases)	T:100 – 130°C, 20-40 bars	Steam heating
6.	Adip	Diproponal amine	COS, H_2S, CO_2 mercaptans, acid gases (NG, SG, refinery gas)	Wide flexibility in operation conditions	P:20-25 kg/cm^2 , T:35°C – 38°C
7.	Unisol Atlantic	Methanol + KOH	CO_2		
8.	Mercapsol	Cresols + Naphthenic acids	Mercaptans (gases & gasoline)		
9.	Tannin solutizer	Organic salts + Potassium phosphates	H_2S, CO_2 gas		
10.	Vetrocoke	Sodium potassium arsenite sol. (K_3 As_2 O_3)	CO_2, NG, RG		
11.	Battersea	Aromatic amines (alkyl salts)	SO_2 (gas)		
12.	Flour Econamine	Aqueous sol. of primary alkyl amine/ diglycolamine (HO–C_2 H_4 O–C_2 H_4 – NH_2)	H_2S, CO_2 (NG, SG, RG)	Sol. 40-60% P : upto 80 kg/cm^2	Steam strippings P : 80 kg/cm^2 T : 180°C
13.	Purisol	N-methyl pyrriolidone	H_2S/acidic constituent (Gas)	Pressure 80 kg/cm^2 T 30°C	
14.	Rectisol	Methanol + KOH	CO_2, H_2,,S, NH_3, COS, HCN gum formers (gas)	35 kg/cm^2	
15.	Selexol	Dimethyl ether of polyethylene glycol	SO_2, CO_2 (NG, SG)		
16.	Sulfinol (Shell)	Sulfolane, alkanol amino and water	H_2S, COS, CO_2 Mercaptans (NG, SG, and LNG)	80 kg/cm	

(*Table Contd...*)

Sl. No.	*Name of the process*	*Chemicals involved*	*Constituents removed*	*Operating conditions*	*Regeneration*
17.	Flour solvent	Anhydrous organic compounds propylene carbonate (Diglycolamine)	O_2 and H_2S from NG, SG	30-40% sol. P : upto 80 kg/cm^2	Steam stripping at 180°C and 80 kg/cm^2
18.	SNPA-DEA	Diethanol amine (modified)	$H_2S + CO_2$ (NG)	P : 50-75 kg/cm^2 T : Low (30°C)	
19.	Takahax	Alkaline sol. (PH 8.5) Sodium 1, 4 naphtoquinone 2 sulfonate as redox catalyst	(NG and SG)		

1.3.1.1. Absorption-Desorption

The gases are selectively absorbed in suitable solvents and then desorbed. The absorption is usually a physical process, however it may be even chemical absorption. The removal of SO_2, CO_2, NO, etc. is basically by chemical absorption. Hydrocarbon gases are mostly separated by physical absorption; propane, butane are highly soluble in light hydrocarbon oils, permitting the recovery up to 70-80%, with a purity approaching 100%. Some gases like acetylene may be absorbed by solvents like dimethyl formamide. Even aromatics can be separated by using tetra ethylene glycol.

Almost all olefins and diolefins can be separated by selecting a suitable solvent. Ethylene, propylene, butene, butadiene may be separated by a mono ethanol diamine solution of cuprous nitrate/chloride, due to varied solubilities (shown in Table 1.5) under different pressures. The ethanolamine and metal salt mixtures can absorb CO and acetylene in addition to olefins. Absorption is done at low temperature, while desorption is carried out at 50°C. Silver fluoroborate is found to be better than amine, as it is not affected by the presence of acetylene-carbon monoxide mixtures. $AgBF_4 \cdot 2C_2H_4$ is formed during absorption which easily decomposes.

Table 1.5. Solubilities of Some Unsaturated Hydrocarbons in Monethanolamine-CuCl at 20°C

Hydrocarbon	*Pressure (atm.)*			
	1	5	10	20
Ethylene	8.4	15.8	21.2	24.2
Propylene	1.1	4.3	6.1	—
n-Butene	1.0	—	—	—
Butadiene	10	—	—	—

Thus choosing best operating conditions any single constituent can be separated. Similarly iso-butene from butane mixture may be separated by 65% sulphuric acid at 35°C by absorption, where other olefins do not react with the acid at that condition. Further, where the boiling points of many components are close, fractionation fails hence alternative routes are sought. Sometimes azeotropic or extractive distillation may be useful. Butenes are separated conveniently from *n*-butane by using extractive distillation; the added component being furfural. By addition of a solvent the relative volatility of one component can be shifted; as an illustration

1-Butene and *n*-butane have relative volatilities 1.046 and 0.871 respectively; in presence of furfural the volatilities shift to 1.718 and 2.02. Paraffins and olefins of C_4 fraction can be separated by simple distillation because of the closeness of boiling points. It is observed relative volatility of saturated hydrocarbons increases more than that of unsaturates in presence of furfural as given below :

	B.P. °C	*Relative Volatility*	*Relative volatility in presence of furfural*
i Butane	– 11.7	1.209	2.6
n-Butane	– 0.6	0.871	2.02
1-Butene	– 6.3	1.05	1.72
iso-Butene	– 6.9	1.07	1.70
Cis-Butene	– 3.5	0.77	1.06
Trans-2-Butene	– 0.9	0.84	1.19
Butadiene	– 4.5	1.00	1.00

Infact the separation of butanes follow a serial order. Firstly, *i*-butane is removed from mixed C_4 fraction. Later, distillation is recalled to separate *i*-Butane (BP-11.7°C) from *i*-butene (BP-6.3˚C) as overhead product leaving bottom product as a mixture of *n*-Butane (BP-0.6°C) and 2-butene (0.9°C). Both the overhead and bottom products are distilled with third component, furfural, in separate columns. The relative volatility of paraffin increases in presence of furfural, thus aiding the separation. Fig. 1.3 shows such a distillation with furfural as solvent.

Aqueous acetone solutions are also useful in extractive distillation (20% Water + 80% Acetone). Acetone-water mixture is convincingly used to separate butane and butene streams into individual components. Absorption with extractive reflux has been successfully used to split ethane and propane[20] streams. The most useful diene of C_4 fraction is butadiene, and is removed from other olefins by chemical absorption method or using extractive distillation.

Butadiene is separated from C_4 streams by absorbing in a solution of copper ammonium acetate, containing about 17 to 18% of copper. Two or three columns are required for complete absorption of butadiene from butene fractions. These columns operate at less than room temperature (0°C). Iso-butene is easily removed from C_4-fraction by extractive distillation. Butene-butadiene fraction is absorbed in series of absorbers. The solution is heated to remove butadiene vapours, unabsorbed butenes-leave from the absorber top, while regenerated

Legend
1. First fractionator
2,4. Extractive distillation
3,5 Stripping columns
6. *i*-Butane, 1-Butene
7. *n*-Butance, 2-Butene
8. *i*-Butane
9. *i*-Butene
10. *n*-Butane
11. *i*-Butane

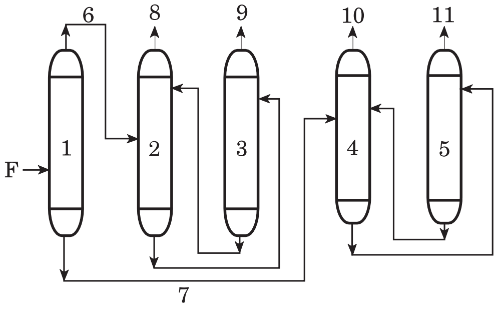


Fig. 1.3. Separation of C_4 Components by Extractive Distillations.

butadiene escapes from the stripper. Perhaps, further purification of butadiene is required. Isoprene is also similarly separated by using acetone solution.

1.3.1.2. Compression and Liquefaction

This technique is suitable specially if a mixture contains a component, which when compressed and cooled liqefies easily, keeping the remaining components unaffected. Gas when compressed at bubble point condenses, of course, if the bubble point is high, say greater than 30°C, it can be easily liquefied by cooling. Depending upon the concentration of the component in the mixture, simple cooling or application of pressure or both have to be resorted to. The dew point of the component is given the maximum credit. This process is mostly used in combination with other operations. Sometimes, casing head gases are compressed and extracted with gas oil fractions to remove the light gasoline fraction, which again reflects the application of the process.

1.3.1.3. Low Temperature Fractionation

In this operation whole mixture is cooled and liquefied. This liquefied mixture (liquid) is subjected to distillation at low temperature. The production of low temperature can be done by external cooling agencies or by self expansion against resistance or no resistance. The effectiveness of this technique has resulted in cheap production of polymer grade olefins. Different feed stocks ranging from ADU, casing head to cracker gases can be liquefied. Separation of a gas containing C_1 to C_3 components is discussed here.

The dried gas when cooled to 55 to 60°C under a pressure of 35 atmospheres, ethane-ethylene fraction condenses, while methane, nitrogen, hydrogen and carbon-monoxide remain as gases. Hence it is desirable to operate the column more specifically, reflux drum under those conditions. After the non-condensable gases are removed, the liquid fraction containing ethane-ethylene can be distilled separately in a coulmn that contains 60 plates and operates at 20 kg/cm^2 pressure. The reflux is maintained around – 30°C. This way ethylene is separated out as distillate and ethane as residual product. So far, the above mixture has been dealt assuming up to C_2 fraction is available. In case C_3 fraction is also available, this is first liquefied by using a separate column operating at – 10°C under 25 kg/cm^2 pressure. Usually a 35 plate column in desired to separate C_3 fraction from all the more volatile fractions upto C_2.

After collecting the C_3 fraction in liquid state, a separate column of the same order is pressed into service for separation of propylene from propane. From this, it is clear that the increasing pressure naturally elevates the operating temperature or *vice versa*. Modern method of producing liquefied petroleum gas is by turbo expansion technology. Such technique has been in operation in India at Duliajan for the production of LPG. The plant produces 60,000 tonnes LPG from the natural gas liquefaction. LPG being higher boiling component can be liquefied first and taken out before liquefying methane.

Turbo expansion(12) technology differs from Joule—Thompson expansion in one respect only. In Joule–Thompson expansion, there is no external work done, whereas in Turbo-expansion, the gas is allowed to do some work *i.e.* driving turbines for compression, while it suffers cooling(19).

The feed gas is first compressed up to 20 MPa in stages and allowed to expand in turbines, as a result, temperature goes as low as – 100°C. Turbo expansion technology or Joule-Thompson expansion effect is invincible where natural refrigerants (may be useful up to –40°C) fail. A more sound method called cascade cooling is economically employed to substan-

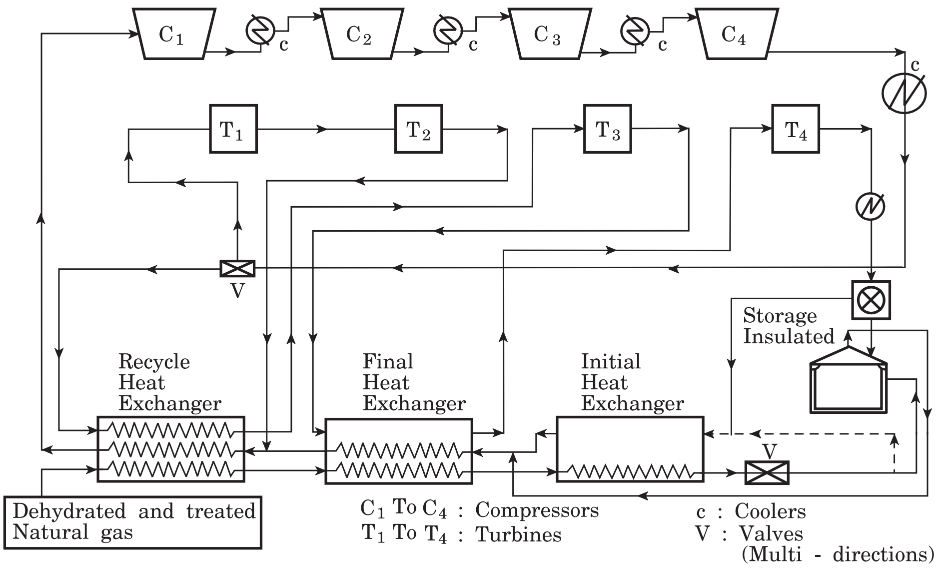


Fig. 1.4. Natural Gas Liquefaction.

tiate the simple principle of natural refrigeration. In this method, the easily condensable component is liquefied first, this acts as a refrigerant for the second liquefaction, the resultant of which is employed for cooling the most vehement one. It may be illustrated further like this, propane is first condensed by using water at not more than 50°C and at a pressure of 1.9 MPa. The boiling point of propane at ordinary pressure is – 43°C. So, this is permitted to act as a refrigerant to ethane fraction, which can be liquefied at – 33°C under a pressure of 2 MPa. Ethylene boils at – 103°C at ordinary pressure, hence this component can safely condense methane, at – 100°C under a pressure of 3 MPa. Thus, methane faction can be liquefied much above its boiling point (–161˚C) under pressure. The system is evenly balanced because of the critical temperatures and pressure as shown below :

	B.P. at 760 mm Hg *°C*	*Critical pressure* *kg/cm^2*	*Critical Temperature* *°C*
Methane	– 161.5	45.0	– 81.55
Ethane	– 88.6	47.5	+33.3
Ethylene	– 103.8	50.9	9.7
Propane	– 42.0	41.0	+97.8
i-Butane	– 11.72	35.0	+135.6
n-Butane	– 0.5	36.4	+153.2
Butadiene	– 4.41	42.0	152.2
i-Pentane	32.3	32.0	177.0
n-Pentane	32.2	33.6	177.4

C_4 and above fractions are usually available in liquid state. Fig. 1.5 illustrates the separation of gaseous constituents by using low temperature condensation and fractionation.

Purified gas is dried to remove moisture and compressed to 35 atmospheres. After compression it is cooled by process heat removers to as low as possible (around 15°C). This mixture is sent into column (1), where the highly condensable gases (Propane and Butane) liquefy, which are drawn out from the bottom of the column. The top product is cooled in a cooler to – 8 to – 10°C again by process coolers and streamed into fractionator (2), where the imposed pressure is sufficient to condense C_3 and C_2 fractions. Overhead fraction is a gas consisting of methane and some liquid and transferred to column (3). From the top of the column (3), methane comes out. The liquid product mainly C_2 fraction joins the stream of ethane-ethylene fraction obtained from column (4). This column (4) takes up the bottoms of column (2) as feed, which contains C_2, C_3 and C_4 fraction. The column (4) fractionates the mixture into C_2 stream as overhead and the bottoms, remaining liquid. Ethane-ethylene mixture is separated in long distillation column (5). Overhead of this column is ethylene, thus ethane forms the bottom product. The bottoms of column (4) are mixed with the bottoms of column (1) and fractionated to get C_3 fraction as top product and C_4–C_5 fraction as bottoms in column (6). Propane-Propylene fractionation is done in another column (7). Ethane-Ethylene splitter is shown in Chapter 3.

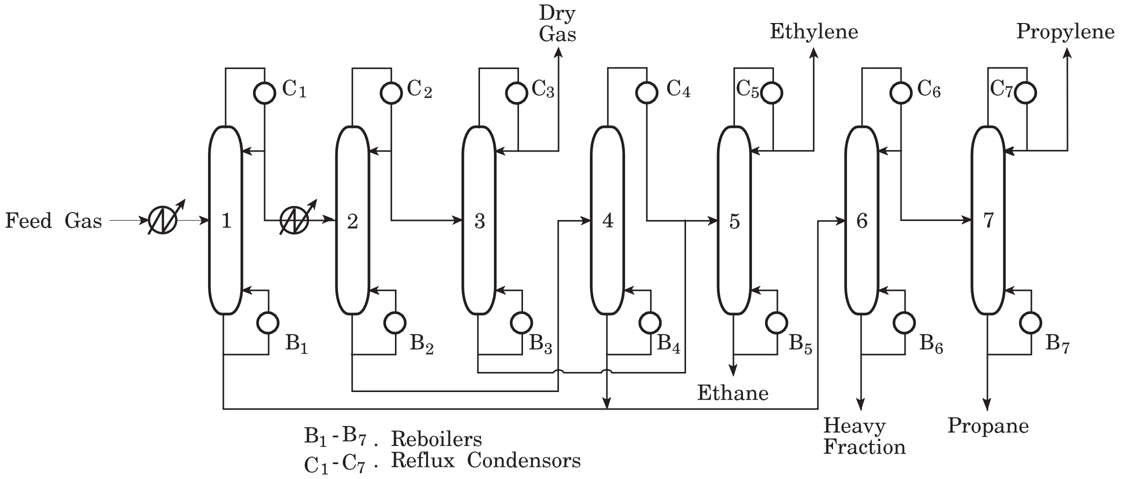


Fig. 1.5. Low Temperature Fractionation.

Propane or propylene obtained serves as the initial refrigeration system for incoming feed. Ethane-ethylene fraction cools the top product of column to condense methane. Effective cooling by out going cool gases markedly improves the economy of the process. Propane can be very easily liquiefied at room temperature simply by application of pressure.

1.3.1.4. Adsorption

In the earlier stages of application, adsorption was considered to be an operation of purification. Various kinds of impurities ranging from colour donating substances to corrosive and toxic chemicals were attended by this process. Use of charcoal in masks at war fields or bone charcoal for bleaching sugar solution were authentic. Tswett's application of selected adsorbents for separation and isolation of pigments and natural colours, has gradually instituted chromatography, a modern tool of chemical analysis. In all these applications natural adsorbents have been gradually replaced by synthetic ones. The use of natural absorbents, like bentonite clay, Fullers earth, bauxite has been received with wild acclaim for decolorisation of lube oils in petroleum industry. Though the hydrodesulphurisation technique has gained momentum to interlace all the petroleum and chemical industries, still orthodox refiners are continuing the old clay treatment process.

Synthetic absorbents like silica gel, molecular sieves, zeolites have been permeated into petroleum industry, the survival of petroleum industry without these has become a question.

Separation of paraffins from aromatics whose boiling range do not permit the conventional techniques, has been successfully done by this technique. Based on the selective or preferential adsorption, Molex process (Molecular sieves) works for removal of normal paraffins from either branched chain paraffins or aromatics. Also detergents manufacturing is based upon the selective removal of paraffins from other constituents (gasolines and kerosenes). The adsorbability is governed by the physical and chemical properties of adsorbates and the nature and structure of adsorbents. As a highlight, ethylene has been successfully separated from cracked gas mixtures, which is described below.

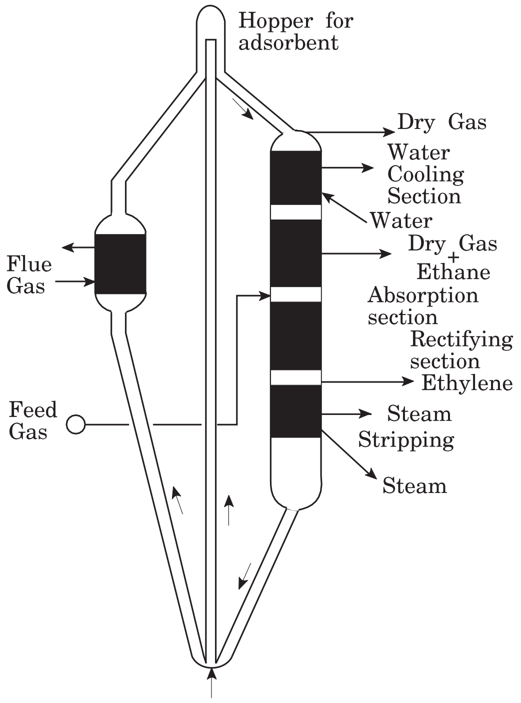


Fig. 1.6. Hypersorber.

The unit namely, hypersorber is shown in Fig. 1.6 contains 4 chambers. The feed gas enters the section (3) and rises to adsorption chamber, where the heavy unsaturates are adsorbed, the adsorbent, in this system being activated charcoal. Light gases like H_2, CH_4 are not adsorbed and escape as such through top section. The downward travelling catalyst reaches bottom section where heating is done to expel the adsorbed ethylene (265°C). Heating is done by circulating dowthern mixture or high pressure-superheated steam. The outgoing streams usually go through cyclones, which catch any charcoal dust. The desorbed adsorbent once more heated (for complete regeneration) and elevated to the bin above the top of the hypersorber. Proper distribution is done by distributors at the entrance of each section. A highly efficient hypersorber can yield 98% ethylene from a concentration of 6% in inlet feed, at a purity of 98 to 99%.

1.3.1.5. Special Techniques

Special techniques are invited when the individual techniques fail to prescribe economic operation. For a close economy, two or more methods are congenially joined together. Fig. 1.7 describes a combined absorption and fractionation unit for separation of refinery cracked gases into dry stream and olefins or feed stocks for petrochemical industry.

Feed gas under a convenient pressure (8 to 10 atms) is first sent into depropaniser absorber (1), where a solvent fraction (C_7–C_{10}) trickles down. This solvent rapidly absorbs C_3 and above components. The top gas contains unabsorbed methane, ethane and propane fractions along with other non condensables like air, H_2S, hydrogen, etc. The fat solution goes to the second column called debutaniser, the overhead shall be butane fraction and residue contains high

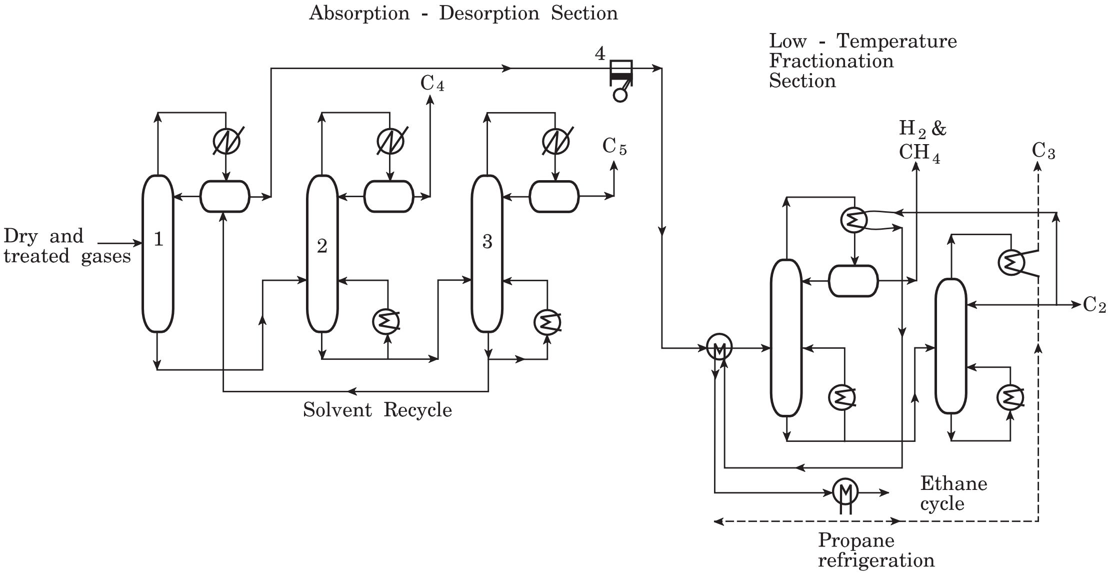


Fig. 1.7. Absorption-Low Temperature Combination for Separation of Gases.

proportions of pentane. Pentane is stripped off in the column (3). The heavier bottoms are recirculated as solvent. The unabsorbed gases are compressed (4) (30-35 atm) cooled and dried and then sent to low temperature fractionation battery. This system has been already described (Fig. 1.5.).

Another combination is partial liquefaction-fractionation. In this process the cooling efficacy results in condensing C_2 and heavier fractions. Thus, hydrogen and methane remain in gas phase. The dry gas is separated for heating purposes and the concentrates are processed in liquid phase. LPG recovery from associated gas or natural gas is a fit example in this direction and the major steps involved are :

First Stage: Cooling the whole mass of gas to 30°C under 35 atmosphere pressure to liquefy C_4 and above constituents.

Second Stage: The uncondensed gas is subjected to severe conditions, *i.e.* upto +30°C, and 20 atmosphere pressure, whereby propane condenses leaving ethane and ethylene in gaseous form.

Third Stage : Ethane and ethylene are liquefied and fractionated.

Fourth Stage: Dry gas constituting CH_4 and H_2 is separated from ethane/ethylene mixture, and this mixture is used as a refrigerant.

Fifth Stage : The heavy bottoms of first stage unit are processed for C_3 and heavy ends.

1.4. Separation of Aromatics

Most useful aromatics are benzene, toluene and xylene. All these being liquids at room temperatures, precise fractionation can separate. However, when they are in fractions of close boiling ranges, paraffins will hurdle the separation. Aromatics from paraffins can be separated by azeotropic distillation or by liquid extraction. So, preferably, aromatics as a group may be separated from these by azeotropic distillation. It is apparent that paraffins are separated by extractive distillation, while aromatics require azeotropic distillation. The principle underlying azeotropic distillation is that added component forms a constant boiling mixture (usually less than the b.p. of individual components) which can be easily condensed and further fractionated. Industrially liquid extraction is used to separate aromatics from cracked feeds. Solvents like liquid sulphur dioxide, dimethyl formamide,(24) dimethyl sulphoxide(25) and ethylene glycols(26) etc. are in much use in industry. All these solvents preferably extract aromatics from non-aromatics.

The most suitable source of light aromatics (BTX) is reformate of naphtha (80–140°C) or cracked naphtha fraction. The description of these methods appear here.

1.4.1. Azeotropic Separation of Toluene

Any thermally cracked or catalytic reformed stocks contain at-least 18% toluene. This toluene fraction in close boiling cut (100–115°C) is first separated from the main stream by distillation. Mostly used azeotropic solvents are methanol and methyl-ethylketone. Methanol has a tendency to form azeotrope with toluene. Azeotropic mixture contains 55% methanol. Fig.1.8 describes the operation in detail. Methanol and feed mix enter the column (1), where methanol forms a top product with naphthenes and paraffins. This product enters the tower (3). The bottoms of column (1), contain methanol and aromatics as an azeotrope enters the column (2). The top product is mainly methanol and the bottom product is toluene of the purity 96-98%, which is further refined to eliminate unsaturates either by treating with sulphuric acid or by distillation. In the column (3) methanol is replaced by scrubbing with water thus setting free hydrocarbons from the bottom of the column, the liquid wastes is taken into column (4), where fractionation separates methanol as a top product from water. The methanol is sent back to column (1) to begin the operation.

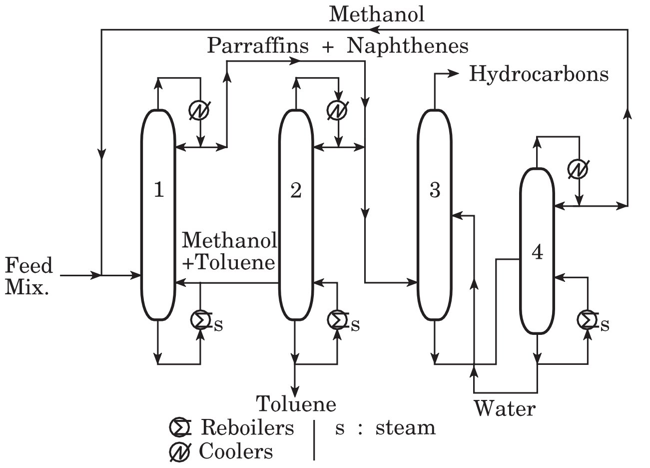


Fig. 1.8. Azeotropic Distillation for Toluene.

1.4.2. Extractive Distillation : Separation of Styrene

Styrene is obtained as byproduct during cracking of naphtha for ethylene and it constitutes about 4 to 6%. The cracked fraction can be used as a raw material without any treatment for recovery of styrene although it is highly advantageous to tailor the fraction to C_8 cut only, to rise the concentration of styrene to greater than 30%, (Boiling range of such stream is 125–148°C). Specially styrene O-xylene separation is a difficult thing because of close boiling

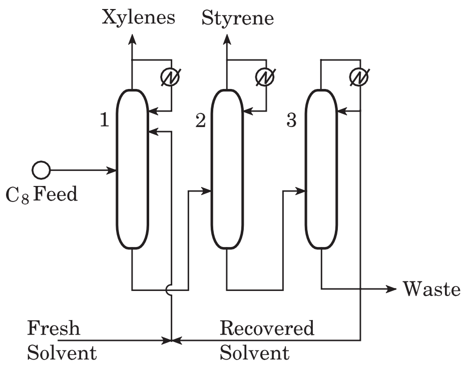


Fig. 1.9. Styrene by Extractive Distillation.

ranges of these two. Extractive distillation is successful in separation of these two. Fig. 1.9 explains the operation. Initial separation may be done by extraction or distillation to concentrate C_8 fraction from the rest. Separated C_8 fraction is sent into an extractive distillation unit, where a suitable solvent encounters the feed. The solvent styrene form a high boiling mixture and crude xylenes leave the tower from the top of column (1). The residue obtained from the bottom of this column contains styrene, a high boiling mixture and crude xylenes leave the tower from the top of column (1). The residue obtained from the bottom of this column contains styrene and solvent. This solvent mix is distilled again in a second column (2) to free styrene as a top product. Rich mixture of solvent and heavy ends formed due to polymerisation of styrene go into a separate column (3), where pure solvent is set free from the bottoms of the column. Polymer wastes are discarded. To prevent polymerisation of styrene small amount of inhibitor is added. STEX(27) process uses a special solvent for this operation, though phenol is the best suggested one.

1.4.3. Aromatics separation from Reformates

Full range naphtha when subjected to catalytic reforming paraffins cyclise through dehydrogenation reaction. The cyclic compounds together with isomerised paraffins boost octane number. Hence, this process has become a major refinery operation to produce quality gasoline. The same process has become exceptionally faithful to produce aromatics from paraffin rich stocks. Depending upon the carbon atoms present in the feed, the reformate turns out to contain the same number of carbon atoms, but in cyclised or isomerised form. So it may be suitably chosen C_6/C_7/C_8 atoms to produce benzene, toluene, xylene respectively. After the reaction, the reformate may be enriched with aromatics up to 40 to 50% depending upon the catalyst and the process variables. The rich reformate is extracted with solvents like ethylene glycols, dimethyl formamide, dimethyl sulphoxide, sulpholane or liquid sulphur dioxide etc. Snam Progettis(28) new solvent N-formylmorpholine has also become a competitive solvent in this field. A brief description on extraction of aromatics by ethylene glycols is furnished in Fig. 1.10.

Ethylene glycol mixed with water forms a solvent for aromatics. Aromatic rich stock heated to 150°C under a pressure of 8-10 bars is sent into the extractor (1); where the udex solution comes in contact with the aromatic rich stock. The raffinate from the top goes into a water washer (3), where solvent is washed off by a spray can of water. From the top, raffinate is obtained; and by steaming the remaining solvent stains can be removed. The extract from the extractor goes into a fractionator (2), where the top product containing aromatics and small amount of solvent is finally distilled in a column (5) to get aromatics and solvent from the bottom of the column to join the extractor. Raffinate washings are collected and separately fractionated in a column (4) to drive off excess water to maintain the degree of dilution of the solvent, *i.e.* 80-90%. Solvent recycling is 5 to 6 times to hydrocarbon feed. Ethylene glycol is suitable to extract only light hydrocarbons, while the other solvents such as DMF, DMSO liquid sulphur dioxide are used for improving smoke point of kerosene.

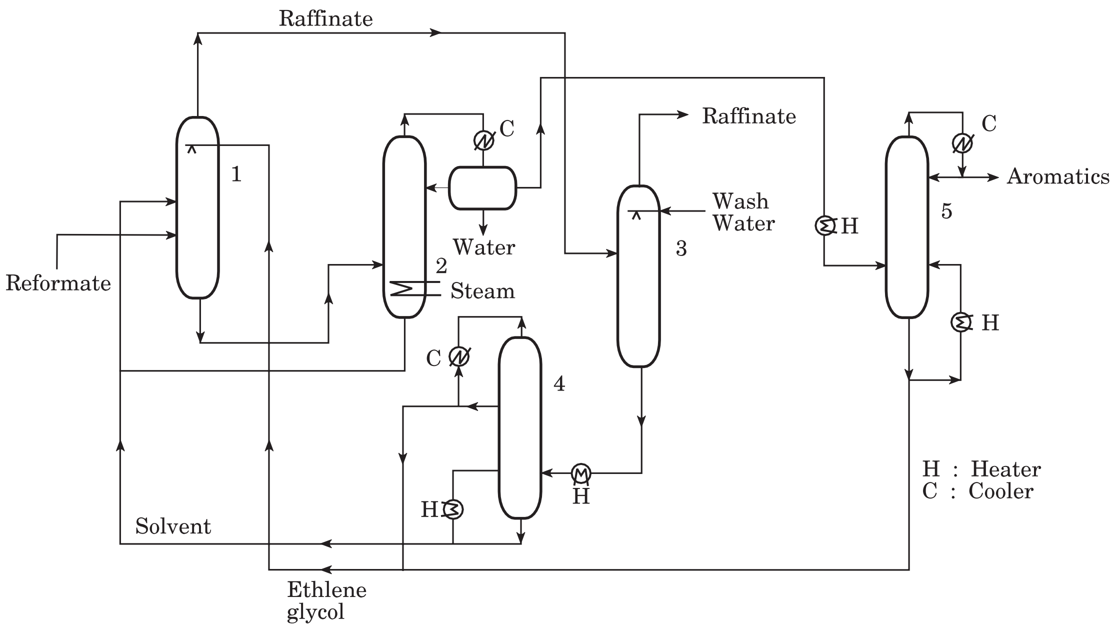


Fig. 1.10. Udex Extraction Process.

1.4.4. Separation of Aromatics by Crystallisation

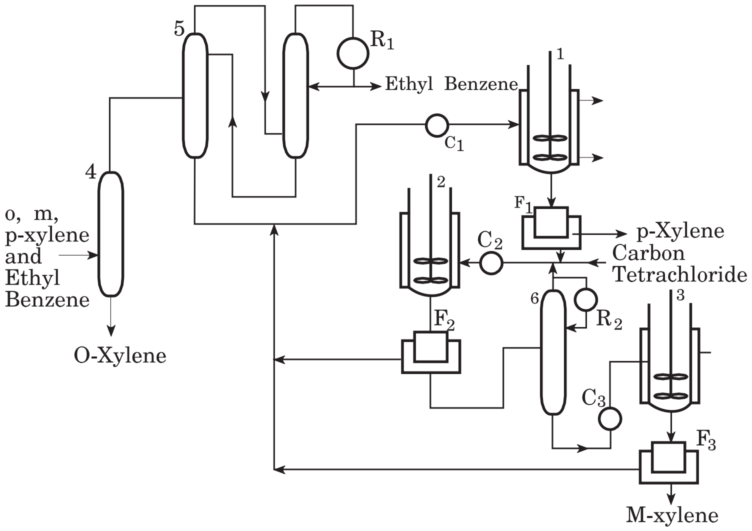
Azeotropic or extractive distillation is an invincible tool for separation of aromatics from paraffins of the same boiling range. However, these methods fail when separation of C_8 aromatics to individual components is attempted. There are four isomers of C_8 aromatics whose boiling points are in close range as given below :

Component	*Melting point °C*	*Boiling point °C*	*Density gm / cm*
O-xylene	– 25.2	144.4	0.880
p-xylene	+ 13.3	138.4	0.861
m-xylene	– 47.8	139.1	0.864
Ethyl benzene	– 95.0	137.2	0.867
Styrene	– 31.0	145.2	0.902

It may be guessed how difficult it should be to separate these individual components from a mixture by conventional fractionation alone. So a different procedure involving the advantages of difference in melting points and boiling points is taken up. *p* and *m*-xylenes can be separated by fractional crystallisation, while O-xylene can be separated by distillation from ethyl benzene. As shown in Fig. 1.11, first fractionator (4) separates all the four components to O-xylene as bottom residue and overhead as a mixture of p and m xylenes and ethyl benzene. O-xylene is removed as bottom product. The reflux in these columns is maintained at 60 to 70. Usually, such large columns are split into series of 3 columns, to diminish the construction costs, difficulties further smooth maintenance is also possible. Now *p* and *m* xylenes are to be separated in cooler (C_1). *p* and *m*-xylenes are first cooled to – 20°C. This starts crystallising p-xylene, while m-xylene remains as liquid. The crystals of p-xylene from the crystalliser (1) are separated in a centrifuge (F_1). The separated crystals still contain some m-xylene carrys p-xylene to 10%, hence an altogether different procedure has been recommended.

P-xylene and m-xylene mixture can be submitted to extractive crystallisation using n-pentane as solvent, so that the eutectic crystallisation may be avoided. Another method is to follow adductive crystallisation using carbon tetra chloride as solvent. The former method was developed by Phillips, while the later method is used in USSR. To improve the purity of p-xylene, the recovered p-xylene is mixed with carbon tetrachloride and cooled to – 78°C in a cooler (C_2) and crystallised (2). A complex crystalline substance melting at – 40°C results, which on distillation yields p-xylene and carbon tetrachloride. The complex from the crystalliser is centrifuged (F_2) and the filtrate is sent into the first crystalliser (1). Carbon disulphide is regenerated in column (6) to join the process. The bottoms from the column are cooled again in a cooler (C_3) to – 70°C and sent into crystalliser (3). The crystals are again separated in a centrifuge (F_3), the mother liquor from the centrifuge contains p-xylene concentrate and is sent into the first crystalliser. The crystals from centrifuge-3 show a solid phase of m-xylene about 85% and this can be purified in a separate unit if desired. Many methods of purification are available as discussed below :

Sulphonation is used to separate m-p-xylenes. When sulphonation is done to m-p-xylenes mixture, only m-xylene is found to be susceptible. The sulphonated product is extracted with water or any solvent and hydrolysed to get back m-xylenes.



1,2,3 Crystallisers
4-6 Fractionating Columns (100-300 Plates)
C_1 – C_3 Coolers
F_1 – F_3 Centrifuges
R_1 – R_2 Condensers

Fig. 1.11. Fractional Crystallisation for Separation of C_8 Isomers.

Another method appears in literature which describes the oxidation of m-xylene to phthalic acid with air at a temperature of 200°C under a pressure of 15 to 30 atm. (Amoco oxidation).

A supplementary to the above methods is understandably isomerisation technique(29). When ethyl benzene concentration is not favourable for extraction or separation, it may be converted to other xylenes by isomerisation catalysts. This method has been developed in view of economy by ICI(30), using non-noble catalysts at atmospheric pressure and at a temperature of 100 to 500°C maximize p-xylene.

1.4.5. Solid Adsorbents

Specific adsorbents with well defined pore size, like molecular sieves are credited with an excellent performance of separating parffins from aromatic or a particular isomer from host of isomers of same carbon atom. Parex process has suggested that p-xylene can be effectively separated from other C_8 isomers. Iso Siv(20) process has been in operation for concentrating n-paraffins from kerosene or gasoline fraction. In this process molecular sieve of size 5A is used.

In Parex process adsorption takes place at a termperature of 150–175°C and under a pressure of 10 kg/cm^2, preferably in liquid phase only. By this method purity of p-xylene obtained is found to be 99.5%.

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