PETROCHEMICAL INDUSTRIES

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First Registered on 25 August 2010; Received after Corection on 8 September 2010
Publication Approval on : 30 September 2010

ABSTRACT

Petrochemical processes begin with relatively few basic raw materials, expand into a complex network of chemicals and converge into materials that serve specific functions as consumer products. Then raw material base for the petrochemical industry primarily depends upon the type of intermediates and final products required by industry and consumer. Almost all petrochemicals are derived from three sources: synthesis gas, olefin and aromatic.

Production of those three petrochemical sources and the derivative chemicals are described briefly.

Key words*: Petrochemical feedstocks, their derivatives, petrochemical industry.*

I. INTRODUCTION

Petrochemical processes begin with relatively few basic raw materials, expand into a complex network of chemicals and converge into materials that serve specific functions as consumer products. Then raw material base for the petrochemical industry primarily depends upon the types of intermediates and final products required by industry and the consumer. Almost all petrochemicals are derived from three sources:

- Carbon monoxide/hydrogen (synthesis gas) from steam reforming of natural gas (methane)
- Olefins from thermal reforming of ethane, propane -butane (LPG) or distillates in the olefin center
- Aromatics from catalytic reforming.

There are also refinery streams used for Petrochemical (Table 1). The three main source for petrochemicals lead to products which are marketable items in their own right, as well as raw materials for a great many other petrochemicals used both as intermediates and as finished products. Production of synthesis gas, low olefins and low aromatics, and their chemical derivatives are described briefly.

II. SYNTHESIS GAS

A. Production of Synthetic Gas

Synthesis gas, *syn gas*, is a general term used to designate various mixtures of carbon monoxide and

Table 1
Refinery Streams use for Petrochemicals

Refinery Stream	Petrochemical
	Basic Petrochemicals
FCC Offgas	Ethylene
FCC Olefin	Propylene, Butylene
Reformate	Benzene, Toluene, Xylene
	Petrochemical Intermediates
LPG	Olefin
Naphtha	Olefin
Gasoil	Olefin
FCC Ethylene	Etylbenzene
FCC Propylene	Methylethylketon
FCC Butylene	Cumene, Isopropanol, Oligomer
Kerosene	n. Paraffin
FCC Light Cycle Oil	Naphthalene

hydrogen. The mixture of CO/H_2 can be produced from almost anything containing carbon and hydrogen from methane, coal, to crude oil residues.

Two general types of reactions are used for the production of syn gas, i.e. partial oxidation and steam reforming. Steam reforming is the most important process, when methane or natural gas is used as the carbon–hydrogen sources. Partial oxidation is primarily used for heavy fuel. Table 2 gives the compositions for the steam reforming of methane to produce a 3 to 1 ratio of hydrogen to carbon monoxide.

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

Partial oxidation of methane

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2$$

The shift reaction is used produce pure hydrogen from synthesis gas

$$CO + H_2 \rightleftarrows CO_2 + H_2$$

Steam reforming process of methane is also used in the fertilizer industries, methanol plant and hydrogen plant for hydrocracking complex .

B. Chemical from Syn Gas

1. Ammonia

Pure hydrogen is produced from Sys Gas. Hydrogen combined with atmospheric nitrogen is used for the production of ammonia.

$$N_{2(g)} + 3\ H_{2(g)} \rightleftarrows 2\ NH_{3(g)}$$

The main consumer of ammonia is the fertilizer industry (about 80%). Anhydrous ammonia is utilized as a fertilizer by direct application to soil, and in the form of various compound such as ammonium nitrate, urea and ammonium phosphate. Ammonia is also used to produce plastics, resin, fibers and explosives.

2. Urea

Carbon dioxide, a side product of ammonia plant reacts with ammonia to produce area. The production of urea is based on the two–step reactions of carbon dioxide and ammonia. The NH3 / CO_2 mole ratio is about 3:1. In the first step, ammonium carbamate is formed

$$CO_{2(g)} + 2\ NH_{3(g)} \rightleftarrows NH_2\ COONH_{4(s)}$$

The second step is the decomposition of the carbamate to urea and water.

$$NH_2COONH_{2(s)} \rightleftarrows NH_2CONH_{4(s)} + H_2O_{(g)}$$

Urea is an important solid fertilizer containing about 45% nitrogen. The fertilizer use of urea account for about 75% of its production. Other ureas are used as animal feeds (10%) and adhesives, plastics, and resins (15%).

3. Nitric Acid

Nitric acid is commercially produced by oxidizing ammonia with air. The simple reaction is assumed, as follows:

$$4\ NH_{3(g)} + 5\ O_{2(g)} \rightarrow 4NO_{(g)} + 6\ H_2O_{(g)}$$

$$2\ NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$

$$3\ NO_{2(g)} + H_2O_{(l)} \rightarrow 2HNO_{3(ag)} + NO_{(g)}$$

Nitric acid is mainly used for the production of ammonium nitrate. It is also used as a nitrating agent for paraffins and aromatic compounds. The major compounds derived directly or indirectly from methane are given in Figure 1.

III.LOW OLEFINS

A. Production of Low Olefins

Steam reforming process of gas and distillates produces low olefins. The three most important ole-

Table 2
Composition of Reformed Gas and Partial Oxidation Gas

Production Process	Volume % dry sulfur free				
	CO	H_2	CO_2	N_2 + A	CH_2
Steam–natural gas reforming	15.5	75.7	8.1	0.2	0.5
Partial oxidation–heavy fuel oil	47.5	46.7	4.3	1.4	0.3

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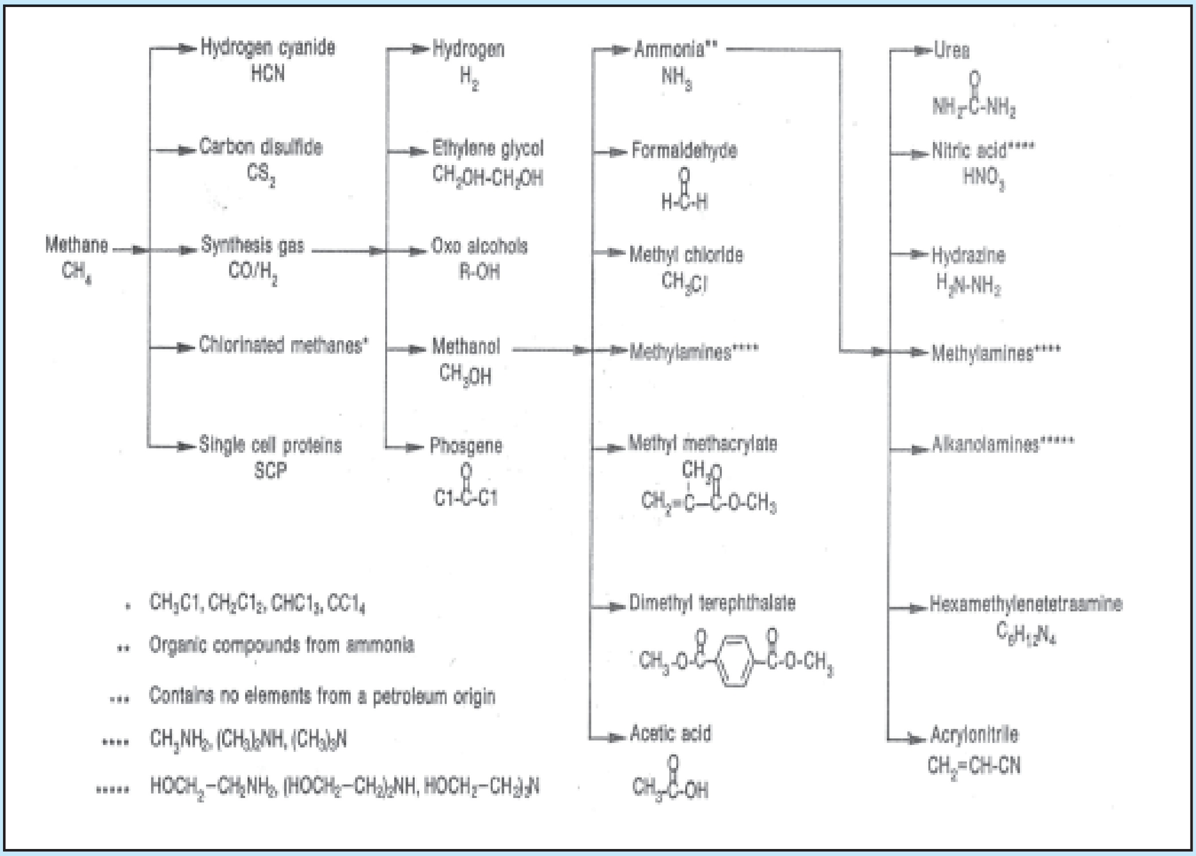

Figure 1
Major compounds derived directly or indirectly from methane

fin used for the production of petrochemicals are ethylene, propylene and butadiene. However these products are inseparable. There are generally produced in various ratios by cracking of feedstock as shown on Table 3.

In both countries of United States and Europe, heavier feedstocks are playing a greater role in ethylene production.

One of the advantages of naphtha over gas feed–stocks is wider spectrum of coproducts therefore a variety of coproducts can be obtained. The additional pyrolysis of gasoline (liquid products) causes for the additional BTX formed (Table 4).

B. Chemical from Low Olefins

1. Ethylene

A basic reason why ethylene $CH_2 = CH_2$ is a prime raw materials for petrochemicals is that it is readily available at low cost and in high purity. Ethylene reacts by addition with low cost material such as oxygen, chlorine, hydrogen chloride and water to produce petrochemical compounds, moreover the reactions take place under relatively mild conditions and usually with high yields. It enters into the production of about 30% of all petrochemicals. Derivates of ethylene are used for the production of plastics (65%), antifreeze (10%), fiber (5%), and solvents (5%).

Ethylene and many ethylene derivatives are used to produce polymers, which is the largest percentage of ethylene utilization, such as polystyrene, polyester and polyvinyl chloride.

2. Propylene

Propylene, $CH_3 – CH = CH_2$, often offered as the crown prince of petrochemical. It is superficially similar to ethylene, however each of which has many differences either in production or uses.

Petrochemical demand for propylene is about one–half of the demand for ethylene. This is somewhat surprising because the added complexity of the

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Table 3
Typical Yields from Various Feedstocks (Including Ethane Recycle)

Feedstock	Products wt. %				
	Ethylene	Propylene	Butane	Aromatics (BTX)	Other
Ethane	84.0	1.4	0.4	0.4	12.8
Propane	44.0	15.6	3.4	2.8	34.2
n-Butane	44.4	17.3	4.0	3.4	30.2
Light Naphtha	40.3	15.8	4.9	4.8	34.2
Full Range Naphtha	31.7	13.0	4.7	13.7	36.9
Reformer raffinate	32.9	15.5	5.3	11.0	35.3
Light Oil Gas	28.3	13.5	4.8	10.9	42.5
Heavy Gas Oil	25.0	12.4	4.8	11.2	46.6
Waxy Distilate	28.3	16.3	6.4	4.5	44.5
Crude Resid	21	7	2	11	59
Crude Oil	32.8	4.4	3.0	14.4	45.4

propylene molecule should permit a wider selection of markets. The propylene utilization are as follows, polypropylene–29%, acrylonitrille 15%, acrylic acid – 2% and others 13%.

The major uses of propylene oxide are in the production of flexible foams (48%) and propylene glycol (25%). The remaining propylene oxide are usually produced for rigid foams, non–foams, dipropylene glycol, polypropylene glycol and isopropyl amines.

3. Butene

The chemical application of 1 butene (CH_2= CH–CH_2–CH_3), 2 butene (CH_3–CH=CH–CH_3) and iso–butene (CH_2–CH CH_3–CH_3) are presented in Figures 2 and 3.

4. Butadiene

It was noted that while the assured future of the butadiene, CH_2=CH–CH=CH_2 lies on synthetic rubber the potential of butadiene is in its chemical versatility. Today only about 7% of butadiene production is utilized in other than direct polymer formation. Butadiene has not lived up to its potential as a chemical intermediate (Figure 4). The polymer distribution is : styrene–butadiene rubber (50%), polymers (20%), and other rubbers (10%).

Table 4
Typical Once–Through Yields
from Naphtha Feedstock*

Products**	Cracking Severity	
	Low	High
Methane	10.3	15
Ethylene	25.8	31.3
Propylene	16.0	12.1
Butadiene	4.5	4.2
Butanes	7.9	2.8
BTX	10	13
C5 +	17	9
Fuel oil	3	6
Other***	5.5	6.6

+ sp. gr. 60/60°F 0.713
Boiling range °C 32 – 170
Aromatic 7
** Weight percent
*** Ethane (3.3 and 3.4%), acetylene, methyl acetylene, propane, hydrogen

IV. LOW AROMATICS

A. Production of Low Aromatics

Catalytic reforming process of heavy naphtha produces reformate containing low aromatics (BTX). The composition of the C6–C8 aromatic of reformate is shown in Table 5.

Catalytic reforming process of heavy naphtha is an important process in the aromatic center.

B. Chemicals from Low Aromatics

Benzene, toluene and xylenes, (BTX) are aromatic hydrocarbon, with a wide use as petrochemicals. They are important precursors for plastics such as nylon, polyure-

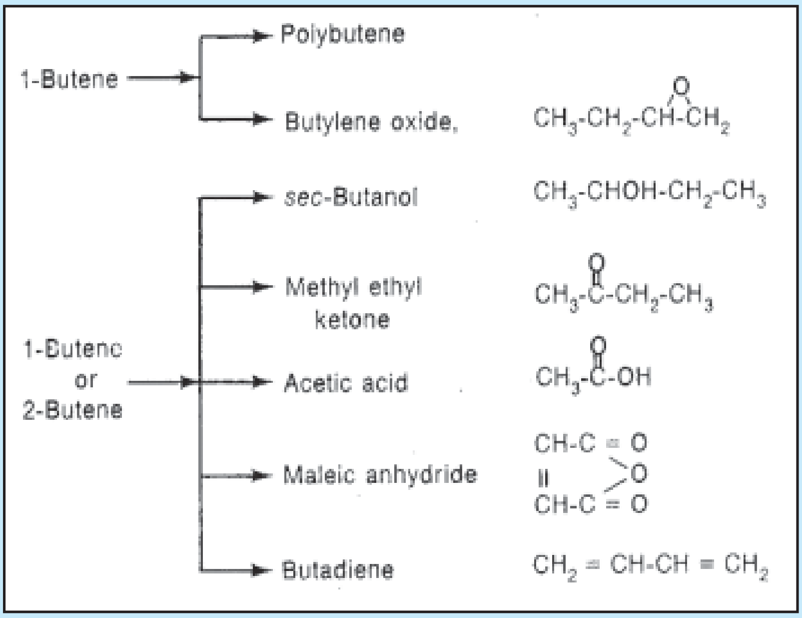

Figure 2
The chemical application of the *n* – butanes

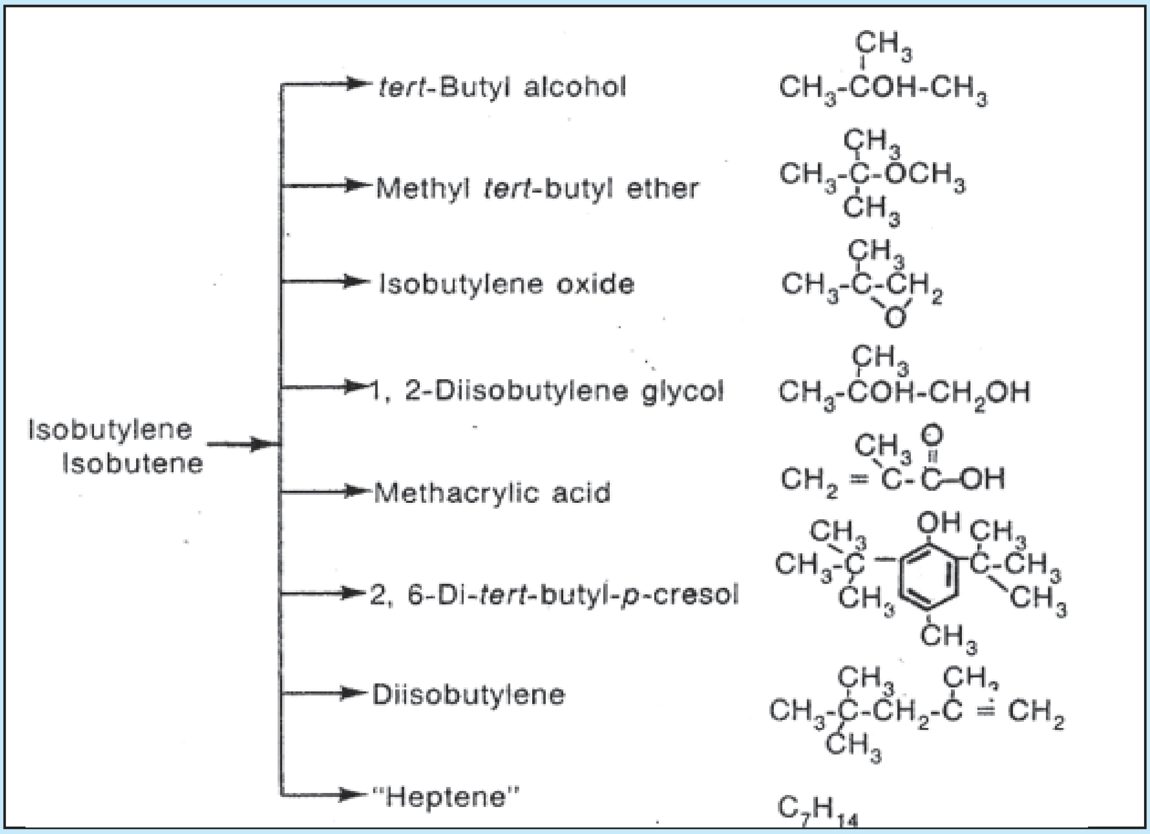

Figure 3
The chemical application of isobutylene, exclusive of polymer formation

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thane, polyester, alkyd-resins, and phthalate plasticizers. These represent the large scale applications. On the lesser scale they are precursors for insecticides, weed killers, medicinal, and dyes.

1. Benzene

Benzene C_6H_6, is the simple aromatic hydrocarbon and so far this aromatic compound is the most widely used in petrochemical industries. The initial derivates of which in turn are used to make consumer product.

The final products are frequently polymers which means the chemical benzene is a large volume petrochemical. Initial used of benzene are as follows: Ethylbenzene ethylene – 50%, cumene – 15%, cyclohexane – 15%, nitrobenzene – 5%, maleic anchydride – 4%, and other – 11%. The styrene is produced by dehydrogeration of ethylbenzene. The styrene market is as follows: polystyrene – 61%, styrene butadiene rubber – 9%, acryconitril butadiene styrene – 7%, unsaturated polyester – 7% and other – 8%.

Cyclohexane, C_6H_{12}, is produced by hydrogenation of benzene. Cyclohexane is used almost exclusively in the production of intermediates for nylon fibers and resins, with 60 percent to nylon 66 and 30 percent to nylon 6.

2. Toluene

The application of toluene in petrochemical industries are as follows: solvent – 35%, toluene diisocyonate – 21%, benzyl chloride – 6%, benzoic acid – 6%, phenol – 3%, trinitrotoluene – 3%, and

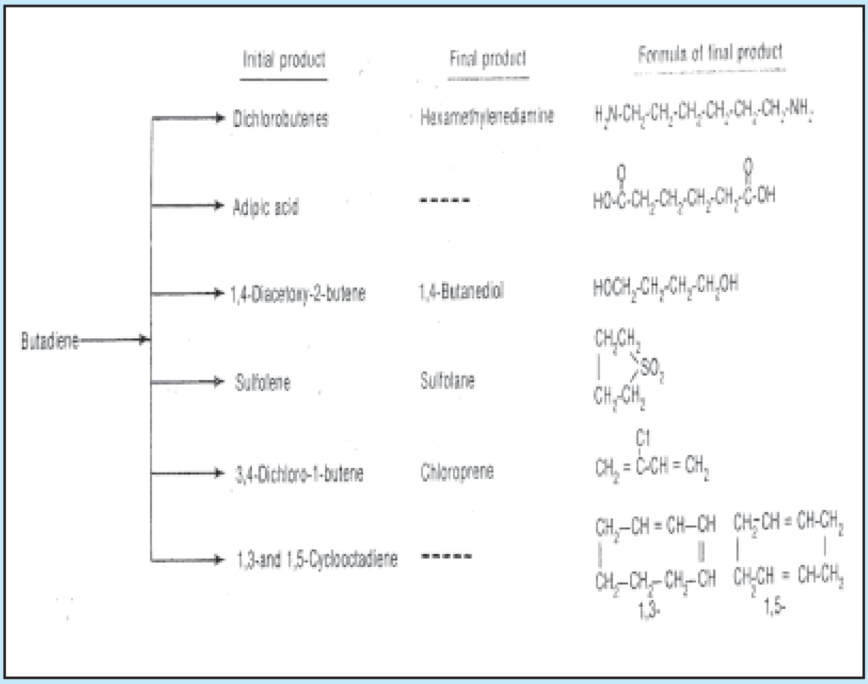

Figure 4
The principle industrial compounds derived from butadiene

Table 5
The composition of the C6 – C8 Aromatic of Reformate Structure

Structure						
Name	Benzene	Toluene	O.xylene	M.xylene	P.xylene	Ethyl Benzene
Vol %	10.3	33.7	12.9	21.7	8.1	9.3

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other including export – 26%. The major endproducts from the chemical use of toluene are shown in Figure 5.

3. The Xylenes

The xylenes are obtained from refinery reformate streams where the yield or mixed xylenes plus ethylbenzene (the C_8 aromatics) is greater than that of the combined yield of benzene and toluene. The weight percent of the C8 aromatics composition of reformate is as follows: o.xylene – 20.1%, m.xylene – 40.4%, p.xylene – 18.3% and ethylbenzene 21.2%.

a. Ortho Xylene

About 75% of oxylene is oxidized to produce phthalic anhydride. The single largest use (48%) of phthalic anhydride is for the production of plasticizers for polyvinyl chloride, (PVC). The second most important use (24%) is in the production of polyester resins; 20 percent is used for alkyd resins.

b. Metha Xylene

Meta xylene is the least of the three isomeric xylenes used in petrochemical industries. At present the major usage m-xylene is isomerization to the more desirable aromatic hydrocarbons such as : o – and p– xylenes. The most important petrochemical interest is its oxidation to isophthatic acid. An interesting new synthesis is oxidative ammonolysis to isophthalonitrite. Isophthalic acid is produced via liquid phase oxidation of *m*–xylene by using of ammonium sulfite $(NH_4)_2SO_3$.

The use of isophthalic acid are similar to those of the other phthalic acids. This polyesters have better toughness, resistance to abrasion, resiliency and free from cracking and cracking reactions.

c. Para-xylene

Virtually the only use of p–xylene is for production of terephthalic acid, TPA, and dimethyl tereph

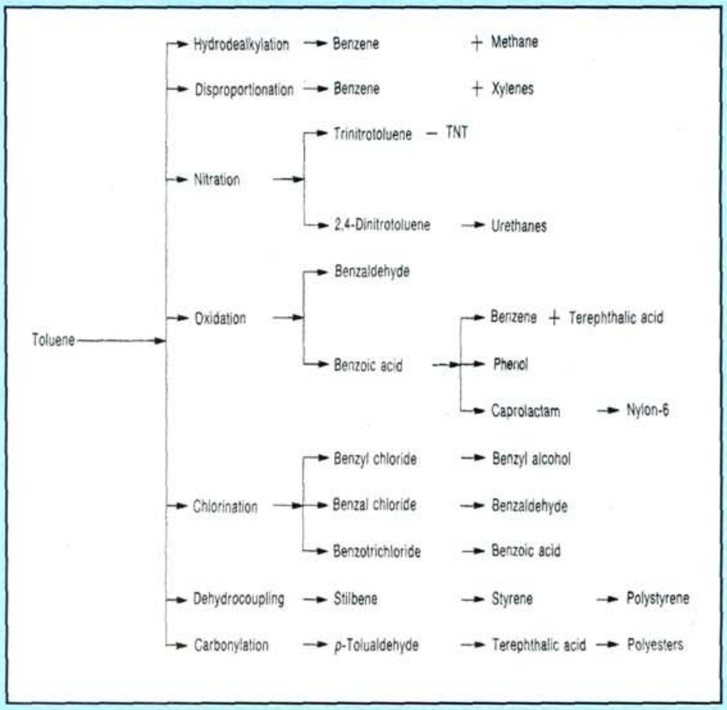

Figure 5
he major and endproducts from the chemical use of toluene

Table 6
Petrochemical Industries in Indonesia

Fertilizer Industries	: Asean and PIM (Aceh), Pusri (South Sumatera), Kujang (West Java), Kaltim (East Kalimantan)
Methanol Plant	: Bunyu (East Kalimantan)
Petrochemical Industries	: Gresik (East Java)
Hydrogen Plant	: Refinery (UP. II Dumai, UP.V Balikpapan and UP. VI Balongan)
Olefin Center	: PT Chandra Asih, Cilegon
Aromatic Center	: UP.IV Pertamina Cilacap
Polypropylene	: UP.III Pertamina Plaju
Purified Therephthelate Acid	: UP.III Pertamina Plaju.

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thalate, DMT. Pure fiber grade terephthalic acid is called PTA. Current production capacity is about evenly split between PTA and DMT. The trend is toward PTA expansion rather than DMT.

The two p–xylene derivatives PTA and DMT, have only one major use, i.e. the synthesis reactivity to polyethylene terephthalate fiber (85 percent) and film.

However, at least two other types of terephthalate esters are growing in importance. These are unsaturated polyesters and polybuthylene terephthalate, PBT, which are available as thermoset plastics. PBT is one of the fastest growing injection molding plastics. A lesser extent TPA is used as an intermediate substance for herbicides, adhesive, printing inks, coatings, paints, and animal feed supplements. Several petrochemical industries built in Indonesia are as shown in Table 6.

V. CONCLUSION

Feedstock source of petrochemical process are mainly based on the three following molecules i.e. synthesis gas, low olefin and low aromatics. These three main sources for petrochemical products which are marketable items is their own right, as well as raw materials for a great many other petrochemicals used both as intermediates and as finished product.

Steam reforming processes are used in the fertilizer industry, methanol plant and hydrocracking process. While thermal reforming is used in olefin plant. catalytic reforming process is applied in aromatic center.

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