



## CHAPTER II

### CATALYTIC REFORMING

Catalytic reforming, an important refinery process for octane improvement, is used to designate a process by which the molecule structure of naphthas is changed, or reformed, with an intent of lessening the knocking tendency of those naphthas in internal combustion engines [5]. Also, the reforming process is used to synthesize aromatics -particularly benzene, toluene, and  $C_8$  aromatics -from selected naphtha fractions.

In this chapter, a review of introductory description of the products from reforming, feedstocks for reforming, and catalytic reformer, together with detailed accounts of the commercial process is presented.

#### 2.1 Distillation Column

Refinery processes are the processes that separate crude oil, which is a liquid mixture consisting principally of hydrocarbons, to many products used as fuels or petrochemical feeds--such as liquefied petroleum gas (LPG), naphtha, kerosene, gas oil, lubricating oil and heavy fuel oil, and asphalt. Most refinery processes can be grouped into one of three classes [6] as follows:

1. Separation, usually distillation, gives the desired type of compounds,
2. Conversion, usually cracking, changes molecular weight and boiling point,
3. Upgrading, e.g., hydrotreating, meets product-quality specifications.

An overall flow diagram of refinery processing steps is shown in Figure 2.1 and 2.2. Crude oil is fed into distillation units to separate into semiproducts. Light and middle semiproducts are generally fed to upgrading units (e.g., alkylation, extraction, catalytic reforming and hydrotreating units) to improve product quality. Heavy semiproducts are often fed to conversion units (e.g., hydrocracking, steam cracking, catalytic cracking, coking and visbreaking) to increase middle products and produce heavy products. Details of those units have been described in many references [6, 7, 8]

## **2.2 Products from Reforming**

Catalytic reforming in a petroleum refinery produces high-octane blending stock for motor fuel and also produce high-value aromatic hydrocarbons. Hydrogen is a valuable reforming product and its yield is the source of part or all of the hydrogen used for hydrotreating, hydrocracking, or hydrorefining processes.

A reformer that is operated to make high-octane blending stock is a motor fuel reformer. The primary product from reforming is called reformate. Because reformer feedstocks contain paraffins, further processing such as extraction is necessary to recover aromatics of marketable purity. After removal of aromatics from the reformate, the remainder is called raffinate. In some refineries, a catalytic reformer may operate part time as a motor fuel unit and part time as a BTX unit. The position of the catalytic reforming unit (or cat reformer) in a typical fuels refinery processing scheme is shown in Figure 2.1.

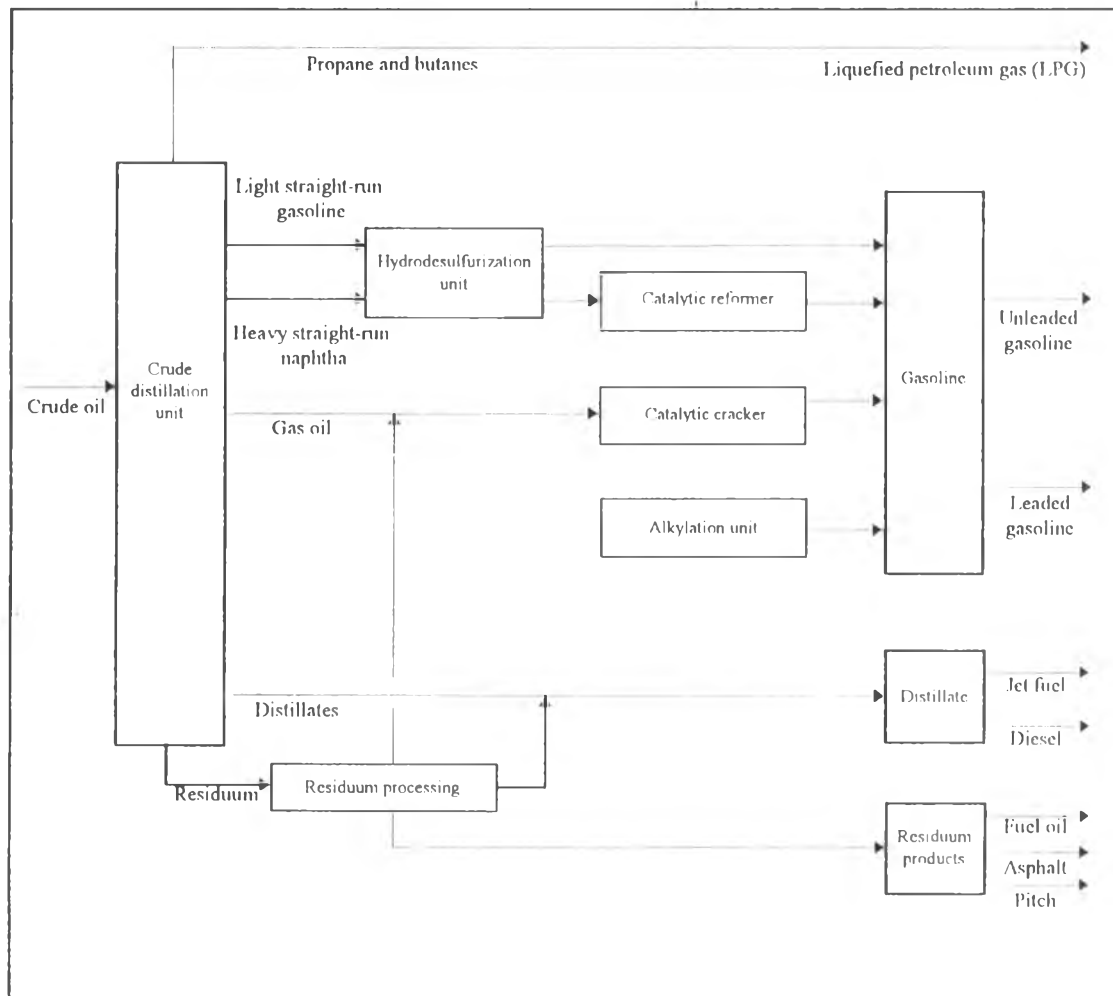


Figure 2.1 Motor fuel refinery with catalytic reforming [4].

### 2.3 Feedstocks for Reforming

The typical feedstocks to catalytic reformers are streams which from crude distillation are light straight run (LSR) naphtha and heavy straight run (HSR) naphtha. Both these streams are in the gasoline boiling range (about 80-400 °F). These are composed of the four major hydrocarbon group: paraffins, olefins, naphthenes, and aromatics (PONA). Typical feedstocks and reformers products have the following PONA analyses

Component	Vol. %	
	Feed	Product
Paraffins (P)	45-55	30-50
Olefins (O)	0-2	0
Naphthenes (N)	30-40	5-10
Aromatics (A)	5-10	45-60

When the stream goes directly to motor fuel, it is called gasoline in the refiner jargon. If the stream (that is, the feedstock) is charged to a process unit, it is generally called naphtha.

In Figure 2.2, the light straight run fraction is hydrodesulfurized and blended directly to gasoline. The pentanes and hexanes in this boiling range are not converted to the desired aromatics in a catalytic reforming unit because they are not good feedstock of this unit. The heavy straight run naphtha is hydrodesulfurized and then charged to the catalytic reforming unit. The product is blended with other refinery stocks to make finished gasoline.

Thus, the feedstock to the catalytic reforming unit from the crude unit is gasoline boiling range hydrocarbons, which are in the raw crude. These are separated from other crude hydrocarbons by fractionation. The gasoline that obtained directly from crude oil (HSR) is almost always of such low octane number that a refiner cannot use it in the motor fuel. The other refinery blending stocks are usually not high enough in octane number to raise the motor fuel blends to the required octane number specification. So the purpose of the catalytic reforming unit is raise the octane number of gasoline to a higher octane number.

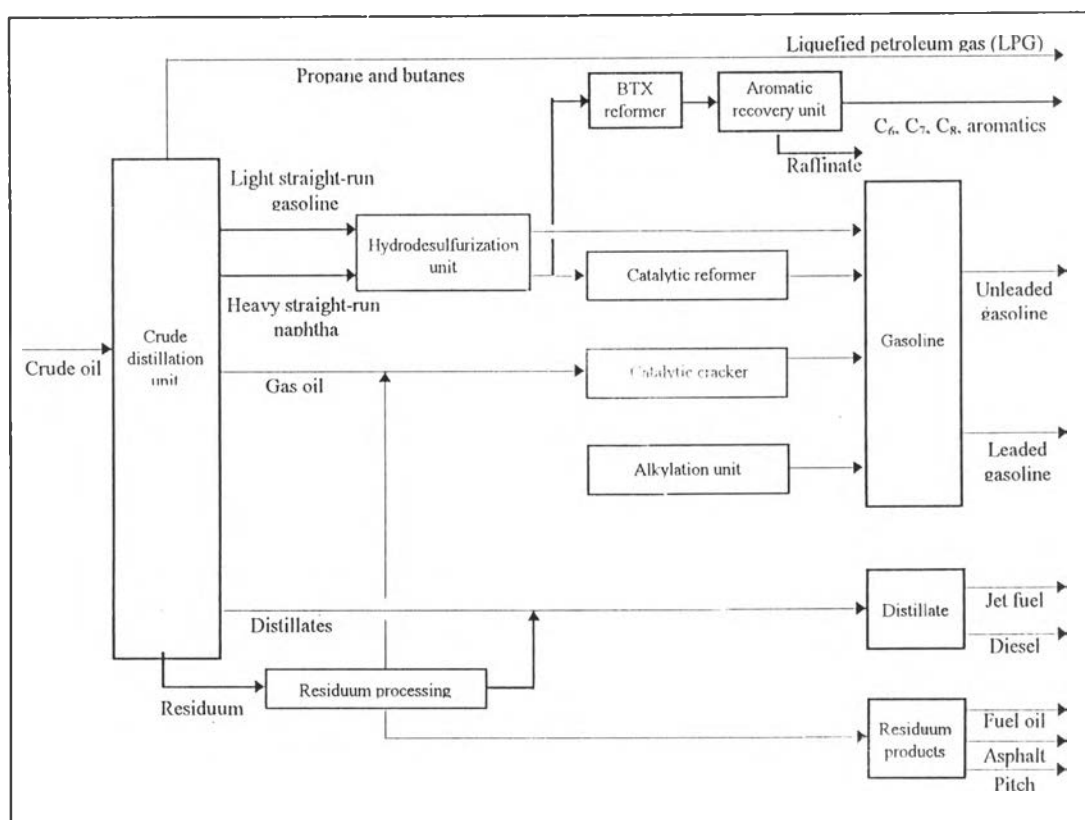


Figure 2.2 Refinery with motor fuel and BTX catalytic reforming [4].

## 2.4 Catalytic Reforming for Aromatics

Although catalytic reformers are most widely used for increasing octane number, many refiners find it economical to reform for certain aromatic hydrocarbons that can be sold as petrochemicals, usually at a much higher price than gasoline. These aromatics are benzene, toluene, and xylenes.

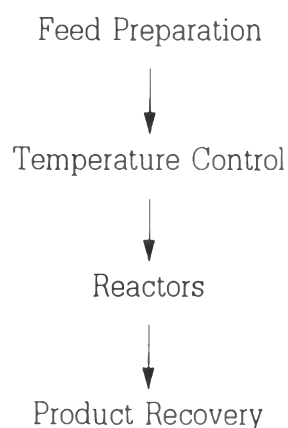
Catalytic reforming unit is particularly suited to yield these aromatics because refinery naphtha feedstocks contain a significant amount of naphthenes, which in the reformer are dehydrogenated to aromatics, and of paraffins, which are cyclized to aromatics. Operating conditions in reformer reactors are such

that aromatics, once formed, are relatively stable and resist destruction or conversion to nonaromatics.

The refinery process scheme of Figure 2.1 must be changed to produce marketable aromatics. A new BTX catalytic reformer would be added. The installation of fractionation and extraction facilities would be required to separate and purify the benzene, toluene, and xylenes to specification-grade aromatics. The feedstock to the BTX reformer would likely be a straight-run naphtha. The refinery configuration would then be as shown in Figure 2.2.

## 2.5 Process Design of Catalytic Reformers

The process design of a catalytic reforming unit follows the basic configuration of most refinery catalytic process units. The generalized flow scheme is:



Each component of the flow scheme is engineered to the needs of a particular process. For example, the reactor of a fluid cat cracker (FCC) differs in size, shape, and metallurgy from that of a catalytic reformer, but each is designed so desired reactions can take place.

The reaction section of an FCC unit rarely has more than one reactor. A catalytic reformer may have from three to five reactors in its reaction section. Variations within a unit are necessary, but the basic flow scheme is still recognizable.

Figure 2.3 shows the basic elements of a catalytic reformer for a step-by-step description of the process.

### **2.5.1 Feed Preparation**

The charge, or feedstock, to the cat reformer is a naphtha that has been processed in a feed-preparation unit to remove contaminants such as sulfur, nitrogen, arsenic, and lead. These contaminants are either temporary or permanent poisons to the catalyst and must be eliminated for satisfactory catalyst performance.

The feed-preparation unit itself is a catalytic unit using a cobalt-molybdenum (Co-Mo) or a nickel-molybdenum (Ni-Mo) catalyst. Hydrogen is included with the feed to the feed-preparation units. These feed-preparation units are called hydrodesulfurization (HDS) units, or hydrotreaters.

After passing over the Co-Mo or Ni-Mo catalyst, the naphtha goes to a stripper or fractionator that removes the hydrogen sulfide, ammonia, water, and light hydrocarbons formed in the hydrotreater reactor. The feed stripper could be either on the tail end of the hydrotreater or on the front end of the reformer. In the flow scheme (Figure 2.3), the reformer naphtha charge is fractionated to the correct end point, probably at the crude unit. Only the initial boiling point is adjusted in the feed stripper.

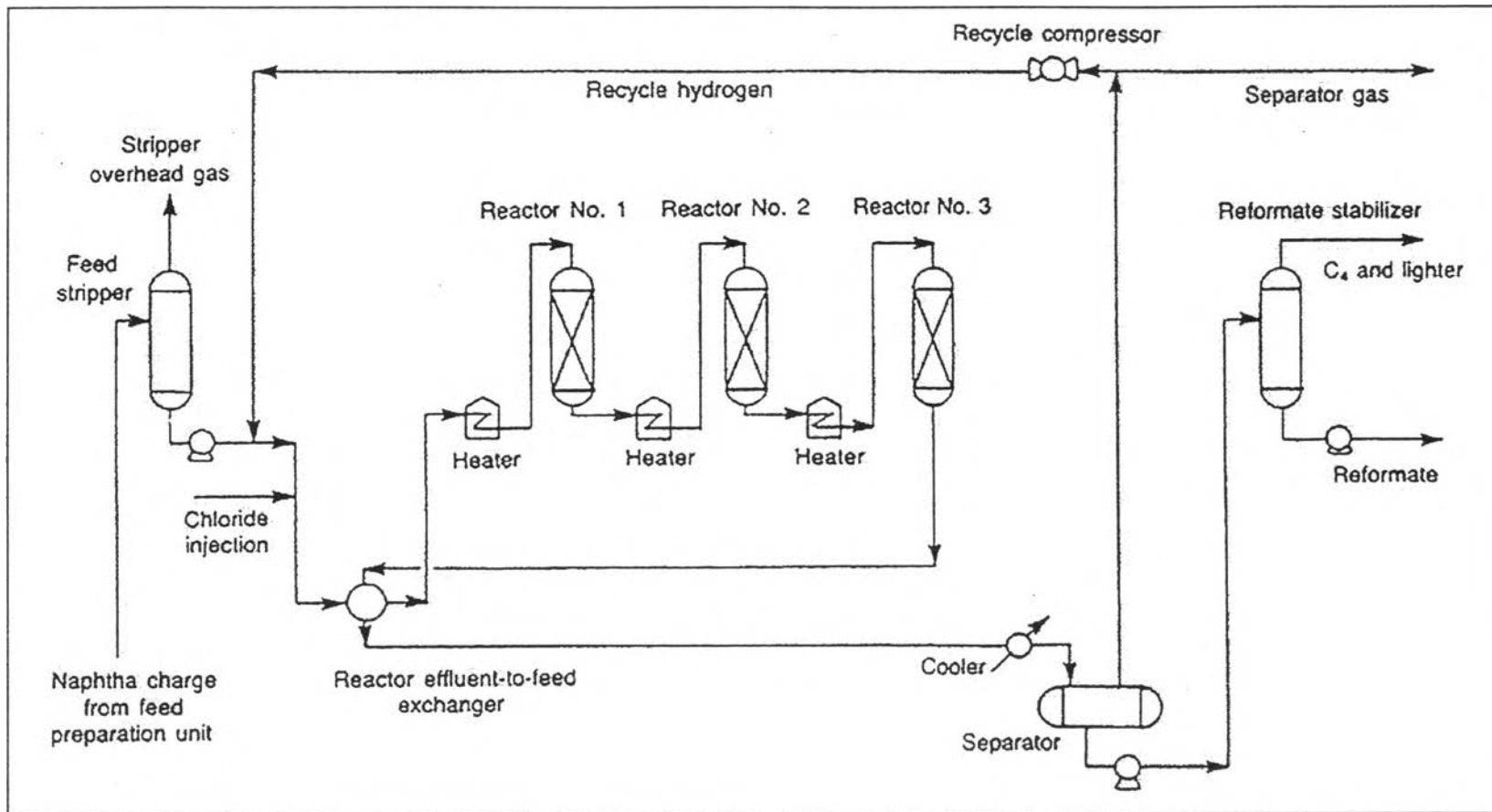


Figure 2.3 Process flow scheme of a catalytic reformer [4].



### 2.5.2 Temperature Control

The reactor charge must be raised to the proper temperature for the reforming reactions to occur when the charge contacts the catalyst. As shown in Figure 2.3, total reactor charge is heated, at first by heat exchange with effluent from the last reactor, and is finally brought up to the No. 1 reactor inlet temperature in the charge heater. (Effluent is total vapor flowing out of the last reactor.)

The reactor effluent-to-feed exchanger is one key to energy conservation in a catalytic reformer. The reactor effluent, which may be at temperature as high as 950-1,000 °F, must be cooled to 90-125 °F for flash separation-separation of vapor and liquid without fractionation of hydrogen from the reformate.

The reactor effluent-to-feed exchanger is sometimes called the combined feed exchanger. This exchanger cools reactor effluent and, at the same time, adds heat to the incoming total reactor charge. In reformers built in the 1950s and 1960s, this heat exchange consists of several banks of heat exchangers, arranged for parallel flow. Newer units use one large single-pass vertical exchanger.

### 2.5.3 Reactor

Catalytic reforming is a vapor-phase process. After passing through the reactor effluent-to-feed exchanger and the charge heater, the total reactor charge is 100% vapor and is ready to contact the reforming catalyst at reaction temperature.

The flow scheme (Figure 2.3) shows three reactors. Reformers have been built with four or five reactors. Although the Figure 2.3 flow sheet shows all reactors of the same size, reactors sizes are different in many units, with the smallest reactor in the No. 1 position and the largest as the last reactor.

Some units originally built with three reactors have been revamped by adding one or more reactors. The additional reactors increase catalyst volume, which permits increased time between catalyst regenerations, increased charge rate, or higher-octane-number reformate.

The major reactions, such as dehydrogenation, are endothermic and very fast. The first contact with catalyst causes a rapid decrease in temperature. Very quickly the temperature in the reactor drops so low that the reaction rate becomes too slow for commercial operation. It is not unusual in the No. 1 reactor to have a temperature decrease between inlet and outlet of 180-280 °F. For this reason, catalytic reformers are designed with multiple reactors and with heaters between reactors to maintain reaction temperatures at operable levels.

As total reactor charge passes through the reactor train (three or more reactors in series flow), the reactions become less and less endothermic and temperature differential across the reactors decrease. In fact, the last reactor may show zero endotherm or, in some cases, a small temperature increase.

The flow scheme of Figure 2.3 shows a separate heater for each reactor. A number of units have heaters arranged this way, but there are also units with two or more heating coils in one large heater. The coils are separated within the heater by a bridgewall arrangement. A bridgewall is firebrick between heating coils.

#### 2.5.4 Product Recovery

The effluent from the last reactor, at temperatures from 950-1000 °F, is cooled by heat exchange with the reactor charge, then further cooled by air and water exchangers to 100-125 °F.

The stream then enters the separator vessel (called the product separator), where flash separation of hydrogen and some of the light hydrocarbons- primarily methane and ethane takes place. The flashed vapor, containing 60-90 mol% hydrogen, passes to a compressor and then circulates to join the naphtha charge from the feed stripper. The hydrogen circulating to the naphtha charge is called hydrogen recycle. Excess hydrogen from the separator is yielded to fuel gas or to hydrogen-consuming units in the refinery hydrotreaters.

The separator liquid, comprised mostly of the desired reformate product but also containing hydrogen, methane, ethane, propane, and butanes, is pumped to the reformate stabilizer or fractionator. Reformate off the bottom of the stabilizer is sent to storage for gasoline blending or, in the case of a BTX reformer, to an aromatic-extraction unit. Some refiners separate the stabilizer to leave sufficient butane in the reformate to meet Reid vapor pressure (Rvp) specifications when making gasoline blends.

#### 2.6 Reformer Classification

The flow diagram of Figure 2.3 is purposely simplified. This reformer can be classed as one of four types of reformers generally used in the petroleum industry. The four reformer classifications are as follows.

### 1. Semiregenerative.

This means the reformer processes feedstock for a time and then shuts down for regeneration and rejuvenation of the catalyst. The time between regeneration is called cycle and is expressed in months (a cycle is sometimes reported as barrels of feed per pound of catalyst). Cycles vary from three months to three years. A cycle may be terminated for a number of reasons, but the most common is poor catalyst performance. This shows up as a loss of reformate yield or as too high reactor-inlet temperatures approaching the maximum allowable for reactor metallurgical construction.

The generation procedure, which includes rejuvenation, restores the catalyst to fresh-catalyst condition. The reformer, as a semiregenerative unit, will have a few connections not shown in Figure 2.3 for regeneration purposes. These connections allow addition of air and nitrogen or oxygen and nitrogen, injection of hydrogen chloride, instrumentation, and neutralizing solution to be circulated. The catalyst in a semiregenerative unit is expected to retain its usefulness over multiple regenerations and to have an ultimate life of 7-10 years or longer.

### 2. Nonregenerative.

Some reformers do not regenerate catalyst because the cycle is long enough for the refiner to justify replacing-instead of regenerating-the catalyst. The reformer of Figure 2.3 can easily operate in this manner.

### 3. Cyclic.

The unique feature of a cyclic reformer is that it has a special valving-and-manifold system so any reactor can be isolated and regenerate catalyst while the other reactors are reforming. In contrast to a semiregenerative reformer,

which requires a shutdown of the entire unit to regenerate catalyst, a cyclic unit can continue operation over long periods between shutdowns. Note, however, that a cyclic unit can operate as a semiregenerative reformer.

Since the usual reason for regeneration is to burn off carbon that has fouled the catalyst, a cyclic unit can reform at lower pressure and higher severity than semiregenerative units, even though rapid coking results. The cycles (switching reactors in a cyclic unit) vary from a few hours to weeks or months. Although the reactors can be operated in any sequence, the last reactor is usually the one taken off-line for regeneration.

#### 4. Moving-bed or continuous catalyst regeneration.

These units, as the names imply, permit the catalyst to be moved continuously through the reactors, to be withdrawn from the last reactor, to be regenerated in a regeneration section, and to be returned to the first reactor as fresh catalyst. Compared to a fluid cat-cracking unit, the rate of catalyst flow in a reformer is very slow. Whereas FCC catalyst circulation is measured in tons per hour, reforming catalyst circulation is a few hundred or a few thousand pounds per hour.

The moving-bed reformer operates in a semiregenerative mode by shutting down the regeneration section. In fact, a number of new units are designed to operate initially as semiregenerative, with the provision that a regeneration section can be added later.

For this work, the case study is the catalytic reforming unit of the plant No. 2 in Bangchak Redinery. It is an important unit conversion the crude to reformate (rich in aromatics), shown in Figure 2.4.

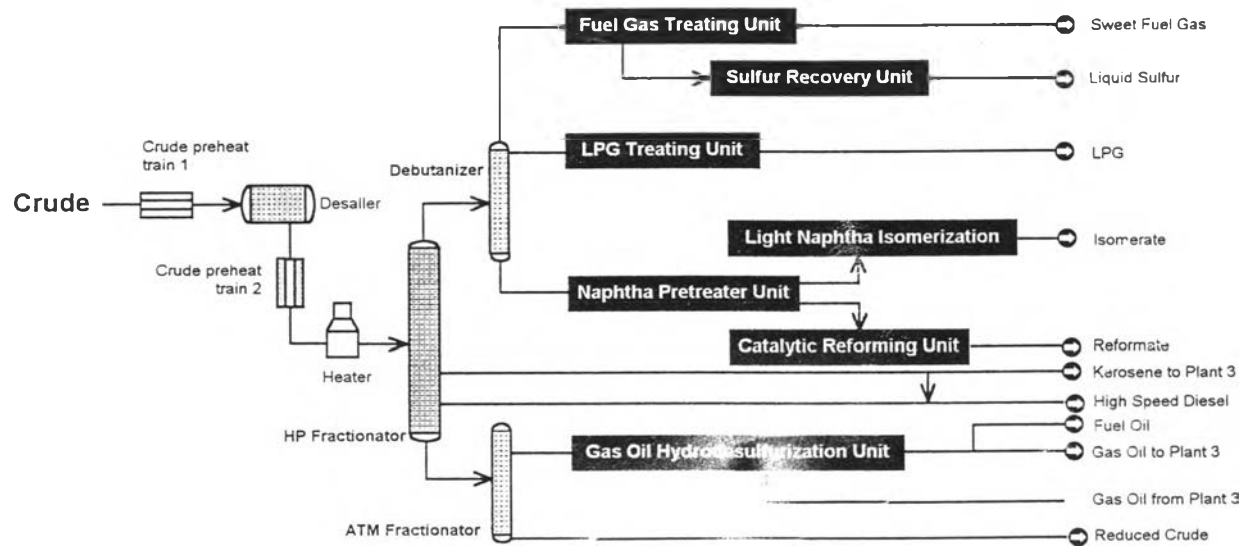


Figure 2.4 Overall Process of Plant No.2 in Bangchak Refinery.