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THE ENVIRONMENTAL PROTECTION MEASURES OF PETRO-CHEMICAL REFINERY INDUSTRIES

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ABSTRACT

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The discovered reserves of oil and gas in the world have increased substantially, and the investment in exploration and development has enlarged. Petrochemical refining and ethylene capacity growth is accelerating. Although the growth rate of energy demand has declined, it is still in the rising stage. Fossil energy is still the main part of the energy structure and will soon become an important part of the energy structure. Therefore, clean energy transformation is imperative and facing challenges.

This thesis work describes the status quo of petrochemical enterprises and the importance of promoting cleaner production, briefly introduces the common processes and devices in petrochemical units, and at the same time gives the treatment methods for oil leakage and pollutant emissions in production. Finally, it analyzes the world's new technologies for the production of clean gasoline, and also extends to the future development trend. It is concluded that the petroleum processing industry should continue to develop in the direction of cleanliness, intelligence and refinement.

Key words
Cleaning technique, Desulfurization, Environmental protection, Fossil Energy, Pollutant emission, Petrochemical, Refinery industry

CONCEPT DEFINITIONS

List of abbreviations

API	American petroleum institute
CDHDS	Catalytic distillation hydrodesulfurization
FCC	Fluid catalytic cracking
FCCU	Fluid catalytic cracking unit
GARDES	Gasoline aromatization and desulfurization
HCN	Heavy cracked naphtha
LCN	Light cracked naphtha
MPa	Megapascal

List of definitions

DEMET	A technology about chemical regeneration of fluid catalytic cracking equilibrium catalyst.
GARDES	Full name is Gasoline aromatization and desulfurization. A technology during gasoline production from Research Institute of Petroleum and Petrochemical & China University of Petroleum.
ISAL	A technology of hydrodesulfurization and octane number recovery during gasoline production from Venezuelan INTEVEP corporation.
ISO	A hydrogenation technology during diesel production from DuPont company using Liquid phase packed bed reactor instead of trickle bed reactor.
Octane Number	Octane number is an indicator of the resistance of the fuel (gasoline) used by vehicles to shock and explosion. The octane number of gasolines directly depends on the proportion of various hydrocarbons in the gasoline. If the octane number is low, the exhaust emissions will increase.
Prime-G, Prime-G+	A technology of Gasoline desulfurization during gasoline production from IFPEnergiesNouvelles.

RID0S	RID0S is a low sulfur and low olefin gasoline production technology from Sinopec Research Institute of Petroleum Processing.
RSDS	A technology of selective hydrodesulfurization during gasoline production from Sinopec Research Institute of Petroleum Processing.
RSH	Mercaptan, general term for non-aromatic compounds containing mercapto functional groups.
RSR’	Thioether, a class of compounds with general formula R-S-R.
RSSR’	Disulphide, a class of compounds with general formula R-S-S-R.
SCANfing	A technology of selective hydrodesulfurization during gasoline production from ExxonMobil corporation.
SLHT	A new hydrogenation technology during diesel production. It is the upgrade of SRH.
SRH	A technology of hydrogenation during diesel production based on a large number of liquid-phase products circulating and carrying dissolved hydrogen into the reaction.

ABSTRACT

CONCEPT DEFINITIONS

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1 INTRODUCTION

On the basis of a summary of cleaner production concepts proposed by many countries, the United Nations Environment Programme defines cleaner production as: a new and creative way of thinking about the production process of products, which means that the production process and products continue to use overall prevention environmental strategy with a view to reducing human and environmental risks. For products, it means reducing the adverse impact of the entire life cycle of the product from raw material use to final disposal. For the production process, it means saving materials and energy, eliminating the use of toxic raw materials, and reducing the amount and toxicity of waste before discharge in the production process. (Wang 2012).

From the definition of cleaner production, it can be seen that the concept of cleaning production is actually aimed at energy saving, consumption reduction and pollution reduction. By replacing toxic products, toxic raw materials and energy, using large amounts of petrochemical refining process and equipment, to improve operation technology and management methods, maximize the use of resources and energy, improve product quality while reducing production costs, and strangle pollution in production. Reducing pollutant emissions and investment in terminal treatment to maximize economic and environmental benefits through above ways. It is based on the production of the enterprise, and the optimization and upgrading are of great significance to the sustainable development of the enterprise.

According to the data from International Energy Agency, petroleum-based fossil energy occupies a chief position in the primary energy demand and energy structure, and will still dominate in the future (IEA 2020). With the further improvement of people's living standards worldwide, the awareness of environmental protection keeps rising, therefore the contradiction between industrialization development and environmental quality will become more acute, and the world's requirements for clean-fuel standards also increase continuously. For this purpose, the promotion of clean production has an important significance. Green and low-carbon lead to enormous changes in the energy landscape. The shortage of energy resources, the deterioration of the ecological environment, and the aggravation of climate change have become global challenges. Since the 21st century, sustainable development has gradually become a consensus. Countries are paying more attention to low-carbon environmental protection and have issued a series of important policies to restrict or slow down the use of traditional energy. For example, in 2011 in Europe, all gasoline and diesel fuels were required to have a sulfur content of less than 10 μg/g (Wang & Wang 2017, 8), further restricting olefins and aromatic hydrocarbons in gasoline and fused aromatic hydrocarbons in diesel fuel. Faced with increasingly prominent environmental pollution and resource constraints, the world's energy has accelerated its transition to diversification, cleanliness, and low carbonization. Clean production in the refining chemical industries must reduce pollution from the source, adopt advanced process technology and equipment and other measures to improve resource utilization efficiency, reduce or avoid the generation and emission of pollutants, in order to reduce or eliminate the harm to human health and the environment. (Li 2009).

This thesis is a literature review, without laboratory work. In the situation of environmental protection measures and green production requirements for petrochemical enterprises are increasingly strict controlled by the world. Based on the previous research on pollution treatment. This thesis is aim to summarize and analyze the main treatment measures for pollution emissions and the technologies used in the production of petroleum products, speculate about future challenges, put forward corresponding countermeasures against it, and point out the next research direction.

2 THE SIGNIFICANCE OF CLEANING PRODUCTION AND SITUATION OF PETROCHEMICAL REFINERY INDUSTRY

The emergence of cleaner production is the historical necessity of the rapid development of human industrial production. In 1960s and early 1970s, due to the rapid economic development, the world ignored the prevention and control of industrial pollution, resulting in increasingly serious environmental pollution. (Zhang 2011).

The environmental problems have gradually attracted the attention of governments of all countries, and corresponding environmental protection measures and countermeasures have been taken. However, through the ceaselessly practice, it has been found that this method, which focuses on the control of emissions (in the terminal), makes the discharged pollutants reach the discharge standard. Although terminal treatment plays a certain role in a certain period of time or in some areas, it does not fundamentally solve the problem of industrial pollution. Because of the development of production and the increasing variety of products, as well as the improvement of people's environmental awareness, more types of pollutants discharged from industrial production, the emission standards of regulated pollutants (especially toxic and harmful pollutants) are stricter, and the requirements for pollution control are also higher. (Shi 2015).

In order to meet the requirements of emission, enterprises need to spend a large number of funds which increases the cost of governance to a large extent, but still, some requirements are hard to meet. Besides due to the limited technology of pollution control, it is difficult to eliminate pollution completely. Because the general method of terminal pollution control is to pass necessary pretreatment first, and then conduct biochemical treatment before discharge. However, some pollutants are not biodegradable pollutants, only diluted emissions, which not only pollute the environment, but also cause secondary pollution if they are not properly treated. Some of the pollutants only transfer physical form. Waste gas becomes wastewater, wastewater becomes waste residue, waste residue is stacked and buried, which pollutes soil and groundwater, forms a vicious cycle and destroys the ecological environment. Only focusing on the terminal treatment method will not only investment is needed, but also some recyclable resources (including unreacted raw materials) are not effectively recycled and lost, resulting in increased consumption of raw materials, increased product costs, and reduced economic benefits, thus affecting the enthusiasm and initiative of enterprises in pollution control. Therefore, the promotion of cleaner production must be carried out from the start and the terminal at the same time. (Shi 2015).

Cleaner production is the technical carrier of circular economy, which is also an effective way for sustainable development of economy, protection of ecological environment and rational use of resources. With the rapid development of human civilization, the rapid deterioration of the global ecological environment is a major crisis facing human development in the 21st century, which has become one of the focuses of the international community. At the same time, as a long-term dominant resource in the energy structure, oil production scale is gradually increasing, and the change of the nature of crude oil means that it may bring more pollution and more resources utilization. (Wang & Wang 2017).

Fossil energy accounts for 80 % of the world's energy structure, and oil plays an main role in it. The fluctuation of the oil industry will cause changes in the world's politics, economy and lifestyles of human. According to the investigation, the importance of oil will not change much in the next few years or even decades (IEA 2020). As a highly polluting energy industry, oil refining is generally subjected to high-temperature and high-pressure conditions in its production process, and it has strong destructive power to the natural environment. Some of the materials produced are flammable, explosive and poisonous. If the environmental protection work of oil refining engineering will not be strengthened, then soon, the social and economic benefits brought by petroleum energy will be offset by the losses caused by environmental degradation. Today, the world's refining and chemical industry has matured, and petrochemical products are developing in a more professional and refined direction, and facing difficulties such as shortage of resources, energy shortage and environmental pressure. In order to facilitate the centralized processing and utilization of oil products, to achieve efficient and reasonable utilization of energy and optimization of technological processes, to save the unit input costs of safety facilities, the average scale of petrochemical refinery processing has gradually increased (TABLE 1) (Robert 2015).

TABLE 1. The average size of world petrochemical refinery (Adapted from Wang & Wang 2017, 9)

Region	2000s 10^4tons	2010s 10^4tons	2015s 10^4tons
Asia Pacific	492	754	878
Western Europe	689	724	750
Eastern Europe	564	583	615
Middle East	666	823	836
Africa	355	358	373
North America	558	701	752
South America	477	499	441

The table above reflect the coverage of pollution emissions of the petrochemical refinery will be wider. At the same time, from the current situation, crude oil is becoming heavier and lower in quality world-wide. (TABLE 2). However, according to OPEC's forecast, the market's demand for light oil is gradually increasing, and the cleanliness of oil products is becoming stricter. (Wang & Wang 2017).

TABLE 2. Changes in the nature of world crude oil (Adapted from Wang & Wang 2017, 9)

Term	2000s	2010s	2015s
API gravity	32.5	32.4	32.3
Sulfur content (%) in crude oil	1.14	1.19	1.25

With the continuous deterioration of resources, under the changing market structure and strict environmental protection requirements, it is very important to strengthen the emission control and the improvement of new technology in production. It can not only save enterprise funds , but also reduce the damage to the environment. (Wang & Wang 2017).

3 PREVENT OIL LEAKAGE

Petroleum is a relatively complex mixture, mainly composed of hydrocarbons and non-hydrocarbons, of which hydrocarbons account for 95 %-99.5 %, and non-hydrocarbons are mainly oxygen, nitrogen, sulfur, chlorine, silicon, phosphorus, non-metallic elements and a small amount of heavy metal elements. The oil mainly refers to crude oil and its preliminary processed products (including gasoline, kerosene, diesel, heavy oil). These petroleum products are highly toxic to humans and animals, especially aromatic hydrocarbons represented by polycyclic and tricyclic rings. They can enter humans or animals through breathing, skin contact, and dietary intake, affecting the normal function of liver, kidney and other organs function seriously or even cause cancer. In addition, it also has the effect of interfering with and destroying the living environment of creature and affecting the normal physiological functions of living organism, so it needs to be paid more attention to. (Chang 2008).

In many cases, the pollution caused by crude oil leakage in refining and chemical enterprises is easily despised. Most people pay attention to the emission of pollutants. In fact, the transportation of crude oil from oil field to petrochemical refinery factory is a long process, which leakage will happen frequently, and the damage caused by the leakage of crude oil is much more serious than expected. For example, the oil spill in the Gulf of Mexico in 2010s caused the local marine life to be destroyed, and many species even died out. At the same time, it caused a more terrible impact under the sea level: a large number of corals died, and the food chain was interrupted, resulting in a vicious cycle of ecology. The local fishery production was reduced, and the economic loss was incalculable, at the same time residents were facing serious health problems. (Zhao 2010).

3.1 Pollution from oil leakage

Pipeline transportation is a common method in petroleum transportation. Over time, the steel pipe will react with the surrounding environment, resulting in corrosion of the steel and cause crude oil leakage (Wang & Li, 2012). When oil leaks into the soil, oil contaminants will invade all corners of the soil along the void channels in the soil. In the process of spreading in the soil, pollutants will change the water permeability and permeability of the soil and will change the proportion of organic matter in the soil. In addition, because there are aquifers, groundwater and air in the soil, its pollutants will also affect the safety of surface water and air. (Yu 2019).

Petroleum contaminants are a relatively complex mixture, which contain some soluble salts. These salt substances enter the soil together with the pollutants and accumulate and move in the soil, causing the salinization of the soil. The hydrolysis of these accumulated salt substances in the soil changes the acid-base balance of the soil, which may cause the change of soil pH. (Yu 2019).

When the soil is contaminated by leaked oil, the groundwater and soil are connected, so once the soil is contaminated, the water body it contains is also contaminated. Petroleum hydrocarbons entering the water body will change the physical, chemical and biological characteristics of the water and affect its original function. First, the salt substances contained in the petroleum pollutants will be hydrolyzed to change the acidity and alkalinity of the water, and the oils they contain exist in the form of floating oil, dissolved oil, emulsified oil. Consumption of 3-4 mg of oxygen, when the thickness of the oil film on the water surface is greater than 1 micron (Guo 2019), can isolate the exchange between the water body and the air, resulting in the decrease of dissolved oxygen in the water, causing the organisms in the water to die due to lack of oxygen, resulting in the water body deterioration makes the water body lose drinking and other functions; secondly, the long-term use of oil-contaminated water bodies for irrigation of crops will cause secondary pollution of the soil and will also have toxic effects on the crops, such as affecting the lodging resistance, the ability of pests and diseases directly leads to a reduction in crop yields. (Li, Yu & Liu 2017).

Typical crude oils can lose up to 45 % of their volume by evaporation in a few days (Fingas 2015). The petroleum contaminants that invade the soil also contain some volatile organic compounds (mainly low-boiling components). Under certain environmental conditions, these volatile components will volatilize into the atmosphere and pollute the air. Various poisoning symptoms will occur after people and animals breathe the polluted air. For example, acute poisoning of benzene starts from the respiratory tract. Leukemia and immune system destruction can occur when exposed to an environment with a concentration of less than 44 mg/L. Therefore, how to deal with the air in the polluted soil also needs people's attention. (Yu 2019).

3.2 Cleaning measures to the leakage

The best method to clean the oil leakage is to ensure the sealing during transportation (Wang & Li 2012 8). Oil is mainly transported through pipelines or oil tanks on vehicles, so appropriate pipelines and tanks should be used to prevent leakage and reduce oil volatilization. Even if the oil leakage is caused by uncontrollable force, there are some methods that can be used to deal with the leaked oil and avoid pollution as much as possible. (Zhong, Wang & Sun 2018).

3.2.1 Measures to prevent leakage

The suitable storage tank can be selected, and more advanced sealing technology can be used. Oil tanks with external floating roof or internal floating roof have a good protection for light crude oil. These kinds of tanks can effectively control the evaporation of crude oil and avoid the safety hazards caused by low-flash point and light components. Concerning to heavy oil, horizontal dome-roof tank should be used in the transportation. (Zhong, Wang & Sun 2018).

Strengthening the control of oil pipeline is an important method to control the leakage. Improve the cleanliness of oil pipeline is to control the extent of corrosion. Pre-plating steel on the inner surface of pipeline to control the corrosive gas content. Simultaneously also process the outer surface to ensure the rigidity of the pipeline. During pipeline installation, the connection area needs to be inspected carefully to ensure the quality of tightness, the performance of the pipeline must be strictly tested before used. After application, regular inspection is required. Use pipeline leak detection technology which will analyze the pressure and flow to find the leak at the first time. By using the anti-corrosion methods above, it is effective to deal with leakage in pipeline. (Wang & Li 2012).

Another way to reduce oil leakage is to prevent evaporation. Prevent the evaporation of oil gas is to conduct comprehensive inspection of pipeline breathing valves and hydraulic safety valves to guarantee the normal working condition. And need to make maintenance frequently. The oil hole, the light transmission hole and the sealing of the valve should also be checked frequently to reduce the evaporation and avoid the leakage of oil. Changes in temperature will cause changes in the physical properties of petroleum, therefore reduce the evaporation of oil by reducing the oil temperature changes which need cooling measures such as installing spray-water device on the oil tank, adding an insulating layer on the surface of the oil tank, and applying light-colored paint on the oil tank. At last, collect the vaporized oil by using gas collection tanks, absorbers and recovery devices to prevent air pollution caused by the evaporation of oil gas are necessary. (Zhou 2018).

3.2.2 Remediation of the environment that has been contaminated by the leak

Today, there are physical methods, chemical methods and bioremediation to deal with the pollution from the leakage. Physical method refers to a method of treating and repairing contaminated soil by physical means, mainly including isolation method and incineration method. The isolation method is relatively simple, which refers to the use of clay or other substance to isolate the pollution of the oil spill from the surrounding environment. The advantage of this method is that the repair cost is lower, and it is suitable for areas with poor permeability. It simply prevented the migration of pollutants, cannot deal with pollutants, so this method cannot be used as a permanent repair method. The incineration method utilizes the characteristics of petroleum-based materials that are easily combustible or volatile under high temperature characteristics, so that the pollutants are separated from the soil to achieve the purpose of treating petroleum pollutants. Calorific value and moisture content need to reach the requirements in this process. The advantage of this method is that the treatment method is relatively simple, but it contain serious disadvantages, such as the organic matter composition of the burned soil will also burn, which will make the soil lose the ability to continue farming crops; in addition, the process of burning petroleum pollutants will produce toxic and harmful gas will cause secondary pollution. (Wen & Zheng 1994).

Commonly used chemical treatment methods include dosing, soil washing and extraction in chemical remediation. The dosing method is to drill a certain wellhead in the contaminated soil and then inject a certain amount of chemical oxidant (commonly used oxidants are chlorine dioxide, hydrogen peroxide, potassium permanganate) or straight directly spray the contaminated soil and achieve the purpose of purifying the contaminated soil through chemical reaction with it. The advantages of this method are short time, high efficiency and low cost, but the disadvantage is that the injected oxidant will destroy the original organic matter and living microorganisms in the soil due to its strong oxidizing properties. (Turlough, Stuart, Terry & Brent 2002).

The law of soil washing is to prepare active agent and water into a certain solution to wash the contaminated soil. Related studies have shown that petroleum contaminants are not attached to all soil particle surfaces but only to some soil particles such as clay and silt. Therefore, before washing the contaminated soil needs to be screened and classified. The disadvantage of this method is that the operation is more complicated, and it is only suitable for multi-void and permeable soil. (Yu 2019).

The extraction method is based on the principle of similar miscibility, using corresponding organic solvents to extract organic pollutants in contaminated soil and then separate and recover. The advantage of this method is that it can maximize the recycling of resources, but the disadvantage is that the process is complicated, the cost is high, and it is only suitable for soil pollution in a small area. (Yu 2019).

Biotechnology to treat soil oil pollution is a relatively new method of soil remediation. The principle of this method is based on the fact that petroleum pollutants are also an organic matter, and most of the organic matter is degradable. Therefore, this method uses the absorption and transformation of microorganisms or other organisms to convert the pollutants into harmless carbon dioxide (CO_2) and water (H_2O). In this way, the pollution of the soil is reduced or even removed. Studies have shown that the total amount of microorganisms degrading oil in the soil accounts for 0.13-0.5 % of the total bacteria. When there is oil pollution, the number of microorganisms will increase to more than 10 % (Li 2004). At present, more than 200 kinds of microbial remediation technologies such as bacteria, fungi and algae can be used. It is generally believed that fungi decompose crude oil easier than bacteria, and bacteria are stronger than algae. In the process of microbial remediation, the intensity of soil pollution, the nature of the soil, and environmental conditions (temperature, humidity, pH.) will affect the degradation rate of pollutants due to the activity of microorganisms and enzymes. According to the way of treating soil, it can be divided into in-situ repair and ex-situ repair. In actual engineering applications, both are applied. In summary, the microbial treatment technology is relatively simple in operation, low in cost and strong in site adaptability, followed by low cost, no secondary pollution and good treatment effect, with significant social and environmental benefits. (Hu 2008).

4 MAIN UNITS AND PROCESSES OF THE PETROCHEMICAL REFINERY

The general petrochemical refinery is mainly composed of petrochemical refining process units and auxiliary facilities. The role of refining process unit is to process crude oil into liquid light fuel and heavy fuel, including gasoline, kerosene, light diesel, heavy fuel including heavy diesel and special fuel for boiler. In addition, the crude oil can be decomposed into lubricating oil, gaseous hydrocarbon, liquid hydrocarbon, chemical raw material, asphalt, petroleum coke, paraffin. Through the refining process unit. The typical production units are as follows. (Li 2009).

In the whole process of crude oil refining, the first main process is atmospheric-vacuum distillation (FIGURE 1). Atmospheric-vacuum distillation process includes desalting and dehydration of crude oil, initial distillation, atmospheric distillation, and vacuum distillation. During desalting and dehydration, the crude oil extracted from the underground contains a certain proportion of water, which contains mineral salts. If the water content in the crude oil is large, it is not conducive to the stability of the distillation tower and easy to damage the distillation tower. In addition, the excessive moisture will delay the heating time, increase the heat absorption, and increase the cost of raw materials. The mineral salt contained in the water will produce corrosive salt scale in the distillation process, which will be attached to the pipeline, and will increase the flow resistance of the crude oil, slow down the flow speed, and increase the fuel consumption, so the crude oil needs to be desalted and dehydrated. In initial distillation process, after desalting and dehydration operation, the crude oil shall be heated by heat exchanger. When the temperature reaches 200-250 ℃, it can enter the initial distillation tower. Here, the residual water, corrosive gas and light gasoline in the crude oil are discharged, which reduces the burden of the tower, ensures the stable state of the tower, improves the product quality and recovers as much crude oil as possible. When it comes into atmospheric distillation, the oil from the previous step enters the atmospheric furnace through the delivery pump and is heated. The heating requirement is about 360 ℃, and then enters the atmospheric tower. After condensation and heat exchange, some of the oil gas separated from the tower top become gasoline, some become kerosene and diesel. The last is vacuum distillation, main process unit of vacuum distillation is the vacuum tower, which is used for secondary processing and deep processing of heavy oil from the atmospheric tower. (Li 2009).

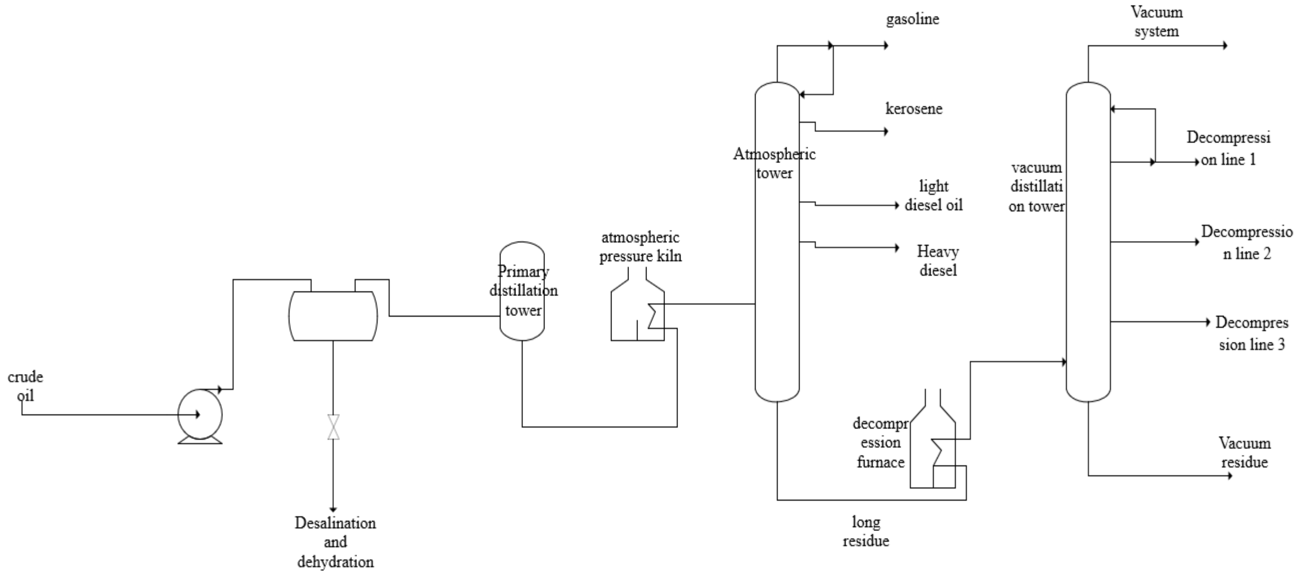

FIGURE 1. Atmospheric-Vacuum distillation unit (Adapted from Li 2009).

Depending on the demand, crude oil may also be delivered to Fluid Catalytic Cracking Unit (FCCU), the raw material in the process of FCCU is heavy oil that needs secondary processing and deep processing. Through this process, heavy oil can be split into light oil we need. The main steps include reaction regeneration system, fractionation system, absorption stabilization system. In reaction regeneration system when the heavy oil from atmospheric-vacuum distillation unit is heated to 400 ℃, it is pumped into the lifting reactor, combined with light oil refining, and then contacted with catalyst to generate vaporization reaction. The inlet steam is blown into the lifting reactor to achieve the lifting effect. The whole reaction of fluid catalytic cracking (FCC) takes place in the lifting reactor, only cost a few seconds, and then the oil gas leave along the top of the lifting reactor. During fractionation system, the oil gas after the upper sequence reaction then enter the fractionator. Through the role of the fractionator, the intermediate products such as FCC rich gas, crude gasoline, oil refining and oil slurry are produced. FCC rich gas and crude gasoline enter the next system, absorption stabilization system. In absorption stabilization system rich FCC gas enters into the air compressor for boosting and cooling, so there is condensed oil, which is pumped to the bottom of the absorption tower. The crude gasoline enters the top of the absorption tower in the form of absorption liquid to absorb the carbon molecules inside to produce rich absorption oil. The rich absorption oil and condensed oil are mixed together, and enter the top of desorption tower through pump, then enter reabsorption tower and stabilization tower. Finally, liquefied gas and stable gasoline are separated (FIGURE 2). (Li 2009).

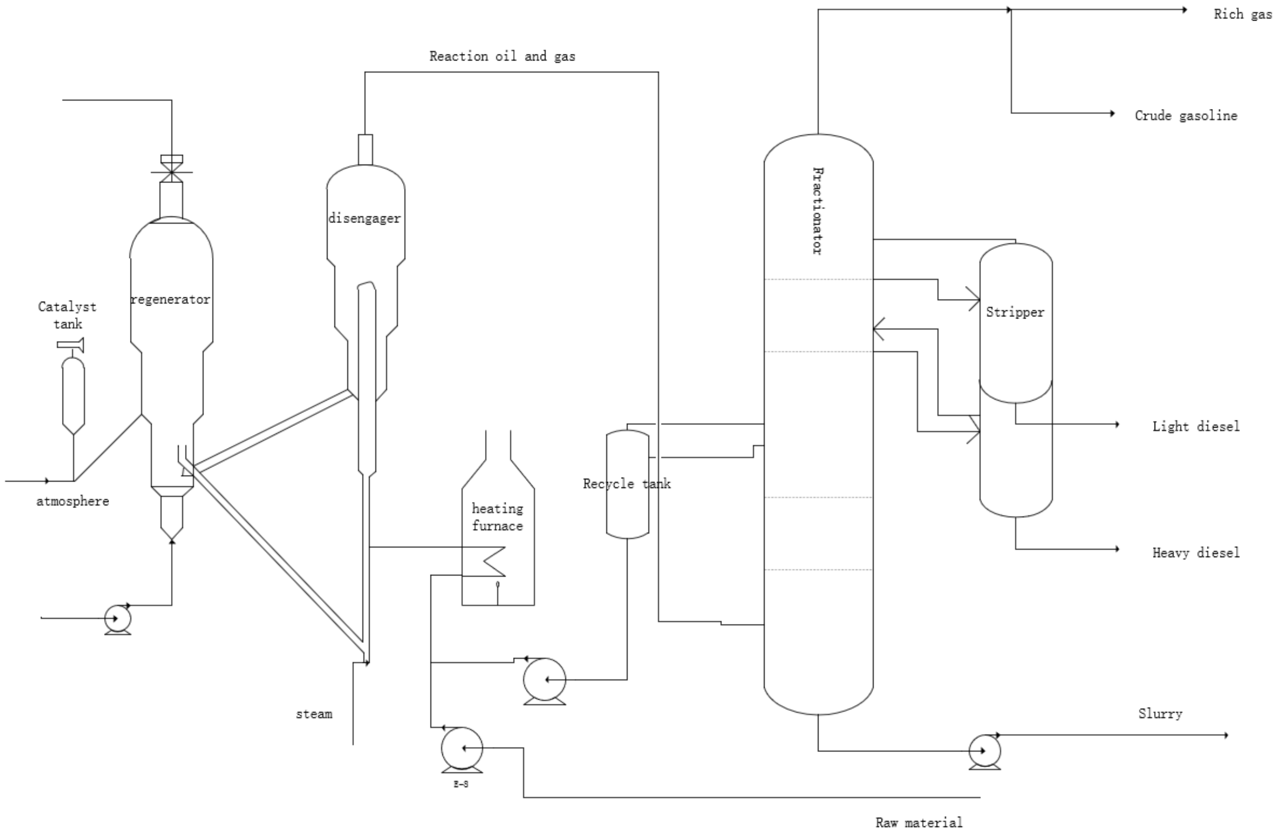

FIGURE 2. Fluid catalytic cracking unit (Adapted from Li 2009).

If the petroleum products with high octane number and aromatics are produced, catalytic reforming is required. The catalytic reforming process includes pre-fractionation and pre-hydrogenation, reforming reaction, post hydrogenation and stabilization treatment, catalyst regeneration. At first, in pre-fractionation and pre-hydrogenation, pre-fractionation refers to the removal of light fraction below 60 ℃ in the pre-fractionation tower and the purpose of pre-hydrogenation is to remove the toxic substances such as arsenic, sulfur and nitrogen that affect the activity of catalyst, to saturate the olefins so as to reduce the carbon deposition on the surface of catalyst, also prolong the service life of catalyst. After the end of the previous step, the product meets and mixes with the circulating hydrogen, then enters the reforming reactor after heat exchange and heating. The temperature inside is 500 ℃. This reaction is mainly a strong endothermic reaction. Reforming reaction is usually carried out in several stages, which is mainly to avoid temperature drop rapidly of each reaction. (Zeng 2009).

The whole reaction is divided into several sections, which not only ensures that the reaction temperature meets the requirements, but also ensures the quality. of the whole reaction. In post-hydrogenation and stabilization, it is difficult to extract olefins under unsaturated conditions, So post-hydrogenation will need to make olefins saturated as much as possible to achieve the purpose of extraction. The reaction temperature of post-hydrogenation is 320-370 ℃, and the whole process is carried out by catalyst. The last important step touch on catalyst regeneration, catalyst also has a certain service life, the main impact is that when the surface carbon deposition is too much, the catalyst will fail, so reducing the carbon deposition on the catalyst surface can greatly extend the service life of the catalyst. Regeneration of catalyst mainly refers to combustion of catalyst in nitrogen to eliminate carbon deposition on the surface (FIGURE 3). (Zeng 2009).

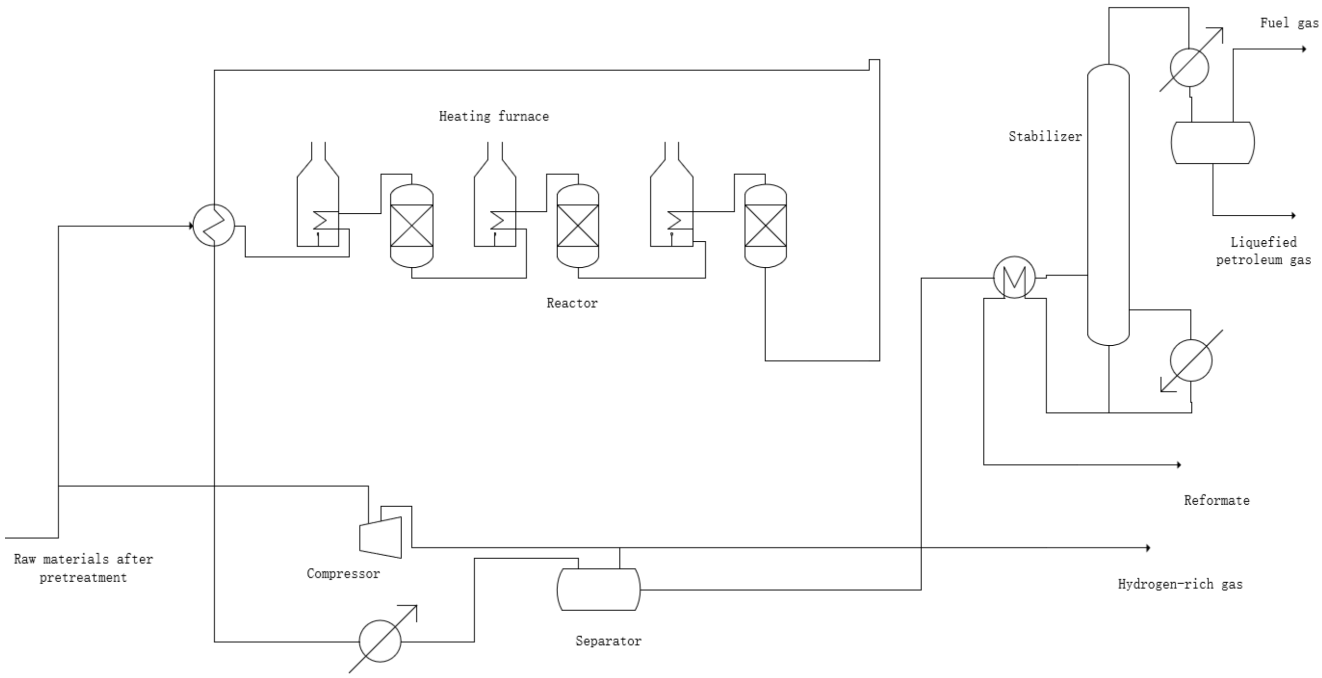

FIGURE 3. Catalytic reforming unit (Adapted from Li 2009).

Hydrofining is an important process for desulfurization and changing octane number in petrochemical industry, hydrofining requires a wide range of raw materials, which can be used for both gasoline kerosene and heavy oil. Its main process includes heating reaction, separation of generated oil. During heating reaction, the raw material meets and mixes with the circulating hydrogen. After heating to the reaction temperature, it enters the reactor and reacts through the catalyst layer. In the reactor, the catalyst is placed in layers and plays a good catalytic role. In separation of generated oil, after the reaction of the previous sequence, the product is separated from oil gas in the separator. The output gas is hydrogen and hydrogen sulfide in circulation. The other product hydrogenated oil in the separator needs to enter the fractionator for further operation until the products such as gasoline and diesel are separated (FIGURE 4). (Zeng 2009).

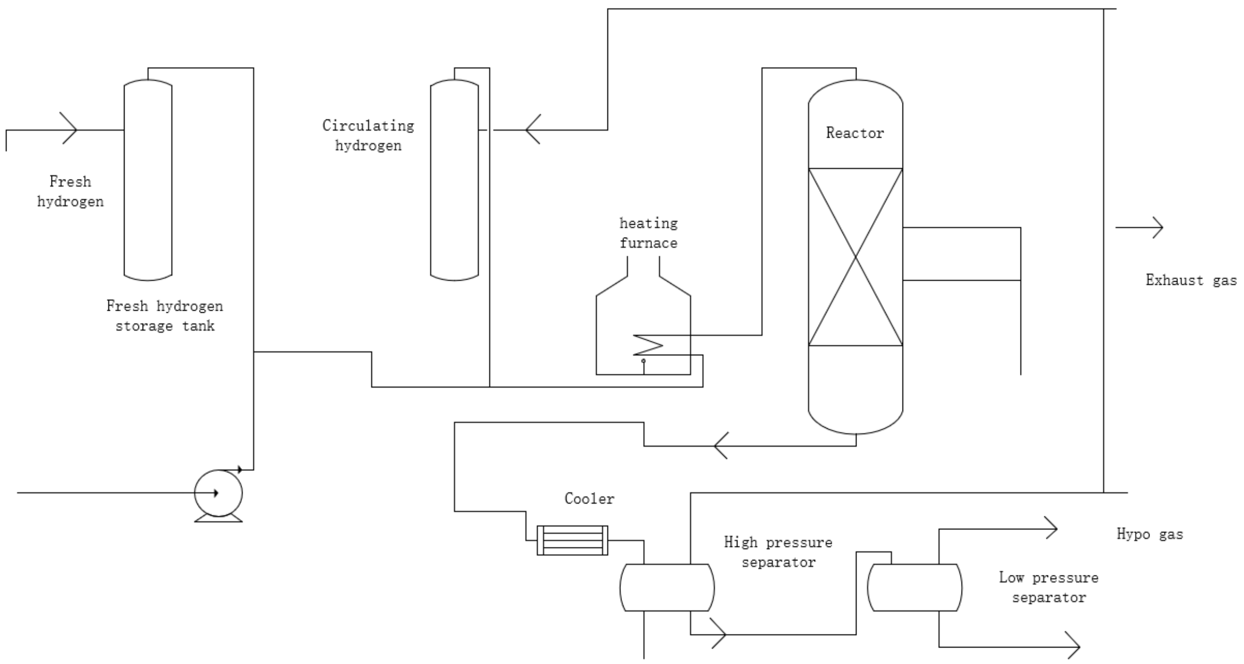

FIGURE 4. Hydrofining unit (Adapted from Li 2009).

In the main process of delayed coking, after heating, the temperature of the raw oil reaches 350 ℃, and then it enters the bottom of the coker fractionator for heat exchange with the coker. In this way, not only light oil can be produced, but also raw materials can be continuously heated at the same time. The product is heated before entering the coke drum. Then the products are pyrolyzed and condensed in coke tower. High temperature oil gas come out of the coke tower and enter the fractionating tower. After fractionation, coking gas, gasoline, diesel and circulating oil are produced. The process unit behind the fractionator is the coke drum. After using the coke drum for a period of time, pay attention to the internal decoking, otherwise will affect the service life of the coke drum and the product quality (FIGURE 5). (Zeng 2009).

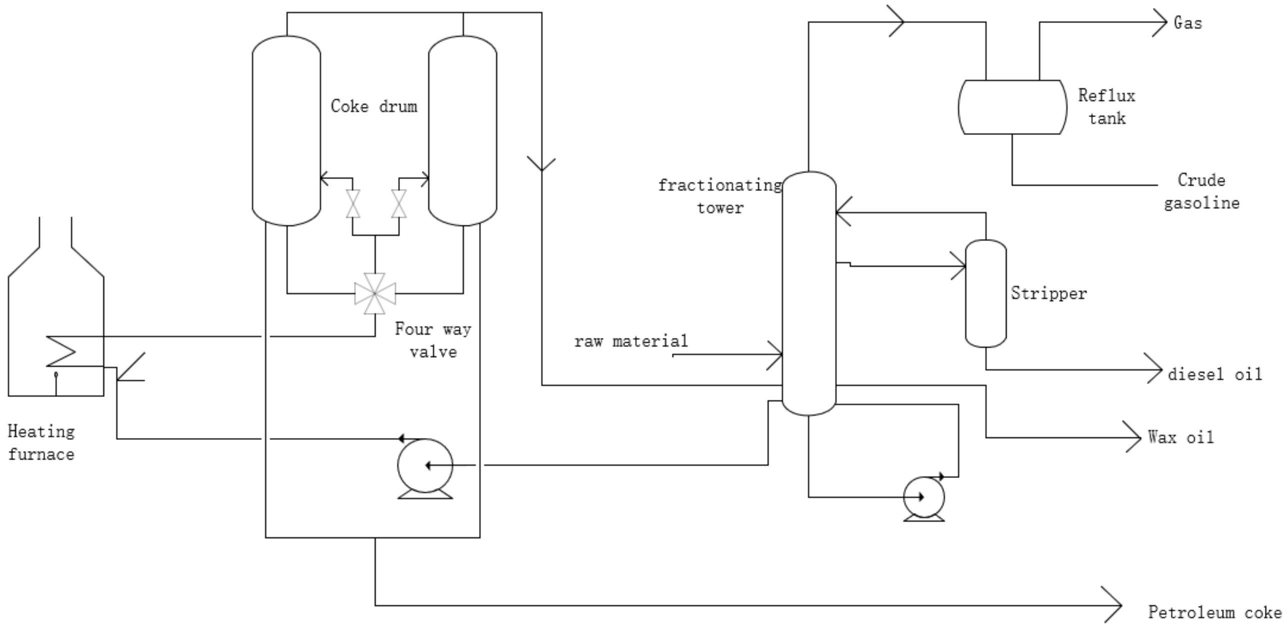

FIGURE 5. Delayed coking unit (Adapted from Li 2009).

The above mentioned five aspects are brief description of the refining and chemical units. It can be seen that the refining and chemical processing of petroleum is an extraordinarily complex process. In these complex processes, there are many device processes that can be improved to achieve the goal of cleaner production. (Zeng 2009).

5 ENVIRONMENTAL PROTECTION MEASURES IN EMISSIONS FROM PETROCHEMICAL REFINERY INDUSTRIES

For the discharged pollutants, enterprises should pay attention to the optimization of technical structure in the production process as well as the end treatment to reduce the emissions. For the inevitable waste, they should use a variety of comprehensive treatment methods to strive for no residue. At the same time, try to recycle the recyclable pollutants as resources. In this way, not only the enterprise funds will be saved, but also meet the world's emission standards, so as to be responsible for human society and the environment.

5.1 Air pollution and treatment measures

Before the analysis of air pollution, it is necessary to understand the main components of air pollutants, their main properties and mechanism of action. During the petroleum refining process, hydrogen sulfide, nitrogen oxides, sulfur dioxide will be emitted into the air (Guo 2008, 7). They are also common pollutants in the atmosphere which have caused economic and health losses to people. Many of the losses are irreversible which cannot be simply repaired and cleaned (Huang 2004, 17).

5.1.1 Air pollutants

In the process of oil mining and petroleum refining, a large amount of hydrogen sulfide gas will be produced. The main sources of hydrogen sulfide in the refining production process are some raw oil and most natural gas, hydrogen sulfide can be present in other raw materials or products in the refining process. Even a small amount of hydrogen sulfide will appear during the maintenance of the equipment. Hydrogen sulfide can be produced in many devices, such as atmospheric-vacuum distillation units, FCCU, delayed coking units, and hydrocracking units. When refining sulfur-containing crude oil, under the action of high temperature and catalyst, the polymer organic sulfide is decomposed and reduced to hydrogen sulfide and other low molecular sulfides. Hydrogen sulfide is a strong nerve toxicant and has stimulating effect on the mucosa. At low concentration, hydrogen sulfide will cause local irritation of the respiratory tract and eyes. The systemic effect on the person will be more critical with the higher concentration, showing symptoms of central nervous system and asphyxia. (Guo 2008).

Another generated pollutant is sulfur dioxide, the harm of sulfur dioxide is multifaceted. It will not only damage the respiratory tract of humans and mammals, but also damage the genetic material of animals. In addition, the damage of sulfur dioxide to the environment, especially the plants and microorganisms in the environment, cannot be ignored. Sulfur dioxide in the flue gas is discharged into the atmosphere and then exposed to light. Oxygen and particulate matter in the atmosphere catalyze chemical reactions to produce acidic substances such as sulfuric acid under multiple conditions, when pH changes, the growth of aquatic organisms and crops will be affected. When the pH is less than 6, most crops cannot survive, when the pH is less than 5.5, fish cannot survive, and when the pH is less than 4, most existing organisms will die. (Huang 2004).

The petrochemical refinery is the main source of sulfur dioxide emissions from the petrochemical industry. According to the EPA's statistics of 145 refineries in the United States in 1999s, the annual sulfur dioxide emissions of the petrochemical refinery alone reached 396,000 tons. The main sources of sulfur in the refinery are the sulfur contained in the raw oil and the sulfur in the fuel used in the heating furnaces or boilers of the refinery equipment and the self-provided power station. According to the nature of the difference, the waste gas emitted by the refinery can be divided process waste gas and combustion waste gas. Among them, sulfur recovery device and catalytic cracking device are the main emission sources of process waste gas, while the waste discharged from heating furnace boiler and flare are combustion waste gas. Basically, the main sources of sulfur dioxide emissions from all refineries are the same. The heating furnaces and boilers have the highest sulfur dioxide emissions, about 50 %, followed by catalytic cracking devices, with emissions of 15-33 %. However, the sulfur dioxide emissions of the FCCU of high sulfur content crude oil processing plants are remarkably high, which can account for 50 % of the total. The sulfur recovery unit accounts for 10 %, the torch accounts for 10 %, and the remaining units account for 10 %. (Huang 2004).

Concerning nitrogen oxides, The chemical formula of nitrogen oxide is NOx, which is a general term for a variety of substances composed of two elements, nitrogen and oxygen (N and O). There are many types of nitrogen oxides, including nitric oxide, nitrogen dioxide, nitrous oxide, nitrous oxide. Most of the nitrogen oxides are gaseous substances in the standard state, and only nitrous oxide is solid. In addition to nitrogen dioxide, all nitrogen oxides have extremely unstable chemical properties. When exposed to light, changes in humidity and changes in temperature, they are easily converted into nitrogen dioxide and nitric oxide. Therefore, the main pollutants in the atmosphere are them. Since nitric oxide (NO) is easily converted to nitrogen dioxide (NO_2) under aerobic conditions, the nitrogen oxide pollutants that need to be treated are all NO_2. Nitrogen dioxide is a gas with a pungent odor. It does not burn itself, but it can support combustion and has strong oxidizing properties. In addition, NO_2 is very toxic and has a stimulating effect on human respiratory system. Nitrogen oxides are also one of the main substances that form acid rain. When there is a large amount of nitrogen oxides in the air, after the ultraviolet rays of the sun are irradiated, it is easy to produce a chemical effect with the hydrocarbons emitted by the automobile exhaust, and a light blue harmful substance, that is, a nitro compound and eventually photochemical smog is generated. If people inhale photochemical smog, it will cause irritation and great toxic effects on the human respiratory system. It will stimulate the eyes, mouth, nose and lungs of the human. Living in this environment for a long time will damage the functions of the human bodies. (Wang 2013).

The main sources of nitrogen oxide emissions are flue gas from catalytic cracking regeneration. In the reaction regeneration system, when the to-be-generated catalyst is burned again, the catalyst is scorched to remove the coke deposited on the catalyst due to the reaction, the activity of the catalyst is restored, and then returned to the reaction system for recycling. The nitrogen oxides produced in the general combustion process are composed of fuel-type nitrogen oxides and thermal-type nitrogen oxides. Fuel-type nitrogen oxides are nitrogen oxides produced by the conversion of nitrogen-containing compounds in the fuel during combustion, and the amount of production mainly depends on the type of fuel and the combustion method. Thermodynamic nitrogen oxides are formed by the reaction of nitrogen in the air with oxygen at high temperatures (above 1500k). (Liu 2014).

Nitrogen oxides emitted from power boiler flue gas in oil refineries are also one of the largest pollution sources factor of nitrogen oxide emissions from the entire plant. Since the petrochemical refinery production process requires a large amount of steam power, which is used to heat the device, process consumption or power turbine, most of the refineries need to be equipped with power boiler systems. Due to the amount of steam required in the petrochemical refinery, the general neat consumption is about 500t / h. To remove the steam generated by the preheating boiler in the plant, the power boiler needs to supplement the production steam of about 100 t/h. (Liu 2014).

Nitrogen oxides also will come from heating furnace burning flue gas, enough heat is required in the production of the oil refining industry to ensure the normal reaction of the oil product. Each oil refinery is equipped with multiple sets of heating furnaces, generally more than 10 units. The nitrogen oxide content in the flue gas of the heating furnace is generally between 100-300 mg/m^3. Although the concentration is not high, the emissions cannot be ignored. (Liu 2014).

5.1.2 Treatment measures to air pollutants

At present, the main treatment measures of hydrogen sulfide are physical method, chemical method and biological method. physical methods mainly include physical absorption methods which use organic solvents as absorbents and activated carbon adsorption. There are oxidation method and chemical precipitation method in chemical method. The oxidation method generally purifies hydrogen sulfide gas to hydrogen sulfide into elemental sulfur, and chemical precipitation method is to add certain chemical agents to the wastewater to make it directly chemically react with hydrogen sulfide in the water to form a precipitate. (Zhang 2009).

When hydrogen sulfide dissolves in water, there are biological methods to deal with which include contact oxidation method and anoxic biological oxidation. Contact oxidation method is mainly based on the biofilm attached to the carrier and is an efficient water treatment process for purifying organic wastewater. Anoxic biological oxidation method is to anaerobic oxidation of hydrogen sulfide in wastewater with photosynthetic sulfur bacteria to convert hydrogen sulfide into sulfur and then recover it. (Zhang 2009).

In the actual production of petroleum refining and chemical enterprises, the treatment technology of hydrogen sulfide is mainly realized by the desulfurization process. The hydro refining process is widely used in various processes in refineries and is a general term for the catalytic upgrading of various oil products under hydrogen pressure. It refers to the hydrogenolysis reaction of various non-hydrocarbon compounds in oil products under certain temperature and pressure, in the presence of catalyst and hydrogen, and then removed from the oil products to achieve the purpose of refining the oil products. The main chemical reaction of hydro refining: Hydrofining can saturate the olefins in the raw oil and remove harmful components such as sulfur, oxygen, nitrogen and metal impurities. Its main reactions include desulfurization to generate hydrogen sulfide, then is denitrification to produce ammonia, then is deoxidize to produce water, after that is hydrogenation of olefins, the last is hydrodemetallization. (Zhang 2009).

For sulfur dioxide, there are basically three ways to treat the sulfur dioxide pollutants in the FCCU flue gas: catalytic cracking raw material hydrogenation pretreatment, the use of sulfur transfer aids and end-of-pipe treatment of regenerated flue gas. Feedstock hydrogenation pretreatment has become the development trend of the global catalytic cracking process. This process can reduce the sulfur dioxide content of regenerated flue gas and can also reduce the sulfur content in catalytic cracking products, but the investment and operating costs of this technology are exceptionally large. In comparison, the use of sulfur transfer aids is more economical and reasonable. This technology does not require any modification of the existing FCCU, so it will not incur costs, but this technology has limited emission reduction effects and cannot be used alone Emissions reduction requirements. In terms of flue gas terminal treatment, for the control of sulfur dioxide in flue gas, there are not many desulfurization methods that can be practically applied to catalytic cracking devices, only three flue gas desulfurization facilities are applied in the petrochemical refinery industries: Mobil wet flue gas scrubbing, Berg EDV wet method and Wet flue gas acid production (TABLE 3). (Wang 2013).

TABLE 3. Flue gas desulfurization facilities (Wang 2013).

	theory	effect
Mobil Wet Flue Gas Scrubbing	The alkaline liquid enters the Venturi tube together with the flue gas, and the washing liquid forms a thin film on the wall of the necking section, and then the inlet at the throat is divided into small droplets. Due to the existence of the relative velocity difference, the gas and the droplets in the event of an inertial collision, sulfur dioxide can be removed.	The removal rate of sulfur oxide and dust can reach more than 90 %
Berg EDV wet method	The smoke from the regenerator enters the spray tower and is immediately cooled to the saturation temperature rapidly, and then contacts with the spray droplets containing the desulfurizer to remove particulate matter and SOx	Sulfur dioxide removal efficiency reaches 90 %, and particulate matter can also be removed
Wet flue gas acid production	This process can be used to remove SOx from catalytic cracking and regeneration flue gas, and produce commercial grade (mass fraction 93-98.5 %) concentrated sulfuric acid	Sulfur dioxide conversion rate reaches 95 %

In the treatment measures to nitrogen oxides, There are several process, one is fixed bed residue hydrogenation process, its characteristics include reaction pressure 10-20MPa, reaction temperature 370-420 ℃, relatively low temperature, residual oil conversion rate 15-25 %, converted residual oil can be used as low sulfur Combustion oil or resid FCC feed, coking raw materials, mature technology, simple equipment, easy to operate, but the operation is greatly affected by raw material impurities, and it is prone to blockage. It is generally used for processing residual oil materials with a content of nickel and vanadium less than 150ppm. Another is ebulliated bed residue hydrogenation process, this process characteristics include reaction pressure 15-21Mpa, reaction temperature 400-470 ℃, can process heavy materials with a content of nickel and vanadium higher than 700ppm, this method has a long operating cycle, high catalyst utilization efficiency, and residue the conversion rate is 60-90 %, but the operation and equipment are complicated, which requires high investment. Another one is suspended bed residue hydrogenation process, characteristics include reaction pressure of this process is 10-30MPa, reaction temperature is 450-480 ℃, and special low-quality raw materials can be processed, but this method is still in the experimental stage. Last one is moving bed residue hydrogenation process characteristic is that the old catalyst can be discharged continuously or intermittently, and the new catalyst can be added continuously or intermittently, so that the catalyst in the reactor can always maintain activity, and can be used as a pre-system for the fixed bed reactor to prolong the service life of the fixed bed. (Liu 2014).

5.2 Water pollution and treatment measures

In addition to the traditional catalytic reduction and redox absorption methods, residual oil hydrogenation technology and wax oil hydrogenation technology will also be used in the petrochemical refinery. For the nitrogen oxides generated in the combustion of the heating furnace, air-classified low-nitrogen burner, fuel-classified low-nitrogen burner, three-stage low-nitrogen burner, and flue gas cycle burner can be used as devices to reduce the emission. It can be calculated to reduce nitrogen oxide emissions by 30-60 % by the above devices. (Wen & Zhao 2013).

5.2.1 Water applications and wastewater in petrochemical refinery

A large amount of industrial water is required during crude oil processing and production，an oil refinery with relatively complete production facilities consumes 30 to 50 times the amount of crude oil processed. Oil refining wastewater can be divided into the following types: First is wastewater in the refining process which are generated from production devices, include drainage of the tower, tank and oil-water separator of the oil refining plant, which is the main source of pollution. Second is oily wastewater, it mainly comes from the pump cooling water of the oil refining device, the crude oil and heavy oil intermediate tank drainage, the ground flushing water, and the tower and condenser drainage. Third is other water, including cooling water and domestic sewage. The last is sulfur-containing wastewater. (Gong & Wang 2006).

5.2.2 Treatment measures to wastewater

At present, oil refineries generally take the following measures to prevent and control water pollution. Reform the production process and reduce the amount of sewage discharged, in the production process of oil refineries, it is a positive and effective measure to control water pollution by using non-polluting and less polluting processes and equipment as much as possible to compress the pollution source and reduce the amount of pollutants. (Qi 2008).

The proportion of hydrofining in secondary refineries of oil refineries has increased rapidly. The use of hydro refining can reduce the amount of wastewater discharged and the degree of pollution, eliminating the difficult problems of high-concentration sulfur-containing, phenol-containing waste lye and alkali residue. Some oil refineries have adopted shell-and-tube surface condensers instead of atmospheric condensers, and vacuum pumps instead of steam jet pumps, eliminating atmospheric condenser drainage. Some oil refineries use a reboiler instead of direct steam for stripping to reduce the amount of sewage discharged, and some studies have used natural gas or dry gas instead of steam stripping. (Qi 2008).

Comprehensive utilization of water resources and recycle the useful substances. Most of the newly built oil refineries have sulfur recovery devices, and the sulfide in the recovered gas is used to produce sulfur. The condensed water (commonly referred to as acidic water) at the top of the fractionation tower of the secondary processing unit of oil refining contains high concentrations of pollutants such as hydrogen sulfide, ammonia and phenol. At present, many plants have an acid water stripping device to recover ammonia, and the hydrogen sulfide stripped off together with the ammonia sulfide gas discharged from other devices is sent to the sulfur recovery device. Some factories use high-concentration phenol-containing wastewater to recover phenol by electrostatic extraction. Some oil refineries recover naphthenic acid from the straight-washed alkaline washing waste liquid, sodium hydrosulfide and sodium sulfide from the waste alkaline liquid, and sulfuric acid from the acid residue. (Qi 2008).

Reduce freshwater consumption and compress sewage discharge, oil refineries are trying to use air cooling instead of water cooling, which greatly saves the amount of fresh water. Many old plants that use direct current water cooling are gradually switching to circulating water systems. Some factories have widely adopted ways to reuse and purify wastewater for reuse. (Qi 2008).

In addition to the above-mentioned regular sources of pollution, special attention should be paid to the prevention and control of those complex impact sources of pollution, which must be considered when designing and constructing facilities. At first promote the diversion of production waste-water: On the basis of investigating and researching the pollution sources of the petrochemical refinery, reforming the production process and compressing the discharge volume, a plan for waste-water clean-up and diversion was formulated so that different methods of waste-water treatment can be treated. Pay attention to the rationality that is beneficial to governance, easy to manage, and economic and technological when formulating a plan for cleaning up and diversion. The drainage system of newly built oil refineries mostly adopts the diversion system, and some old factories have also transformed the drainage system of the confluence system into a diversion system. It is generally divided into four systems: oil-free wastewater (salt-containing wastewater), oil-containing wastewater, process wastewater and domestic sewage. (Qi 2008).

Secondly is the pretreatment of wastewater (during the process in workshop). The high-concentration sulfur-containing, phenol-containing, ammonia-containing waste-water and waste alkali residue discharged from the refinery production process are first pretreated in the production workshop, which can not only reduce the pollution load of the waste-water treatment plant, but also recycle the waste-water Useful substance. (Qi 2008).

5.3 Solid waste and treatment measures

Solid waste is one of the most easily recycled pollutants. Solid waste has a strong spatial and temporal attribute. In the eyes of some people, the substance is solid waste yet may be resources in the eyes of others. The solid waste here may have great use value in other areas. Today, it is solid waste. Tomorrow, it may become resources. That is to say, solid waste is a misplaced resource, and "resource attribute" is the natural attribute of solid waste. It should be noted that some organic solvents, sludges and other semi-solid and slurry fluids are also regarded as solid waste. (Hao 2015).

5.3.1 Solid waste in petrochemical refinery

The solid waste of petrochemical industry has the following characteristics, on the one hand, the content of organic matter is high. The loss rate of crude oil treatment is 0.25 %, most of which is in solid waste. Most of the solid waste generated is organic waste liquid. In addition, the sludge oil content in the tank bottom mud pool is higher than 60 %. The oil acid and waste alkali residue from alkali refining of the oil refining business division contain 5-10 % oil, 10-15 % naphthenic acid and 10-20 % phenol. Besides, it contains many kinds of hazardous waste. For example, the acid-base waste residue from oil refining contains not only organic matters, but also free acid-base and sulfide with high toxicity and corrosiveness. More than 60 % of the substances in the organic waste liquid are hazardous waste. The bottom mud of the tank is inflammable and explosive, this mud is also belonging to dangerous substances. However, there are many ways to recycle solid waste. If proper physical transformation and smelting are adopted, useful materials can be obtained. (Yang 2004).

5.3.2 Treatment measures of solid waste

The conventional methods and technologies for the treatment of chemical waste include landfill, incineration, incineration thermal energy utilization technology. First is landfill method, a typical measure to fill solid waste into large pits or depressions to promote the restoration of landform and maintain ecological balance. According to the characteristics of different hazardous waste, different landfill methods should be adopted. Another is incineration, generally toxic, high-energy organic waste will be incinerated. Due to the continuous improvement of incineration method in engineering application, it is mainly reflected in combustion method improvement, in details are the burner design, such as the new type of internal type, adiabatic radiation burner. Also reflected in the improvement of catalytic combustion mainly focuses on the research and development of the new catalyst used, as well as the improvement of traditional catalytic combustion by adopting a suitable catalytic adsorption concentration process to reduce secondary pollution. The improvement of heat energy utilization technology is also a reflection, mainly focuses on the configuration of the efficiency system of heat energy recovery of high-temperature exhaust gas. The main theme of industrial development in the future is circular economy. Chemical waste takes the route of resource reuse, which is the call of the times and the inevitable requirement of modern industrial development in the world. Because many of the waste generated by refining enterprises are highly toxic and contain harmful substances, it cannot be simply landfilled or incinerated. (Hu 2003).

Typical refining and chemical enterprises also need to deal with sludge, catalyst and alkaline waste. Concerning sludge treatment, the oil sludge in the refinery has a high calorific value and contains a certain amount of water, which is suitable for the incineration heat recovery process. The combined process of rotary kiln and heat recovery with tail gas treatment can be adopted. The rotary kiln incinerator is built with insulating bricks in the cylindrical metal shell and placed horizontally. Through the overall rotation of the furnace body, it can achieve uniform mixing and move along the inclined angle to the discharge end. The whole furnace is divided into dry section, spontaneous combustion section and incineration section, which is conducive to promoting the mixing and release of flue gas and oil sludge, increasing its combustion efficiency, and suitable for oil sludge with certain humidity. The energy consumption of sludge treatment by incinerator is high. (Yang 2004).

In the treatment of catalyst, the applied catalytic addition is mainly divided into cracking catalyst and hydrogenation catalyst. Cracking catalyst is mainly composed of aluminosilicate zeolite with particle size of 20-200 μm. In the process of fluid bed catalytic cracking, some of the deactivated catalysts are discharged into the atmosphere with tail gas because the particles are too small to be recovered. Because crude oil contains a certain amount of nickel and vanadium and other heavy metals, they will deposit on the surface of catalyst during cracking process, which will be discharged into the atmosphere together with catalyst, and become one of the sources of particulate pollutants. DEMET process can be used to treat cracking catalyst. Hydrogenation catalyst is mainly composed of cobalt, nickel, tungsten, molybdenum and other transition metals supported on alumina. The catalyst can be treated by the following methods: baking first, adding solvent according to the proportion of 1:1, removing the metal on the catalyst, and then treating the catalyst by chemical method to restore its catalytic performance. For Alkaline waste, after the alkaline residue is de-oiled by heating, concentrated sulfuric acid is added for neutralization reaction. After the reaction, useful products can be obtained, but acidic liquid may be produced, may cause secondary pollution. Carbon dioxide neutralization method can also be used to recover alkaline materials, or use Alkaline residue in other production, such as cooking liquid in paper industry. (Wang 2007).

6 PROMOTING CLEAN PRODUCTION IN THE PROCEDULE OF PETROCHEMICAL PRODUCTION

Oil refining enterprises have many petroleum products, and their quality standards have become increasingly strict. Research institutions around the world have been looking for breakthroughs in the processing technology of petroleum products to cope with the changing market demand and standards. Nowadays, in the processing of petrochemical products such as gasoline, diesel and ethylene, many new technologies have been applied to the actual production (Ye, Zhang, Li & Nie 2019, 72), which can effectively improve the efficiency of resource utilization and reduce the generation of pollutants. It has broad economic and social benefits (Wang & Wang 2017).

6.1 Technological process of refined oil

Both gasoline and diesel are the main fuels of automobiles. With the development of the automobile industry, the consumption of automobile fuels has gradually increased, and a large amount of automobile exhaust emissions have caused air pollution. In order to meet the emission standards (FIGURE 6), it is necessary to reduce the amount of sulfur, olefins and aromatics in the finished oil, and at the same time make the gasoline octane number meet the requirements. (Sun 2018).

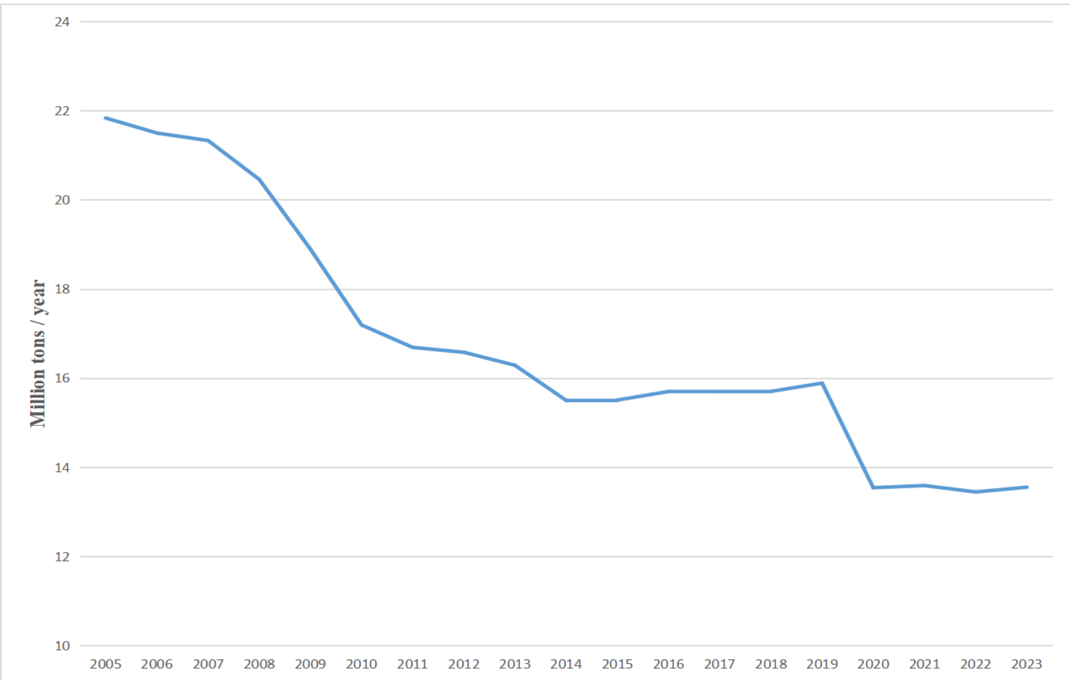

Figure 6. Allowed sulfur content in oil products. (Adapted from IEA 2019).

6.1.1 Introduction of gasoline production cleaning technologies

Automotive gasoline is mainly composed of FCC gasoline, reformer gasoline, alkylated gasoline, isomerized gasoline and straight run gasoline. The highest proportion is FCC gasoline, which is the main research object of clean oil production. It should be noted that all new desulfurization and octane number changing technologies are upgrading of above-mentioned hydrofining process, thus no new treatment device and process are added. Before describing and analyzing each clean gasoline production process, the principle of hydrodesulfurization should be mentioned first. (Wang 2011).

To understand the principle of hydrodesulfurization, it is necessary to understand it from a micro perspective. As mentioned earlier, oil is a complex mixture even if it is processed into gasoline or diesel products. It mainly contains such elements as carbon, hydrogen, oxygen, nitrogen and sulfur. Among them, hydro， carbon and oxygen account for 95-97% of the total. Sulfur removal is to reduce the total sulfur content, so that the proportion of carbon, hydrogen and oxygen increases. After combustion, carbon dioxide and water are discharged to achieve the purpose of cleaning. The way of desulfurization is through the different bond energy between the various elements, under special conditions, the sulfur elements in the oil are discharged in the form of other compounds through chemical reactions (TABLE 4). The bond energy of C-S bond is the smallest and hydrodesulfurization is the easiest, and C = C bond is easy to be saturated by hydrogenated. (Wang 2011).

TABLE 4. Chemical bond energy of major elements in petroleum (Adapted from Liu 2018).

bonds	C-H	C-C	C=C	C-N	C-S	N-H	S-H
bond energy kJ/mol	413	348	614	305	272	391	367

Gasoline hydrodesulfurization is mainly to convert sulfur compounds in gasoline fractions into hydrogen sulfide under the action of catalyst in hydrogen environment (FIGURE 7), and then remove hydrogen sulfide from the reaction effluent by means of vapor-liquid separation, fractionation or stripping. As the olefin and aromatics hydrogenation saturation are considered in gasoline hydrogenation, the octane number will be reduced, so gasoline hydrogenation will affect the catalyst high demand for selectivity. Special attention should be paid to the selection of catalyst during the process. For the same catalyst, when the desulfurization rate is similar, such as 98% and 95%, although the difference is only 3%, the change of olefin saturation rate is incredibly significant, from 35.1% to 59.6%, far exceeding the change of desulfurization rate. It is exceedingly difficult to select the catalyst with the same desulfurization rate. If the olefin saturation rate is compared under the condition of similar desulfurization rate, it may bring a serious error or even lead to the wrong direction. Nickel-Tungsten (Ni-W) catalyst system and Cobalt-Molybdenum (Co-Mo) catalyst system are the most commonly used metal combination in hydrofining. In the fields of denitrification and deep desulfurization, Ni-W catalyst performs well, but its selectivity is poor in the process of hydrogenation. Therefore, cobalt molybdenum catalyst is mainly used in hydrofining process. (Wang 2011).

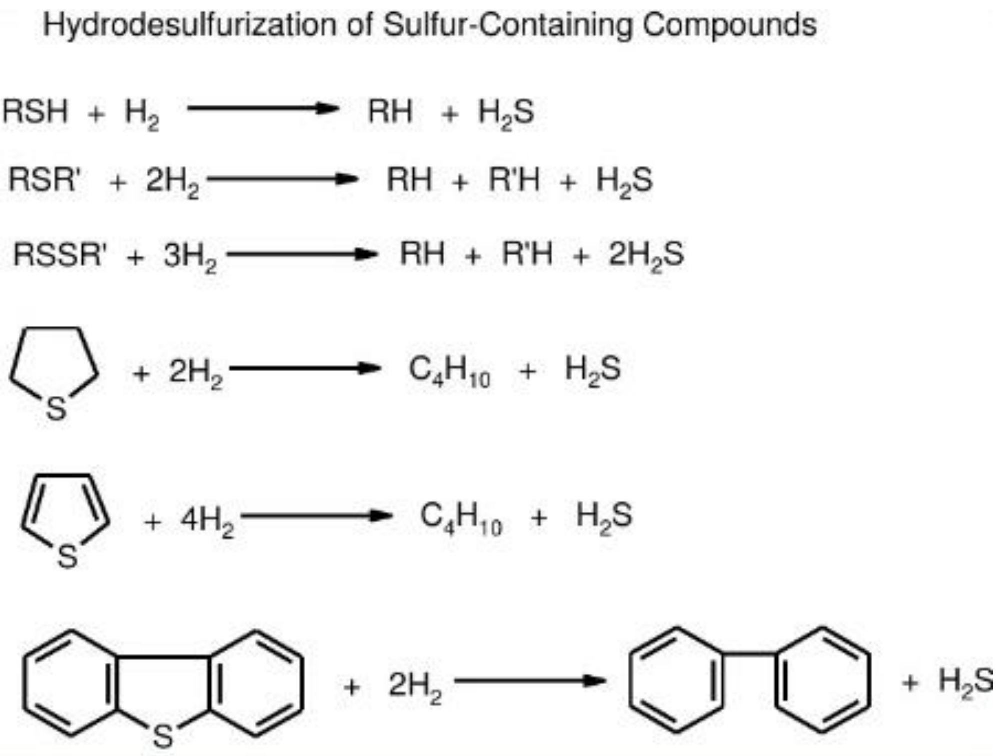

FIGURE 7. Main reactions in the hydrodesulfurization process (Liu 2018).

Clean gasoline production technology mainly includes selective hydrodesulfurization technology and hydrotreating octane number recovery technology. The selective hydrodesulfurization technology mainly includes RSDS, prime-G and CDHDS. The product gasoline has high quality, low sulfur content, and octane number, which is widely used in industry. Hydrotreating octane recovery technology mainly includes the technologies of GARDES, ISAL and RID0S. The production of clean gasoline has the advantages of low sulfur, low olefin and high octane, but there are some problems, such as high operating conditions and high energy consumption. (Ye, Zhang, Li & Nie 2019)

RSDS technology is divided into fractionator and selective hydrogenation unit. FCC gasoline is divided into light component (mainly LCN) and heavy component (mainly HCN) according to the properties of feedstock and the requirements of final product. After the mercaptan is removed by alkali washing, HCN enters into the selective hydrogenation unit for desulfurization. Finally, the final product is obtained by mixing the desulfurized LCN with HCN. The desulfurization rate of RSDS technology is over 80%, have small loss of octane number, and oil quality can meet the production requirements. More than 90% of the sulfur in the finished gasoline comes from FCC gasoline, so the removal of sulfur in FCC gasoline is the key to determine the sulfur content of the finished gasoline. (Liu, Zhai, Gao & Wang 2016).

Another technology is Prime-G+, Prime-G+ technology is developed by Axens of France, which is an improved selective hydrodesulfurization technology based on the previous Prime-G technology. This technology uses a double catalyst system to selectively hydrodesulfurization FCC gasoline， the main structure of the fixed bed reactor is composed of three parts: selective pre-hydrogenation of raw materials, fractionator and selective hydrodesulfurization unit. There are three kinds of reactions in the selective hydrogenation unit, first is the selective hydrogenation saturation of diene components, second is the olefin isomerization reaction, and the last is the conversion of light sulfur compounds (mercaptan and thioether) into heavy sulfur compounds.

In the first part of Prime-G+ process, appropriate catalyst and appropriate process conditions are needed to be selected to saturate the diene components in FCC gasoline under the premise of keeping olefins as much as possible, so as to avoid the deactivation of catalyst due to the carbon deposition of diene on the catalyst. In the second part, the olefins in FCC gasoline are converted into thermodynamic equilibrium components by double bond isomerization. Through this reaction, alpha olefins can be converted into other isomeric olefins, thus increasing the octane number. Because the hydrogenation activity of isomeric olefins is weaker than alpha olefins, a large number of isomeric olefins can be generated to reduce the loss of olefins in the process of gasoline upgrading. (Wang 2011).

In the separator of Prime-G+, FCC gasoline treated by selective hydrogenation unit is divided into light component (mainly is LCN) and heavy component (mainly is HCN) according to different boiling points. LCN contains almost no sulfur, but most of the olefins in gasoline. Because there is no need to be hydrotreated, it retains the olefins with high octane number. Another advantage of the separator is that it reduces the scale of the selective hydrodesulfurization unit. The sulfur content in HCN is high and the olefin content is low, so the deep hydrodesulfurization is carried out in the selective hydrodesulfurization reactor (Wang 2011). Prime-G+ has the advantages of low hydrogen consumption, high space speed, high liquid yield, low olefin hydrogenation activity, no aromatics saturation, cracking and other side reactions, low octane number loss (FIGURE 8). (Meng, Zhou & Sun 2014).

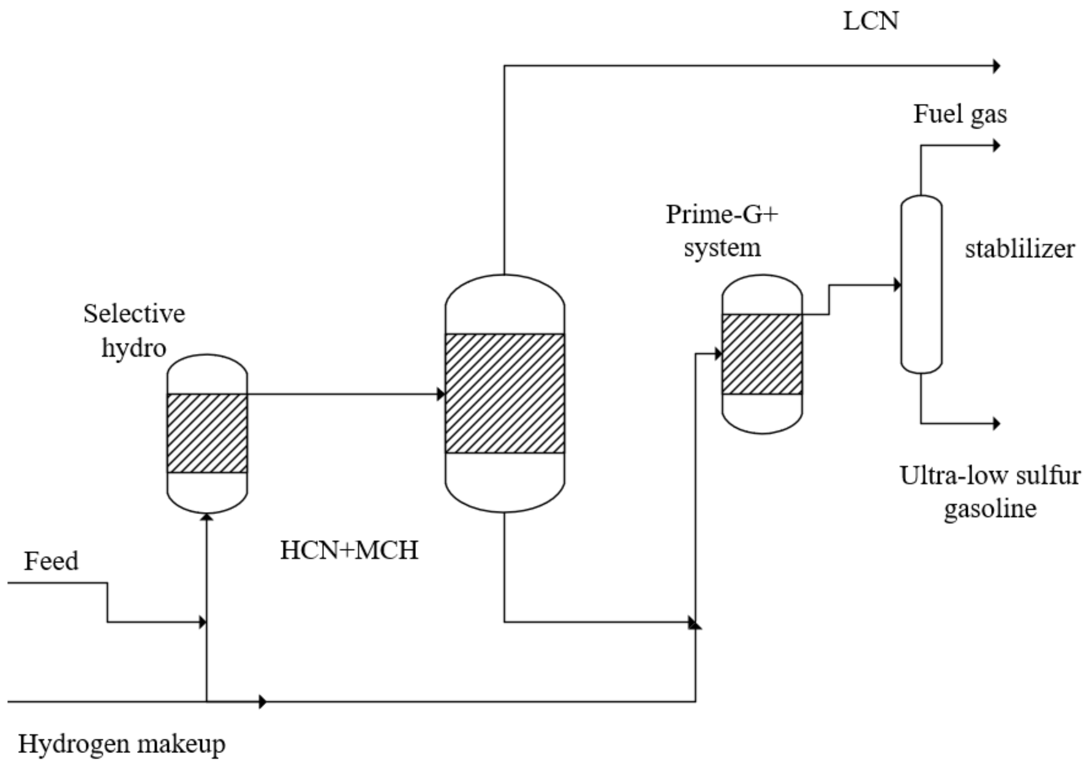

FIGURE 8. Process of Prime-G+ technology (Adapted from Wang 2011, 16)

Cdhydro / CDHDS technology is a selective hydrogenation technology developed by CDTECH company of the United States. It combines hydrodesulfurization and catalytic distillation in a reactor to realize the removal of sulfur content and diene hydrocarbon in FCC gasoline and the separation of light heavy components. The whole distillate gasoline and hydrogen enter the CDhydro catalytic distillation tower, and the mercaptan and diene in the distillate will undergo etherification reaction under the catalyst condition, realizing the simultaneous removal of mercaptan and diene, and the generated thioether compounds will enter the heavy fraction . The diene in the fraction is hydrogenated to produce mono-olefin under the condition of catalyst, which improves the stability of gasoline. The isomerization of the fractions increases the octane number of the gasoline. The heavy fraction flows out from the bottom of the tower to the next section of CDHDS hydrodesulfurization, and the light fraction is distilled from the top of the tower. (Huang, Ke & Bao 2016).

CDHDS process mainly involves hydrodesulfurization of sulfur compounds in heavy fractions and hydro saturation of olefins. The heavy fraction is distilled, and hydro desulfurized in catalyst bed. The light fraction has low sulfur content and high olefin content. The heavy fraction is desulfurized under high temperature and high hydrogen partial pressure at the bottom of the tower. The distribution of the whole reaction can realize the efficient desulfurization of the fraction, and at the same time inhibit the saturation reaction of the olefin. Cdhydro / CDHDS technology uses the characteristics of catalytic distillation unit to select suitable operation conditions to control the effect of selective hydrodesulfurization, with clear process flow, strong operability, easy operation and low investment cost. Cdhydro / CDHDS technology can meet the requirements of clean oil production and realize the separation of light and heavy fractions, which is a high-level desulfurization technology. (Huang, Ke & Bao 2016).

SCANfing technology is a selective hydrodesulfurization technology developed by ExxonMobil company, and Akzo noble company jointly develops catalyst. The main unit of SCANfing technology includes four parts: pretreatment hydrogenation saturation unit, selective hydrodesulfurization unit, amine scrubber and stripper. FCC feed gasoline and hydrogen are mixed and heated to enter the saturation unit of diene hydrogenation to saturate diene and prevent its polymerization and coking from blocking the pipeline. After heat exchange, the saturated products enter the selective hydrodesulfurization unit, and then they are cooled and separated by amine scrubber and stripper to obtain the final products. The purpose of SCANfing technology is to reduce the consumption of hydrogen in fixed bed reactor at low temperature and low pressure. SCANfing technology is not widely used in developing countries. In 2016 ExxonMobil’s Beaumont refinery, a set of SCANfing selective catalytic cracking and hydrogenation process unit was installed to upgrade the existing process to produce qualified gasoline products with low sulfur content and low octane. (Gérard, G, Kaldor & Kerby 2000).

For GARDES Technology, the principle of this technology is to pre hydro desulfurize the whole FCC distillate gasoline to realize the heavy mercaptan. After hydrogenation, the whole distillate enters the fractionator to realize the cutting of the light and light fractions. The light fraction is directly taken as the top of the product tower, and the heavy fraction enters the selective hydro desulfurizing unit. Under the action of the catalyst, the macromolecular sulfide is removed efficiently and selectively, and the product enters the next octane number recovery and supplement the desulfurization unit realizes small molecule sulfide removal and olefin isomerization and aromatization reaction. At last, the light and light fractions are mixed and exported as desulfurization clean gasoline products. The GARDES technology is a combination technology of selective hydrodesulfurization and octane number recovery developed for high sulfur and high olefin FCC gasoline, which has wide applicability. According to the content of sulfur and olefin in the raw oil and the requirements of the final product oil, the GARDES technology can optimize the process parameters and catalyst grading to achieve the efficient removal of sulfide and recover the octane number of the product oil. (Xu 2015).

ISAL technology is developed by Venezuelan INTEVEP company. The main body of the process is divided into two reactors. The first reactor adopts fixed bed method to realize desulfurization of raw oil under low pressure. The second reactor is an octane number recovery device, which can reduce the content of olefins and aromatics in the feed oil, to maintain a high-octane number. This technology uses a new type of gallium- chromium molecular sieve catalyst. The catalyst does not contain noble metals. Its acidity, surface area and particle size have been carefully selected. It has the functions of desulfurization, denitrification, olefin reduction, isomerization and cracking. On the surface of the catalyst, the small cracked molecules can undergo molecular rearrangement reaction and be reformed into high octane number components, thus solving the problem of the octane number serious reduction because olefin saturation which is a problem that traditional technologies cannot deal with at all (Wang 2011). ISAL technology can reduce the sulfur content of FCC gasoline to less than 30 microgram/g and reduce the octane number loss of gasoline. ISAL technology can be used to process FCC full distillate gasoline, or FCC light gasoline and heavy gasoline, with diversified operation, high yield and high-octane number retention. The other parts are the same as the traditional hydrogenation process, so no special operation procedure is needed, and the investment operation cost is low. (Huang, Fan & Bao 2005).

RID0S technology is a hydrotreating octane number recovery technology developed by Sinopec Petrochemical Research Institute. The technology is to separate LCN and HCN from feedstock oil at 70-100 ℃, in which LCN is desulfurized by conventional alkali washing and extraction to avoid olefin hydrogenation saturation and to preserve the octane number of feedstock oil. HCN was desulfurized by hydrofining, and then the product was isomerized, and octane number was restored under the action of octane number recovery catalyst. RID0S technology adopts layered loading and hydrogen injection in the middle to improve the applicability and operation flexibility of crude oil, which can be applied to various FCC gasoline feedstocks. (Li, Shi & Yang 2014).

6.1.2 Introduction of diesel production cleaning technologies

The development direction of clean diesel production technology is to further reduce sulfur and polycyclic aromatic hydrocarbons in diesel oil and increase cetane number. At present, the main application technology is still diesel oil hydrogenation technology, which can be divided into conventional fixed bed hydrogenation process and liquid phase hydrogenation process. The conventional fixed bed process is almost the same, with the newly developed high activity catalysts as the core, such as stars and Nebula series catalysts of Albemarle catalysts, central series catalysts of criterion Catalysts & technologies, TK of Haldor Topsoe Series catalysts and Axens HR series catalysts. Most of the representative high activity hydrotreating catalysts can produce ultra-low sulfur diesel oil with sulfur content less than 10 mg/G under the existing plant conditions. (Wang & Wang 2017).

The liquid phase reaction is adopted in the liquid phase hydrogenation technology, the traditional hydrogen circulation system is canceled, the hydrogen is dissolved in the raw oil, and sufficient hydrogen is dissolved through the liquid circulation to meet the needs of the hydrogenation reaction. Representative liquid phase hydrogenation processes include: ISO heating hydrogenation technology of DuPont company, SRH Liquid phase circulating hydrogenation technology jointly developed by Sinopec Luoyang Engineering Corporation and Fushun Research institute of petroleum and petrochemical, SLHT liquid phase circulating hydrogenation technology jointly developed by China Petrochemical Engineering and Construction Corporation and China Petrochemical Institute of Sciences. (Wang & Wang 2017).

6.2 Cleaning technological process of other petroleum derivatives

As a typical petrochemical product, ethylene plays an important role in refining and chemical enterprises. Ethylene unit is large-scale to compare with other units in petrochemical refinery, require large amount of energy consumption. At present, many ethylene plants in the world adopt optimized energy-saving technology, which reflects the economy of large-scale ethylene production and makes its products more competitive in the market. Energy saving optimization technology includes optimizing ethylene energy system, improving thermal efficiency of cracking furnace, and using advanced ethylene separation process. (Hong 2012)

The most important part is the optimization of energy system, a method of optimizing design of heat exchange network, pinch technology, was put forward in 1970s. This method gradually developed into the main theory of energy integration technology in chemical process. Pinch technology can not only be used to optimize the heat exchange network, but also to set up heat engines and heat pumps, improve production capacity, reduce production water consumption and reduce pollution emissions. This technology is widely used in ethylene splitting decomposition to optimize the heat exchange network, so as to reduce the energy consumption and emissions of ethylene plant. (Gao, Lie & Yang 2010).

Second most important is to improve the thermal efficiency of cracking furnace, cracking unit is an important unit in ethylene production, and its energy consumption accounts for about 70-85 % of the total energy consumption. With the increasing of ethylene plant specifications, the energy consumption of cracking cannot be ignored. Then is the energy saving of quench system, quench system is used to recover the energy from cracking furnace and reduce the temperature of gas. Therefore, the energy consumption of ethylene processing can be reduced by changing the operation conditions of quench system and effectively recovering heat. Oil scrubber is the key equipment of quench oil system. Improving the gas-liquid contact of oil scrubber is conducive to improving the cooling of cracked gas. After above parts is the energy saving of cracked gas compression system, in ethylene production, the energy consumption of compressor accounts for about 20 %, so reducing the energy consumption of compressor can reduce the energy consumption of ethylene plant. The compression ratio of cracking gas compressor is exceptionally large. In order to reduce the power consumption of compressor, multi-stage compression is adopted. Then is energy saving of separation system, the energy consumption of separation system in ethylene plant accounts for about 10-15 %. In the same separation system, energy saving is achieved through different combinations of various units. In the separation system, in order to reduce energy consumption, relevant energy-saving technologies are adopted, such as heat pump distillation for distillation tower, multiple refrigeration for refrigeration system and catalytic distillation for hydrogenation system. At last is the energy saving of distillation tower, distillation is an indispensable separation process in ethylene plant, and energy consumption accounts for about 10-15 %. (Wang 2009).

At present, the energy saving of distillation is mainly reflected in changing the operating conditions and changing the process. To change the energy saving operation, the reflux ratio should be considered, the feed should be preheated, and the appropriate feed position and feed state should be selected. In order to change the process, a new tower structure should be considered, such as adding an intermediate condenser and an intermediate reboiler and using heat pump distillation. (Hong 2012).

7 FUTURE DEVELOPMENT PROSPECTS OF CLEANER PRODUCTION IN PETRO-CHEMICAL INDUSTRY

With the heavy quality and inferior quality of crude oil and the light weight, high quality and cleanliness of petroleum products, the cost of refining has risen sharply, and the profit space of refining and chemical enterprises has been severely squeezed. Ultimately, by optimizing oil refining production and achieving refined production, the value of each petroleum molecule can be used to achieve the molecular-level optimization of petroleum resources. (Zhang, Wang & Xue 2016).

With the development of modern analytical instruments, especially full two-dimensional gas chromatography, high-resolution mass spectrometry (tandem mass spectrometry, time-of-flight mass spectrometry, Fourier transform ion cyclotron resonance mass spectrometry) and selective ionization techniques (field ionization, field resolution, electrospray , atmospheric pressure photoionization), the refining industry practitioners' perception of crude oil has rapidly increased from the previous fraction level to the molecular level. The molecular identification and characterization technology for crude oil and various fractions has developed rapidly, which has greatly improved the understanding of the utilization and conversion laws of petroleum resources, so that it has reached the level of understanding at the molecular level. The technologies formed on this basis can be generally called molecules oil refining technology. (Zhang, Wang & Xue 2016).

The core of molecular refining technology is the characterization of petroleum molecules and molecular-level comprehension and simulation of the petroleum conversion process. Using these comprehension, on the one hand, it can provide strong technical support for the development of new petroleum refining processes, new catalytic materials, and new petroleum processing equipment, To provide guidance for the emergence of new molecular refining technology; on the other hand, it can further develop the process simulation and system optimization of the refining process to the molecular level, and provide the basic conditions for the refined management of the refining process. (Zhang, Wang & Xue 2016).

8 CONCLUSIONS

The quality of the world's crude oil is continuing to decline, and as one of the world's major energy sources, oil will still directly affect human society in the future. How to carry out clean production in the refining industry is related to the fate of each of individual. Nowadays, the awareness of environmental protection in the world is becoming stronger. Every country, industry and individual are actively promoting the production and life of environmental protection and green, and the requirements for the energy industry are stricter. Oil refining industry is a high energy consumption, high pollution and high-risk industry, so oil refining enterprises also bear more important responsibilities than other industries. Cleaner production activities run through all aspects of plant production, and it is a long-term and gradually standardized work. At the source, it is necessary to minimize the loss of leakage. In terms of emissions, the enterprise should actively improve technology and recycle pollutants generated by comprehensive utilization. In production, enterprise should apply new equipment and technology, save resources and enhance the sustainable development capacity of clean energy industry.

Since the 21st century, the world's refining and chemical technology has made progress. The technological development of clean oil production, heavy oil processing, olefin raw material diversification, high value-added chemical product production and other technologies has been constantly breaking through to meet environmental protection policies and market demand, so as to make people's lives better. From the perspective of crude oil leakage, once an oil spill occurs, it not only presents a fire hazard, but also easily pollutes the surrounding environment. For oil storage and transportation, each petrochemical refinery enterprise should use more suitable equipment. For the leakage of pollutants, from the previous point, the bioremediation method is the best method, but this method is not popular. For some small oil processing enterprises, from the perspective of intuition that simple physical landfill or incineration is easier, so environmental protection agencies should strengthen control and promote the use of bioremediation to deal with leakage pollution. From the perspective of emission, although the pollutants discharged into the environment can be eliminated to a certain extent, the terminal treatment cannot fundamentally solve the problem. Regardless of the status of the pollutants, new technologies should be used to reduce the emission of harmful substances. The best method is recycling, which not only reduces pollution emissions but also saves resources and costs. From the perspective of the products produced, the fuel produced by the new process is cleaner and more efficient, with less damage to the engine, less exhaust gas, higher economic benefits, and better environmental protection. However, the action of promoting new technology cannot be stopped. In the future, the focus of development will be still on cleaning, intelligence and refinement, while realizing green production and continuously improving product quality. In the future, refining and chemical enterprises should continue to promote cleaner production, to make cleaner production reach a new level.

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