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Bachelor Thesis

Coking of Coal:

Perspectives for Mongolia

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Nalaikh, 2018-08-10

Statutory Declaration

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I hereby affirm that I provided the submitted bachelor thesis

Coking of Coal: Perspectives for Mongolia

independently and without undue external help. I did not use any sources other than those stated. In case that the work is additionally submitted on a data medium, I declare that the written and the electronic form are identical. The work was not submitted in the same or similar form to any examination authority.

Nalaikh, 2018-08-10

Munkhtsetseg Amaljargal

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Symbol	Meaning	SI unit
A	Coefficient in correlations	various
B	Coefficient in correlations	various
c_p	Molar heat capacity at constant pressure	$\mathrm{J/(K\,mol)}$
C	Coefficient in correlations	various
D	Coefficient in correlations	various
E	Coefficient in correlations	various
F	Helmholtz free energy	J
G	Gibbs free energy	J
T	Temperature	°C, K
T_b	Boiling point	°C, K
T_m	Melting point	°C, K
ppm	Parts per million	

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1 Introduction

Mongolia is rich in coal, copper, rare earth, and gold ores. In the past 20 years, the Mongolian economy strongly relayed on the mining sectors. The mining industry contributed around one-quarter to Mongolia's gross domestic product in 2014. Unfortunately, this number is only a result of the export of the minerals as raw materials. No mining company produces the final product from an ore deposit in Mongolia. On the one hand it is a pity that Mongolia earns less income than what would be possible, but on the other hand, there is a free market waiting for companies to develop the mineral processing sector.

In this research, I studied one of the advanced coal processing technologies, i. e. coal coking. The main reason to choose coal is its availability with 37.4 billion tons of proven coal reserves in Mongolia. The range of coal type includes lignite, sub-bituminous, bituminous, and premium-bituminous coal. Mongolia became the 5th largest exporter of coking coal due to active mining in the south Gobi area. Based on current coking coal mining deposits, there is a chance to produce coke in order to add value to the raw material.

The coke has a significant role in a metallurgical plant due to its high calorific value and other characteristics. As Mongolia has no own blast furnace metallurgical plant, and as the Chinese coke demand is still growing, thus Mongolian coke could be exported to China.

This study aims at a preliminary design for a coke-making plant based on available coking coal feed. To do that, coking technologies, products, and by-products need to be studied.

This thesis focusses on theoretical process design and development tools and does not have an experimental part. In order to develop the design of the coke-making plant, the systematic process systems engineering approach is followed with its procedure on the functional level, the physics level, and the embodiment level.

The first chapter introduces fundamental information of the research work. After the study of the fundamentals of coke technologies, the functions are determined. The functional level chapter introduces the very basic flowchart of the plant and reveals the must-have functions of the processing steps.

On the physics level, all physical and safety properties of the substances that are evolved during the coke-making process are clarified. Based on the physical properties, especially the boiling point ranges, the separation technologies are chosen. Worldwide coke-making technology is developed very well regarding their separation units. The chosen techniques are explained in the physics level chapter. The final study sector is the exemplary simulation of a separation sequence. The simulation is performed on the Aspen Plus program. In order to have mass balance, the plant capacity is calculated and then become a base for the simulation analysis. The last process analysis chapter introduces the result of the simulation process and their descriptions.

2 Coal in Mongolia

2.1 Coal Deposits in Mongolia

Mongolia covers an area of about 1.6 million square kilometers. The landscape of Mongolia consists of mostly steppes and mountain ranges, which stretch along the western and southwestern regions and the Gobi desert in the south. Mongolia is rich in mineral resources, especially coal resources. Coal is the most dominant factor of energy resources because of its availability. Mongolia features 15 large-scale coal-bearing basins and more than 320 places of coal deposits covering all around Mongolia. Mongolia is ranked 10th in the world, by coal reserve. According to the Mineral Resource and Petroleum Authority of Mongolia, Mongolia has 173.3 billion tons of estimated geological resources and 37.4 billion tons of proven coal reserves [1]. Such reserves include the coal types “bituminous”, “premium bituminous”, “sub-bituminous” and mostly low-rank “lignite coal”. Currently, there are 49 active coal mines in Mongolia, and they produce about 33.3 million tons of coal per year.

In Mongolia, the deposition of coal-bearing strata belong to the Carboniferous, which lasted from 323.3 million years ago (Mya) to 298.9 Mya, the Upper Permian which spans from 298.9 Mya to 251.9 Mya, the Lower-Middle Jurassic from 201.3 to 145 Mya, and finally the Lower Cretaceous time which lasted from 145 to 66 Mya. Fig. 2.1 summarizes the age and tectonic regime of coal-bearing stata in different parts of Mongolia. The average carbon content of Carboniferous coal is highest with $82.7\,\%$, followed by Jurassic and Cretaceous with $75.3\,\%$ and $66.3\,\%$ respectively. The volatile matter of the Carboniferous is lowest with $24.8\,\%$ and highest for the Cretaceous coal with $45.2\,\%$. The lowest value of moisture content relates to Permian coal which has an average moisture of 0.8 %. Pennsylvanian[1] coal has a moisture content of 2.5 % and Cretaceous coal has a quite high moisture content of 9.6 % [2].

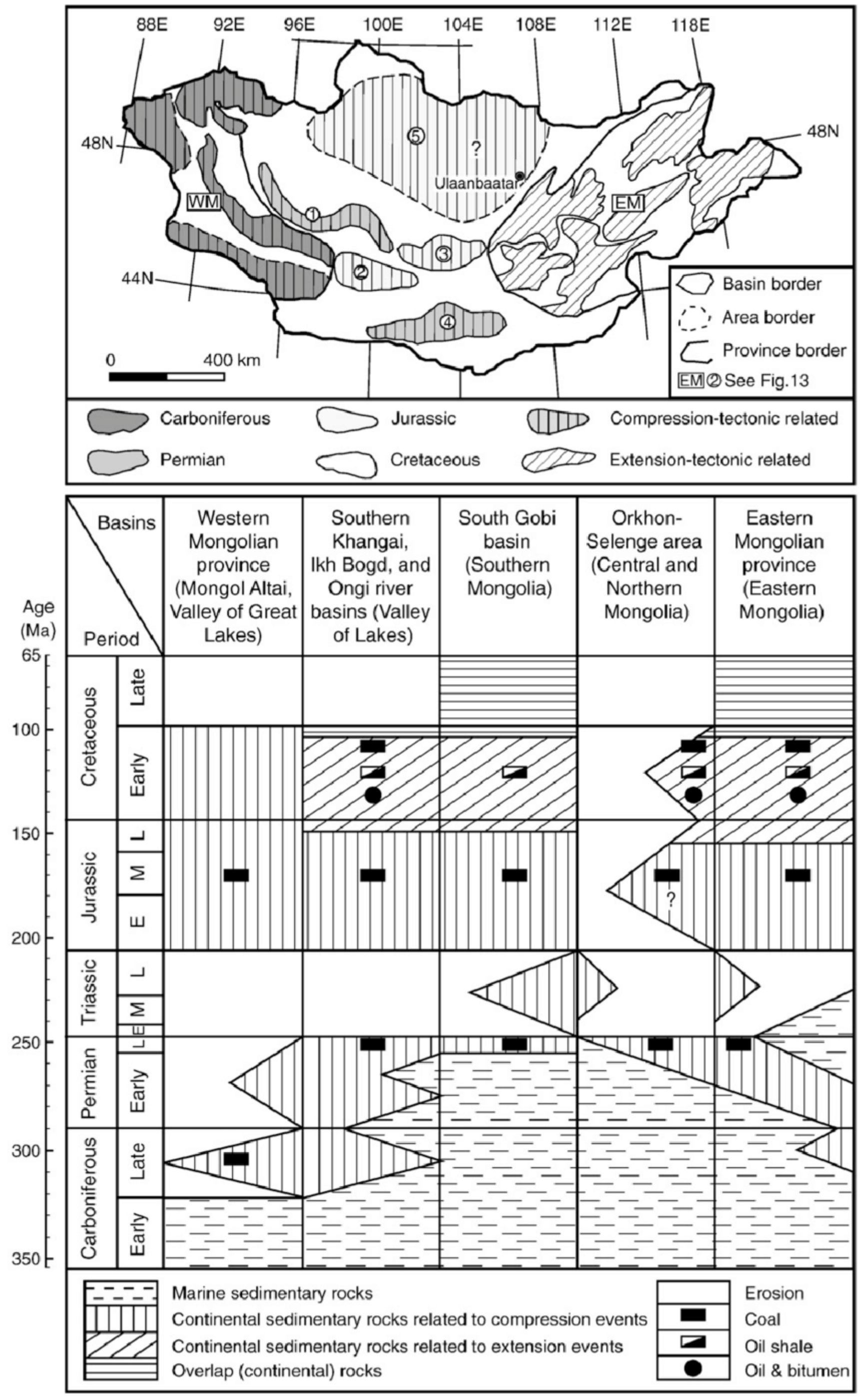

Figure 2.1: Summary of age and tectonic regime of coal-bearing strata in different parts of Mongolia. [2]

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[1] a sub-group of the the Carboniferous

Carboniferous coals were found in Western Mongolia. The Mongol-Altai, Kharkhiraa, Bayan-Ulgii, and Trans-Altai basins belong to western Mongolia. Several deposits are operating within the Mongol-Altai coal basin, including Khushuut, Maanit, Khuren gol, Tsagaan gol and Zeegt. The basin has total estimated coal resources of 10 billion tons and a proven reserve of 49 million tons. The formation has more than ten seams with an average thickness of $4\,\mathrm{m}$ to $18\,\mathrm{m}$. The Mongol Altai basin is characterized by high to low volatile bituminous coal. The Kharkhiraa basin is located in the northwest which includes Khuden, Nuurst khotgor, and Khartarvagatai mining deposits. This basin has total resources of 4.8 billion tons and proven reserves of 172.5 million tons. The average moisture content of coal from the Kharkhiraa basin is $1.3\,\%$ to $4\,\%$, and it contains $30\,\%$ of volatile matter. The sulfur content is about $0.5\,\%$, and the calorific value of the coal is from $29.5\,\mathrm{MJ/kg}$ to $33.8\,\mathrm{MJ/kg}$. Based on those coal quality quantities, it belongs to the high volatile bituminous coal type.

Fig. 2.2 informs about age, rank and areal distribution of coal accumulation in Mongolia with resources.

Jurassic coals were typically found in central and northern Mongolia. The most significant representatives are the Ongi River and Orkhon-Selenge basins. Those basins comprise the Alagt-sakhir, Khotgor, Bayantseeg, Tsagaan-Ovoo, Ulaan-Ovoo, Shariin gol, Nalaikh, and Mogoin gol deposits. The Ongi river basin has total resources of 1.5 billion tons and proven reserves of 42.6 million tons. The resource in the Orkhon-Selenge basin is 7.7 billion tons, and the proven reserve is 408.8 million tons [2].

Cretaceous coals in the eastern Mongolian provinces are Choir-Nyalga, Choibalsan, Sukhbaatar, Tamsag and East and Central Gobi. Within the region, over 90 deposits have been discovered, and all coals are characterized as lignite and sub-bituminous coal. The total coal resources of the eastern Mongolia coal basin are 108.3 billion tons with proven coal reserves of 6.5 billion tons. The most prominent representatives are the Baganuur coal mine and the Shive-Ovoo coal mine. The Baganuur coal deposit is a small depression filled with Jurassic and Cretaceous rocks between the Onon and the Choir-Nyalga basins. The Baganuur coal deposit is the largest surface coal mine in the country which has a significant role of supplying most of Mongolia's central region coal demand including the capital city Ulaanbaatar.

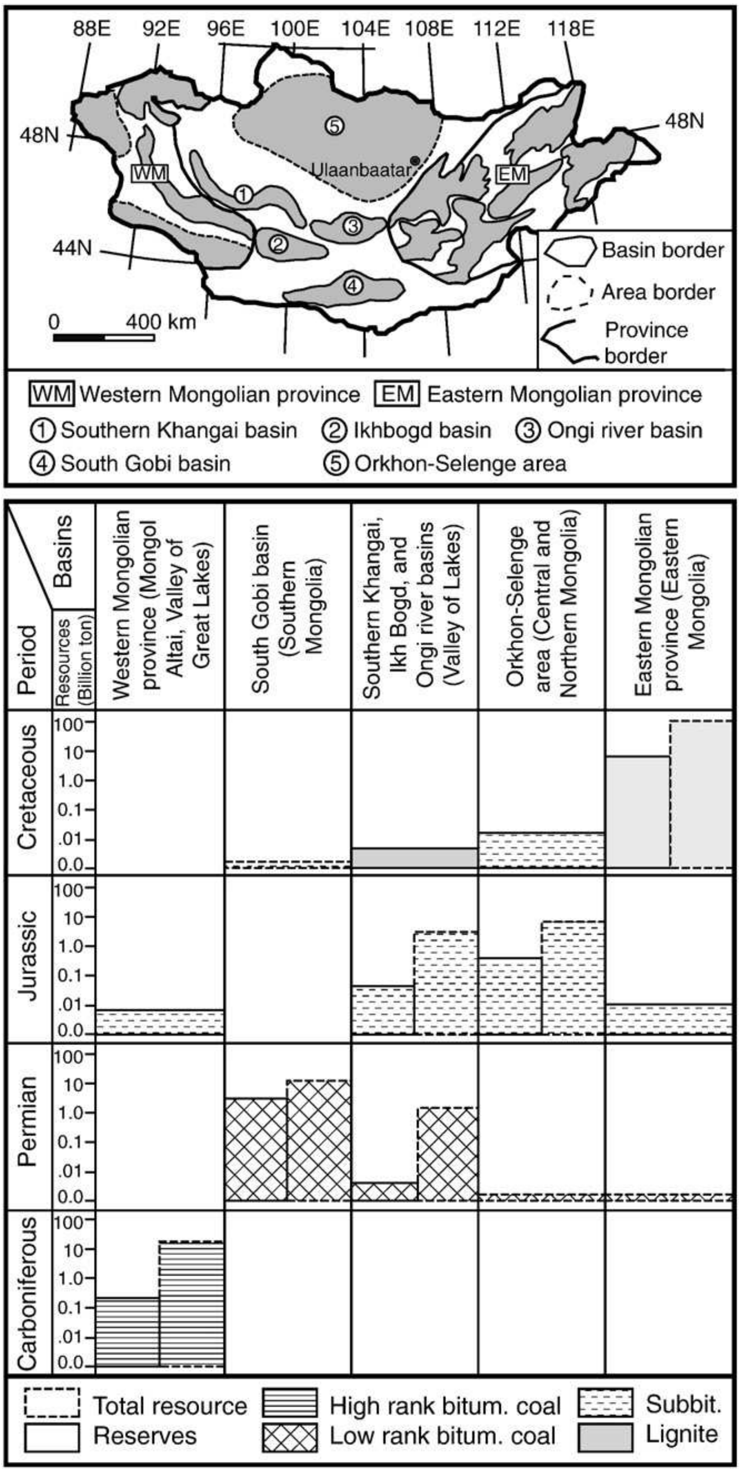

Figure 2.2: Age, rank and areal distribution of coal accumulation in Mongolia with resources [2].

It has total estimated coal resources of 812 million tons and proven reserves of 400 million tons. Due to the coal characteristics, the main consumers of the Baganuur coal deposit are thermal plants. Due to consumer demand, the Baganuur coal mine produces 5 million tons of coal per year. Further on, it will increase the output to over 6 million tons annually. The mean thickness of the coal deposit is $27\,\mathrm{m}$ with a moisture content of $31.8\,\%$ to $35.9\,\%$, ash content of $12\,\%$ to $17\,\%$, sulfur content of $0.3\,\%$ to $0.5\,\%$ and a calorific value of $13\,\mathrm{MJ/kg}$ to $15\,\mathrm{MJ/kg}$. Moreover, other coal deposits such as Aduunchuluun and Khulstnuur belong to the Choibalsan coal basin which has total resources of 14.9 billion tons and proven reserves of 213.2 million tons. Bulangiin khooloi and Bayantsogt belong to the Tamsag coal basin which has total resources of 32 billion tons and proven reserves of 190 million tons. Talbulag from the Sukhbaatar basin has total resources of 4.3 billion tons, including 68 million tons of proven reserves, Khootin khonkhor from Central Gobi basin and Khirmiin khural from East Gobi coal basin are the biggest lignite coal deposits. The total resources of the Central Gobi and East Gabi basins are defined as 13.2 billion tons and 23.5 billion tons, respectively. The quality of those basins is quite low, i. e. the coal contains volatile matter of $40.5\,\%$ to $47.3\,\%$, and ash of up to $25\,\%$ [3].

Permian coals are found in the south Gobi region of Mongolia. The quality of Permian coal is bituminous and premium bituminous coal. It covers 40 000 square kilometers within the total estimated resources of 13 billion tons, 2.9 billion tons of which are proven reserves. The South Gobi basin contains coking coal reserves. The primary representative is the Tavan Tolgoi coal deposit which is considered as one of the strategically significant coal deposits. The Tavan Tolgoi coal deposit has a total estimated resource of 6.4 billion tons. Of this quantity, 1.8 billion tons are coking coal, and 4.6 billion tons are thermal coal. The coking coal deposits exist not only in the south Gobi but in western Mongolia as well. However, coking coal deposits in the western area have a better quality of coking coal, Tavan Tolgoi has more advantages regarding the location and exploration [4].

Mongolia became the 5th largest exporter of coking coal in the world in 2013 because of the development of the Tavan Tolgoi coal deposits. The Tavan Tolgoi coking coal deposit consists of the Tsankhi, Ukhaa Khudag, Bor Tolgoi and Southwest and Eastern coalfields. The Tsankhi coal mine owns the most of the area of the Tavan Tolgoi deposit. The coal quality of the Tavan Tolgoi coal basin is determined by the moisture content, which is between $0.5\,\%$ and $2.3\,\%$, the ash content of $12.5\,\%$ to $27\,\%$ and a calorific value between $32.4\,\mathrm{MJ/kg}$ to $33.7\,\mathrm{MJ/kg}$. As it is a huge deposit, the coal is distributed in 18 coal-bearing layers, and the total thickness of the coal vein is $190\,\mathrm{m}$. Each seam has relatively different properties caused by their formation process. For example, the Ukhaa Khudag coal mine is evaluated that the mining area has three main zones which are called affected, fresh and zero. The fresh zone has a constant high quality, but the zero zone has a low quality which meets the quality of thermal coal. The Ukhaa Khudag (UHG) coal mine owns 6 percent of the overall Tavan Tolgoi deposit which covers 29.62 square kilometers. All the mines in the Tavan Tolgoi deposits are open surface mines which are further differentiated as open-cast and open-pit mines. The open-cast mining technique extracts the mineral while reclamation takes place in other parts of the mine simultaneously. In open pit mining the reclamation takes place after the extraction is completed. The UHG is an open pit mine which has a total estimated resource of 315 Mt, 218 Mt of which is proven reserve. In the entire Tavan Tolgoi coal basin, only the UHG coal mine has a coal handling and preparation plant. That is a literal example of using all the licensed area with high efficiency. As mentioned before, the coal properties are not the same at every seam. Therefore, to use the coal reserves effectively, coal handling and preparation plants are necessary for all mining companies, especially in the south Gobi region. The production capacity of UHG is 15 million tons of raw coal per year. As products, UHG produces about 7 million tons of hard coking coal and 3 million tons of thermal coal annually.

Speaking of the coal processing sector in Mongolia, UHG built the very first coal handling and preparation plant (CHPP) in 2011. The CHPP consists of three modules which can process 15 million tons of raw coal annually. They produce more than $70\,\%$ of the received coal as hard coking coal and export it to a Chinese cokemaking plant.

Lignite coal is used in Mongolia also as raw coal. The Mongolian government is interested in coal liquefaction and coking plants. However, due to the lack of money and other issues, Mongolia could not build it until now although it wanted to. For coal coking technology, as mentioned above, Mongolia has enough resources. Moreover, most importantly, it is easy to accomplish because

Mongolia has significant coking coal deposits that are currently exploited. Furthermore, washed hard coking coal is also produced in a Coal Handling and Preparation Plant which is ready to be developed on a bigger scale.

2.2 Current Coal Coking Plants in Mongolia

The modern industry requires a high throughput of goods with value-adding technologies. The higher technological development leads to the economic growth of the country. That criterion applies globally. According to the Mineral Resource and Petroleum Authority of Mongolia [1], Mongolian competitiveness ranks 109th out of 133 countries. Mongolian economy strongly relates to the mining sector. However, most of the heavy industries utilize simple technologies. Accounting mining occupies about 81.9 % of the overall exports and from that number 97 % uses poor technology or export products without a value-adding[1]. However, as a developing country, Mongolia has a great enthusiasm to advance heavy industry technologies. In the past 10 years, there have a few companies shown interest in the coking process. Since Mongolia has a substantial reserve of coking coal, coking technology can be developed in Mongolia.

Currently, there are one coal coking plant and one semi-coking plant in Mongolia. The coke-making plant is called ”ENC” LLC which is located in the Bayan-ovoo, South Gobi. The project study started in 2005, and the plant commenced in February 2008 with a capacity of 300 thousand tons of metallurgical coke annually. The chosen cokemaking technology is the non-recovery process which produces 13 thousand tons of tar annually. As a plan, the company exports the coke produced as well as the tar to China. However, the company could not reach the full plant capacity due to technical and other issues. Unfortunately, the plant could reach only 40 % of the planned capacity. The company was active in the beginning, but the current situation of the plant is not clear. Nevertheless, as a very first cokemaking plant in Mongolia, ENK brought the idea of producing coke as a domestic product.

The semi-coking plant, so-called ”NACO” LC, was established in Darkhan industrial campus, Darkhan-Uul province in 2010. The plant can receive 100 thousand tons of coking coal and produces 50 thousand tons of semi-coke and 6 thousand tons of briquette annually using the non-recovery process. The baking process takes place in the coke oven in the temperature range of 450 to $650\,^{\circ}\mathrm{C}$. The productions are semi-coke, tar, and coke oven gases. The produced semi-coke is sold to the local consumers.

Besides those two plants, there is one cokemaking plant planned to build. Since 2009, the Mongolian government has been trying to start a huge industrial project which is called Sain-shand heavy industry park. This enormeous project includes a cokemaking plant with an annual capacity of 2 million tons of coke. The purpose of the cokemaking plant would be to supply coke to the metallurgical plants in the industrial park.

3 Coke Fundamentals

3.1 Chemical Nature of Coking Coal

Coal is the sedimentary rock comprised mainly of organic detritus deposited in a swampy environment. In other words, coal is a combustible fossil fuel, formed from vegetal matter such as woody material, bark, spores and leaves that accumulated under the conditions of high pressure and temperature within a long time. Coal formation began in the geological period of Carboniferous which is from 360 million years ago (Mya) to 290 Mya. Coal is divided by its quality into several types. However, the coal quality refers to coal formation time and region. Also factors like climate, latitude, vegetation, peat accumulation rate and the burial history effect to the coal quality. According to the Statistical Review of World Energy in 2018, world coal proven reserves amount to 1035 billion tons [5]. By quality, 52 % is higher rank coals including anthracite (1 %) and bituminous (51 %) and other (48 %) is lower rank coals which determined as lignite (20 %) and sub-bituminous coal (28 % [6].

An initial stage of coal formation is peat. The peat is covered by sand and silt which causes the high pressure in the peat environment. Due to increasing pressure, the peat became harder and denser. Spontaneously, chemical reactions of losing oxygen, hydrogen, and sulfur in the form of gaseous compounds will have occurred in the peat. That physical and chemical processes together increase the content of carbon of the peat. Based on that formation the coal is classified into 5 ranks which are peat, lignite coals, sub-bituminous coals, bituminous coals, and anthracite. The chemical composition of peat is close to the plant, and it is not considered as coal. Attributes of peat are high moisture content and a large number of pores. Compared with coal itself, the calorific value is very low. Lignite, also called brown coal, is the youngest and the first rank in coal. Brown coals are mainly used in thermal power plants.

The maceral groups are inertinite, exinite[1] and vitrinite. They determine the carbon, hydrogen, and nitrogen composition. The vitrinite is the most important maceral which is responsible for determining the coking behavior of bituminous coals. The chemical structure of bituminous coal is described as more than half of the carbon being organized into aromatic nuclei containing on the average 2-3 fused rings. Each aromatic nucleus contains hydrogen atoms. The substituents are partly phenolic hydroxyl and carboxyl oxygen, and partly aliphatic carbon atoms that are composed of in such a way as to constitute hydroaromatic rings and to serve as linkages connecting the aromatic nuclei. Besides, there is a minor proportion of short alkyl chains and non-aromatic alicyclic rings. The ability to fuse is important in bituminous coals which allows them to be called coking coal. The average vitrinite amount in bituminous coal is around 60 % to 70 %. That proportion can be increased in the coking coal washing plant. Inertinite and exinite play a minor role in the bituminous coals. Those are the resin and waxy material of plants or highly evolved plant remains in coal. The proportion of the inertinite is higher than exinite in the bituminous coal [7].

3.2 Coke Manufacture

Coke is the solid carbonaceous, and upgraded version of coking coal which is an essential feed in the iron and steel making industry. Over 90 % of the total coke production is used for the metallurgical purpose and the remaining 10 % are called foundry coke. Foundry coke is used for foundries in furnaces for melting metal and in the preparation of molds. China is the largest coke producer in the world, producing 448 million metric tons of coke in 2015, and that is more than 60 % of the world coke production. The following top coke producers are Russia with 40 million metric tons, Japan with 37 million metric tons and India with 30 million metric tons in 2016 [8]. In the past 10 years, only China shows a considerable growth of coke production which increased by 326 million metric tons. Other countries kept coke production constant or decreased it.

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[1] synonym of liptinite

The cokemaking process can be broken down into two main technologies, the by-product process, and the non-recovery process. Those are differentiated by the concept of recycling or cleaning side products from the coking process. The commonly used and up-to-date technology is the by-product coke oven process. Because of the nonhomogenous behavior of coal particles, coking coals must be pulverized and then blended before they enter the coke oven. Blended coals are fed into several ovens which are sealed and heated at high temperatures for typically about 15 to 18 hours. The baking time is determined by the coal mixture, volatile matter, moisture and ash content, and other desired properties of the coke. From the thermal distillation process, output streams are separated into two. One of them is the main solid product, which remains in the oven, coke. It is pushed to the quenching tower, where coke is cooled with spray water, and then the coke is screened and stored. Another stream is coke oven gas that goes to further stages to recover by-products such as tar, ammonia, light oils, phenolic, and other aromatic chemicals. The nonrecovery process is sometimes called heat recovery cokemaking, which uses coke oven gases like steam in the power plant. There is no recovery of the by-products.

The core coking process takes place in the coking furnace. The coking coal, with a carbon content of around 75 to $90\,\%$ and moisture content of up to $10\,\%$, is baked under the condition of high temperature (900 to $1200\,^{\circ}\mathrm{C}$) at a slow heating rate (2 to $5\,\mathrm{K/min}$), in the absence of oxygen. Bertling et al. [9] mention that the coal is converted into coke zone by zone from the furnace wall to the center, and those zones are named drying, softening, and semi-coking. The zones are shown in the figure 3.1. First, the moisture evaporates from coal caused by contact with the furnace wall. Then volatile matter and other hydrocarbons are distilled from coal above $250\,^{\circ}\mathrm{C}$. That process is called pre-degassing, and it continues until $350\,^{\circ}\mathrm{C}$ is reached. In the next zone between $350\,^{\circ}\mathrm{C}$ and $480\,^{\circ}\mathrm{C}$, the so-called plastic zone, pore generation will happen on the microscopic scale. Volatile matter migrates from the coal particle through the vitrinite. This causes the volume of pores to increase and the particle to soften. Thus, coke swells. On the macroscopic scale, the rate of change and pore formation reaches a maximum at mid $400\,^{\circ}\mathrm{C}$. Indeed, structurally, vitrinites of coking coal have a sufficient number of molecular cross-linkages that are relatively weak $\mathrm{C{-}H}$ bonds, rather than the more stable $\mathrm{C{-}O}$ bonds or double bonded carbon. Around the middle of the coking time, the softening zones meet in the middle of the oven, where they unite to form the semi-coke zone. After 500 °C, the coal particles start to shrink and resolidify. Once the coke oven temperature reaches 900 °C, coking is nearly completed. As a result, bituminous coals are transformed into grey, hard and porous coke and the carbon concentration increases. This cokemaking process behaves similarly to the way that coal behaves in the coalification (carbonization) process.

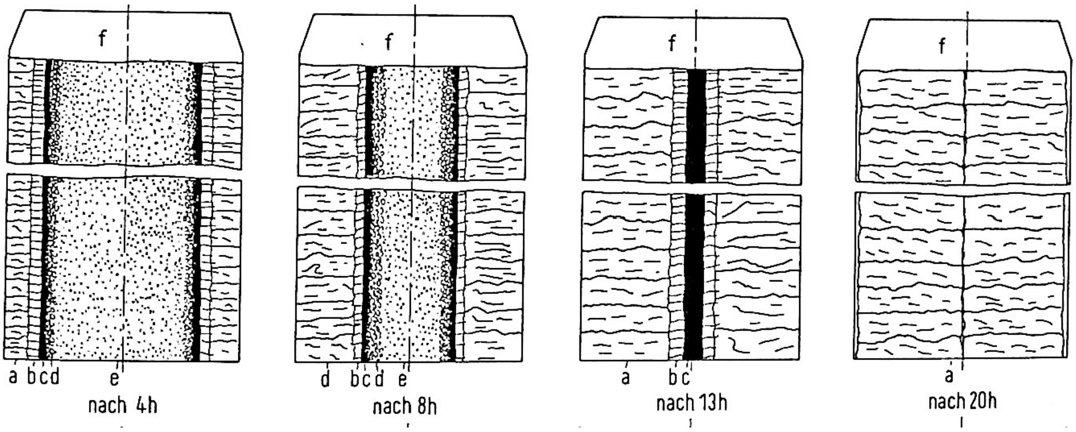

Figure 3.1: Coking zones after 4 h, 8 h, 13 h, 20 h in the coking chamber after [9]: a. 600 to 1100 °C, coke; b. 480 to 600 °C, semi-coke; c. 350 to 480 °C, plastic range; d. 100 to 350 °C, predevolatilized coal; e. 0 to 100 °C, coal and moisture; f. gas collection

As a result of baking in the coke oven chamber, coal becomes:

- More aromatic and less aliphatic
- Carbon dioxide is eliminated from carboxyl group
- Water is eliminated from hydroxyl groups
- Methyl groups exit as methane
- Condensation to C—C bonds and C-rings

Chemical Properties: In the process of making iron or steel in the blast furnace, coke is the most suitable fossil fuel to enable the process. Coke has three major roles. The primary role is to generate heat for the chemical reactions and the melting of slag and metal. The second role is to produce gases for the reduction of iron oxides. Moreover, the last role is to support the process of melting by providing a porous support. Regarding those three major roles, coke has to fulfill certain requirements. Carbon content, moisture, volatile matter, ash and sulfur content are important parameters to take into account. Fixed carbon is the fuel portion of the coke. Therefore, its concentration needs to be high. As mentioned before, other parameters are considered as impurities and need to be kept as low as possible. Coke moisture should be around $1\,\%$ to $6\,\%$, the ash content should be between $8\,\%$ and $12\,\%$, the volatile matter should be less than $1\,\%$.

Physical Properties: In the cokemaking process, the coke strength, the coke stability and the coke strength after reaction (CSR) are the most important parameters regarding the physical properties. Above all, coke size plays a basic requirement for these physical properties. The size is controlled by screening. Typically, a mean optimum size should be in a range of 50 to $55\,\mathrm{mm}$. Coke strength is related to the coal rank. The stability determines the capability of the coke to how it resists breakage at a normal temperature. CSR values represent the coke potential to break into smaller size under the environment of the high temperature, CO, and CO_2. The coal rank, coal rheology, inert contents and coking conditions influence the CSR. For a good quality coke, CSR index should be high. Generally, keeping the value of CSR, the coke quality can be controlled.

3.3 Environmental Aspects

The cokemaking process is a kind of chemical process which eliminates some chemicals, especially volatile matter, using heat. China as the primary producer of metallurgical coke has a big issue with significant pollution from the coke industry. However, pollution from the cokemaking process can be controlled by the technology itself. Several technological developments occurred in the history of the cokemaking process. Globally, two leading technologies exist. However, Chinese cokemaking technologies are divided into more than these two. Along a long time of development of technology, coke demand, and governmental regulations, China developed more detailed versions of cokemaking technologies. Due to mass production of coke, the Chinese government has strict environmental regulations on the pollutions from the cokemaking plant. Starting from 1996, the State government in China issued to close all old cokemaking plants that have old technology which is harmful to the environment.

The two basic technologies are mentioned in section 3.2. In addition to that, in China, there are five different categories including indigenous ovens, modified indigenous ovens, vertical coke ovens and heat recovery ovens. Indigenous and modified indigenous ovens are quite old technologies which have only one kiln without any installation to recover pollutants. Nowadays, most countries stop using those two technologies. The advanced, up-to-date technologies are machinery ovens (by-product ovens) and vertical ovens. They are able to recover most chemicals from the coke oven gas and other by-products. The latest technology is called “heat recovery ovens”, also known as the non-recovery process, that burns all the volatile matter and tars in order to get heat [10]. The main input of the cokemaking process is coking coal, and coke is the main output which is the most interesting material that we want to produce. However, depending on the technology, by-products such as tars, coke oven gases (carbon monoxide, carbon dioxide, methane and other hydrocarbons), light oils, ammonia, aromatic chemicals (like benzene, toluene, xylene, and naphthalene), and phenols are recovered from raw coke oven gases. Generally, in order to produce clean coke oven gas, all those ammonia, tars, aromatic chemicals, and light oils are removed from raw coke oven gases. If those materials could not be recovered, then they would affect the environment [11].

3.3.1 Emission aspects of the cokemaking process

The fugitive air emissions are produced along the cokemaking process. The fugitive air emissions include pollutants which are produced from leakages from doors, coal crushing, pushing, blending, coal handling and coke quenching, combustions stacks, coke sizing, screening, handling, and storage. Those fugitive emissions can be measured as particulate matter (PM). Besides PM, there are other chemical substances which could be emitted into the air. Those are sulfur dioxide, nitrogen oxides, numerous organic compounds including polycyclic organic matter, volatile organic compounds (VOC), and others. VOCs originate from coke oven leaks, coke pushing, and coke quenching. Also, other emissions such as sulfur dioxide, nitrogen oxides, and carbon monoxide are emitted from coke oven leaks [12]. Every country, especially the top producer countries have their own regulations, which regulate the limits. For instance, according to the World Bank Group report for coke manufacturing pollution prevention, PM emissions should be less than $50\,\mathrm{mg/m^3}$, and VOC emissions should not exceed $20\,\mathrm{mg/m^3}$.

3.3.2 Environmental impacts of emission

Emissions from pushing, quenching, and battery stacks affect human health including chronic health disorders (blood disorder, damage to the central nervous system, and respiratory lesions) and acute health disorders such as irritation of skin and eyes. Benzene and toluene in the air may affect the central nervous system and cause dizziness, sleepiness, and headache in the short-term inhalation. Long-term inhalation may cause severe disorders. Employees who work in cokemaking plants have reported an increase in lung cancer: The high content of polycyclic aromatic hydrocarbons in the air increases the lung cancer risk [10] and cancer of the trachea, kidney, and other sites.

The United States Environmental Protection Agency classifies coke oven emissions as Group A carcinogens and links them to lung cancer. To decrease emissions, the sources of emission need to be controlled.

Each step, where emissions can escape from the process, can be controlled by suitable actions. If there are leaks on the doors or lids that cover the charging ports, then those leakages can be stopped by using luting materials. Emissions from mechanical steps, like handling, crushing, sizing, screening, and storing of coke, can be collected and sieved in baghouses. Flue gases, such as sulfur dioxide that is emitted from the coke baking process or hydrogen sulfide which escapes from the desulfurization process, usually is controlled by maintaining oven walls and using additional gas cleaning equipment [13].

3.3.3 Wastewater aspects and their impacts on the environment

Besides emissions, there are other significant aspects regarding wastewater. In the cokemaking process, quenching and cooling of coke oven gases are must-have functions. After coke is produced in the coke oven batteries, it is delivered to the quenching tower, where water spray cools it. Because of the direct contact of water spray and hot coke particles, some portion of the water evaporates in the cooling process, and the excess water is collected and recycled. As it is recycling water, it is polluted by fine coal particles that must be separated or disposed of. This quenching process consumes a huge amount of water that impacts the water resource of the local area. Furthermore, it transfers pollutants, such as VOC, from the wastewater to the atmosphere surrounding the quench tower. If pollutants from the quenching with water process are considerably high, then a dry quenching method can be used which has minimal air emissions and uses no water. However, that is a more complicated process than wet quenching and more expensive. The second sector that uses water is the cooling of by-products.

Major wastewater streams are generated from the cooling of ammonia, tar, and other aromatic chemicals. Each ton of coal converted to coke produces about 100 liters of wastewater. That wastewater is salty and may contain a small portion of benzene, suspended solids, phenols, a significant amount of ammonia, polycyclic aromatic hydrocarbons (PAH), cyanides and other constituents that increase the biological and chemical oxygen demands. Wastewater from the cokemaking process is not directly recyclable, but it can be treated in settling tanks to remove total suspended solids, oils, and tars. For the removal of ammonia, hydrogen sulfide and hydrogen cyanide a steam stripping process can be used. Biological treatment and filters are used in the final stages of treating wastewater. If wastewater is not treated and directly discharged into the environment, then it causes massive damage to the freshwater ecosystems, mostly due to phenol, PAHs, and heavy metals.

3.4 List of Requirements

The cokemaking process is advanced coal beneficiation technology. It has the most significant influence on the iron and steel industry. Most likely, the cokemaking plant is part of an iron or steel making plant. Sometimes, the coke is called “blast furnace coke” as well. In this section, we will consider design specifications regarding some basic requirements for the cokemaking plant, standards requirements and wishes to progress.

3.4.1 The set of requirements for products from the coke oven plant

1) All output streams and their chemical characteristics must be determined.

   Depending on the chosen technology, output streams of the cokemaking plant are different. However, the most common outputs have already been studied in the longtime history of the cokemaking process. The main output is the coke. Side-products are residue tar, ammonia, naphthalene, toluene, benzene, xylene, coke oven gases, and light oils. Chemical and physical characteristics are shown in chapter 5. All those side-products can be produced if the cokemaking plant has a by-product treatment plant which comprises many steps to treat and separate the by-products. There are two main processing sectors that must be included in order to have by-products, which are tar distillation and coke oven gas treatment.

2) Coke yield must be higher than 70 %.

   Along the development of the cokemaking process, from the middle of the 19th century, technology has improved a lot by increasing the coke yield from about 33 % to 65 %. Currently, the coke yield becomes stable with an average coke yield of 65 % to 75 % of the input mass. The modern cokemaking technology concentrates on the highest possible yield of coke and quality to ensure optimal coke performance in the iron and steel making plant. The most of the cokemaking plants in the world produce the coke with a yield of 75 %, which also is our requirement.

3) The main and side products must fulfill consumer standard requirements.

   The chemical and physical specifications have to be met. The essential parameters of good coke are shown in table 3.1. The optimal size of coke is a very basic property, the coke reactivity index (CRI)[2] and the strengths of coke before after reaction (CSR) [3] would play a big role in the coke quality requirements. CSR should be at minimum 61 %, or higher.

Table 3.1: Coke Chemical and Physical Properties

Parameters	Specification
Moisture	1 to 6 %
Ash content	$<$ 10 % of dry matter
Volatile matter	8 to 12 % of dry matter
Sulfur	0.5 to 0.9 % of dry matter
Fixed carbon	79 to 81 %
Calorific value	28 to 31 MJ/kg
Mean size	50 to 55 mm
Coke strength after Reaction (CSR)	61 to 70 %
Coke reactivity index (CRI)	21 to 25 %

4) The primary product, the side products, and the emissions must fulfill all the local and worldwide regulations.

   Regulations that are formulated by the World Health Organization, State Environmental Protection Administration (Chinese environmental regulation), Environmental Protection Agency (American national standards), and Ministry of Environment and Green Development (Mongolian national standards for emission) have to be taken into account. Cokemaking is a global technology. In Mongolia, there is no such specific regulation for coke oven emission and tars. However, air quality standards and other country's standards for coke oven emissions, tars, and wastewater discharge regulations can be taken that are accepted elsewhere. Emissions from coke oven batteries should be observed and recorded for four

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[2] Percentage weight loss of coke after reaction with carbon dioxide to form carbon monoxide under conditions specified in ISO 18894:2018 [14]

[3] Strength of coke after reaction with carbon dioxide in the CRI test, measured as the percentage retained on either a 10,0 mm or a 9,5 mm sieve after tumbling under conditions specified in ISO 18894:2018 [14]

consecutive pushes each day for each battery. The minimum and maximum temperature of the flue gas should be established.

The limitation of visible emissions from coke oven doors are restricted to 4 % leaking doors for the tall batteries (the height of the oven is 5 m or more) and 3.3 % for short batteries (the height of the oven is less than 5 m). The standard requirement of the quenching process is that each quench tower should have baffles that cover at least 95 % of the cross-section area. According to SEPA, 2012, emission standards for PM, sulfur dioxide, and nitrogen oxides are limited to 1.0, 0.5, and $0.25\,\mathrm{mg/m^3}$ at the plant boundary, respectively. The standard values for PM at crushing and screening, feeding, coke pushing, and oven flue gas are limited to 30, 50, 50, and $30\,\mathrm{mg/m^3}$, respectively. And wastewater regulation from cokemaking plant requires (shown in table 3.3) a pHof 6.0 to 9.0, suspended solids (up to 30 mg/L), cyanide (less than 1 mg/L); biochemical oxygen demand (BOD) and chemical oxygen demand are 30 mg/L and 100 mg/L, respectively, oils (less than 10 mg/L), hexavalent chromium (up to 0.5 mg/L), ammonia-nitrogen (20 mg/L), and zinc (less than 5 mg/L [15]. The average wastewater generation rate should be less than $0.3\,\mathrm{m^3}$ per ton of coke production.

Table 3.2: Emission Standards for Coke Ovens [10]

	PM $[\mathrm{mg/m^3}]$	SO_2 $[\mathrm{mg/m^3}]$	NO_x $[\mathrm{mg/m^3}]$
Concentration at plants boundary	1.0	0.5	0.25
Crushing and screening	30		
Feeding	50	100	
Coke pushing	50	50	
Oven flue gas	30	50	500

5) Production rate must be determined.

The production rate can be considered as a capacity of the cokemaking plant. The capacity is expressed as the maximum average rate at which entities can flow through the system. There are a variety of factors that relate to the determination of the capacity. The first factor would be the demand for coke. How much of coke could we sell annually? There are a series of iron

Table 3.3: Wastewater Effluent Requirements

Parameter	Specification
Wastewater per t of coke	$0.3\,\mathrm{m}^3$
pH	6 to 9
Suspended solids	$< 30\,\mathrm{mg/L}$
Biological Oxygen Demand (BOD)	$< 30\,\mathrm{mg/L}$
Chemical Oxygen Demand (COD)	$< 100\,\mathrm{mg/L}$
Ammonia	$< 20\,\mathrm{mg/L}$
Phenols	$< 1.0\,\mathrm{mg/L}$
Cyanide	$< 1.0\,\mathrm{mg/L}$
Benzene	$< 15\,\mathrm{mg/L}$
Naphthalene	$< 1.0\,\mathrm{mg/L}$
Hexavalent chromium	$< 0.5\,\mathrm{mg/L}$
Zinc	$< 5.0\,\mathrm{mg/L}$
Oils	$< 10\,\mathrm{mg/L}$

and steel making plants existing in the northern part of China where we could deliver the produced coke. The next factor is the lifetime of the cokemaking plant. The typical lifetime of the coke oven batteries are 30 years, but the reserves of coking coal must be taken into account in order to determine the lifetime of the plant. Based on the lifetime range then a size of the plant can be defined. The plant size and their process functions determine the capacity. The average cokemaking plant capacity in the U.S is $1.36 \times 10^6\,\mathrm{t}$ annually. In Japan, the “Nippon Coke and Engineering” technology enables an annual production capacity of $1.9 \times 10^6\,\mathrm{t}$ of coke per plant. However, in this study, the coke production rate would be assumed regarding coking coal feed that UHG produces daily or annually.

6) Wastes from cokemaking plant must be disposed of properly.

The rate of the wastewater generation should be less than $0.3\,\mathrm{m}^3$ per ton of coke. The disposal of the solid residues and wastewater are must be treated regarding the limitation values in the wastes (limitation standards for wastewater effluents shown in table 3.3). Moreover, treated wastewater should be discharged into soakage, sewer or drains. Solid wastes should be discharged into the specific landfill, well isolated from groundwater.

7) By-products must be recovered.

As mentioned above, the coke yield must be higher than 70 % of feed coal. Then 25 to 30 % of the parent coal would be by-products, emissions, and wastes. Practically, about 20 to 25 % of the feed coal is converted into the by-products including tar, coke oven gases, ammonia, naphthalene, toluene, benzene, xylene, and other vapors. Products specifications are shown in the 3.4.

Tar consists of more than a hundred polycyclic aromatic hydrocarbons. Tar is separated from the main stream of raw coke oven gas which is generated in the coke ovens. The temperature of this gas stream is about 760 to 870 °C and firstly, it is shock cooled by spray flushing liquor in the gooseneck. Using this spray, the temperature of the raw gas can be decreased until it is between 80 to 100 °C, and from the cooled gas, tar precipitates and various components condense from the vapor phase. Precipitated tar is collected in the tar collector; then the liquor is separated in the tar decanter. Finally, the tar is stored.

After the tar is removed, the ammonia must be recovered from coke oven gas either as an aqueous solution or as ammonia sulfate salt. Furtherly, naphthalene and crude benzene should be recovered as a result of the further cooling process. Crude benzene contains mostly benzene, toluene, and xylene. Those aromatic chemicals must be recovered step by step. In order to separate crude benzene mixtures, specific separation agents and other technology are required.

Table 3.4: Typical products and by-products from one ton of coal [16]

Products	Amount	Specification
Coke	700 to 750 kg	
Coke breeze	40 to 90 kg	
Tar	30 to 45 L	
Ammonia liquor	60 to 135 L	99.7 %
Ammonia sulfate	10 to 13 kg	99.9 %
Coke oven gas	270 to 330 m^3	99.3 %
Light oils	10 to 15 L	
-Naphthalene	4 to 6 L	99.8 %
-Toluene	1.5 to 2 L	99.6 %
-Benzene	2.5 to 4.5 L	99.9 %
-Xylene	2 to 2.5 L	99.7 %

8) Additional reagents must be determined.

   In the process of recovering by-products, there are several media used. Depending on the chosen recovery technology, additional reagents will be determined.

9) Recovered by-products should be used on purpose.

   Aromatic chemicals are widely used in the field of chemical, pharmaceutical, and dye industries. Aromatics such as xylene, naphthalene, and phenol are used in the production of polymers. Benzene is used for making nylon, nitrobenzene, dyes, and pharmaceuticals. Naphthalene is important in the production of phthalic anhydride. Moreover, the recovered tar from raw coke oven gas can be distilled in the next processing step that leads to the production of phenol, and other industrial chemicals.

3.4.2 The set of requirements for design specifications

1) The location of the cokemaking plant should be near the coking coal deposit and coking coal washing plant.

   Most of the coke products are used for metallurgical purposes, especially for the blast furnace which makes them a part of the iron and steel industry. Most of the cokemaking plants are built next to the blast furnaced metallurgical plant. In Mongolia, there is a one iron making plant which exists in northern Mongolia, called Darkhan Metallurgical Plant (DMP). DMP produces reinforcing steel bar, round steel bar, steel square bar, and steel angle using scrap iron in the high power electric arc furnace. This means DMP does not use coke for melting scrap. Instead, DMP uses graphite electrodes. That is why our cokemaking plant should be located next to the coking coal deposits in the South Gobi where we have quite many reserves, accounting for 2.9 billion tons of coking coal, and active mines.

2) Ergonomics and quality of the plant must be environmentally friendly to the employees and locals.

   The coke oven battery is the heart of the cokemaking plant where the coke is produced. The average age of the worldwide installed coke oven batteries is over 25 years. The technical life range of coke oven batteries is 30 to 40 years of age. However, they have an economic life of 25 years, and if older they cause high maintenance cost. In the USA, 40 % of the coke oven batteries are over 30 years of age and 25 % are over 40 years of age. They might produce a lot of emissions and wastes and make the cokemaking process quite expensive. In order to have well-qualified plant and coke, modern and new coke oven batteries should be chosen. Although the installation cost is higher at the beginning, maintenance cost is reduced. The quality of the plant directly relates to the environmental impacts. As mentioned before, the cokemaking plant needs to fulfill all the environmental regulations.

3) Plant process must be controlled by an automatic control system.

   The Cokemaking process will produce masses of coke. The process should be continuous to keep the plant on balance. In the continuous technology, each process function must be adjusted in certain conditions and must not be interrupted by external effects. When a failure occurs, quick actions for finding the error and then maintenance or correction must be made as quickly as possible. For these needs, industrial control systems are abundant in the processing technology. The control system can be installed as partly or fully automatic control system. Especially, coke oven batteries must have the control system for heating and pushing.

4) The plant must have HAZOP analysis, all the safety tools, safety guidelines in the boundary of plant environment.

   A Hazard and Operability Study (HAZOP) is a systematic examination of the whole plant including all operations in each process phase. HAZOP is a technical risk assessment that is useful to identify and evaluate possible incidents and problems that may occur in the working field. Based on all safety analysis regarding operations and human health, safety guidelines should be made for all and safety tools must be provided and installed.

5) Transportation system must be established in an economic and environmentally friendly way.

6) Storage of the coke must be built concerning leakages and product loss.

The coke storage must be designed with a completely roofed and walled structure surrounding the coke product. The design of the storage must prevent the escape of fugitive emissions. The storage must follow all the regulations regarding construction schedule, interim fugitive emission plan, emission monitoring plan and contingency plan.

4 The Process on the Functional Level

4.1 The Basic Flowsheet of the Coking Process

The functional level is the very first stage of process systems synthesis. In this principal level, we will determine our very basic flowsheet of a cokemaking plant. Basic needs such as input and outputs have to be specified. The functions and their subfunctions have to be defined, and the relationship between functions and subfunctions will be determined here.

Based on the list of requirements, our technology choice would be the most common by-product process which means we want to recover all by-products from the coke oven. Figure 4.1 illustrates the major process functions in a schematic diagram. The flowsheet diagram shows the process functions from the preparation of coking coal to the finished product “coke” that is delivered to the metallurgical plant. The main focus will be on the coal coking process. We tried to sum up all the essential functions of the by-product process of cokemaking. The cokemaking process consists of mainly two sections; one is the coke production line and another one is the by-product recovery line.

4.1.1 Coke production line

The coke production line starts with the blending of various kinds of coking coals that are differentiated by their chemical and physical quality. Basically two or more low, medium, or high volatile coals that need to have low ash and low sulfur content. The blending process plays an important role for the strenght of coke. Diez et. al.[17] mentions in his article that 70 % of the coal quality depends on the selection of coals and their blending. The blended coals have to be crushed so in this way coal can be pulverized uniformly. The feed to the coke oven batteries must have a same size, and the size selection influences the strength and the quality of the coal. After crushing function, coal will be discharged into ovens.

The coke bake function will take place in coke oven batteries. The coal is baked under the condition of high temperature and absence of oxygen. The general temperature would reach 1000 °C to 1200 °C at a slow heating rate of 2 to $5\,^{\circ}\mathrm{C/min}$. The moisture and volatile matter, (CO_2, and light hydrocarbons) are evaporated from the organic macromolecular structure when the coal is heated to 350 °C. At the next level of heating from 350 °C to 500 °C degradation of the coal structure will happen. At this range of temperature the pore generation rate of coal reaches a peak. As a result, coal becomes softer and swells. After 500 °C, the coal starts to shrink and resolidify. It leads to a structural reorganization of a semicoke to coke. This whole baking process proceeds for 15 to 18 hours to produce perfect blast furnace coke. The baking time is related to coal properties, blend, and production rate. From coke oven batteries, two streams will be generated. Mainstream is a solid product coke that remained in the oven and another stream is raw coke oven gas.

The mainstream leaves the coke oven batteries by being pushed to the quenching tower. In the quenching tower, coke is cooled by a shock water spray. This shock cooling process is required to prevent the coal from burning after revealing to air. After the coke is cooled, the coke is screened Coke with the proper size for the blast furnace operation is delivered to the coke storage.

4.1.2 By-Products production line

The second stream, that is formed from coke oven batteries, raw coke oven gas (crude gas) proceeds to the by-product recovery plant. As shown in the figure 4.1, the recovery plant consists of several functions which are branched down from the coke bake function. Crude gas accounts for 25 % to 30 % by weight of the parent feed and consists of water vapor, coke oven gas (H_2, CH_4, CO, CO_2, and hydrocarbons), tar, aromatic chemicals, and light oils. Crude gas is collected in gas collection main. The temperature of the existing crude gas is about 760 °C to 870 °C. At first, this temperature must be cooled down until 80 °C. Due to cooling process of crude gas tar is precipitated and goes to the tar decanter where tar is seperated from the looking agent and other condensed compounds. The yield of the tar would be 3 % to 5 % of the crude gas. After the tar is removed, the gas goes to the ammonia recovery. The next function would be to recover naphthalene. In order to recover the naphthalene, the gas needs to be cooled again. Then we have the function to separate light oils which lead to crude benzene compounds. Crude benzene is a mixture of benzene, toluene, and xylene. The recovery method would be the distillation of crude benzene where we can separate those chemicals. After tar, ammonia, and crude benzole removal, the crude gas is nearly purified and the final function of the by-product recovery plant would be to remove H_2S and HCN. Finally, clean coke oven gas is produced and collected. It then goes to coke oven batteries to support the combustion system.

4.2 Descriptions of By-Products

Tar: The carbonization process of coal breaks down organic compounds into simpler compounds. That process leads to the formation of various types of aromatic chemicals within a range from volatile benzene to pitches. Tar is an great source of aromatic chemicals including polycyclic aromatic hydrocarbons (PAHs), phenolic compounds, tar acid compounds, and oxygenated and nitrogenated aromatic bases. Tar can be further distilled after it is produced from the crude gas. The products such as benzene, toluene, xylene, carbolic oil, naphthalene oil, wash oil, and coal-tar pitches could be fractionated. Ammonia: Ammonia (NH_3) is the simplest pnictogen hydride. The most of the ammonia, accounting about 88 %, is used in fertilizers. Naphthalene: Naphthalene is the simplest volatile PAH. The crude gas from coke oven batteries contains naphthalene that condensates typically about at 50 °C to 55 °C. Naphthalene is the basis for the synthesis of phthalic anhydride, that is used in the preparation of plasticizers, dyes, resins and other specific chemicals. BTX: The crude benzole, so called BTX fraction, is mostly composed of benzene, toluene, and xylenes. BTX is essential for the petrochemical industry. Benzene is the most important compound in the crude benzole that becomes a basis of a lot of products such as nylon, phenolic compounds, and polystyrene which used in the production of plastic materials. Toluene is used for chemicals and pharmaceutical products. Xylene is used in the production of polymers such as polyesters, aramids, and benzobisoxazoles. 2018-08-10 23:56

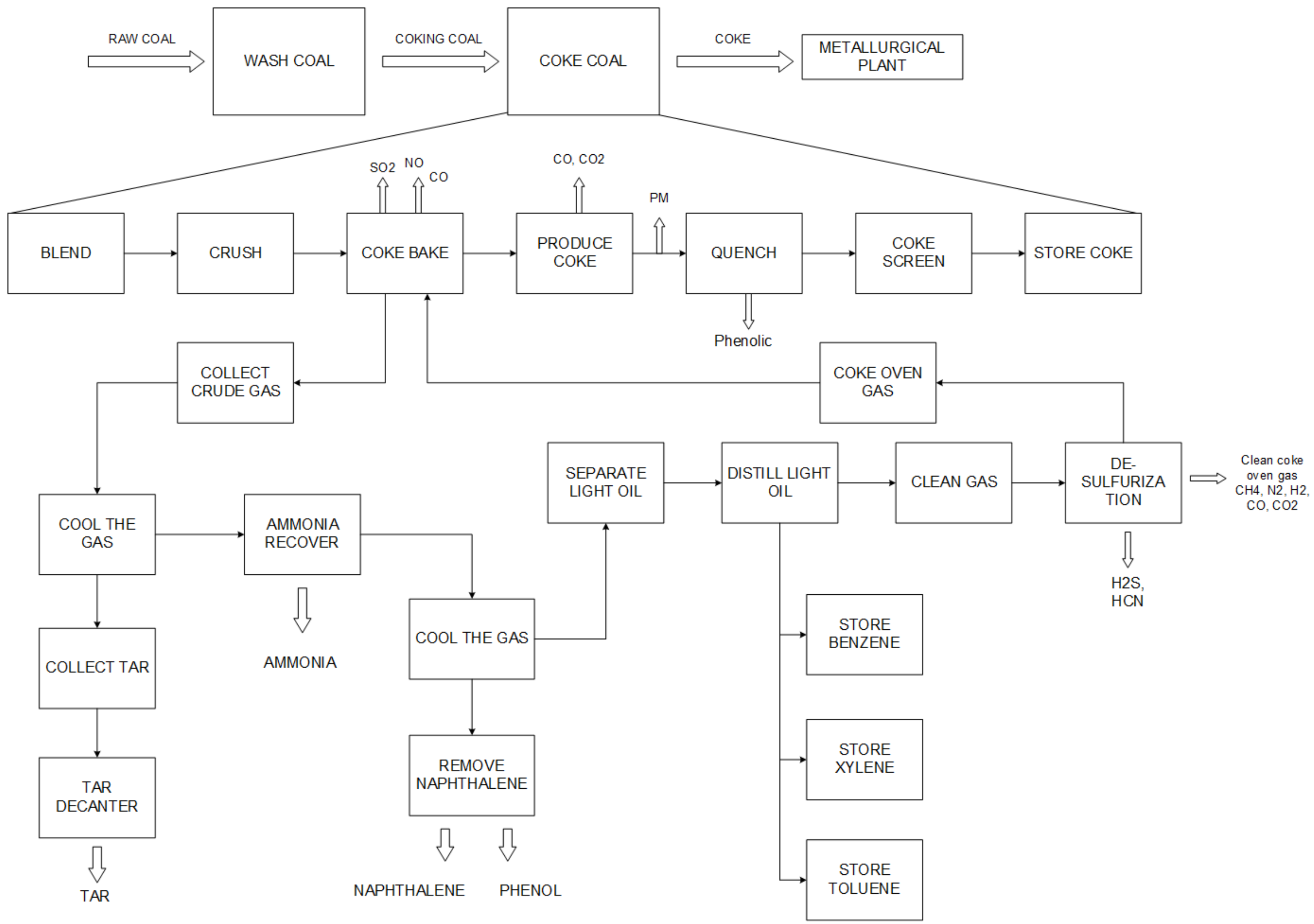

Figure 4.1: The basic flowsheet of the coking process

5 Physical Properties

5.1 Physical Properties of Chemical Substances in the Coke-making Process

Physical properties (see Table 5.1) include formulae of substances, CAS numbers, melting and boiling points, critical data, densities, liquid phase heat capacities and maximum emission concentrations according to German standards.

5.2 Ideal Gas Heat Capacities

The ideal gas heat capacities for toluene, naphthaliene, the xylenes and other substances follow the polynomial (Shomate equation). The coefficients are given in 5.2 and 5.3, respectively.

$$c_p = A + BT + CT^2 + DT^3 + ET^4 \tag{5.1}$$

$$c_p = A + BT + CT^2 + DT^3 + \frac{E}{T}^2 \tag{5.2}$$

5.3 Safety and Hazards Data

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Table 5.1: Properties of chemical substances in the coke-making process [18] and [19] and maximum immission concentrations according to TA Luft [20, 21]. The substances are in the order or their boiling points.

Name	Formula	CAS Number	Melting point [°C]	Boiling point [°C]	Critical temperature [K]	Critical pressure [bar]	Liquid phase density at 25 °C [kg/m^3]	Liquid phase heat capacity at 25 °C [J/(K mol)]	TA Luft limit [mg/m^3]
Hydrogen	H_2	1333-74-0	−259.2	−252.9	33.2	13.0			
Nitrogen	N_2	7727-37-9	−210.0	−195.8	126.2	34.0			
Carbon monoxide	CO	630-08-0	−205.0	−191.51	132.86	34.935			80
Methane	CH_4	74-82-8	−182.5	−161.5	190.6	46.1			
Carbon dioxide	CO_2	124-38-9	−56.6	−78.4	304.13	73.773	710.50 [a]		
Hydrogen sulfide	H_2S	7783-06-4	−82.0	−60.0	373.15	90.0	775.20 [b]	73.52	3
Ammonia	NH_3	7664-41-7	−77.7	−33.3	405.4	113.33	602.76 [c]	80.16	30
Sulfur dioxide	SO_2	7446-09-5	−72.0	−10.02	430.64	78.84	1367.7 [d]	93.06	0.05
Nitrogen dioxide	NO_2	10102-44-0	−11.2	21.2	431.4	10.1		141.72	0.04
Hydrogen cyanide	HCN	74-90-8	−14.0	25.6	456.7	50.0	680	73.52	3
Benzene	C_6H_6	71-43-2	5.5	80.08	562.05	48.94	873.67	137.87	5
Thiophene	C_4H_4S	110-02-1	−38.0	84.0	579.4	57.0	1059	124.5	50 [e]
Toluene	C_7H_8	108-88-3	−95.0	111.0	593.2	41.263	862.24	157.49	50 [e]
p-Xylene	C_8H_{10}	106-42-3	13.0	138.0	617.3	35.2	858	197.75	50 [e]
m-Xylene	C_8H_{10}	108-38-3	−48.0	139.0	618.4	35.4	861	182.66	50 [e]
o-Xylene	C_8H_{10}	95-47-6	−24.0	144.4	631.3	37.0	876	189.25	50 [e]
Phenol	C_6H_6O	108-95-2	40.5	181.7	694.3	59.3			50 [e]
Naphthalene	$C_{10}H_8$	91-20-3	78.2	218.0	748.6	41.1			50 [e]
Pyrene	$C_{16}H_{10}$	129-00-0	145.0	404.0	936.0	26.1			0.05[f]

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[a] at 64.342 bar
[b] at 20.173 bar
[c] at 10.032 bar
[d] at 3.9238 bar
[e] all organic substances combined
[f] all polycyclic aromatic hydrocarbons combined

Table 5.2: Coefficients for calculating the ideal gas heat capacities at constant pressure in $\mathrm{J/(mol\,K)}$ for toluene, naphthalene and the xylenes [19]

	A	B	C	D	E	T_{min}[K]	T_{max}[K]
Toluene	-24.097	5.2187×10^{-1}	-2.9827×10^{-4}	6.1220×10^{-8}	1.2576×10^{-12}	200	1500
o-Xylene	0.182	5.1344×10^{-1}	-2.0212×10^{-4}	-2.1615×10^{-9}	2.3212×10^{-11}	200	1500
m-Xylene	-16.725	5.6424×10^{-1}	-2.6465×10^{-4}	1.3381×10^{-8}	1.5869×10^{-11}	200	1500
p-Xylene	-17.360	5.6470×10^{-1}	-2.6293×10^{-4}	1.1217×10^{-8}	1.6544×10^{-11}	200	1500
Naphthalene	67.099	4.3239×10^{-2}	9.1740×10^{-4}	-1.0019×10^{-6}	3.3896×10^{-10}	50	1500

Table 5.3: Coefficients for calculating the ideal gas heat capacities at constant pressure in $\mathrm{J/(mol\,K)}$ for chemicals in the coke-making process [18]

	A	B	C	D	E	T_{min}[K]	T_{max}[K]
Ammonia	19.995 63	49.771 19	−15.375 99	1.921 168	0.189 174	298	1400
Carbon monoxide	25.57	6.09	4.05	−2.67	0.13	298	1300
Carbon dioxide	24.99	55.19	−33.69	7.95	−0.14	298	1200
Sulfur dioxide	21.43	74.35	−57.75	16.35	0.09	298	1200
Nitrogen dioxide	16.11	75.89	−54.39	14.31	0.24	298	1200
Hydrogen sulfide	26.88	18.68	3.43	−3.38	0.13	298	1400
Hydrogen cyanide	32.69	22.59	−4.37	−0.41	−0.28	298	1200
Nitrogen	28.98	1.85	−9.65	16.63	0.0001	100	500
Hydrogen	33.06	−11.36	11.43	−2.77	−0.16	298	1000
Methane	−0.7	108.48	−42.52	5.86	0.68	298	1300

Table 5.4: Safety data of chemicals substances in the cokemaking process [22]

	Explosion limits		Ignition	Flash	TLV value	Flammability
	Lower limit [% by vol. in air]	Upper limit [% by vol. in air]	Temperature [°C]	Point [°C]	TWA [a] [ppm]	
Carbon monoxide	12.5	74.2	609	-191	25	4 [b]
Methane	5	15	537	-188	1000	4
Carbon dioxide	-	-	-	-	5000	0 [c]
Hydrogen sulfide	3.9	45.5	232	-82.4	1	3 [d]
Ammonia	13	28.0	651	-	25	1[e]
Sulfur dioxide	-	-	-	-	2	0
Nitrogen dioxide	-	-	-	-	3	0
Hydrogen cyanide	5.6	40	538	-17.8	10	4
Benzene	1.2	8.0	497.78	-11.63	0.5	3
Thiophene	1.5	12.5	-	-1	-	3
Toluene	1.1	7.1	-	6	20	3
p-Xylene	1.1	7.0	528	27	100	3
m-Xylene	1.1	7.0	527	27	100	3
o-Xylene	0.9	6.7	463	32	100	3
Phenol	1.3	9.5	-	79	5	2[f]
Naphthalene	0.9	5.9	525	80	10	2
Pyrene	-	-	-	-	-	0

---

[a] TLV - TWA = Threshold Limit Value in Time-Weighted Average 8h/day

[b] Extremely flammable - materials that will rapidly or completely vaporize at atmosphere pressure and normal ambient temperature or that are readily dispersed in air and will burn readily

[c] Not flammable - materials that will not burn under typical fire conditions, including intrinsically noncombustible materials such as concrete, stone, and sand

[d] Highly flammable - materials that can be easily ignited under almost all normal temperature conditions

[e] Flammable - materials that must be preheated before ignition will occur

[f] Moderate flammable - materials that must be moderately heated before ignition will occur and includes combustible liquids and solids and semi-solids that readily give off ignitible vapors

Table 5.5: Impacts of chemicals on humans (Hazard statements)

	Physical damage		Intoxication	Cancerogic	Teratogenic	Mutagenic
Carbon monoxide	Extremely flammable	-	Toxic if inhaled	Specific organ toxicity	May damage	-
Methane	Extremely flammable	-	Harmful if inhaled	-	Suspected damage	-
Carbon dioxide	Cold or liquid phases affects to eyes, skin	-	Harmful if inhaled	-	-	-
Hydrogen sulfide	Burns easily	Serious eye and skin irritation	Fatal if inhaled	Specific organ toxicity	-	-
Ammonia	Burns skin and eyes	Skin corrosion, eye damage	Fatal if inhaled	Specific organ toxicity	-	-
Sulfur dioxide	-	Skin corrosion, eye damage	Toxic if inhaled	-	-	-
Nitrogen dioxide	Oxidizing gas	Serious eye damage	Fatal if inhaled	Specific organ toxicity	Suspected damage	
Hydrogen cyanide	Extremely flammable	Irritation to skin and eyes	Fatal if inhaled	Specific organ toxicity	-	-
Benzene	Highly flammable	Serious eye and skin irritation	Aspiration hazard	May cause cancer	-	May cause genetic defects
Thiophene	Highly flammable	Serious eye and skin irritation	Toxic if inhaled	Specific organ toxicity	-	-
Toluene	Highly flammable	Skin corrosion	Aspiration hazard	Specific organ toxicity	Suspected damage	-
p-Xylene	Burns easily	Skin corrosion, eye damage	Aspiration hazard	Specific organ toxicity	-	-
m-Xylene	Burns easily	Serious eye and skin irritation	Aspiration hazard	Specific organ toxicity	-	-
o-Xylene	Burns easily	Serious eye and skin irritation	Aspiration hazard	Specific organ toxicity	-	-
Phenol	Burns easily	Serious eye and skin irritation	Acute toxicity, oral and dermal	Specific organ toxicity	-	Suspected damage
Naphthalene	Burns easily	Serious eye and skin irritation	Acute toxicity, oral	Suspected damage	-	-
Pyrene	-	Skin corrosion, eye damage	May cause repiratory irritation	-	-	-

6 Physics Level

6.1 Coke Oven Gas Treatment

The by-products of the cokemaking technology are recovered from the main gas stream (crude gas). The raw crude gas is produced during the process of coal coking. It consists of various types of hydrocarbons and other chemicals. The primary objective of the treatment plant is to produce a clean coke oven gas (COG) after removing condensable and valuable components. The typical clean gas composition ranges are shown in the table 6.1. From these compositions, the H_2, CH_4, CO, and other hydrocarbons play an important role in clean COG.

Table 6.1: Raw and Clean coke oven gas composition [23] [24] [25]

Parameter	Composition	
	Raw COG [% by volume]	Clean COG [9] [% by volume]
Hydrogen	52 - 59	53 - 62
Nitrogen	1.9 - 5.7	6.4 - 12.3
Carbon monoxide	4.5 - 7.0	4.6 - 6.3
Carbon dioxide	1.4 - 2.1	1.5 - 2.7
Methane	26 - 33	22.6 - 25.7
Ethane	0.7 - 1.1	0.1 - 2.9
Ethylene	2.0 - 2.8	< 0.02
Hydrogen sulfide	0.4 - 1.2	< 0.05
Hydrogen cyanide	0 - 1.2	< 0.09
Other hydrocarbons	2	< 0.3

Clean COG has a net calorific value (coke oven gas produced from hard coking coal) of about $20\,\mathrm{MJ/(N\,m^3)}$ [23]. Thus, it is used for supporting the combustion system of the coke oven batteries. As described in chapter 4, the COG treatment plant consists of various stages, and each by-product requires own recovery method. The most of the separation methods would be performed based on the boiling point of the substance.

In order to produce clean coke oven gas, there are several separation techniques needed for the several chemical substances of crude gas. There are various separation methods involved in mixtures. The most known separation processes are chromatography, crystallization, filtration, evaporation, decantation, distillation, and fractioning. The various methods are applied according to the separation problem of the mixture. For instance, distillation is used for separating liquids in solution, filtration is used for separating the mixture of solids and liquids. Therefore, the separation techniques must be chosen based on the chemical and physical properties of the mixture. By relevant properties, the most appropriate separation techniques to separate by-products from the raw coke oven gas mixture can be chosen.

In coke oven treatment case, the boiling point will play a big role in the separation operation. The boiling point difference can tell how separation could be performed. The table 5.1 shows the typical physical properties of substances that are included in the crude gas. In the table, the boiling point is arranged in order from low to high boiling point. The order will show that COG compositions are clearly separated at the top part which is low boiling point range ($-60\,^{\circ}\mathrm{C}$ to $-259.2\,^{\circ}\mathrm{C}$) from other substances that need to be removed. There is a great temperature difference between COG composition and hydrocarbons, accounting at least $60\,^{\circ}\mathrm{C}$, namely, benzene has the boiling point of $80.08\,^{\circ}\mathrm{C}$ but hydrogen cyanide $25.6\,^{\circ}\mathrm{C}$. That great difference makes the separation process much easier which means there will be no problem to separate aromatic chemicals from benzene to pyrene (in table order) from COG. But in the order of substances, the boiling point of hydrogen cyanide ($25.6\,^{\circ}\mathrm{C}$) and nitrogen dioxide ($21.2\,^{\circ}\mathrm{C}$), and also p- ($138\,^{\circ}\mathrm{C}$), m- ($139\,^{\circ}\mathrm{C}$), o- ($144.4\,^{\circ}\mathrm{C}$) xylenes are very close to each other. That shorter difference will be problematic in terms of the separation process.

Due to a smaller difference of the boiling points of three isomers of xylene, xylenes will be separated as one component. There will be no separation process for the xylene isomers. Thiophene and benzene have close boiling point as well $84\,^{\circ}\mathrm{C}$ and $80.08\,^{\circ}\mathrm{C}$ respectively, but thiophene will be separated in the tar separation process with other tar components.

6.2 Separation Technologies for By-Products

Heuristic rules are widely used for process design. There are quite a number of selection rules for the separation methods. In order to select the most efficient separation sequence, heuristic rules give a guideline for the selection process. As shown in the process flowsheet 4.1, several separation technologies are needed. Following two heuristic rules are applied for the separation processes for by-products.

1) Heuristic rules for separation operations [26]:
    1a) Aim at high separation factors
    1b) Prefer distillation
    1c) Consider separation operations that introduce foreign substance only as a second choice
    1d) Prefer separation operations with proven technological experience
    1e) Consider extreme process conditions as a second choice
    1f) Prefer fluid phases over solid phases
    1g) Pay attention to a reasonable relation between the costs of chosen separation operation and the value of the product
    1h) Avoid deterioration of the product or keep it low
2) Heuristic rules for separation sequences[26]
    2a) To reduce the separation load, divide and mix streams
    2b) Prefer sequences that remove corrosive, poisonous or otherwise hazardous substances as early as possible
    2c) If components are present in excess, separate them as first

2d) Prefer sequences that divide the feed stream to a separation unit into two equimolar process stream

2e) Place difficult separations at the end of a sequence and separate in a line of falling separation factors. Perform easy separation first

2f) If components are to be obtained with high purity, place their separation at the end of the sequence

2g) In distillation sequences, prefer those sequences that deliver the components with highest purity specifications as head products

2h) In distillation sequences, prefer those sequences that place the components in direct series

2i) Pay attention to the thermal coupling of condensation and evaporation for difficult distillation separations at the end of a separation sequence

2j) Prefer sequences with side withdrawals for components or fractions whose boiling temperatures are not too near to the boiling points of other components and that do not require high purity

Based on those heuristic rules, following separation sequences are determined. Due to its separation design for by-products from the cokemaking process, by-products physical, chemical, and safety properties are concerned firstly then based on heuristic rule 2b and 2e, separation sequences are determined as tar - ammonia - naphthalene - light oil separation - desulfurization.

6.2.1 Tar separation

Tar is a mixture of various polycyclic aromatic chemicals, accounting for more than 200 chemicals that are identified in the coal tar. The high valued components are naphtha-type compounds, benzene, toluene, xylenes, thiophene, and methylcyclohexane. Those chemicals have the boiling point range between 80 °C to 130 °C shown in the table 5.1. During the coking process, tar components are mixed with the overheated gases and reach a temperature above 700 °C. Under this high-temperature condition, tar changes its physical and chemical behavior, becoming more aromatic and condensed. Since tar becomes easy to condensate and it exists as droplets in the crude gas, tar would be the easiest separation unit to perform in the recovery plant, rule 2e. Moreover, coal tar separation will decrease the crude gas stream load 2a. That is why the very first separation sequence becomes the tar separation.

The hot crude gas, which is produced from coke oven batteries, has a quite high temperature of $750\,^{\circ}\mathrm{C}$. That temperature must be decreased for further by-product recovering processes. An initial cooling stage typically uses aqueous liquids to quenching the hot crude gas. Aqueous liquids, also called flushing liquor, contain dissolved ammonia, water, and dissolved neutral oils. This aqueous shock spray cools the hot crude gas to 70 to $100\,^{\circ}\mathrm{C}$. During this process, the most of the tar components are condensed due to their dew point. Precipitated tar components, which are mixed with flushing liquor, are separated from the crude gas and delivered to the tar and liquor separation stage.

The next stage for separating tar would take place in the tar decanter. The decanting stage consists of the tar-liquor separation, and the separation of solid particles. The tar-liquor separation is a gravity separation that splits the condensed tar from flushing liquor based on the density difference. As mentioned above, the aqueous liquid contains ammonia-type compounds and other oils, besides water. But those compounds can not influence the density of water, $1000\,\mathrm{kg/m^3}$. Tar has a specific gravity of 1100 to $1200\,\mathrm{kg/m^3}$ on average. Separated tar is collected in the dewatering tank and the flushing liquor stream stream is recycled to the primary cooling stage.

According to Bertling et al. [9], the amount of the tar is 2.0 to $5.5\,\%$ of the dry coal. From this amount, 60 to $70\,\%$ of the tar components are eliminated from the crude gas stream in the primary cooling tower. For further elimination of the tar components in the crude gas, there is an electrostatic precipitator (ESP) used after the primary cooling stage. ESP is widely used to clean the gas based on the electron charges. Here, remained tar components can be removed. The figure 6.1 shows a schematic diagram of the tar separation unit operation. Using these stages, 3.5 to $4\,\%$ tar in the dry coal can be eliminated.

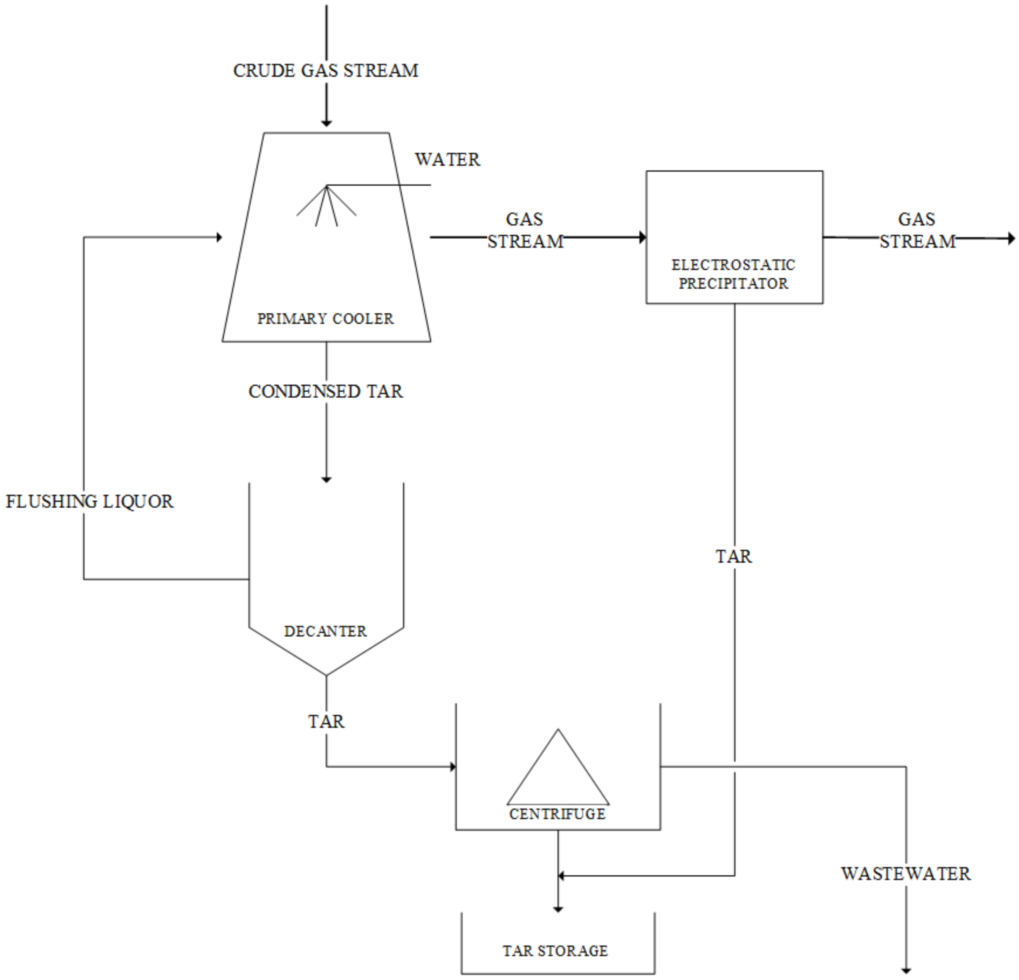
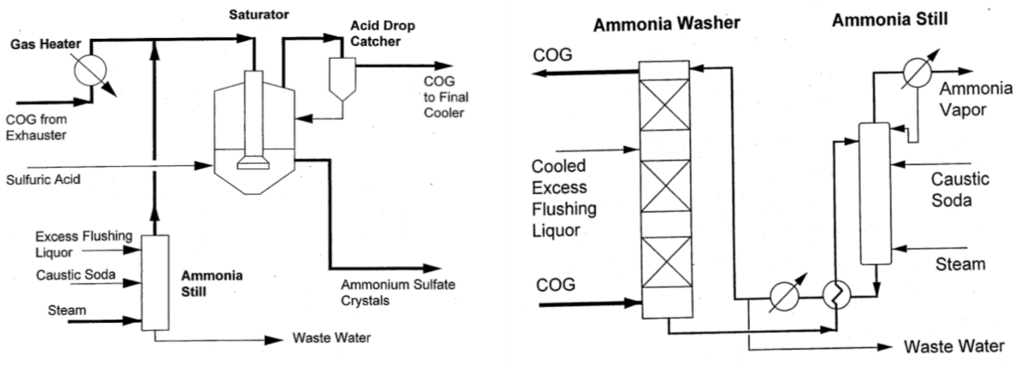


Figure 6.1: Schematic diagram of tar separation

6.2.2 Ammonia removal

As mentioned in the rule 2b, corrosive, poisonous or otherwise hazardous substances should be removed as early as possible, ammonia removal takes place just after tar separation. Ammonia reacts with hydrogen sulfide and hydrogen cyanide. The reaction leads to a corrosion problem to the carbon steel. And additionally, ammonia is hazardous for the environment. The threshold limit value for 8 hours of exposure per day is limited to 25 parts per million (ppm). Ammonia has a low boiling point of $-33.3\,°\mathrm{C}$, the explosive upper limit is $28\,\%$ by volume in the air. Due to those safety statements ammonia must be recovered with an appropriate specification. As mentioned in table 3.4, ammonium sulfate purification value must be kept at $99.9\,\%$. The separation method of ammonia leads either to ammonium sulfate salt or to an aqueous solution after absorption with



(a) Schematic diagram of ammonium sulphate process [27]

(b) Schematic diagram of water wash process [27]

water. Both are proven technologies for ammonia removal.

The process that removes ammonia from the crude gas by the absorption method is commonly used in a COG treatment plant. In this method, ammonia is recovered in the solution of ammonium sulfate and sulfuric acid. The crude gas passes through the ammonium saturator tank where sulfuric acid is added as a reagent. The ammonia in the crude gas reacts with sulfuric acid and forms crystals of ammonium sulfate which means ammonia is recovered by crystallisation. The schematic figure of a ammonia saturator is shown in figure 6.2a. In order to begin the crystallisation process in the saturator, the amount of sulfuric acid should be at 5 to 10 %. The recovered ammonium sulfate crystals are washed and then centrifuged in order to prepare it for sale.

Another process for removing ammonia from crude gas is the direct water wash process 6.2b. The process is based on the absorption of ammonia in water. The wash process takes place in the ammonia washer where a spray of water absorbs ammonia. There are two types of design options; the spray type absorber with respray stages or a packed tower. This process is efficient at low temperatures of the crude gas of 20 to 30 °C. The temperature must be kept in an optimum range. If the crude gas temperature drops too much, naphthalene will precipitate. The good point of using the water wash process is that the recycled liquor and other water streams can be used in the washer. The disadvantage of this process is that ammonia absorbed in the spray needs further distillation to separate ammonia from the water. However, Bertling et al. [9] explain that this ammonia separation method can be used as a prerequisite for another advanced separation technology which is ammonia and hydrogen sulfide removal from crude coke oven gas. This scrubbing method has a great advantage which combines a desulfurization process with the ammonia liberation. The schematic diagram is shown in the figure 6.3. This combination process will be used in our cokemaking plant.

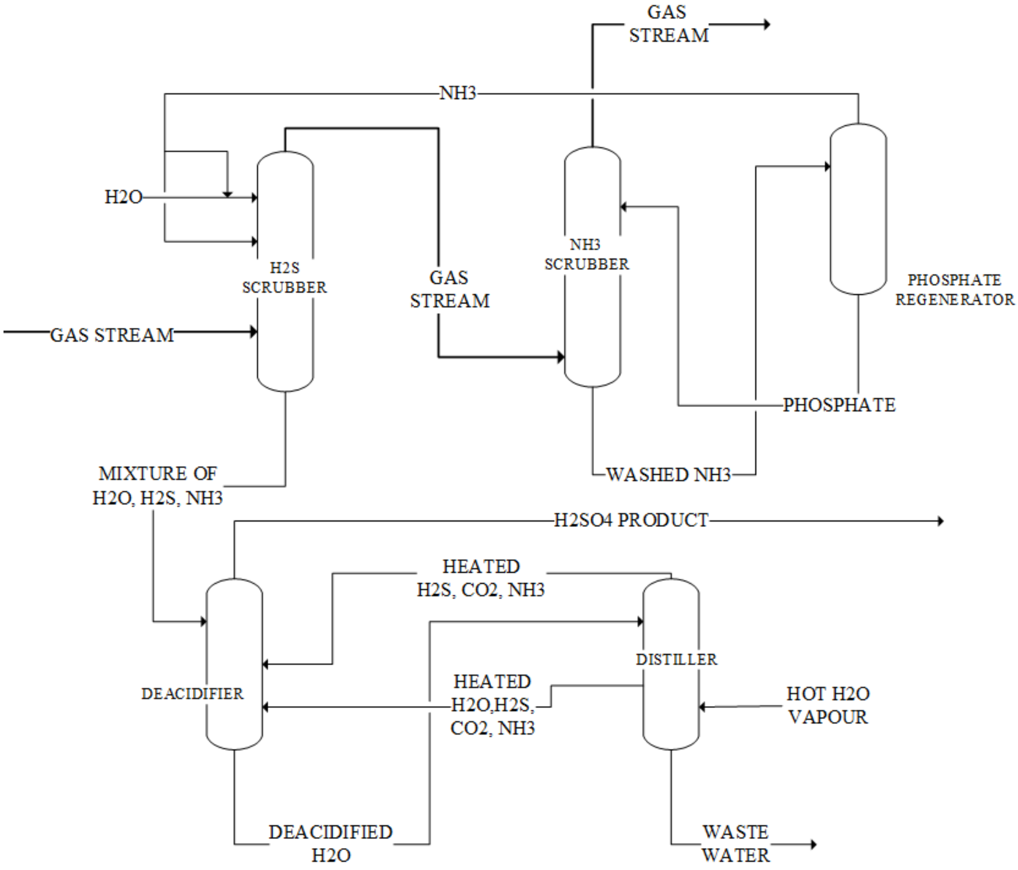


Figure 6.3: Ammonia and Hydrogen sulfide separation diagram

Weber et al. [28] mentions that this combined separation technology is a continuous process which incorporates two scrubbers, two distillation columns, and one de-acidifier column. Ammonia is scrubbed by the solution of mono ammonium phosphate that can be recycled in the operation.

The scrubbed ammonia can be in two phases, both liquid and vapour, the liquid phase is mixed with the water stream of the first scrubber and the vapor form is supplied individually to the hydrogen sulfide process in the separation column. The reason is to support the liberation of hydrogen sulfide more extensively and selectively with ammonia. Weber et al.[28] also mention that within ammonia as a supporting medium to the hydrogen sulfide scrubber, about 98 % of the sulfur can be eliminated from crude coke oven gas. The washed ammonia and hydrogen sulfide are passed through the de-acidifier column. The acidified water is removed from the de-acidifier column and then delivered to the final distillation column where NH_3, H_2S, and H_2O are liberated by hot water vapor. Those vapors are set free from the column and recycled to the de-acidifier where it supports the heating in the column. The final product stream of the entire eliminated ammonia and hydrogen sulfide are released from the top of the de-acidifier column and delivered to the H_2SO_4 plant.

As mentioned before, the removal of ammonia and sulfur must be included in the coke oven gas treatment plant. The technological options for both processes are widely available but they are expensive and require quite much equipment. This combination method saves cost and works efficiently as far as it is fulfilling the specifications of the by-products.

6.2.3 Naphthalene removal

The boiling point of naphthalene is as high as 218 °C, the threshold limit value in the air is 10 ppm, and it has an explosive upper limit of 5.9 % by volume in the air. As pointed out in rule 2c, if the substance is present in excess then it could be recovered first. The temperature of the mainstream crude gas is close to the dew point of naphthalene thus it can be removed just after ammonia. Unlike ammonia, naphthalene is easily condensed.

Naphthalene can be recovered by the second spray water cooling stage, which is required for the further process. When the ammonium sulfate process is used in the previous stage then the crude gas temperature is supposed to increase due to the chemical reaction in the saturator. The crude gas temperature can reach 50 to 60 °C. This temperature must be reduced to not more than 25 °C. Within this cooling process, naphthalene and water vapors are condensed and removed from the mainstream, crude gas. If the water wash process is used then the temperature is supposed to be near the dew point of the naphthalene which means that a few Kelvin of temperature drop is needed in the second cooling process. The naphthalene separation process is shown in figure 6.4. The main gas stream comes from the head of the ammonia scrubber column. The temperature of the gas that leaves the ammonia scrubber is about 20 to 30 °C. Once that it enters into the secondary cooling process, the naphthalene is precipitated and leaves from the bottom of the cooler with the washing water. In the next step naphthalene is separated from water in the decanter, then it continues to the storage. Based on this separation process, 0.5 % of the mother coal feed is recovered as naphthalene.

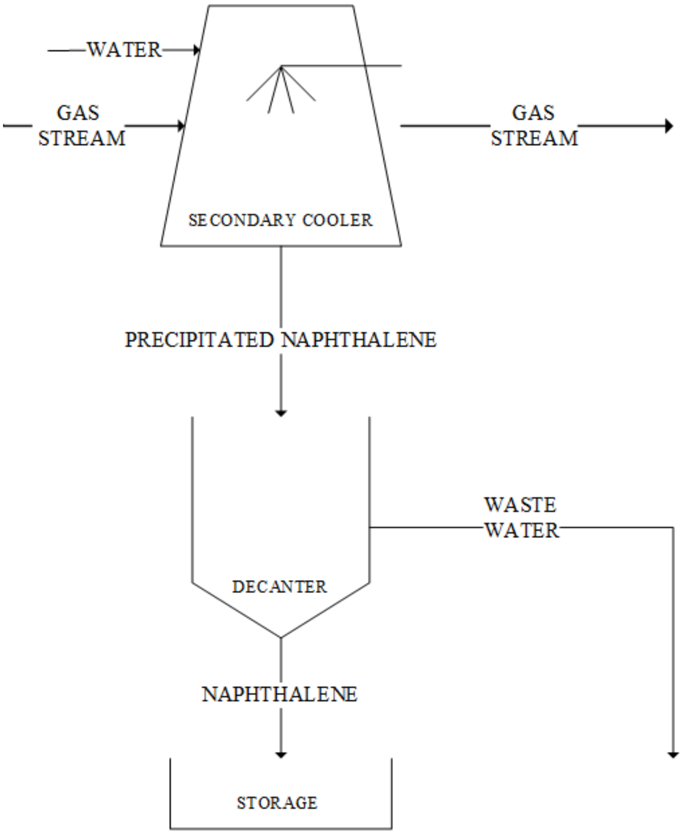


Figure 6.4: Naphthalene separation diagram

6.2.4 Light oil separation

The light oil separation from the crude gas is the next separation sequence in the coke oven gas treatment plant. The crude gas contains 20 to $40\,\mathrm{g/m^3}$ of crude benzene. Light oil fractions contain aromatic and non-aromatic hydrocarbons between C_5 to C_8 but as Bertling et. al. [9] describes, mainly it is composed of a mixture of 65 to 80 % benzene, 15 to 25 % toluene, and 5 to 7 % xylenes, which have boiling points 80.08 °C, 111 °C, and 138 to 144.4 °C, respectively. Those compounds are called the BTX fraction. The BTX fraction can be separated and the individual constituents can be sold with revenue. Since it is worth to recover the BTX fractions, the light oil must be separated from the main gas stream.

The light oil exists as a vapor in the crude gas. An absorption process is suitable for separating the gas mixtures and to purify the gas. The absorption process takes place in the absorption column under the high pressure and low temperature. In the absorption operation, heavy petroleum wash oil is used as a solvent. The role of the solvent is to scrub the light oil from the crude gas.

Even if it is mentioned in the rule 1c that preferring foreign substances is only second choice, in the light oil case, the scrubber is definitely needed to absorb the light oil from the crude gas. The wash oil can remove the light oil with an efficiency of about 95 % from the crude gas. The petroleum wash oil is composed of hydrocarbons such as naphthalene, quinoline, alkyl naphthalenes, biphenyl, acenaphthene, dibenzofurans, and fluorene [29]. To simplify the absorption process, diphyl is used as the absorbent. Diphyl is a mixture of 1 part diphenyl and 3 parts diphenyl ether and used in the industry as a heat transfer medium.

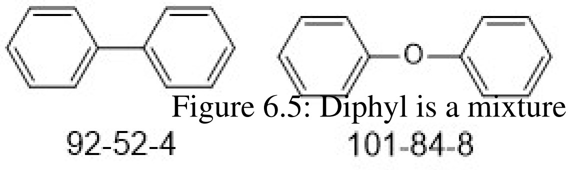


Figure 6.5: Diphyl is a mixture of 1 part Diphenyl and 3 parts Diphenylether

The crude coke oven gas enters at the bottom of the scrubber and the crude benzene would be washed out by the wash oil which is introduced to the top of the scrubber as a spray. There are several scrubbers suitable for the crude coke oven gas such as a packed, tray, and gravity spray towers. But the most extensively used scrubber is packed tower which has high efficiency. The washed crude benzene, which includes 90 to 95 % of the scrubbed light oil, leaves from the bottom of the tower and debenzoled coke oven gas is leaving from the top of the tower. The bottom product (wash oil with light oils) will go through the further distillation column where the benzene, toluene, and xylenes are distilled. The distillation process operates based on boiling point ranges. The distillation process has three distillation columns in series. Benzene has the lowest boiling point, thus it is distilled first. And the following fractions would give toluene and xylenes. During the distillation processes, the wash oil can be regenerated and recycled to the light oil scrubber.

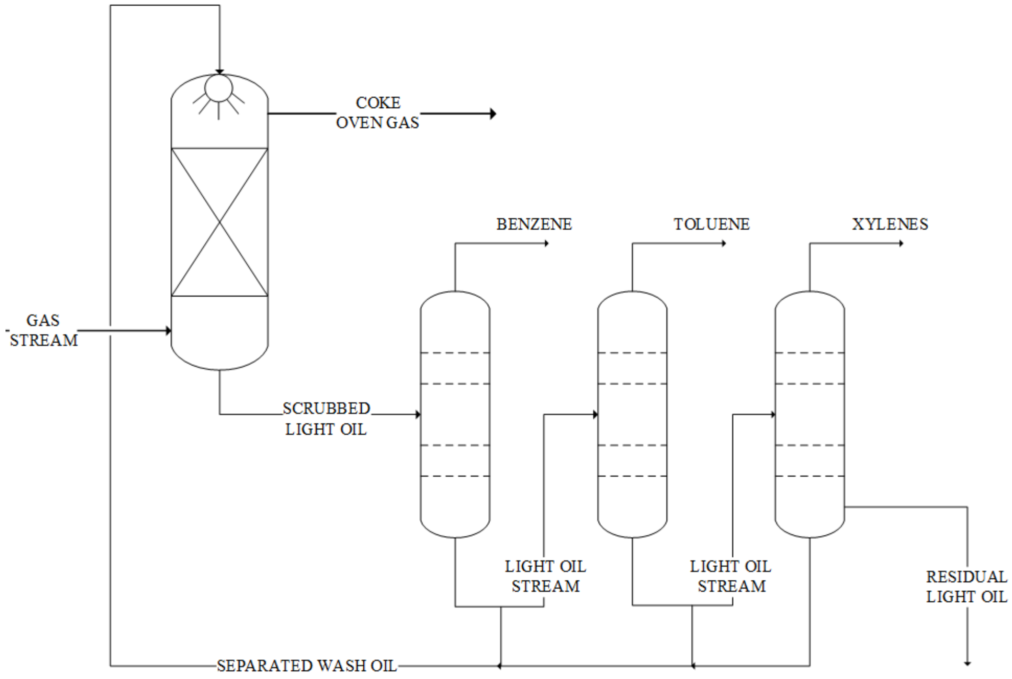


Figure 6.6: Light oil separation diagram

6.2.5 Hydrogen sulfide removal

The initial request for the content of the sulfur should be less than 1 %. Of this amount, about 60 % remains in the coke, 3.5 % in the tar and the rest of the sulfur remains in the crude gas, accounting to 4 to 12 $\mathrm{g/m^3}$ of H_2S which is contained in the crude gas. Sulfur in the form of H_2S, SO_2 or

SO_3 is a harmful component in the products and in the environment. The presence of hydrogen sulfide in the coke oven gas leads to corrosion of the equipment and catalysts poisoning in the cokemaking plant. Hydrogen sulfide is an extremely flammable substance, it is fatal if inhaled and very toxic to aquatic life. Those impacts require the desulfurization of the COG.

There are several techniques regarding the desulurization process, namely dry process, wet oxidation, and wet neutralization process. Dry COG cleaning process uses iron hydroxide as absorbent and it absorbs sulfuric acid and sulfide as reactants. But the dry desulfurization process is not common yet, the most common process is a wet cleaning technique. The oxidative wet scrubbing process produces sulfur by absorbing it in the alkaline solution. In the solution, H_2S reacts with oxygen and produces sulfur. As a result of the dry and wet oxidation desulfurization process, sulfur can be recovered as a single element. Wet neutralization processes produce hydrogen sulfide as a product. The neutralization technique works based on the absorption-desorption process in which the absorption takes place in the cold or under pressure and desorption occurs when the solution is heated. Ammonia NH_3 solution is used as an absorbent because it is included in the COG treatment process. Once hydrogen sulfide is converted into ammonium sulfide, then ammonia and sulfur can be separated in thermal desorption process.

6.3 Coke Oven

The heating system of the coke oven can be direct or indirect. There are the following four different systems regarding heating the coke oven chamber.

a. Heated surface : The heat transferred through ceramic or metallic heating walls. In this case raw material must be dry as possible. The heating rate of this system is 1 to $10\,\mathrm{K/min}$.

b. Circulation gas: The heat transferred by hot inert gas within direct contact of gas and coal. This system can be used if the fed material is permeable enough to the gas. And also it is suitable for low baking coals.

c. Fluidized-bed: This is a direct heating system that the heat transferred by hot gas within the support of fluidized-bed movement. Due to fluidized behaviour, the heat can be transferred through the coal uniformly.

d. Flow stream: In this heating system, the heat transferred by heated gas within intensive high speed. The speed can reach up to $104\,\mathrm{K/min}$.

The most applicable and modern coke ovens are designed as a regenerative of heating with indirect heated surface system. The coke battery consists series of coke ovens that are separated by the space where hot gas flows and heat the walls. The horizontal coke oven chamber is the most efficient choice for the coke oven due to its thermal advantages, low operating cost, and a long durability for high performance [9]. The typical chamber has a volume of 20 to $52\,\mathrm{m}^3$ within a height of 4 to $7\,\mathrm{m}$, length of 12 to $17\,\mathrm{m}$, and the width of the single chamber is about 400 to $500\,\mathrm{mm}$. The total size of the coke oven battery directly depends on how many coke oven chambers would be included and furthermore, the number of the chamber depends on how much coke is produced.

As determined in the requirement section, 60,000 tons of coking coal will be fed to the coking plant and daily production rate would be 45,000 tons of coke. The table 6.2 shows the real working hours and production rates in time manner, namely, the daily production rate would be about $1875\,\mathrm{t/h}$ and about 16 million tons of coke per year. If a single chamber has $100\,\mathrm{m}^3$ of volume then it can contain about $83\,\mathrm{t}$ of coking coal. The coke residence time is 20 hours. Based on those assumptions, the size of the coke oven can be determined by simple calculations. In order to produce $45\,000\,\mathrm{t}$ of coke per day, 5 coking batteries, each has about 100 coke oven chambers, will be required.

The sketch diagram of the coke oven chamber is shown in the figure 6.7. As shown in the diagram, the oven is heated by hot flue gas and it can be regenerated at the bottom of the chamber. In order to reach the temperature of above $1000\,^{\circ}\mathrm{C}$ at the generation of hot flue gas it is essential to preheat the air before it mixed with the gas.

After 18 hours of coal baking process, pushing machine pushes baked coke from the oven to the quenching car in order to make a room for the next coal feed. During the carbonization process coke oven gas is collected at the top of the chamber and delivered to the COG treatment plant by pipelines. Dumped hot coke is delivered to the quenching tower and then passed through the

Table 6.2: Production parameters

Parameter	
Calendar working days	365
Calendar overall month	12
Calendar overall time	8760
Hours in a day	24
Maintenance break days	14[1]
Possible working hours in a day	24
Possible working days in a year	351
Possible working hours in a year	8600
Real working hours in a year	8600
Timely capacity	1875 t/h
Daily capacity	45 000 t/d
Annual capacity [tonn per year]	16 125 000

crushing and screening section. Finally, coke is stored in the storage.

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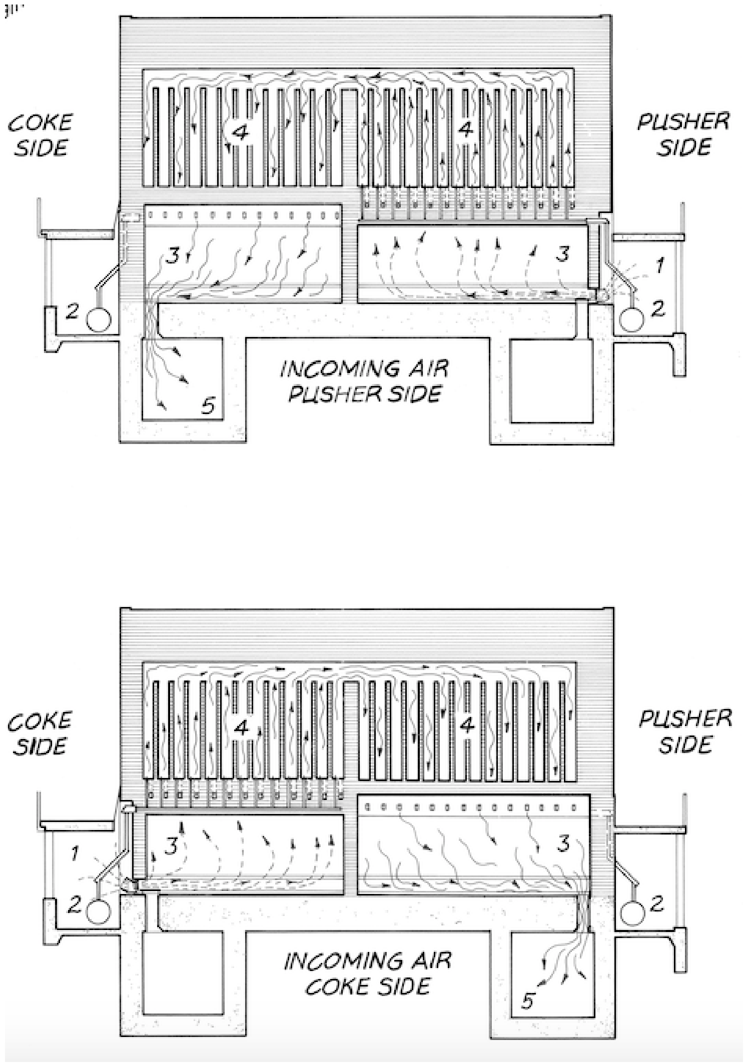

Figure 6.7: Diagrammatical sketch of regenerative coke oven by Koppers 1952; [30] 1. Air box where outside is pulled into regeneration chamber; 2. Gas main; 3. Regeneration Chamber; 4. Flues; 5. Exhaust flue which carried waste gasses to stack

7 Process Flowsheet

The figure 7.1 introduces the final version of process flowsheet. The coking process starts with blending. In order to have well blended coal, the plant will use 3 to 4 types of coal. Coal types are different in their chemical and physical properties. Coals are discharged to the conveyor belt from coal bunkers and delivered to hammer crusher. Crushed coal delivered to the coal storage bin. The second blending process will occur. This time crushed coal is mixed with coke breeze or small amount of oil. The addition of finely sized coke breeze increases the coal cohesion and at the same time cracking of the coke is reduced. The suitable oil addition keeps the bulk density of the coal [9]. The mixed coal then goes to the blender in order to have uniform blend. The next step would be coking process. The coke oven is descriped in the chapter 6.3. The coke oven gases are collected in COG main, is located at the roof of coke ovens, and delivered to COG treatment plant which is explained in the chapter 6. The coke from the coke oven is discharged into quenching car that transports hot coke to the quenching tower. The quenching car directly goes inside of the quenching tower where the hot coke is cooled by the spray water. Due to contact between hot coke and water, the water is immediately evaporated. A large amount of water vapour, includes fly ash and fine particles, leave the tower at the top. The typical quenching tower is contsructed with water recovery in the middle of the tower. So, the water vapour can be condensed. The condensed water leaves the tower and recycled to the spray water stream. There is an another stream that leaves the tower which is phenol. The phenol is separated from coke during the quenching process. That is highly toxic substance in aqueous form. Thus, it has to be separated and disposed properly. Final stages of the coking process would be screening and storage. In the screening process very fine particles of coke, so called coke breeze, is separated and then goes to the coke breeze bunker.

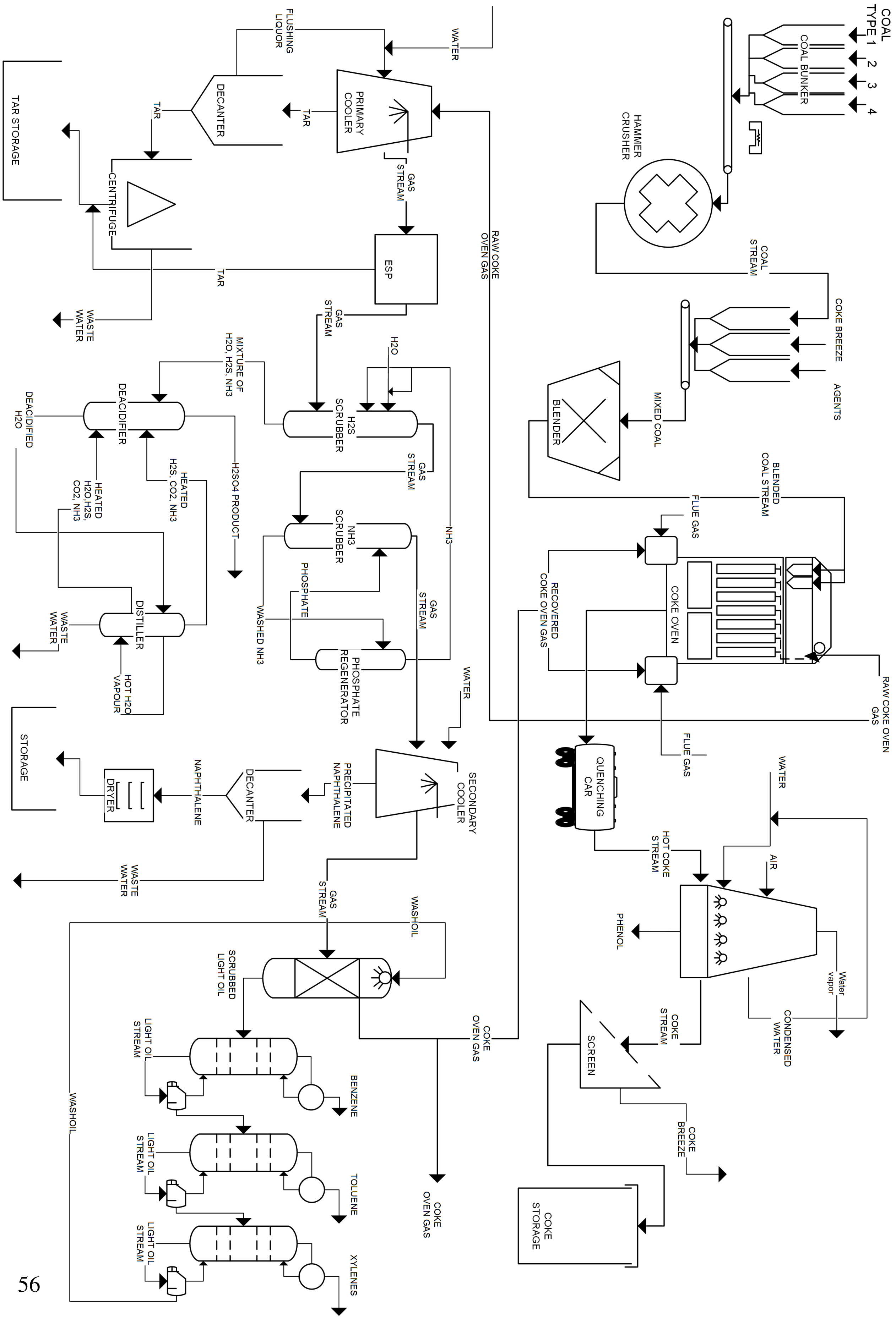

Figure 7.1: Process Flowsheet of cokemaking plant

8 Process Analysis

8.1 The Basis for the Process Analysis

As mentioned in the list of requirements, the annual coke production rate is calculated regarding UHG coking coal production rate. In order to determine the plant capacity, the overall mass balance should be developed in the processing system. Figure 8.1 shows the mass balance of the cokemaking plant.

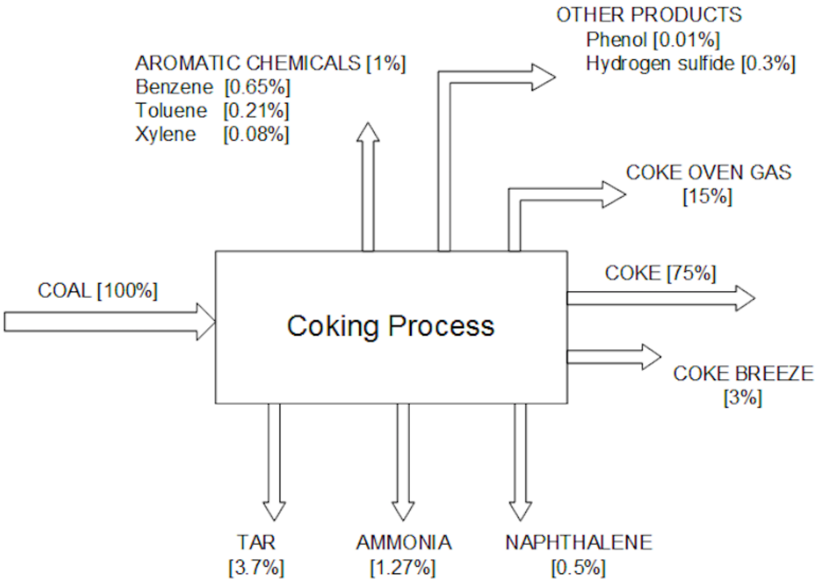

Figure 8.1: Process mass balance

The feed (coking coal) enters the plant, 75 % of feed becomes coke and 15 % of the coke oven gas will be produced. Remaining 10 % distributed into other by-products such as tar (3.7 %), coke breeze (3 %), ammonia (1.27 %), aromatics chemicals (1 %), naphthalene (0.5 %), and phenol and hydrogen sulfide together take (0.31 %).

The UHG coal handling and preparation plant has the capacity of 60000 tons per day. If the cokemaking plant is built next to the UHG coal mine area and uses coking coal what they produces, then the annual capacity of the cokemaking plant would be nearly 16 million tons of coke. If the plant works 351 days in a year, daily and timely capacity would be 45 000 t/d and 1875 t/d, respectively 6.2. The table 8.1 shows other by-productions yield.

Table 8.1: Quantity and Composition of products from cokemaking plant

Process products	Amount [%]	Amount [t/d]	Amount [t/h]
Coal input	100	60,000	2500
Coke product	75	45000	1875
Coke oven gas production	15	9000	375
Coke breeze (fine coal)	3	1800	75
Tar recovery	3.7	2220	92.5
Ammonia recovery	1.27	762	31.75
Naphthalene recovery	0.5	300	12.5
Crude benzole	1	600	25
Hydrogen sulfide	0.3	180	7.5
Phenol	0.01	6	0.25
Tar composition			
- Naphthalene	0.36	216	9
- Naphthalenehomologue	0.2	120	5
- Phenol	0.02	12	0.5
- Phenolderivate	0.06	36	1.5
- Pitch	1.99	1194	49.75
Crude benzole fractions			
- Benzene	0.651	390.6	16.275
- Toluene	0.217	130.2	5.425
- Xylene	0.080	48.0	2
- Nonaromatics	0.028	16.8	0.7
- Naphthalene	0.006	3.6	0.15
- High boiling compounds	0.028	16.8	0.7

From the table, it is coherent to see the crude benzole production rate which is calculated as 25 t/d. This much crude benzole should be eliminated from the crude coke oven gas. In this process analysis section, the light oil separation process will be simulated on the Aspen Plus program. The process flowsheet is designed in the 6.2.4. The intention to the simulation analysis is to prove the assumption for the BTX yield and determine design specifications such as the height and amount of medium.

8.2 Simulation

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9 Summary

For this thesis study, I successfully completed the process design flowsheet. Based on the research of fundamentals of coal carbonization process and coke manufacture, I decided to choose by-product cokemaking process out of several options. The by-product technology is comparatively efficient and environmentally friendly process. The main point of this coking technology is to treat the crude coke oven gas. During the process of coal carbonization at high temperature and an absence of oxygen, the coke and coke oven gases are formed in the coke oven. $75\,\%$ of the mother coal feed is transformed into coke production and remaining $25\,\%$ becomes coke oven gas. This $25\,\%$ of mass can be treated and sold its own purpose. At the beginning of the study work, I made a list of requirements where I expressed my technology wishes. This way, I made my line through the study. That led to the by-product process system.

In the functional level, I drew a basic flowsheet of the by-product coking technology. Based on research, I wanted to have separated tar, ammonia, naphthalene, benzene, toluene, xylenes, and finally clean coke oven gas. That particular by-products require special separation technologies. Before I study separation processes, the typical physical properties of chemical substances, which is included in those products, are identified. The physical property table showed a significant difference in the boiling points. So, then I understand why boiling points play a big role in the separation process. It is because the temperature difference makes the chemical separation easier and efficient. In order to determine the separation sequence, heuristic rules for separation operation and sequences are helped me a lot. Based on heuristic rules I explained why separation pattern is developed in a way its drawn in the flowsheet. After that I chose the separation technologies for the by-products. The underlined separation technologies were ammonia and BTX recovery operations. As described in the ammonia removal, the separation process can recover ammonia as well as hydrogen sulfide. Sulfur is must leave substance in the coke oven treatment plant. Thus, the combination of ammonia and sulfur liberation technology is chosen. For the BTX recovery part, absorption and distillation column are used in order to separate the benzene, toluene, and xylenes from coke oven gas.

Finally, I made a simulation analysis for the light oil separation process in the process analysis part. Cokemaking plant capacity is assumed as 45 thousand tons of coke per day. In order to produce this much coke daily, overall 5 coke oven batteries, each has 100 coke ovens, will be required. After I did some simple calculations, our estimated coke plant will produce $375\,\mathrm{t/h}$ of coke gas, of which $25\,\mathrm{t/h}$ crude benzole. This number became my simulation feed basis. As a result of simulation for the light oil separation, I successfully recovered benzene, toluene, and xylenes in the distillation column. At the stage of absorption process we could separate $95\,\%$ of light oil from coke oven gas which means still $5\,\%$ of light oil is included in clean coke oven gas.

In summary, metallurgical coke can be produced in Mongolia. Mongolia has a numerous amount of coking coal that can be used as a feed for the coking plant. If the coking plant can be integrated with metallurgical plant then the importance of the Mongolian coke would be increased. This study summarized the coking technology in the perspective of Mongolia that can be used in a way of environmentally friendly. Further studies of this thesis can be widened regarding economical aspects or simulation analysis for the rest of the process and even it is important to study coal blending stage in terms of how it influences to the coke yield.

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