
Study of the Mechanism of Coke Formation of Oil Residue and Coal Raw Materials

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Abstract: This thesis examines how temperature affects the coke obtained from coal pitch and oil residue. The types of coke suitable for use as electrodes and anodes have been identified. A review of existing technologies capable of solving problems with the use of coal tar pitch has been conducted. Studies and experiments were conducted on the coking of heavy feedstock with different chemical composition (HGO FCC, tar and coal pitch). Three experiments were conducted using each feedstock (FCC, tar, coal pitch) for a period of 5 hours. To find out the effect of residence time on the coking, three sets of experiments for each feedstock were performed by first heating the samples for 4 hours to the set temperature and maintaining this temperature for another 5 hours (9 hours in total). The dependence of the heating mode of the coking chambers on the material balance was studied. Samples of the coke formed from the coking were studied at the laboratory to determine the possibility of using them as anode in the aluminum industry and electrode in steel industry. The relevance of the work is explained by the good applicability of the coking process both for processing heavier types of oil raw materials, increasing the depth of selection of light distillate fractions.

Keywords: Coking, Petroleum Coke, Coal Tar Pitch, Tar, FCC, Anode Grade

1. Introduction

The depletion in reserves of light and medium crude oils has focused interest in heavy oils. There is currently high demand for 20° - 25° API quality crude oil because the production of light and other similar crude oils has been declining in recent years. To meet this demand of light oil, heavy oil from the reservoir and residual oil have to be upgraded. One of the widely used upgrading process is coking. Coking is a refinery unit operation that upgrades material called bottoms from the atmospheric or vacuum distillation column into higher-value products and, as the name implies, produces petroleum coke [1].

The coking process is capable of accounting for up to 30 wt% of the product as produced coke. Though coking is the most preferred surface upgrading technology by refiners, high coke formation and low liquid product are some of the demerits. The various products are useful by different industries, hence it is important to know how different feedstocks and operating conditions affect the products.

Since the percentage of coke and distillates formed are

affected by the type of feedstock and operating conditions, this thesis seeks to compare distillates to coke production of various feedstocks at different operating conditions. The purpose of this research is to propose a methodology for obtaining high quality coke that can be used as anode and electrode. Figure 1 shows the change of world petroleum demand structure.

The objectives of this research are:

1. to find out how temperature changes affect coking of FCC, tar and coal pitch;
2. to find out how increase in residence time affect coking of coal and oil residue;
3. to compare coke yield from coal and oil residue;
4. to investigate the structure and composition of coke from FCC, tar and coal pitch;
5. to compare the coke to distillate yield of FCC, tar and coal pitch;
6. to propose a methodology for obtaining quality coke that can be used as anode or electrode.

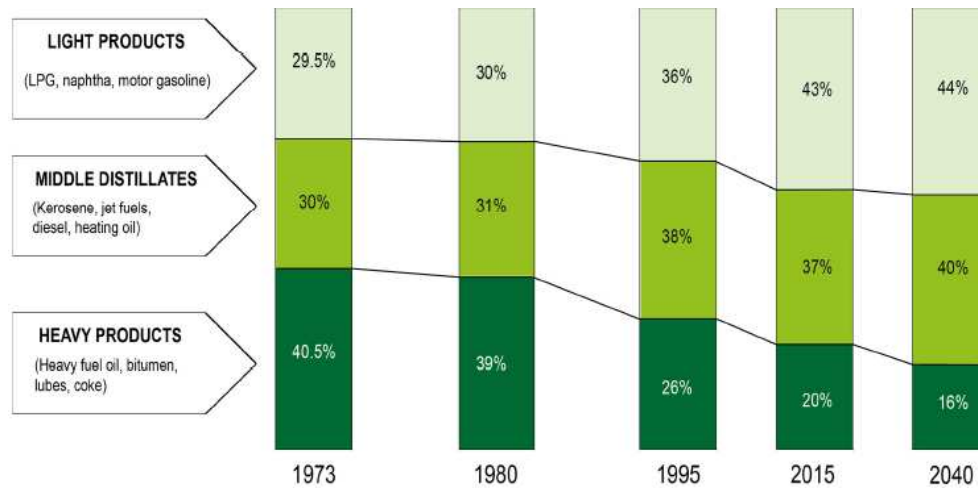


Figure 1. Change of world petroleum demand structure (weight%) [2].

2. Literature Review

2.1. Mechanism of Coke Formation

Coke obtained from oil residue is known as petroleum coke (pet coke). Petroleum coke is a final carbon-rich solid material derived from refining. Petroleum coke is obtained from a final cracking process that breaks long chain hydrocarbons of petroleum into shorter chains. This process takes place in units termed coker drums or coker units. Heating is done in the furnace to start cracking and the reactions are completed in the coke drums [3]. These processes are termed coking processes. Petroleum coke is also produced in the production of synthetic crude oil, or syncrude from bitumen. Figure 2 is an image of petroleum coke showing different types and sizes of coke.

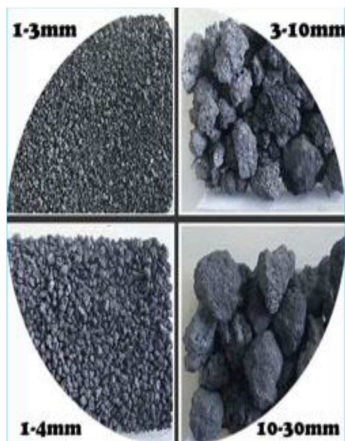


Figure 2. Petroleum coke [4].

Coke can also be obtained from coal. There are two types of reactions that occur in the formation of coke from coal [5]. These are:

1. the cracking reactions, which consist of the rupture of carbon-carbon bonds. These reactions produce components that are less polymerized than coal and of

which will yield higher percentage of liquids at the pyrolysis temperature. The rupture of C-C bond in the process leads to the formation of two radicals. These two radicals become saturated with hydrogen which is supplied by the second type of reaction;

2. reactions of aromatization and condensation occur. The dehydrogenation of saturated rings and recombination of aromatic groups with one another by the formation of aromatic C-C bonds liberates hydrogen. The liberated hydrogen leads to the formation of a solid carbon residue. This is formed either from the initial raw material components or the intermediate substances that are formed. These processes occur in a relatively low pressure range (0.5 to 20 bar) and in a relatively high temperature range (430 to 850°C) [6].

2.2. Feedstock Characterization Affecting Coking

The most commonly used feedstocks for delayed coking are heavy residues such as vacuum residue and atmospheric residue. However, feedstocks like gilsonite, lignite pitch, coal tar pitch, refinery hazardous wastes, and used plastics have been used over the years [7]. To obtain high quality needle coke, sometimes highly aromatic blends of heavy oil are processed.

The molecular weight of the aromatic fraction is 600 to 750 which is slightly higher than saturates. The aromatics have an average carbon number in the range of 41 to 53. They are simple structures compared to resins and asphaltenes. Their low micro-carbon residue (MCR) value of 3.7 wt% show that they have a low tendency to form coke. Aromatics also have a low heteroatom content.

These are viscous and volatile enough to be distilled with hydrocarbons. Resins consist of an appreciable amount of aromatic carbon content (40–53%) with intermediate paraffin chain length. The resin fraction acts as the dispersant for the asphaltenic component in the maltene phase [8].

Conradson carbon residue is the most important characteristics in determining the quantity of coke that will be produced from any particular feedstock. A high CCR leads to high coke yield. It reveals the coke-forming propensity of

the feedstock. Since, in most cases, the objective of delayed coking is to maximize the production of clean liquid products and minimize the production of coke, the higher the CCR, more difficult it is to achieve the same [9].

2.3. Coking

The decline in conventional oil production has led to the increase in production of heavy oil. This means that refiners will have much oil residue. To meet the demand for transportation fuel delayed coking which is known to be very effective in processing heavy oil is used. Needle coke obtained from delayed coking process is a highly sought-after product, which is used in electric arc furnaces (in the form of graphite electrodes) in steel making applications. Residues obtained from processing heavy oil have low value and hence delayed coking is used to improve the low value residue into lighter products and to obtain petroleum coke as a by-product. Needle coke which is a high quality coke is normally produced specifically for use as feedstock for other industries [10].

Fluid Coking converts heavy hydrocarbons to lighter products. Heavy hydrocarbons that are normally converted are atmospheric residue, vacuum residue, bitumen, deasphalter bottom and fluid catalytic cracker (FCC) bottom. It is continuous fluid bed technology that converts heavy hydrocarbons into lighter products thermally.

Fluid coking produces a wide range of gases and liquids. The gases that are produced are further processed to give fuel gas (C₂), C₃ which undergoes alkylation at the alkylation unit or liquefied petroleum gas (LPG) and C₄'s. The liquid products are typically cut into three fractions. Coker naphtha is normally hydrotreated and used as reformer feedstock. The naphtha from fluid coking can also be used for mogas blending [11].

Flexi-coking was introduced to convert the coke generated to fuel gas by gasifying the petroleum coke. Coke particles obtained in flexi coking vary in chemical and physical properties [12]. Flexi coking differs from fluid coking only because of the presence of gasification unit in flexi-coking. In flexi coking there is complete or partial gasification of the petroleum coke to yield a fuel gas. It is different from the bulk liquid-phase coking in delayed coking. In flexi coking there is a burner that burns the accumulated coke and causes coking on the surface of the circulating coke particles. The vacuum residue is first pre-heated and then sprayed onto the hot coke particles heated in the burner. This is done by partial combustion of coke produced in the previous cycle. Since small coke particles circulate between the reactor and the burner, the large surface area of the reactor and burner provides efficient heat transfer and rapid coking. After recovering the fine coke particles the products of the coking are sent to a fractionator. Heavy liquids that sticks to the surface of the coke particles are then removed. This is done by applying steam to the bottom of the reactor in a scrubber to strip them off. The reactor and the burner operate at temperatures of 510 – 570°C and 595 – 675°C, respectively [13]. Coking is rapid because of higher temperatures, this leads to higher liquid and lower coke yield.

The demand for high value petroleum products is increasing. Coking upgrading is done to convert the low value residues to more valuable liquid and gas products [14]. The common objective of the three coking processes is to maximize the yield of distillate products in a refinery by rejecting large quantities of carbon in the residue as petroleum coke. The distillates obtained from coking are gas, gasoline, gasoil, and vacuum gas oil.

3. Methodology

The evaluation process began with the identification and selection of samples where samples of coal pitch, fluid catalytic cracker (FCC) residue and tar were collected. Equal quantities of the samples were used for the experiment and as the temperature and time were increased the quantity of sample used was decreased. About 100g of samples were measured for the coking experiment at a temperature of 450°C. When the temperatures for all samples were increased to 480°C and 510°C the samples used were decreased to about 40 g. and 30 g. respectively since increase in temperature increased the cracking rate and hence the samples were decreased for the ceramic container used to be able contain all the coke formed without spillage.

3.1. Feedstock Sampling

A good oil residue and coal pitch evaluation depends on good sampling protocols followed and the due diligence done. It was ensured that sampling followed oil feedstock sampling protocol. Three FCC samples, three coal pitch samples and three tar samples were taken for analysis. This was done at a constant time of 5 hours and all experiment repeated at a constant time of 9 hours (4 hours heating to set temperature and 5 hours holding). Coal pitch samples were grounded into fine particles using crucibles to expose a larger surface area and make the coking effective.

3.2. Preparation of Equipment and Tools

3.2.1. Cleansing of Apparatus for Sampling

Ceramic containers were cleaned and kept in a desiccator cabinet to keep them dry. Tongs were used to lift all containers that were not supposed to be touched to prevent moisture and impurities from affecting the measurements. Round bottom flask were washed with toluene and distilled water and kept dry. Scoopula was used to scoop and clean metallic container.

3.2.2. Sample Measurement

The mass of empty ceramic flask, round bottom flask were measured with a measuring balance and recorded. Samples were then put into the ceramic flask and their masses recorded. The mass of samples used were not equal since the mass was reduced as temperature of the coking and residence time were increased. This was done to prevent spillage of the coke formed to enhance accurate mass measurement of the coke. Reduction in the weight of sample used had no effect on the experiment results since percentage of the feedstock

that formed coke was what was calculated for each sample. Samples were kept at room temperature. Ceramic flasks were kept in a desiccator to absorb all moisture and keep them dry.

3.3. Laboratory Analysis

Samples of FCC, coal pitch and tar after being sealed in a reactor to make them air tight were placed in a furnace. The pipe of the reactor was then connected to the distillation

chamber as shown in the figure below. After setting up the furnace and the distillation chamber the furnace was switched on for coking to be done at set temperatures. The distillates formed were collected by a conical flask and their masses measured. The mass of the coke formed for all samples was also measured. Figure 3 shows a set-up of the furnace and distillation chamber that were used in the coking process.

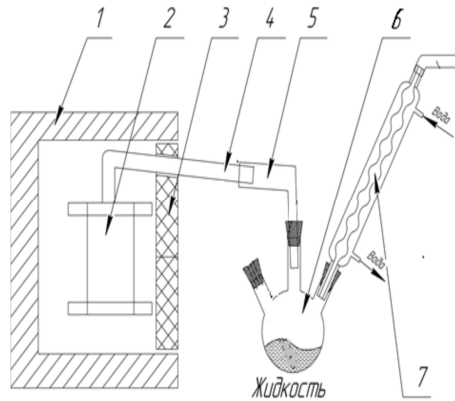


Figure 3. Furnace and distillation chamber setup.

1 – furnace, 2 – reactor, 3 – refractory screen; 4 – removal of gaseous and liquid coking products; 5 – alonge; 6 - three-neck round bottom flask; 7 - reflux condenser.

4. Results and Discussions

A summary and descriptive statistics of the results of the samples of FCC, Coal pitch and tar that were analyzed are presented in table 6 and the parameters compared with standard guidelines.

4.1. Results

Table 1. 5 hours heating.

HEATING FOR 5 HOURS.			
TEMPERATURE (Degrees Celcius)	450	480	510
TAR			
Percentage of distillate (%)	61.458%	72.956%	75.919%
Percentage of Coke (%)	27.882%	17.357%	7.777%
FCC			
Percentage of distillate (%)	71.705%	88.567%	88.909%
Percentage of Coke (%)	20.681%	7.706%	6.55%
COAL PITCH			
Percentage of distillate (%)	46.4%	46.706%	43.856%
Percentage of coke (%)	43.7%	42.116%	43.556%

Table 2. (9 hours). 4 hours heating up, 5 hours holding.

(9 HOURS). 4 HOURS HEATING UP, 5 HOURS HOLDING.			
TEMPERATURE (Degrees Celcius)	450	480	510
TAR			
Percentage of distillate (%)	69.833%	71.807%	68.938%
Percentage of coke (%)	16.755%	15.276%	15.078%
FCC			
Percentage of distillate (%)	76.683%	81.547%	84.049%
Percentage of coke (%)	10.721%	9.825%	9.165%
COAL TAR PITCH			
Percentage of distillate (%)	32.974%	35.18%	37.344%
Percentage of coke (%)	47.46%	46.244%	44.4%

4.2. Equipment

Furnace, beam balance, desiccator cabinet.

4.3. Observation

Percentage of coke by weight decreased for all three samples when the operating temperature was increased. Percentage of distillate by weight also increased as temperature was increased. Coal pitch gave the highest yield of coke in both experiments. FCC produced a coke, which is highly crystalline. The ash content of coke formed from FCC was low (< 2%).

5. Conclusion

We have investigated the dependence of coke yield on temperature and feedstock properties.

1. Coke yield is directly proportional to increase in temperature.
2. The results show that analyzed coke has a low ash and metallic content in FCC and tar. Their structure showed open porosity. Hence, these feedstocks can be used in the production of anode for aluminum smelting.
3. Coal pitch has the highest coke yield among the three feedstocks. It has a needle-like structure and can be used for electrodes in steel production.

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