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MASTER'S THESIS

Project of East Siberian Crude Oil Processing Equipped with Delayed Coking Unit
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ABSTRACT

In addition to light products, delayed cokers produce valuable coke such as anode coke and needle coke. The production of these useful light products and coke has made it profitable and interesting for the refinery industry to look into the processing of heavy oils as oil reserves continue to decline. In this thesis, a laboratory delayed coker was constructed and modeled in a software (Aspen Hysys) to estimate light fractions and coke that can be produced from a sample of crude oil obtained from the Vankor Oil field.

Beginning with the crude properties testing procedures to find out the compositional properties of sample, distillation under atmospheric and vacuum conditions. The distillates/fractions obtained is examined through gas chromatography, FIA analysis, density of each fractions including the crude, and lastly the Sulphur content measuring. The results stipulated the profile of the crude to be heavy with a Sulphur percentage of 0.72 by mass and a density of 0.920kg/m3 at 15 °C. After employing other refining processes such as reforming and isomerization, light fraction such as gas oil fraction formed the major straight run fractions, while the employment of the delayed coking process gives additional 3.2 % by weight of naphtha and alkylation 1.14 wt.%.

The results from the software model showed that the production light fractions and coke can be optimized by varying parameters such as temperature and pressure using variables such as light fractions and coke yield. However, in the work the amount of coke produced was linked to the variable maximum light fractions but quality coke. These and other issues are discussed in the thesis. Keyword: REFINING, ASPEN HYSYS, SIBERIAN CRUDE, OPTIMIZATION VARIABLE.

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INTRODUCTION

Crude oils are grouped according to their API gravity as light crude oils (30 – 49.9), medium crude oils (22.0 29.9), heavy oils A (14 – 21.9), heavy oils B (10 – 13.9) and extra-heavy oils (below 9.9) [1&2]. Light crude oil is easier refined for production of light valuable hydrocarbon products like naphtha, gasoline and diesel by separation methods (for example distillation); also, high yields of these products are achieved without using deep conversion technologies. On the other hand, heavy oil which normally has low hydrogen to carbon ratio (H/C ratio), high content of contaminants (Sulphur, Nitrogen, Nickel, Vanadium) produce low yields of light hydrocarbon products when they are distilled or processed. For example, only 50% of the bitumen can be recovered by vacuum distillation [2&3]. Therefore, the use of deep conversion technologies is necessary to transform the heavy petroleum fractions, also called residue, into more valuable hydrocarbon products.

Compared with refined products such as gasoline and aviation turbine fuel, there is relatively little in the literature on the analysis and characterization of crude oils. Indeed, for many years, there were relatively few ASTM methods specific to crude oils, although several ASTM methods had been adapted for their analysis. This situation may have resulted, at least in part, from the historical tendency of refinery chemists to independently develop or modify analytical methods specific to their needs and, subsequently, for the methods to become proprietary. In recent years, the unique problems associated with sampling and analyses of crude oils have received more attention, and many standardized methods for determining specific crude oil features have been published.

The world economy is largely dependent on the availability of fuels to power the significant growth of most industries including aviation, manufacturing and automotive industry. However, due the unstable nature of oil prices on the international market and natural disasters such as the current outbreak of covid-19, there is significant strain and losses on capital investment to most refinery industries.

1.1 Problem statement

According to Martinez et al (1997), as light petroleum resources have become increasingly scarce and reserves of heavy oil remain available around 40 trillion barrels of heavy oil are available, the oil industry has been forced to increase the amount of low quality heavy feedstocks processed in coking units to meet market demands for fuels. Consequently, the production of some useful coke in delayed coking units has increased the profitability of refineries. This research shows the crude oil analysis by laboratory work for a sample that was obtained from Vankor fields and its potential to produce useful coke. The appropriate process scheme for refining will be selected based on the results obtained from the feedstock and crude oil analysis.

The quality of any coke produced by delayed coking is inherently dependent on the quality of the feed material, thus only certain petroleum heavy residues can produce anode grade quality coke. This coke quality is dependent on the molecular composition such as heavy metal content and ash content of the delayed coker feed which in turn governs the kinetics of the coking reaction and the coke microstructure. The coke microstructure controls the electrochemical and mechanical characteristics of the coke inclusive of the Coefficient of Thermal Expansion (CTE).

1.2 Objectives of the investigation

1. A crude oil sample was obtained from the Vankor oil field, Russia. A laboratory set up was used to process this sample to Gases, Gasoline, Naphtha, Kerosene and Diesel, Gas Oil and Vacuum residue.

2. A heavy oil process called delayed coking was used to convert these Vacuum residues into:

- Gas;
- Naphtha;
- Coker gas oil;
- Coke.

3. To analysis the type of coke produce by the sample

2 Literature Review

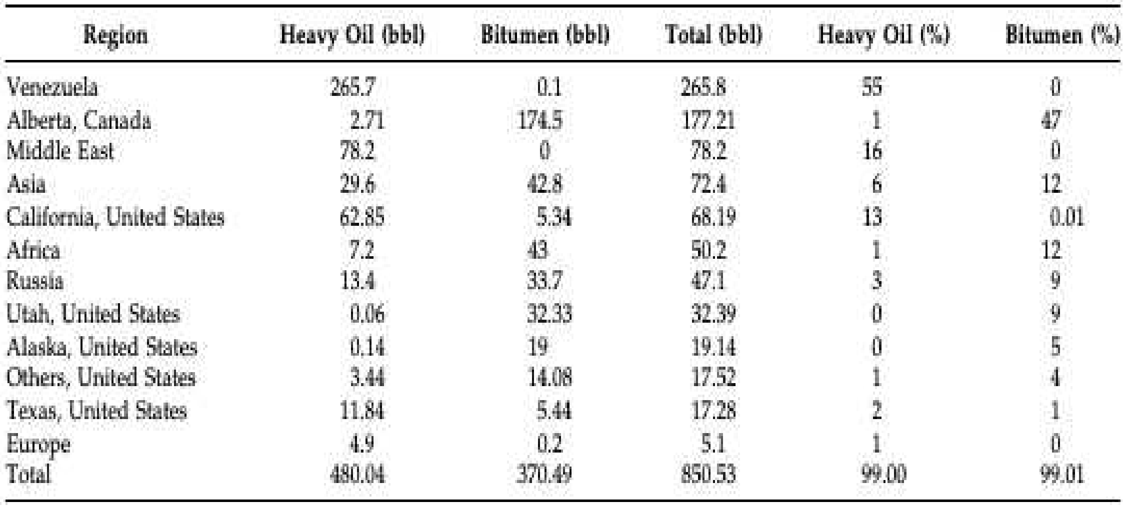
2.1 East Siberian crude oils

For the last 150 years, commercial oil production has been ongoing in Russia and elsewhere in the former Soviet Union. By 1900, almost one-third of the world's oil was being produced in the Russian Federation. This expansion of the oil industry continued into the 20th century in conjunction with the development and production of two of the world's largest oil fields: the Romashkino in the Volga-Ural Basin and the Samotlor in west Siberia [3] According to Shanazarov (1948), most Siberian oil prospects were not considered exploitable especially before 1931, with the exception of the Lake Baikal area, which has natural gas and oil and where early drilling for hydrocarbons began in 1902 [4]

Several technological advances came from Imperial Russia and the former Soviet Union, such as, reputedly, the world's first oil well, drilled in the late 1840s in present-day Azerbaijan, and, incontrovertible, the world's first multilateral horizontal well in Bashkortostan, drilled in the 1950's, more than 40 years ahead of the west. The world production of conventional reserves is predicted to peak as early as the 2030's and as a result of these predictions, a steadily growing interest in unconventional resources such as heavy oil and bitumen has been observed. The projected scarcity of the conventional hydrocarbon supply, along with the new development of in-situ technologies, has focused attention toward the huge heavy-oil and bitumen reserves of Russia, particularly in the eastern Siberian platform.

Recently, the U.S. Geological Survey estimated that the Russian Federation has 13.4 billion bbl of technically recoverable heavy oil and 33.7 billion bbl of technically recoverable bitumen [5]. To the extent that the estimates are accurate, the supplies of Russia represent approximately 3% of the projected heavy-oil and 9% of the projected natural bitumen resources in the world (Figure 1; Table 1).

Table 1 - Major world heavy-oil and bitumen resources.*



Region	Heavy Oil (bbl)	Bitumen (bbl)	Total (bbl)	Heavy Oil (%)	Bitumen (%)
Venezuela	265.7	0.1	265.8	55	0
Alberta, Canada	2.71	174.5	177.21	1	47
Middle East	78.2	0	78.2	16	0
Asia	29.6	42.8	72.4	6	12
California, United States	62.85	5.34	68.19	13	0.01
Africa	7.2	43	50.2	1	12
Russia	13.4	33.7	47.1	3	9
Utah, United States	0.06	32.33	32.39	0	9
Alaska, United States	0.14	19	19.14	0	5
Others, United States	3.44	14.08	17.52	1	4
Texas, United States	11.84	5.44	17.28	2	1
Europe	4.9	0.2	5.1	1	0
Total	480.04	370.49	850.53	99.00	99.01

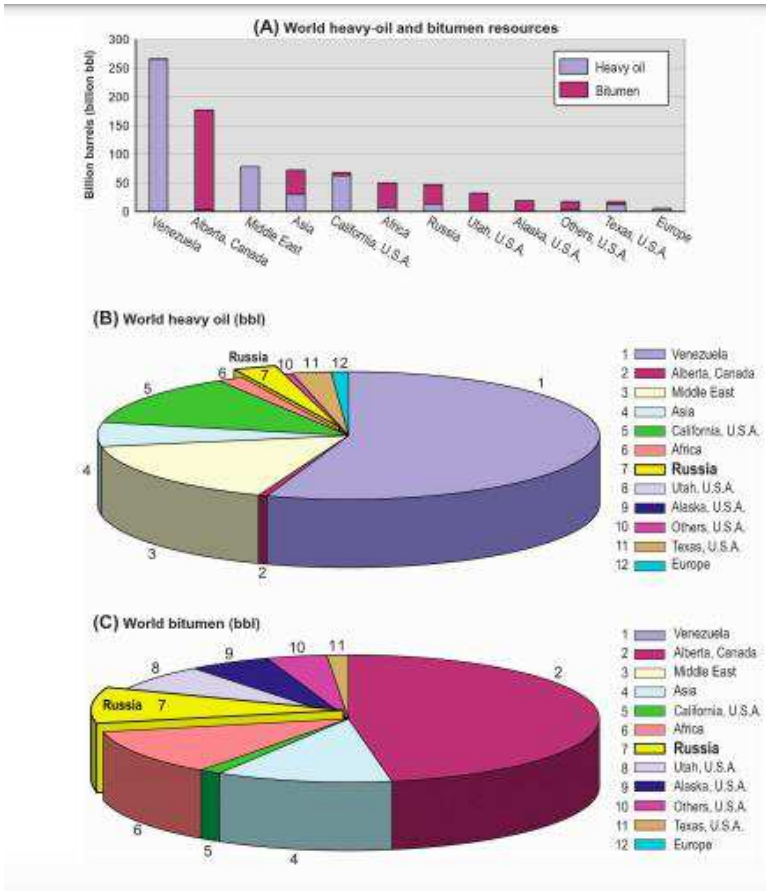


Figure 1- Major world heavy-oil and bitumen resources.

(A) Histogram showing the main deposits (blue = heavy oil; purple = bitumen). (B) Pie chart of heavy oil deposits. (C) Pie chart of bitumen deposits (Hein, 2006; Meyer and Freeman, 2006; Meyer et al., 2007; Humphries, 2008).

In the past, natural bitumen fields in Siberia were considered uneconomic mostly because of the unfriendly climate and remote location and the lack of an integrated pipeline network and technologies required to extract from predominantly frozen ground. In Canada, technological advances have made in-situ recovery of bitumen relatively commonplace in remote areas of northeastern Alberta, where overburden is generally higher than 50 m (164 ft) and occasionally shows discontinuous permafrost [6].

The import of western technological advances, including steam-assisted gravity drainage (SAGD), cyclic steam stimulation, and expanding solvent-SAGD, along with refined methods of geosteering, directional drilling, and measuring while drilling, may, in the future, successfully overcome comparable challenges impeding in-situ development of oil sands in eastern Siberia.

2.1.1 Russian Oil Supply and Reserves Estimates

Under the Soviet Union, Russian oil production peaked in the mid-1980s at approximately 13 million bbl per day (Figure 2). In 1991, the fall of the Soviet Union caused a 50% drop in production of conventional crude, which reached a low of approximately 6.5 million bbl/day in the late 1990s (Figure 2). Since then, daily oil production from the Russian Federation has steadily climbed.

In 2007, Russia was one of the largest conventional oil producing countries and was the second largest oil exporter after Saudi Arabia. Despite the global financial crisis, Russian oil companies maintained their 2008 production volumes in the first half of 2009. The oil production of Russia rose 0.4% in March 2010, from 10.08 million bbl/day the previous month to 10.12 million bbl/day. Over the long term, this rise is unsustainable, primarily because of declining production from mature conventional oil fields. Although, undoubtedly, some conventional resources remain to be discovered, production of current Russian conventional crude oil is projected to increase no more than 5 to 15% per annum above current rates, peaking by 2036. Without new unconventional production from regions like eastern Siberia, the crude output from Russia will plateau and, perhaps, begin to decline.

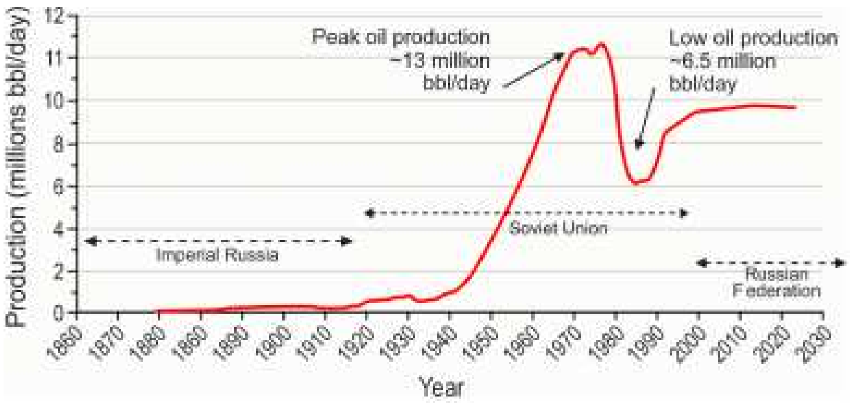


Figure 2 - Russian conventional oil production, based on a compilation of historical sources (for Imperial Russia and the former Soviet Union) from 1860 to 2000 and Russian Federation year on-year production growth from 2000 to 2008 [6&7].

In addition to the technological challenges, the scarcity of data has hampered the development and exploration of the vast bitumen and extra heavy-oil deposits of the Siberian platform. As one example, only three Russian natural bitumen deposits were identified in the review of Walter (1974) of the world's major oil sand deposits. Today, conservative estimates of more than 51 billion bbl for the Siberian heavy-oil and bitumen deposits have been published [7].

The regional geologic assessment of Meyer and Freeman (2006) shows more than 40 occurrences in its northern and northeastern margins; the 15 largest occurrences are shown in Figure 3. However, of these, only the Olenek deposit (Figure 3, number 1) has been studied in sufficient detail to enable reliable estimations of discovered bitumen in place and a detailed geologic understanding of the emplacement, diagenesis, and physical properties of the natural bitumen in the area [8]

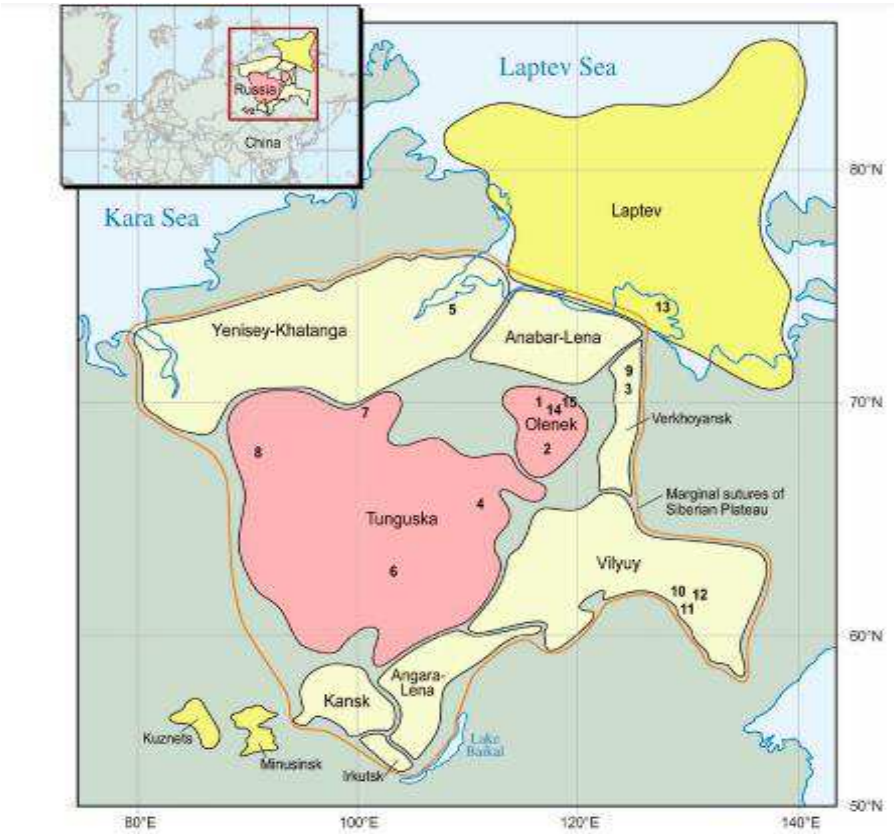


Figure 3 - Map of the sedimentary basins of the Siberian platform, Russia.
Main heavy-oil and bitumen deposit locations:
(1)Olenek;(2)EastAnabar;(3)Chekurovka;(4) Siligir-Markha;(5) Rassokha;
(6)Chun'ya;(7) Medvezh'ye; (8) Turukhan; (9) Bulkur; (10) Tuolba;(11) Amga; (12) Sina;
(13)Ust'-Lena; (14) Kuoyka;and (15) Sololisk. Dark pink color denotes uplift areas;yellow color
denotes basins (Meyer and Freeman, 2006;modified from St. John,1996).

2.2 Composition of crude oils

Crude oil is a complex mixture of literally hundreds of different hydrocarbon compounds and some compounds such as sulphur,nitrogen and heavy metals. It contains some high molecular weight molecules that will not vaporize even at the low pressures and relatively high temperatures in vacuum distillation units and they are called residue. Crude oil is made up of organic compounds, heteroatom compounds (S,N,O), hydrocarbons (C, H), metals and organic (Ni, V, Fe) and inorganic (Na+, Ca++, Cl-) compounds. Compounds that are made up of only elements of carbon and hydrogen are called hydrocarbons and constitute the largest group of organic compounds in petroleum. There could be as many as several different hydrocarbon compounds in crude oil. Hydrocarbon compounds have a general formula of CaHb, where a and b are integer numbers.

Hydrocarbons are generally divided into four groups: (1) paraffins, (2) olefins, (3) naphthenes, and (4) aromatics (Figure 4). Among these groups, paraffins, olefins, and naphthenes are sometimes called aliphatic compounds, as different from aromatic compounds. The lightest hydrocarbon found as a dissolved gas is methane (CH4), the main component of natural gas. Olefins are not usually found in crude oils, but produced in a number of refining processes.

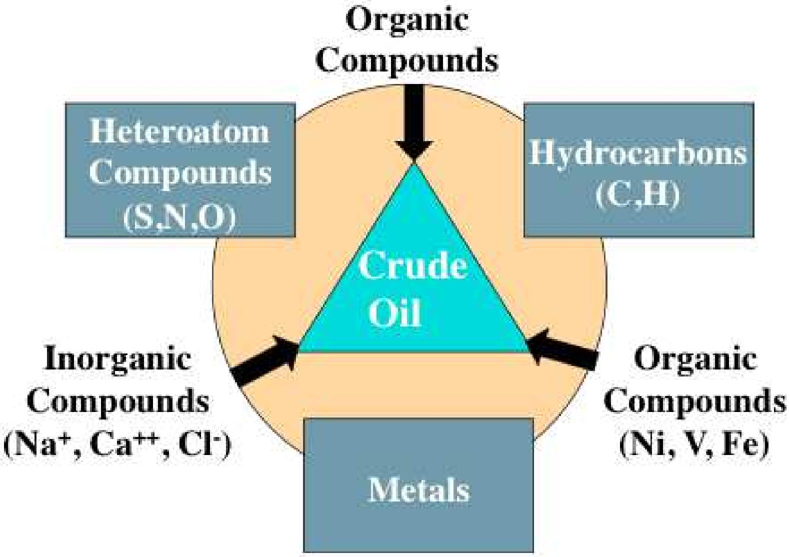


Figure 4 - Constituents of crude oil Source

2.3 Assay

Crude oil assays provide a combination of physical and chemical data that uniquely describe or characterize a crude oil and allow for the evaluation of quality parameters. Each crude oil feedstock has unique characteristic properties and constitution. Likewise, the assay provides valuable information that is utilized to assess refining characteristics and is used in various Linear Program (LP) modeling and optimization tools. Overall, crude oil assay provides the refiner with the data needed to make informed decisions in the areas of crude selection, scheduling and planning. It is also a valuable tool that aids in the optimization of various refining processes.

The assay can be an inspection assay or comprehensive assay. Testing can include crude oil characterization of whole crude oils and the various boiling range fractions produced from physical or simulated distillation by various procedures. Information obtained from the petroleum assay is used for detailed refinery engineering and client marketing purposes. Feedstock assay data is an important tool in the refining process. A typical crude assay should include the following major specifications:

-API Gravity
-Total Sulfur (% wt)
-Pour Point (°C)
-Viscosity
-Nickel (ppm)
-Vanadium (ppm)
-Total Nitrogen (ppm)
-Total Acid Number (mgKOH/g)
-Distillation Data
-Characterization factor KUOP, KW

2.3.1 Density, specific gravity and API gravity

Density is defined as the mass per unit volume of a substance. It is most often reported for oils in units of g/mL or g/cm3, and less often in units of kg/m3. Density is temperature-dependent. Density, specific gravity (SG) and API gravity values are used to monitor quality during the production of crude oil, and to establish its price in trading. The density of crude oil and liquid hydrocarbons is usually reported in terms of specific gravity (SG) or relative density, defined as the density of the liquid material at 60°F (15.6°C) divided by the density of liquid water at 60°F. At a reference temperature of 15.6°C, the density of liquid water is 0.999 g/cm3 (999 kg/m3), which is equivalent to 8.337 lb/gal (U.S.). Therefore, for a hydrocarbon or a petroleum fraction, the SG is defined as:

SG(60∘F/60∘F), or (15.6℃/15.6℃) = (Density of liquid at 60°F in g/cm3)/(0.999g/cm3).

Two density-related properties of oils are often used: specific gravity and American Petroleum Institute (API) gravity. Specific gravity (or relative density) is the ratio, at a specified temperature, of the oil density to the density of pure water. The API gravity scale arbitrarily assigns an API gravity of 10° to pure water. API gravity is calculated as:

$$\frac{145}{specific\ gravity * \left(\frac{60}{60}\right)\ \mathrm{°F}} - 131.5$$

Depending on their origin, crude oils can differ substantially as to the chain lengths of the constituent hydrocarbons and additional components (such as sulfur) and are therefore grouped into two categories, light and heavy:

i) Light crudes normally have a low density (e.g. below 900 kg/m3), and API gravity of 30° or more.

ii) Heavy crudes, by contrast, usually have densities above 1000 kg/m3 and API gravity of less than 20°.

These oils show considerable differences in their chemical and physical properties, requiring different methodological approaches for their testing. Oils with low densities, and hence low specific gravities, have high API gravities. The price of a crude oil is usually based on its API gravity, with high gravity oils commanding higher prices. API gravity, density, and specific gravity at 15°C, can be interconverted using Petroleum Measurement

2.3.2 Viscosity

Viscosity, commonly depicted by the symbol μ, is a physical property of a fluid that describes its tendency/resistance to flow. A high-viscosity fluid has a low tendency to flow, whereas low-viscosity fluids flow easily. Newton’s Law of Viscosity provides a physical definition of viscosity. Power requirement to transport (e.g., to pump) a fluid depends strongly on the fluid’s viscosity. Interestingly, the viscosity of liquid decreases with increasing temperature, while viscosity of gases increases with increasing temperature. Among petroleum products, viscosity constitutes a critically important characteristic of lubricating engine oils. Viscosity of liquids is usually measured in terms of kinematic viscosity, which is defined as the ratio of absolute (dynamic) viscosity to absolute density ($\nu = \mu/\rho$).

Kinematic viscosity is expressed in units of centistokes (cSt), Saybolt Universal seconds (SUS), and Saybolt Furol seconds (SFS). Values of kinematic viscosity for pure liquid hydrocarbons are usually measured and reported at two reference temperatures, 38°C (100°F) and 99°C (210°F) in cSt. However, different reference temperatures, such as 40°C (104 °F), 50 °C (122 °F), and 60 °C (140 °F), are also used to report kinematic viscosities of petroleum fractions. The viscosity of crude oils can be measured using a standard method (ASTM D86-11).

2.3.3 Pour Point

The pour point of a crude oil, or a petroleum fraction, is the lowest temperature at which the oil will pour or flow when it is cooled, without stirring, under standard cooling conditions. Pour point represents the lowest temperature at which oil is capable of flowing under gravity. It is one of the important low-temperature characteristics of high-boiling fractions. When the temperature is less than the pour point of a petroleum product, it cannot be stored or transferred through a pipeline. Standard test procedures for measuring pour points of crude oil or petroleum fractions are described in the ASTM D97 (ISO 3016 or IP 15) and ASTM D5985 methods. The pour point of crude oils relates to their paraffin content: the higher the paraffin content, the higher the pour point.

2.3.4 Distillation and Boiling Points

The boiling point of a pure compound in the liquid state is defined as the temperature at which the vapor pressure of the compound equals the atmospheric pressure or 1 atm. The boiling point of pure hydrocarbons depends on carbon number, molecular size, and the type of hydrocarbons (aliphatic, naphthenic, or aromatic).Complex mixtures such as crude oil, or petroleum products with thousands of different compounds, boil over a temperature range as opposed to having a single point for a pure compound. The boiling range covers a temperature interval from the initial boiling point (IBP), defined as the temperature at which the first drop of distillation product is obtained, to a final boiling point, or endpoint (EP) when the highest-boiling compounds evaporate. The boiling range for crude oil may exceed 1000 °F. The ASTM D86 and D1160 standards describe a simple distillation method for measuring the boiling point distribution of crude oil and petroleum products. Using ASTM, D86 boiling points are measured at 10, 30, 50, 70, and 90 vol% distilled. The points are also frequently reported at 0%, 5%, and 95% distilled. ASTM D1160 is carried out at reduced pressure to distill the high-boiling components of crude oil.

2.3.5 Concentration of Various Contaminants

In addition to hydrocarbons, crude oil contains heteroatom (S, N, metals) species that need to be removed if their concentrations are higher than the specified thresholds. Other impurities in crude oil include salt and sediment and water. The acidity of crude oil is also important particularly for concerns of corrosion in pipes or other process units. Carbon residue of a crude oil indicates the tendency to generate coke on heater tubes or rector surfaces. All of these contaminants and properties of crude oils are measured using standard methods, as described in this section.

2.3.6 Metals

Metal content in crude oils can provide valuable information about the origin of those oils, potentially aiding in identifying the source of oil spills. Crude oil assays often include nickel and vanadium contents due to the detrimental effects of these metals on catalysts used in cracking and desulphurization processes. In lubricating oils, metal contents can provide information on both the types of additives used in the oil and on the wear history of the equipment being lubricated. ASTM method D 5185 - Standard Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), (ASTM D 5185) can be used to determine over 20 different metals in a variety of petroleum product

2.3.7 Yield on Crude

Yields on crude data are still widely reported in the oil assay literature, providing information on the yield of specific fractions obtained from a crude oil. Although by no means universal, the below fractions are commonly used.

Table 2- standard petroleum fractions and their corresponding true boiling point (TBP) cut points

Product	TBP Cut Points, °C
Light straight-run gasoline	C5-70
Light naphtha	70-100
Medium naphtha	100-150
Heavy naphtha	150-190
Light kerosene	190-235
Heavy kerosene	235-265
Atmospheric gas oil	265-343
Vacuum gas oil	343-565
Atmospheric residue	>343
Vacuum residue	>565

3.0 Refining processes

3.1 Desalting and Distillation

Distillation is usually considered as the first process in petroleum refineries, in many cases. However, desalting should take place before distillation (Figure 5).

Salt dissolved in water (brine) moves the crude stream as a contaminant during the production or transportation of oil to refineries. If salt is not taken away from crude oil, serious damage can occur, especially in the heater tubes, due to corrosion or rusting caused by the presence of Cl. Salt in crude oil also causes reduction in heat transfer rates in heat exchangers and furnaces and increases overall energy consumption.

The three stages of desalting are:

1. adding dilution water to crude;
2. mixing dilution water with crude by a mixer;
3. dehydration of crude in a settling tank to separate crude and sediment and water (S&W).

Desalting can be performed in single-stage or two-stage units. The amount of water wash and the temperature of the mixing process depends mainly on the crude API gravity [9].

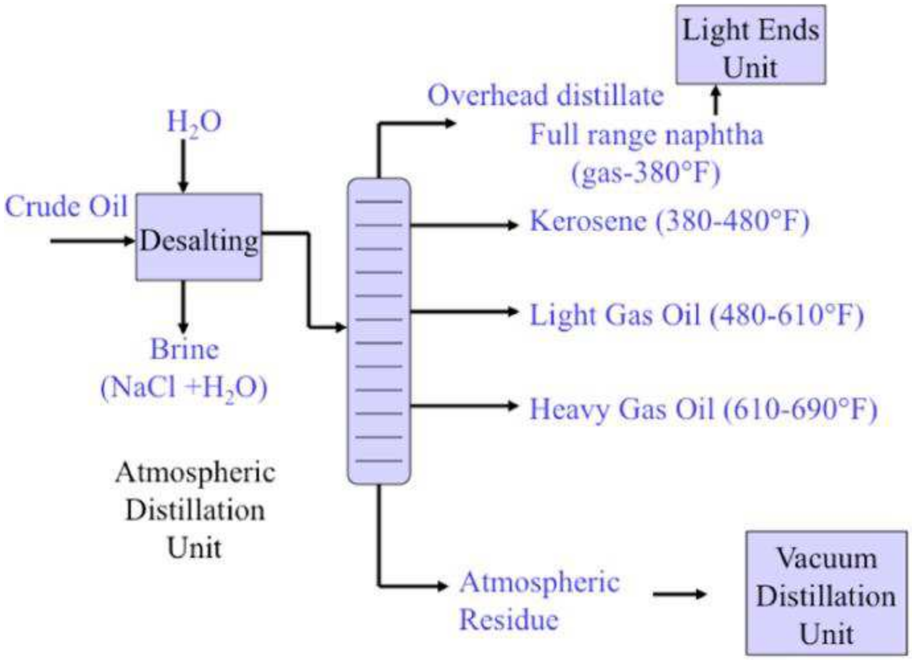


Figure 5 - Desalting and fractional distillation of crude oil.

Distillation separates hydrocarbon compounds into distillate fractions according to their boiling points or volatility. Compounds with low boiling points (volatile) tend to vaporize more easily than heavy compounds, and this forms the basis of the concept of separation using distillation. In a distillation column, light components are removed from the top of the column, and the heavier part of the mixture appears in the bottom. For a crude that is a mixture of several hydrocarbons, some very light compounds such as ethane and propane only appear in the top product, while extremely heavy and non-volatile compounds such as asphalts only appear in the bottom. Figure 5 shows a simple diagram of atmospheric and vacuum distillation units and the fractional separation of the crude oil into different boiling fractions with the indicated boiling ranges. The lightest compounds found in crude oil come out from the top of the distillation column (referred to as overhead distillate, or full-range naphtha) and are sent to the Light Ends Unit (LEU) for further separation into LPG and naphtha, as discussed later. The side streams separated in the atmospheric distillation column give fractions that include the "straight-run" products called kerosene, and light and heavy gas oils. The residue from the atmospheric distillation column generates two side streams, light and heavy vacuum gas oils, and vacuum residue from the bottom. All of these distillation products are subjected to subsequent processing to produce light and middle distillate fuels and non-fuel products, as described in the following sections starting with LEU.

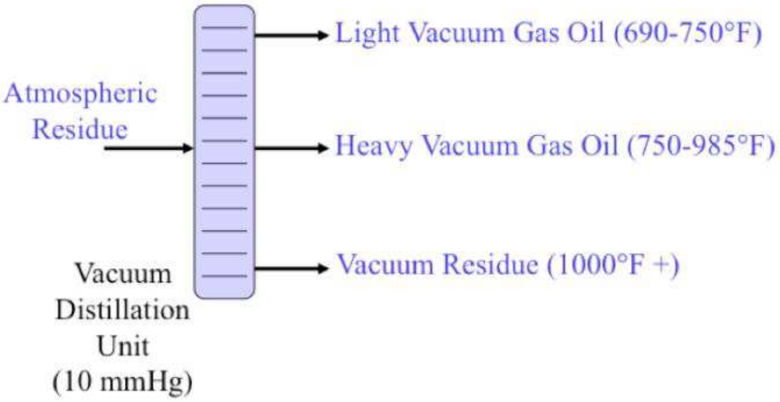


Figure 6- A schematic diagram of the Vacuum distillation unit

3.2 Light Ends Unit

As shown in Figure 7&8, the Light Ends Unit is made up of a sequence of distillation processes to separate the overhead distillate product from the atmospheric distillation column into five streams consisting of methane and ethane (C2 and lighter), to propane (C3), butane (C4), light naphtha, and heavy naphtha. The fraction C2 and lighter is used as fuel gas in the refinery to provide heat or generate steam. Propane and butane are sold as liquefied petroleum gas (LPG) after removing H2S. Light naphtha fraction that consists of C5 and C6 paraffins (pentane and hexane) is sent to the gasoline blending pool as straight-run gasoline, while the heavy naphtha fraction (rich in cycloalkanes, or naphthenes) is sent to a catalytic reforming process to produce gasoline with a high octane number.

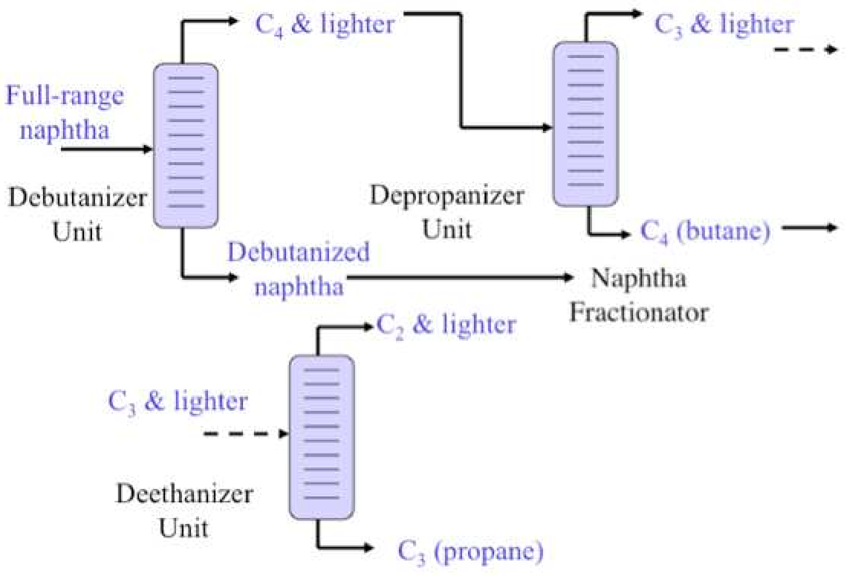


Figure 7- Distillation unit for light ends

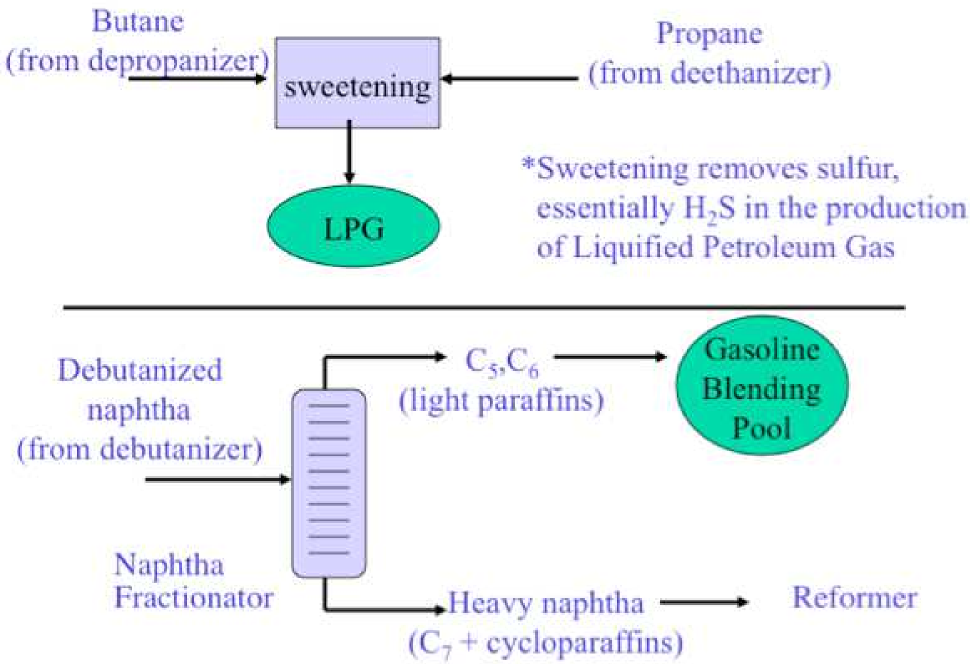


Figure 8- Separations in light ends unit.

3.3 Catalytic Reformer

Catalytic reforming transforms low-octane straight run naphtha fractions (particularly heavy naphtha that is rich in naphthenes) into a high-octane, low-sulfur reformate, which is a major blending product for gasoline (Figure 11). The most valuable byproduct from catalytic reforming is hydrogen, which is needed in refineries with increasing demand for hydrotreating and hydrocracking processes. Most reforming catalysts contain platinum supported on alumina, and some may contain additional metals such as rhenium and tin in bi-, or tri-metallic catalyst formulations. Ideally, for catalytic reforming, the naphtha feedstock needs to be hydrotreated before reforming, to shield the platinum catalyst from poisoning by sulfur or nitrogen species.

The principal reactions in catalytic reforming include dehydrogenation of naphthenes to aromatics (with significant quantity of hydrogen as byproduct) and cracking/isomerization of n-paraffins into i-paraffins. The principal product from catalytic reforming is called reformate, consisting of C4 to C10 hydrocarbons. Reformate has a high octane number because of high concentration of aromatic compounds (benzene, toluene, and xylene) produced from naphthenes. With the more stringent requirements on benzene and total aromatics limit in US and Europe (less than 1% benzene, 15% total aromatics), the amount of reformate that can be used in gasoline blending has been limited, but the function of catalytic reforming as the only internal source of hydrogen continues to be important for refineries.

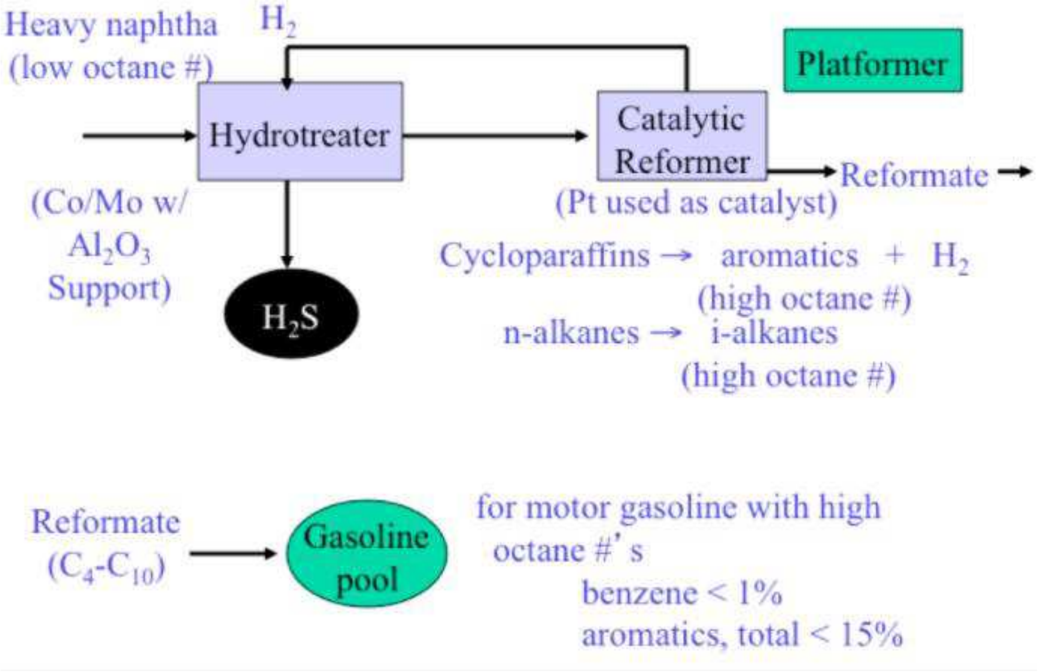


Figure 9- Catalytic reforming.

3.4 Catalytic Hydro treatment

Catalytic hydro treatment can be used as a pretreatment step to protect catalysts from crude oil contaminants such as heteroatom (S, N, O) compounds, as well as metals (mainly Ni, V) just like with the catalytic reforming in the previous section, . Hydro treatment is also used as a major finishing process in a petroleum refinery. Shifting to the side stream products from the distillation column, kerosene and light gas oil fractions can be hydrotreated to remove the heteroatoms to produce the final products of jet fuel, and diesel fuel, as shown in Figure 3.4. Particularly strict sulfur limits are imposed on diesel fuels so that the particulate emissions from diesel engines can be reduced. In the U.S., the government regulations [10] require that highway and non-road locomotive and marine (NRLM) use diesel fuel that meets a maximum specification of 15 parts per million (ppm) sulfur by 2014, with a full compliance for highway use and non-road diesel fuel since December of 2010.

Note in Figure 5 that typical catalysts used for hydrotreating are Co and Mo compounds supported on alumina (Al2O3). Jet fuel consists of C10 to C15 hydrocarbons, and diesel fuel consists of C15 to C20 hydrocarbons. Analogous to octane number for gasoline, a performance parameter for diesel fuel is cetane number (n-C16H34, n-hexadecane) that measures, in contrast to octane number, the tendency (not resistance) of diesel fuel to ignite upon compression with air. As a side note, light gas oil fraction is not typically used in the U.S. for producing diesel fuel, but sent to catalytic cracking to make gasoline.

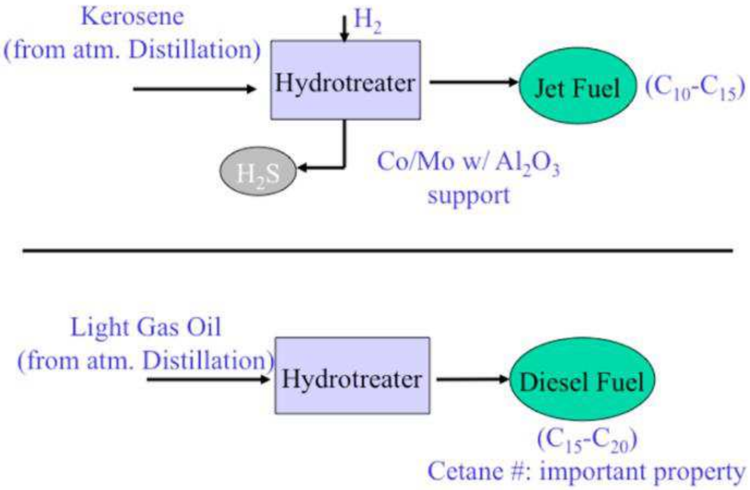


Figure 10- Catalytic hydrotreatment of jet fuel and diesel fuel.

3.5 Conversion of Heavy Gas Oil

Moving down on the side streams of the distillation column, heavy gas oil constitutes the next fraction in line. Some generic conversion processes for the heavy distillates, such as heavy gas oil (consisting of C20 to C25 hydrocarbons), are shown in Figure 13. These processes, aimed at reducing the molecular size or the boiling point of gas oil compounds, involve thermal cracking or catalytic cracking. A mild thermal cracking process, called visbreaking, is applied to reduce the viscosity of the feedstock, and it is more frequently applied to residual fractions, such as vacuum distillation residue. A more severe thermal cracking of heavy gas oil can be used to produce LPG and ethylene and light and middle distillates from heavy gas oil. A highly aromatic byproduct from thermal cracking is called ethylene tar. Ethylene is an important petrochemical feedstock, while ethylene tar can be used as feedstock to produce carbon blacks. Catalytic cracking is more frequently used for conversion of heavy gas oil to gasoline.

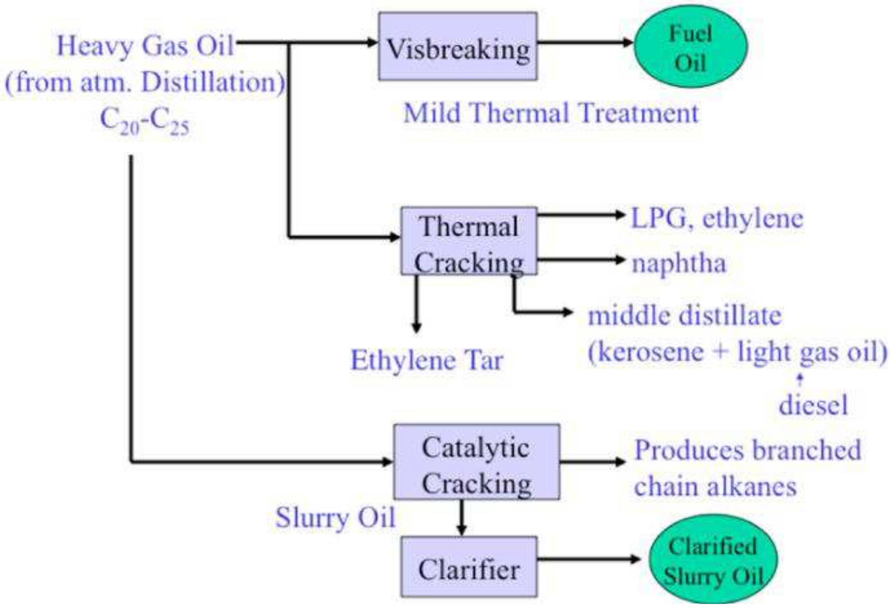


Figure 11- Conversion of heavy gas oil.

A particular process of catalytic cracking, Fluid Catalytic Cracking, is almost exclusively used worldwide in heavy gas oil and light vacuum gas oil conversion. This process produces high octane gasoline primarily, with important byproducts, including LPG, light olefins and i-alkanes, light cycle oil (LCO), heavy cycle oil (HCO), and clarified slurry oil (also called decant oil), as shown in Figure 13 and 14. LCO is used in the U.S. to produce diesel oil by hydrocracking, and decant oil can be used as fuel oil, feedstock for carbon black manufacturing, and to produce a special type of petroleum coke called needle coke. Needle coke has a microstructure that makes it a good precursor to graphite electrodes that are used in electric-arc furnaces to recycle scrap iron and steel. The manufacturing of graphite electrodes, using a byproduct from FCC used to produce gasoline, is considered a principal interface between petroleum refining and the iron and steel industry [9&10].

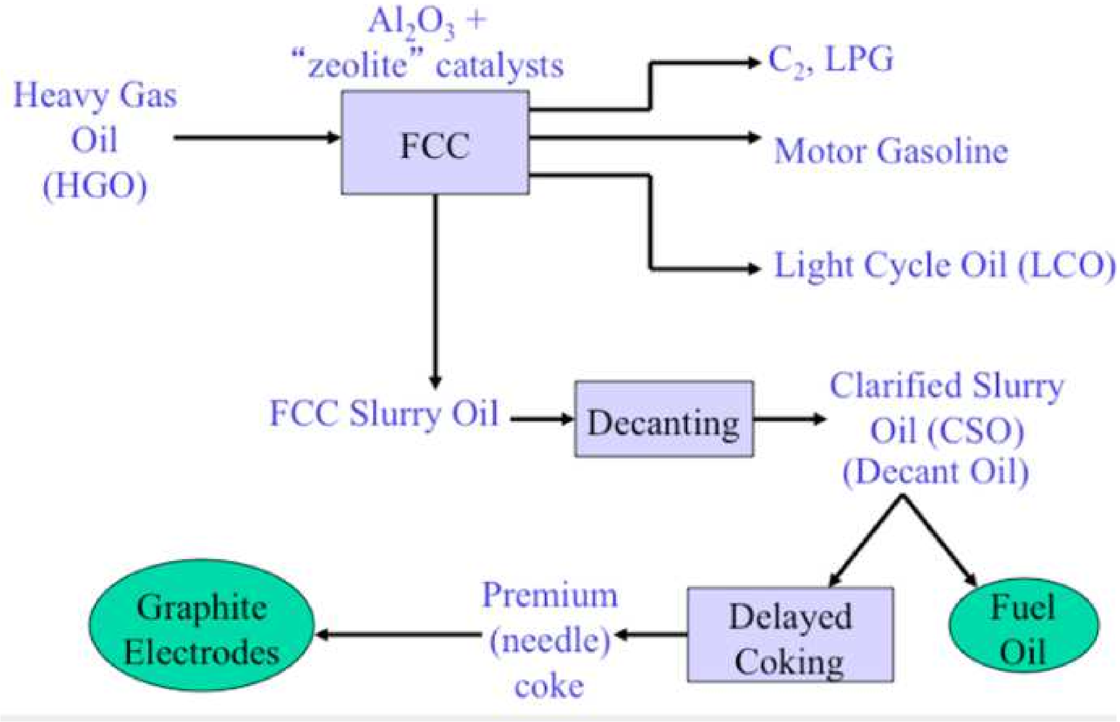


Figure 12- Fluid Catalytic Cracking (FCC) of heavy gas oil.

3.6 Conversion and Processing of Vacuum Gas Oils

Moving to the vacuum distillation column, the vacuum distillates, and light vacuum gas oil (LVGO) and heavy vacuum gas oil (HVGO) can be processed by some advanced FCC processes. However, hydrocracking is more frequently used to convert LVGO and HVGO into light and middle distillates, using particular catalysts and hydrogen. Similar to LCO, the LVGO and HVGO fractions from vacuum distillation tend to be highly aromatic. Catalytic hydrocracking combines hydrogenation and cracking to handle feedstocks that are heavier than those that can be processed by FCC, because of excessive coke deposition on the catalyst in the absence of hydrogen. Middle distillates (e.g., kerosene and diesel fuel) are the principal products of hydrocracking. In addition to light and middle distillates, hydrocracking also produces light distillates and LPG, as shown in Figure 13.

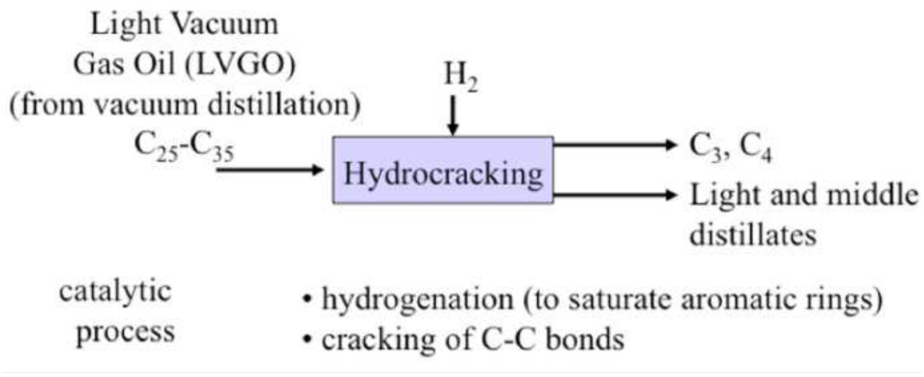


Figure 13. Hydrocracking of light vacuum gas oil.

HVGO can also be used as a feedstock to produce lubricating oil base stock, through a sequence of solvent extraction processes to remove aromatic hydrocarbons by furfural extraction, and to remove long-chain paraffins by dewaxing (Figure 16).

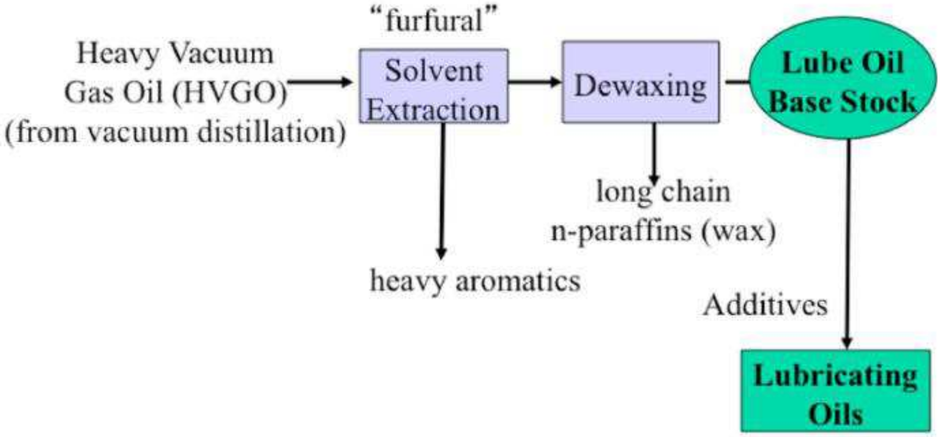


Figure 14- Solvent extraction and processing heavy vacuum gas oil.

3.7 Processing and Conversion of Vacuum Distillation Residue

The heaviest and the most contaminated component of crude oil is the vacuum distillation residue (VDR), also referred to as the bottom-of-the-barrel. There are multiple processing paths to upgrade VDR into usable products. One process is called deasphalting, which removes the heaviest fraction of VDR as asphalt that is used mainly to pave roadways. The lighter fraction obtained in the deasphalting process, deasphalted oil (DAO), can be used as fuel oil after hydrotreatment (Figure 15).

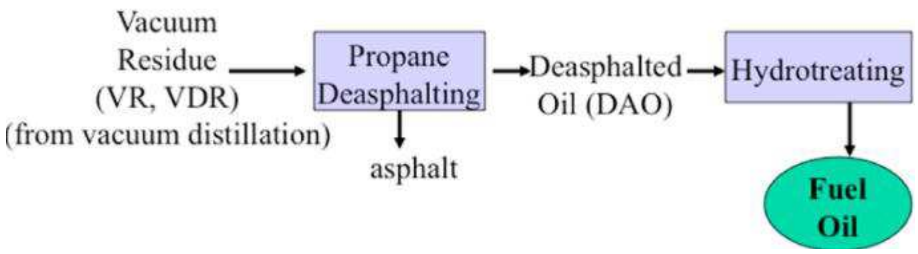


Figure 15- The deasphalting process

Thermal processes, such as visbreaking and coking, also provide options for upgrading VDR, which is normally a solid at ambient temperature. As shown in Figure 18, the visbreaking operation involves mild thermal cracking, with the primary purpose of producing a relatively low grade fuel oil (with a much lower pour point than VDR) and byproducts such as middle and light (naphtha) distillates and LPG.

The yield of these byproducts would normally not exceed 10%wt of VDR. As a general rule in refinery conversion processes, producing a lighter product with a higher H/C ratio (e.g., fuel oil, middle distillates, LPG) from a feedstock (e.g., VDR) would require the simultaneous formation of a heavier product (e.g., coke) with a lower H/C ratio than the feedstock. Clearly, this compensation is dictated by the hydrogen balance, or hydrogen distribution among the products. With no external hydrogen entering the conversion unit (as it would in hydrogenation, or hydrocracking reactions), making a product(s) with a higher H/C ratio than that of the feed would require making other product(s) with a lower H/C ratio than that in the feedstock. In the case of visbreaking, what enables the production of lighter (or lower viscosity) fuel oil and other products from VDR is the formation of small quantities of coke with an extremely low H/C ratio. Hence, the term disproportionation describes this unequal distribution of C or H in the conversion products, or losing (rejecting) C in the coke that accumulates on reactor tubes and is periodically burned out to clean the reactor tubes.

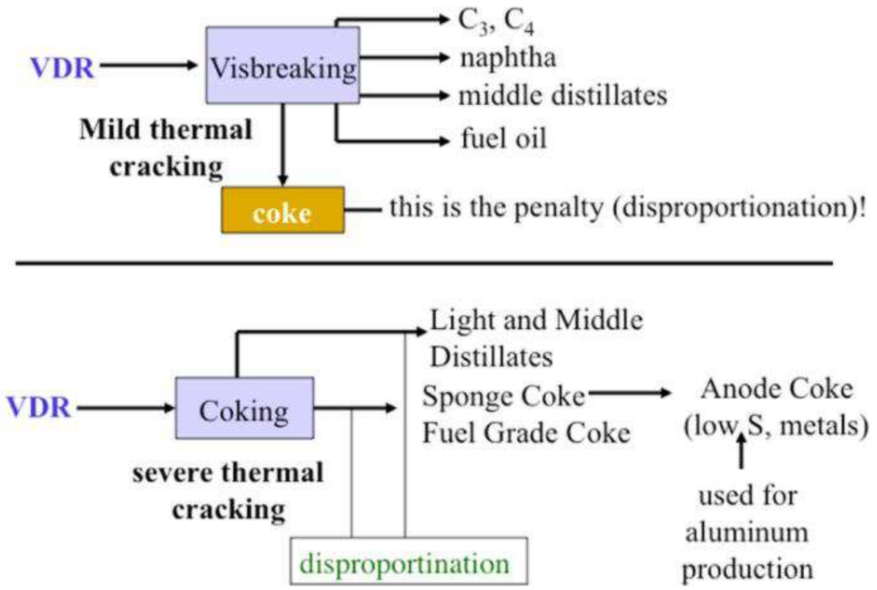


Figure 16-Thermal processing of VDR by visbreaking, or coking processes.

As different from visbreaking, coking involves severe thermal cracking with intentional production of coke with a low H/C, so that lighter fuels can be obtained from VDR (by disproportionation), as can also be seen in Figure 18. The product coke obtained from VDR with relatively low heteroatom concepts, termed sponge coke, can be used in manufacturing carbon anodes that are used in electrolysis of alumina (Al2O3) to produce aluminum metal. This is another important interface between petroleum refining and metals industries, similar to the coke produced from decant oil used for making needle coke for manufacturing graphite electrodes to operate electric-arc furnaces, as mentioned before.

3.8 Paths for Upgrading Heavy Oil

It should be clear from this quick tour of a refinery, that the most valuable products from a refinery include light distillates (gasoline) and middle distillates (jet fuel and diesel). These products are mostly paraffinic and contain relatively short paraffin chains, or small molecules, or, in other words, high H/C ratios. In this context, one could summarize the overall goal of petroleum refining as managing the H/C ratio of the products for the optimum distribution of hydrogen into products to maximize profits. Controlling the H/C ratio of the products would require either lowering the C content of the products (i.e., carbon rejection), or increasing the H content (i.e., hydrogen addition). The animation below depicts these two major paths for upgrading heavy oil (or crude oil) with some examples for each path.

The processes, coking, solvent extraction (e.g., deasphalting), visbreaking, and catalytic cracking reject carbon in the coke (carbonaceous) product so that lighter products (with high H/C) ratios can be obtained in these processes. Carbon in the coke or in the heavier product is considered to have been rejected (and potentially lost) since the carbonaceous byproducts have much lower value in comparison to those of the lighter products. In contrast, hydrogen addition, as in the processes of hydrogenation and hydrocracking, enables the conversion of all the carbon present in heavy oil (or crude oil) to high value products without rejecting, or sacrificing, any. The hydrogen addition processes cost much more than carbon rejection processes, because producing hydrogen and the catalysts used in hydrogen addition processes are very expensive.

4. Experimental Methodology

4.1 Density measurement

4.1.2 Apparatus

-Sample vessel
-Mettler Toledo DM45 Delta Range Density Meter

4.1.3 Reagents

Six different types of samples, and the below listed solvents were used during the experiments;

-Crude oil;
-Atmospheric residue;
-Fuel oil;
-Kerosene;
-Diesel oil;
-Vacuum fraction;
Rising solvent.

4.1.4 Procedure

DE45 Density Meters measured the density of gases, liquids and solutions using the oscillating body methods. Turned on the device, and applied 20°C. Then waited for the device to hit 20°C. The sample was placed in the sample vessel, and replaced into the sample changer. The analysis was started with one click on the touchscreen of the master instrument. The sample changer used pressurized sampling to fill the measuring cell. Pressurized sampling avoided bubbles in the cell. A first measurement was performed after a few minutes, and the cleaning started to remove the sample by using an initial rising solvent. Repeated the same procedure for the same sample to reduce errors.

Figure 17 – Mettler Toledo DM45 Delta Range Density Meter

4.2 Atmospheric Distillation

4.2.1 Apparatus

-SETA atmospheric distillation unit;
-Distillation flask;
-A graduated cylinder;
-Calibrated measuring cylinder (receiver);
-Weighing scale;
-Liquid in glass thermometer of 400 °C capacity;
A round bottom flask supporting coke.

4.2.2 Reagents

Crude oil (without water content), 100 mL;

4.2.3 Procedure

The weights of the distillation flask and the cylinder to receive distillate are weighed and recorded on the weighing balance. Weighed and recorded the weight of boiling chips. Measured 100 ml of sample in a cylinder and poured into the distillation flask. The liquid thermometer provided with a snug-fitting cork is placed tightly into the neck of the distillation flask (refer to figure 19 for SETA distillation unit). The distillation flask with the thermometer was placed into the distillation unit with the second neck rightfully placed into the condensing section of the SETA Atmospheric unit, and the bottom of the flask on the heating mantle of the distillation unit. The tap was opened and water level controlled to facilitate condensation. Turned on the heating system, and once the sample started boiling, the temperature at which the sample started to boil was recorded as the initial boiling point (IBP). The first drop was waited for and temperature recorded, after which, the heater was adjusted severally in order to obtain droplets speed of about 2 (two) droplets per second.

Figure 18-SETA Atmospheric Distillation unit

The temperatures at which 10 %, 20 %, 30 %, 40 % and 50 % volumes of distillate are obtained are recorded. Also, the percentage volume of distillate obtained at 200 °C and 300 °C are recorded. To avoid cracking of the sample, it was ensured that temperatures in excess of 350 °C were not used. Heating was discontinued and the system was allowed to cool to ambient temperatures. The distillation flask was disconnected, weighed and the final weight of the distillation flask recorded and its content collected.

The final percentage volume of the distillate obtained is recorded. Weighed and recorded the weight of the receiving cylinder and the distillate. After the necessary data are collected, the percent loss is determined by deducting the total recovery percentage from 100. The percentage of completed recovery is the sum of recovery percentage and residual percentage point.

4.3 Vacuum Distillation

4.3.1 Apparatus

-Distillation flask (500mL capacity);
-Weighing scale / Analytical balance of sensitivity 0.01 g;
-Calibrated measuring cylinder (sample);
-Flask supporting;

The laboratory distillation unit (HDV632) has in-built vacuum-jacketed column assembly, vapor temperature measuring device, receiver of borosilicate glass, vacuum gage, pressure regulating system, cold traps, low pressure air or carbon dioxide source to cool the flask and heater at the end of the distillation, low pressure nitrogen source to release the vacuum in the system, safety screen, coolant circulating system (see Figure 11).

4.3.2 Reagents

- Atmospheric residue, 100 mL;
- Silicone grease;
- Silicone oil;
- Toluene (technical Grade).
-

4.3.3 Procedure

The weight of the cylinder without the sample is weighed and recorded. 200 ml of sample was measured in a cylinder and the weight of the cylinder with the sample was taken. The condenser coolant temperature was set to 30 ° C below the lowest vapour to be observed in the test. A suitable grease was used to lubricate the spherical joints of the distillation apparatus. Cleaned the surfaces of joints before applying the grease.

Evacuate the system until the pressure exceeds 0.133kPa. The heater was turned on when the desired pressure level had been reached and applied heat to the flask as quickly as possible. The vapour time, temperature, and the pressure at the volume percentage fractions were recorded with the help of the computer. Used the automatic method for this laboratory work. Lowered the flask heater 5 to 10 cm, and cooled the heater and flask by fan-cooler. The device was cleaned by using toluene as a sample and finally the device was turned off.

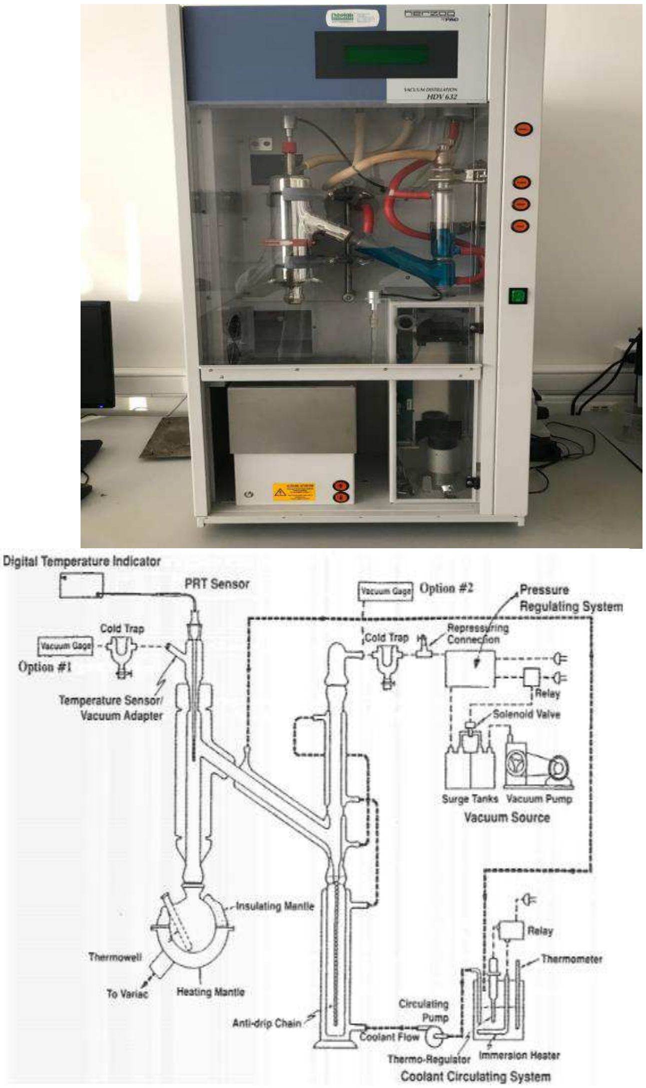


Figure 19 – Assembly of the laboratory vacuum distillation unit (HDV 632)

4.4 coking

4.4.1 Apparatus

-Ceramic container
-Oven (temperatures above 1000 C)
-Fine sand

4.4.2 Reagent

-Vacuum residue

4.4.3 Procedure

Vacuum residue was placed in the ceramic container and weight was taken and recorded accordingly. The residue was uniformly covered with sufficient fine sand and placed in a metallic vacuum container. The metallic container was tightly closed and placed in the vacuum oven for about 3 hours. Temperatures moved from 100 °C to 450 °C and were held for above 1 hour before descending and finally cooled. The metallic container was taken out of the oven and opened to take out the coke formed in the ceramic container. The container was further heated in a more powerful oven at a temperature above 1200 °C for 1 hour 30 minutes. (see figure 12). The coke was allowed to cool down and separated from sand for further analysis.

Figure 20-Nabertherm Oven (temperature range 30-3000°C)

5. Results and discussions

5.1 Crude oil assay analysis

Several tests were conducted on the sample to determine the properties of the sample and they are listed in the table below.

Table 3- Assay properties of sample from laboratory analysis

Properties	Vankor Oil field
Specific density @ 20 °C, kg/m 3	920.7
CCR	21%
Kinematic viscosity, mm 2 /sec	
20°C	6.14
30°C	5.18
40°C	3.31
50°C	2.73
60°C	2.34
Freezing point, °C	+13
Fractional composition	
I.b.p.	91.2°C
amount of fraction i.b.p.-180 °C, vol%	25
amount of fraction 180-240 °C, vol%	34
amount of fraction 240-300 °C, vol%	42
Group composition (Content, % wt.)	
Asphaltenes	1.4
Resins	3.5
Saturated (paraffins + naphthenes)	76.2
Aromatic hydrocarbons	18.9

5.1.1 Distillation fractions evaluation (ASTM D86)

Atmospheric distillation is carried by the evaluation of recovered amounts of fraction under elevating temperature and is vital to predict the operating condition in the scale-up scenario as well as to determine the yield and the quality of the outputs. The experiment was done based on ASTM D86 which was used to measure the crude distillation curve under atmospheric pressure conditions. ASTM D86 is known as the simplest technique to identify the fractions percentage based on the boiling point report. The test could obtain as much as 50, 60, to 90% of vaporized volume as per reported.

However, due to the heavy hydrocarbon cracking occurrences at high temperature, the operation was terminated after the temperature of 300 C. The results shown in Table 2 below illustrate the amount of vaporized fraction recovered in the temperature rising. The observed initial boiling point (IBP) at 91 °C is noticed by the present of the first drop in the collecting flask. To draw the statement by comparing with average heavy oil data, 91 °C IBP indicates that the sample from the Vankor field is heavy oil. The ASTM D86 method shortfalls in the gas fraction percentage observation, causing the data evaluation missing, and assumption of 91 °C IBP accounted for the majority naphtha fraction with gas included. The next steps are to determine the corrected temperature reading and corrected actual loss to 101.3 kPa by reading and calculating from the distillation curve generated ASPEN HYSYS.

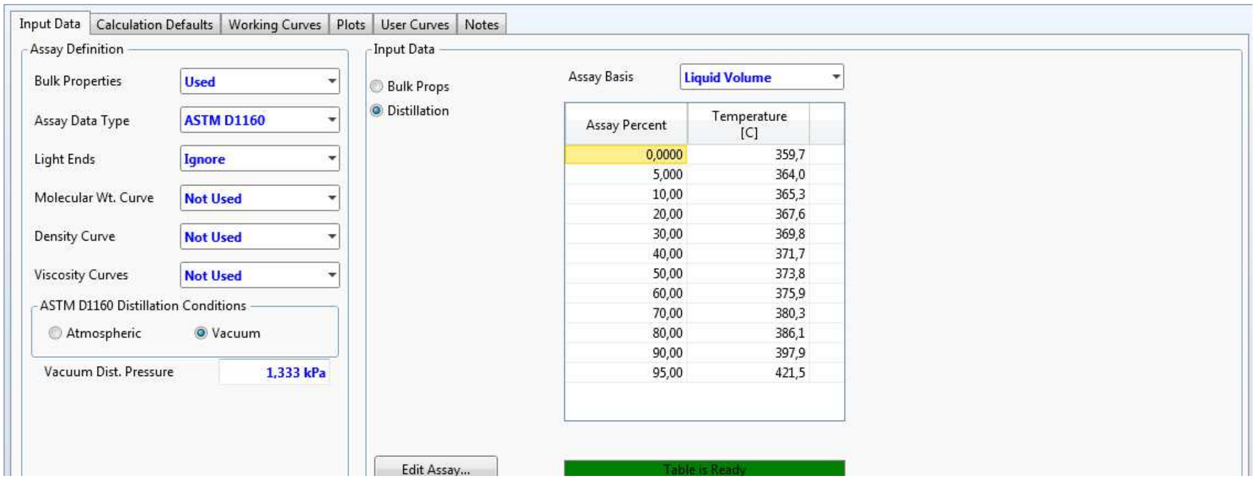
Table 4- Recovery percentage with their corresponding temperatures.

Recovered (%)	Temperature(°C)
0	91
10	97
16	134
20	156
22	168
26	189
29	221
32	252
35	281
43	301

5.1.1.1 Simulations

Aspen Hysys simulation software was used to simulate both atmospheric and vacuum distillation and their corresponding calculations. For the purpose of simulation in Aspen Hysys, the above necessary properties were input into our simulation work to generate recovery and distillation curves which were close to the manually calculated figures.

Temperatures and percentage recovery generated from Atmospheric and Vacuum distillation are input in the interface below in Aspen Hysys to create an assay for the sample.



Assay Definition

Bulk Properties: Used

Assay Data Type: ASTM D1160

Light Ends: Ignore

Molecular Wt. Curve: Not Used

Density Curve: Not Used

Viscosity Curves: Not Used

ASTM D1160 Distillation Conditions: ○ Atmospheric ● Vacuum

Vacuum Dist. Pressure: 1,333 kPa

Input Data

○ Bulk Props

● Distillation

Assay Basis: Liquid Volume

Assay Percent	Temperature [C]
0,0000	359,7
5,000	364,0
10,00	365,3
20,00	367,6
30,00	369,8
40,00	371,7
50,00	373,8
60,00	375,9
70,00	380,3
80,00	386,1
90,00	397,9
95,00	421,5

Figure 21- Input data from Vacuum distillation unit

point	moles	cum moles	NBP [C]	mole wt	Mass density[kg/m3]	Viscosity1 [cP]	Viscosity2 [cP]
0	-	0	49,7541262	77,16615009	669,9588373	0,319980628	0,172749827
1	0,03	0,03	56,65111883	80,06027614	679,1752587	0,33917083	0,183825192
2	0,03	0,05	70,34119145	85,99087066	696,197198	0,300458504	0,187303748
3	0,02	0,08	83,84416183	92,09000484	711,4571608	0,339167724	0,207283604
4	0,02	0,10	97,1017675	98,57264373	725,1026719	0,382922915	0,229168329
5	0,02	0,12	110,0927657	105,3349005	737,3147294	0,432020913	0,253080016
6	0,02	0,14	122,3840689	111,9525067	747,9186195	0,485753814	0,280197012
7	0,02	0,16	133,9451794	118,2675931	757,1343235	0,541501201	0,306099949
8	0,02	0,18	145,2407389	124,7111624	765,5005666	0,602189361	0,333713262
9	0,02	0,20	156,4068388	131,3665513	773,2155816	0,66870906	0,363373385
10	0,02	0,22	167,5853461	138,3337482	780,4459221	0,742297143	0,395545238
11	0,04	0,26	188,8970192	152,5317733	793,0632729	0,929392328	0,467711996
12	0,04	0,29	221,422194	176,7674657	810,0430455	1,35852617	0,611534978
13	0,03	0,32	252,2782235	202,9226192	824,4477522	1,991620684	0,796825522
14	0,03	0,35	280,6682662	229,8240673	836,8596703	2,896202646	1,026799123
15	0,03	0,38	293,4464063	242,7844894	842,3002078	3,456371167	1,155063893
16	0,03	0,41	297,2041047	246,6888157	843,8896008	3,644850317	1,1963027
17	0,03	0,43	300,9618032	250,6329687	845,4753408	3,845638417	1,239288432

Figure 22 -calculations and simulations generated by software (Aspen Hysys).

The software calculates and generates a distillation curve after all data are entered correctly. And this assay becomes the basis for simulation and for all other processes to be performed. It also corrects the boiling point range and generates the corresponding viscosity as temperature changes by generating TBP recovery. This can be easily read from the distillation curve generated by the software. See curve below.

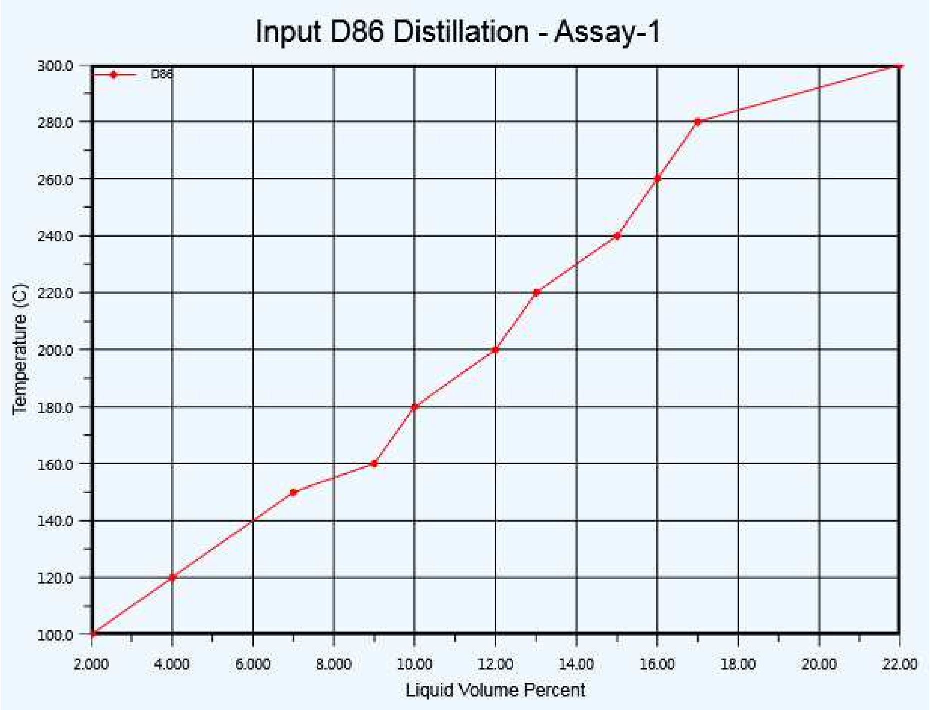


Figure 23- Boiling points (°C) of sample generated by Aspen Hysys

5.1.2 Vacuum distillation fractions evaluation

ASTM D1160 was used for analysis. As much as 63% of the AR collected from the non-vaporized fractions from atmospheric distillation process was further analyzed based on the boiling point of each recovered volume percentage. Table 5 below describes clearly the result along with the adjustment to the atmospheric temperature profile.

Table 5- Adjusted recovery and temperatures

Recovered (%)	Temperature (°C)	ATM Temperature (°C)
0	159.7	359.7
5	163.1	364
10	164.1	365.3
20	165.9	367.6
30	167.7	369.8
40	169.2	371.7
50	170.8	373.8
60	172.5	375.9
70	176.4	380.8
80	180.6	386.1
90	190.1	397.9
95	209.1	421.5

5.1.2.1 Simulations

In a similar manner, recorded values obtained in laboratory experiments for vacuum distillation were input in the software to generate the distillation curve and calculate the recovery. The software also generated the various boiling point ranges (TBP) and the corresponding viscosity.

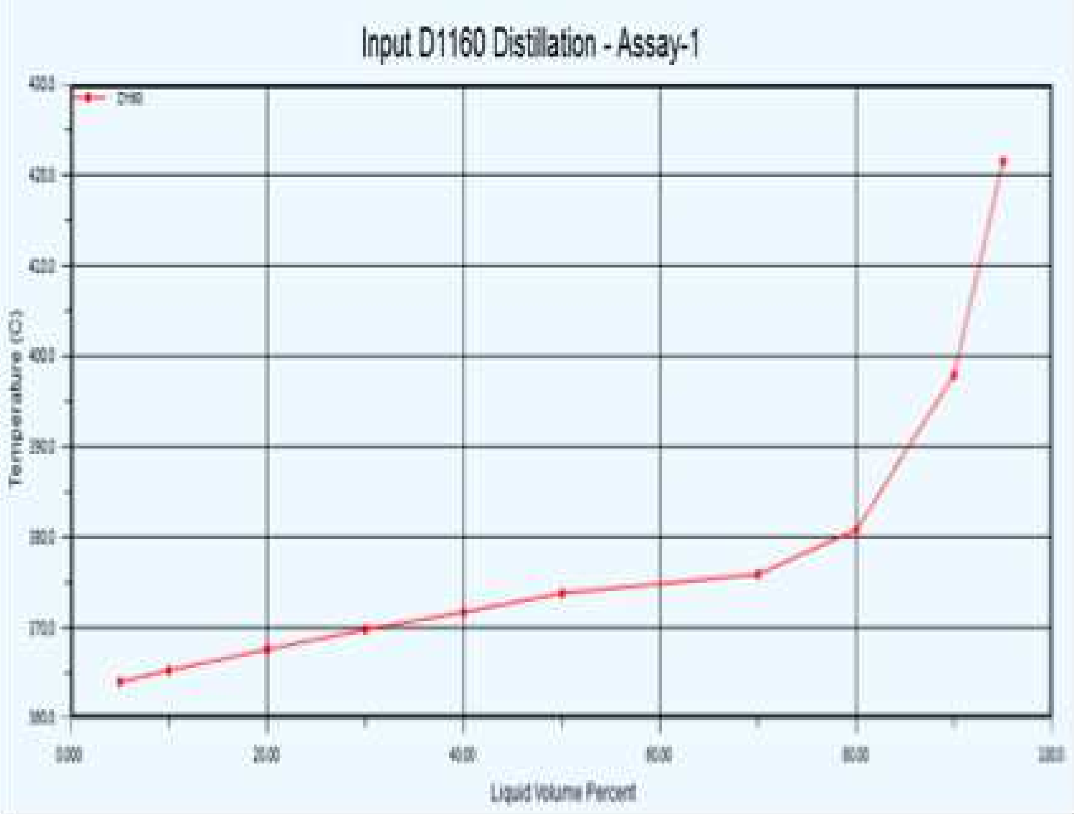


Figure 24- Vacuum distillation curve generated after simulations

5.2 Refinery process

5.2.1 Desalting and Atmospheric distillation

Desalting is a water-washing operation performed initially at the production field and thereafter at the refinery site for additional crude oil cleanup, where the salt and water content specifications are even more rigid because of their negative effect in the downstream processes due to scale formation, corrosion, and catalyst deactivation. Table 11. shows the detailed material balance of the desalting process. First, it is preheated before being sent to the separator column to strip out the gaseous fractions. This reduces the pressure accumulation on the second furnace and to achieve better separation in the CDU. Before entering the CDU, the oil is intensified up to 370 °C in the furnace heater and the top stages of the CDU are maintained at 1.2-1.5 bar.

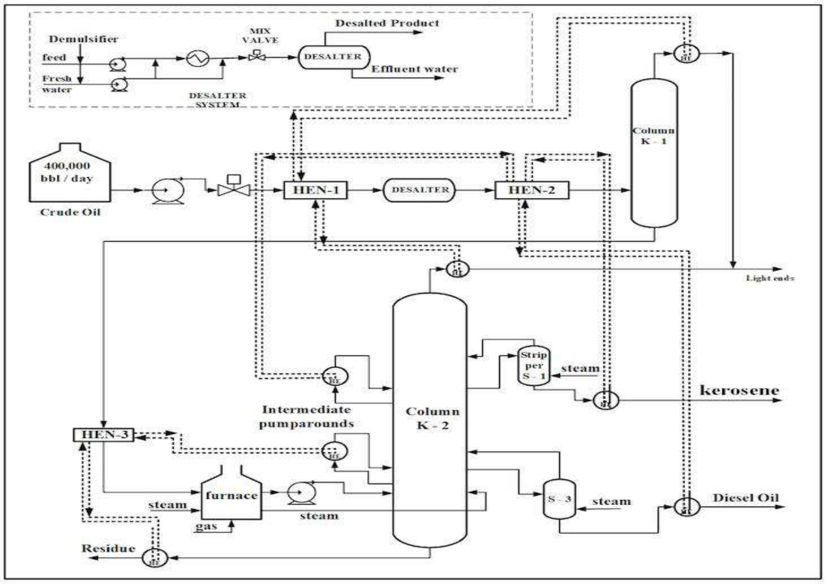


Figure 25 – A Schematic diagram of the crude desalting and distillation unit

The overhead light-ends and SR Naphtha which dispatch at the top stage are then mixed together with the K-1 stripped gas to the stabilizer K-3, prior entering, it is heated by heater. The middle distillate products (kerosene and diesel) are leaving with output temperature of 180 to 260 °C. On the other hand, the AR (atmospheric residue) output temperature is reduced (from 340 °C) by heat exchange with CDU feed before being transferred to the VDU. The above displayed design was selected based on the functionality to separate each fractions with optimum purity and reduced the number of columns in CDU which translated as reduced in pressure drops and operation handlings [11].

Table 6 – Material balance of the desalting system

Feed and products		wt % on feedstock of process installation	wt % on crude oil	ton/day
Input	crude oil	101	101	8301.36
Output	desalted oil	100	100	8219.17
	Water and salts	1	1.00	82.19
Total	-	101	101	8301.36

The design capacity assumption is made on a mass basis with inflowing feed of crude oil from desalter at 8219.17 ton/day that is 300000 barrels per year. Table 12 obtained by manual calculation, with a total loss of 0.4 % and 63.10 % of AR.

Table 7 – Material balance of the atmospheric distillation

Feed and products		wt % on feedstock of process installation	wt % on crude oil	ton/day
Input	Desalted oil	100.00	100.00	8219.17
Output	Top product (gases)	0.57	0.57	46.85
	Light Naphtha	5.29	5.29	434.79
	Heavy Naphtha	10.07	10.07	827.67
	Kerosene	9.69	9.69	796.44
	Diesel Oil	17.08	17.08	1403.83
	Residue	53.30	53.30	4380.00
	Lost	4.00	4.00	328.77
Total	-	100.00	100.00	8219.17

It can be noticed that the sample contains a high amount of the bottom of the products especially Residue. Hence, it is necessary to undertake further processes catalytic and thermal upgrading to achieve optimal plant productivity.

5.2.2 Vacuum distillation unit

The topped AR feed is fed after being heated below the cracking temperature zone before entering the flash zone of VDU. The steam jet ejector is used to maintain the vacuum at 20 – 40 mmHg of absolute pressure. The range of operating temperature at flash zone at 390 – 420 °C chose for further vaporization of overhead products and middle vacuum fractions. Wet type of VDU is used over the dry type that needs a high amount of injected steam to reduce the partial pressure of oil [12].

The wet is not preferred because total steam in the range of 36 – 60 kg/m^3 per AR feed is needed to run the process. The dry type as shown in Figure 22.below utilizes its own effectiveness of the vacuum in heavy oil vaporization. However, the column design will be far smaller in comparison with dry type and the application of overhead pre-condenser is eliminated in the process. However, the dry VDU has higher flash zone operating temperature (380 °C for wet VDU), boot cooling circuit is strictly required to prevent coking formation and plug the plates.

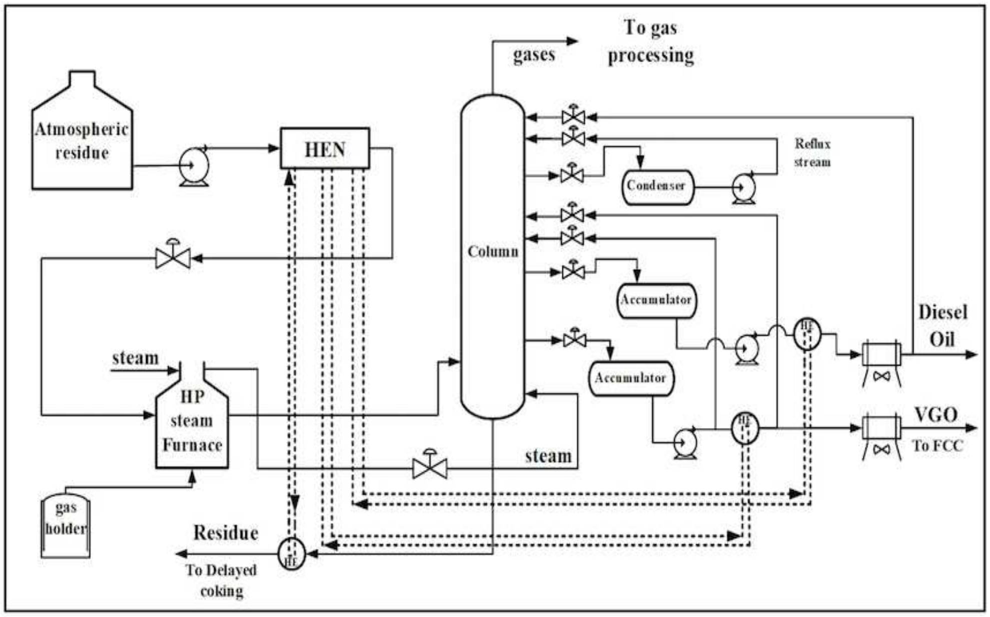


Figure 26 – A schematic diagram of the crude distillation unit

Additionally, as the modern design of vacuum units, dry VDU runs at lower flash zone pressure and lower pressure drops in the internals of the column. Thus, the reflux zone with fractionation trays might be replaced by a low pressure drop spray section.

Table 8 – Material balance of the vacuum distillation

Feed and products		wt % on feedstock of process installation	wt % on crude oil	ton/day
Input	Atmospheric residue	100	53.3	4380.82
Output	Top product (gases)	0.29	0.15	12.7045
	Diesel oil	10	4.8	438.082
	VGO	50.5	27.45	2212.31
	Residue	38.61	20.58	1691.43
	Losses	0.6	0.32	26.28
Total	-	100	53.3	4380.82

Consequently, the material balance from TBP was calculated, and theoretically compared then translated into mass percentage. The loss accumulated over a period of testing was found to be 0.6 % out of the total AR feed. Interestingly, diesel fraction was produced at a relatively high percentage at 10.48 % from total AR. The VR is then subjected to the further process of delayed coking while VGO to fluidized catalytic cracking for catalytic upgrading to recover lighter fractions.

5.2.3 Delayed coking

Less-valuable feedstock received from VDU bottom (VR) is upgraded to lighter fraction recuperation by thermal treatment. Thermal-cracking which occurs in delayed coking under slow pace increases the H/C ratio of the feed.

The gas oil discharged at temperatures ranging between 490 – 510 °C with operating drum temperature of 485 – 505 °C in 5 – 6 atm (illustrated in Figure 23) [13]. Pressure and 24 hrs of coking reacting period, translated to a sum of 48 hrs for the whole cycle of the operation including coke draining, coke cutting, and drum heat-up [14].

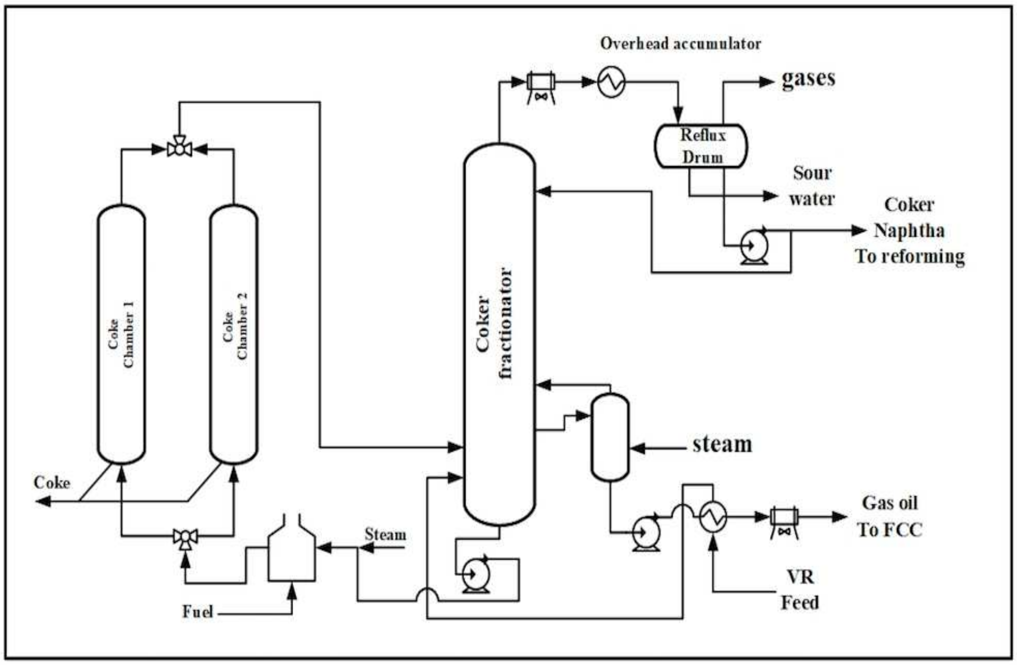


Figure 27 – A schematic flow diagram of a delayed coking

The diameter of the drum and the height is merely depending on the feed for the design consideration. The temperature from the discharge line of the coker drum to the fractionator is ranging around 440 – 445 °C. Delayed coking is preferred over fluid, contact and flexi coking because it offers the most optimal CDE % (Conradson Decarbonizing Efficiency) at 99.8 % and has minimum cost of investment as well as operating cost. And the quality of the produced coke is fairly superior to fluid coking.

Table 9 – Material balance of the delayed coking

Feed and products		wt % on feedstock of process installation	wt % on crude oil	ton/day
Input	Vacuum residue	100.00	20.58	1,700.20
Output	Gases	6.89	1.42	117.14
	Coker naphtha	15.62	3.21	265.57
	Gas oil	47.81	9.84	812.87
	Coke	29.20	6.01	496.46
	Losses	0.48	0.10	8.16
Total	-	100.00	20.58	1,700.20

5.2.3.1 Simulations

For optimization purposes, a delayed coking unit was constructed in Aspen Hysys using the previous generated Assay and all necessary properties.

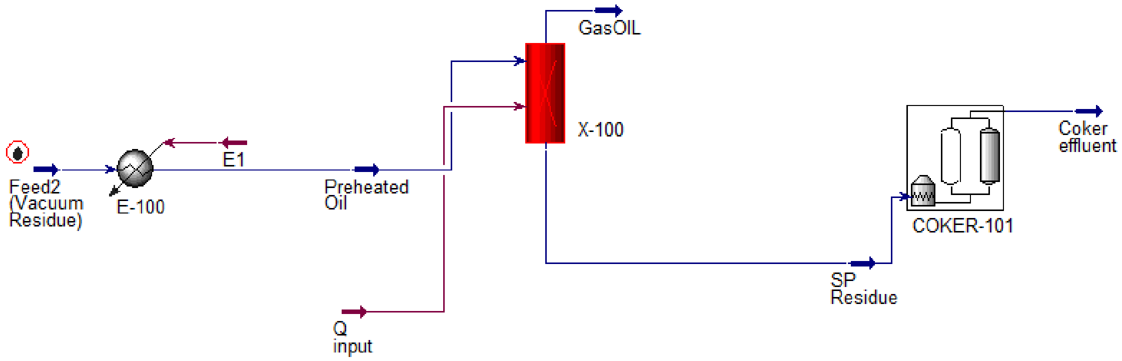


Figure 28- Flow sheet diagram of the delayed coking unit generated by Aspen Hysys

5.2.3.2 Optimization

For the purpose of optimization, different temperatures were used while all other parameters were held constant to see the effect on product yield from the modelled delayed coker in Aspen Hysys. Several series of optimizations were run to determine how changes in parameters would affect the optimum operating conditions. Three parameters were held constant and three remained constant from series to series. The three parameters held constant were the feed, pressure and residence time. The parameter that varied from series to series was temperature. For each series, the gas oil and other light fractions values increased as the temperature increased. In this work maximum light fractions and quality coke production are favored.

Therefore, the expected conditions are temperature at 530 C and high pressure. At a high gas oil value, minimum coke production results in the optimum operating conditions. Selected results are presented on Table 10.

Table 10- Product yield for different temperatures.

		TEMPERATURES									
PRODUCT YIELD%		480	485	490	495	500	505	510	515	520	**525**
H2S	**GAS**	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06
Fuel Gas		.83	.97	.11	.25	.38	.5	.61	.71	.81	.9
C3 Paraffins	**COKE NAPTHA**	.83	.84	.87	.91	.94	.98		.03	.06	.08
C3 Olefins		.65	.66	.68	.69	.7	.71	.72	.73	.74	.75
C4 Paraffins		.04	.06	.09	.11	.13	.14	.16	.18	.19	.21
C4 Olefins		.67	.68	.69	.71	.72	.73	.74	.75	.76	.77
C5-350F		1.69	1.94	2.18	2.42	2.64	2.85	3.05	3.23	3.41	3.57
350-650F	**GAS OIL**	5.79	6.14	6.47	6.8	7.11	7.41	7.68	7.94	8.19	8.42
650+F		2.02	2.6	3.17	3.71	4.22	4.69	5.12	5.51	5.85	6.17
Coke	**COKE**	9.42	8.01	6.63	5.31	4.05	2.8	1.8	0.8	9.88	9.03

The results from the above simulations indicated that more liquid fractions are produced as the temperature increases and a lesser amount of coke is produced as the temperature increases. For the purpose of my research the temperature 480 C was chosen for its sufficient coke and gas oil yields.

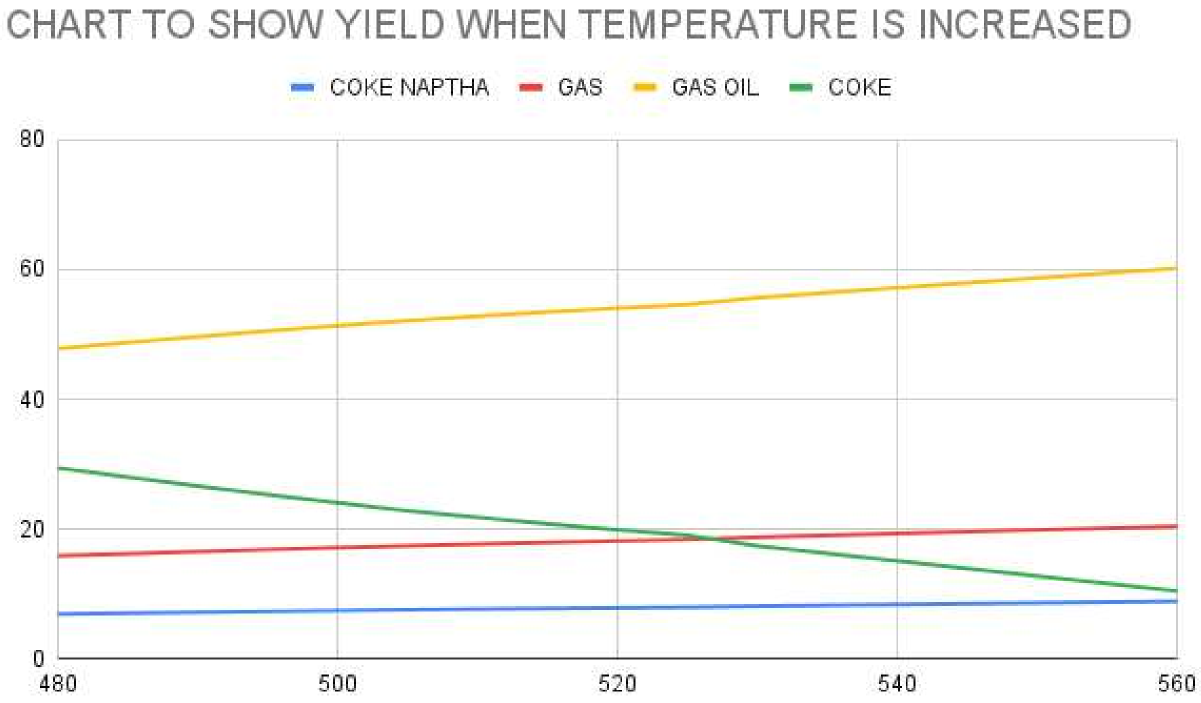


Figure 26- Delayed coking product yield during optimization simulations in Aspen

5.2.4 Light ends unit

The feed receives light ends from CDU and coker naphtha from delayed coking (see Figure 26) initially heated by heat exchanger, then gas separated by stabilizer. The bottom product separated to light naphtha and heavy naphtha by boiling point in the fractionator.

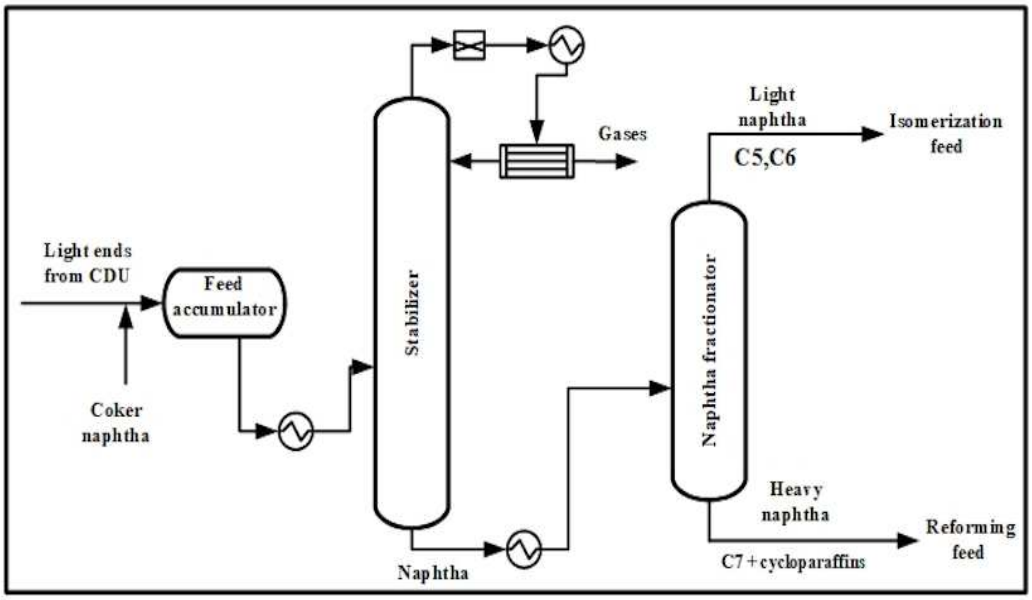


Figure 27 – A schematic flow diagram of a light ends unit

Table 11 – Material balance of the light ends unit

Feed and products		wt % on feedstock of process installation	wt % on crude oil	ton/day
Input	Light ends from crude (LN, HN, gas)	85.2	16.23	1309.31
	Coker naphtha 35 % LCN and 65 % HCN	14.8	2.82	350.46
Total	-	100	19.05	1,659.77
Output	Gases	2.68	0.51	44.43
	Light naphtha	31.93	6.08	529.73
	Heavy naphtha	65.39	12.46	1085.6
Total	-	100	19.05	1659.77

5.2.4 Isomerization Process

Straight run light naphtha obtained after distillation is the primary source of the selected Par-Isom$^{\text{TM}}$ process. Although the catalyst is solidly resistant to contamination such as to sulfur deactivation and water, the pretreatment of HDS (by

NiMo catalyst) is recommended for higher quality of isomerate and as an assurance for the smooth operation of isomerization [15].

Figure 27.depicts the pretreatment of C_5/C_6 and conversion of the desulfurized feedstocks into higher octane end-products of branched isomerates. The hydrogen sulfide as the HDS product outperformed at 99 % efficiency with 0.1 wt.% in total of the LN feed shown in Table 18. The unreacted hydrogen then is recycled with additional mark-up fresh H_2. Prior to the isomerization reactor, the existing iso-pentane in the desulfurized LN is extracted from the DIP tower and pumped to the isomerate mixing valve. On the other hand, the bottom of DIP (majority n-alkanes) is ejected to be isomerized [16].

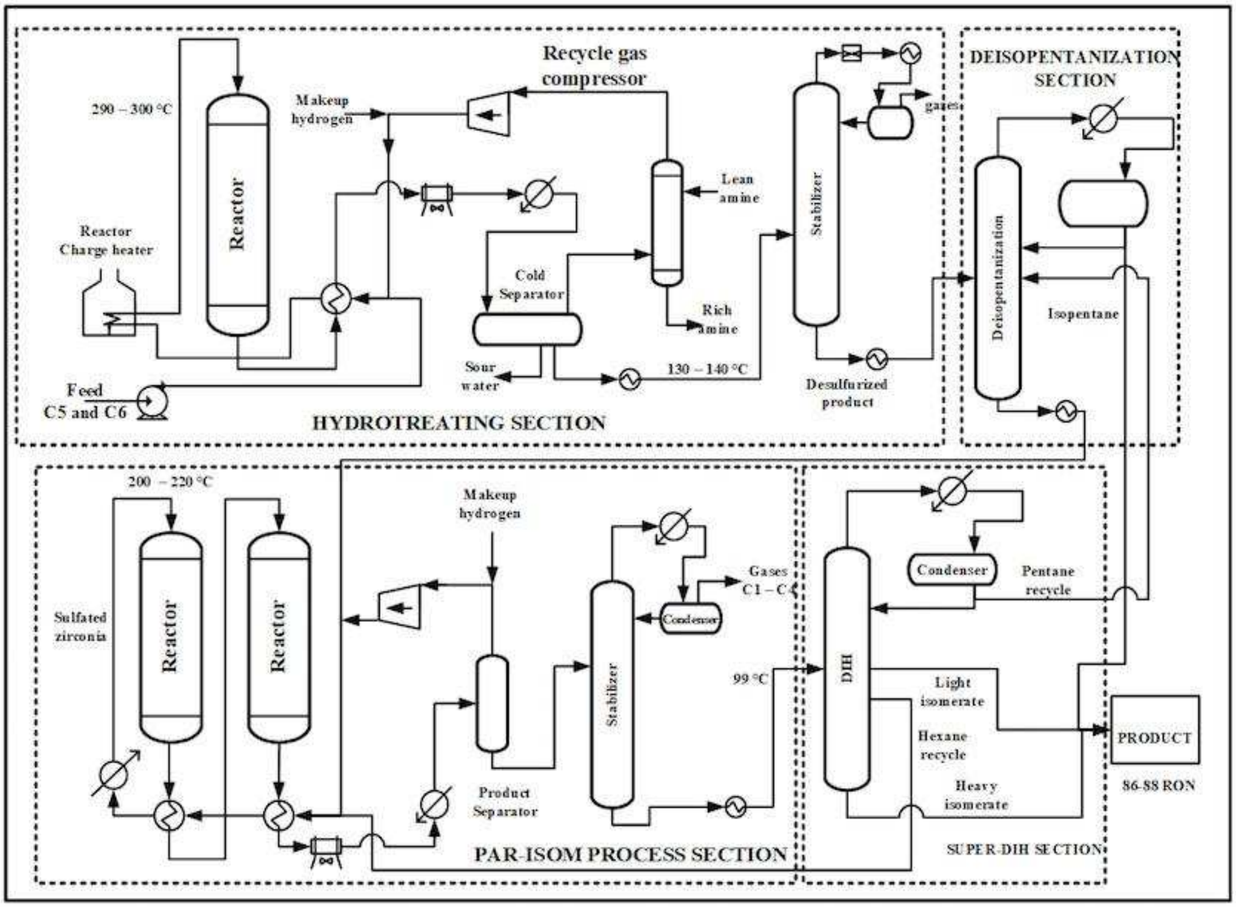


Figure 28 – A schematic flow diagram of an isomerization unit

Table 12 – Material balance of the isomerization pretreatment (HT) process

Feed and products		Weight per 101.5	Weight per 100	wt % on crude oil	ton/day
	Light naphtha	100	99.01	6.08	529.73
	Hydrogen	1	0.99	0.06	5.244
Total	-	101	100	6.02	524.49
Output	Desulfurized product	97.35		5.92	515.69
	Hydrogen sulphide	0.28		0.017	1.48
	gas	1.98		0.12	10.49
	Losses	0.39		0.024	2.07
Total	-	100		6.08	515.69

The desulfurized light naphtha is then passed to the heat exchanger and preheater before entering the two sets of reactors and the temperature rises gradually to 180 – 210 °C (activation temperature). The reactor pressure and liquid hourly space velocity are at 15 – 35 bar and 1.0 – 3.0 hr^{-1} respectively, though, the H_2/HC ratio at 1.0 – 2.0 in molar basis. Par-Isom™ is chosen based on several highlighted features in-hand to offer. Sulfated metal oxide catalyst with minor amount of platinum (Pt) is utilized by employing modified zirconia as acid site for modern variant of technology provides higher stability to contaminants in comparison with UOP Panex I-82 or conventional zeolite isomerization catalytic process [16]. The incorporated UOP PI-244 modified sulfated zirconia oxide is also superior in terms of octane number obtaining, up to 88 RON can be achieved by recycling of the unreacted n-alkanes, and operates in lower temperature of reaction in comparison with zeolites.

As an ideal choice of catalyst, PI-244 as well offers full performance with the benefit of eliminating the necessity of constructing a gas compressor loop, and slashes the injection of chloride for maintaining the activity of acid side and required caustic for neutralizing the products. Economically, UOP Par-Isom™ is more viable from a CAPEX perspective when set side by side with UOP Panex when DIH recycling technology is added. Lastly, modified zirconia PI-244 is able to be regenerated by simple oxidation and cheaper in comparison to zeolite catalyst regeneration [17].

Table 13 – Material balance of the isomerization process

Feed and products		Weight per 101.1	Weight per 100	wt % on crude oil	ton/day
Input	Desulfurized product	100	98.91	5.92	515.69
	Hydrogen	1.1	1.09	0.064	5.11
	Total	101.1	100	5.856	510.58
Output	Isopentane	67.06		3.93	342.39
	Isohexane	27.99		1.64	142.911
	gas	3.96		0.23	20.22
	Losses	0.99		0.058	5.055
Total	-	100		5.86	510.58

Initial readings indicate that 95.05 % of isomerate yield is achieved; it is measured in terms of iC_5/nC_5 and $2,2\text{-DMB}/nC_5$ ratios shown in Table 19. The gas amounting up to 3.96 % consisting of tail gas/ dry gas will be sent to the gas processing unit for further separations while 0.99 % of total feed loss is mainly affected by the formation of coke on the surface of the catalyst.

5.2.5 Reforming

The incoming heavy naphtha is received from SR HN plus extra recovered naphtha from delayed coking. The blended feeds are initially treated in HT process under NiMo catalyst to enhance the HDN and higher hydrogenation activity, the mechanism and operating condition is identical to the isomerization feed pretreatment process which operates under controlled cracking temperature ranging from 290 – 300 °C, which is sufficed to eliminate 99 % of the existing sulphur content in the feed. The hydrogen mass flow percentage is computed to be 1.1 wt.% of the feedstock sum of 101.1%. Tail gas and LPG are stripped off from the stabilizer, resulting in the remaining C_{7+} to proceed to the reforming reactors depicts in Figure 29.

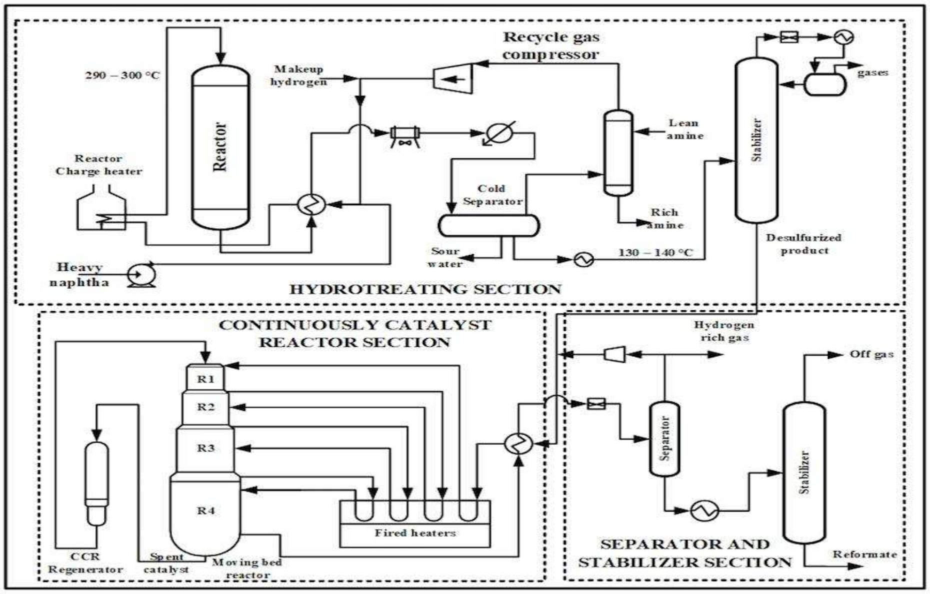


Figure 29 – A schematic flow diagram of a reforming unit

The UOP CCRRP (Continuous Catalytic Regeneration Reformer Process) with over 500 units installed around the world is decided to be employed in the process design referred to its numbers of quality trademark compare to semi-regenerative (SR) and cyclic (CR) process. Consisting 3 – 4 reactors in series with low operating pressure of 50 psig averagely and extreme reacting temperature of 515 – 528 °C, CCRRP capable of reaching optimum production RON at 95 – 108, 10 points higher than SR and 4 points than CR [18]. The catalyst system adopts the moving-bed type, where the system as well offers no obligation of shutdown during the operation for regenerating the catalyst due to being actively/continuously activated in the special regenerator by ordinary oxidation and hydrogen is generated non-stop at higher catalyst activity and yield. In addition, the amount of formed hydrogen is the highest among the three configurations.

Table 14 – Material balance of the reforming pretreatment (HT) process

Feed and products		Weight per 101.5	Weight per 100	wt % on crude oil	ton/day
	Heavy naphtha	100	98.91	13.32	827.67
	Hydrogen	1.1	1.09	0.14	9.01
Total	-	101.1	100	13.18	818.66
Output	Desulfurized product	97.39		12.83	797.3
	Hydrogen sulphide	0.29		0.05	2.37

	gas	1.93	0.25	15.8
	Losses	0.39	0.05	3.19
Total	-	100	13.18	818.66

Furthermore, in terms of catalyst selection, alumina oxides are widely known to offer highest support stability where the acid catalyst from different metals usually utilize Pt, Re, or Sn. Apparently, the modern research has found that trimetallic Pt-Re-Sn, where Pt as metal site with promoter of Re and additional Sn deposited on the support of γ-alumina (Al_2O_3) with constant/periodically induced acid (Cl) to maintain acidity level of the catalyst, along with presulfided impregnation, resulted as Sn-Pt-Re/Al2O3–Cl provides a perfect alternative for the highest acidity activity that promotes more isomerization eventuality. The proposed catalyst was also observed to have a higher resistance to coke deactivation and higher selectivity to aromatic and iso-paraffins, affected by the greater conversion of isomerization and cyclization in the acid side of the catalyst.

Table 15 – Material balance of the reforming process

Feed and products		wt % on feedstock of process installation	wt % on crude oil	ton/day
Input	Desulfurized product	100	13.18	818.66
Output	Reformate	85	10.91	695.86
	Off gas	9	1.15	73.68
	Hydrogen	5	0.64	40.93
	losses	1	0.13	8.19
Total	-	100	12.83	818.66

In comparison with conventional Pt/Al_2O_3 catalyst, the coke formation is decreased in addition to Re and Sn, as well as hydrogenolysis reaction is lowered in comparison to monometallic Pt/Al_2O_3. At 0.1% addition of Sn, table 2 shows that the stability and activity of the catalyst are increased in comparison to both Pt and Pt-Re catalyst. Although, addition of higher concentration of Sn would deteriorate the acid sides dispersion which means, lesser produced iso-paraffins occurrence. However, the addition of 0.1 Sn produces more aromatic compounds at a low benzene rate, but the i-C_7 and remaining isomerized products are boosted.

Additionally, the disruption caused by Sn and Re addition create dynamic behavior on the catalyst which affects a lower hydrogenolysis reaction to happen. On the other hand, to maintain the acidity, Cl injection is required. Although, It is important to point out that commercial Pt-Re/Al_2O_3 catalysts are normally pre sulfided in the commercial units at the start of the run because the catalyst has high initial hydrogenolysis activity that needs to be suppressed for proper operation and product quality [18]. If the catalyst is not passivated by this procedure at start-up, temperature runaways in the reactor can be expected to occur. The poor selectivity to aromatic and i-C7 isomers found for these catalysts is mainly due to the absence of presulfidation.

Hence, the reformate using 0.1 Sn embedded catalyst would give higher isomerized compounds (iC_6/iC_7) in the reformation in comparison with toluene as per cited. Though, there is recorded loss of 1 % accounted to coking from the total amount of desulfurized HN, while H_2 for 5 % and gases 9 % is computed consecutively as shown in Table 15.

5.2.6 Kerosene HT

The SR kerosene with boiling point ranging from 160 – 240 °C is recovered by distillation column under atmospheric pressure. The SR kerosene normally found contains a heteroatomic component of sulphur in the presence of mercaptans, benzothiophene, and alkylated benzothiophene. The tightening regulations standardized lower content below 3000 ppm in 2010, and the threshold is continuously lessened [13].

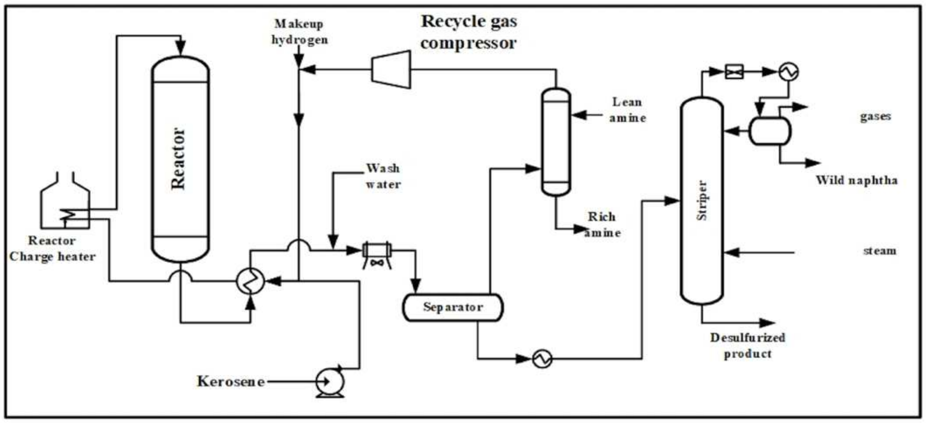


Figure 30 – A schematic flow diagram of a hydrotreating of kerosene unit

The initial amount of sulfur content that could be stated as sweet SR kerosene was determined at 307.331 ppm. Once-through HT process as Figure 39. Illustrates is capable of eliminating 97 – 99 % of sulfur under operating pressure of 15 – 30 bar and reactor temperature of 300 – 340 °C. LHSV of 2 – 4 hr^{-1} is regularly applied using hydrogen feed to HC ratio of 36 – 48 std m^3/m^3. Co-Mo-S/alumina catalyst is preferred over Ni-Mo-S because the need of HDS is more than HDN and aromatic saturation. Therefore, as the most economic catalyst for HDS, Co-Mo-S is able to remove the sulphur content to the designated number by consuming a lesser amount of hydrogen in comparison with Ni-Mo or Ni-W.

Table 16 – Material balance of the SR kerosene hydro treatment (HT) process

Feed and products		Weight per 101.7	Weight per 100	wt % on crude oil	ton/day
Input	Kerosene	100	98.33	9.69	796.44
	Hydrogen	1.7	1.67	0.16	13.17
Total	-	101.7	100	9.53	783.27
Output	Desulfurized product	96.05		9.15	752.33
	Wild naphtha	1.37		0.13	10.73
	Hydrogen sulphide	0.32		0.03	2.51
	gas	1.87		0.18	14.65
	Losses	0.39		0.04	3.05
Total	-	100		9.53	783.27

Moreover, the computed details achieved (Table 16) using 1.2 wt.% of hydrogen as input resulted in 96.05 desulfurized kerosene with overall sulfur content less than 15 ppm.

5.2.7 HT gas oil

The current trend of ULSD (Ultra-low Sulfur Diesel) around the refining industry required by the EPA has pushed the HT efficiency to reach the utmost potential by above 97 % of HDS recap with the outcome of lower than 15 ppm sulfur weight percentage. The origin of the obtained crude oil has a particular advantage in which the carried-off sulfur to the SR diesel down to approximately 480.687 ppm found during the crude assay analysis.

Hence, the focus can be switched towards the cetane number (CN) improving process in the selected design as depicted in Figure 30. above. To satisfy that purpose, Ni-Mo-S/alumina catalyst is favored with its higher saturation activity than Co-Mo type, hence, the CN uplifts. Based on the literature, Ni-Mo catalyst covers two-times folded of the CN uplift in comparison to Co-Mo or smart catalysts.

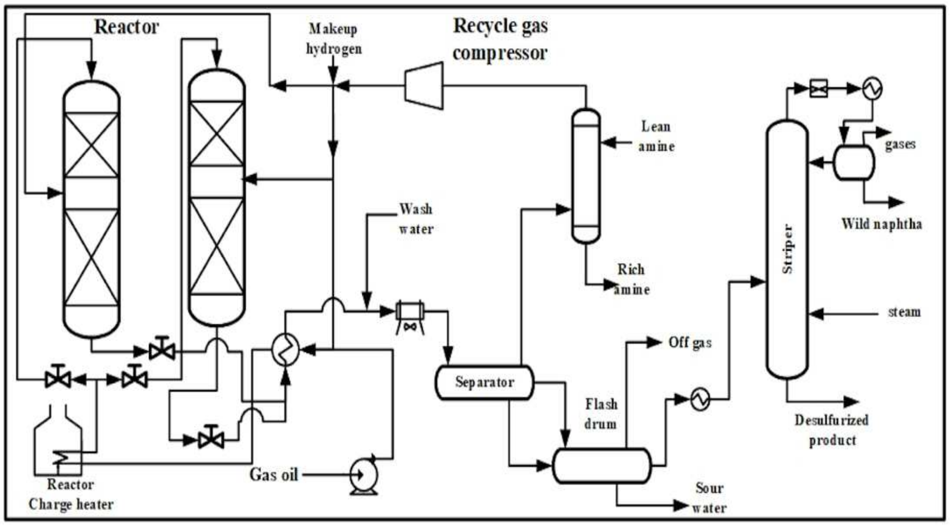


Figure 31 – A schematic flow diagram of a hydrotreating of gas oil/diesel unit

Typically, mercaptans, benzothiophene (BT), alkylated benzothiophene, and dibenzothiophene presented in gas/diesel oil can be readily desulfurized by both types of common catalyst [13]. Therefore, the concentration of paraffinic compounds which can be enhanced when the PAN formation is reduced is stimulated by the proper selection of catalyst (in this case Ni-Mo type).

Table 17– Material balance of the SR gas oil hydro treatment (HT) process

Feed and products		Weight per 101.7	Weight per 100	wt % on crude oil	ton/day
Input	Diesel oil/ Gas oil	100	98.33	22.41	1,841.91
	Hydrogen	101.7	1.67	0.37	30.76
Total	-	100	100	22.04	1,811.15
Output	Desulfurized product	95.48		21.04	1729.29
	Wild naphtha	1.36		0.3	24.63
	Hydrogen sulphide	0.51		0.11	9.24

	gas	2.26	0.5	40.93
	Losses	0.39	0.09	7.06
Total	-	100	22.04	1,811.15

The sketched design is also done under consideration of the unique surrounding condition of Russia, which has a freezing winter and summer. Consequently, two modes of reactors are required to be commissioned to satisfy the demand of winter-diesel with lower pour point and gel point to lower than – 10 °C CFPP (cold filter plugging point) min. The operating condition designated is 15 – 40 bar and reactor temperature of 320 – 350 °C. LHSV of 1 – 3 hr^{-1} is regularly applied using hydrogen feed to HC ratio of 36 – 48 std m^3/m3.Hydrogen is injected in two sections, the middle column injection as quenching for controlling the cracking and coking generations. Organic peroxide can be used to improve CN, while anti-gel additives are employed for winter diesel. Though, the computed output of HT desulfurized diesel to the storage tank can only reach 95.48 wt.%, it is affected by the produced gaseous fractions at 2.26 wt.%. The desulfurized product (17.07 wt.%) was sent to storage with the fuel oil product (220 – 350 ^{0}C)

5.2.8 Saturated gas process

The collected gaseous fractions of both condensable and non-condensable gases from various sources such as CDU, VDU, reforming, and isomerization accommodate mostly saturated/alkane groups. The separation of those gases to magnify the producibility of the refinery is vital. Hence, 4 chain splitter columns are engaged as an improved process integration (illustrates in Figure 32) in the process to mainly recover the i-butane as main precursor on alkylation, n-butane as additional feed to gasoline mixing pool, and non-condensable gas for heating source of refinery furnaces, while propane serves as end-product of LPG.

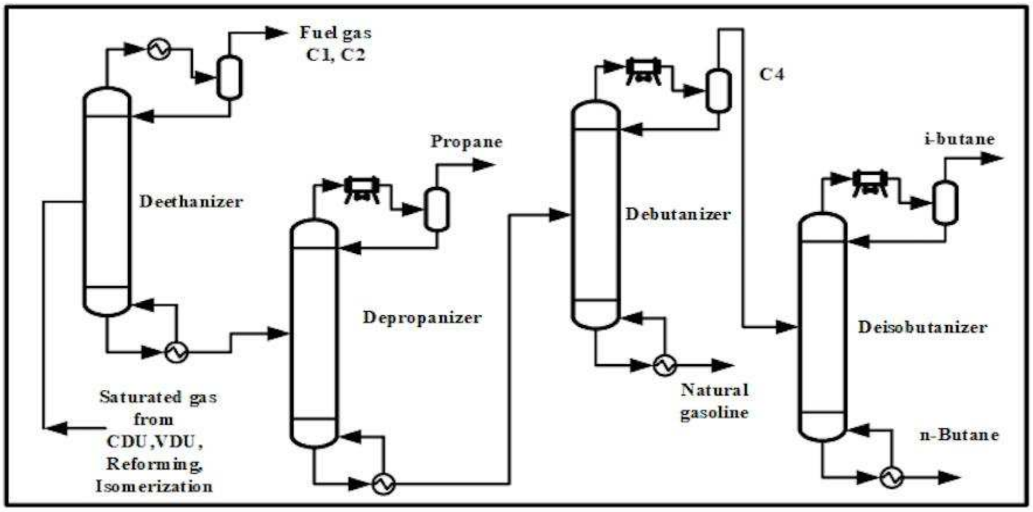


Figure 32 – A schematic flow diagram of a saturated gas process unit

HP separator column with devoted pressure of 31 – 33 bar is used for the deethanizer with typical number of trays of 25 – 35 and the feed stage slightly above the center of the column can achieve up to 70 % efficiency without reflux. The depropanizer using lower pressure of 17.50 bar with more trays of 35 – 40 holds efficiency of 90 % without reflux. Debutanizer and deisobutanizer employing LP separator operate at 5 and 6.50 bars with 38 – 45 and 85 – 95 trays respectively and may offer 90 % separation efficiency in the absence of reflux for both splitters.

Table 18 – Material balance of saturated gas process

Feed and products		wt % on feedstock of process installation	wt % on crude oil	ton/day
Input	Gases from CDU	36.31	0.57	46.85
	Gases from VDU	9.55	0.15	12.7045
	Gases from reforming	45.86	0.64	20.87
	Gases from isomerization	8.28	0.12	10.49
	Total	100	1.48	90.91
Output	Gases (C1,C2)	6.5	0.096	5.91
	Propane	21.6	0.32	19.63
	i-butane	16.1	0.24	14.63
	n-butane	33	0.49	30
	C5 and more	21.4	0.32	19.45

	Losses	1.4	0.021	1.27
Total	-	100	1.48	90.89

By the literature citations, it is computed the individual components of HC as shown in Table 18. 16.1 wt. % of iC_4 totaling 90.88 tones/day as the feedstock of alkylation will be reacted with captured olefins. And C_{5+} might be either induced to the isomerization process or straight to the gasoline mixing pool.

5.2.9 Unsaturated gas process

Unlike the previous mix of bulk saturated gas streams, the gases from FCC and delayed coking compromised high amounts of olefins aftermath of the dehydrogenation reactions also the operating condition effect of both processes and FCC's catalyst thermodynamic behavior.

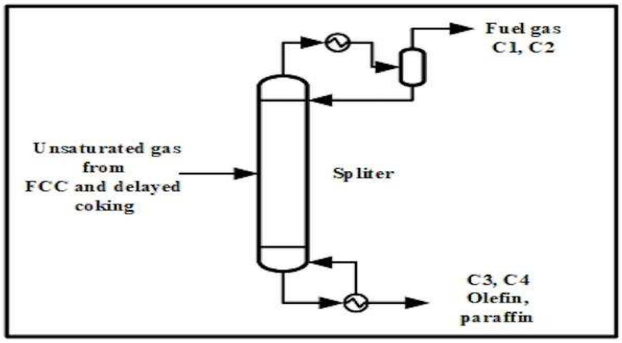


Figure 33 – A schematic flow diagram of an unsaturated gas process unit

The splitter with average number of stages from 35 – 40 consisting of a reboiler and condenser to increase the stream purity has the feed stage appropriately at 27th stage from the bottom of the column. The reflux ratio to obtain as high as 99% isolation of targeted compounds is regularly ranging from 0.4 – 0.5 L/F with partial condensation type.

Table 19 – Material balance of unsaturated gas process

Feed and products		wt % on feedstock of process installation	wt % on crude oil	ton/day
Input	Gases from delayed coking	100	1.42	117.14
	Total	100	1.42	117.14
Output	Gases (C1,C2)	33.5	0.48	39.24
	C3,C4 (paraffin, olefin)	63.5	0.9	74.38
	Losses	3	0.0426	3.5142
Total	-	100	1.422	117.13

The overhead of tail/dry gas is used similarly to support the refinery utility as fuel gas by adding more than 1,300 ton/day to the system. The separated rich olefinic gases of C_3 and C_4 accounting 63.5 % which equal to 2,557.41 ton/day are applied as the secondary feed to alkylation along with isobutane fractions. This method is incorporated to suffice the sum of feed required to perform the alkylation in the plant.

5.2.10 Alkylation

An auxiliary unit which can be parted in the refinery system which is able to convert low-boiling point fractions such as C_3 & C_4 gases into high octane number of gasolines. The produced gasoline is highly branched paraffinic (isoheptane and isooctane) which is favorable to balance the aromaticity and to reduce the required amount of oxygenates (MTBE, ETBE) as octane improver during blending stage. Some refineries strongly consider during the master-plan design stage over alkylation adaptation as a formidable alternative, however, the decision mostly depending on the number of produced olefins and characteristics of the feedstock in term of the composition of the embedded iso-butane in nature of the crude itself.

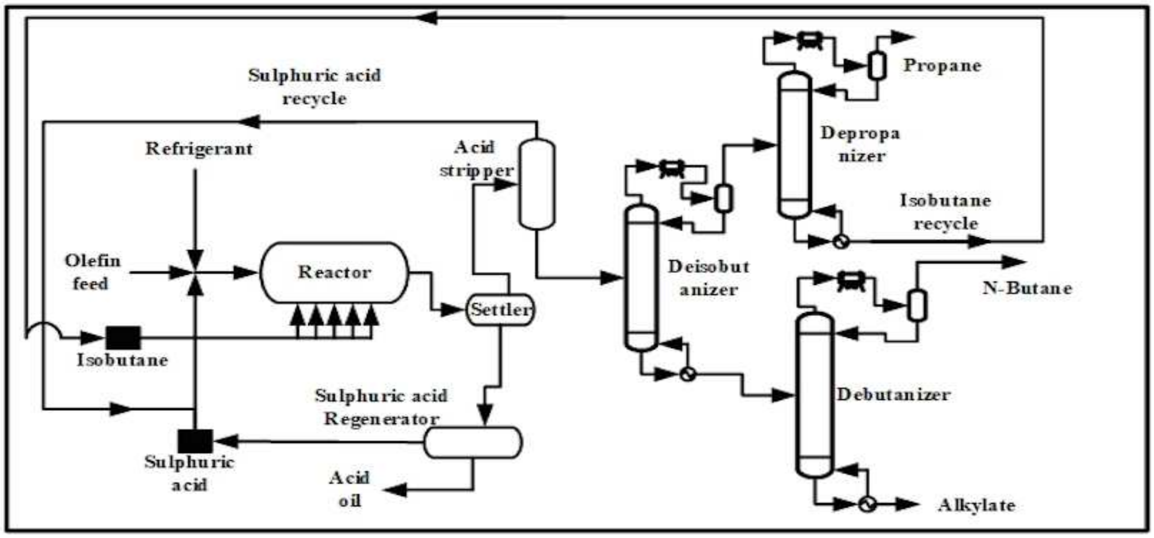


Figure 34 – A schematic flow diagram of an alkylation unit

The premium gasoline blending stock (alkylate) with low Reid vapor pressure, clean burning, and have high antiknock effect is produced over two options to be picked, SAAU (sulphuric acid) HFAU (hydrofluoric acid) units [50]. The acid homogeneous catalyst acts as action formation-arrangement agent in the process before pairing and chain termination process mechanism. The process operating condition for maximum yield of alkylate and conversion percentage is below 90 °C with reactor pressure from 15 – 20 bar, and isobutane/olefin ratio of 10 – 15, along with olefins space velocity of 0.2 – 0.5 hr^{-1}. The catalyst of H_2SO_4 offers higher octane rating of product and higher activity on alkylation reaction, as well as it is less hazardous than HF to humans, however, the regeneration of this catalyst required 6 – 18 hours.

Table 20 – Material balance of alkylation process

Feed and products		Weight per 101.5	Weight per 100	wt % on crude oil	ton/day
Input	C3,C4 (paraffin, olefin)	100	71.43	0.9	74.38
	I-Butane	40	28.57	0.24	14.63
Total	-	140	100	1.14	89.01
Output	Propane	2.9		0.03	2.58
	N-Butane	16.9		0.19	15.04
	Alkylate	80.2		0.92	71.39
Total	-	100		1.14	89.01

The scavenged isobutane and olefins was done by gathering the potential stream and employing a splitter tower in the segregation process. 40 wt.% of highly purity of iC_4 feed is reacted with 100 wt.% of unseparated C_3 & C_4 which still mostly contain higher alkane compounds of propane and butane instead. Hence, the predicted produced alkylate exhibits the percentage of 80.2 %, amounting with the daily average output of 2,871 ton for additional exclusive gasoline feedstock for mixing. The alkane constituted in the C_3 & C_4 streams are not overcoming the reaction process under the devoted operating condition, hence, they are sent as striped gases in fractionators.

5.2.11 Claus Sulphur recovery unit (SRU)

SRU is one of the crucial units to represent the Sulphur management process in petroleum refineries apart from the used amine treating process (ATP). By Claus elemental Sulphur recovery mechanism, up to 99 % of elemental Sulphur can be yielded by integrating tail gas clean-up unit (TGCU) using an inlet containing high (above 50 %) of H_2S. The entire process is straight-forward by employing an HP furnace reactor and a series of catalytic reactors and condensers. SRU involves at least two-steps of reaction of partial oxidation of H_2S to SO_2 and elemental Sulphur from SO_2 reacts with H_2S [19].

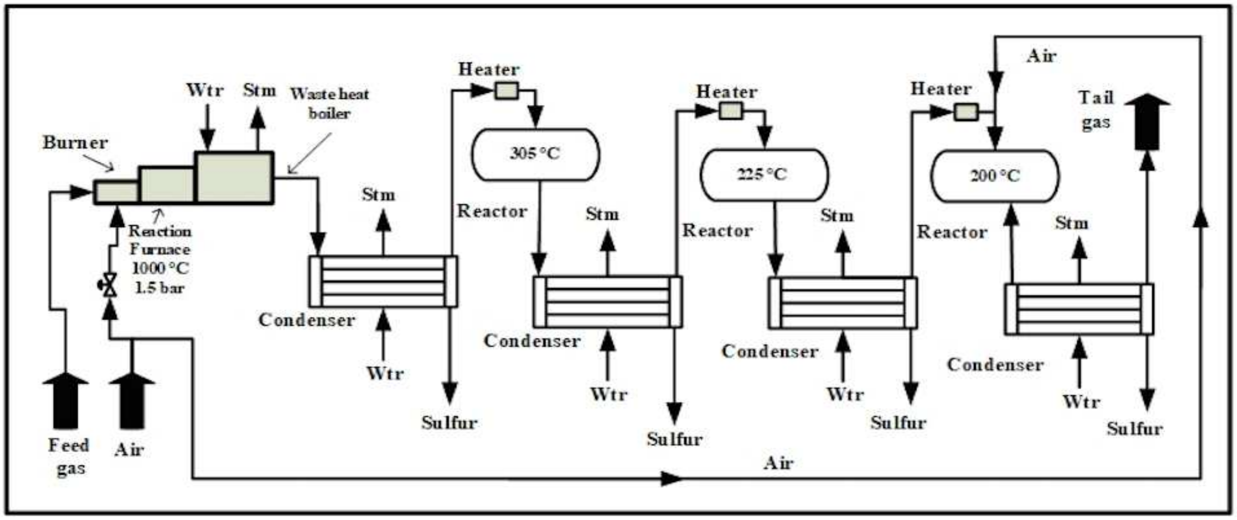


Figure 35 – A schematic flow diagram of a Claus sulfur recovery unit

The first stage of the process converts H_2S to Sulphur dioxide and to Sulphur by burning the acid gas stream with air in the reaction furnace above 850 °C (1000 °C selected at slightly above P_{atm}). This provides SO_2 for the next phase of the reaction. The tail gas outlet is cooled in a condenser before being discharged to the incinerator. The common range of the SO_2 in the tail gas is usually around 10,000 – 30,000 ppm. The first reactor with above 300 °C, here, 60 – 65 % of S produced, followed by 25 – 30 % for the second reactor, and 5 – 8 % for the last reactor operating at cooler conditions of 200 °C. The efficiency is merely depending on the environmental perspective for the applied process.

Table 21 – Material balance of Claus sulfur recovery

Feed and products		wt % on feedstock of process installation	wt % on crude oil	ton/day
Input	Hydrogen sulphide	100	0.74	32.57
Output	Sulphur	95.4	0.71	31.07
	Tail gas	4.6	0.03	1.5
Total	-	100	0.74	32.57

According to Gary, the recovery system has more than 94 % efficiency [23], resulting in more than 30 ton/day of elemental Sulphur being produced. The elemental Sulphur can be palletized or granule formed which is usually used in commercial production of sulphuric acid for sulphate in fertilizer or other chemical industries.

5.2.12 Coke Analysis

The quantitative assessment of coke morphology based on the Raman spectroscopic characterization indicated that the coke from the sample was a transition-type coke. This is good because such coke can be used for anode production which is highly useful in the aluminum industry [26&30].

Table 22- Absorption and wave numbers of coke from sample

Wave number	Absorption
1349,483	43,8419
1587,855	33,02392
542,6357	5,6436
813,3075	1,9387
2547,804	3,58767
3354,651	4,17069
1976,744	3,62894
1534,884	27,45166
1281,654	32,06505

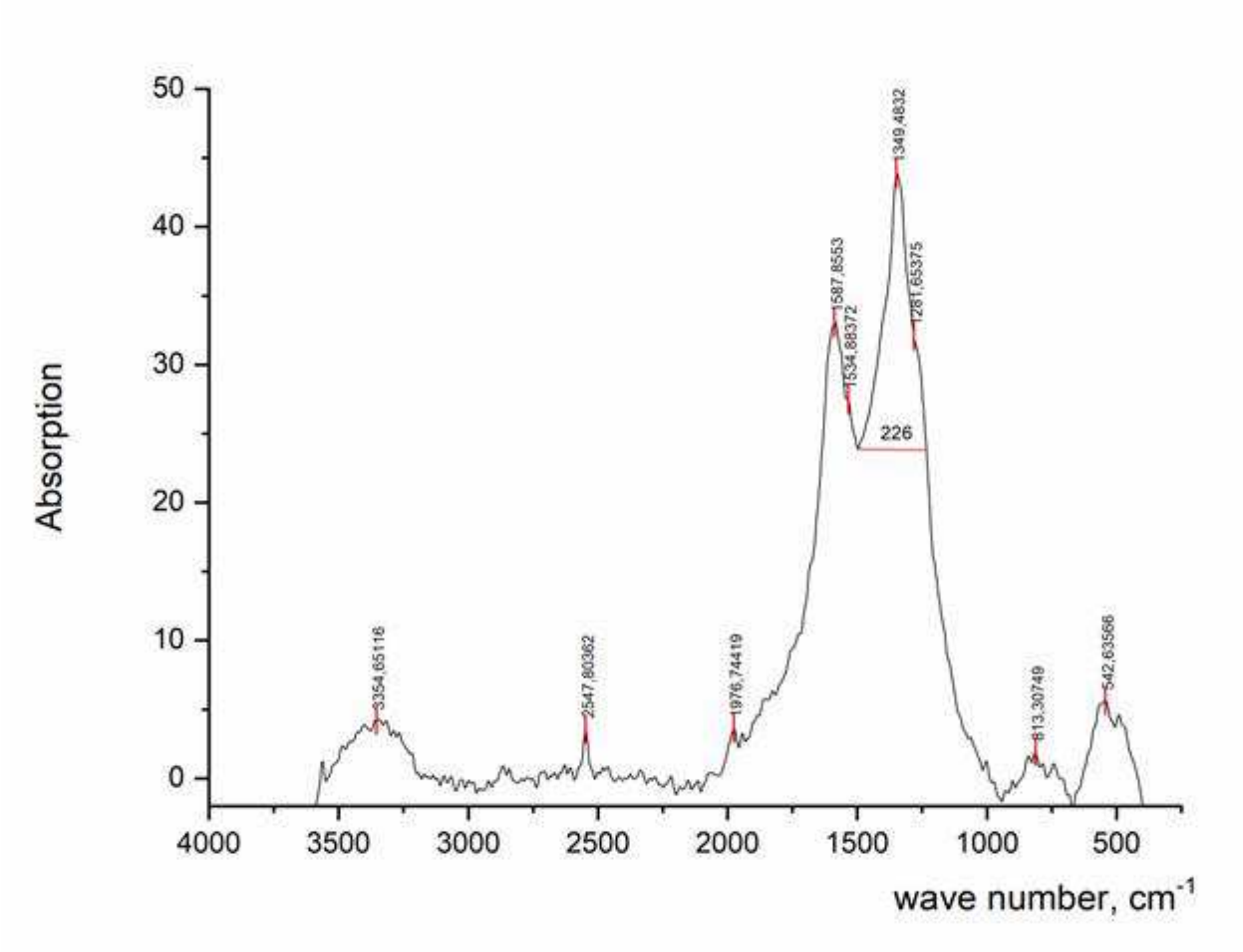


Figure 36-Fitted curves for the first-order Raman spectrum of coke.

5.3. Refinery Block Diagram

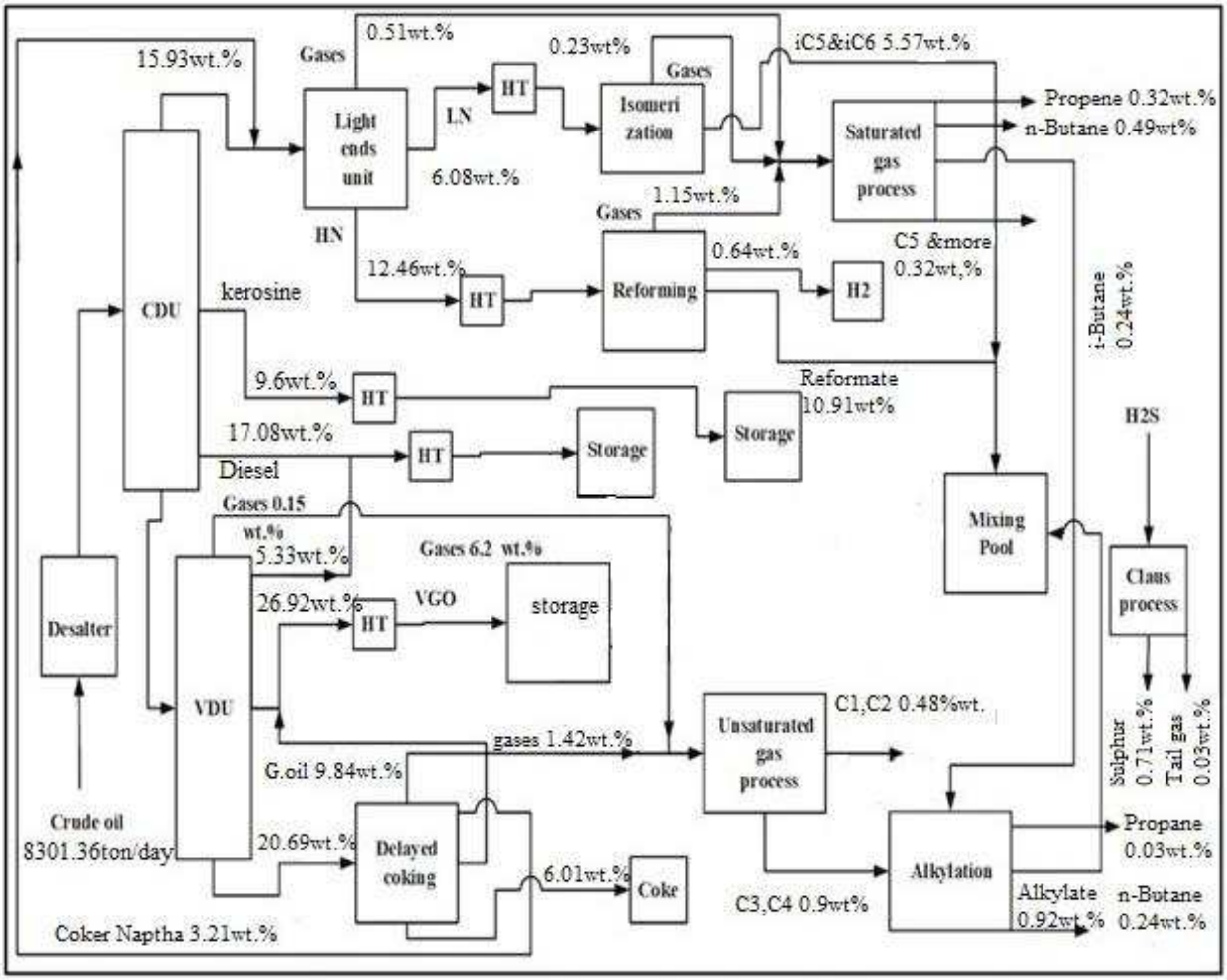


Figure 37 - A block diagram to show refinery layout

CONCLUSION

At the end of the research and experimental simulations of unknown crude oil from the Vankor field, major refinery processes and coke analysis were successfully performed and brought to a closure. However, there are many areas that can be further investigated such as TBP analysis of assay which is a detailed evaluation procedure. Also, catalytic cracking processes should also be explored to increase the potential of light fractions from sample. Major feedstock analysis of the crude including atmospheric distillation to measure specific product yield, distillation under vacuum, gas chromatography (GC), chemical properties examination under fluorescent indicator adsorption (FIA), the percent of sulfur, and modeling delay coking using a software (Aspen Hysys). Also, the coke produced from the laboratory experiment was sent for further analysis and using RS analysis, the type and quality of coke from the sample was determined.

Atmospheric distillation yielded about 27% kerosene and diesel with about 53% residue and this confirm the high Conradson carbon of 21wt.% and from the bottom VR which amounted to 26.92 %, however, the recuperation of upgraded value material can further press down the coke produced to be lesser, 6 % and even lower from the overall incoming feed of crude. Additional contribution of catalytic and thermal upgrading, namely coking, reforming, isomerization and alkylation, contribute as minimum as 812 ton/day of coker gas oil and 3.21 wt. % recovered naphtha.

On the other hand, more preferred isomerate paid off the conceptual design with expected of gaining close to 5.89 % of iso-alkane under Par-Isom. However, the selected trimetallic catalyst with small deposited Sn increases the ratio of reacted heavy naphtha towards branched paraffinic compounds in reforming reactors. The sulfur content was determined to be 0.72 wt. %, it indicates the crude has the potential to produce coke and further analysis of coke supported this analogy. Even though the initial sulfur has a very low tendency to degrade the catalyst as if it is sour, accumulation of sulfur in form of H_2S in gaseous fraction especially coming from the residual process strongly being suggested on being treated under adequately higher severity in compare with HT for SR middle distillate and naphtha. Low viscosity found in comparison with light Siberian crude, with magnitude of 5.37 mm^2/s at 20 °C provides lesser dependence of energy to pump the crude into the CDU, for instance.

The conclusion can be drawn based on 0.920 g/cm^3 of crude density at 20 °C that is strongly categorized as heavy crude with a potential to produce anode coke on commercial bases. Coke was tested via the Raman Spectroscopy analysis, the morphological and liquid crystal structure (also termed as mesophase) indicated the that coke produced was a transitional-type which can be used to produce anode coke for commercial purposes. The production of coke was optimized by variation of parameters such as temperature so that high temperature favors production of more liquids and smaller coke and vice versa.

LIST OF ABBREVIATIONS

Abbreviation	Detail description
API	American petroleum institute
ASTM	American Society for Testing and Materials
LP	Linear programming
GC	Gas chromatography
MS	Mass spectrometry
ICP	Inductively coupled plasma
AES	Atomic emission spectrometry
PAH	Polynuclear aromatic hydrocarbons
LVGO	Light vacuum gas oil
MVGO	Medium vacuum gas oil
HVGO	Heavy vacuum gas oil
IBP	Initial boiling point
EP	Final boiling point, or endpoint
HDS	Hydrodesulfurization
MTBE	Methyl tert-butyl ether
TAME	Tert-amyl methyl ether
ISO	International organization of standardization
LPG	Liquefied petroleum gas
VDU	Vacuum distillation unit
CDU	Crude distillation unit
SDA	Solvent deasphalting
DAO	Produces deasphalted oil
CLO	Clarified oil
FIA	Fluorescent indicator adsorption
IPA	Isopropyl Alcohol
FBP	Final boiling point
BP	Boiling point
VR	Vacuum residue
EDXRF	Energy dispersive X-ray fluorescence
LHSV	Liquid hourly space velocity
SG	Specific gravity
LSC	Light Siberian Crude
HPLC	High performance liquid chromatography
HT	Hydro-treating
PEG	Polyethylene glycol
SR	Straight run
AR	Atmospheric residue

CDE	Conradson Decarbonizing Efficiency
FCC	Fluid catalyst cracking
PNA	Polynuclear aromatic
UOP	Universal oil product
HN	Heavy naphtha
LN	Light naphtha
CCRRP	Continuous Catalytic Regeneration Reformer Process
RON	Research octane number
RS	Raman Spectroscopy
ULSD	Ultra-low Sulfur Diesel
CN	Cetane number
BT	Benzothiophene
HC	Hydrocracking
ETBE	Ethyl tert-butyl ether
HFAU	Hydrofluoric acid units
SRU	Sulphuric recovery unit
ATP	Amine treating process
TGCU	Tail gas clean-up unit
VOL.	Volume
WT.	Weight
XRD	X-rays Dominated Regions

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MASTER'S THESIS

Project of East Siberian Crude Oil Processing Equipped With Delayed Coking Unit

04.04.01 Chemistry

04.04.01.05 Petroleum Chemistry and Refining

Research supervisor	Candidate of Chemical Sciences, Associate Professor	Vladimir Safin
Graduate		Nuamah A. Charles

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