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Processing of Mongolian Heavy Oil Residue and Oil Sand

Bachelor Thesis

by

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Ulaanbatar, May 16, 2021

Statutory Declaration

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I hereby affirm in lieu of an oath that I provided the submitted bachelor thesis

Processing of Mongolian Heavy Oil Residue and Oil Sand

I did not use any sources other than those stated. In case that the work is additionally submitted on a data medium, I declare that the written and the electronic form are completely identical. The work was not submitted in the same or similar form to any examination authority.

Ulaanbaatar, 16.05.2022 — Place, Date

Signature

Acknowledgment

I would like to express my deepest appreciation to prof. Dr. -Ing. Manfred Hampe for supervising and guiding me. His invaluable advice has been a great experience.

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Special thanks to my family for providing for my needs and supporting me every day.

Abstract

This thesis work aims to study the characteristics of crude oil from Tamsag-Bulag Block-19 and oil sand from the Bayan-Erkhet deposit. Besides characteristics, cracking of atmospheric residue and pyrolysis of bitumen processing has been focused on.

The water content, density, viscosity, flashpoint, pour point, and content of hydrocarbon tests are performed according to ASTM standards on crude oil and >350°C residue. To determine the hydrocarbon content, the SARA method is carried out. Atmospheric and vacuum distillation were performed in laboratory conditions. Thermal cracking and catalytic hydro-cracking are performed on >350°C residue and distilled in Glass Tube Oven and fractionated light, medium, and heavy fractions. For catalytic hydro-cracking, 1 wt.% Ni-Mo/Al_2O_3 catalyst and 5MPa hydrogen gas are filled in the reactor with the sample.

The sand oil from the Bayan-Erkhet deposit is tested. Bitumen is separated from the sand by chloroform as solvent and evaporated. Almost 7 kilograms of bitumen is separated from 5 kilograms of sand oil. The yield of bitumen is 14.8%. The penetration of the needle, softening point, ductility, flashpoint, pour point and the SARA analysis are tested on bitumen.

Pyrolysis is tested on raw sand oil. Heated up to 600°C. Formed gas was directly condensed and collected in the flask. Due to loads of gas formation and short condenser, few amounts of gas are lost between 400-550°C. The test is carried out until there is no droplet from the condenser. Pyrolyzed product is distilled into light, medium, and heavy fractions.

The yield of light and medium fractions of an overall distillation of crude oil including cracking and distillation of pyrolysis is compared. A medium fraction and the light fraction from pyrolysis were the highest. To get the fractions, the bitumen is only pyrolyzed and distilled but crude oil is distilled, cracked the >350°C residue, and then distilled.

From the result, the sand oil of the Bayan-Erkhet deposit in Mongolia has the potential to supply the demand for petroleum products when the scarcity of crude oil increases.

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1 Introduction

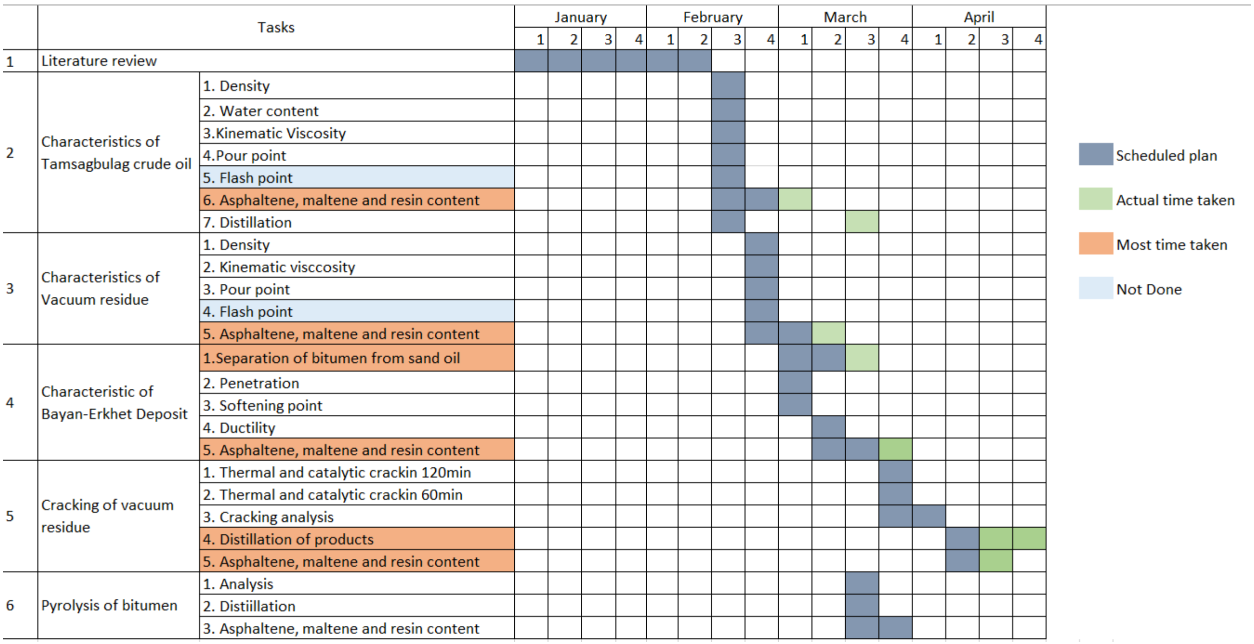
The goal of this thesis work is to decrease the percentage of inefficient heavy residue and to increase the amount of an outcome by processing the heavy residue with thermal and catalytic hydrocracking. Additionally, bitumen from the sand oil has the potential to yield a gas oil by heat treatment to break down the long chain.

The crude oil sample was taken from the Tamsagbulag XIX block and the sand oil sample is from the Bayan-Erkhet deposit. Tamsagbulag XIX block is located in Matad soum, Dornod province, Mongolia. Bayan-Erkhet sand oil deposit is located in Bayanjargalan soum, Tuw province.

The research questions are:

1. What are the characteristics of Tamsagbulag crude oil and Bayan-Erkhet sand oil?
2. How to process the heavy residue and bitumen?
3. Is sand oil able to substitute crude oil in the future in Mongolia?

This thesis work has 2 experiment objects which took 3 months to finish. During the experiments, I have learned new methods and skills. However, there were a man and equipment errors to fail some experiments which delayed the work schedule. The thesis work schedule is shown in Table 1.



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1	Literature review		🟦	🟦	🟦	🟦	🟦	🟦										
2	Characteristics of Tamsagbulag crude oil	1. Density							🟦									
		2. Water content							🟦									
		3.Kinematic Viscosity							🟦									
		4.Pour point							🟦									
		⬜ 5. Flash point							🟦									
		🟧 6. Asphaltene, maltene and resin content							🟦	🟦	🟩							
		7. Distillation							🟦				🟩					
3	Characteristics of Vacuum residue	1. Density								🟦								
		2. Kinematic visccosity								🟦								
		3. Pour point								🟦								
		⬜ 4. Flash point								🟦								
		🟧 5. Asphaltene, maltene and resin content								🟦	🟦	🟩						
4	Characteristic of Bayan-Erkhet Deposit	🟧 1.Separation of bitumen from sand oil									🟦	🟦	🟩					
		2. Penetration									🟦							
		3. Softening point									🟦							
		4. Ductility										🟦						
		🟧 5. Asphaltene, maltene and resin content										🟦	🟦	🟩				
5	Cracking of vacuum residue	1. Thermal and catalytic crackin 120min												🟦				
		2. Thermal and catalytic crackin 60min												🟦				
		3. Cracking analysis												🟦	🟦			
		🟧 4. Distillation of products														🟦	🟩	🟩
		🟧 5. Asphaltene, maltene and resin content														🟦	🟩	
6	Pyrolysis of bitumen	1. Analysis											🟦					
		2. Distiillation											🟦					
		3. Asphaltene, maltene and resin content											🟦	🟦				

🟦 Scheduled plan
🟩 Actual time taken
🟧 Most time taken
⬜ Not Done

Table 1 Planned schedule of experiments

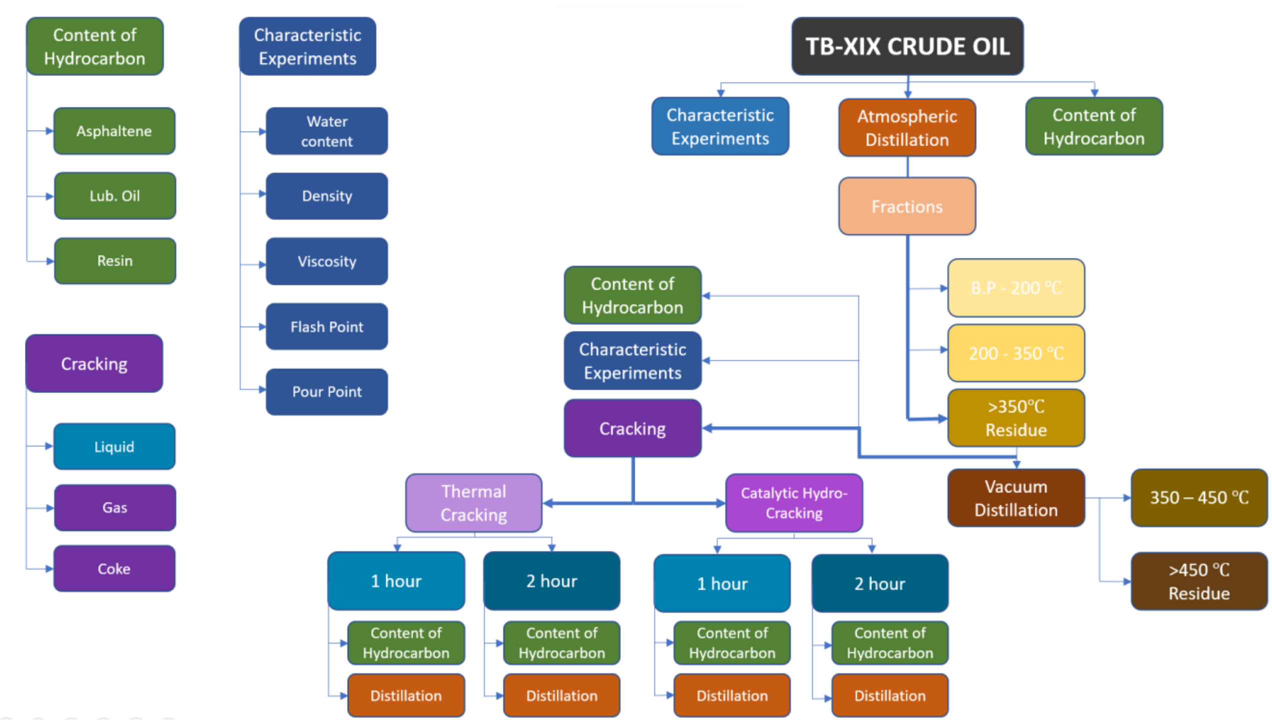


Figure 1Experiments on Crude Oil

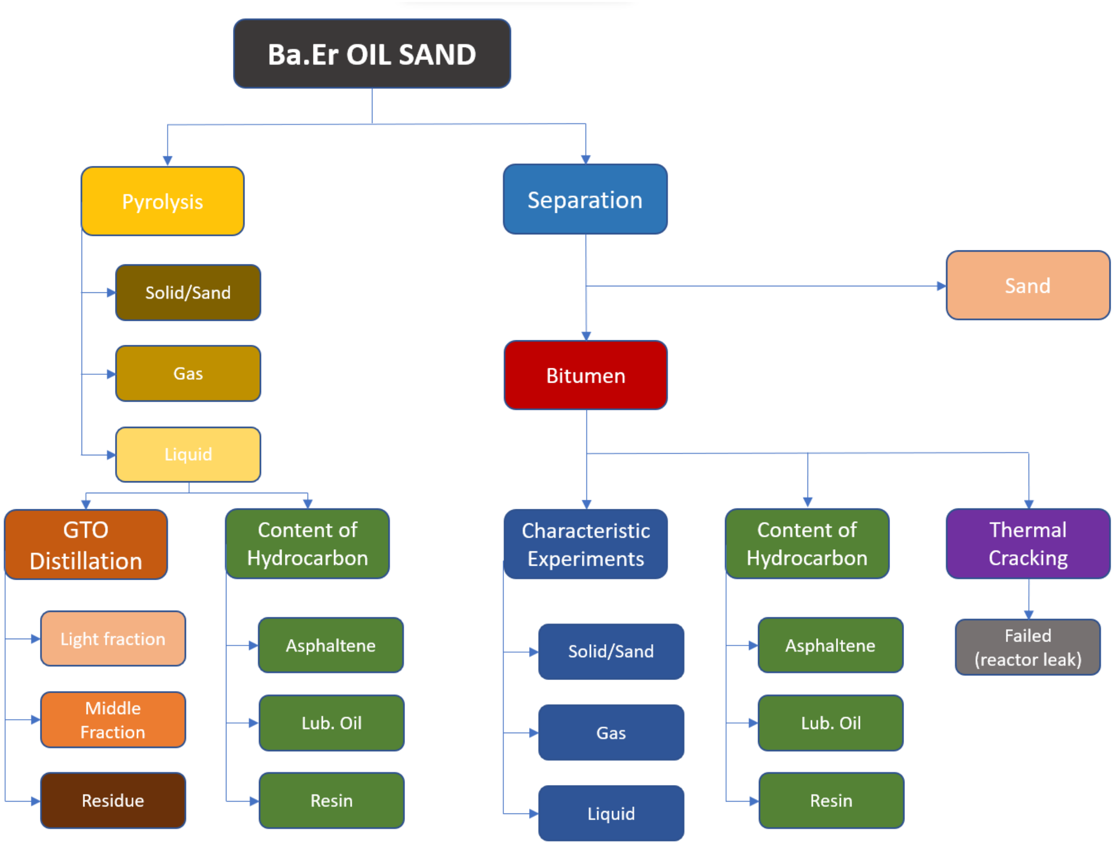


Figure 2 Experiments on Sand Oil

1.1 Mongolian Crude Oil

Besides metals and minerals, Mongolia has an abundant reserve of crude oil and oil sand. Even so, our country is 100 percent dependent of import oil products. Between 1950 and 1964, our country had an oil refinery but it was shut down due to political issues. However, exploration and production of oil has started in 1998. Since then 33 blocks have been explored and only 3 blocks are advanced in production. Between 2003 and 2019, approximately 65 million barrels of crude oil has been produced and imported from these 3 blocks. The proven reserve of these 3 blocks is 320 million barrels. (1)

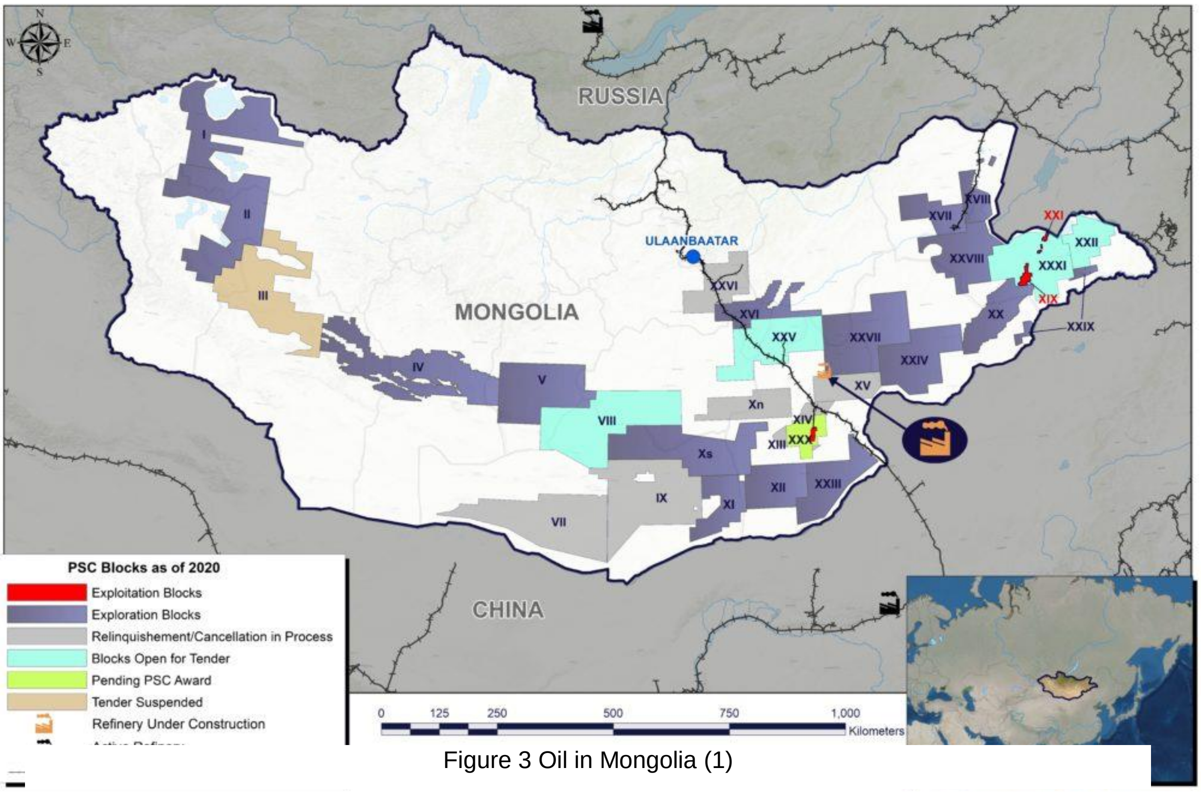


Figure 3 Oil in Mongolia (1)

Currently, a new oil refinery is being built at Dornogovi aimag, Altanshiree soum. With the collaboration of the Indian government, Mongolia got the possibility to process and refine its own crude oil. The refinery has a capacity of processing 1.5 million tons of oil annually. This project gives advantage to stabilize the import-dependent sensitive price of oil products in Mongolia. Also, it has an opportunity for employment and increases the number of specialized engineers in this field.

1.2 Crude oil

Crude oils are composed of a great variety of hydrocarbons. Hydrocarbons (HC) with one to four carbon atoms (methane – butane) are gaseous at room temperature, and hydrocarbons with more carbon atoms are liquid at room temperature (pentane, hexane, etc.). Hydrocarbons with more than seventeen carbon atoms per molecule are solid at room temperature as pure compounds, but these are usually dissolved in the liquid portion of the crude oil (2).

Crude petroleum is a mixture of compounds boiling at different temperatures that can be separated into a variety of different generic fractions by distillation (3).

Crude oil processing starts with the distillation. After vacuum distilling at 350ºC, the remaining thick liquid would be the heavy residue. The residue has a higher boiling point because of the longer hydrocarbon chain. The long-chain could be broken down into lighter hydrocarbons. Cracking is the main process to treat the residue.

1.2.1 History

Crude oil is a naturally occurring fossil fuel. It was formed underground with high pressure and high temperature. It took hundreds of millions of years to form from the remains of dead organisms. Which makes crude oil a non-renewable source.

The crude oil product and demand were expanding, which depends on technology development. For example, firstly, crude oil derivatives such as asphalt and pitch were rarely used in the medieval ages for coating the ship to protect it from sinking which used the hydrophobic characteristic of crude oil. Besides hydrophobic characteristics, the ancients used flammable characteristics for heat and light.

In 1859, the first successful oil well was drilled by Edwin Drake in Pennsylvania. Before this event, crude oil was rarely produced which makes it less useful. At that time, the first distillation was processed in the Batch operation of coal distillation which was producing just a few fractions of oil. However, the Batch reactor was modified with thermal cracking step to increase the yield. The crack distillation process was developed. The heavy part of the oil was heated and cracked until coke remained. Russia was also playing a big role in the processing of crude oil. In 1875, continuous crude distillation was developed.

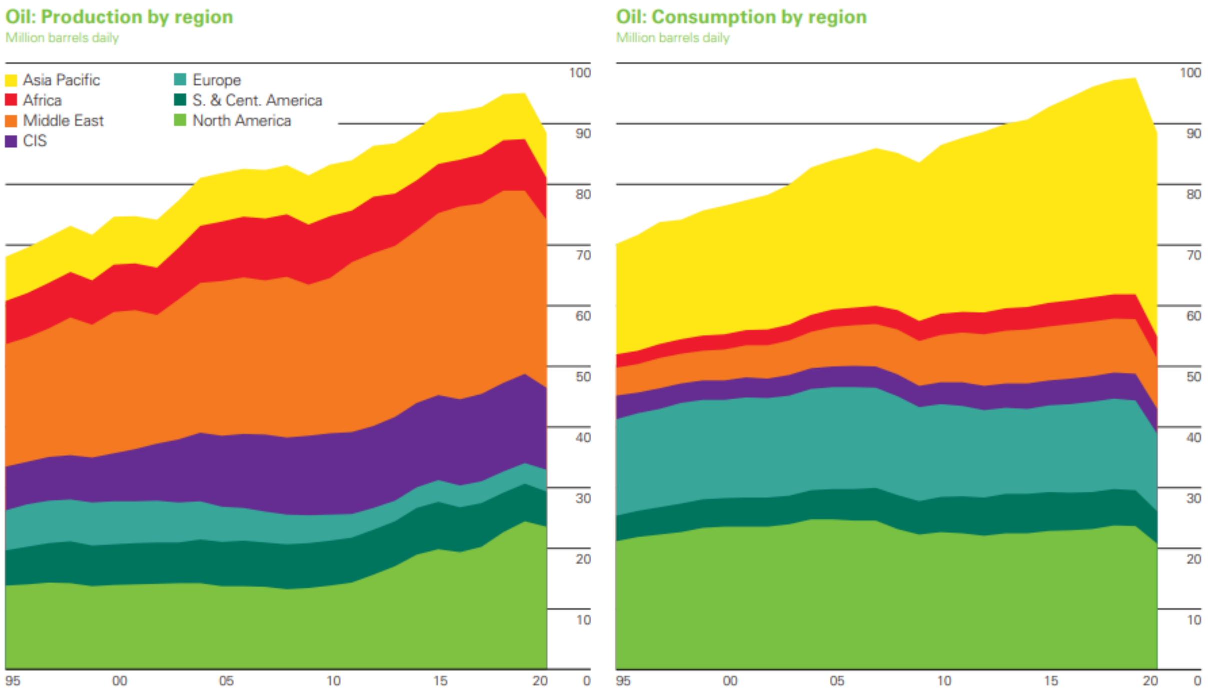
In the 19th century, crude oil was refined to produce mostly kerosene for lamps and other middle products such as pitch and lubricating oil. The lightest and heaviest fractions were just burnt that time because there was no demand.

20th-century crude oil demand was huge compared to the 19th century because of the fast expansion of electricity and motorization. Electricity was substituting the usage of lamp oil and motorized vehicles were increasing the demand for gasoline which lead to the development of thermal cracking processes which was the Burton process in 1912.

This demand for gasoline was increasing dramatically. In 1920, the thermal cracking developed, and Dubbs process increased the yield of gasoline from 30 percent to 50 percent. The Houdry catalytic cracking process was the next improvement in refining in 1930. The process used molybdenum-on-alumina catalysts in the presence of hydrogen at high temperatures and pressure. (2)

1.2.2 Reservoir and consumption of the world

In 2020, the proven world reserve was recorded as 1732.4 thousand million barrels. The world production per day is 88391 thousand barrels. On the other hand, the consumption of the world is estimated 88696 thousand barrels (4).



Oil: Production by region

Million barrels daily

Oil: Consumption by region

Million barrels daily

Graph 1 Oil production and consumption by region (4)

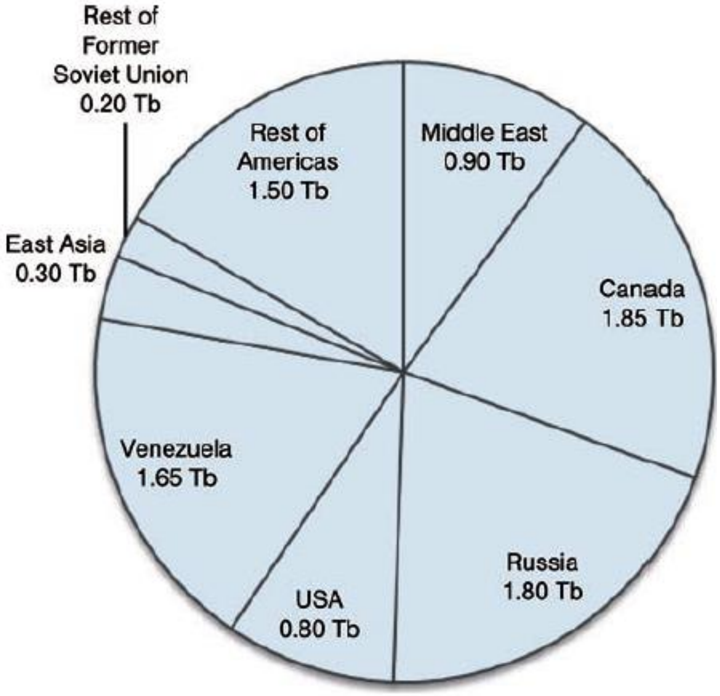
From the statistics, roughly 40 years are left to consume the proven reserve of oil. It has been almost 165 years since the production of oil. Year by year, the reserve of crude oil will be decreasing. From the history behind, we can see that demand has been increasing rationally to technical development and the population of the world. Therefore, in this supply-and-demand scenario, it is expected that the existing peak in conventional oil production will decline within the next two to three decades and production of oil from residua, heavy oil, and tar sand bitumen will increase significantly.

1.3 Sand oil / Sand bitumen

Oil sand is a mixture of mostly sand, clay, water, and a thick, molasses-like substance called bitumen. Bitumen is a mixture of hydrocarbons and asphaltic or tarry material. In Canada, the term ‘tar sands’ is also used, and elsewhere they may be referred to as unconventional oil. It is soluble in hydrogen sulfide, chloroform, and other organic solvent. Bitumen mostly contains asphaltene and resin and a low amount of sulfur, oxygen, and nitrogen (5).

Construction is the primary application for refined bitumen. It is mostly used in the paving and roofing industries. Bitumen is also used as a water and electricity insulator. From organic decomposition, it produces solid, liquid fuel, coke, sulfur, and hydrogen products. In Mongolia, the road of Nalaikh is paved with the bitumen from the Bayan-Erkhet oil sand deposit in 1990.

Unlike crude oil, sand oil is still in its developing stage. Year by year, new reservoirs are proven. The United States Geological Survey (USGS) and others estimate that the world endowment of VO in both clastic (sandstones, cemented, or unconsolidated sand deposits) and carbonate rocks are on the order of 9.0 Tb (1430 10^9 m3), more than double the conventional OOIP resource of roughly 4.50 Tb (5).



Graph 2 Geographical distribution of VO in the world (5)

A natural bitumen classifies into three types natural solid bitumen (asphaltite), natural viscous bitumen (asphalt), and natural liquid bitumen (maltene). Also, bitumen could be produced from the heavy residue of crude oil which is called crude oil bitumen.

2 Refining Methods

Crude oil in its natural form has no value to consumers. It must be transformed into products that are usable in the marketplace. To get the desired product, it is separated by physical and chemical properties from crude oil. Heat, pressure, catalyst, and chemicals are used in various operations and conditions to get up to 2000 individual refinery products with different specifications (6). Typical refinery products with their carbon content and boiling ranges are shown in Figure 3.

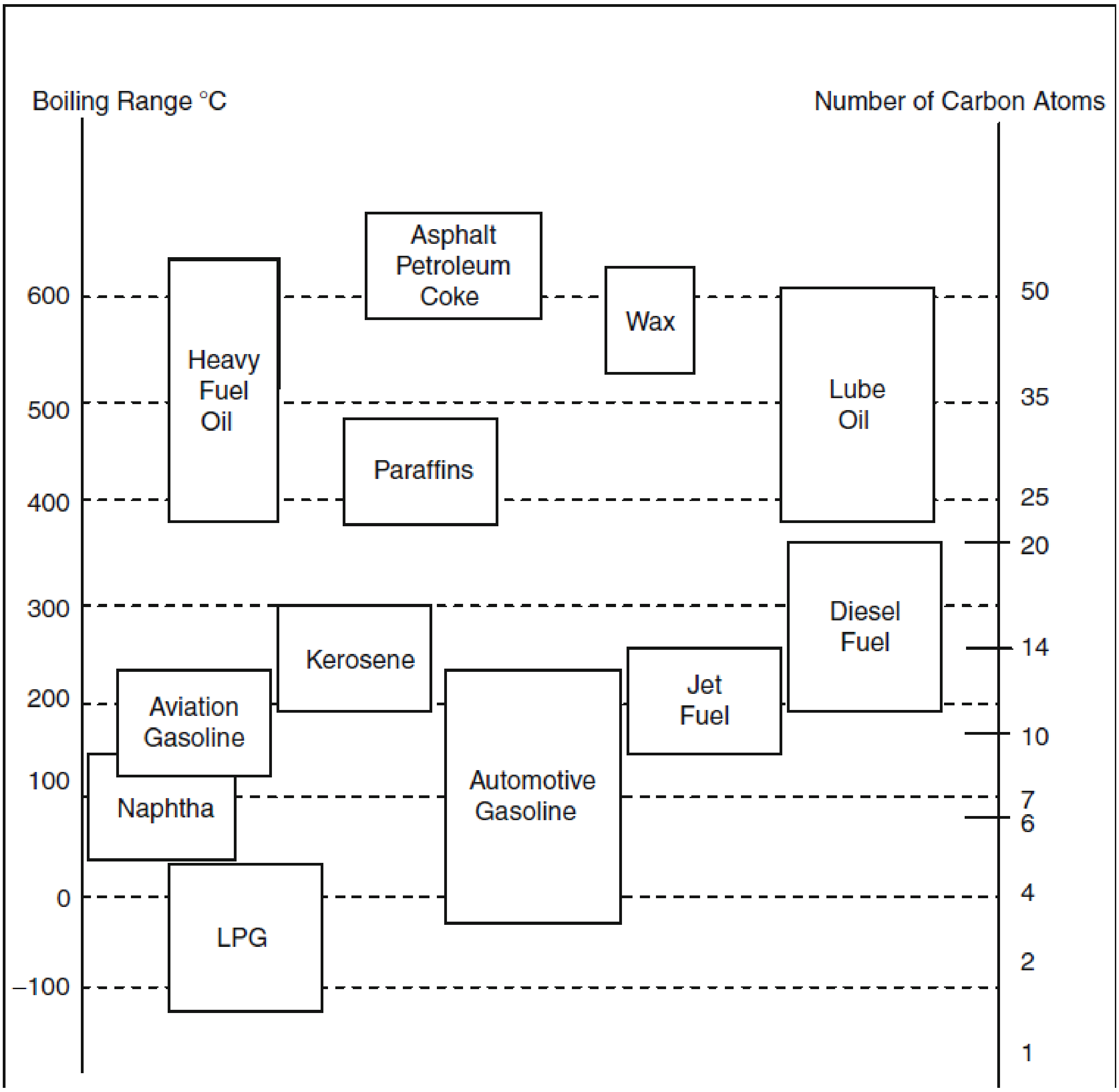


Figure 4 Principal petroleum products with carbon numbers and boiling ranges (6)

Crude oil should be desalted and dewatered before distillation. Distillation is the first process of physical separation. After it is separated, the top middle, and bottom products move to the next process of chemical separation such as cracking, reforming, and hydrotreating.

2.1 Distillation

2.1.1 Desalting and Dewatering

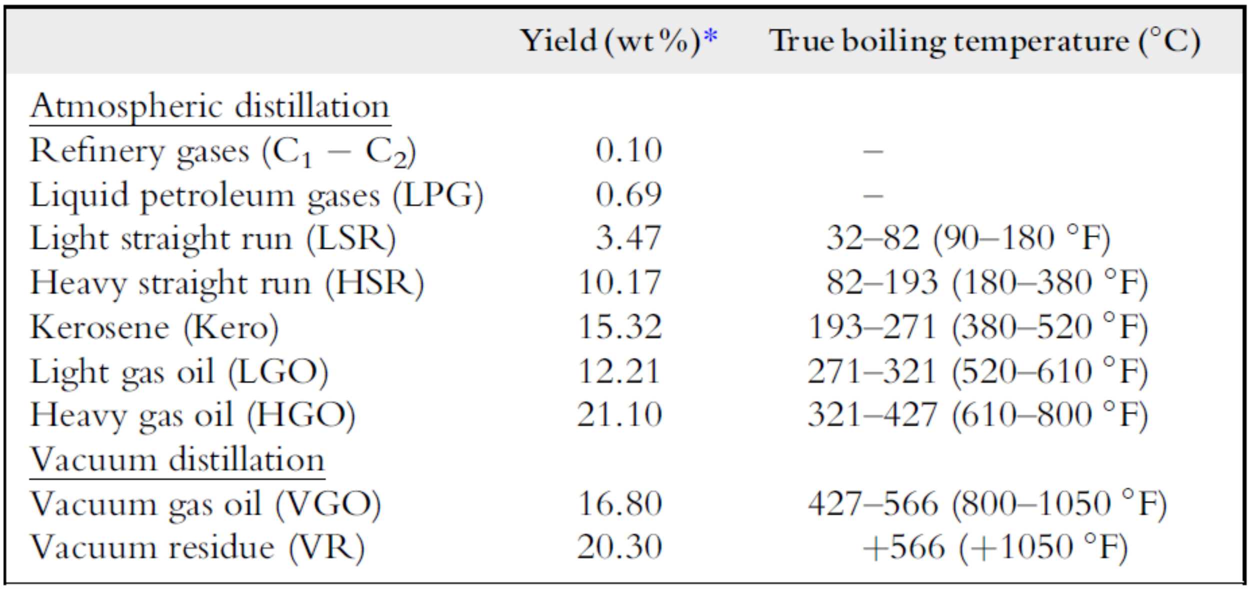
Simply, crude oil is pumped through a well from an underground reservoir. Crude oil could be containing any salt, dirt, gas, and water. Before the distillation process, crude oil should be pretreated such as desalting. Desalting is a water-washing operation performed at the production field and at the refinery site for additional crude oil cleanup. Otherwise, impurities could cause operating problems during the refinery process, such as equipment corrosion and catalyst deactivation.

2.1.2 Atmospheric and Vacuum Distillation

Atmospheric distillation is the first step in crude oil processing. The crude oil is separated into fractions of different boiling ranges (2). Continuously operated fractionation columns are used to perform fractional atmospheric distillation of crude oil. The required heat for fractionation is supplied by fired tube furnaces.

Hydrocarbon fraction with a boiling point above 360° C would not be recovered by atmospheric distillation because above this temperature cracking of heavy products start. Therefore, the atmospheric residue should move to the next vacuum distillation. The higher-boiling oil fractions can be evaporated under similar temperature conditions as in the gas oil section of atmospheric fractionation due to the reduced pressure (to 10 mm Hg or less) in vacuum columns. The final boiling point of a full-range vacuum gas oil (feedstock for a catalytic cracker) would correspond to 550° C at atmospheric conditions (2).

Table 2 shows the yield and boiling point of different products from distillation.



	Yield (wt %)*	True boiling temperature (°C)
Atmospheric distillation		
Refinery gases ($C_1 - C_2$)	0.10	–
Liquid petroleum gases (LPG)	0.69	–
Light straight run (LSR)	3.47	32–82 (90–180 °F)
Heavy straight run (HSR)	10.17	82–193 (180–380 °F)
Kerosene (Kero)	15.32	193–271 (380–520 °F)
Light gas oil (LGO)	12.21	271–321 (520–610 °F)
Heavy gas oil (HGO)	21.10	321–427 (610–800 °F)
Vacuum distillation		
Vacuum gas oil (VGO)	16.80	427–566 (800–1050 °F)
Vacuum residue (VR)	20.30	+566 (+1050 °F)

Table 2 Crude distillation product (6)

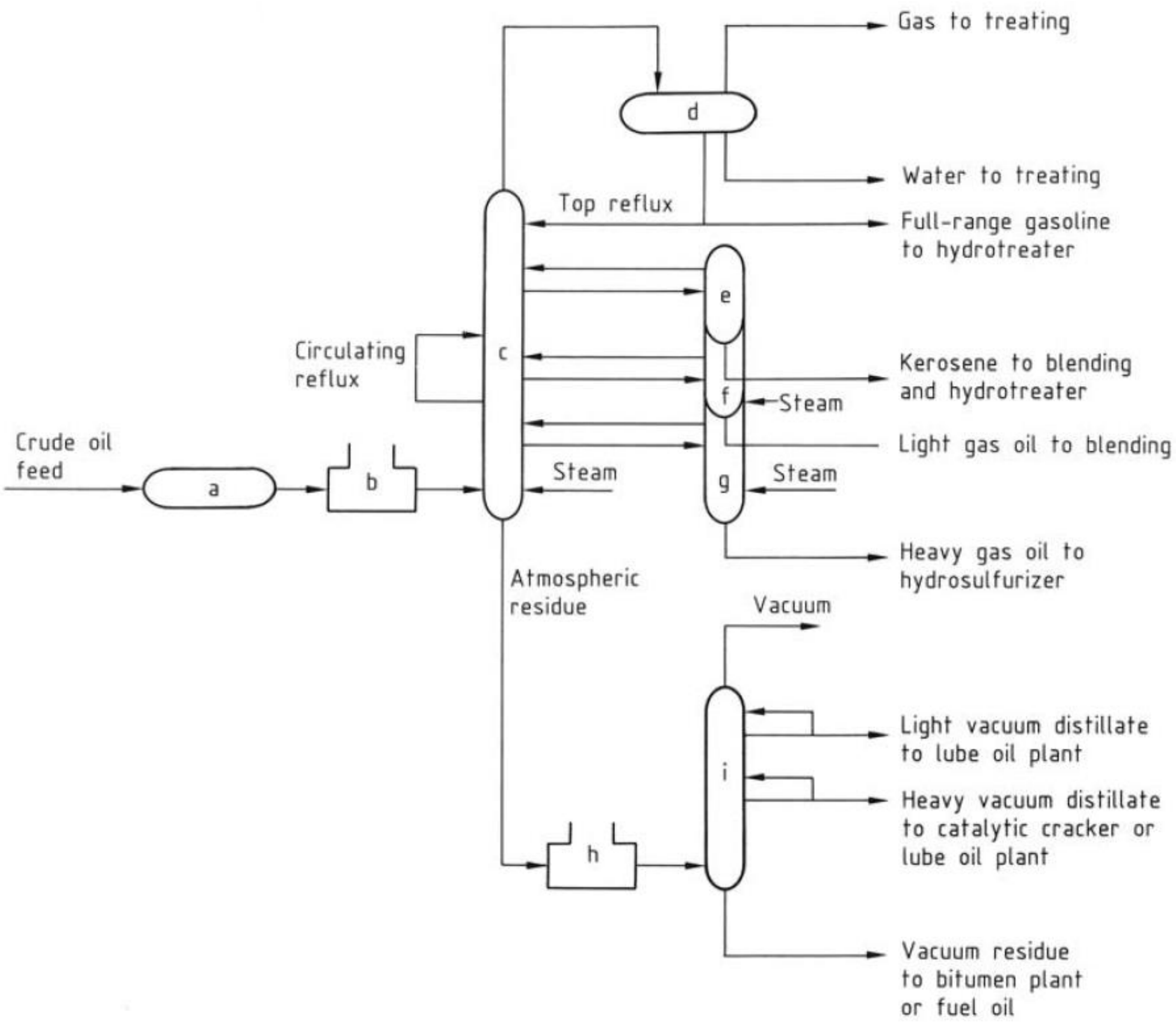


Figure 5 Schematic representation of crude oil distillation including crude desalting and vacuum flashing a) Crude desalter; b) Crude heater; c) Main fractionator; d) Overhead accumulator; e) Kerosene stripper; f) Light gas oil stripper; g) Heavy gas oil stripper; h) Vacuum heater; i) Vacuum flasher (2)

Figure 5 shows the scheme of crude oil distillation process with desalting and vacuum flashing. Crude oil from the production well is already desalted and dewatered, but there could be remaining salt and water which could corrode the equipment or mislead the further operations with catalyst.

The column top product vapor is condensed and separated into gas and gasoline in the overhead accumulator (Figure 5. (d)) then part of the gasoline is pumped back into the column as reflux. In a kerosene stripper, lighter fractions are stripped off by superheated stream and products are moved to the next treatments such as hydrotreating, blending, gas treating, and reforming. Vacuum residue is carried to next processes such as visbreaking, catalytic cracking, coking, and deasphalting.

2.2 Cracking

2.2.1 Thermal Cracking

One of the first conversion processes utilized in the petroleum industry was the thermal cracking of higher-boiling materials into lower-boiling products. This process is known as thermal cracking. In the early 1900s, this process was created to make gasoline from "unwanted" higher-boiling materials. The cracked product is usually a lighter and more fuel-efficient.

Temperatures of 455°C 540°C and pressures of 100-1000 psi are used in the majority of thermal cracking procedures; the Dubbs process is an example of an early thermal cracking operation(3).

Crude oil consists of paraffins, naphthene and aromatic. Thermal cracking breaks down higher-molecular-weight hydrocarbons of heavy residue into light ones. With the heat, huge amount of energy inserts in which breaks the C-C bond to form free radical. Chemical reaction of thermal cracking is endothermic and the free radical chain reaction. Also, olefins form during the chain reaction.

The relative ease of cracking of different types of hydrocarbons with the same molecular weight is generally presented in the following order: (1) paraffins, (2) olefins, (3) naphthenes, and (4) aromatics. To avoid any misunderstanding, paraffins are the least stable, while aromatics are the most stable.

The free radical chain reaction consists of 5 stages:

1. Initiation reaction: is a process that occurs when a single molecule breaks apart into free radicals. In this reaction, the two free radicals are formed by breaking the bond between two carbon atoms.

$$CHCH_3 \rightarrow 2CH_3\cdot \ (3)$$

2. Hydrogen abstraction reaction: The free radical takes a hydrogen atom from another molecule.

$$CH_3\cdot + CH_3CH_3 \rightarrow CH_4 + CH_3CH_2\cdot \ (3)$$

3. Free radical decomposition reaction: Where free radical decomposes into olefin and hydrogen ion.

$$CH_3CH_2\cdot \rightarrow CH_2{=}CH_2 + H\cdot \ (3)$$

4. Radical addition reaction: the radical reacts with an alkene to form a single and larger free radical

$$CH_3CH_2\cdot + CH_2{=}CH_2 \rightarrow CH_3CH_2CH_2CH_2\cdot$$

5. Termination reaction: occurs when two free radicals react to produce a product by recombination and disproportionation reactions.

$$CH_3\cdot + CH_3CH_2\cdot \rightarrow CH_3CH_2CH_3$$

$$CH_3CH_2\cdot + CH_3CH_2\cdot \rightarrow CH_2{=}CH_2 + CH_3CH_3 \quad (3)$$

Besides those reactions, many other reactions occur s

2.2.2 Catalytic Cracking

The catalytic cracking is thermal decomposition in the presence of catalyst. The catalytic cracking replaces thermal cracking in production of gasoline because the product is richer in branched and cyclo- paraffins, and aromatics which improves quality of gasoline. It results the maximum derivatives of butene and butane.

The commissioning of the first catalytic cracking plant in 1936 (Houdry process, United States) initiated a new era in petroleum refining. Until then, thermal cracking of distillates had been the governing conversion process, the role of which was taken over very soon by catalytic cracking. This development was particularly influenced by the increased demand for high-quality transportation fuels during World War II (2).

Advantages over thermal cracking:

1. Lower production of C1 and C2 hydrocarbons
2. Lower cracking temperature
3. Higher octane rate
4. Higher cracking reaction rate

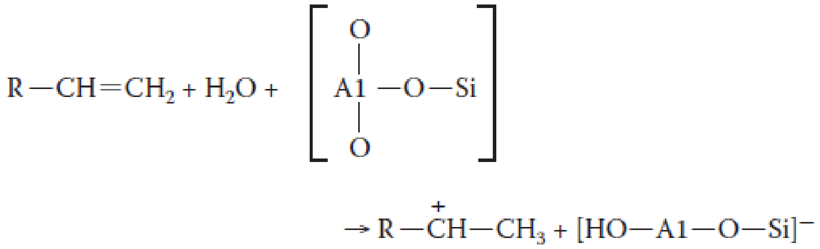
The first used acid catalysts were 87% silica (SiO_2) and 13% alumina (Al_2O_3). Now it is substituted by crystalline aluminosilicates (zeolites). The process condition is 900°F-1000°F and 10-20 psig. The variations of process are fixed bed, moving bed and fluidized bed.

Thomas suggested that carbonium ions are generated by a tiny amount of thermal cracking of n-paraffins to create olefins, and that this is the process. These olefins absorb a proton from the catalyst, forming big carbonium ions that disintegrate into small carbonium ions and olefins according to the beta rule (carbon–carbon bond scission occurs at the carbon in position beta to the carbonium ions and olefins). By transferring a hydrogen ion from an n-paraffin to generate a tiny paraffin molecule and a new big carbonium ion, the small carbonium ions promote the chain reaction. Consider the borrowing sequence for n-octane as an example of a typical n-paraffin hydrocarbon cracking process (7).

Step 1: Initiation reaction – mild thermal cracking

$nC_8H_{18} \rightarrow CH_4 + R --- CH=CH_2$ (7)

Step 2: Proton shift



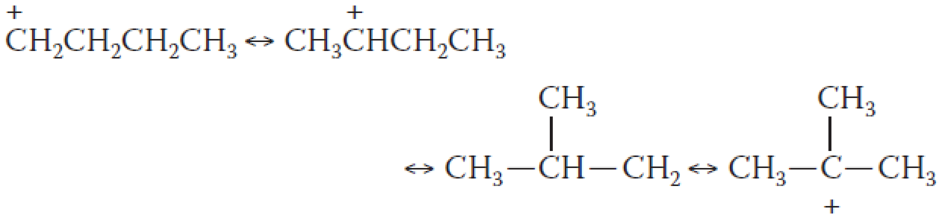
$$R-CH=CH_2 + H_2O + \left[\begin{array}{c} O \\ | \\ Al-O-Si \\ | \\ O \end{array}\right] \rightarrow R-\overset{+}{C}H-CH_3 + [HO-Al-O-Si]^-$$

(7)

Step 3: Beta scission

$$R-\overset{+}{C}H-CH_3 \rightarrow CH_3CH_2=CH_2 + \overset{+}{C}H_2CH_2CH_2CH_3$$ (7)

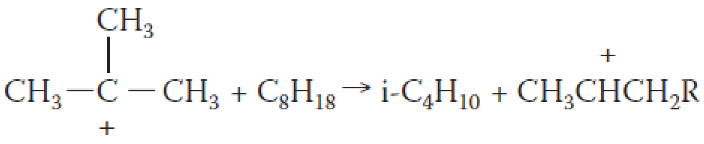
Step 4: Rearrangement to get more stable.



$$\overset{+}{C}H_2CH_2CH_2CH_3 \leftrightarrow CH_3\overset{+}{C}HCH_2CH_3 \leftrightarrow CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2 \leftrightarrow CH_3-\underset{+}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

(7)

Step 5: Hydrogen ion transfer



$$CH_3-\underset{+}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + C_8H_{18} \rightarrow i\text{-}C_4H_{10} + CH_3\overset{+}{C}HCH_2R$$

(7)

3 Methodology

3.1 Water Content of Crude Oil

If the crude oil has a content of water, it could negatively affect to precision of experiment results of its properties. Therefore, crude oil sample should be dewatered firstly. Water can be stored in crude oil in three states as dissolved, emulsified and free water (8).

The Dean-Stark method is commonly used to determine the content of water. Crude oil is dissolved in an organic solvent and azeotropically distilled. Toluene is used as a solvent. 100 grams of crude oil and 100 ml of solvent are added to a cylindrical flask and mixed for 5 minutes. A little piece of ceramic is added to boil it evenly. Then the flask is connected with Dean-Stark glassware and a condenser as shown in Figure 4b. Heated at a constant rate with 1-2 drops from the condenser. Distillation is done for 30 to 60 minutes. Since water is denser than toluene, water is collected at the bottom of the Dean-Stark glassware. Volume of the water is observed from the measurement of glassware. The percent of water (X, %) is calculated as follows:

$$X = 100 * \frac{V}{G}$$

V – Volume of water in the collector (ml),

G – Mass of the crude oil sample (g)

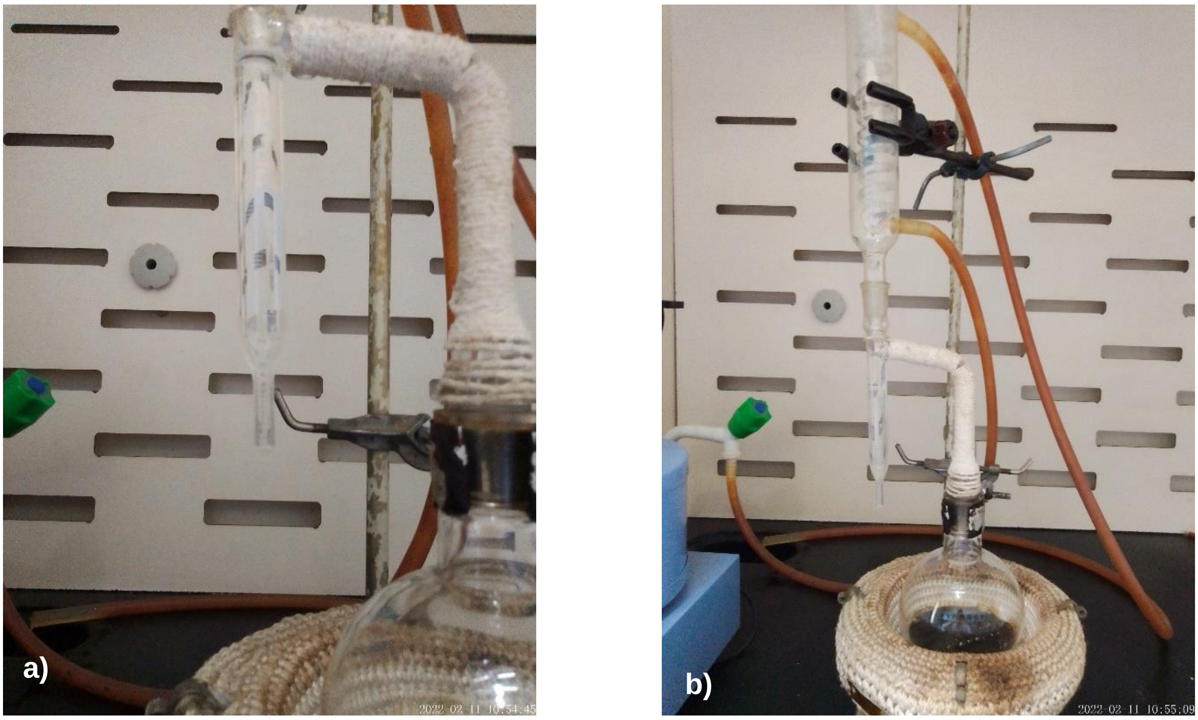


Figure 6 a) Dean-Stark glassware, b) Dean-Stark apparatus

3.2 Density

The Density and the specific gravity are two properties that have wide use in petroleum industry and we could expect the quality and characteristic of crude oil with these properties.

Density is defined as the mass of a unit volume of material at a certain temperature in grams per cubic centimeter. Specific gravity is the ratio of the mass of a volume of a material to the mass of the same volume of water, and it is determined by two temperatures: the temperature at which the sample and water masses are measured, and the temperature at which the sample and water masses are measured.

The API gravity scale was created in 1921 as a modification of the Baume scale, which was established in 1916 by the United States National Bureau of Standards. In the petroleum industry, the API gravity scale is commonly used to establish quality and property correlations of crude oils, fractions, and products. As a result, the economic value and price of crude oil rises in tandem with its API gravity. API gravity, on the other hand, has been proven to correlate with a range of crude oil qualities. Sulfur, nitrogen, metal, and asphaltene concentration, for example, tends to rise as API gravity lowers (9).

$$API\ gravity\ at\ 60°\mathrm{F} = \frac{141.5}{Specific\ Gravity\ at\ 60\ °\mathrm{F}} - 131.5 \quad (9)$$

From this equation we can see API gravity and density has reversely dependent. When API gravity is low, it shows heavy crude oil with high density. Also, density is variable to temperature. When temperature increases, density of petroleum product decreases. There are methods of determining density according to ASTM standards, such as hydrometer, digital density meter and pycnometer.

$$\rho^{t} = \rho^{20} - \gamma(t - 20) \quad (8)$$

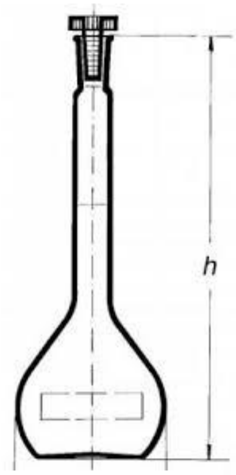


Figure 8 5 ml pycnometer

Figure 7 pycnometers in a 20C water tub

Pycnometer (Figure 7) method is performed to determine the density of crude oil. Parallel experiment is conducted to be more precise. It is operated at 20℃ constant temperature, pycnometer is placed at water bath for 30 minutes to maintain 20℃ (Figure 8). After settled for 30 minutes, pycnometer is refilled up to the 5 ml line. Mass of empty and filled pycnometer is weighed. Density is calculated as follows(8) :

$$m = m_2 - m_1$$

$$\rho = \frac{m_3 - m_1}{m}$$

$$\rho_4^{20} = (0.99823 - 0.0012)\rho + 0.0012 = 0.99703\rho + 0.0012$$

m – water number of pycnometer.

m_1 – mass of empty pycnometer

m_2 – mass of pycnometer with water

m_3 – mass of pycnometer with crude oil

ρ – visible density

ρ_4^{20} – Density at 20℃

Oil class	API
Light	API>31
Medium	22<API<31
Heavy	10<API<22
Extra heavy	API<10

Table 3 Oil classification by API

3.3 Viscosity

The viscosity of a crude oil or petroleum fraction indicates its resistance to flow or pumpability. When viscous oils flow through pipes, the pressure loss is larger. The kinematic viscosity is measured in centiStocks (cSt) or 1mm2/s. ASTM D445 measures viscosity at 37.8°C and ASTM D446 measures viscosity at 99°C.

The viscosimeter (Figure 9) is filled with testing crude oil or petroleum product and placed in thermostat (Figure 11). After settling in thermostat (Figure 11) for 30 or 60 minutes, a rubber pipette filler sucks up the air and elevate the crude oil above the line of viscosimeter. Then, crude oil in viscosimeter flows down to the next level, when time is recorded and repeat it several times. Kinematic viscosity (υ) is calculated by multiplying average time taken (τ) with viscosimeter constant (C). Dynamic viscosity (η) is calculated by multiplying kinematic viscosity (υ) with density (ρ) at the same temperature.

$$\nu = C * \tau \quad (8)$$

$$\eta = \upsilon * \rho \quad (8)$$

Figure 9 Used Viscosimeter with constant 1.016

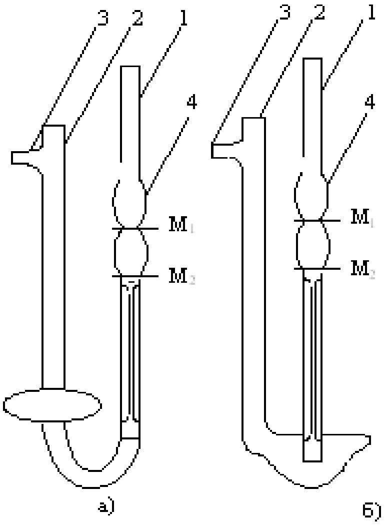


Figure 11 Pinkevich Viscosimeter

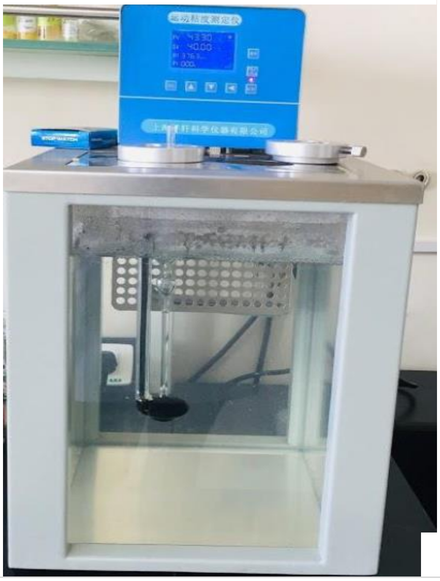


Figure 10 Thermostat

3.4 Pour point

After heating, the sample is cooled at a defined rate and its pour property is examined at intervals of 3℃. The lowest temperature at movement is not flowing of the sample is observed and recorded as the pour point. Lighter petroleum products tend to have higher pour point and heavier fractions tend to have lower pour point.

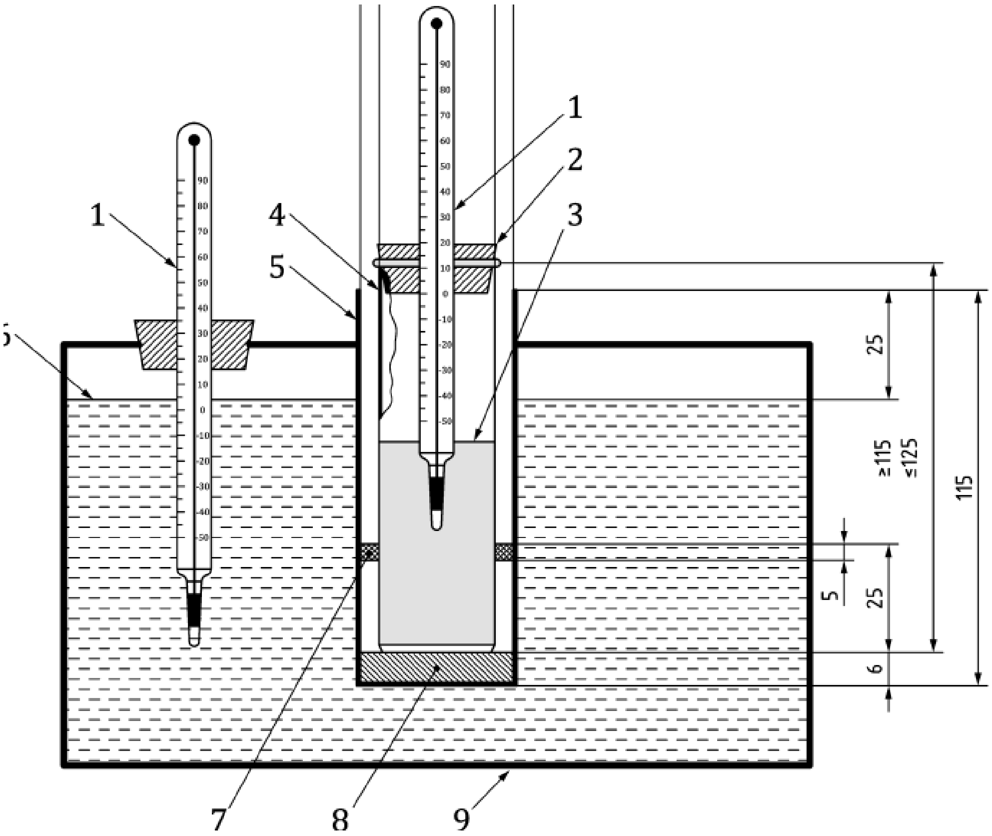


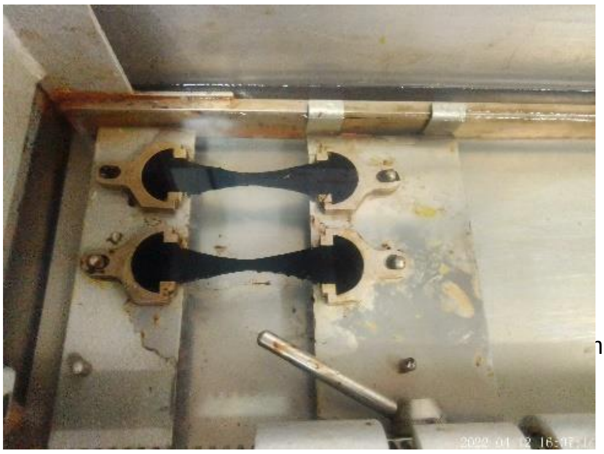
Figure 12 Pour point determining (10)

3.5 Separation of Bitumen from Oil Sand

The bitumen from oil sand could be separated with hot water or organic solvent. In this experiment, bitumen is separated with chloroform. To calculate bitumen content from oil sand, 100 grams of sample is weighed and added into clean flask with cap. Chloroform is added in flask and shook frequently. Dissolved bitumen is filtered and evaporated chloroform in rotary evaporator. Extracted chloroform is added to flask with sand, dissolving is repeated until the dissolved solution turns into colorless. Then bitumen is separated after evaporating chloroform. Bitumen content of oil sand measured usually between 5-20%.

3.6 Ductility

The property of bitumen which allows it to undergo deformation or elongation is called ductility of bitumen. The ductility of bitumen is measured by the distance in centimeter. Bitumen sample will elongate before breaking when it is pulled by standard specimen at specified speed and temperature.



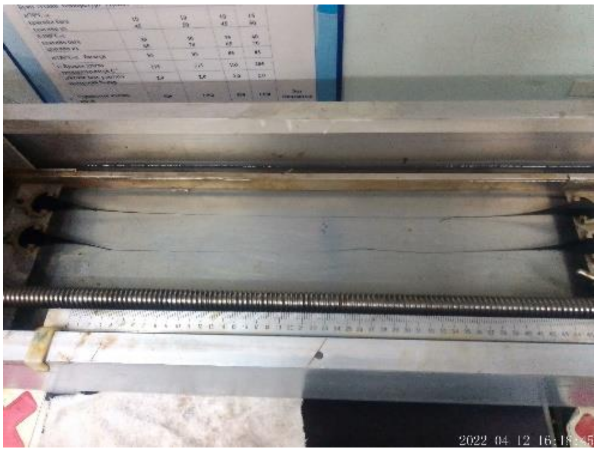


Figure 14 Ductilimeter sample cast

The petroleum product is heated and fill it into the cast (Figure 12) and cooled down. Cast should be lubricated in order to remove sample clearly. Then placed in ductilimeter with 25℃ water bath. After is set, the sample is stretched with speed of 5 cm/s. The length is recorded when the sample fractures.

3.7 Penetration

The penetration test for bitumen determines its hardness or softness by measuring the depth of penetration with a standard loaded needle in five seconds while keeping the temperature of the bitumen sample at 25 °C. The less distance a needle can penetrate the more viscous the bitumen is. As a result, viscous bitumen has a lower penetration value. From the result bitumen can be classified into penetration grades according to ASTM D946-09 standard.

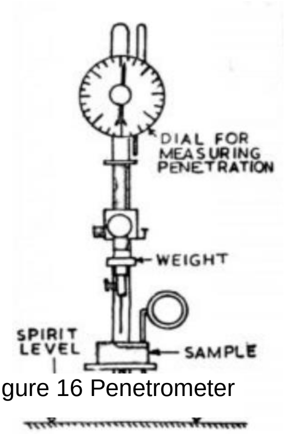


Figure 16 Penetrometer

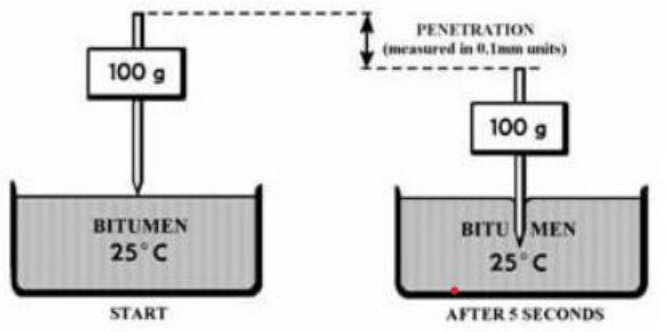


Figure 15 Needle penetration

3.8 Softening Point

A ring-and-ball contraption submerged in distilled water can be used to measure the softening point of bitumen. The softening point is calculated as the average of the temperatures at which the two disks soften enough for each bitumen-encased ball to fall 25 mm. Bitumen is heated and molded into a ring. The apparatus consists of 1000 ml beaker, thermometer, heater, ring and the ball. Figure 15 shows the experiment procedure. The beaker of water is heated constantly. Eventually, temperature increases and the bitumen softens, then the ball sinks down with bitumen. Temperature is recorded when the softened bitumen touches the below platform which is 2.5 cm from the ring level.

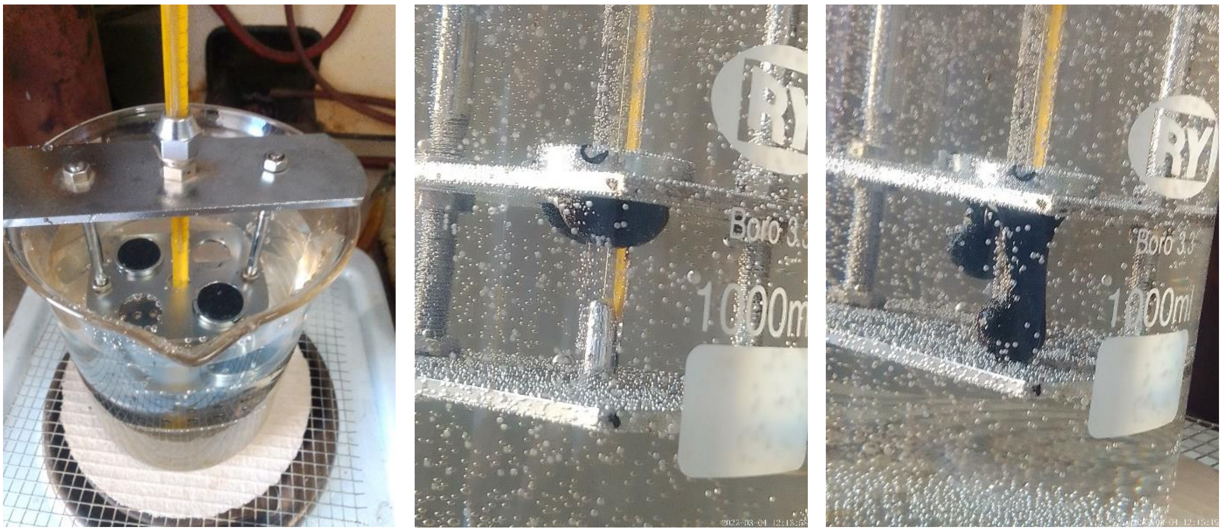


Figure 17 Softening point of bitumen

3.9 Content of Hydrocarbons

Content of hydrocarbon test is experimented on crude oil, bitumen, heavy residue of distillation and on fractions of cracked heavy residue. It is the most time consumed and the most important test of property.

Content of hydrocarbon is achieved by SARA analysis method. The concept is based on solubility of paraffins and aromatics. Soxhlet apparatus is the main equipment of this method.

3.9.1 Sample Preparation

Sample amount is taken depending on the Soxhlet apparatus volume. First step is to dissolve crude oil in n-hexane with 1:40 ratio respectively. Precision of weighing of sample is important in order to calculate the contents. 40:1 n-hexane solution is settled in dark with cap for 24 hours (Figure 19). As a result, asphaltenes are separated as solid precipitation in solution.

To separate asphaltene, Erlenmeyer flask, tared Gooch crucible funnel and filter paper are used (Figure 18). Must be cautious on asphaltene precipitate not to escape into the flask with maltenes. After filtering, filter paper with asphaltene is folded into paper packet. Since, few amounts of maltene is absorbed in filter paper with asphaltene, packet is placed in Soxhlet. N-hexane solution is placed in a round bottom flask which is set up with the Soxhlet and the condenser.

3.9.2 Extraction of Asphaltene

When solution in the round bottom flask starts to boil, gaseous hexane is condensed in condenser and drops into Soxhlet. Soxhlet fills up to siphon level and flows back into the round bottom flask. While Soxhlet is filling up, absorbed maltene from packet dissolves in n-hexane.

Figure 19 Filtering asphaltene

Figure 18 Dissolving crude oil in n-hexane, 1:40

After solvent in Soxhlet turns colorless, maltene and n-hexane solution is changed with the round bottom flask with chloroform. Same process repeats with chloroform as a solvent to dissolve asphaltene in the packet. When Soxhlet solvent turns colorless asphaltene separation comes to the ending. Chloroform is extracted with rotary evaporator, then placed in fume hood until all chloroform evaporates. Mass of the beaker with asphaltene weighed (precision of 0.0001g) until it is stabilized.

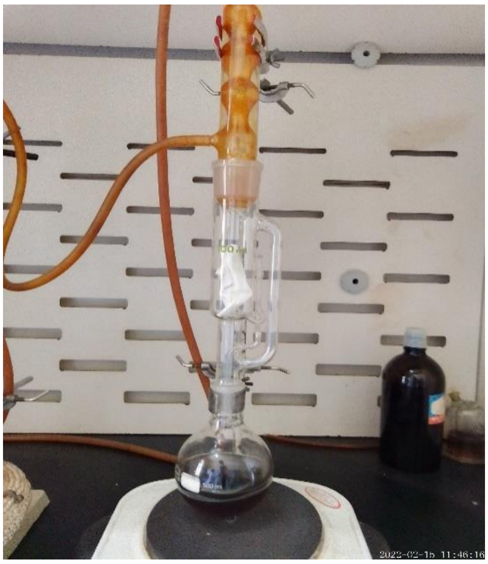


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Figure 20 Extracting asphaltene

Figure 21 Evaporating solvent

3.9.3 Extraction of Oil Constituents

N-hexane is extracted from the solution of oil constituents, resin and moves to the next process to extract oil constituents with an activated silica gel and n-hexane as the solvent. Activated silica gel is occupied in the thimble of Soxhlet. Clear cotton must be added first at the bottom of thimble in order to prevent silica gels wash off through siphon. Oil constituents and resin is added at the top of silica gel in the thimble and extracted oil constituents with n-hexane solvent. Resin trapped at the top layer of silica gel and oil constituents dissolve and flow through the siphon into the round bottom flask. After 4-6 hours, oil constituents completely separated from resin. The round bottom flask with oil constituents is washed with chloroform after evaporating n-hexane with rotary evaporator and stayed in warm place until the solvent evaporates and mass stabilizes.

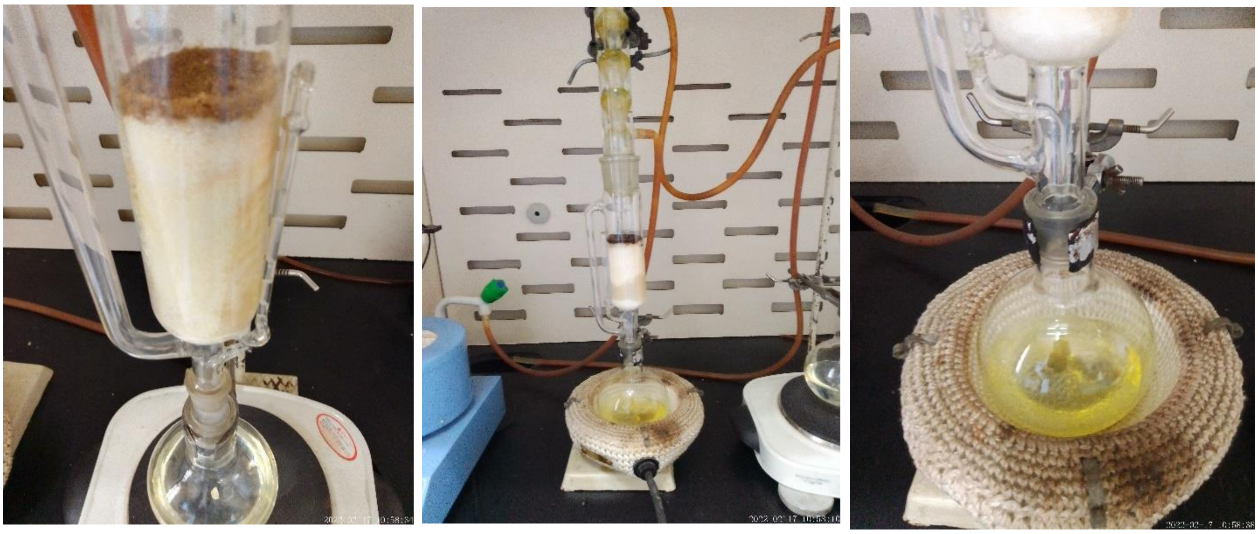

Figure 22 Extraction of oil constituents with activated silica gel

3.9.4 Extraction of Resin

After extraction of oil constituents, we get the Soxhlet with only resin on top of the activated silica gel. Extraction of resin resumes with ethanol-benzol 1:1 solvent. Same process as previous repeats. As a result, ethanol-benzol and resin solution is collected in the round bottom flask. Solvent is evaporated and washed the flask with chloroform to get all of the resin. Beaker with resin is stored in warm to evaporate all solvents and weighed the mass of resin. Silica gel is used again after activating in furnace.

Figure 23 Content of crude oil from TB-XIX

Figure 24 Extraction of resin

3.10 Distillation

3.10.1 Crude Oil Laboratory Distillation

Distillation apparatus consists of boiling flask, connecting tube, thermometer, condenser, receiving flasks and vacuum motor. It was possible to heat up to 200℃ for atmospheric distillation (Figure 25 a) due to capacities of equipment. Atmospheric residue is distilled vacuum (Figure 25 b) up to 250℃ by thermometer value with pressure of 3-8mm Hg which gives >450℃ in the flask.

Fractions of b.p - 200℃, 200 - 350℃, 350-450℃ and >450℃ residue had achieved from crude oil distillation. Above 350℃, cold water flow of condenser should be stopped due to heavy fractions condenses and chill which blocks the way in the condenser. Because of the blocked tube, pressure and temperature in flask increases. Condenser could be heated from outside to melt the heavy fraction. Sudden unblock could cause spillage of crude oil into collecting flask or could explode.

Figure 25 a) Atmospheric distillation, b) Vacuum distillation

3.10.2 Distillation of Cracked Products

Thermal and catalytic hydro-cracking had done with 1 hour and 2 hours. 4 liquid products accomplished. In order to get fraction results to compare, distillation had done. Since the reactors of crack has small volume, liquid product was very small in amount between 5 – 8 grams.

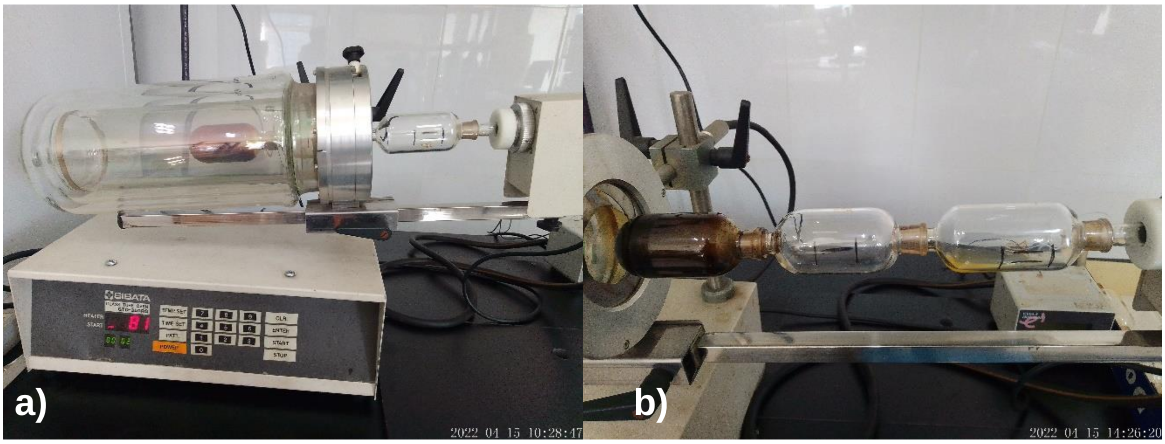

Figure 26 a) Glass tube oven, b) Flasks in series

Glass tube oven (Figure 26 a) is used to distill cracked liquid product. It is suitable to distill small amount of sample. It consists of 3 layers of glass tubes, temperature controller, pressure controller, rotary motor, and 3 flasks in series (Figure 26 b). The light fraction is obtained at 45kPa and 190℃. Heat rate was set at 4℃ per minute. When temperature reaches 190℃, it is held at same condition for 30 minutes to distill all light fraction or it could be stopped before if light fractions does not form. Medium fraction is achieved at 210℃ and 2kPa.

First and second flasks rotate in the tube and fractions condense in third flask. After fractions distilled, mass balance I calculated and change the series of flasks to next distillation. Huge heat rate could lead to failure when sample is sucked up into other two flasks.

3.11 Cracking

>350℃ residue is cracked 4 different times. Thermal cracking and catalytic hydro-cracking is performed for 1 hour and 2 hours each. 15 grams of sample is loaded into 50 ml fixed bed reactor. 3 steel balls added in order to mixing inside while the furnace (Figure 27 b) moves up and down by the pivot. After precise amount loads into reactor (Figure 27 a), catalyst is added and capped tightly. Then, air is washed off by nitrogen for thermal and hydrogen for catalytic hydro-cracking. When pressure reaches the desired amount the gas valve is closed tightly. Lastly, reactor is inserted (Figure 27 c) into 450℃ hot furnace. Conditions of cracking is listed in Table 3. After passing 1 or 2 hours, the heater and motor are turned off and stayed in room furnace to cool down.

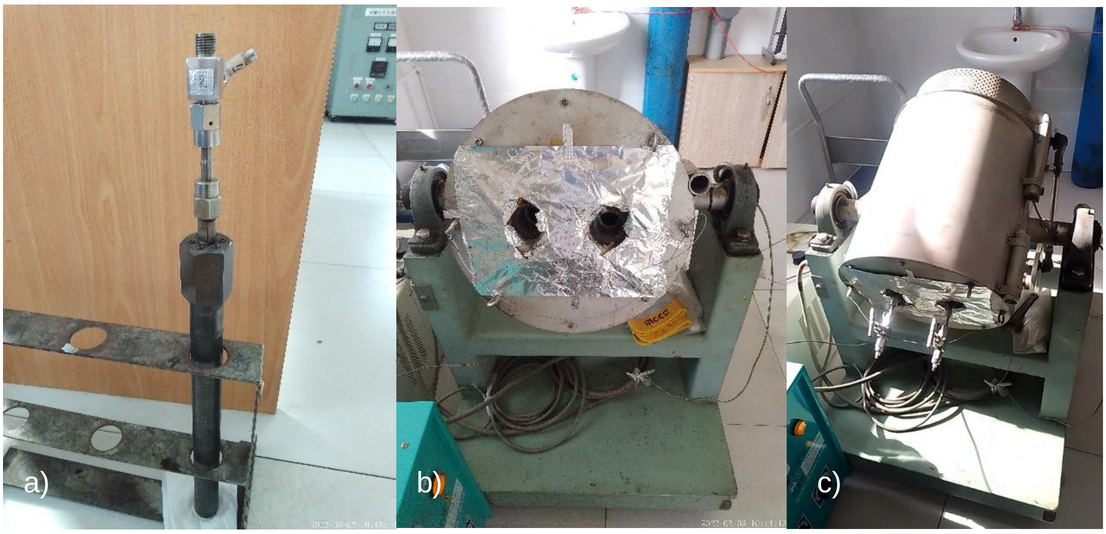

Figure 27 a) Reactor, b) Heater warming up c) Reactor in process

	Thermal Cracking	Catalytic Hydro-cracking
Temperature (℃)	450	450
Pressure (Mpa, atm)	4 atm	5MPa
Gas	N_2	H_2
Time	1 and 2 hours	1 and 2 hours
Catalyst	-	NiMo 1%, S 1%

Table 4 Cracking condition

After the reactor is cooled down, first gas amount is measured with syringe. Liquid product is collected in flask with cap. Since the liquid product is soluble in toluene, reactor is washed off with toluene and stored in flask with cap. The product which is not soluble in toluene is the solid product, coke. Coke is cleaned off with acetone and collected in the flask. Acetone evaporates in room temperature and only coke remains in the flask. Toluene flask is filtered and extracted in Soxhlet. Solid precipitate mass is added to coke product. After toluene is extracted by rotary evaporator, residual liquid mass is added to liquid product for mass balance.

3.12 Pyrolysis

Pyrolysis (Figure 28) is the process of heating oil sands to a temperature high enough for the organic components to break down into smaller hydrocarbon molecules. Light gases and condensable vapor make up the product stream, leaving solid coke residue on the sand. Oil sand (Figure 30) was heated up to 550℃ until there is no condensed droplet. Reactor had capacity load 2 kg oil sand. After loading the oil sand into reactor, it was sealed tightly with bolts. If bitumen leaks through the bolt, it is able to cause fire. The cap has one outlet down to condenser. Light

Figure 30 Pyrolysis

Figure 28 Uncondensed gas

Figure 29 Oil Sand

hydrocarbons condense through condenser and collected into receiving flask. Pyrolysis must go under fume hood. Due to high heat rate, a lot of gas forms. Condenser cannot catch excess gas (Figure 29) and gas escapes. Extracted liquid should store in flask with cap in the dark.

Figure 31 shows the residual sand. Since, the color is blackish it could be dissolved in organic solvent to extract residual bitumen. The sand could be used for construction raw material for concrete or backfill.

Figure 31 Residual sand from pyrolysis

4 Experimental Results

4.1 Properties of crude oil and >350℃ residue from TB XIX block

4.1.1 Water content

The crude oil sample was taken from the tank which was ready to export. It could be pretreated. Crude oil boiled in Dean-Stark apparatus for 30 minutes. Toluene was blurry, Dean-Stark glass ware reheated in hot water bath and cooled again. After 15 minutes toluene turned colorless and there was no boundary of toluene and water. There was no water content in TB-XIX crude oil (Figure 6 a).

4.1.2 Density

Density was measured in parallel 2 pycnometers. Since crude oil is dark black, it was unable to see 5 ml line. Reheating in hot water bath a pycnometer with sample is recommended. In this way sample would become less viscous and gets easier to read the volume of sample. Filter paper is used to remove excess sample via absorption. The density at 20℃ is calculated by $\rho_4^{20} = 0.99703\rho + 0.0012$. The density of crude oil and >350℃ residue is shown in Table 4.

20C V=5ml		**Crude oil**		**>350 residue**	
		1	2	1	2
Empty mass	m1 (g)	11.5204	12.2316	11.5204	12.2316
Mass with water	m2 (g)	16.4237	17.1878	16.4237	17.1878
Mass with sample	m3 (g)	15.6287	16.3817	15.8104	16.5841
Water number	M (g)	4.9033	4.9562	4.9033	4.9562
Visible density	p (g/cm3)	0.837864295	0.837355232	0.87492097	0.87819297
Average p	(g/cm3)	**0.837609764**		**0.876556971**	
Density at 20C	(g/cm3)	0.836322063		0.875153597	
API at 60F (15.5C)		37.69319281		30.1859035	

Table 5 Density Calculation

4.1.3 Distillation of Crude oil

Atmospheric and vacuum distillation performed for TB-XIX crude oil. Fraction between boiling point and 200°C is fractionated from atmospheric distillation. Boiling point was 39°C. Also, fractions of b.p-200°C, 200-350° and 350-450°C is fractionated after atmospheric distillation from vacuum distillation. Residue in flask is counted as >450°C vacuum residue. Table 4 shows the result of distillation.

Fractional Distillation		
T(°C)	Mass (g)	Percentage (%)
B.P-200	22.2106	**10.59**
200-350	58.8646	**28.07**
350-450	54.2380	**25.86**
>450	74.3868	**35.47**
Sample taken	209.700	100

Table 6 Fractional Distillation

Figure 32 Fractional distillation

Figure 32 shows heavy fraction, middle fraction and light fraction respectively from left hand side.

4.1.4 Viscosity

There are kinematic and dynamic viscosities to calculate. The kinematic viscosity is calculated by multiplying time taken to flow through viscosimeter and viscosimeter constant. Time is recorded at temperature of 40 and 30 degrees of Celsius for crude oil and 50°C for >350°C residue. Test is done 11 times and calculated the average time. It was faster to flow when the temperature is higher. Temperature for residue is set at 50°C because it was taking long time and hard to see the flow due to low viscosity.

Dynamic viscosity is calculated by multiplying kinematic viscosity by density of same temperature as kinematic viscosity. First step is to convert density of 20°C to density of 30, 40 and 50°C. This equation is used convert density: γ is correctional factor

$$\rho^{t_2} = \rho^{t_1} - \gamma(t_1 - t_2)$$

Density of crude oil at 30°C and 40°C:

$$\rho^{40} = 0.8376 - 0.000725(20 - 40)$$

$$\rho^{30} = 0.8376 - 0.000725(20 - 30)$$

Density of >350°C residue at 50°C:

$$\rho^{50} = 0.87656 - 0.000673(20 - 50)$$

Viscosity Constant C=1.016 mm2/s2	**Calculating viscosity**		
	Crude Oil		>350°C residue
	T=40°C	T=30°C	T=50°C
	t (s)	t (s)	t (s)
1	12.94	41.19	32
2	12.87	35.37	30
3	13.44	42.57	31
4	12.5	38	31
5	12.5	34.88	31.47
6	12.54	41.07	31.57
7	13.19	36.9	31.47
8	12.9	39.69	32.3
9	12.59	35.8	31.62
10	12.78	47	31.2
11	12.88	39.58	32.16
Average	12.83	39.27727273	31.43545455
Kinematic viscosity (v mm2/s)	**13.03528**	**39.90570909**	**31.93842182**
Density (g/cm3)	0.850822063	0.843572063	0.895343597
Dynamic viscosity (η MPa*s)	**11.09070382**	**33.66334133**	**28.59586147**

Table 7 Viscosity calculation

4.1.5 Flash point and pour point

	TB-XIX Crude oil	>350 Residue
Freezing point T (C)	13	17
Flash point T (C)	48	62

Table 8 Pour and Flash point

From Table 7, >350 residue has higher pour point than crude oil because residue has higher density and viscosity than crude oil.

4.1.6 Hydrocarbon content and element analyze

Hydrocarbon contents	TB-XIX Crude oil		TB-XIX >350 Residue	
	(g)	(%)	(g)	(%)
Total mass of Sample	1.0297	100	0.9538	100
Asphaltene	0.0101	0.9808682	0.0148	1.551688
lub.oil	0.937788	91.073905	0.8425	88.33089
Resin	0.081812	7.9452268	0.0965	10.11743

Table 9 Hydrocarbon content

Element analysis	Mass (%)
Carbon	84.409
Hydrogen	11.011
Nitrogen	1.254
Sulfur	0.76
Oxygen	-

Table 10 Element analysis on crude oil

4.2 Cracking of heavy residue >350ºC

4.2.1 Cracking results

Thermal cracking	2 hours		1 hour	
Sample mass (g)	15.1		12.28	
	(g)	(%)	(g)	(%)
Gas	2.460	16.291	0.800	6.515
Liquid	12.351	81.795	10.878	88.586
Solid	0.287	1.898	0.600	4.890
Total	15.098	99.984	12.279	99.991

Table 11 Thermal cracking result

Catalytic hydro-cracking	2 hours		1 hour	
Sample mass (g)	14.83		14.46	
	(g)	(%)	(g)	(%)
Gas	0.450	3.034	0.490	3.389
Liquid	14.048	94.727	13.703	94.761
Solid	0.331	2.233	0.168	1.159
Total	14.829	99.995	14.360	99.309

Table 12 Catalytic cracking result

4.2.2 Distillation of cracked heavy residue

Distillation of Thermal cracked liquid product	2 hours		1 hour	
Sample mass (g)	9.12		6.64	
	(g)	(%)	(g)	(%)
B.p-220C	1.33	14.5833	0.9	13.554
220-350C	2.51	27.5219	2.07	31.175
Residue	5.28	57.8947	3.67	55.271

Table 13 Distillation of thermal cracked liquid product

Distillation of Catalytic Hydro-cracked liquid product	2 hours		1 hour	
Sample mass	7.02		10.4606	
	(g)	(%)	(g)	(%)
b.p-220C	2.5	35.613	2.551	24.387
220-350C	2.33	33.191	3.7675	36.016
residue	2.19	31.197	4.1421	39.597

Table 14 Distillation of catalytic hydro-cracked liquid product

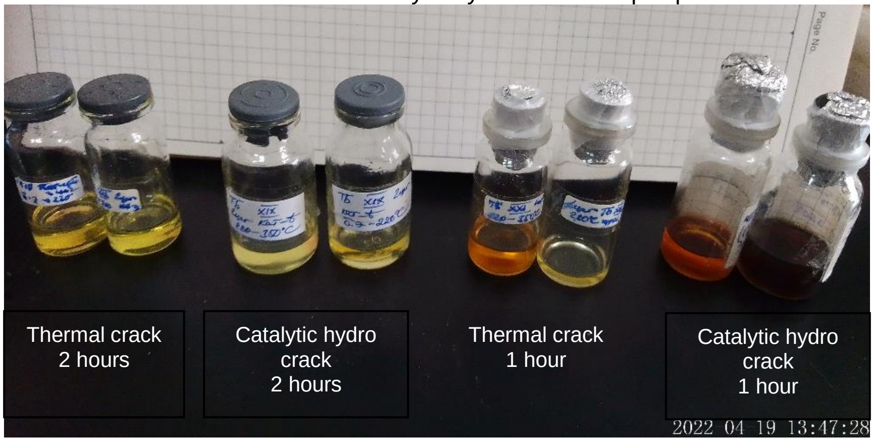

Figure 33 Light and medium fractions of cracked liquid

4.2.3 Content of hydrocarbon

Cracking	Catalytic hydro-cracking		Thermal cracking	
Time	1	2	1	2
Asphaltene	1.85	2.00	2.17	1.69
lub.oil	93.94	92.62	92.86	92.71
Resin	4.21	5.37	4.97	5.59

Table 15 Content of hydrocarbons of Cracked products

4.3 Properties of oil sand from Bayan-Erkhet deposit

4.3.1 Separation Density Ductility Softening Point Penetration Flash point

Property	Result
Bitumen content in Oil Sand (%)	14.8
Penetration of needle at 20°C (0.1 mm)	36.6
Ductility at 25°C (cm)	66.45
Softening point (°C)	55
Flash point (°C)	225
Density (g/cm3)	1.14

Table 16 Properties of Bitumen from sand oil

4.3.2 Content of hydrocarbon

Hydrocarbon Contents	Mass (g)	Mass (%)
Sample mass	1.0512	100
Asphaltene	0.0823	7.83
lub.oil	0.3527	33.55
Resin	0.5869	55.83
Loss	0.0293	2.79

Table 17 Hydrocarbon content of bitumen

Element analysis	Mass (%)
Carbon	76.974
Hydrogen	10.652
Nitrogen	1.398
Sulfur	0.57
Oxygen	-

Table 18 Element analysis of bitumen

4.3.3 Distillation of Pyrolysis product

Fractions	Content (wt.%)
b.p-220C	37.45
220-350C	51
Residue	11.55

Table 19 Distillation result of pyrolysis liquid product

5 Conclusion

1. Tamsagbulag XIX crude oil is light oil by API according to Table 3 and 5. The lower pour point (Table 8) of crude oil shows, it tends to be more aromatic. From distillation of crude oil, light fraction yield is low and >350C residue yield is high (Table 6). Lubrication oil has highest content, 91% of crude oil. Resin-Asphaltene content is low (Table 9). From element analysis (Table 10), sulfur content is 0.9 wt.% which classifies into sour crude oil.
2. Thermal and catalytic hydro-cracking tested on >350°C residue for 1 and 2 hours. Thermal cracking condition was 450°C, 4 atm of N_2 for 1 and 2 hours. Catalytic hydro-cracking condition was 450°C, 5MPa of H_2, 1wt.% Ni-Mo/Al_2O_3 catalyst and 1wt.% sulfur for 1 and 2 hours. Catalytic hydro-cracking for 2 hours yielded most light fraction and converted 65.1% (-39.977) residue into light and medium fraction. In Table 18, for 1-hour Thermal Cracking, it shows 61.3% of crude oil is >350 residue and by cracking 24.304 of 61.338 is converted into light and medium fraction.

	Initial distillation (wt.%)	1-hour Thermal Cracking (wt.%)		2-hour Thermal Cracking (wt.%)		1-hour Catalytic Hydro-Cracking (wt.%)		2-hour Catalytic Hydro-Cracking (wt.%)	
		Recovery	Total	Recovery	Total	Recovery	Total	Recovery	Total
B.P-200	10.592	7.365	17.957	7.317	17.908	14.175	24.766	20.692	31.284
200-350	28.071	16.939	45.010	13.808	41.879	20.934	49.005	19.285	47.356
>350	61.338	-24.304	37.033	-21.125	40.213	-35.109	26.229	-39.977	21.360

Table 20 Compared distillation result of cracking

3. Bayan-Erkhet sand oil deposit is unconventional heavy oil. Lubricating oil content is much lower comparing to crude oil and asphaltene, resin content is much higher. Lubricating oil is lower than 40% and asphaltene-resin content (Table 19) is more than 60% which classifies Bayan-Erkhet viscous bitumen into “asphalt”. From elemental analysis (Table 17), content of sulfur is 0.57%, it is lower than sulfur content of crude oil.

Hydrocarbon	Crude oil (wt.%)	>350 Residue(wt.%)	Bitumen (wt.%)
Asphaltene	0.98	1.55	7.83
lub.oil	91.07	88.33	33.55
Resin	7.95	10.12	55.83

Table 21 Comparison between contents of hydrocarbon if crude oil and bitumen

4. Pyrolysis test is heat up to 550°C. From 40-100°C first condensed drop collected. Between 400-550°C, gas formation was moderate. From distillation, 51% is diesel product, 37.45% is gasoline product and heavy fraction is 11.55%. Crude oil 2-hour Catalytic Hydro-Cracking has fraction of 47.36%, 31.284% and 21.36 respectively. From this comparison between pyrolyzed sand oil and catalytic hydro-cracked crude oil, pyrolysis of bitumen has higher yield of diesel fraction and light fraction. Which proves that sand oil is feasible to substitute crude oil for demand of petroleum product in the feature.

6 Reference

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