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Pre-Treatment of Heavy Crude Oils for Refining

Faith Uchenna Babalola and Alfred Akpoveta Susu

Abstract

The economic unattractiveness of heavy crude oils in the global oil market scene is fast changing due to the looming scarcity of light oils. There are huge reserves of heavy oils to which refiners are being reluctantly attracted. The fully developed conventionally available refineries are, however, incapable of processing these heavy crudes without some major modifications of both process and equipment, which will be capital intensive. This thrust promises to be very viable and yield great benefits since heavy oil is relatively cheap. Process and equipment modification begins with the required pre-treatments of these heavy crudes to facilitate efficient and cost-effective refining. Low API gravity, high amounts of impurities, and high viscosity are the major challenges addressed in the pre-treatment section. An option for a unit for the removal of some impurities for some special heavy oils is proposed. This should be followed by a multi-stage desalting unit that may be replaced with a centrifuge and a preliminary hydrotreating unit.

Keywords: heavy oil, pre-treatment, desalter, contaminants, impurities, efficient refining

1. Introduction

With the depletion in global reserves of light crude oil over the past few decades, the attention of refiners and researchers has been shifted to heavy and extra-heavy crude oils in recent times. It is estimated that global heavy oil reserves are over 3 trillion bbl, which can supply the world's energy needs for the next 100 years [1]. Refining processes for light crudes have been well developed and the products yield high economic value; this is in contrast with the more complex and more costly processing of refining heavy crudes which is less expensive but yields less attractive products. The trade-off, however, lies in the fact that these heavy crudes are currently becoming more abundant, and also with further development in their processing technologies, higher quality products will emerge and the return on investment will become quite attractive. It is estimated that there is twice the quantity of heavy crude in reserves than light crude and this ratio is most likely to increase in favor of heavier crudes.

The primary challenges in processing heavy crude oils are poor flowability due to high viscosity, low API gravity (<20°), and the presence of higher amounts of impurities than in light crudes. With treatments that increase flowability and remove impurities, the refining task is reduced to mainly cracking processes to yield desired products such as gasoline and middle distillates. Various technologies have been employed to improve heavy oil flowability in pipelines. Due to high viscosity

and hence high pressure drop, pumping cost is extremely high and so energy intensive; alternative solutions to higher pumping power include pre-heating of the crude by heating of the pipes, dilution with light hydrocarbon fluids, oil-in-water emulsification, and partial upgrading [2, 3]. Flowability enhancement technologies for transporting heavy oil are outside the scope of this chapter but are available in literature [4, 5].

Upgrading of heavy oils is achieved by either a carbon-rejection process, a hydrogen-addition process, or a combination of both. These technologies produce light oil fractions, which can be processed in conventional refineries and, therefore, also fall outside the scope of this work but can be found in open literature [6]. To enhance refining, heavy crudes are first sent to pre-treatment units either on the drilling site or in the refinery to condition them for easy processing and render them equipment-friendly.

2. Unconventional crude oils

With global changes in technology and economy come concomitant changes in the definition of conventional and unconventional petroleum crudes. Generally, today, conventional oil includes light crude oil with natural gas and its condensates, while unconventional oil consists of a wider category, including heavy oil, extra-heavy oil, oil sands, gas to liquids, and other liquids. Conventional oils are cheaper and easier to produce and process than unconventional oils. These categorizations, however, may not remain fixed over time. With technological development, resources hitherto considered unconventional may migrate to the conventional category. According to the US Department of Energy (DOE), "unconventional oils" have not yet been strictly defined [7]. In fact, it has been argued that common classification of unconventional oils based on production techniques is imprecise and time-dependent. No universally accepted definition of "conventional" and "unconventional" oil has been accepted by the International Energy Agency [8].

2.1 Heavy and extra-heavy crude oils

Heavy oils are characterized as having boiling points above 650°F (343°C). These oils are termed "heavy" because of their relatively high density or specific gravity; they also have higher viscosity and heavier molecular composition. Heavy oils have an API gravity of less than 20° [9], and in 2010, the World Energy Council defined extra-heavy oils to have an API gravity of less than 10° and a reservoir viscosity of 10.000 centipoises or less [10]. Below an API of 10°, a heavy oil will sink in water rather than float and is termed extra heavy.

Heavy oils contain asphaltenes and resins; they are dense and viscous (heavy) due to the higher percentage of aromatics and naphthenes than alkanes. They also contain high amounts of nitrogen, sulfur, oxygen, and heavy metals. They have a higher proportion of compounds with over 60 carbon atoms and, hence, higher boiling points and higher molecular weights than light oils.

2.2 Transportation of heavy crude

Most existing pipelines are designed for light crude oil transportation and so cannot accommodate heavy oil unless they are modified. To transport heavy oil in these existing pipelines, diluting or drag reducing agents (DRAs) are added to the heavy oil. Sometimes, light oil is mixed with the heavy oil to enhance flowability, which, of course, reduces the value of the light oil [5]. With modifications of the

pre-treatment unit proposed here to adequately handle water/oil emulsions, dilution with water may be a preferred method of improving flowability.

2.3 Environmental impact

Heavy oils have higher amounts of impurities and undesirable contaminants especially sulfur, metals, and nitrogen which impact negatively on the environment. Sulfur causes acid rain and combines with hydrogen to form hydrogen sulfide which is a major air pollutant. Sulfur also causes corrosion in pipelines and downstream equipment. Heavy metals, which are present in heavy oils, cause catalyst poisoning and fouling of process equipment and are toxic thereby posing disposal problems. At last, more carbon dioxide is generated both in the processing of heavy oils and in the consumption of products of heavy oil stock due to higher carbon-to-hydrogen ratio than in light oil [11].

3. Unwanted constituents and impurities

Some impurities in heavy oil occur as natural unwanted constituents of the oil, such as nitrogen, sulfur, oxygen, acids, and salts, while others are acquired by the oil during production; these include water and insoluble solids. These impurities and the processes for their removal are discussed in this section.

3.1 Effects of impurities

The impurities in heavy oil are responsible for its low economic value because they constitute a lot of problems to the pipelines, processing equipment, and the environment. Sulfur causes fouling in the equipment and environmental pollution in the form of hydrogen sulfide; nitrogen forms gums that lead to catalyst deactivation; oxygen can reduce the calorific value of the fuel; heavy metals such as nickel, vanadium, and lead are harmful to the environment and cause corrosion in process equipment and deactivate catalysts. Salts and acids also cause fouling of equipment, while insoluble solids cause plugging in pipes [1, 6, 7]. The list of the effects of impurities appears endless but suffices it to state here that the removal of these impurities is crucial to environmental preservation, process efficiency, and product quality.

3.2 Pre-treatments

Here, the various pre-treatment processes that ensure significant reduction or complete removal of impurities in heavy oils before they are taken to the refining process units are discussed. These pre-treatments mitigate downstream consequences which include corrosion and fouling of equipment, catalyst poisoning, more elaborate water treatment process, and higher energy cost. It is also worthy of note that prior to pre-treatment, the delivery system, handling and storage of the feed (heavy oil), goes a long way to affect the pre-treatment system requirements, efficiency, and cost [1].

3.2.1 Demulsifying

Crude oil emulsion is formed as dispersed water phase in an oil medium. The water globules are protected by an oil layer which prevents their coalescence. This protective oil layer increases in mechanical strength with time (aging) due to long

storage, thus stabilizing the emulsion. Agitation during transportation in pipes has a yet more stabilizing effect on emulsions due to high shear, which leads to smaller sizes of water droplets. Smaller droplets are relatively more stable than larger ones; hence, it is more challenging to demulsify the crude oil emulsion at the refinery than at the production site [12]. Chemical demulsifiers or emulsion breakers are used to break the crude oil emulsion into oil and water phases. They destroy the interfacial film and enhance the coalescence of the water droplets. Some chemical demulsifiers include amines, polyhydric alcohols, acids, and polymers [13].

The quality of a demulsifier is determined by the rate of oil separation from water, amount of water left in the crude oil after separation, and quality of separated water for disposal. It is desirable to have a fast separation rate, a low amount of residual water in the crude oil, and a low percentage of oil in the separated waste water. Both the water phase and its dissolved salt contents need to be removed because they lead to corrosion in the refinery equipment. Dehydration in thermochemical steel tanks at temperatures as low as 50–55°C is effective for demulsifying heavy oil emulsions as well as stage-wise electrode-assisted desalting units [14]. Other demulsification techniques, such as biological, membrane, electrical, and microwave irradiation, have also been employed in the oil industry [15]. Low-temperature demulsifiers in delivery and storage facilities are used to improve feedstock quality and optimize desalter operations [16]. Some factors that need to be addressed in order to enhance demulsification and oil-water separation are discussed here.

a. *Agitation*: This should be minimized during transportation, pumping, and storage and avoided wherever possible to reduce the mechanical strength of the interfacial film between the water and the oil phases. Mechanical chokes and flow obstructions can be employed to reduce agitation, though a necessary degree of agitation is required to achieve an adequate mixing of the demulsifiers into the bulk of the oil-water emulsion.

b. *Heat*: When heat is applied to an oil-water emulsion, the viscosity of the oil is increased to enhance its flow, water expands and breaks the interfacial film, there is a higher rate of droplet collision leading to faster coalescence, and density difference between the oil and the water is increased. All these result in an increased rate of phase separation. There is, however, an optimum amount of heat requirement beyond which it can become disadvantageous and lead to loss of low-boiling hydrocarbons.

c. *Time*: The retention time, during which the emulsion is held at the treating temperature, affects the separation efficiency. Longer retention time results in greater separation efficiency. Conventional crudes are treated for about 10–30 minutes, while heavy oils would require a much longer retention time [12].

d. *Solids*: The presence of solids, whether oil-wet or water-wet, has a further stabilizing effect on emulsions and so needs to be removed, especially fine particles [17, 18].

3.2.2 Deasphalting

Heavy oils contain significant amounts of asphaltenes which, if not removed, will decrease the efficiency of the refining process and reduce product quality. Asphaltenes comprise a dark brown to black solid with no definite melting point but foams and swells when heated leaving a carbonaceous residue. Their molecular weight can span from 1000 to 100,000 [19]. Some common solids such as

asphaltenes and waxes may be removed with the water after being water-wetted or dispersing them into the oil.

They contain hydrocarbons and heteroelements, namely oxygen, nitrogen, and sulfur. In asphaltenes, hydrogen-to-carbon ratio varies over a very narrow range of between 0.5 and 1.15%. Larger variations are seen in their heteroelement contents: oxygen varies from 0.3 to 4.9%, sulfur varies from 0.3 to 10.3%, and nitrogen varies from 0.6 to 3.3% [20].

The heteroatoms (sulfur, oxygen, and nitrogen) in asphaltenes cause other problems such as corrosion, catalyst deactivation, and environmental pollution. Solvent deasphalting processes have been used to significantly remove asphaltenes from heavy oils at mild temperature conditions [21]. In this process, an alkane (the solvent) is injected into the heavy oil feedstock to disrupt the dispersion of the oil components and, hence, cause the polar constituents to precipitate. Alkane solvents, most common of which is propane or a mixture of propane and butane, are used to obtain a good yield of deasphalted oil [22].

Practically, any conventional deasphalting process and equipment can be used. For example, the residual oil supercritical extraction (ROSE) process, which is currently used for residue fraction as feed, may be easily adapted and modified to accommodate the whole crude feedstocks. Some of the adaptations to address will include increasing the solvent/oil ratio, increasing the temperature, and the mixing effect, which may involve the use of pumps, mixing valves, or medium speed centrifuges. The deasphalted whole crude, after separation, may contain some of the solvents but has much less asphaltenes and metal content. The deasphalted crude stream is passed through a flash vaporization step to recover the solvent for reuse before it goes for refining [21].

The Solvahl process is a solvent deasphalting process suitable for application to heavy oils, extra-heavy oils, tar sands, and bitumen. It removes the asphaltene constituents, gives very high yields of deasphalted oil, and reduces metal content in the viscous feedstock. Various solvents used in this process include liquid propane, butane, pentane, hexane, and heptane depending on downstream process objectives and feedstock properties [23].

Solvent recovery for reuse is a crucial part of the deasphalting unit because the solvent is expensive and its ratio to the oil feed is high. Solvent recovery from the deasphalted oil is carried out at a high temperature of about 200°C. Carbon dioxide can be employed to effectively separate the solvent from the deasphalted oil at a much lower temperature of about 40°C. This is achievable due to the increase in the interaction between the CO_2 and the solvent [24].

Some classes of asphaltenes, which are insoluble in paraffin solvents, are removed using aromatic solvents. The drawback, however, is the high solvent-to-oil ratio required to remove most of the asphaltenes and the consequent high cost of solvent recovery. Asphaltene removal achieves sulfur content reduction, API gravity increase, viscosity reduction, and improvement in other oil properties. Some conventional deasphalting processes are done at the crude production site to upgrade heavy oil and bitumen but may also be carried out as a pre-treatment in the refinery. Deasphalting is achieved under high-temperature condition, which simultaneously achieves cracking and upgrading of the heavy oil. Subsurface deasphalting may be done for heavy oils using solvents but will not be addressed here.

3.2.3 Demetallization

Most crudes, especially heavy oils, contain various metals in different concentrations ranging from 1000 to a few million ppm depending on the origin of the crude. These metals are mainly sodium (Na), potassium (K), lithium (Li), calcium (Ca),

strontium (Sr), iron (Fe), cupper (Cu), silver (Ag), manganese (Mn), tin (Sn), lead (Pb), cobalt (Co), titanium (Ti), gold (Au), chromium (Cr), vanadium (V), and nickel (Ni). These metals are present either as inorganic salts or as organometallic compounds such as porphyrins. They are accumulated in resins and asphaltenes and need to be removed to their barest minimum if not completely before refining because they lead to catalyst deactivation and corrosion in equipment and contribute to "acid rain." The water-soluble salts, such as sodium chloride and magnesium chloride, produce hydrochloric acid which is very corrosive. Calcium and magnesium combine with carboxylic acid to form soaps which act as emulsifiers and so are undesirable. Most of these metals combine with naphthenic acids to form complex organometallic compounds, while others are present as oil-soluble metalloporphyrins. These metallic complexes contain asphaltenic aggregates which have low reactivity; thus, most conventional metal removal methods require severe conditions [25]. The water-soluble salts are significantly removed during the desalting step before refining. The most abundant of trace metals in crude oils are nickel and vanadium which cause catalyst poisoning. It is, therefore, easier and preferable to demetallize heavy crudes before refining. The existing methods of demetallization can be broadly classified into three, namely:

i. thermal and chemical methods, where the nature of the organic matrix is modified;

ii. solvent and adsorption methods, where the metal-containing compounds are separated from the oil; and

iii. unconventional methods, where electric fields, magnetic fields, or radiation is employed [26].

Currently, demetallization is most commonly achieved during hydrotreating, deasphalting, and hydrocracking [27]. However, the efficiencies of these processes are greatly hampered by the presence of the metals that poison the catalysts. It has been reported that for greater effectiveness in metal removal, the usual hydrotreating catalysts should be dosed with very small amounts of active metals belonging to the sixth and seventh subgroups of the periodic table [28]. The chemical reaction, by which metals (especially the more common nickel and vanadium) are removed, is given in Eq. (1). By a sequence of two mechanisms, the porphyrins are first dehydrogenated to form precursor species which thereafter undergo ring-cleavage reactions leading to metal deposition on the catalyst surface.

$$(MP) + H_2 \rightleftharpoons (MPH_2) \longrightarrow M + PH_2 \qquad (1)$$

where MP is the metalloporphyrin, MPH_2 is the intermediate hydrogenated metalloporphyrin, M is the deposited metal, and PH_2 is the resulting hydrocarbon.
Using chemical methods, metalloporphyrins react with an acid as given in Eq. (2):

$$MP + HX \rightleftharpoons MX + PH \qquad (2)$$

where MP is the metalloporphyrin, HX is the acid, MX is the metal-acid complex, and PH is the resulting hydrocarbon [28].
It is, therefore, very necessary, especially for heavy metals, that a pre-treatment step be employed to first reduce or remove these harmful metals. There are newer technologies for metal removal, such as solvent extraction, by which up to 51% vanadium and over 65% nickel can be removed using cyclohexane and other

organic solvents. Other methods include oxidation, electrochemical process, immiscible ionic liquid extraction, and adsorption [29]. Some natural and synthetic zeolites have been successfully employed to selectively remove nickel and vanadium [25, 30]. A special challenge encountered in the removal of calcium due to the presence of calcium naphthenate (CaNA) that is formed from calcium cation and the anion of naphthenic acids has been reported. An aqueous solution, containing a calcium-removal agent, was successfully employed to completely remove calcium from heavy crude oil [31].

3.2.4 Denitrogenation

Nitrogen is one of the major heteroatoms but is also present in crudes as nitrogen-containing compounds which need to be removed from crude oil to avoid downstream problems. Common nitrogen-containing compounds are mainly in form of complex structures such as porphyrins and quinolines as well as simple ones such as pyridine (C_5H_5N) and pyrrole (C_4H_5N), which are prone to free radical addition reactions to form gums and amines. These react with acid catalysts and cause deactivation [32]. Nitrogen content in most conventional oils is <0.3 wt%, but in heavy crudes, it can be as high as 1 wt% and can exceed that in some high nitrogenous crudes [33]. They are more thermally stable than sulfur compounds and so require higher heat to be removed. Though organonitrogen compounds occur at such low levels, they are undesirable because they cause catalyst poisoning in the refining process and generate a pollutant (NOx) upon combustion [34].

Hydrotreating units serve for effective denitrogenation and are the benchmark against which other methods are measured. Of the common heteroatoms, nitrogen is relatively more difficult to remove [35]. Hydrodenitrogenation removes nitrogen by forming other compounds such as ammonia, which are then separated from the oil. This method of nitrogen removal leaves the hydrocarbon part of the nitrogenous compound in the oil. A typical dehydrogenation reaction removes nitrogen in the form of ammonia as shown in Eq. (3). The common catalysts are cobalt, nickel, and molybdenum disulfide but are combined in appropriate ratios for the particular feedstock.

$$R_3N + 3H_2 \longrightarrow 3RH + NH_3 \qquad (3)$$
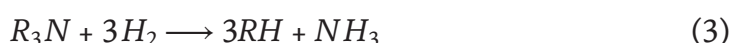
Other methods, however, are also applicable: these remove the nitrogen-containing compounds completely from the oil thereby reducing the hydrocarbon content of the oil itself. One such method is liquid-liquid solvent extraction that exploits the difference in solubility parameters and employs polar solvents, acidic solvents, ionic liquids, and deep eutectic solvents [32]. Some others are liquid-solid solvent extraction, physical adsorption and chemisorption between the solid adsorbent and the nitrogen-containing compound [36]. Adsorption beds can be packed with activated carbon, silica gel, resins, polymers, and zeolites [37, 38]. Nitrogen limit is not directly given in fuel specification but is indirectly specified as gum content, storage stability, and thermal stability.

3.2.5 Deoxygenation

Oxygen is present as one of the heteroatoms and in other forms in oxygen-containing compounds that are natural contaminants in crude oil. A wide variety of oxygen-compounds have been identified in literature. More than 20 such compounds (containing both oxygen and nitrogen) in amounts significant enough to be regarded as above trace amounts have been reported [14]. Some of these

compounds, being weakly acidic, are responsible for petroleum acidity and include carboxylic acids, cresylic acid, phenols, and naphthenic acids. Oxygen content in crude oils can vary from 0.05 to 1.5 wt%. Generally, heavy oils contain larger amounts of oxygen than light oils [39]. Naphthenic acids can be extracted using dilute caustic solutions; other oxygen-containing compounds, which are non-acidic, include esters, ketones, and amides but are quite negligible. These compounds along with sulfur are simultaneously removed during hydrotreating and other processes. Much of the unwanted oxygen is actually in the produced water, which is removed in the desalter. There is no special process to selectively remove oxygen alone from crude oil.

3.2.6 Desulfurization

Sulfur is a major drawback in the pricing of oil products because it contributes most significantly to equipment fouling and environmental pollution. Sulfur-containing compounds in crude oils vary in nature and concentration with boiling range; with the heaviest fraction, it containing the highest amount of sulfur. Compounds that contain aliphatic sulfur (sulfides and thiols) have been found easier to remove than compounds containing aromatic sulfur (thiophenic compounds), which are present in higher proportions in heavy crude oils [40]. High percentage removal of sulfur (above 70%) can be achieved using combined oxidants ($KMnO_4$-H_2O_2) in a formic acid catalyzed reaction system [41].

Conventional high-pressure hydrodesulfurization process is being replaced by more effective oxidative desulfurization (ODS) at mild conditions without hydrogen pressure but with various catalysts. ODS is sometimes assisted and further enhanced with ultrasound technology and the use of ionic liquids [42]. This has become necessary due to the shift in global oil supply from light to heavy oil, which usually has higher sulfur content. Microwave irradiation can also be used as a pre-treatment for heavy crude oil where the sulfur content is not relatively high though fragmentation and recombination reactions may not be avoidable [43]. Currently, however, most desulfurization processes are carried out during refining and not as a pre-treatment (except for crudes with very high sulfur content), and if as a pre-treatment, then it serves also to upgrade the feedstock.

3.2.7 Desalting

The desalting process derives its name from the fact that soluble salts in the crude oil enter the aqueous phase and are easily removed by phase separation in the desalter. The wash water to oil ratio is 3–4 for light oils of API > 30° and 7–10 for light oils of API < 30°; a pH of 6 is ideal for the wash water and may be adjusted using caustic soda or acid [44]. For the case of heavy oils, however, with API < 20° but >10°, much higher water volume ratios will be required.

The desalting unit is where virtually all the aforementioned pre-treatments take place to some extent apart from the deasphalting step. For heavy and extra-heavy crude oils, however, there may be need to include one or more of the above specific pre-treatment steps to be carried out before the general desalting process. This may be warranted if the heavy oil has a peculiar need for such a step; otherwise, a two or three stage desalting unit may very-well serve all the purposes needed to achieve about 90% removal of contaminants from the heavy crude. This is because heavy crudes have higher proportions and wider ranges of contaminants such that a one-stage desalting process alone will not be adequate to pre-treat them for efficient refining [1]. In a typical single-step desalting unit as shown in **Figure 1**, the crude oil is pumped from storage through a heater, and fresh water, dosed with demulsifying
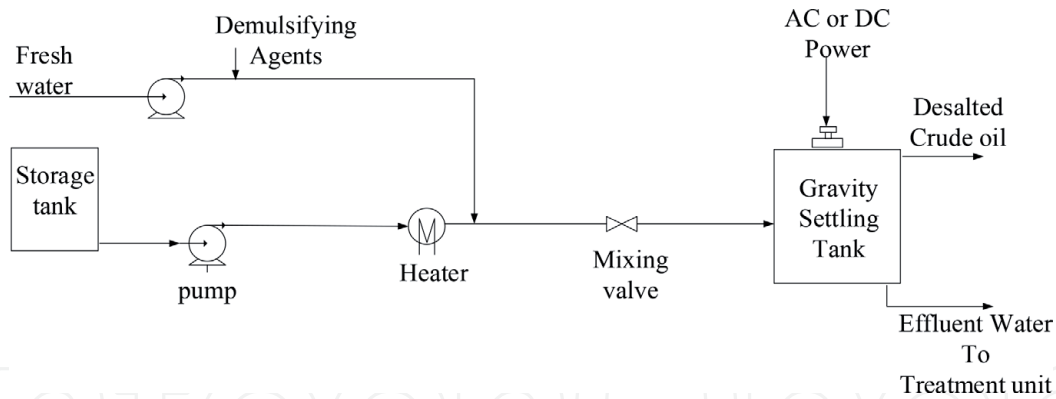
Figure 1.
Single-stage desalting unit.

agents, is added to the oil stream, which goes through a mixing valve for proper mixing. The stream then enters the gravity settling tank, where the water phase settles by gravity at the bottom of the tank, while the oil phase remains above it.

The separation of the oil from the water phase in the gravity settling tank is often aided by installing two electrodes between which an electrostatic AC or DC field is created with a potential of between 12,000 and 35,000 volts [45, 46]. These values are, however, most likely going to increase significantly in the desalting of heavy oils. The electrostatic field promotes coalescence of water globules and enhances separation. Effluent water is sent to water treatment unit, while the desalted crude is drawn from the top of the settling tank to the refinery for processing.

For heavy crude oils, however, except for crudes with exceptionally low amounts of contaminants, the desalting unit given in **Figure 2** is recommended, where the subunits in blue outlines are included for necessity. As the crude is pumped from storage, part or all of it is first diverted to a special treatment unit as the special need of the particular crude may require.

3.2.7.1 Special treatment unit

The traditional desalting and dehydration process was fully developed for light crudes of relatively high API gravity and low viscosity, but with the proportional increase in available heavier crudes, modifications have become necessary for effectiveness and efficiency in the desalting process. Heavy oil, especially with high contaminants, may be desalted after it is passed through its own special purification unit to significantly reduce the particular contaminant in question. For example, heavy oil with very high sulfur content can be first passed through a microwave irradiation unit before desalting [43]. Also, an adsorption packed bed with appropriate zeolite grades could be used to selectively reduce metal ions for a heavy crude, which is contaminated with a specific heavy metal [25]. Another possible case is a minor deasphalting unit using solvent extraction [21].

From the special treatment, the fresh water with demulsifying agents is added before the back-mixing by the mixing valve and then the stream flows to the first gravity settling tank. With the obvious need for a second gravity settling tank, the oil is sent to it for further separation, while the effluent water from the first settling tank is sent to water treatment unit. The desalted oil from the second tank goes to the final step in the pre-treatment section which is the hydrotreatment unit before it is sent to the refinery for processing, while the water from the bottom of the second tank is recycled as shown (**Figure 2**). This proposed arrangement is expected to achieve excellent results for the pre-treatment of
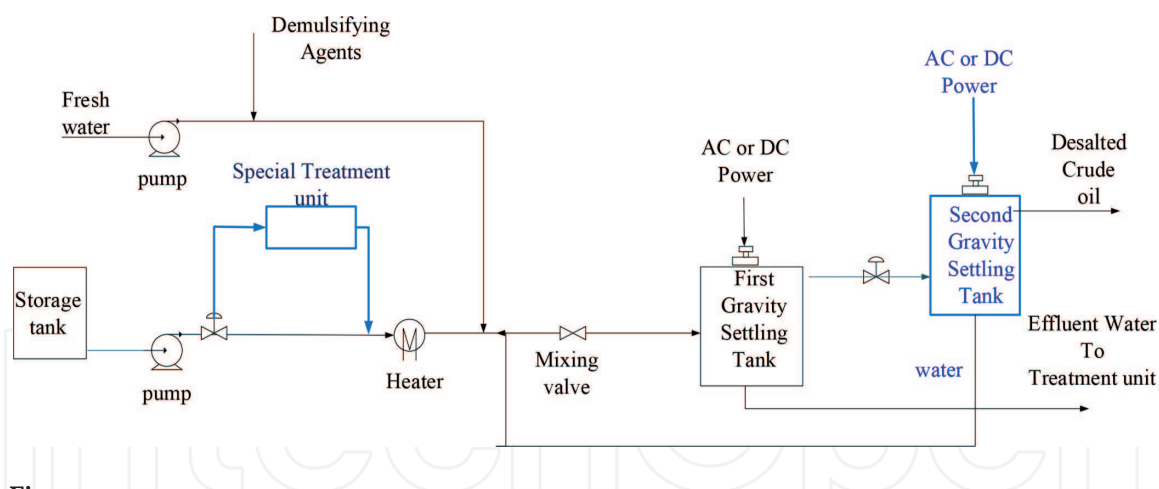
Figure 2.
Two-stage desalting unit with special treatment option.

heavy crudes. This special treatment unit may be bypassed if it is not required for a feedstock with minimal contaminants.

3.2.7.2 Multi-stage desalter

Heavy oils contain higher percentages of impurities and contaminants which cannot be removed by the conventional single-stage desalter. A two- or three-stage desalting unit will be required depending on the degree of contamination. A two-stage desalting unit is shown in **Figure 2**.

3.2.7.3 High-speed centrifuge

The limitations of the desalting process when treating heavy crude oil of API gravity of less than 20° and greater than 10° and of high viscosity can also be overcome by using a high-speed centrifuge. Well-designed high-speed centrifuges combine efficiency, reliability, product quality, and environmental friendliness. Gravity settling tanks are not very effective with heavy crudes even with the aid of an electrostatic field (AC or DC) due to their high viscosity. With a single-stage centrifuge technology, excellent separation between the oil and water phases is achievable [1]. The use of centrifuges leads to lower costs in energy consumption (in the electrostatic field), lower temperature and pressure in the operating conditions of the desalter, and less material and handling costs due to lower water-oil ratio and less amounts of demulsifying agents.

3.2.8 Hydrotreating

Hydrotreating is one major way of removing sulfur and other contaminants present in crude oil fractions. It can be applied at different stages of the refining process to different streams as required [47]. For the pre-treatment of heavy oils, however, hydrotreating needs to be employed primarily in its simplest form to significantly reduce or remove sulfur which can be as high as 8% by weight [19]. This unit is recommended to be placed immediately after the desalting tank and so serve as the last unit in the pre-treatment section before the refining process. Here, the desalted oil is mixed with hydrogen and heated to between 340 and 425°C, pressurized to about 14 MPa, and then passed over a suitable catalyst. Some commonly used catalysts are mainly cobalt, nickel, and molybdenum oxides

on alumina. Biocatalysts have also been explored but have not yet become commercially attractive [32, 42, 44, 48].

In the hydrotreating unit, the primary target element is sulfur but many of the contaminants, which have been discussed earlier, are also removed simultaneously through several reactions as mentioned below:

- *Hydrodesulfurization* (HDS) reaction, which occurs between sulfur-containing compounds and hydrogen, leads to the removal of sulfur in the form of hydrogen sulfide. Eq. (4) shows such a reaction between ethanethiol (C_2H_5SH) and hydrogen (H_2). The hydrogen sulfide gas is captured and converted into elemental sulfur and sulfuric acid.

$$C_2H_5SH + H_2 \longrightarrow C_2H_6 + H_2S \qquad (4)$$

- *hydrodenitrogenation* (HDN) by which nitrogen is removed mainly as ammonia;

- *hydrodemetallization* (HDM) by which metals are removed by being deposited on the catalysts;

- *hydrodeoxygenation* (HDO) by which oxygen is removed as water; and

- *hydrodearomatization* (HDA) by which olefins, naphthenes, and aromatics get saturated with hydrogen and become paraffins. Minor cracking also takes place to produce light alkanes.

The numerous products from the hydrotreating unit (HTU) are cooled using a series of heat exchangers then charged into a high-pressure gas separator, where hydrogen sulfide, ammonia, and the unreacted hydrogen are separated from the hydrotreated crude. The gases are sent to a scrubber with ethanol amine or other basic solutions to remove hydrogen sulfide for sulfur recovery, while hydrogen is recycled [49].

4. Modification requirements for heavy oil pre-treatment

Crude oil pre-treatment is a requirement before refining to remove contaminants which may be naturally part of the crude or acquired during production. A simple single-stage desalter can achieve sufficient purity when handing light crudes [16]. For heavy crudes, however, it is imperative to introduce some modifications since the conventional desalter will not be adequate. These modifications begin with the storage and pre-treatment process and extend all the way to the refining process and equipment. In the pre-treatment unit, a packed bed to achieve a significant degree of deasphalting, demetallization, deoxygenation, or denitrogenation should be introduced as an option at the beginning of the process depending on the particular need of the feedstock. The gravity settling tank (desalter) should be in two stages or may be replaced with a single high-speed centrifuge desalting tank. After desalting and the separation of the oil from the water phase, the desalted crude oil can then be partly hydrotreated in a mini hydrotreatment unit, particularly for heavy crudes with very high sulfur content. This applies to heavy crudes with >10–20° API gravity. **Figure 3** shows a schematic diagram of our proposed modification of the pre-treatment unit for efficient handling of heavy crude oil.
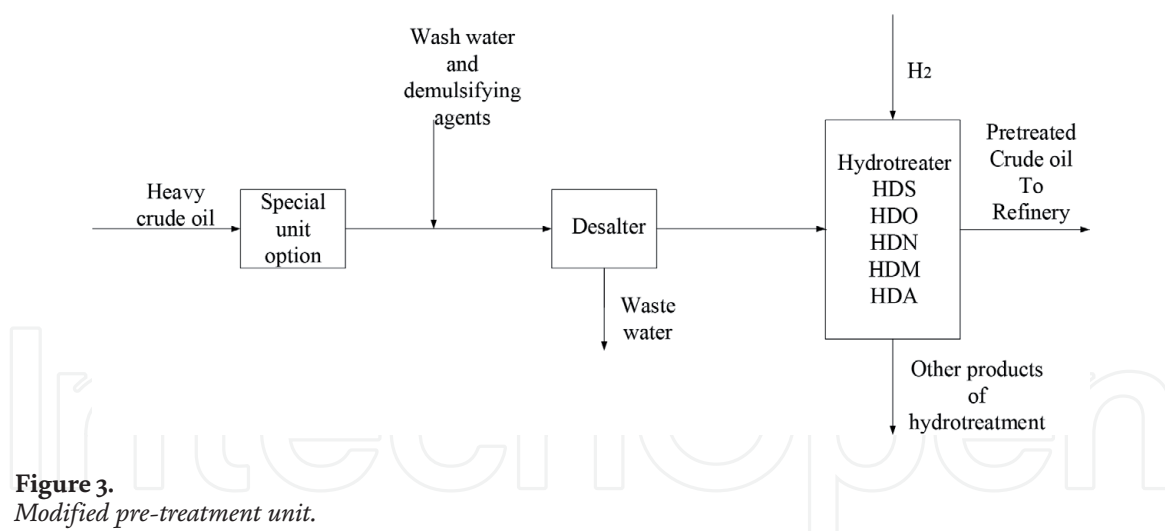
Figure 3.
Modified pre-treatment unit.

In the near future, extra-heavy crudes with an API gravity of <10° will be desalted in units with yet further modifications. This is because the API gravity of water is 10° and a crude with 10° API cannot be separated from the water phase by gravity. For extra-heavy oil, however (API < 10°), gravity settling tanks or centrifuges will still serve for phase separation; but in this case, waste water will be drawn from the top of the tank, while desalted crude will be drawn from the bottom.

5. Cost implications

Currently, heavy crude oil is more expensive to produce (upstream) but yields less economic returns to the producer because of the challenges encountered in its processing and the lower quality of its products; on the other hand, lighter crude is cheaper to produce and easier to process, and therefore, it is more expensive. With the economic turn of events lately, much of the global lighter crude reserves have been greatly depleted, while heavy crude reserve is in over-abundance, and refiners are now beginning to prefer to buy heavy crudes which are cheaper and modify their processes and equipment which is capital intensive. There is, however, a trade-off because the process modification is a one-time investment, while the long-term good product yield eventually compensates with a high return on investment. The development of new technologies for processing heavy oils needs to be rapid enough to forestall the effects of the dwindling supply of conventional crudes. It is also expected that in the course of process modifications, new technologies will serve to significantly reduce anticipated cost and favor heavy oil production. For example, in a modified desalting unit, the use of a high-speed centrifuge eventually results in significant savings in energy and material cost. This is due to lower temperature and pressure conditions, less amounts of required demulsifying agents, less quantity of wash water, and therefore less waste water generation. As refiners invest more in processing heavy oil, producers will more likely be motivated to invest in its production. The economic face of the oil market is likely to experience new paradigms as heavy oil processing technologies begin to compete with light oil refineries. For light oils, cost of refining, depending on oil configuration and refinery size, can vary widely from 4 to 15 USD/bbl, while for heavy oils, it is in the range of 20–22 USD/bbl [50, 51].

In basic refinery economics, the cost of crude oil and the price of refined products are highly volatile and nearly unpredictable because they are affected by economic, political, and environmental factors. Since refiners have no control

over these factors, operational efficiency, which is measured by the ratio of output to inputs, is the basis for profit maximization and can be increased through continuous innovation [50]. As a determinant of profitability, facility expansion for complexity to handle a wider variety of feedstocks can impact on profitability up to the tune of 0.5 USD/bbl [51]. This implies that modifying the pre-treatment section of a refinery to handle heavy crude oils for efficient refining into "attractive" products is economically favorable. Since heavy oils are cheaper than light oils and the cost of crude oil is the largest input cost of a refinery, processing cheaper crudes into higher-value products through process modification usually improves profit margins. The increased global demand for lighter petroleum products made from heavier crudes (quality gap) drives downstream investors toward more complex refineries. A refinery's complexity is measured by its range of capacities to "add value" by its processes to a crude feedstock. The most common cost-based measure of complexity for refineries is the Nelson Complexity Index (NCI). It provides a relative measure of the construction cost of a refinery based upon its capacity to upgrade. The simplest topping refinery is assigned an index of 1.0 against which all others are measured. The higher the NCI number of a refinery, the more its complexity, cost, and capacity to add value to crude feedstocks. Since 2005, global trends have been toward refineries of higher complexities through newer technologies; hence, older refineries with low NCI numbers are fast fading out as lower-value crudes (such as heavy oils) increase in relative abundance. A refinery with a fluid catalytic cracker, alkylation, and hydrotreating units has an NCI of about 7.0, while an inclusion of hydrocracking, coking, and reforming units can raise its NCI number to about 14.1 [51].

For the pre-treatment section, therefore, the proposed necessary modification here will definitely cause a minor increase in the NCI number of the refinery due to the additional pieces of equipment. An overview of NCI numbers of complex refineries shows a wide range from 5 to 14 [52]; therefore, it is estimated that the pre-treatment section contributes only about 1–1.5% of the total NCI number and, hence, total cost of the refinery. The bulk of the refinery cost is in the refining processes and not in the pre-treatment; consequently, the pre-treatment equipment cost is certainly less than 2% of the total cost of the refining equipment with the modification proposed in this chapter even for pre-treating the most challenging heavy oil feedstocks.

6. Conclusion

It can be concluded from the issues discussed in this chapter that a modification of the conventional oil pre-treatment unit is required to ensure the adequate removal of impurities from heavy crude oils. First, a special optional unit is introduced at the beginning of the pre-treatment unit to treat crudes with any extremely high level of a particular contaminant such as heavy metals, asphalt, or sulfur. Second, the desalting stage is carried out in two stages aided by electrostatic fields, and third, the desalted crude is sent to a mini pre-hydrodesulfurization unit before it goes for proper refining. With high purity of pre-treated crude, refining processes will be enhanced, product quality will improve, and downstream problems will be reduced to their barest minimum or completely eliminated.

Conflict of interest

The authors declare no conflict of interest.

Appreciation

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