LITERATURE SURVEY

2. LITERATURE SURRVEY

Petroleum heavy distillates and residues are necessary raw materials for the production of valuable light fuel products. The efficient conversion of these resources to useful products requires knowledge of the chemical compositions of the complex mixtures. A great deal of efforts has been exerted by petroleum chemists to develop analytical methodologies to obtain detailed structural information on petroleum fractions.

The composition of the crude oils becomes more complicated as the boiling range of the components increases. The structural diversity of the hydrocarbons increases astronomically with molecular weight. Thus, the extreme sample complexity of heavy fractions makes compositional analysis by the isolation of individual compounds a practical impossibility. Therefore, separation and isolation must be accomplished in the structure features of the compounds rather than the individual compounds.

Major work in the compositional and structural analysis of high boiling petroleum distillates (360 – 525 0C) was implemented in the early 1970s under API project 60, to support an upgrading program in the US refinery industry [1-6]. An analytical scheme was developed for the separation and identification of major component types in the high-boiling distillates of crude oils. Since then, petroleum chemists have been modifying the API project 60 in order to develop more efficient and less time-consuming separation and characterization methods [7-11], applied high performance liquid chromatography (HPLC) for the separation of olefins, saturates and aromatic hydrocarbons from the high-boiling distillates and residues of shale oil and whole shale oils. Hsu *et al.* [12] successfully utilized the ultrahigh resolution capabilities of Fourier Transformer Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) for measurement of complex hydrocarbon mixtures.

Hydrodesulphurization of residues in fixed-bed processes is a well-established residue upgrading process which requires specific catalysts designed to desulphurize the feed and to remove contaminants [13-15]. Until recently the aims of these processes were mainly to produce fuel and distillate satisfying the specifications imposed by regulations, notably for SO_x emissions of power plants. These specifications are going to be even more drastic in the near future and will require more severe hydroprocessing of residues.

The increasing severity of the products specifications as well as the change in the demand of products will lead to a shift of the main objective of residue upgrading processes from hydrodesulphurization (HDS) to conversion. In addition, improvement of hydrodenitrogenation (HDN), aromatic hydrogenation (HDA), and Conradson carbon reduction (HDCCR) performances will be sought after in order to reduce better feeds for residue catalytic cracking units (RCC).

R. Santamaria-Ramìrez and others [16] studied the Pyrolysis of three petroleum pitch residues of different aromaticities under varying experimental parameters of pressure, temperature and soak time in order to provide detailed information of factors which influence formation of anisotropy or mesophase in the resultant semi cokes. Carbon anodes for aluminium industry and graphite electrodes for the steel industry, as well as many smaller applications, use delayed cokes (sponge- and needle-coke) as major constituents in their formulations [17]. In turn, delayed cokes are made by the industrial processes of delayed coking, where selected petroleum residues or feedstocks are heated in vertical cylindrical drums at inlet temperature of about 500° C. The feedstock is converted to a coke (of varies qualities) via a mechanism involving the formation of mesophase [18, 19].

Greinke [20] reviewed the early stages of the chemistry of petroleum pitch carbonization (kinetics and mechanisms), and referred to the important of mesophase formation. Mochida *et al.* [21] reviewed the chemistry and industrial operations in the production and utilization of delayed cokes. Ultimately it is the

chemistry of the Pyrolysis system which controls the structure and properties of the resultant semi cokes / cokes / carbons. But, the chemistry, in turn, is a function not only of the chemical properties of the original feedstocks, but also of the physical parameters incorporated into the system, such as carbonization capacity (size of the reactor), heating rate, soak time, final reaction temperature and the pressure within the system. Dependent on how the Pyrolysis system is constructed, e.g., whether or not volatile material is lost from or retained within the Pyrolysis system, these physical parameters control the chemical composition of the feed stock as it paralyzed through to a semi coke [22, 23].

Romero-Palazón [24] and Rodrìguez-Reinoso *et al.* [25] showed how multiphase systems within bulk paralyzing systems influence coke quality and how gas evolution (amount and temperature of evolution) also influence coke quality, controlling how and when mesophase formation occurs. Santamarìa-Ramìrez *et al.* [22,23] surveyed those effects, chemical and physical, which influence mesophase growth and coalescence of mesophase within semi cokes.

The effectiveness of the conversion of petroleum feedstocks into more valuable products is adversely affected by crude oil tendency to form coke as measured by carbon residue content (Micro Carbon Residue Test – MCRT). Heavy crudes have high MCR (Micro Carbon Residue) content and thus are expensive to refine. Metals, particularly vanadium and nickel, also adversely affect crude oil conversion processes by poisoning catalysts. Sulfur and nitrogen are also undesirable and must be removed from crude oil to meet the stringent requirements for high-value fuels. Both desulphurization and denitrogenation processes are expensive as they require large amounts of expensive hydrogen [26].

2.1. Composition of Heavy Residues:

Petroleum heavy distillates and residues are valuable raw materials for the production of fossil fuel products. The efficient conversion of these resources to useful products requires a knowledge of the chemical composition of the complex

mixtures. The previous work in this laboratory involved the development of methods for the separation and analysis of compound types in high-boiling petroleum distillates [27- 30]. As an extension of this work, McKay *et al.* in a series of three papers [31, 10, 11] describe the separation and characterization of petroleum residues.

Much of the previous characterization work on petroleum residues and asphalts has been performed [32-35]. The separation of these high-molecular weight mixtures becomes possible as chromatographic techniques were developed. Kleinschmidt [36] developed a method to separate asphalts into fractions of asphaltenes, white oils, dark oils, and asphaltic resins. The separation of asphalts using the method of Corbett [37], produces fractions of saturates, naphthenes, aromatics, polar aromatics, and asphaltenes. The "SARA" method developed by Jewell and co-workers [38] separates petroleum residues into fractions of saturates (S), aromatics (A), Resins (R), and asphaltenes (A). Bunger [39] modified the separation techniques developed by the API project-60 to separate both tar sand bitumen and petroleum residues into seven non-hydrocarbon fractions and two hydrocarbon fractions. The properties, characterization and issues of petroleum asphaltenes were briefly reviewed by Eric [40].

2.2.Characterization of Asphaltenes Molecular Structure:

It is well-known that asphaltenes, the heptane - insoluble / toluene - soluble fraction of oil, are the cause of an array problems associated with either thermal and catalytic processing of petroleum residues or recovery of crude oil. With respect to catalytic hydroprocessing, asphaltenes adversely affect the overall rate of hydrodesulphurization [41], act as coke precursors which in turn lead to catalyst deactivation [42], and may limit the maximum level of conversion achievable in hydrocracking process due to sludge formation [43]. Asphaltenes are also responsible for the high viscosity of residues [44] and, in the case of tiebreaking, both the process severity and the stability of the product strongly depend on the asphaltenes content of the feed stock and its tendency to form coke. Finally, the

tendency of asphaltenes to precipitate during crude oil recovery can cause a sharp decline in oil flow or even blockage of the well [45].

In the above circumstances, structural characterization of petroleum asphaltenes is a subject of considerable interest since a deeper knowledge of their molecular structure can be a valuable aid in achieving a better comprehension of their behavior during conversion processes and crude oil recovery. Elucidation of structural characteristics of the asphaltenes has been a subject widely investigated by means of numerous analytical techniques, and different models have been proposed [46, 47]. Dickie and Yen [48], mainly on the basis of results of X-ray analysis, proposed that petroleum asphaltenes consist of large sheets containing 100 – 300 carbon atoms and joined by aliphatic chains, Figure-1. Subsequently the use of proton nuclear magnetic resonance (^{1}H NMR) spectroscopy in conjunction with other analytical techniques [49 – 53], such as infrared (IR), and gel permeation chromatography (GPC), led to a picture of asphaltenes molecules consisting of one or more fused ring systems with a lower degree of condensation and containing naphthenic structures associated with the aromatic core. Unit sheets of moderate size are seen as joined by aliphatic bridges and bearing alkyl side chains with an average length between 4 and 5 carbon atoms. The simultaneous use of ^{1}H NMR and ^{13}CNMR allowed a more accurate determination of several average structural parameters such as the aromatic carbon fraction, the average number per alkyl side chain and the percent of substitution of aromatic carbon [54, 55]. Lately, the application of more sophisticated NMR techniques, provided a more detailed description of carbon–type distribution [56– 58].

Gel permeation chromatography (GPC) has been extensively used for molecular size determinations of large molecules such as petroleum asphaltenes[59-61]. GPC separates molecules on the bases of linear molecular size, and the samples elute in decreasing order of molecular length. The GPC has previously been used to separate a wide range of molecular sizes in coal derived liquids which are a complex mixture of hydrocarbons similar to heavy petroleum

crude. One of the limitations of GPC is that the total number of peaks which can be resoled is limited compared with other modes of liquid chromatography.

However, relatively larger samples can be analyzed without sacrificing much of the resolution in 20 to 40 minutes. Unlike adsorption chromatography, in most cases, GPC columns do not retain any portion of the sample for all practical purposes. Regardless of the molecular size distribution, the analysis time is dependent on the solvent flow rate and the number of columns used, not on the sample size.

To get more information from set of experimental data, several mathematical methods which combine data from NMR, elemental analysis, molecular weight determinations and density measurements have been proposed [62 – 65].

With the decline of conventional crude oil production, procedures have begun to exploit heavy oil reservoirs and offshore fields resulting in increased production problems associated with asphaltenes deposition. These asphaltenes deposits have the potential to disable production operations anywhere from the oil reservoir to the production lines and storage tanks. To develop effective methods for mitigating asphaltenes deposition, it is first necessary to model asphaltenes measurements of asphaltenes properties such as molar mass and density as well as some precipitation data with which to tune the model.

It has proven difficult to achieve consistent asphaltenes property measurements because they are a solubility class and not a pure component. Typically, crude oils are separated into four solubility fractions, illustrated before, namely, Saturates (S), Aromatics (A), Resins (R), and Asphaltenes (A) (SARA). The saturates generally consist of naphthenes and paraffins. The aromatics, resins, and asphaltenes appear to form a continuum of polynuclear aromatic species of increasing molar mass, polarity, and heteroatom content. There is no clear distinction between asphaltenes and resins. Consequently, the amount of

asphaltenes extracted from a crude oil depends on the type of solvent, dilution ratio, contact time, and temperature [66].

The effect of time on the amount of asphaltenes is shown in Figure-2. The yield increases over the first few hours reaching a plateau after approximately 24 hours. Figure-3 shows the effect of adding more solvent, i.e., increasing the solvent-to-bitumen ratio. The yield increases and reaches a plateau at solvent-to-bitumen ratios above approximately 25 cm^3/g. the amount of precipitation depends on the solvent, for example, the precipitation curves in Figures (2 & 3) shift upward as the carbon number of an *n*-alkane solvent decreases below seven. The curves shift downward as temperature increases since the solubility of the asphaltenes increase with increasing temperature [67].

The importance of temperature solvent, solvent-to-bitumen ratio, and contact time is well established and standard separation procedures have been developed in an effort to obtain consistent asphaltenes fractions. It is general practice to use *n*-pentane to extract asphaltenes if the de-asphalted oil is to be further subdivided by adsorption chromatography into resins, aromatics, and saturates. If higher-carbon-number alkanes are used, less asphaltenes are separated and significant amounts of residual *"Asphaltenic Resins"* adsorb permanently on the chromatographic column. *n*-heptane is commonly used as the separating solvent for asphaltenes studies because asphaltenes properties do not vary significantly with the carbon of the solvent for *n*-heptane and higher-carbon-number alkanes [68]. A solvent-to-bitumen ratio of 40 cm^3/g. is used for most separation methods and the recommended contact time is 12 to 16 hours for *n*-pentane and overnight (16 to 24 hours) for *n*-heptane separation. In most cases, separation is carried out at ambient conditions for convenience.

The final step in most separations, washing the asphaltenes filter cake with solvent, is not standardized. Asphaltenes properties can be very sensitive to small amounts of resins and therefore may be sensitive to the amount of washing. Alboudwarej and others [69]. Studied the sensitivity of asphaltenes properties to

separation techniques. They extracted asphaltenes with three different levels of washing from four source oils. In all cases, increased washing decreased asphaltenes yield and slightly increased both asphaltenes density and molar mass, while decreasing the solubility of the extracted asphaltenes. They also used the Soxhlet method which removed the largest amount of resinous material and yielded asphaltenes with significantly different properties from conventionally washed asphaltenes. Since more resinous materials removed, the Soxhlet method allows a more direct comparison between asphaltenes from different sources.

Studies of the nature of trace element species have demonstrated that the asphaltenes are the major trace element host, although chemical species have not been determined [70,71]. Except for vanadium, little is known about the bonding of metals in the asphaltenes structure although heteroatoms (N, S, and O) are probably involved. By definition, petroleum asphaltenes comprise the portion of crude oil or oil-sand bitumen that precipitate on addition of an excess of low-molecular weight straight-chain alkane solvent [72 –74], such as pentane or heptane. Petroleum asphaltenes are brown to black, amorphous solids of high molecular weight and contain small amounts of nitrogen, sulphur and oxygen. (generally less than 10 weight percent) present in part in functional groups that may be involved in metal complexing. Several models have been proposed concerning that physical and chemical nature of asphaltenes in oil-sand bitumen and crude oils. Speight and Moschopedis [74] proposed that the individual asphaltenes molecules are effectively dispersed in the hydrocarbon matrix by the resins, which provide a structural transition from the complex polar asphaltenes to the less polar hydrocarbon matrix. Other authors [75, 76] have obtained results which suggest that asphaltenes are not physically different in nature from the non-asphaltenes (e.g., the resins) in the hydrocarbon mixture and are dispersed or interspersed throughout the petroleum matrix. Asphaltenes have also been considered as colloidal suspensions with the colloidal particle, or micelle, being comprised of clusters of asphaltenes molecules associated principally via $\pi - \pi$ interactions [77–79]. In a study of the colloidal nature

of crude oil by ultracentrifugation, it was concluded that asphaltenes precipitates contained substantial amounts of Maltenes and that some asphaltenes were strongly retained in the Maltenes solution [80]. These studies confirm that there is no qualitative difference in the physical nature of the asphaltenes and resins.

The principal factor in determining whether a species precipitates as an asphaltenes is the physical chemistry of the solution under the conditions of separation [81]. The composition of the asphaltenes precipitated depends on the nature and proportion of straight-chain alkane used as a solvent, and in general, the amount of precipitate recovered decreases with increasing alkane carbon number [82]. Speight and Long [73] and Long [72] consider that asphaltenes precipitating with a given straight-chain alkane consist of two types of molecules, namely, less polar materials of higher molecular weight and more polar materials of lower molecular weight. These two "end-members" would represent a range of compounds precipitated with a given solvent.

Chromatographic separation of asphaltenes has played an important role in the elucidation of asphaltenes structure [75, 83-85]. Most of the chromatographic characterizations of petroleum asphaltenes have been done with size exclusion chromatography (SEC) to separate asphaltenes on the basis of molecular size. This method of separation is subject of certain limitations: *FIRSTLY*, the technique separates on the basis of molecular size rather than molecular weight, *SECONDLY*, there is a lack of suitable well characterized homologous series of compounds for calibration purposes, as has been noted by Dark [86], and *THIRDLY*, there is the possibility of adsorption of highly polar petroleum components on chromatographic substrates. Little work has been reported of separation based on functionality other than on acid-base behavior [11].

Long and Speight [73], Long [72], and Speight *et al.* [87] have attempted to define asphaltenes and have proposed a classification scheme for asphaltenes based on functionality as well as molecular weight and these authors note that chromatographic separation of asphaltenes with solvents of increasing polarity

provides a method of classifying asphaltenes. Such a classification relates asphaltenes properties (i.e., solubilities) to composition (i.e., nature of functional group, heteroatom contents, molecular size, etc.) and represents a useful concept for relating the nature of trace element species in asphaltenes to composition.

Large proportions of crudes processed in oil refineries are set aside as distillation residues which are of relatively little commercial value. Therefore, more detailed structural characterizations are necessary before improved process routes to upgrade these materials can even be contemplated. Vacuum residues are complex hydrocarbon mixtures, their more intractable parts are the more polar and larger molecular mass components. The latter are less abundant compared to the lighter and better-known components of crude oils, but are more difficult to characterize and to upgrade.

Most analytical techniques applied to complex mixtures, however, suffer from the masking effect of the more abundant materials on the less abundant components. Fractionation is, therefore, a necessary first step in attempting to obtain more complete descriptions of the larger mass and more polar fractions in residues and tars [88, 89]. Suelves *et al.* [90] have compared molecular mass distributions and several structural features of two petroleum vacuum distillation residues and their fractions. The residues have been fractionated using solvent (n-heptane) separation and Column Chromatography. The residues and the separated fractions have been characterized by size exclusion chromatography (SEC) and by ultraviolet-fluorescence spectroscopy (UV-F).

Liquid adsorption chromatography on classical adsorbents is most often used for the group analysis of high-boiling petroleum fractions, i.e., their separation into saturated hydrocarbons, mono-, di- and polyaromatics, and polar aromatic compounds. Gustav and others [91] studied the optimization of the preparative separation of petroleum Maltenes by liquid adsorption chromatography on dual silica gel-neutral alumina column. the conditions of this separation, i.e., the volume of the mobile phases used, their composition and flow-rate were optimized

on the base of detailed analysis of the chromatographic fractions obtained using elemental analysis (carbon, hydrogen, nitrogen and sulphur with oxygen by difference), UV spectrophotometry, ^{1}H NMR and vapor pressure osmometry.

Column chromatography [92] is often used in the group-type analysis of heavy petroleum fractions, but the resolution between group-types is often poor because the properties of adsorbents vary from one brand to another brand, even from one batch to another batch, and there is no adequate detector for monitoring the separation procedure. The mass spectrometry (MS) group-type method (ASTMD 2786, ASTMD3239) can provide more detail compositional data for vacuum gas oil (VGO). If, however, the composition of the sample is different from that assumed by the method, the results may be very inaccurate [93]. Yongzhi *et al.* [94] used preparative liquid chromatography (LC) with two columns (Silica Gel and Alumina) to separate vacuum gas oil (VGO), Coker gas oil (CGO), and heavy cycle oil (HCO) into saturates, monoaromatics, diaromatics, polyaromatics and resins. the separation procedure was monitored on-line by refractive index (RI) detector and ultraviolet (UV) absorption detector and monitored off-line by synchronous fluorescence spectrometry. To confirm the separation between fractions, they analyzed some fractions by gas chromatography (GC) and mass spectrometry (MS). Finally they compared the separation results from their studies with the MS group-type methods (ASTM D 2786, ASTM D 3239).

In the history of the evolution of the petroleum science and technology, the use of the true boiling point (TBP) distillation to establish the property – yield curve and the use of Universal Oil Products (UOP) K factor as a criterion of classification and correlation of properties of petroleum products was accepted as a common practice [95]. However, due to the limitations of the TBP and UOP factor, they have difficulties when applied to the characterization of heavy petroleum residua, hence a new method based on the supercritical fluid extraction and fractionation (SFEF) and a new characterization factor, UOP K_H was

proposed and had shown some success. For the assay of the properties of natural petroleum and petroleum products, the use of the **TBP** distillation analysis was accepted as a common practice, and has been proven very useful for design and operation of refinery units. For the characterization and correlation of properties of petroleum and petroleum products of various origins, the **UOP** factor was introduced by Watson and Nelson in 1933 [96] as:

$$K = \frac{\sqrt[3]{T_{BR}}}{S} = \frac{1.216\sqrt[3]{T_{BK}}}{S}$$

Where T_{BR} is the average boiling point, [° R = ° F + 460], T_{BK} is the average boiling point [K = ° C + 273], S is the density of petroleum products at 15.6° C referring to the density of water at 15.6° C. The TBP distillation and the UOP factor have made great contribution to the petroleum science and technology in classification of petroleum and correlation of properties of petroleum products and have been accepted worldwide. However, when applied to petroleum residua, or even to heavy oils, difficulties are often encountered in two aspects:

1- In the TBP distillation, the highest temperature of distillation must be kept below 350° C at which the petroleum begins to decompose. Even using the highest feasible vacuum, the fraction that can be distilled over at this temperature may have normal boiling point at around 550° C. for many heavy crudes, this is about 40 – 50 % distilled, leaving almost half of the crude untouched. It was found by Guanghua [95] that a new method of separation based on the supercritical fluid extraction an fractionation (SFEF) can affect separation of heavy petroleum and residuum at much lower temperature and still give enough quantity of each fraction for characterization of its properties.

2- In analyzing the UOP factors of petroleum products, Guanghua [95] found out that this index was closely related to the density and molecular weight of the said petroleum fraction.

The Principle of the SFEF of Petroleum Residua:

It is well-known that the solution ability of a solvent increases with the increasing density of the solvent near the critical region of the solvent. Therefore if the petroleum residua were brought into contact with a suitable supercritical solvent, a certain percentage of the residua will be dissolved into the supercritical fluid (SCF). Upon reduction of the system pressure, this portion of the residuum will precipitate out. This phenomenon is well-known as the retrograde condensation. By stepping the pressure of the system progressively, the solution power of the solvent will increase and fraction of more difficult soluble will be extracted out in succession. This operation is more or less similar to the TBP distillation except that the variable is the total pressure of the separation system instead of the temperature in TBP distillation.

2.3. Spectroscopy:

Vacuum residues are extremely complex mixtures of thousands of non-polar compounds [97, 98]. The application of mass spectrometer group-type analysis to high boiling petroleum fractions has been restricted because it is necessary to employ costly and lengthy separation to reduce the number of interferences caused by the great variety of components. It is well known that high resolution mass spectrometry eliminates many of these interferences. Petroleum group-type analysis by high resolution mass spectrometry was studied by E.J.Gallegos and others & Lumbikin [99, 100] and they have found that the data from the high resolution mass spectrometer are sufficiently reproducible to take advantage of the small mass differences and thus eliminate the physical separation. In 1951, R.A. Brown [101] was the first which use spectral information for analyzing for compounds rather than for individual compounds. His procedure applied to gasoline received immediate and nearly universal acceptance in the petroleum industry. Increasing demand for processing of high boiling petroleum stocks

caused interest in extending group-type analysis to these materials. O'Neal and Wier [102]. Conventionally, double focusing mass spectrometry has been used to analyze the compound type distributions of constituent molecules [103, 104]. The mass scale requires trimming down to narrow segments for achieving high resolution and repeating the measurements to cover a desirable mass range due to a limit of the mass resolving power. Prevalence of high magnetic field **FT-ICR MS** *(Fourier Transform- Electron Ionization Cyclotron Resonance Mass Spectrometry)* may facilitate the molecular level characterization of complex mixture across the whole mass range at once because of its high-resolution and high-sensitivity.

Several research groups have applied **FT-ICR MS** to analyze constituents in petroleum distillates, diesel fuel or heavy crude oil [105 – 112]. Fourier Transformer Infrared Spectroscopy **(FT-IR)**, is one of the available analytical methods for interpreting the structure of asphaltenes and it has been used to characterize functional groups in these compounds.

Residual oils (Residues) possess high social and economic significance. The determination of chemical composition such as saturates, aromatics, resins, asphaltenes (SARA) and element content (i.e., hydrogen, sulfur, and nitrogen), and physico-chemical properties such as density, viscosity, and carbon residue of those samples present major analytical challenges.

In refineries today, most of the preceding properties are still been analyzed by conventional methods, which are usually tedious and time consuming. For example, the most widely used method for SARA analysis now is traditional elution chromatography (EC), which uses the aluminium oxide column and ingredient elution with mobile phases having different polarity. Each fraction solution is collected and the solvent in it is removed by evaporation, and the SARA contents are determined gravimetrically. These techniques take about two days to analyze the sample, and consume a lot of poisonous solvents. The development of

fast and accurate analysis methods for those properties has become an urgent task to the process control for residues processing.

Near infrared (NIR) spectroscopy in combination with multivariate calibration techniques has received much attention during the past decades. The advantages of speed, accuracy and simplicity make NIR spectroscopy become one of the most popular alternatives to wet chemistry procedures for determining the physico-chemical parameters of sample. The widespread use of NIR technology is found in analyzing petroleum products properties, such as octane number, hydrocarbon group type compositions of gasoline [113].

Mid-infrared (MIR) spectroscopy has also been used in determining the physical and chemical properties of petroleum and petrochemical products, and good results as same as NIR have been received by MIR [114, 115]. Because of its operational simplicity and high repeatability, NIR spectroscopy is still industrially preferred for the analysis of light petroleum fractions.

The opaque and viscous features of residuals make NIR measurements very inconvenient. The use of attenuated total reflection (ATR) geometry can simplify and expedite the MIR measurement to a considerable degree. The ATR has an accurate light path length, which depends on the number of inter reflections when light passes through the crystal and assists in improving the repeatability of spectral measurement. Moreover, in contrast to NIR, the spectral bands in MIR are fundamental bands that are specific, sharp and sensitive include the absorption bands of aliphatic C-H bond and additional bands originating from groups containing aromatics, oxygen, sulfur, and nitrogen. The MIR region is attractive for residues analysis because most of the useful information can be possibly extracted by chemo-metric methods.

Yuan Hongfu *et al.* [116] indicate that there are only a few examples of MIR technology used in the determination of physical and chemical properties of heavy petrochemical products. They focus on the simultaneous determination of multi-properties, for example, SARA, density, viscosity, carbon residue, hydrogen,

sulfur, nitrogen, and element contents of three types of residual oils *(Atmospheric Residue, Vacuum Residue, and Hydro Cracked Residue)* using MIR ATR-cell coupled with multivariate quantitative and qualitative calibration methods.

Chung H. and Ku M.L. [117] have determined API gravity of atmospheric residue by the use of MIR spectrometer with an ATR probe and partial least square (PLS) method. Brian K. Wilt *et al.* [118] have studied the determination of asphaltene content in crude oils by MIR spectroscopy. Nave Aske *et al* [119] have also used MIR ATR-cell to determine SARA components of crude oils.

2.4. Upgrading Of Heavy Residues:

The fluid catalyst cracking (FCC) process plays an important role in heavy oil upgrading. It converts heavy petroleum fractions into valuable light products such as gasoline, diesel, and olefins. Over the years, many improvements have been made on the FCC process. These include the development of very active Zeolite cracking catalysts that allow FCC reactions to be completed in short contact time in the riser reactors, and innovative engineering design of FCC reactor components and peripheral units. These improvements enhance FCC process yield by optimizing catalytic cracking reactions and minimizing undesirable secondary cracking reactions.

Another important aspect of the FCC operation is the feedstock selection. Since FCC is a catalytic and heat integration process, tremendous efforts have been devoted to establish the FCC feedstock specifications to meet the process constraints such catalyst deactivation and heat load requirement. To meet these requirements, the metal and concarbon residue (CCR) content of FCC feedstock are usually kept at certain critical levels either by fractionation or pretreatment. However, to maximize the profit margin of refinery units, it is extremely important that the FCC operators have prior information on the product yield of various feedstocks.

The effect of feedstock properties on FCC product yield has been reported extensively Chumming Xu *et al.* [120] studied the correlation between feedstock SARA components and FCC product yield. They concluded that:

1- The FCC reaction studies on deasphalted oil (DAO) indicate that most of gasoline yield originates from the saturate fraction of DAO.
2- Aromatic fraction of the DAO contributes to gasoline and diesel yields.
3- Most of the coke yield is from resins fraction of DAO.
4- The saturates and aromatics fractions produce only a small amount of cock.
5- Generalized empirical correlations were developed predicting the FCC gasoline, diesel, light oil and coke yields as a function of feedstock SARA composition. These yield correlations can be used to set the upper limit of feed stock resins content for commercial FCC operations.

The term hydroconversion is used to signify processes by which molecules in petroleum feedstocks are split or saturated with hydrogen gas while tumbling boiling ranges and impurities content from petroleum fractions. hydroprocessing is a broad term that includes hydrocracking, hydrotreating, and hydrofining. To meet the gradual changes in petroleum stipulate, in particular a reduced demand for heavy fuel oil, advanced technologies for residue hydroprocessing are now extremely necessary. Mohan and others [121] reviewed the recent advances on process technologies for upgrading of heavy oils and residua. The thermal, catalytic fixed and ebullated types of hydroconversion are reviewed and discussed.

Two-stage hydrocracking of petroleum residue consisting of hydrogenation (at low temperature), and thermocracking (at high temperature) has been investigated [122].

N. Panariti, *et al.* [123, 124] studied the upgrading of petroleum residues with dispersed catalysts. In part-1 [123] they studied the catalytic activity and selectivity of different compounds in terms of products yields and quality. In the second part, part-2 [124], they studied the hydrotreatment of the petroleum residues in the

presence of dispersed molybdenite within a wide range of operating conditions and catalyst loading.

It was observed that the active carbon (AC), which is neutral or weak base support, has the affinity to heavy hydrocarbon compounds and adsorption selectivity to asphaltenes, and exhibits better ability to restrict coke formation during the hydrocracking reaction of vacuum residue (VR). The mesopore of the active carbon was thought to play an important role for effective conversion of heavy hydrocarbon compounds into lighter fractions restricting carbon formation. The active carbon catalyst for heavy oil upgrading was studied by Hidetsugu Fukuyama and others [125]. They concluded that, in addition to its affinity to heavy hydrocarbon and adsorption selectivity to asphaltenes, and exhibits better ability to restrict coke formation, the active carbon catalyst shows the high activities for the removal of such impurities as sulphur and heavy metals. Thus, the AC catalyst offers prominent application possibilities both in fixed and ebullating-bed in combination with typical commercially available processes for synthetic crude production, upgrader with inline hydrodesulphurization (HDS) and pretreators for hydrocracking of heavy oils. Rafael and Reginaldo [126] studied the catalytic hydroconversion Kinetics of vacuum residue. Kinetics of vacuum residue (VR) hydroconversion are usually obtained in fixed bed, with highest catalyst holdup, or using catalyst as an additive (low catalyst holdup). Under these conditions, the kinetics are expressed either as a function of catalyst quantity or reactor volume. In practice, catalyst holdup in an ebullated-bed reactor remains between the two cited limits, having both thermal and catalytic contributions to conversion and other reactions.

Crude oils typically contain trace amounts of metals with vanadium and nickel being the most common. Usually they are in an oil-soluble form and in conventional refining processes they become concentrated in the residual fuel oil fractions. The deleterious effects of metals in petroleum have known for some times. The metals not only contaminate the products, the metal chelates also cause

poisoning and fouling the catalyst and corrode equipments. Mohammed and Saeed [127] discussed the physical, chemical, and catalytic treatment processes for the removal metals (nickel and vanadium), which are mostly concentrated in the asphaltenes. They also concluded that the AC (Active Carbon) catalyst was confirmed to be effective and suitable for upgrading of heavy oil, especially such heavy oils which contain much heavy metals.

2.5. Structure of Asphaltene Molecule:

The major problem with heavy oil fractions is the complexity of feedstock and analysis of its components. Efforts have been committed in order to analyze crude oil, using different methods have given improved impeding to the understanding of heavy oil composition [118, 48]. Apart from the several other complex structures, asphaltene remains as one of the common uncertain molecules in heavy oil. Asphaltene is thought to be the most complex, high molecular weight, polar and high aromatic in nature molecule present in petroleum. Nevertheless, microstructure of asphaltene residue has been studied [128,129], and has been reported that in general, it is a large aromatic sheet, having high molecular weight, which is build up on each other to form a unit cell and large associated asphaltene molecule. Additionally, few metalloporphyrins are also associated with asphaltene molecule via a π-electronic interaction as shown in Figure-4.