

Review Article

Clay Adsorption Perspective on Petroleum Refining Industry

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Abstract: Clays are the most utilized minerals and considered very efficient and economical sorbents according to their chemical and physical properties. Clays are enjoying rapid popularity in the petroleum refining industry for the various processes such as adsorption and separation. Removal of many components such as sulfur, heavy metals, colors and separation of different hydrocarbon groups of crude oil and petroleum fractions can be carried out by clay adsorption. The present review summarizes the using of clay as adsorbent in several petroleum refining processes such as desulfurization, deasphalting, waste oil recovery, bleaching, corrosion reduction, heavy metals removal and other. One of the simplest, easiest and efficient separation processes used in different industries is adsorption. Review results show that different types of clay are obtainable and used in many applications. Clay adsorption can be enhanced the treatment and finishing of crude oils and petroleum fractions through several modifications such as metals impregnation, acid and thermal activations. Bentonite clays promote the highest adsorption capacity to remove sulfur and a high bleaching potential. Attapulgite clay is effective in decolorization and neutralization any petroleum oil. Impregnation of NiO nanoparticles into kaolin improves the asphaltenes adsorption. Several modified as well as unmodified clays promote the highest removal efficiency of Ni and V from crude oil. Additionally, the adsorption pre-treatment affects the reduction in corrosion yields and the corrosion rate.

Keywords: Clay, Adsorption, Petroleum Refining Industry, Desulfurization, Waste Oil Recovery, Finishing Process, Deasphalting, Bleaching

1. Introduction

Distillation or fractionation of crude oils is the first step into separate fractions of hydrocarbon groups in the petroleum refining. Most of the resultant products are further converted into more valuable products by changing their properties through different conversion processes such as cracking, reforming and other. To produce finished products, various separation and treatment processes, such as extraction, hydrotreating, sweetening and adsorption are consequently treated of the products [1].

Clays are a naturally occurring mineral [2], and considered very efficient sorbents, inexpensive and environmental friendly according to several physical and chemical properties such as high surface area, mechanical stability and thermally inert [3, 4]. Clays are played an important part in petroleum refining industry [3]. They used in several applications as

active components, adsorbents, binders, catalysts and ion-exchanger [3, 5]. Several types of clay such as bentonite, attapulgite, hectorite, kaolin and sepiolite are obtainable and used in different applications [6].

Adsorption process is to be one of the simplest and efficient separation methods, because it can be achieved at ambient pressure, temperature and without use of any expensive materials [5]. Additionally, it seems to be very promising and economical methods and saves energy consumption [7]. Adsorption process is used to treat crude oil and petroleum fractions [5-8]. It plays an important role in the treatment and finishing of petroleum fractions through desulfurization [9], deasphalting [10], bleaching [11] and other [12-14].

Clay percolation treatment was the original method to treat a petroleum fraction through a coarse clay pellets tower. Clay activity lowered through absorbing impurities from the petroleum fraction. To restore the clay activity by remove the

used clay from the tower periodically and burnt it under controlled conditions so as not to sinter the clay. Clay percolation treatment was broadly used for lubricating oils, but clay contacting has been largely replaced [1].

Several types of clay are obtainable and applied in adsorption to treat the petroleum fractions [2, 6, 9-14]. Attapulgite clay can be used to separate crude oils into saturates, aromatics and resins through a chromatography column packed [6]. Bentonite is considered very good adsorbent clay and specifically commonly used as a sorbent according to its layered structure and high surface area ($\sim 800 \text{ m}^2/\text{g}$). Several types of bentonite can be absorbed water up to 100% and oil up to 80% of their dry weight [2]. Another type of clay is sepiolite. It has a surface area lower than bentonite ($\sim 300 \text{ m}^2/\text{g}$), according to its high porosity it has a several applications for paints, cosmetics, bleaching agent, filter support to an industrial adsorbent [15]. Oil adsorption by sepiolite have been reported by a few studies [15, 16].

A finishing step by clay treatment is still used in the production of lubricating oils and waxes. Removing traces of asphaltic materials and other compounds by clay that give lubricating oils and waxes undesirable colors and odors. Often clay treated cracked naphtha to prevent gums formation in gasoline by removing diolefins [1].

The aim of this review is to summarize the applications of the different types of clay through adsorption process in the petroleum refining industry, such as the removal of sulfur compounds through desulfurization, base oil finishing, the recovery of waste oils, the removal of asphaltenes and heavy metals, bleaching of petroleum fractions, the reduction of corrosion.

2. Desulfurization

Sulfur compounds removing from petroleum fractions are essential to produce clean burning fuels can be used environmentally [8]. Sulfur compounds in petroleum fractions can cause several problems such as air pollution, acid rain, poison emission control catalysts and corrosion of parts in engines [8, 17]. Adsorption plays a significant role in petroleum fractions [18] and crude oil desulfurization [19]. The selective adsorption of sulfur compounds in crude oil and petroleum fractions, such as kerosene and diesel oil can be accorded through several clays used as adsorbents including kaolinite, montmorillonite, palygorskite and vermiculite [8, 20].

Different low-cost adsorbents can be used for desulfurization of diesel fuel for removal of sulfur compounds [9, 21, 22]. Bentonite was used to remove sulfur compounds from diesel fuel [7, 23]. Kaolinite showed the maximum desulfurization yield of about 60%, 76% and 64% after 6 hrs adsorption contact time with crude oil, kerosene and diesel oil, respectively [9]. Younis and Simo [22] compared the desulfurization efficiency of Tawke diesel fuel by adsorption through Na-Y zeolite, local clay and activated charcoal. Desulfurization by activated charcoal is about 20%, it is more efficient than by zeolite and clay. Baia et al., [24] studied the

kinetic and isothermal of the adsorption performance of different commercial clays such as attapulgite clay and bentonite clays to remove sulfur and nitrogen compounds from a stream of real diesel. The highest adsorption capacity to remove sulfur and nitrogen compounds was achieved using bentonite clays, probably according to the presence of Brønsted acid sites. However, attapulgite clay was more selective to remove nitrogen compounds [24]. On the other hand, Ahmad et al. [25] concluded that fuller's earth and calcium oxide were ineffective in desulfurization for the treatment of oils found during the pyrolysis of used tires.

Several studies compared the desulfurization ability of different clays with their modifications [7, 23, 26-29]. Montmorillonite (MMT) clay is locally available and can be efficiently used for desulfurization. Modification of MMT clay by metals impregnation increases its adsorption characteristics [28]. Desulfurization by adsorption of commercial kerosene and diesel oil was carried out through different metals impregnated acid modified MMT clay. Metals were wet impregnated on MMT included Fe, Cr, Ni, Co, Mn, Pb, Zn and Ag. Results show that, the highest desulfurization of kerosene and diesel oil of about 76% and 77% was achieved with adsorption through Zn-MMT, respectively. The increasing of the surface area, pore size and pore volume and additionally, the improvement of the surface morphology of the MMT was occurred with Zn impregnation [28].

Desulfurization by adsorption of mercaptans from model oil using bentonite impregnated with Cu^{+2} , Cu^{+1} , Fe^{+3} and MnO_4^{-1} was investigated [26]. Authors concluded that the highest capacity of desulfurization of bentonite impregnated with Fe^{+3} and MnO_4^{-1} can be according to the oxidation of mercaptans. Ishaq et al., [7] studied the removal of dibenzothiophene from model oil using untreated bentonite, acid activated bentonite and magnetite impregnated bentonite as the adsorbents. Magnetite impregnated bentonite exhibits the best performance and the highest capacity in the desulfurization of fuel. It can be according to the catalytic activity of magnetite for the co-conversion or destruction of sulfur compounds. Additionally, the recovery of the magnetite can be easily by using the magnetic separation in the application [7]. Yi et al., [27] also, investigated the sulfur content reduction in model oil as liquid hydrocarbon fuels by adsorption for removing dimethyl sulfide and propylmercaptan using copper (II) impregnated bentonite as adsorbent. Results show that the highest sulfur adsorption capacity was achieved at a Cu (II) loading of 15 wt%, at 150°C of the optimum calcination temperature.

Dynamic and static evaluation of the capacity and efficiency of the sorbents for alkyl dibenzothiophenes removal was studied using silver modified bentonite and raw activated bentonite. Results show that silver ions loaded on bentonite had a higher adsorption of alkyl dibenzothiophenes than the activated bentonite. It can be attributed to silver ions could have complex reactions with alkyl dibenzothiophenes. Additionally, the adsorption capacities of alkyl dibenzothiophenes increased gradually with an increasing of silver ions loading and with a decreasing temperature [23].

Acid-activated kaolinite and bentonite clays, charcoal, petroleum coke and cement kiln dust were selected to adsorb of dimethyl disulfide sulfur compound from petroleum fraction. Acid-activated bentonite showed higher efficiency towards sulfur adsorption, may be according to the structure of bentonite that, the silicate-silicate structure (which produced from the water molecule dissociation in between silicate sheets) possesses Brønsted acid sites. Also, the surface of clay after acid modification would possess positive hydrogen sites. Hence, the bentonite-clay lattice can be disturbing the charge equilibrium by increasing in acid sites, that can be interact more selectively with the sulfur compound [30]. Wan et al., [17] studied a batch adsorption of oxidized sulfur compounds in diesel oil using activated clay at different process parameters. Results show that good adsorption performance in real diesel oil using activated clay batch adsorption. The adsorption parameters as pH, adsorbent dosage and temperature showed an important effect on the sulfones adsorption in diesel oil while contact time and agitation speed were insignificant.

Acid treated attapulgite clay was effective under microwave thermal activation and ultrasonic vibration and its performance was evaluated the desulfurization of simulated gasoline as the feed [29]. The results show that the removal rate of thiophene increased with an increasing amount of hydrochloric acid during modification of attapulgite clay under microwave.

Miller and Bruno [31] studied the effect of clay and organo-clay on the adsorption enthalpies and interaction of common odorants add in the fuel gas industry by using gas chromatography with wall-coated open-tubular column. Results show that, sulfide odorants have larger enthalpies than thiol odorants on surfaces of clay and organo-clay. In addition, the results explain the Lewis acid–base chemistry has significantly difference in enthalpy magnitudes on clay surfaces between the sulfide and thiol odorants.

3. Base Oil Finishing

After extraction and dewaxing, the base oil is still not ready to produce lubricating oils. Lubricating oils are required to employ finishing step, such as clay treatment or hydrofinishing in order to improve color, oxidation stability, thermal stability, reduce foaming tendency and remove residual acidity of base oil [6, 32]. The conventional finishing treatments use many adsorbents such as activated or inactivated clays through percolation cylindrical filters, or by mixing. Clay treatment may be replaced by hydrofinishing process to reduce spent clay disposal problems and other operating restrictions [6], additionally, present better results of yields, selectivity and colour stability.

Clay percolation may be used to remove wax, aromatics and asphalts to produce a variety of lubricating oils. Acid-clay refining, also called “dry refining” is the traditional technique that use sulfuric acid and clay for the manufacture of lubricating oils. This technique is used for oils that form emulsions through neutralization. Dry refining technique is

still used in some refiners for the fabricate of specialty oils and the recovery of used oils [6]. Attapulgite clay is efficient in decolorization and neutralization any petroleum oil. On the other hand, this clay is less effective in the adsorption of aromatics, metals and odorous compounds. However, it was reported that the adsorption of heat activated porocel clay is effective in decolorization, deodorizing, decreasing organic acidity and aromatic type molecules and polar compounds containing sulfur and nitrogen [6]. Porocel clay was described as hydrated aluminum oxide and known as bauxite, while attapulgite clay was described as magnesium aluminum silicate [33].

Mostafa et al., [32] studied the effect of the solvent dewaxing and clay finishing of heavy wax distillate fraction. They concluded that the values of refractive index, density and viscosity are slightly decreased, while, the pour point and average molecular weight are slightly increased of the base oil and a slight improvement is occurred in ASTM color of the finished oil. The content of polycyclic aromatic compounds in the dewaxed oil reduced from 2.5 to 2.26 wt% through clay percolation.

4. Deasphalting

Asphaltenes are the fraction of crude oil and can be soluble in aromatic solvents (as toluene), but insoluble in short straight chain alkanes (as pentane or heptane) [34]. Asphaltenes can be precipitated and deposited through changing in pressure, temperature, composition and shear rate [35]. As a result, in petroleum industry, asphaltenes consider to be the major source to several complications such as clogging of pipelines, surface facilities, pumps, safety valves and fouling, which can affect production, transportation, storage and the refinery processes. These complications produce a large capital and operational costs in petroleum industry [35, 36]. The most significant commercial application of adsorption is the removing of asphaltenes or resin compounds from lubricating oil stocks using acid activated bentonite, Fuller's earth and bauxite [37]. Asphaltenes can be adsorbed on different clays and modified clays such as kaolin, illite and bentonite and others [10, 38-40]. Also, different surface active materials such as attapulgus clay, fuller's earths, silica or alumina can be used to separate resins from maltenes via adsorption through preparative liquid chromatography, followed by desorption with aromatic/polar solvents [36].

The combination of synthesized NiO nanoparticles and mesoporous–macroporous kaolin was studied the asphaltenes adsorption and followed by catalytic steam gasification. Results suggest that the absorbents showed better adsorption, by increased pore size distribution from 200 to 800 °A and have low surface basicity. Additionally, impregnation of NiO nanoparticles into kaolin not only improved the asphaltenes adsorption, but also enhanced the steam gasification of the adsorbed asphaltenes, resulting major products of CO₂ and H₂ [38]. Dean and McAtee Jr [39] concluded that the asphaltenes adsorption onto two different clay minerals

depends on the properties of the clay surfaces and no significant effect of the adsorption process by temperature. In contrast, another study claimed that adsorption of asphaltenes onto mineral adsorbents decreases with increasing temperature according to the size reduction of asphaltenes by aggregation and self-association [41]. Dudasova et al. [10] studied the adsorption of asphaltenes in five different crude oils onto inorganic particles (kaolin, CaCO_3 , BaSO_4 , FeS , Fe_3O_4 , TiO_2 and SiO_2). Results show that no change on the adsorption amount of asphaltenes on mineral adsorbents and clays with contact time after 12 hrs. Besides, the asphaltenes adsorption depends more on the adsorbent type than on the source of asphaltenes. The amount adsorption of asphaltenes increases with increasing the heteroatomic content in asphaltenes.

Kaolinite can be considered active adsorbent for asphaltenes, according to polar sites located at the broken edges and exposed hydroxyl terminated planes in kaolinite structure [10, 40]. Tsiamis and Taylor [42] used the depletion method in toluene for the adsorption of asphaltenes and resin isolated fractions from four different sources onto kaolinite. The results confirm that the adsorption behavior in toluene solution complicated by concentration dependent nano-aggregation of asphaltenes species, while the interactions of resin-resin were weaker, but accompanied by adsorbent particle aggregation.

Several studies focused on the asphaltenes removal before catalytic conversion using different processes such as extraction, hydrogenation and adsorption. Before catalytic processes such as hydrocracking and hydrodesulfurization in refineries, adsorption pre-treatments can be used to minimize or prevent catalyst poisoning resulting from deactivation by minimizing or preventing coke formation and removing metallic compounds [43].

5. Bleaching

Bleaching or decolorizing applications can be applied using clay [44]. Bleaching process is physical adsorption by weak bonds between the dark coloured compounds in oil and the clay adsorbent [37]. Bleaching by clays can be used for some oils and chemicals industries such as [45]:

- Mineral oils for special applications such as transformer oils, turbine oils and medicinal white oils;
- Paraffin and waxes using in the food industry;
- Regeneration waste oils for re-refined lubricating oils;
- Rolling oils used as lubricants;
- Removal of bituminous substances from mined crude sulfur in a refining process;
- Removal of olefin hydrocarbons from aromatic hydrocarbons such as benzene, toluene, and xylene.

Used oil bleaching can be occurred using raw bleaching clay, activated bleaching clay, amorphous silicates and activated carbon [46]. Bentonite clay has a high bleaching potential, it is mostly used to remove the color and smell of the product [47]. Clay is recovered and can be used as filler in asphalt, bituminous mixture and cement industry [44].

Bleaching capacity of different types of clays can be enhanced by many methods in an efficient and economical way. Thermal activation can be used to activate bauxites, bentonite and palygorskite-sepiolite clays [45]. Acid activation of clays was reported by several researchers [37, 45, 47]. Acid activation can be affect the physicochemical properties of bentonites and galuconite [37, 48]. It was concluded that acid bentonite clays are usually used as oil bleaches, which can favor the adsorption of aromatic color compounds and decrease the adsorption of others compound, mainly naphthenic acids and sulfur compounds [48].

Karim et al., [11] compared various types of clays for decolorizing dark lubricant oils. They concluded that the local clays (yellow bentonite, brown bentonite) need acid activation treatment to improve their decolorizing ability, because their decolorizing efficiency was lower than activated China clay and Iranian clay. On the other hand, Kaolin was efficient for bleaching lubricating oils, according to its decolorizing power and can be considered as good bleaching clay [11]. The surface area of smectites or bentonites increased several times larger after the acid activation, for about 200 to 300 m^2/g , resulting that the acid-activated clays is used to adsorb the coloring matter dissolved in oil [45]. Aziz et al., [37] characterized and used different types of clays as bleaching earth for the decolourization of acid treated and untreated used lubricating oil. Best results of decolourization obtained using local acid activated clay. Freundlich isotherm was more applicable than Langmuir isotherm by the different clays for the decolourizing of used lubricating oil.

6. Heavy Metal Removal

Catalyst deactivation and adverse effects on the economy of crude oil refining can be occurred in the presence of heavy metals in crude oil. Clay adsorption can be played significant role in the elimination of heavy metals [12, 49]. It was found that several modified as well as unmodified clays give the highest removal efficiency of Ni and V from crude oil [49]. Kukwa et al., [12] studied the kinetics of adsorption removal of Ni and V from crude oil using NH_4Cl modified primitive clay. The removal percentage of metals increased with the increasing of adsorbent dosage and contact time. The result fitted the Lagergren's pseudo second order kinetics model higher than the Lagergren's pseudo first-order model. Modified primitive clay is therefore competitive among low cost adsorbents that can be used for Ni and V elimination from crude oil [12]. Oduola and kwonna [50] studied the removal of heavy metals and trace elements from waste lubricating oil by acid activated Ukpok clay as an adsorbent. The best adsorption removal of metals obtained using 2 mol/L concentrations of sulfuric acid to activate the clay. The initial concentrations of Ca, Pb, Zn and Ba were 804, 398, 222 and 0.1 mg/L and reduced to 3.6, 5.6, 0.01 and 0.01 mg/L, respectively.

7. Corrosion Reduction

Naphthenic acids (NA) contribute to the acidity of crude

oils and one of the main aggressive compounds present [51]. NA are the major sources of corrosion in the oil refinery equipments such as pipelines and distillation units [52]. Additionally, the higher concentrations of NA in crude oils reduce the quality and market at a lower price [53]. Silva et al. [48] studied the reducing of corrosion by removing NA from a light petroleum fraction using two commercial adsorbents (clay and activated alumina). Both adsorbents proved a high reduction of the total acid number (TAN) in the residual oils. It was observed that the adsorption of acid composites of the oil significantly influenced by the thermal pre-treatment of clay. Additionally, the pre-treatment by adsorption affected the reduction in corrosion yields and the corrosion rate of the mild steel coupons decreased in the residual oils originated from the adsorption processes for both adsorbents [48]. Xiaohui et al., [13] studied the adsorption of NA from dewaxed vacuum gas oil during lube base oil refining using a commercial grade activated clay. The results show that the Dubinin-Radushkevich isotherm fitted a better experimental data than other isotherms and the kinetics of adsorption followed the pseudo-first order kinetic equation. The thermodynamic data evidences that the adsorption process was possible as an endothermic process. The results could explain that the NA adsorption can be occurred during lube base oil processing at refineries by activated clay [13]. NA separation from sour crude oil was studied through adsorption of the acid using local activated clays. Results show that the ability of Muscovite clay to reduce TAN of sour crude oil and to remove NA was higher than the Zeolite clay. Clay activation by alkali was recommended to reduce the cost of activation process, because the price of NaOH is much less than that of H₂SO₄ [54].

8. Waste Oil Recovery

Waste oil is considered a valuable and an important resource of energy [14, 55, 56]. Waste oil is recovered using several techniques including chemical technique (acid/clay) [14], physical technique such as distillation [56], thin film evaporation [57] and solvent extraction [58]. One of the important technique for refining and recovery waste oil is adsorption using several adsorbents [14, 58, 59].

The re-refining of waste lubricating oil using acid activated Ukpok clay as an adsorbent was investigated. The best performance of adsorption on the waste lubricating oil was achieved with activated clay using 2 mol/L concentrations of sulfuric acid. The performance improvement of the acid activated clay may be according to the increasing of their surface area and large pore volume. The results indicate that adsorption using acid activated clay improved the physico-chemical properties of the lubricating oil by enhancement density, viscosity, pour point, flash point, and decrease TAN, moisture and sulfur content. The best kinetic data was fitted by the Pseudo-second order kinetic model [50]. On the other hand, adsorption treatment using sm400 activated clay as an adsorbent was studied to restore the physico-chemical parameters of the used transformer oil.

Results show that the used transformer oil was purified, but its quantity decreased during adsorption. Additionally, treated oil was eco-friendly and had green chemistry uses [60].

Many studies investigated the recovery of waste oils using acid/clay treatment [14, 55, 58, 62]. In this technique waste oil is treated with strong acid and followed by clay adsorption. Abu-Elella et al., [55] studied the treatment of waste engine oils using four different acids (sulfuric acid, phosphoric acid, acetic acid and formic acid) followed by clay earth adsorption treatment. The results show that the formic acid followed by clay treatment improve the flash point of the treated oil. Additionally, the kinematic viscosity improvement of the oil was achieved by comparing with fresh engine oil using the sulfuric acid, acetic acid and formic acid followed by clay treatment. On the other hand, the phosphoric acid-clay treatment has no significant action on the kinematic viscosity and flash point of the treated oil. Josiah and Ikiensikimama [63] studied the effect of the acid desludging and the activated clay adsorption ratio from the recovery of waste engine oil. The recovery increased by increasing the ratio with a maximum recovery of about 83%.

Other studies investigated to recover waste oils by comparing between various techniques [14, 59, 61]. The most re-refining techniques of waste oil used as the following: firstly, pre-treatment using filtration or heat, then i) either vacuum distillation followed by hydrogen finishing or clay treatment, ii) solvent extraction followed by clay treatment and iii) chemical treatment followed by hydro-heating. Udonne [61] compared different recovery techniques of used lubrication oils: acid-clay, distillation-clay, acid treatment and activated charcoal-clay, and concluded that the viscosity improved from about 25.5 cs for used lubrication oil to about 86 cs, 89 cs and 81 cs of treated oil for distillation, acid/clay treatment and activated/clay treatment, respectively. Ahmad et al., [64] reported about the obtaining of useful fuel-like products through the conversion of spent lubricating oil using prebaked clay as adsorbent followed by pyrolysis over coal ash as catalyst. The results show that the using of coal ash in low concentration evidenced good activity and selectivity toward the liquid pyrolysates formation having fuel value comparable with diesel fuel.

Solvent extraction followed by adsorption treatment was found to be one of the competitive techniques for the recovery of waste oil [14, 58]. Emam and Shoaib [14] compared two techniques for recovery of waste oils collected from different sources. First technique was solvent extraction followed by clay treatment and the second technique was acid treatment followed by clay-percolation. Also, treated oil characteristics were compared with virgin base oil. The results show that a best characteristics quality of the treated oil was obtained using acid/clay-percolation and a higher yield of about 83% was achieved using solvent extraction/clay treatment [14]. Mohammed et al., [58] evaluated the performance of six extracting solvents, followed by adsorption treatment using different adsorbent materials (such as almond shell, walnut shell, eggshell and acid activated clay) to treat waste lubricants. Acid activated clay treatment provided the best

results of treated oil. The properties of waste oil were changed by acid activated clay treatment as the following: the increasing of viscosity and flash point were from 38.3 cst and 178°C to 85 cst and 238°C, respectively, whereas, the decreasing of density, pour point and colour were from 912 kg/m³, -6°C and 0.53 to 896 kg/m³, -13.2°C and 0.12, respectively. Daham et al., [62] reported the specifications of the two types of base oil recovered using solvent extraction (MEK and 1-butanol) followed by activated bentonite clay adsorption as the following: viscosity at 100°C 8.3, 9.2 cSt, flash point 210, 223°C, pour point -17.4, -22.2°C, TAN 0.25, nil, color 3.0, 2.5 and ash 0.03, 0.002, respectively.

9. Conclusions

Clays are played an important role in petroleum refining industry. Clays are very efficient and economical sorbents according to their properties. Different types of clay such as bentonite, attapulgite, hectorite, kaolin and sepiolite are obtainable and used in different applications. Adsorption is very important process in petroleum industry. Clay adsorption plays an important role in the treatment and finishing of crude oils and petroleum fractions through desulfurization, deasphalting, bleaching, corrosion reduction, heavy metals removal, waste oil recovery and other. Additionally, clay modifications through metals impregnation, acid and thermal activations, etc. can be enhanced the adsorption treatment and finishing of crude oils and petroleum fractions.

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The hydrogenation of hydrocarbon fractions from petroleum refining is a forefront issue recently adopted by refineries worldwide. The process involves the incorporation of suitable catalytic systems under hydrogen atmosphere to upgrade hydrocarbons into similar derivatives of better gasoline properties. Therefore, the clay-supported catalysts have good refining potentials for upgrading fuel feeds.

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17. Froment, G. F. et al. Petroleum refining refers to the separation as well as reactive processes to yield various valuable products. Therefore, a key issue in the petroleum refining is to deal with multicomponent feed streams and multicomponent product streams. Usually, in chemical plants, we encounter streams not possessing more than 10 components, which is not the case in petroleum refining. Therefore, characterization of both crude, intermediate product and final product streams is very important to understand the processing operations effectively.

3.2 Overview of Refinery processes.

Source: HANDBOOK OF PETROLEUM REFINING PROCESSES CHAPTER 1.5 LINEAR ALKYL BENZENE (LAB) MANUFACTURE Andrea Bozzano UOP Des Plaines, Illinois INTRODUCTION The detergent industry originated in the late 1940s with the advent of sodium alkylbenzene sulfonates, which had detergency characteristics far superior to those of natural soaps. These techniques used a variety of adsorbents and desorbents. Adsorptive separation techniques based on the molecular sieve action of 5-Å... zeolites have dominated this industry since the mid-1960s. Keywords: Petroleum refinery; clay; clay-modified catalysts; acidic-clay; pillared-clay; kaolin; montmorillonite.

1. INTRODUCTION. species were buried partially in kaolin through adsorption. coke deposition was not changed significantly. However Petroleum refining industry has been continuously developed, which includes processes that are based on the catalysts. Catalysts by clays have attracted much interest recently and an important catalytic application in petroleum refining industry. Clays and their modifications are used extensively for various processes such as catalytic cracking, hydrocracking, isomerization, alkylation, etc.