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Treatment and disposal of refinery sludge

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Abstract

Crude oil is a major source of energy and feedstock for petrochemicals. Oily sludge, bio-sludge and chemical sludge are the major sludges generated from the processes and effluent treatment plants of the refineries engaged in crude oil refining operations. Various types of pollutants like phenols, heavy metals, etc. are present in the sludges and they are treated as hazardous waste. Oily sludge, which is generated in much higher amount compared to other sludges, contains phenol (90-100 mg/kg), nickel (17-25 mg/kg), chromium (27-80 mg/kg), zinc (7-80 mg/kg), manganese (19-24 mg/kg), cadmium (0.8-2 mg/kg), copper (32-120 mg/kg), and lead (0.001-0.12 mg/kg), Uncontrolled disposal practices of sludges cause degradation of environmental and depreciation of aesthetic quality. Various treatment and disposal practice have been discussed.

Keywords: Petroleum refineries, sludges, environmental impact,

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Introduction

Refinery sludge in particular is an important problem all over the world because of its harmful impact on the environment. Refinery sludge is a complex mixture of hydrocarbons together with clay, sand, inorganic matter, heavy metals and water. It contains a large amount of combustibles with high heating value. The severity of petroleum sludge problem depends on the nature of the crude oil, the processing capacity, the downstream capacities and the design of the effluent treatment plant. Sludge usually accumulates in refineries because of pumps and desalter failures, oil draining from tanks and operation units, periodic cleaning of storage tanks and pipeline ruptures (Kuriakose and Manjooran, 2001). Treatment of sludge is; therefore, important and of great significance element for oil refineries.

So far, techniques that have been employed in petroleum sludge treatment have included sludge disposal in lagoon/pit, incineration, land farming and secure landfill. Although these techniques have been successful; however, they still have been a major challenge to the petroleum industry worldwide. They generally demonstrate an environmental barrier. For instance, treatment of oily sludge through incineration suffers from the escape of some products of incomplete combustion. In addition, ashes produced from incineration contain heavy metals and; therefore, require some kind of environmental-friendly disposal. Likewise, land farming method causes contamination to ground water and soil. In addition, although in secure landfill method, the environmental issues are mitigated, this method requires special arrangement. In order to meet the ever increasing environmental awareness and legislations by which petroleum sludge is no longer landfilled, it becomes more and more essential to develop better techniques to efficiently deal with such sludges.

Development of a technology for conversion of waste feedstock into energy has the potential to address a number of economic, environmental, societal and resource issues. A path for the conversion of waste into energy should be economical; otherwise, fees required for waste disposal management become a credit against the cost of the produced energy. Furthermore, conversion of waste into energy has the environmental advantage of decreasing the number of future landfill sites needed with a contaminant decrease in the associated air and water pollution issues (Wallman et al., 1998).

Several thermochemical conversion technologies (combustion, pyrolysis and gasification) can be utilized for the production of energy from waste. The end products for each of these processes vary and also different energy and matter recovery systems can be used according to the market or requirements. However, gasification in which solid organic matter is converted into a syngas is considered as the most appropriate option as it offers higher efficiencies as compared to combustion or pyrolysis (Bridgwater, 2003). In addition, gasification is central to the development of any sustainable waste based energy and feedstock technologies. Also, syngas mixture produced via gasification can be used in internal combustion engines (ICEs), gas turbines, fuel cells and for hydrocarbon synthesis (Bain, 2004).

Gasification is a viable option for the utilization of oil sludge as ever increasing environmental awareness and legislation demand that oily sludge should be treated at source, as it is no longer acceptable for it to be sent to landfill in lagoons, etc. Gasification is a thermochemical conversion of solid organic material into a combustible gas by partial oxidation at temperatures greater than 500 ^{o}C (Higman and van der Burgt, 2008). The gasifying agent can be air, O_2 or steam. Gas produced is known as product gas, producer gas or syngas. It consists mainly of H_2, CO, CH_4 and CO_2; depending on the gasifying agent used, the dry basis heating value varies from 4-18 MJ Nm^{-3}. If air is used, the syngas is diluted with N_2 and a dry basis heating value between 4-7 MJ Nm^{-3} is obtained (McKendry, 2002a; McKendry, 2002c). Waste into energy conversion efficiencies obtained can be further enhanced through the use of combined cycles to generate electricity. Furthermore, it has been shown that refinery sludge is not only useful for power generation, but also a good source of valuable chemicals which are recovered from the ash produced from the refinery sludge gasification (Hall, 1981; Akay *et al.*, 2005). However, syngas produced from most waste usually contains varying amounts of tars and particulate matters. The applications of the syngas are purification level dependent, so these contaminants need to be removed via gas cleaning up equipment prior to its use for any application. Gas cleaning is important to prevent erosion, corrosion and environmental problems (Bridgwater and Maniatis, 2004; Smith and Shantha, 2007). The presence of tars in the fuel gas is one of the main technical barriers in the waste gasification development and has been the main concern for many researchers. These tars can cause several problems, such as cracking in the pores of filters, forming coke and plugging the filters and condensing in the cold spots and plugging the lines, resulting in serious operational interruptions. Moreover, these tars are dangerous because of their carcinogenic character and they contain significant amounts of energy which should be transferred to the fuel gas as H_2, CO, CH_4, etc. In addition, high concentration of tars can damage or lead to unacceptable levels of maintenance for engines and turbines (Corella *et al.*, 1998).

Tars are defined as a generic term comprising all organic compounds present in the producer gas excluding gaseous hydrocarbons (C_1-C_6) and benzene (Neeft, 2002). Different classifications of tars are found in the literature (Milne *et al.*, 1998; Maniatis and Beenackers, 2000; Padban, 2001; van Paasen *et al.*, 2002; Devi *et al.*, 2005). In general, these classifications are based on: properties of the tar components and the application of producer gas.

Tar removal/conversion for the purpose of syngas cleaning has been a subject of several investigations (Milne *et al.*, 1998; Maniatis and Beenackers, 2000; Padban, 2001; van Paasen *et al.*, 2002; Devi *et al.*, 2003; Devi *et al.*, 2005; Anis and Zainal, 2011). The main target of syngas cleaning is the destruction of tars although the removal of heavy metals is also important. Tar removal methods can be categorized in two types; a primary method in which the treatment is carried out inside the gasifier itself and a secondary method in which the cleaning or conditioning takes place after the gasifier (downstream of the gasifier). Primary methods are of three types: (a) optimization of operating conditions; (b) modification of the gasifier design and (c) addition of catalysts and/or additives in the fuel bed. Secondary methods are characterized by syngas cleaning system and the type of secondary method used is mainly set in accordance to the end application of the syngas and to the main types of contaminants present. Tar removal technologies are classified as physical or chemical. In physical removal systems, gas cleaning systems generally in use are wet scrubbers, gas cyclone separators, baffle filters, fabric filters and electrostatic precipitators by which particulates as small as 5 µm can be removed. Chemical conversion of tars is carried out by thermal or catalytic means. Catalysts used in this method are as those used in the primary treatment (Nair et al., 2003). Syngas cleaning strategies include water scrubbing followed by further cleaning and moisture reduction, low temperature capture of tars and destruction of tars at high temperatures preferably at the gasifier exit temperature.

According to the literature, using the syngas in a power production application, tar concentration in syngas needs to be less than 100 mg/Nm^3 which requires particle and tars reduction efficiencies of 90 % which are required for a satisfactory operation of ICEs using syngas produced in a downdraft gasifier (Devi *et al.*, 2003; Anis and Zainal, 2011).

Crude Oil Refinery and Processing

Petroleum is a complex mixture of organic liquids called crude oil and natural gas, which occurs naturally underground and was formed millions of years ago. Crude oil varies from oilfield to another in colour and composition, from a pale yellow low viscous liquid to heavy black 'treacle' consistencies.

Crude oil and natural gas are extracted from underground, on land or under the oceans, by sinking an oil well and are then transported by pipeline and/or ship to refineries where their components are processed into refined products. Crude oil and natural gas are of little use in their raw state; their value lies in what is created from them: fuels, lubricating oils, waxes, asphalt, petrochemicals and pipeline quality natural gas.

An oil refinery or petroleum refinery is an industrial process plant where crude oil is processed and refined into more useful petroleum products, such as liquefied petroleum gas (LPG), naphtha, gasoline, kerosene, diesel fuel, asphalt base and heating oil. Historically, the first oil refinery in the world was built in 1851 at Bathgate, Scotland, by the Scottish chemist James Young. Figure (1) illustrates a flowchart of a refinery process.

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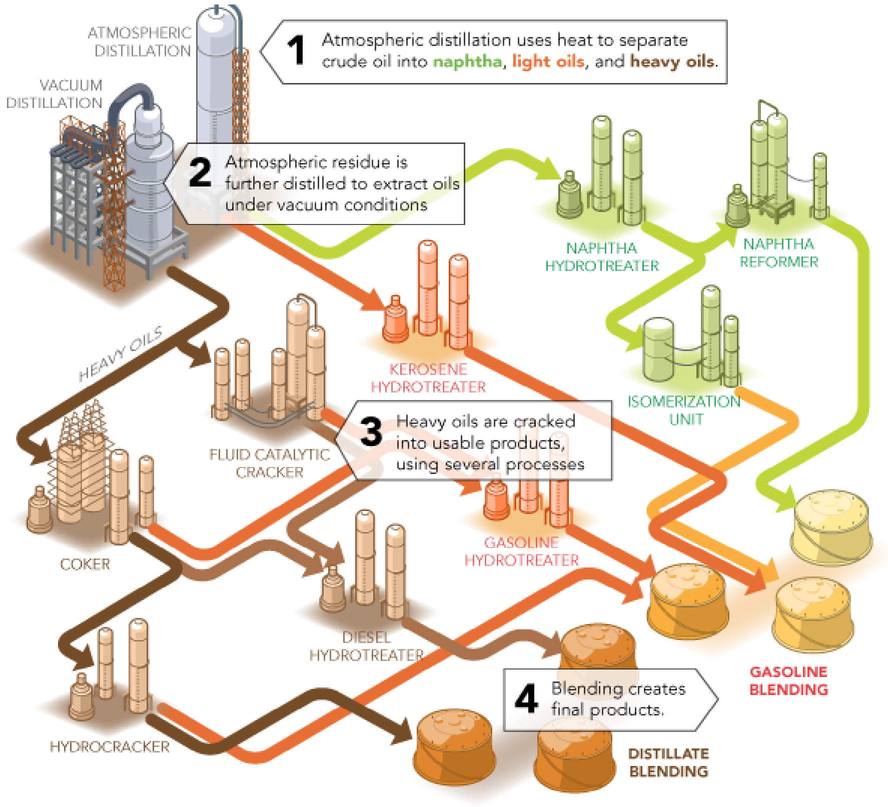

Figure (1) : Flowchart of a refinery process.

http://www.cieng.com/a-11-156-Industries-Refining.aspx

Generally, refinery operations include: fuel production; by-product processing; ancillary operations and waste management (Alshammari et al., 2008). In a petroleum refining process, hydrocarbons of varying molecular masses are separated into fractions through distillation (fractionation). In this process, crude oil from its storage tank is preheated and fractionated in the crude distillation unit. Through a chemical conversion, hydrocarbons are converted into product(s) while impurities are separated out. A lower grade crude oil may require a more complex refining process to remove impurities. Atmospheric distillation, vacuum distillation, reforming, cracking (catalytic cracking, fluid catalytic cracking, hydrocracking and thermal cracking), alkylation, isomerisation, polymerization, hydrotreating and sulphur plants, sulphur recovery plants, delayed coking and blending, etc. are among the processes involved in refineries (Bakr, 2010).

Sources of Sludges in Refineries

Air, water and land can all be affected by refinery operations, since out of a refinery process; both hazardous and non-hazardous solid wastes can be produced. Such wastes include sludge, spent process catalyst, filter clay and incinerator ash (Bakr, 2010). Refineries should be aware of their responsibility to the community and employ a variety of processes to safeguard the environment. The main sludges generated are oily sludge, bio sludge and chemical sludge. Sources of such sludges generation in refineries are schematically shown in Figure (2).

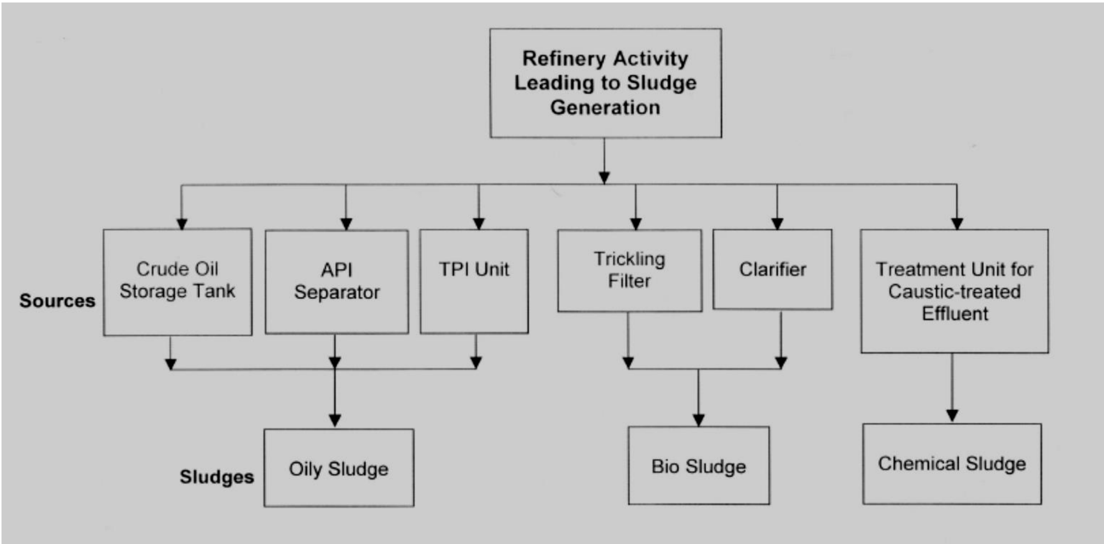

Figure (2): Sources of sludges in refineries (Bakr, 2010).

Presence of oily sludge in a refinery can be as a result of pumps and desalter failures, periodic cleaning of storage tanks, oil draining from tanks and operation units and also as a result of pipeline ruptures (Kuriakose and Manjooran, 2001). It can also be generated while treating wastewater in an American Petroleum Institute (API) separator and Tilted Plate Interceptor (TPI) unit of effluent treatment plants. Biological sludge can be generated during biological treatment of wastewater from trickling filter and clarifier unit. Finally, chemical sludge is generated during the treatment of caustic treated effluent with ferric chloride and polyelectrolyte. In accordance to: nature of crude oil, processing capacity, downstream capacities and design of the effluent treatment plant, etc., the amount of sludge generated is determined (Kuriakose and Manjooran, 2001). Due to rapid expansion of petroleum processing operations; generation of waste has rather been enormous by which a serious threat to environmental quality on the mother earth and its inhabitants is caused. By looking at what is remaining from the natural resources; one should exploit such resources efficiently in a way that even waste is considered as a beneficial matter (Alshammari et al., 2008). In a survey by Kuriakose & Manjooran

(Kuriakose and Manjooran, 2001) it was shown that oily sludge contains approximately 25% water, 5% inorganic sediments such as sand, clay, scales, etc., and the rest 70% hydrocarbons. Table (1) shows the characteristics of a purified refinery sludge (hydrocarbon fraction), while the weight percentages of the metal elements found in the ash following burning are shown in Table (2).

Table (1): Characteristics of a purified refinery sludge (hydrocarbon fraction) (Kuriakose and Manjooran, 2001).

Physical properties	Value
Density at 15 $^{\circ}$C (kg/m^3)	957.3
Pour point ($^{\circ}$C)	42
Wax (%wt)	6
Asphaltenes (%wt)	7.8
Acidity (mg KOH/g)	4.30
Flash Point ($^{\circ}$C)	> 200
Kinematic viscosity at 100 $^{\circ}$C (cS)	30.33
Total sulphur (% wt)	3.43
Ash content (% wt)	4.8

Table (2): The weight percent of the different metal elements in the ash (Kuriakose and Manjooran, 2001).

Element	Weight percentage (wt %)
Iron (Fe)	23.49
Aluminium (Al)	10.57
Calcium (Ca)	1.64
Sodium (Na)	0.57
Potassium (K)	0.46
Nickel (Ni)	0.12
Vanadium (V)	0.23
Magnesium (Mg)	0.65
Zinc (Zn)	0.21
Titanium (Ti)	0.53
Manganese (Mn)	0.10

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Treatment and Disposal of Oily Sludges

Available treatment and disposal methods for refinery sludges are discussed in this section. They include: sludge disposal in lagoon/pit, incineration, land farming and secure landfill of oily sludge. Storing an oily sludge in a lagoon has been commonly used. A lagoon is made with bricks and cement. Although lagoons are used to store an oily sludge, they; however, do not provide a long term and an environmentally friendly solution to ultimately dispose of an oily sludge (Einawawy Amins et al., 1987). In incineration, air in excess amounts is used to achieve complete combustion of waste by which a significant reduction in the amount of waste is secured. Combustion time, temperature and turbulence are important factors in the incineration process. Although it has been used in few developed countries, due to some reasons it has not found a wide application (Patel Naranbhai and Sing, 1999). These reasons include: incomplete combustion by which environmental pollution, by stack emissions, is caused. Also, it requires landfill facilities for the final disposal of ashes which contain heavy metals and require to be disposed of in an environmentally friendly manner. In land farming, as the name implies, waste in certain amounts is landfilled followed by the application of fertilizer and regular planting of crops. Mainly, it depends on the natural in-situ biological decomposition of hydrocarbons by the vast and varied population of microflorain natural soils associated with photo-degradation. Both structure of the soil and humus content can influence the process of hydrocarbon decomposition as they influence oil and water retention, type and population of microflora and the rate of oxygen transfer. This method requires further investigations prior to any large scale applications in the following environmental issues: the presence of oily odour during initial spreading, groundwater pollution due to migration of leachate contaminated with hydrocarbons, phenols and heavy metals and health problems associated with the contact of oily sludge. The last treatment process for refinery sludges is the secure landfill techniques. In this process, waste is isolated by thick layers of impermeable clay and synthetic liner to avoid contamination of air and ground water.

Recently, treatment and disposal of refinery sludge have become a problem of increasing urgency in industrialized societies. Certain methods of treatment and disposal of refinery sludge *do* exist, but they are not entirely satisfactory. Therefore, it is important to develop a technology for adequate treatment of refinery sludge in order to reduce the environmental problem and costs of treatment. It can be assumed that gasification is a suitable technology because it reduces waste volume, removes toxic organic compounds and fixes heavy metals in the resultant solid instead of landfill and/or incineration option. The gasification process converts any carbon containing material into a combustible gas composed primarily of carbon monoxide, hydrogen and methane, which can be used as a fuel to generate electricity and heat, and a little amount of these gases, can be used to dry wet refinery sludge. Typical raw materials used in gasification are coal, biomass, agricultural wastes, sewage sludge, and petroleum based materials. Gasification also adds value to low or negative feedstocks by converting them to marketable fuels and useful products.

Conclusions

The major sludges generated in the refinery are oily, bio and chemical sludge. At present in Libya five refineries are in operation which contribute significantly to sludge generation. Sludges usually contain various pollutants such as phenols, heavy metals, etc. Uncontrolled disposal of sludges on land and in lagoons leads to severe environmental pollution.

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