# Petroleum Oily Sludge and The Prospects of Microwave for Its Remediation

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***ABSTRACT*** *: Petroleum oily sludge, a hazardous waste, which is generated in the refineries and at the production sites has been an important environment and public health issue across the globe and disposal of excess sludge will be forbidden in the near future due to stringent pollution norms. The quantity of the hydrocarbon sludge generated by the refineries and at the production sites is huge and is going to scale up further in future as the demand for petroleum product keeps on growing. Oily sludge generally comprises of a mixture of petroleum hydrocarbons, asphaltenes, long chain paraffinic wax, waste water, sediments and metals. Moreover as the crude reserves is depleting our refiners are aimed to extract as much valuables as possible from the crude and from the left over sludge before disposing it. The present study is aimed at the review work for possible causes of the formation of sludge and the various technologies in use for the remediation of sludge, their limitation and to review the prospects of microwave technology for the remediation of the oily sludge for improving the recovery of valuables from oily sludge and for economical, fast and eco-friendly disposal of treated sludge.*

***Keywords*** *–Asphaltenes, cause of sludge formation, microwave, refinery oily sludge, sludge treatment technologies, wax*



## 1. Introduction

Crude oil is an important source of energy. One of the consequences of crude oil exploration, production and processing activities is the generation of vast amounts of oily sludge [1].Petroleum refineries and production sites unavoidably generate a huge amount of sludge during their storage operations and through on-going operations. The major sludge generated by the petroleum refineries are oily sludge, bio-sludge and chemical sludge[2]. Most of the crude oils have a property to separate into the heavier and lighter hydrocarbons during their storage and transportation. In refineries hydrocarbon sludge is usually generated during cleaning up of crude oil storage tanks, maintenance of associated facilities and pre-export processing i.e. tank farms, desalter failure, oil draining from tanks and operation units, pipeline ruptures and processing of oil [3].About 47000MT of sludge is generated in 2011-12 by Indian refineries [4].The composition of oily sludge varies due to the large diversity in the quality of crude oils, differences in the processes used for oil–water separation, leakages during industrial processes and also mixing with the existing oily sludge. Oily sludge is basically comprises of about 55.13% of water, 9.246% of sediments, 1.9173% of asphaltenes, 10.514% of wax and 23.19% of light hydrocarbons and also a high concentration of heavy metals for instance vanadium is 204ppm,Fe is 0.6% and nickel is 506ppm which makes the oily sludge harmful for the environment and organisms which need to be dealt with for environmental protection. [4].The Ministry of Environment and Forests, Government of India has categorized refinery oily sludge as the hazardous waste and it has become an important environmental and public health issue in India, like other developed and developing countries [5].Because of the hazardous nature of oily sludge, disposal of excess sludge will be forbidden in the near future, thus increased attention has been turned to look into potential technology for sludge treatment. India is the fifth largest energy consumer in the world. There is a growing demand as a result of the rise in population and economic growth. India's petroleum product consumption has grown by 4-5% over the past 10 years and the oil demand in India is expected to rise to 368 MMTPA by 2025 [6].So oil production companies and the refiners are looking for the technologies which are aimed to extract the hydrocarbon from the sludge to the maximum extent and thus to minimize the final treated sludge quantity which can be disposed in a much economical, fast and eco-friendly ways. The present work is aimed to review the causes of sludge formation, the research work done in the field of remediation of sludge and to find out the prospects of microwave for the remediation of sludge and hydrocarbon recovery so as to encourage and facilitate the researchers to work for developing a suitable technology of sludge treatment using microwave.

## 2. Classification of refinery sludge

Based on source and chemical composition the wastes generated in refineries can be broadly classified as follows:

- Hydrocarbon Wastes: It includes API separator sludge, dissolved air flotation float, slop oil emission solids, tank bottoms, FFU sludge, desalter bottoms and waste oils/solvents.
- Spent Catalysts: It includes fluid cracking catalyst, hydro-processing catalyst and other spent inorganic clays.
- Chemical/Inorganic Wastes: It includes spent caustic, spent acids and waste amines.
- Contaminated Soils and Solids: It includes heat exchanger bundle cleaning sludge, waste coke/carbon/ charcoal, waste sulphur and miscellaneous contaminated soils.
- Aqueous Waste: It includes biomass, oil contaminated water (not wastewater), high/low pH water and spent sulphide solutions.

Among the wastes generated in the refineries, the oily sludge has reuse potential if the oil and other components of it can be recovered by proper treatment processes. The breakup of refinery hydrocarbon waste is tabulated in Table 1[7].

*Table 1: Breakup of refinery hydrocarbon sludge*

| TYPES | % w/w |
|---|---|
| API/DAF/IAF SLUDGES | 41.8 |
| WWTP SLUDGE | 30.2 |
| BOILINGFRESH WATER PREPARATION SLUDGE | 13.0 |
| TANK BOTTOM SLUDGE | 7.1 |
| MISCELLANEOUS SLUDGE | 6.7 |
| DESALTER SLUDGE | 0.8 |
| ACID ALKYLATION SLUDGE | 0.3 |



## 3. The formation of crude oil sludge

Most of the crude oils have a property to separate into the heavier and lighter hydrocarbons during their storage and transportation. Such problems are often exacerbated by cold temperatures, venting of volatile components from the crude, and by the static condition of fluid during storage. The heavy ends that separate from the crude oil are found to get deposited on the bottoms of the storage tanks/vessels, commonly known as tank bottoms or sludge.

Paraffin-based crude oil sludge forms when the molecular orbital of individual straight chain hydrocarbons are blended by proximity, producing an induced dipole force that resists separation. As the heavier straight chain hydrocarbons flocculate (heavier meaning predominantly the $C_{20+}$ hydrocarbon molecules), they tend to fall out of suspension within a static fluid, as in the case of storage tanks/vessels where they accumulate on the bottom as viscous gel commonly known as sludge or wax. This newly formed profile stratifies over time as the volatile components within the sludge are expelled with changes in temperature and pressure. The departure of such volatile components results in a concentrated heavier fractions within the sludge, accompanying with increased in density and viscosity, and decreased fluidity. [8]

Formation of asphaltic sludge is because of the tendency of asphaltenes, resins and polymeric compounds to precipitate.The colloidally dispersed asphaltic and related substances in crude oils which are precipitated upon contact with acid are of such a complex nature that they are classified chiefly on the basis of their physical properties [9].The most common classification is as follows:

3.1 Neutral Resins: These substances are high-molecular-weight aromatic hydrocarbons, which are insoluble in alkalise and acids and completely miscible with petroleum oils, including light fractions.

3.2 Asphaltenes: These materials are similar to the neutral resins, but insoluble in light gasoline and petroleum ether. In contrast to the neutral resins, the asphaltenes are precipitated in the presence of an excess of petroleum ether. Both asphaltenes and neutral resins are completely soluble in benzene, chloroform and carbon disulphide.

The asphaltic material present in crude oil is in the form of colloidal particles. Studies have proposed the concept that asphaltenes form the centre of the micelles, with neutral resins absorbed on the surface of the asphaltenes particles [10][11].The substances with the greatest molecular weight and most pronounced aromatic nature form the nucleus. Around this nucleus are arranged lighter and less aromatic constituents and there is a gradual transition to preponderantly aliphatic compounds. It is these adsorbed materials which stabilize the colloidal material. The precipitation of asphaltenes from crude oil by the addition of large quantities of n-pentane is explained on the basis of stripping of the adsorbed aromatic peptizing agents from the asphaltenes. Although the stability of colloidal asphaltenes particles is primarily attributed to adsorbed peptizing agents, other stabilizing factors have been noted. The colloidal material in crude oil is electrically charged. Imposition of a potential across a small body of oil results in electro-deposition of asphaltic material at the positive electrode. It also shows that the neutralization of this charge can result in precipitation of the material. [12]

Other reasons involved in sludge formation are the precipitation of inorganic residue (inorganic salts, sediments, sands, scale and dust). Mixing of non-compatible crudes in the same tank is also a major factor for sludge formation.The Solvent blending number is a parameter relating to the compatibility of oil with different proportions of a model solvent mixture such as toluene/n-heptanes. The oil compatibility model describes about the incompatibility of crude oils when they are mixed during storage and handling [13].

## 4. Composition of oily sludge

The composition of oily sludge is very complex, generally it comprises of oil-in-water, water-in-oil emulsion and suspended solids [14].Oily sludge contains toxic substances like aromatic hydrocarbons, poly-aromatic hydrocarbons [15] and high total hydrocarbon content [16]. Oily sludge is a stable system of suspension emulsion. Hydration and charge lead to the steady dispersion, and a layer or layers of water attached to the surface of the particles causes a combination of barriers [17]. In addition, sludge particles generally bear negative charge. Most particles of oily sludge are attracted to each other rather than repelled. Because of high viscosity, oily sludge is difficult to be dehydrated. Oily sludge is considered as a hazardous solid waste, and its physical–chemical characterization is very complicated. Oily sludge is basically comprises of about 55.13% of water, 9.246% of sediments, 1.9173% of asphaltenes, 10.514% of wax, 23.19% of light hydrocarbons and the high concentration of heavy metals for instance vanadium is 204ppm, Fe is 0.6% and nickel is 506ppm[4].

## 5. Need and ways for sludge treatment

The sludge processing and recovery of the valuables are two major problems faced by the oil companies. Every year, an innovation arises in the petroleum industry pertaining to the utilisation of slop oil and paraffin waxes that is separated from crude oil during storage and pipeline transfers and to minimise the maintenance costs, corrosion and environmental problems related to the remediation of the sludge. Hazardous waste has become an important environmental and public health issue in India, like other developed and developing countries. The Ministry of Environment and Forests, Government of India has categorized refinery oily sludge as the hazardous waste and it has become an important environmental and public health issue in India, like other developed and developing countries [5].Because of the hazardous nature of oily sludge, disposal of excess sludge will be forbidden in a near future, thus increased attention has been turned to look into potential technology for sludge treatment. So refiners have two major agenda for sludge treatment. Firstly is to improve the recovery of valuable oil from oily sludge, and secondly to find a way for economical, fast and eco-friendly disposal of treated sludge. The ways of disposing of sludge can be classified into four major heads:

- Thermal application which is basically incinerating unusable sludge and harnessing heat and gases.

- Dehydration of sludge where the cleaned water is recovered and is returned to the environment, and the hard sludge particles are buried.
- Use of sludge as heat source.
- Biological remediation.

A number of technologies of varying complexity have been proposed, or are currently in use, throughout the oil industry.

5.1 Sludge Treatment Techniques

The oily sludge removed from the storage tanks are subjected to treatments for separation and oil recovery. Many researchers have developed various technologies for the treatment of oily sludge during 1960 to 1970. Many reprocessing plants were severely affected by hazardous waste regulations promulgated in the late 1970s and early 1980s, resulting in the permanent shutdown of large segments of the industry. The various technologies for oil recovery and redemption of the crude sludge include chemical treatments, various distillation processes, cracking, hydro-treating, solvent treatment, and bioremediation. Most of the used oil reprocessing techniques that has survived appears to be based upon the low temperature (less than $300^0$F or $150^0$C) solvent extraction technology or centrifuge method. Some of the conventional methods of sludge treatment are discussed in the following sections.

5.1.1 Manual Cleaning and Incineration

Manual cleaning is the most common and historically has been the low cost method of tank cleaning and recovering oil from sludge. The cleaning is completed by entering the tank and using manual labour to move the sludge either out the door or to pumps stationed in the tank. This method usually takes a long period of time. Using this method, it is difficult to recover the usable hydrocarbons from the sludge that is removed from the storage tanks and thus has very limited oil recovery.This method is labour intensive and personnel spend long periods of time working in a toxic and flammable environment. The majority of the sludge that is removed is usually disposed of as hazardous waste or incinerated. Revisions of the law governing waste treatment and cleaning have toughened regulations on CO and dioxin so that more and more incinerators are being shut down and restrictions on incineration have been multiplying.

5.1.2 Solvent extraction method

Solvent extraction is gaining popularity and credibility as a method of tank sludge oil recovery. Various solvents are used to break down the complex molecules contained in the sludge and render them to their basic constituents – water, crude oil and particulate. This method relies on a chemical reaction and the speed, efficiency and thoroughness of the reaction which are proportional to the exposed surface area of the sludge. Therefore chemical cleaning methods require some sort of mixing apparatus or method of agitation. It has been found that petroleum oil defer in their capability to dissolve the organic components of oil tank sludge. Sludge in addition to their inorganic contents of salt, oxides and other inorganic materials, have been found to contain both waxy and non-waxy(asphaltenes) organic components and that these may be most efficaciously dissolved by appropriate selection of the solvent oil[18].A typical simplified block diagram of slovent extaction process is shown in Fig 1.

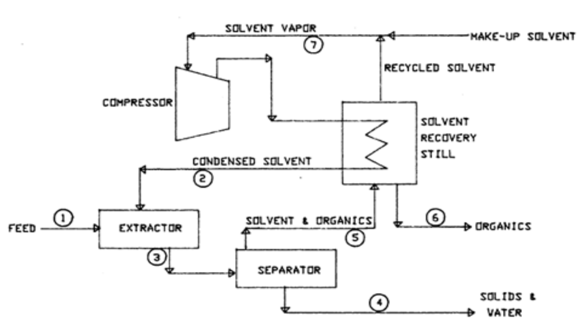


*Figure 1: Simplified block flow diagram of solvent extraction process*

Solvent is allowed to flow into the extractor where non-reactive contact is made with the feed slurry. Organics contained in the sludge are dissolved into the solvent. The extractor contents flow to a decanter where gravity phase separation takes place. The raffinate product, containing the water and treated solids is collected from the bottom of the decanter/separator .The solvent-organic mixture collected from the top of separator is sent to solvent recovery still for oil and solvent recovery.

5.1.3 Ultra High temperature gasification

Ultra high temperature gasification involves thermal oxidation of sludge i.e. heating to a very high temperature (over 1,000°C) using plasma arc without oxygen. It converts the sludge to a valuable pyrogas that can be used as fuel [19].

5.1.4 Oil Sludge Separation using Cyclone

The cyclonic separation is a method of removing the residue and recovery of oil from the oily sludge. A typical setup of oily sludge separation by cyclone is shown in Fig.2 [20].

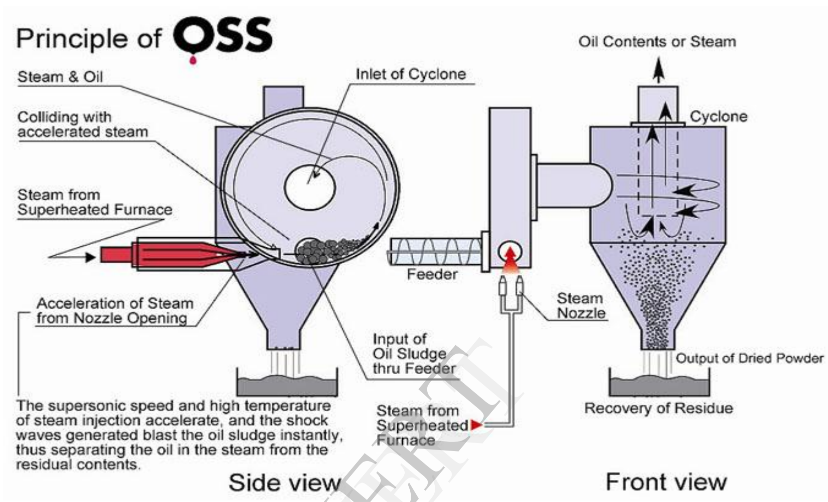


*Figure 2: Oily sludge separation by cyclone*



5.1.5 Oily sludge treatment by application of thermo-chemistry

In this method oily sludge is diluted by heating water and certain chemical reagents are added for extraction of oil from solid-phase. This method was widely used for high oil content, crude oil and oily sands of low emulsification [21].

5.1.6 Bioremediation

The bioremediation technology for the treatment of oily-sludge focuses mainly on basic and applied research on microbial resources for separation of oil from sludge and biodegradation of the residues to address the environmental issues. The activities of bioremediation area are focused to clean up oil spills on land, oily effluent treatment plant (ETP) and tank bottom waste, oil contaminated soil, oil contaminated pond and sea water, oil contaminated drill cuttings, synthetic oil based mud waste by using specific microbial consortium like Oilzapper, Oilivorous – S,Oilivorous - A, KT – Oil zapper, and so on.

5.2 Limitation faced by various sludge treatment processes

Every sludge processing technique has its own advantages and disadvantages. The traditional methods include high heat and chemical utilization, which force the emulsion to separate into water, hydrocarbon and solids. Usually these processes are expensive, energy intensive, low efficiency and require the secondary treatment processes to recover the valuables. These treatment processes might again generate secondary wastes that must also be disposed or treated further for safe or eco-friendly disposal. Solvent extraction methods have limits on VOC (volatile organic compounds) emissions and concerns for worker safety and regulations. Even bioremediation for disposal of sludge was found slow for some refineries for instance in the case study at Mangalore refinery, the time for bioremediation was more than 20 months and the rate of biodegradation of TPH was 0.07 Kg TPH/day/m2 area of bioremediation site [22].

As an alternate, a prospect of microwave heating was studied for sludge treatment to overcome the limitation faced by conventional processes. As microwave can penetrate deeply into the interiors of thick sludge without heating surface and can provide an enhanced separation mechanism.

## 6. Microwave heating approach for sludge treatment

Since Percy Spencer accidentally discovered the possibility of cooking food with microwaves in the 1940s, research on microwave heating have continued unabated. The use of microwaves for heating is well established in society, and is being used in domestic and some industrial processes. There is a potential for this technology which can be introduced and applied to many other industrial heating processes, which offers unique advantages not attained with conventional heating. In this sense, microwave technology is being explored as one method to assist in waste management. The concept of microwave heating for demulsification of sludge-oil emulsion was first introduced by Klaila (1983) and Wolf (1986) in their patents [23][24].In conventional thermal processing, energy is transferred to the material through convection, conduction and radiation of heat from the surfaces of the material. In contrast, microwave energy is delivered directly to materials through molecular interaction with the electromagnetic field. In heat transfer, energy is transferred due to thermal gradients, but microwave heating is the transfer of electromagnetic energy to thermal energy and is energy conversion, rather than heat transfer. This difference in the mode the energy is delivered can result in many potential advantages for using microwaves for processing of materials. Microwaves can penetrate materials and deposit energy and so heat can be generated throughout the volume of the material. The transfer of energy does not rely on diffusion of heat from the surface and it is possible to achieve rapid and uniform heating of thick materials [25].Range of microwave wavelength is shown in Fig.3

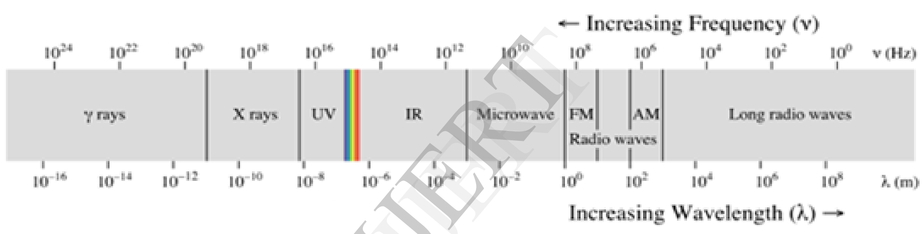




*Figure 3: Range of Microwave wavelength.*

Microwaves lie between infrared radiation and radio waves in the region of the electromagnetic spectrum. More specifically, they are defined as the waves with wavelengths between 0.001m and 1m, which correspond to frequencies between 0.3GHz and 300GHz. For microwave heating, two frequencies are reserved by the Federal Communications Commission (FCC) for industrial, scientific and medical (ISM) purposes are 0.915GHz and 2.45 GHz.

### 6.1 Fundamental principles of microwave

Microwave is an electromagnetic wave consisting of electric and magnetic field components, both perpendicular to each other. Generally, there are three qualitative ways in which a material may be categorized with respect to its interaction with the electric field component of the microwave field:(i) insulators, where microwaves pass through without any losses (transparent), (ii) conductors, where microwaves are reflected and cannot penetrate, and (iii) absorbers [26]. Materials that absorb microwave radiation are called dielectrics, thus, microwave heating is also referred to as dielectric heating. There exist a number of mechanisms that contribute to the dielectric response of materials [25]. These include electronic polarization, atomic polarization, ionic conduction, dipole (orientation) polarization, and interfacial or Maxwell-Wagner polarization mechanisms.

At microwave frequencies, only dipole and Maxwell-Wagner polarizations result in the transfer of electromagnetic energy to thermal energy [27]. The two types of oscillating perpendicular fields that generate microwaves are the electric field and magnetic field. Both the ionic conduction and dipole rotation are responsible for heating of substances [28]. The absorbed energy can interact with materials through either redistribution (formation and rotation) of bound charges i.e. polarization or long range transport of charges i.e. conduction process.The electrophoretic migration of ions under the influence of the changing electric field is called ionic conduction[29]. If the solution offers a resistance to this migration of ions, a friction is generated and the solution is heated. The realignment of the dipoles of the molecule with the rapidly changing electric field is called Dipole rotation [30].

In polar organic-solvent systems, the dipolar polarization mechanism accounts for the majority of the microwave heating effect, while in some carbon-based materials the interfacial polarization accounts for the majority of microwave heating. With respect to the former, dipoles may be a natural feature of the dielectric or they may be induced [31].Distortion of the electron cloud around non-polar molecules or atoms through the presence of an external electric field can induce temporary dipoles. This movement results in rotation of the dipoles and energy is dissipated as heat from internal resistance to the rotation.

On the other hand, the Maxwell-Wagner polarization occurs at the boundary of two materials with different dielectric properties or in dielectric solid materials with charged particles which are free to move in a delimited region of the material, such as π-electrons in carbon materials [32]. When the charged particles cannot couple to the changes of phase of the electric field, the accumulation of charge at the material interface is produced and energy is dissipated in the form of heat due to the so called Maxell-Wagner effect [32].The interaction of microwaves with metals or metal powder may further contribute to the energy absorption effect [33]. The response to an applied electric field is dependent on the dielectric properties of the material [25]. The polarization takes place when the effective current in the irradiated sample is out of phase with that of the applied field. Because the dielectric properties govern the ability of materials to heat in microwave fields, the measurement of these properties as a function of temperature frequency, or other relevant parameters (moisture content, density, material geometry, etc.) is important [34]. The two major effects on the material when subjected to microwave are shown in Fig 3.

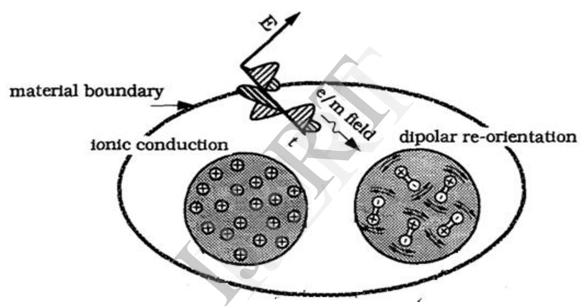


*Figure 3: Effect of microwave on the material.*

6.2 Advantage of microwave heating and research work done in the field of microwave heating

In heat transfer, energy is transferred due to thermal gradients, but microwave heating is the transfer of electromagnetic energy to thermal energy and is energy conversion rather than heat transfer .This difference in the way the energy is delivered result in many potential advantages of using microwaves for processing of materials. Because microwaves can penetrate materials and deposit energy, heat can be generated throughout the volume of the material. The transfer of energy does not rely on diffusion of heat from the surfaces and it is possible to achieve rapid and uniform heating of thick materials.

A review of the literature has shown that a lot of research has been done or being done in the field of microwave heating which suggest the prospects for its use for the remediation of the oily sludge also. The findings are summarized here.

- Nicolas Wolf, in U.S. Pat. No. 4,582,629, 1986, claims a method for enhancing the separation of hydrocarbon and water from an emulsion or dispersion with the application of microwave energy than heating the emulsion using conventional heating means [23].
- Microwave heating provides the higher heating rate, the shorter residence time, and the faster the volatiles arrive to the external cold regions which, in turn, reduce the activity of secondary reactions of vapour phase products. This results in high yields of liquid and reduced deposition of refractory condensable material on the char’s internal surface [35].
- The testing program on microwave separation of oil-water sludge by EPRI Centre for Materials Production, Pittsburgh, US demonstrate the ability of microwave de-oiling to successfully separate a very diverse range of waste sludge into water, oil and solids.[36]

- Menendez and Dominguez have observed greater gas yield and lesser carbonaceous residue in the microwave pyrolysis in their experiments on different wastes, which demonstrate the efficiency of microwaves in carrying out heterogeneous reactions. Some of the heterogeneous reactions observed in pyrolysis processes, such as gasification reactions with CO2 or H2O, have been executed individually at different temperatures under both heating systems [37][38].
- Microwave heating gives a better catalytic effect for specific reactions, such as the methane decomposition reaction. [39].
- Several pyrolysis studies have been conducted using microwaves as a heating source, with lignocellulosic feedstocks that included wood [40][41], coffee hulls[42], rice straw[43], waste tea[44] and wheat straw [45]. As a result of the aforementioned research works, various products were generated, including gas, liquid and solid phase products. The primary factors affecting the product distribution and components include reaction temperature, reaction time, microwave power, particle size, additives, and the original characteristics of feedstock. These researches clearly show the potential of microwave pyrolysis.
- Several studies have revealed the potential of pyrolysis as a disposal method for waste oil [46][47][48].The work has shown that microwave pyrolysis has huge potential as a means of recovering commercially valuable products from waste engine oil. More specifically they realized the potential for recovering gaseous hydrocarbons with light olefins, and liquid hydrocarbon oils containing BTX and benzene derivatives.
- Microwave Pyrolysis techniques for treating plastic waste were initially developed by Tech-En Ltd in Hainault, UK [48]. The process involves mixing plastic containing wastes, which are known to have very high transparencies to microwaves, with a highly microwave-absorbent material such as particulate carbon [49]. The carbon reaches temperatures of around 1000 °C within a few minutes in the microwave field and energy is transferred to the shredded plastic by conduction, providing the efficient energy-transfer associated with microwave-heating processes. From their results it was concluded that microwave pyrolysis provides a more even distribution of heat and better control over the heating process than conventional heating techniques.
- The microwave heating process was examined for water, oil and emulsion samples by Abdurahman H. Nour, Rosli M. Yunus, and Azhary. H. Nour in 2006. Results of their study showed that microwave radiation is a dielectric heating technique with the unique characteristics of fast, volumetric and effective heating and has the potential to be used an alternative way in the demulsification of water-in-oil emulsions. It showed that microwave radiation can raise the temperature of emulsion, reduce the viscosity and accelerate separation process and separation was possible without chemical addition [14].



## 7. Conclusion

At present in India twenty two refineries are in operation which contribute significantly to sludge generation along with the oil production companies. Sludge usually contains various pollutants such as hydrocarbons, heavy metals etc. and uncontrolled disposal of sludge on land and in lagoons leads to severe environmental pollution. A number of technologies of varying complexity have been proposed, or are currently in use, throughout the oil industry for the sludge redemption. Usually these processes are expensive, energy intensive, low efficiency, time consuming and require the secondary treatment processes to recover the valuables.Based on the various research works in the field of microwave technology and the literary review on microwave heating it is quite certain to have a potential for the solution of the basic problem being faced by various sludge treatment processes. So it’s the time for looking up for the new technology based on microwave for sludge processing with the aim to extract the hydrocarbon from the sludge to the maximum extent and thus to minimize the final treated sludge quantity which can be disposed in a much economical, fast and eco-friendly ways. The microwave treatment of sludge using suitable solvent seems to have several advantages. It requires less time, can heat the sludge in the better and more efficient way and thus if used with the suitable solvent can give the better efficiency for oil recovery. Thus microwave treatment gives an avenue to the researchers for developing the technologies for sludge treatment which can minimize the drawbacks faced by conventional techniques.

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