



Original article

A report of the oil spill recovery and treatment technologies to reduce the marine environment pollution

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Abstract

Physical smothering in a long time and toxic components due to the oil spill and oil slick disasters can not only affect directly, very seriously marine creatures, plants and life of other animals but also they pollute the air environment and reduce the health of human. Some activities such as the waterway accidents, the tanker or bilge discharges, and the acts of wanton vandalism are the main causes that pollute the ocean environment. The regulations of many countries such as the prevention of oil spill, reducing maximally the effects of the oil spill, and speeding up the oil spill degradation are to aim at treating and recovering fast, efficiently oil spills and oil slicks. The selection of suitable techniques for oil spill recovery and treatment depends on many factors such as the spilled oil volume, oil type, weather conditions (wind velocity), sea conditions (current velocity and wave height), cost and the fact situations of each country. In this paper, four methods used for oil spill recovery including physical-, chemical-, thermal-, and biodegradation method are introduced. The structure of mechanical devices including booms, skimmers and absorbent materials, the properties of chemicals such as dispersants and solidifies, the methods based on the thermal technologies, the major microorganisms for oil degradation for oil spill recovery, treatment and cleanup are analyzed. Each mentioned method also shows the advantages and disadvantages, as well as its applicability. The selection of suitable method for oil spill recovery purpose on the basis of the available equipment and techniques must be ensure that the collected oil spill volume is the largest, the period of time for recovery process is the shortest, aiming at minimizing the negative effects on the human, marine ecosystem, social economy.

Keywords: oil spill, recovery technology, marine environment pollution, maritime operation

1. Introduction

The oil spill and oil slick have been being considered as toxic substances as discharged into the sea environment and the effects of the oil spill and oil slick on the human, marine life, tourism and entertainment activities, birds and aquatic animals are always extremely serious. Some causes regarding marine oil pollution were reported by the past study, including the accidents from ships/vessels, the operation of the ships/vessels, the shipwreck, and the exploration incidents regarding the oil wells or the oilrigs, the actions of illegal bilge discharges of seawater (Hoang, et al., 2018; Ngo, et al., 2014). As reported, around 5.71 million tonnes of oil was spilled on the water surface from 1970 to 2010 because of the tanker incidents (Hoang and Chau, 2018). After being spilled on the seawater surface, oil slick and emulsions of oil-water are formed. They depend on a number of different factors, which may include the weather and sea conditions, wind and current velocity (affect directly the spreading speed of oil on the seawater surface), drifting in the seawater, the evaporation speed of oil into the air, physicochemical properties of the spilled oil. The changes of the above-mentioned factors result in the significant changes of spilled oil viscosity and density, the interfacial tension force (Musk, 2012). Moreover, some oxygenated contents contained in spilled oil and oil slick are the main causes of the seawater pollution in a long-term (Shadizadeh, et al., 2014). Up to now, there have had several advanced techniques being used to recover and treat the oil spill and oil slick. They are mechanical and in-situ burning methods, bioremediation method, chemical method (including solidifiers or dispersants). The selection of suitable methods for each application needs to be based on the type of the spilled oil, spilled oil volume, the weather and sea conditions, available equipment situations (Al-Majed, et al., 2012; Fingas, 2012; Hoang, et al., 2018). However, the use of chemical methods to treat oil from seawater may have some negative impacts on the environment. Normally, the oil spill incidents in the marine environment are divided into three following classes:

The 1st class: Oil spill is considered as the incidents regarding berthing, the operation of ships/vessels in the port, the oily water discharge from ballast and marine engine room.

The 2nd class: Oil spill is related to the incidents of

shipping or oil exploration, including collisions, fires or other. However, the oil spill incidents, which cause by oil tanker sank, oilrig damage, always tend to affect a large area and to lead to polluting seriously the ocean environment.

The 3rd class: The "unacceptable actions" or "degeneration" of some people or groups in dumping sneakily the oily water or waste oil into the ocean environment with their purpose of saving the money (Singkran, 2013). These actions are considered as ultra criminal ones; they are also different from shipping/maritime accidents.

According to the reported statistics based on the data from 1900 to the present time, yearly, around 2 to 4 large oil spill incidents occur in the world. The most notable oil spill incidents are as followed: (1) In 1978, the spilled oil in Amoco Cadiz, Brittany Bay, Northern West France with 231 thousand tonnes of crude oil; (2) In 1989, the spilled oil incidents of Exxon Valdez ship with 40 thousand tonnes of oil into the ocean, Alaska, United State America; (3) In 2002, 77 thousand tonnes of oil discharged into the ocean by a ship named Prestige, in Northern West, Spain; (4) In 2007, the Hebei Spirit ship discharged 2.7 million gallons of oil into the sea of South West Korea (Craig, 2011; Fingas, 2018; Gasparotti, 2010). In Vietnam, a recent oil spill incident in Ly Son island shown in Picture 1 also affected heavily the ocean environment and the life.



Picture 1: Oil spill and oil slick at Ly Son Island, Vietnam

Obviously, all the oil spills show serious effects on the ecological system, social economy losses. Therefore, finding solutions or methods to recover and treat the spilled oil and oil slick aiming at meeting strategies of the marine environment protection based on IMO

regulations is an extremely urgent issue (Ventikos, et al., 2004). This study reported the published research results of applying the advanced techniques for recovering and treating spilled oil in the maritime field. This review paper introduced the commercial oil physicochemical properties, which were considered as the important factors needed to be determined to use the suitable recovery methods. Moreover, the physical-, chemical-, in-situ burning-, and bioremediation methods were also classified and mentioned. Finally, suitable solutions were suggested based on the oil spill level, weather and sea conditions, and available devices.

2. Oil spill properties

2.1. Physical properties

The physical properties of the oil spill, being solubility, surface tension, kinematic viscosity, pour point, density, are the main parameters affecting significantly the spreading speed, the evaporation speed, the emulsion level with water. However, density is an important parameter to evaluate and predict the behavior of the oil spill in seawater. In fact, the oil spill density is lower than seawater density, hence, the spilled oil floats and lies flat on seawater surface, and spilled oil always tend to spread horizontally when are under high waves and strong wind (Zekri, et al., 2014). Moreover, spilled oil with lower density compared to seawater also shows the increase in the evaporation because the oil spill is thought to contain the light materials and substances. The evaporation of the above-mentioned light materials and substances leaves the heavy materials, which can sink in the seawater column and can interact with seawater components to produce the dangerous sedimentation.

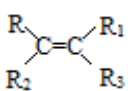
Additionally, spilled oil kinematic viscosity is also considered as a parameter evaluating the level and rate of spreading oil on the seawater surface. Normally, the



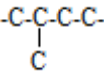
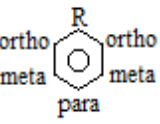
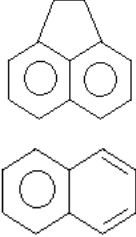
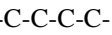
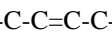
high viscous oil spill is easy to form the chocolate moss, which results in the difficulties in degradation, recovery, and treatment. Moreover, in the case of high ambient temperature, the density and viscosity of spill decreased leading to an increase in the ability of horizontal spreading (Lim and Khimji, 2013). Meanwhile, pour point of the oil spill is related to temperature, this means that spill oil becomes a semi-solid at a higher temperature in comparison with freeze point and it causes the difficulty and complication of oil spill cleanup strategy. Furthermore, the solubility of oil in seawater, which depends on the environmental temperature and chemical structure of hydrocarbon, can occur to produce the pollutant and difficult bioremediation. The solubility of oil is found around from 28 to 31 mg/l (Dave and Ghaly, 2011). On the other hand, the surface tension of the oil spill is inversely proportional to temperature, thus, the oil spill is more prone to spread in warm waters. Spilled oil surface tension affects significantly and quickly the spreading ability of the oil spill, even in the condition of without wind, calm water, and small current velocity.

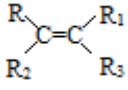

2.2. Chemical properties

The chemical properties of the oil spill are characterized by the hydrocarbon components, which are around 50 to 98% of the oil. Therefore, the chemical properties of the oil spill are very complex. Spill oil also contains the non-hydrocarbon components, which are oxygen, nitrogen, sulfur, and trace metals (Fingas, 2012). Table 1 lists the name of hydrocarbon components of the oil spill, these hydrocarbon components are classified on the basis of nomenclature by The International Union of Pure and Applied Chemistry (IUPAC). Overall, oil is divided into following classifications: saturated-, unsaturated, and aromatic- hydrocarbons, asphaltenes and resins, and refined products (Clayton, 2005).

Table 1: Main classes of hydrocarbons

Primary class	Compounds
Straight chain alkanes, n-alkanes -C-C-C-C-	Propane with chemical formula: C_3H_8 n-Hexane with chemical formula: $CH_3(CH_2)_4CH_3$ n-Dodecane with chemical formula: $CH_3(CH_2)_{10}CH_3$
Straight chain alkenes, n-alkenes -C-C=C-C- 	Cis-but-2-ene with chemical formula: $CH_3CH=CHCH_3$ Pent-1-ene with chemical formula: $CH_2=CH(CH_2)_2CH_3$ Trans-hept-2-ene with chemical formula: $CH_3CH=CH(CH_2)_3CH_3$

<p>Cis -: R is the same as R₁ or/and R₂ is the same as R₃</p> <p>Trans-: R is different from R₁ and R₂ is different from R₃</p>	
<p>Cycloalkanes, a ring with a single bond</p> 	<p>Cyclohexane with chemical formula: C₆H₁₂</p> <p>n-Propyl-cyclopentane with chemical formula: CH₃CH₂CH₂C₅H₉</p> <p>Ethyl-cyclohexane with chemical formula: CH₃CH₂C₆H₁₁</p>
<p>Cycloalkenes, a ring with double bonds</p> 	<p>Cyclopentene with chemical formula: C₅H₈</p> <p>3-Methyl-cyclopentene with chemical formula: CH₃C₅H₇</p>
<p>Branched-chain alkanes</p> 	<p>2-Methyl-propanewith chemical formula: CH₃CH(CH₃)CH₃</p> <p>2,2-Dimethyl-butane with chemical formula: CH₃CH(CH₃)₂CH₂CH₃</p> <p>2,2-Dimethyl-propane with chemical formula: CH₃CH(CH₃)₂CH₃</p> <p>2-Ethyl-hexane with chemical formula: CH₃CH(C₂H₅)(CH₂)₃CH₃</p>
<p>Branched-chain alkenes</p>	<p>2-Methyl-but-1-enewith chemical formula: CH₂=C(CH₃)CH₂CH₃</p> <p>4,4-Dimethyl-cis-pent-2-enewith chemical formula: CH₃CH=CHC(CH₃)₂CH₃</p>
<p>(Alkyl) benzenes</p>  <p>R- ankyl</p>	<p>Benzene with chemical formula: C₆H₆</p> <p>Methyl benzenewith chemical formula: CH₃C₆H₅</p> <p>Ethyl benzenewith chemical formula: C₂H₅C₆H₅</p> <p>(o-Xylene) o-Methyl-toluenewith chemical formula: CH₃C₆H₄(o-CH₃)</p> <p>(m-Xylene) m-Methyl-toluenewith chemical formula: CH₃C₆H₄(m-CH₃)</p> <p>(p-Xylene) p-Methyl-toluenewith chemical formula: CH₃C₆H₄(p-CH₃)</p> <p>1,2-Dimethyl-3-ethyl-benzenewith chemical formula: (1-CH₃)(2-CH₃)C₆H₃(3-C₂H₅)</p> <p>1,2,3-Trimethyl-benzenewith chemical formula: (1-CH₃)(2-CH₃)C₆H₃(3-CH₃)</p> <p>n-Propyl-benzene with chemical formula: CH₃CH₂CH₂C₆H₅</p>
<p>Other aromatic hydrocarbons</p>	<p>Phenol with chemical formula: C₆H₅OH</p> <p>Cresolwith chemical formula: RC₆H₄OH, R is ankyl</p> <p>Hexaclaro-cyclohexane,with chemical formula: C₆H₆Cl₆</p>
<p>Polycyclic aromatic hydrocarbons</p> 	<p>Acenaphthene with 2 rings of benzene and a ring of cycloalkane,with chemical formula: C₁₂H₁₀</p> <p>Naphthalene with 2 rings of benzene,with chemical formula: C₁₀H₈</p> <p>Anthracene with 2 rings of benzene, a ring of cycloalkane and a ring of a cycloalkene,with chemical formula: C₁₄H₁₀</p> <p>Chrysene with 3 rings of benzene, a ring of cycloalkadiene,with chemical formula: C₁₈H₁₂</p> <p>Coronene with 4 rings of benzene, a ring of cycloalkene and 2 rings of cycloalkadiene,with chemical formula: C₂₄H₁₂</p> <p>Pyrene with 3 rings of benzene, a ring of a cycloalkene,with chemical formula: C₁₆H₁₀</p>
<p>Straight chain alkanes, n-ankanes</p> 	<p>Propane with chemical formula: C₃H₈</p> <p>n-Hexane with chemical formula: CH₃(CH₂)₄CH₃</p> <p>n-Dodecane with chemical formula: CH₃(CH₂)₁₀CH₃</p>
<p>Straight chain alkenes, n-ankenes</p> 	<p>Cis-but-2-enewith chemical formula: CH₃CH=CHCH₃</p> <p>Pent-1-enewith chemical formula: CH₂=CH(CH₂)₂CH₃</p> <p>Trans-hept-2-enewith chemical formula: CH₃CH=CH(CH₂)₃CH₃</p>

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<p>Cycloalkanes, a ring with a single bond</p> 	<p>Cyclohexane with chemical formula: C₆H₁₂</p> <p>n-Propyl-cyclopentane with chemical formula: CH₃CH₂CH₂C₅H₉</p> <p>Ethyl-cyclohexane with chemical formula: CH₃CH₂C₆H₁₁</p>

From Table 1, it can be seen that saturated hydrocarbons compose of alkanes with the simplest chemical formula (C_nH_{2n+2}), which only consist of 1 to 40 carbon atoms and saturated hydrogen atoms. It is difficult for alkanes to occur the chemical reaction to other materials. Alkanes are flammable and non-polar compounds, resulting in dissolving difficulty in seawater. However, alkanes composed of 10-26 carbon atoms in the carbon chain are usually easily degraded. Branched-alkanes are found with less degradation than straight-alkanes. Other hydrocarbons with double bonds, triple bonds or two double bonds are also considered as unsaturated molecules. Moreover, cycloalkanes compose of a ring of carbon in their chemical structures.

Aromatic hydrocarbons (AH) are chemical compounds with the aromatic ring. They include some popular compounds such as benzene, toluene, xylenes which compose one aromatic ring, and naphthalene and anthracene with more than 2 polycyclic aromatic rings. Up to now, AHs have been extremely serious pollutants due to potential carcinogens. The degradation of AHs occurs the most sharply under aerobic conditions. Normally, crude oil composes of around 30% of alkanes; 50% of for hydrocarbons such as cycloalkanes, alkenes, alkynes, and dialkenes; 15% of aromatic hydrocarbons; 5% of others.

The compounds of resins and asphaltens with complex chemical structure, which is difficult to analyze, are considered as insusceptible biodegradation. The product of refined oil, that includes unsaturated hydrocarbons formed and produced by the catalytic cracking process, depends on many factors such as crude oil types, or treatment methods.

3. Oil spill and oil slick recovery methods

The issues related to oil spill cleanup and recovery is

often considered as the most debatable because available methods for oil spill cleanup are impossible to recover and treat all oil spills, which are discharged/dumped into the seawater. As using methods for oil spill recovery are classified based on four techniques, being physical methods, chemical methods, thermal (or in-situ burning) methods, and bioremediation methods.

3.1. Physical methods

Physical methods are mainly used aiming two purposes, being zoning the spilled oil area and recovering the spilled oil from mechanical equipment. Firstly, the barriers are used to prevent the spilled oil from spreading and expanding over the seawater surface because the spreading oil is difficult to recover and apply the next applications. A number of as-used physical methods are classified as followed: booms, skimmers, adsorbent. However, the use of which physical methods depends on the many factors, but the purpose of controlling the spilled oil situations must be put on the first (Fingas, 2012; Fingas, 2018).

3.1.1. Booms

Booms are considered as the popular types of mechanical equipment. As mentioned, booms are used to meet the purpose of preventing the oil spill from spreading (Hoang, et al., 2018). However, besides the influence of boom design, the weather and sea conditions such as the current velocity, wind direction, and wave height are the main factors affecting the effective operation of booms. As reported, the optimum conditions for the effective operation of booms include as followed: current velocity lower than 0.4 m/s, wind velocity lower than 5.5 m/s, wave height lower than 1m (Fingas, 2018; Musk, 2012). After being zoned by booms to restrict the oil spill movement, the oil spill are recovered by available devices. Three types of booms

including fence-, curtain-, and fire-resistant boom are shown and classified in Figure 2.

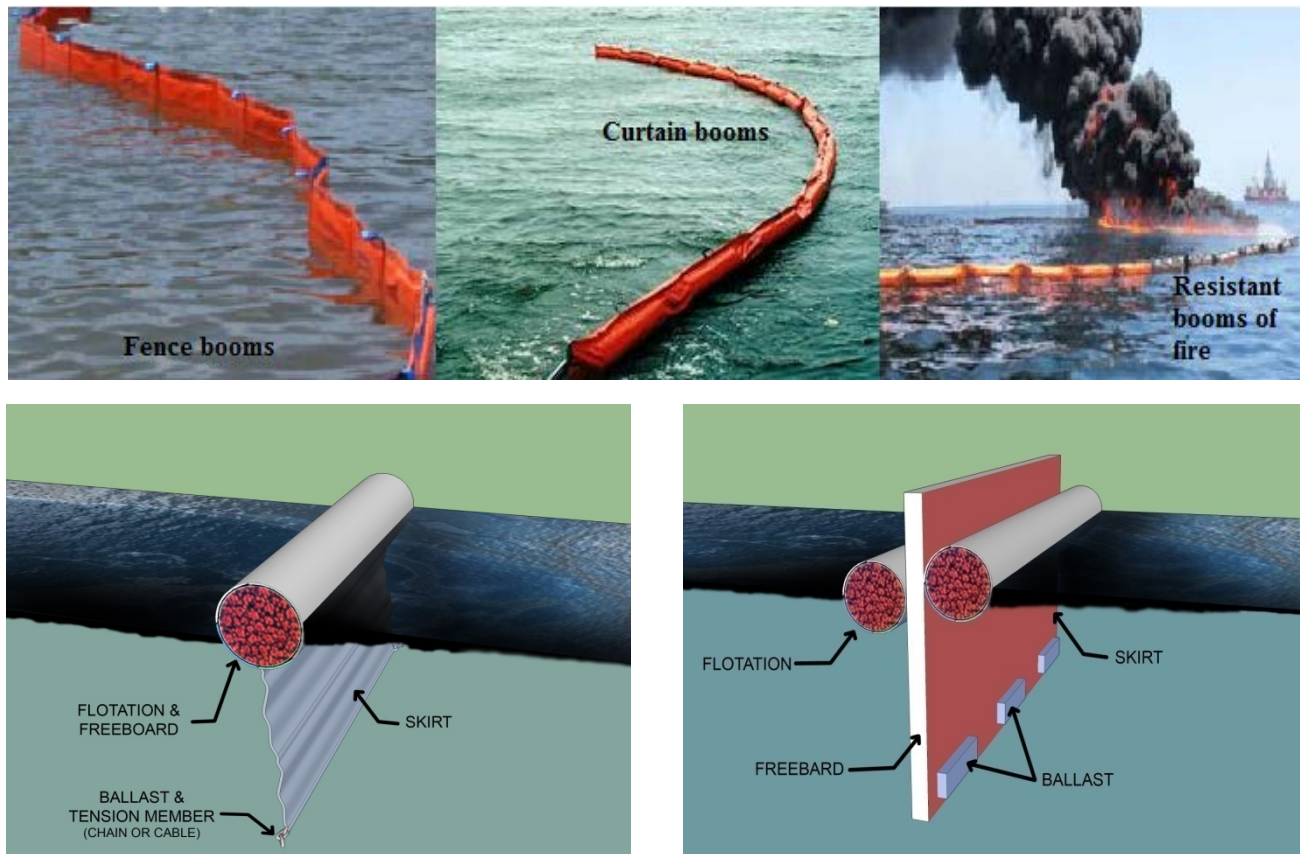


Figure 1: Boom types

Fence booms are designed aiming at the easy-floating structures and are fabricated by rigid or semi-rigid materials. Normally, fence booms are used for floating-oil prevention in the vertical direction with 60% of their height beneath the seawater. In fact, fence boom length is often 15m and the fence boom height is often 300, 600 or 800mm (Group, 2006). The above selection is to link each other easily though special connectors. Some advantages of fence booms include lightweight, minimal space for storage, resistance corrosion, easy clean, highly reliability. However, fence booms are suggested to not be used under strong winds, high velocity of current due to their low stability. On the other hand, low flexibility is also a disadvantage of fence booms.

Curtain booms with large circular and filled-foam chamber can float on the seawater surface. Their structure composes of a flexible skirt under the water and a remaining part on the seawater surface, this floating part on the seawater surface is the structure without being pervious and absorbing water (Lim, et al., 2013). Some light materials are usually used to fabricate curtain booms such as polyurethane, bubble wrap, and polystyrene. Normally, the as-used diameter of curtain booms is the range of 100-500 m, meanwhile, the skirt

length of curtain booms are the range of 150-800 mm. Comparing to fence booms, curtain booms are thought that they are reliable, flexible. However, some disadvantages such as difficult cleanup and storage are also reported (Edoho, 2008).

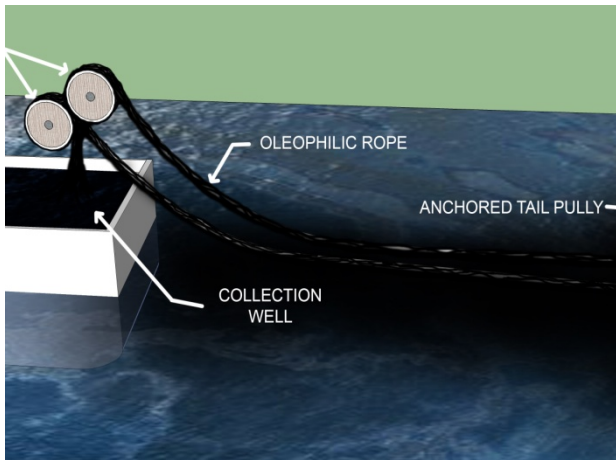
Fire resistant booms are always made of the fireproof materials. This fire-resistant boom type is used to collect oil spill after that oil spill is burnt under. In fact, around 1,500 m² of the area of the burnt oil spill is corresponding to 200m of fire length (Vodyanoy, et al., 2013). Regarding the advantages of fire-resistant booms, they are reliable, and they show the great potential in preventing the bad effects. However, high cost and difficulty in towing due to high weight and size are the disadvantages of fire-resistant booms.

3.1.2. Skimmers

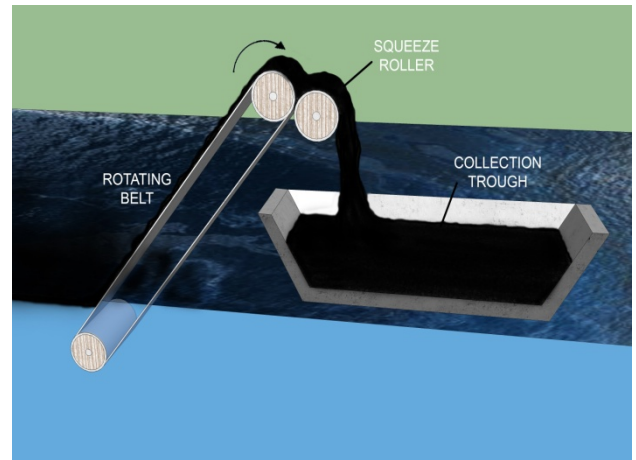
After applying booms to zone the negative effective area of the oil spill, skimmer devices are used along with boom types to collect piled oil from the seawater surface (Ni, et al., 2015). However, the spilled oil properties are usually maintained, thus oil spills after being recovered may be reused. The disadvantages of

skimmers can be thought that they depend on many factors such as weather condition, sea situations, and the floating-oil thickness(Nair, et al., 2017). Moreover, the parameters related to the current, wave and wind affect strongly the work ability of skimmers. However, some advantages of skimmers compared to booms are self-

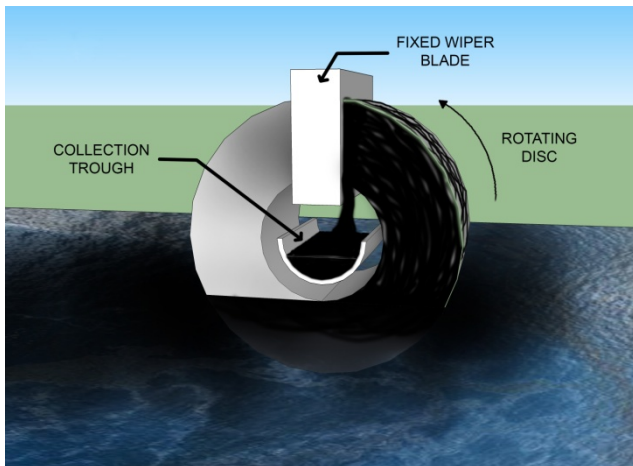
propelled, towed from the shore, and operated by vessels. Skimmers may be divided into 6 types which are shown in Figure 2 and Table 2, they are oleophilic-, weir-, elevating-, submersion-, suction/vacuum-, and vortex/centrifugal skimmer(Musk, 2012).



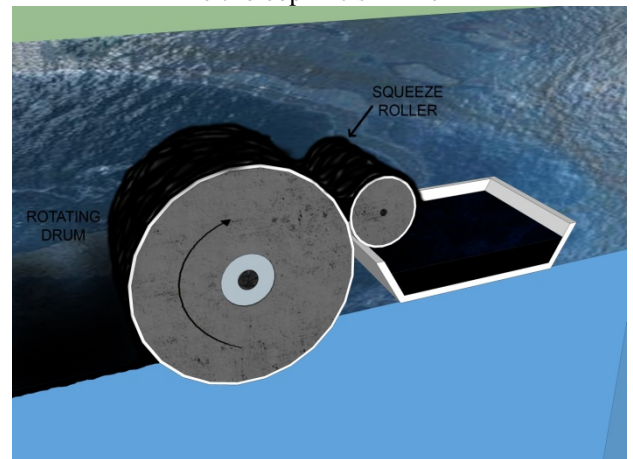
Rope- oleophilic skimmer



Belt- oleophilic skimmer

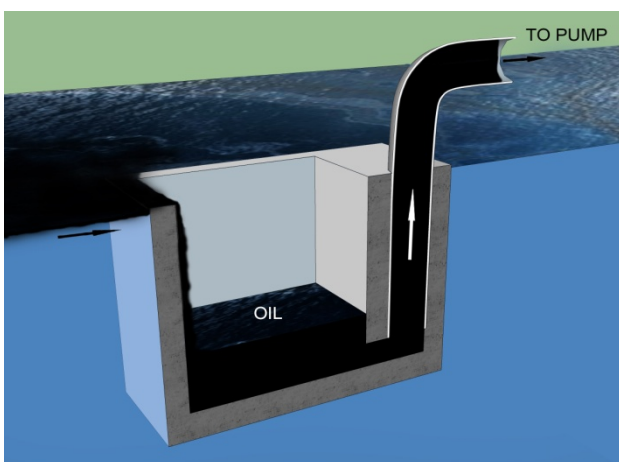


Disc - Oleophilic skimmer

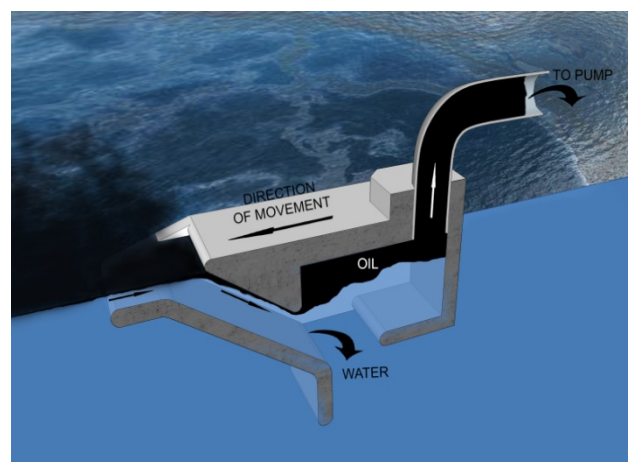


Drum- oleophilic skimmer

Oleophilic skimmers

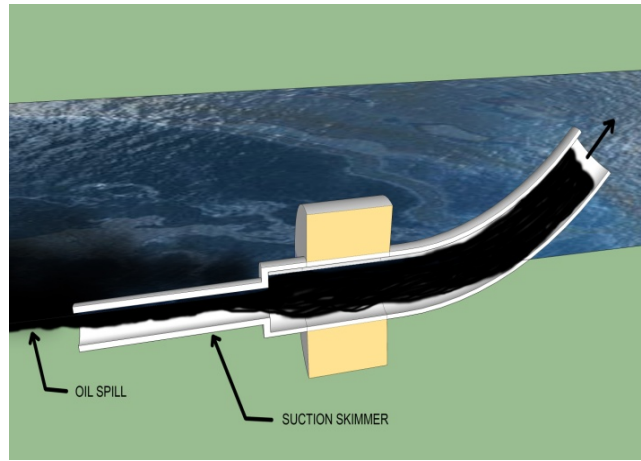
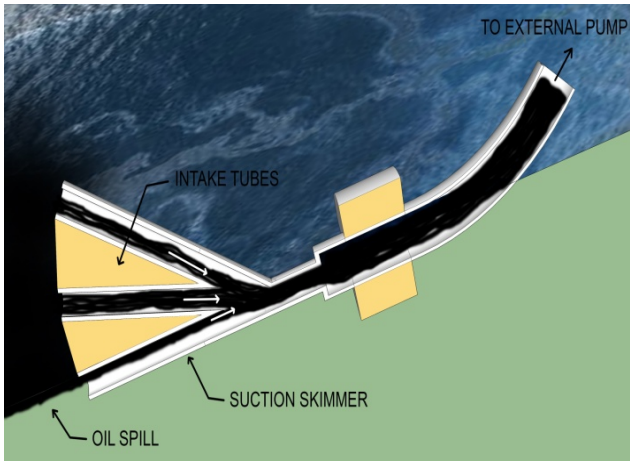


Stationary- Weir skimmers

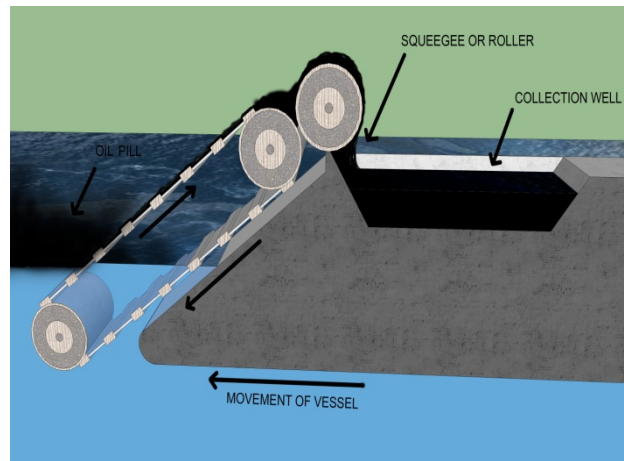
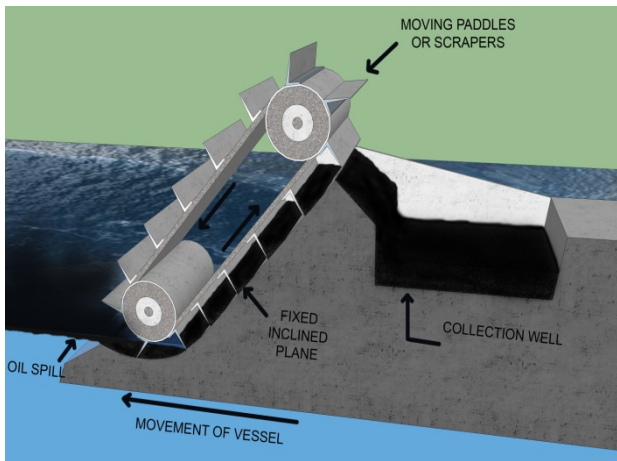


Advancing- Weir skimmers

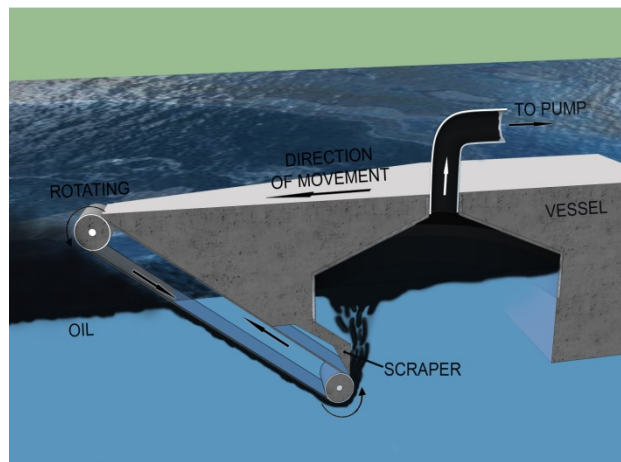
Weir skimmers



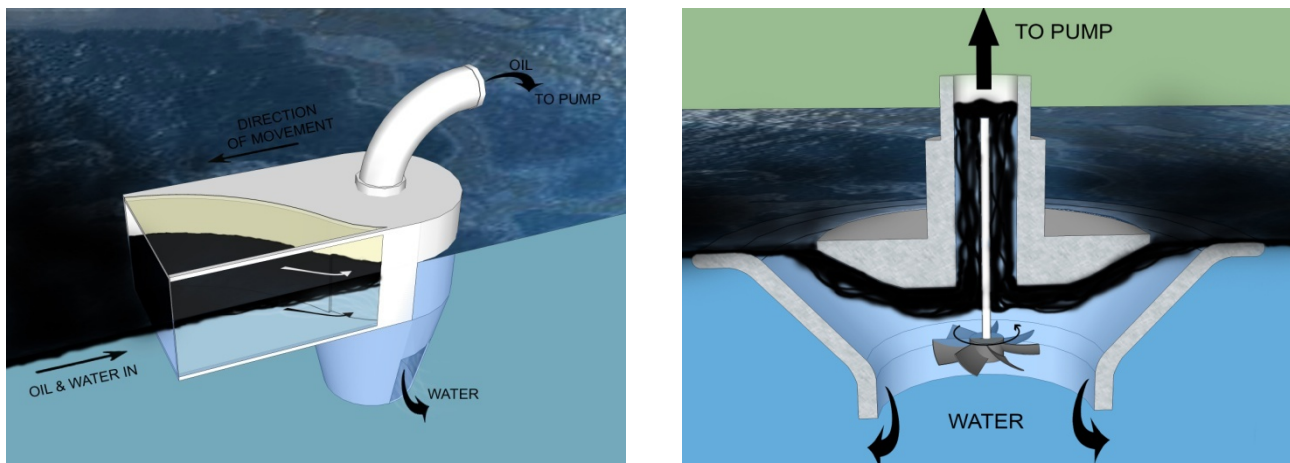
Suction/ vacuum skimmers



Elevating skimmers



Submersion skimmers



Vortex/centrifugal skimmers

Figure 2: Classification of skimmers

Table 2: Oil recovery potential of skimmers[23][24][25]

Types	Operational principle	The range of oil recovery rate (m ³ /h)*	Percent of oil recovery (%)
Oleophilic Skimmer	Oil spill or oil slick adhere on an oleophilic skimmer surface to remove the oil from the seawater surface	0.2 to 50	75 to 95
Weir Skimmer	Based on the gravity to collect spilled oil into a submerged tank	0.2 to 100	20 to 90
Elevating Skimmer	The oil spill is driven to the recovery area by conveyors	1 to 20	10 to 40
Submersion Skimmer	A belt combined with an inclined plane to drive the spilled oil on the seawater surface into a store tank	0.5 to 80	70 to 95
Suction/ vacuum Skimmer	Based on the principle of changing the pressure	0.3 to 40	3 to 90
Vortex/centrifugal Skimmer	Based on the difference in oil density and seawater density	0.2 to 10	2 to 20

*Depends on oil types such as diesel oil, light or heavy crude oil, bunker and other conditions

3.1.3. Absorbent materials

Nowadays, absorbent materials are using to recover the spilled oil for the final step after using booms and skimmers for the previous recovery step. These materials with a high oil absorption capacity are considered applying in the reality. As reported, the use of adsorbents is to convert the spilled from a liquid state into semisolid state aiming at removing spilled oil (Hoang, et al., 2018). Absorbent materials can be divided into three types, being natural organic-, inorganic absorbent-, and synthetic materials. Based on the porous structures of the sorbent material, the absorbent materials show the capacity of retaining spilled oil for collection purpose (Hoang, et al., 2018). According to the type of absorbent materials, the

absorbent materials are usually wrung to recover spilled oil and disposed of safely (Ivshina, et al., 2015). Some factors related to recyclable, oil sorption capacity are used to predict and evaluate the efficient usage of each absorbent materials because the above-mentioned factors are the main ones to determine the time for recovery of spilled oil and harvesting the absorption materials (Hoang, et al., 2018). The spreading of the oil spill before increasing the spilled-oil viscosity to the impossible absorption point is an extremely important requirement. The use of absorption materials was reported as the most effective and cheapest materials for oil spill cleanup (Arbatan, et al., 2011; Shadizadeh, et al., 2014). Table 3 gives the potential of spilled oil recovery based on absorption materials.

Table 3: Oil recovery potential of absorption materials

Types	Classification	Characteristics	The range of oil recovery rate (g/g)*	Percent of oil recovery (%)
Inorganic sorbent	Activated carbon, Silica, Silica gel, Clay, Graphite, Pulverized fly	- Seabed contamination - Harmful effect	- From 2-60 g/g - Silica aero gel with	≈70

materials	ash, Treated-, Treated -, Treated-, Treated silicone, Vermiculite, Zeolite.	- Expensive - Friendly	237 g/g - Expanded graphite with 86 g/g	
Natural organic sorbent materials	Bark-, wood-, and silk-floss fiber, Bird feathers, Collagen sponge, Peat and treated peat moss, Kapok, Silk worm cocoon, Acetylated rice straw and sugarcane bagasse, Cellulose, Cellulose fiber, Raw cotton, Rice Husk.	- The high cost - Low sorption capacity - Limited recyclability - Effective usage	1 – 40	≥75
Synthetic organic materials	Foams of Polyester, Polyethylene, Polyolefin, Polypropylene, and Polyurethane.	- Non-biodegradability - High sorption capacity - Expensive - Not friendly	7-45	≥ 90

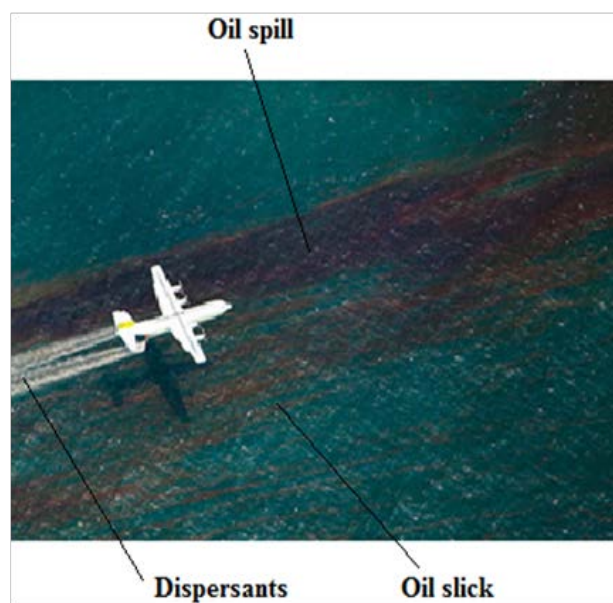
3.2. Chemical methods

These methods are used to treat spilled oil in combination with physical methods. Normally, the main chemicals including dispersants and solidifiers are used in these methods to control spilled oil.

3.2.1. Dispersants

Dispersants, which consist of different surfactants, may be used in the larger area of the sea and. As-used surfactants can solute in both oil and water. As using surfactants for oil spill treatment, the interfacial surface tension between the oil and water reduces (Kleindienst, et al., 2015). This promotes the dispersion and increases the biodegradation of oil in water. The results from the study of (Daling and Indrebo, 1996) showed the sprayed dispersant on oil slick with 15m³ of oil slick treated by the aircraft, and oil slick disappeared after 10 minutes of spraying in comparison with 0.5-1h of treated oil slick by boat. However, the effects of dispersants on the ecological also were reported by some studies. Dispersants may be restrictedly used under the deep water because of fast dilution in the water body, they can produce the toxic components affecting the ecological at the seabed (Lewis, et al., 2010). Recently, some the available dispersants such as Slickgone NS with 1/25 of dispersant/oil, Corexit 9500 with 1/10-1/50 of dispersant/oil, Corexit 9527 with 1/20-1/30 of dispersant/oil, Corexit 9550 with 1/20 of dispersant/oil, Tergo R-40 with 1/20 of dispersant/oil, Ardrex 6120 with 1/25 of dispersant/oil, Shell VDC with 1/20-1/30 of dispersant/oil are widely used. The determination of dispersant ratio for each oil spill incidents aiming at complete treatment is extremely important, this ratio depends on the properties of spilled oil, being medium-, heavy-, or light oil (Neff, 2012; Wang, et al., 2015). The as-used method for treating oil spills and oil slick based

on dispersants, which are controlled by the aircraft, is shown in Picture 2.



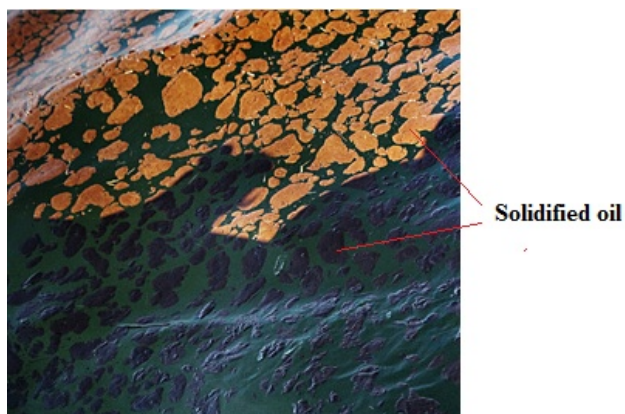
Picture 2: Dispersant sprayed on oil slick by an aircraft

The use of dispersants can get some benefits such as 90% of spilled oil cleanup, the operation ability under rough seas, fast treatment, slowing the formation of oil-water-based emulsion, acceleration of natural biodegradation rate (Kleindienst, et al., 2015). However, some disadvantages including toxic compounds, ineffective usage in calm seawater, and high cost are also reported (Prince, 2015). Especially, it is difficult to use dispersants in the case of thin oil slick.

3.2.2 Solidifiers

Generally, solidifiers for oil spill treatment are usually dry granular materials. They are used to react to the chemical components containing in the spilled oil aiming at converting liquid spilled-oil into a solid materials, which are easily removed (Rosales, et al., 2010). Normally, after using booms, pillows or pads to zone the spilled oil, solidifiers are used for the above-

mentioned purpose of the oil spill recovery to get the spilled oil at solid/semi-solid state (Yan, et al., 2014). This method is illustrated and shown in Picture 3.

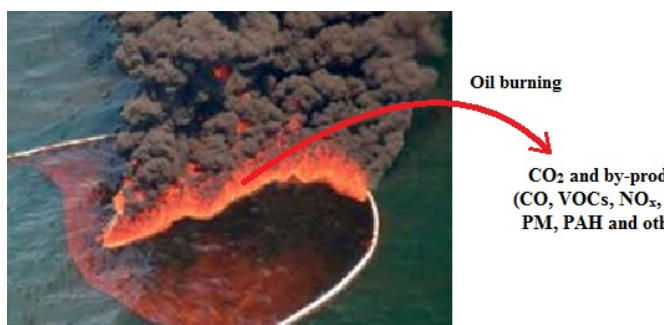


Picture 3: Solidified oil spill after using solidifiers

As reported, solidifiers can be used even rough sea areas, however, the efficiency of using solidifiers depends on the spilled oil properties and composition (Mukherjee, et al., 2014). In fact, solidifiers were not used in the past because it showed the lower efficiency compared to the usage of dispersants (Ren, et al., 2016). Nowadays, some solidifiers such as Spill Green LS, Petro Lock, SmartBond HO, Oil Bond100, Molten wax and Powdered wax with 43, 44, 45, 33, 109 278 at percent of the main chemicals for solidifying the spilled oil respectively are usually being used (Fingas and Fieldhouse, 2011).

3.3. Thermal or in-situ burning method

The oil spill recovery methods and techniques based on thermal engineering or in-situ burning are considered as the simple and quick ones. These method use the thermal sources from outside to burn oil spill or thick oil slick even the spilled oil are still on the seawater surface. Picture 6 illustrates an oil spill treatment by thermal or in-situ burning techniques (Fingas, 2016).



Picture 4: Thermal or in-situ burning techniques

These method sare reported that they can reduce the negative effects of the spilled oil and oil slick on the

marine ecosystem and environment. Deschamps, et al., (2003) has reported that 100-300 tons per hour of spilled oil could be removed by using these methods. Since the 1960s, these methods were widely used for the strategies of treating the oil spill incidents occurred in/on the ice, water, snow through the accidents of broken pipeline, punctured/ broken storage tank or ship accidents in the USA, Canada, Europe (Buist, et al., 2011). To burn the oil spill, a Helitorch equipment is used. A flame thrower type is hanged under the helicopter/aircraft or an oiled rag, after that a type of diesel fuel was thrown from the helicopter/aircraft. In general, these methods may be applied to the large oil spills, although these methods are subjected by the ratification of government due to the toxic emissions from them. Several oil spill incidents in the past including Canada in 1958; Norway in 1988, Exxon Valdez in 1989; Canada in 1993 used these methods for controlling the oil spill and they were considered as the success in using these methods (Fingas, 2016). However, experiences have demonstrated that the methods of oil spill treatment based on thermal or in-situ burning techniques are only effective and useful for the oil spill incidents with enough wide areas aiming at burning the spilled oil volume at the same time. Besides, the layer of spilled oil is also enough thick to maintain the combustion process. To get the best results of using the above-mentioned thermal or in-situ burning techniques, the seawater conditions should be calm, the wind and current conditions should be slow, the place of spilled oil is far from sensitive zones, facilities, equipment.

Thermal or in-situ burning techniques are thought that their advantages will be promoted as conducted in ice, cold conditions or snow because the combustion process can be maintain for a long time. Although thermal or in-situ burning techniques are the effective methods to treat the oil spill incidents, the main constraints of these methods are thought that the secondary fires can be occur. Besides, the effects on the human health, the effects of burnt by-product on the environment are also considered studying more to limit the negative effects. Moreover, the determination of the impact area of emissions, which are produced by thermal or in-situ burning techniques, is necessary. The main chemical components produced by burning the spilled oil such as the CO_x , SO_x , NO_x , PM, VOCs, PAH emission, the emission standard for applying thermal or in-situ burning

techniques, as well as the safety distance are introduced in Table 4.

Table 4: Emission components as using the in-situ burning method for oil spill treatment

Emission components	Emission quantity g.kg ⁻¹ (g emission in comparison with kg burned oil)	USA Standard g.kg ⁻¹ (g emission in comparison with kg burned oil)	Safety conditions
CO ₂	3.000	-	- Wind velocity from 2 to 5 m/s - Safe distance (y) based on PM 2.5: $y = 0.75 * S$ y: safety distance (m) S: square of burning oil area (m ²)
CO	20 - 50	35 g.kg ⁻¹ after 1 hour of burning 9 g.kg ⁻¹ after 8 hours of burning	
SO _x	3	14 g.kg ⁻¹ after 24 hours of burning	
NO _x	5	0.05	
PM	50 - 200	0.5	
VOCs	5	-	
PAH	0.04	-	

3.3. Bioremediation

Biodegradation is a process of oil spill treatment based on microorganisms including two main types as bacteria, and fungi. To degrade, and metabolize the complex

compounds of the spilled oil, the chemical substances are considered as their food resulting in protecting the marine environmental quality (Ivshina, et al., 2015). As reported, the main properties of microorganisms for degrading the spilled oil are given in Table 5.

Table 5: The classification of main microorganisms [2]

Microorganisms	Description	Ability to degrade compounds	
Bacteria	Arthrobacter spp	- Grown on mineral salts - Gram-positive and exponential growth - Use pyridine as its only carbon source	Phenanthrene (C ₁₄ H ₁₀) Methyl-tert-butyl ether, or 2-Methoxy-2-methylpropane ((CH ₃) ₃ COCH ₃) Ethyl-tert-butyl ether (C ₂ H ₅ OC(CH ₃) ₃) Tert-amyl methyl ether (C ₂ H ₅ C(CH ₃) ₃)OCH ₃)
	Brevibacterium	- Short life, asporogenous, aerobic - Gram-positive - Optimum growth from 30 -37°C	Asphaltenes, Petroleum oil
	Dietzia	- Promotion of the activities of HC-degrading - Increasing the hydrogenase and catalase - Speeding up the oil biodegradation process	n-Alkanes with number carbon from 12 to 38 and branched alkanes
	Flavobacterium	- Gram-negative, - Use engine-oil as a carbon source, - - 80 and 90% of oil cleanup, - 30–37°C of optimal temperature	Chlorophenols (HOC ₆ H _{5-x} Cl _x ; 1≤x≤5) include from Monochlorophenol to Pentachlorophenol
	Mycobacterium	- Degrading hydrocarbon with carbon number from C12 and C13	Polycyclic hydrocarbon Pyrene (C ₁₆ H ₁₀) Phenanthrene (C ₁₄ H ₁₀) Diesel oil
	Pseudomonas spp	- High potential for degrading hydrocarbon - The metabolic diversity, the abundant microorganisms, the chemical remediation resistance	4-chlorobenzoate (C ₇ H ₄ ClO ₂)
	Rhodococcus	- Potential producer, high emulsifying index - Suitable for light oil	Polychlorinated-biphenyl (C ₁₂ H _{10-x} Cl _x ; 1≤x≤10) Hexadecane (C ₁₆ H ₃₄) Trichloroethane (CH ₃ CCl ₃) Polycyclic hydrocarbon contains only C, H with many aromatic rings
Fungi	Aspergillus	- The highest biodegradation extent	Pyrene (C ₁₆ H ₁₀)

		- 98% of degradation efficiency	Benzo(a)pyrene (C ₂₀ H ₁₂)
	Candida	- High potential	Toluene (C ₇ H ₈)
	Fusarium	- Degrading hydrocarbon with carbon number C31 - High efficiency	Methyl tert-butyl ether ((CH ₃) ₃ COCH ₃) Tert-butyl alcohol (C ₄ H ₁₀ O)
	Phanerochaete	- Catabolizing oil spill to carbon dioxide	Benzo(a)pyrene (C ₂₀ H ₁₂) Phenanthrene (C ₁₄ H ₁₀) Fluorene (C ₁₃ H ₁₀)

The biodegradation application to the oil spill recovery, treatment and cleanup is a process regarding giving native or non-native microorganisms to speed up the natural biodegradation process. Microorganisms help to protect the affected areas by oil spill risks and prevent the environment from being damaged further. Several enzymatic microorganisms show the ability of degradation of hydrocarbons in fossil fuel such as petroleum, crude oil, diesel fuel (Kleindienst, et al., 2015). Some types of hydrocarbons including alkanes, aromatic contents are considered as the favourite foods of the above-mentioned enzymatic microorganisms. Normally, alkanes containing 10-26 of the carbon atoms are degraded the fastest. Besides, some aromatic contents with low molecular weight such as benzene, toluene or xylene are also biodegraded very fast by enzymatic microorganisms. Nonetheless, it is difficult to degrade some hydrocarbons with complex or complicated structures and high molecular weight because there are fewer enzymatic microorganisms which show the ability of biodegradation of such structures. Fingas, et al., (2011) concluded that the more complex the hydrocarbon structures are, the smaller the biodegradation rates are. Shao and Y, (2009) indicated that the biodegradation process of oil spills is affected by many factors, being nutrient bioavailability, the spilled oil properties, and ambient temperature. Nutrients including nitrogen, dissolved oxygen, and phosphorus compounds are necessary for the metabolic activity of microorganisms in the marine environment. Thus, around from two to four weeks for the biodegradation process of spilled oil is necessary in the case of high concentration of spilled oil. Additionally, the biodegradation needs at least a week for the good suitability of microorganisms with the marine environment. However, the experiences also show that it takes around several months, even several years to complete the whole bioremediation process.

5. Conclusions

The above-mentioned methods for the oil spill recovery, treatment, and cleanup from the accident, incidents disasters related to oil explosion and maritime operation or activities are proposed. Each method also indicates includes its advantages and its disadvantages. However, the selection of what methods for oil spill incidents is very important and that selection should be based on the criteria which are reliability, efficiency, time, oil absorption capacity. Besides, the factors related to weather conditions should be mentioned to choice the most suitable method. Based on the reviewed study, the results are presented as:

Most types of spilled oil can be recovered by physical methods. Beside of their advantages such as high efficiency, simple, easy application, the use of these methods is expensive, complex, high manpower. In addition, these methods must be used before emulsified and collected oil after recovering must be treated, physical methods depend much on the weather and sea conditions, as well as the available device situations.

The use of chemical methods is considered as a quick treatment method under all the weather and sea conditions. Chemical methods show high efficiency and they may be suitable for many types of spilled oil. Some advantages of chemical methods are low manpower, cheap. Nonetheless, the use of chemical methods does not recover any spilled oil, low efficiency with high-viscosity oil. Among chemicals using for chemical methods, dispersants are considered using the most, dispersants suitable for high-viscosity oil spill, stable emulsions and oil slick.

Thermal methods should be considered using because of the released emissions from these methods. They show many advantages such as quick use, high, cheap. However, they are only suitable for open-water area, snow or ice area. However, the unpredicted effects related to air, the threat for marine creatures, and human life are the disadvantages of thermal methods.

Biodegradation is used on the basis of multi-

microorganisms, it is an efficient treating method and suitable for all the weather and sea conditions. The outstanding characteristics are cheap cost, especially the product of biodegradation process are only CO₂ and H₂O. The recovered residues can continuous biodegrading by other types of microorganisms.

Depending on many factors regarding oil spill incidents such as the oil spill level, spilled oil type, weather conditions (wind and current velocity), sea conditions, and the situations of each country, the selection of suitable methods or techniques for oil spill recovery and treatment is extremely necessary. In Vietnam situation, the use of agricultural by-products, which are assisted by mechanical equipment, may be suitable for agricultural and low-middle income country. In the next research, using agricultural by-products for oil spill recovery will be conducted.

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