Analysis of Offshore Oil Spill Pollution Treatment Technology

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Abstract. In recent years, human demand for petroleum resources has been increasing, the exploitation, transportation, and use of offshore oil have also led to frequent offshore oil spills pollution accidents. Once an oil spills accident at sea occurs, it will not only cause waste of petroleum resources and produce economic loss, but also cause great damage to the marine ecological environment. This article reviews the hazards of offshore oil spills pollution, the ways of oil spills, the physical, chemical, and biological treatment technologies of oil spills and gives the prospect.

1. Introduction
In recent years, the energy demand of countries around the world has increased rapidly. Many countries have turned their attention to the development of petroleum resources to the ocean, at the same time, the number of drilling platforms has increasingly appeared at sea. At present, the drilling footprint of human beings has extended from the land to the ocean, the ocean has become an important base for oil development. Although offshore oil development has strict operating safety regulations, accidents on offshore drilling platforms occur from time to time. The oil spilled into the sea not only wastes scarce oil resources, causing huge economic losses, but also severely damages the marine ecological environment. If the oil leakage accident occurs near the sea, it will also seriously affect the production and life of coastal people and even endanger life safety. On April 20, 2010, an oil rig in the Gulf of Mexico named "Deepwater Horizon" caused a large amount of oil spills due to an explosion caused by a fault. It is estimated that an average of 12,000 to 100,000 barrels of crude oil leak into the Gulf of Mexico each day, causing at least 2,500 square kilometers of seawater to be covered by oil. On January 6, 2018, the "Sangji" and the Hong Kong-owned bulk carrier "Changfeng Crystal" collided about 160 nautical miles east of the Yangtze River Estuary, causing the entire ship of the "Sangji" to catch fire. The "Sangji Wheel" loaded with about 136,000 tons of condensate oil was burned for 8 days and sunk at last, bringing huge oil pollution and economic losses. This article mainly reviews the hazards, generation methods and treatment technologies of marine oil spills pollution, in order to make people more aware of the destructive nature of offshore oil spills pollution and popularize the awareness of protecting the marine environment.

2. Hazards of Offshore Oil Spills
Crude oil and its refined products are a complex chemical mixture. When a large amount of oil spills occurs on oil tankers, drilling platforms or other transportation vessels, the oil spills will spread rapidly and cover the sea surface in a large area. It will not only have the danger of explosion and fire,
but also seriously damage the marine ecological environment, endanger marine life, and even poison human health.

When a large amount of oil is leaked to the sea, the seawater will soon be polluted by the hydrocarbons in the oil and inorganic substances such as nickel and vanadium. At the same time, under the evaporation of sunlight, part of the spilled oil becomes oil vapor and enters the atmosphere, which seriously damages the nearby air quality. The fuel covered on the sea surface will drift under the action of wind and waves. When drifts to the coast, it will not only seriously pollute the beach and the tourism industry near the coastline, but also cause incalculable damages to hydropower plants, water plants and salt fields near the coastline.

The oil spills covering the sea surface isolates the atmosphere and seawater, resulting in insufficient oxygen content in the seawater, and the organic matter in the oil spills will oxidize and deplete the oxygen in the water, further reducing the oxygen content in the water, which will suffocate a large number of aquatic life. Seabirds living by the sea usually feed on fishing. When diving and fishing in large spilled seas, their feathers will be contaminated by oil spills, lose their waterproof and heat preservation functions, then died of cold, poisoning or hungry. The oil covered by the sea seriously affects the survival of plankton. Unlike other animals, plankton can not avoid pollution sources, it is particularly sensitive to the toxicity of oil spills. In addition, under the cover of oil spills, plankton can not perform photosynthesis and will soon decay.

There are many ways in which oil spills can harm human health, including inhalation of oil vapors, skin contact, and transmission in the food chain. When recovering oil spills in oil spills areas, workers often inhale a large amount of oil vapor, which contains benzene and its derivatives. This has a slow response to human hazards, headaches, coma, breathing difficulties, abnormal heartbeat. Crude oil leakage in the ocean contains a large number of hydrocarbons, which accumulate in the aquatic organisms' accumulation, passed on by the food chain. When consumed by human, it will endanger human health.

3. Ways of Offshore Oil Spills

At present, the main ways for offshore oil spills into the sea are as follows:

(1) Oil spills and blowouts caused by accidents on offshore drilling platforms. For example, the explosion of the Deepwater Horizon on the Gulf of Mexico offshore drilling platform in April 2010 caused the largest offshore oil spills in the history of the United States.

(2) Leaking oil, discharging oil and accidents of oil tankers caused oil enter the sea directly. Oil tankers are one of the main modes of transportation for international oil trade. Oil tankers often have various accidents leading to oil spills. These accidents can caused by weather, such as storms. There are also oil spills caused by crew error and other major faults such as tanker hull ruptures. Anymore, tanker collided with other ships due to intensive shipping routes can result in oil spills. For example, on November 13, 2002, the Greek tanker "Prestige" encountered a storm while passing through the waters near northwestern Spain, the hull was damaged and sank in two pieces on the 19th. After the "Prestige" sank in the Spanish waters, it caused a large area of oil leakage.

(3) Oil leaking from subsea pipeline. For example, in 2013, the “11·22” Sinopec Donghuang oil pipeline in Qingdao city of China leaked and exploded in a particularly serious accident, causing crude oil to leak into the sea. Part of the crude oil entered the Jiaozhou bay along the rainwater pipeline, with an area of approximately 3, 000 square meters.

(4) Refinery contains waste water that is injected into the sea via rivers. In order to seek economic benefits, some companies took risks, the oil plant directly discharged a large amount of waste oil without any treatment or disqualified after the treatment of various indicators, then the waste oil eventually reached the ocean through rivers. The industrial waste oil discharge is also the reason for the increasingly serious environmental problems.

(5) Man-made oil spills, such as oil spills at sea caused by man-made damage to oil wells or tankers. For example, in 1991, in an attempt to invade Kuwait’s oil resources, the Iraqi army sent troops to Kuwait, which touched the nerves of the US and other Western powers in the Middle East,
which triggered the Gulf War. The Iraqi army ignited its oil wells in Kuwait, which made as much as 1 million tons of oil been spilled, then the direct result was the sea was covered with a thick layer of oil, the seawater was unable to set off waves, surging like mud.

4. Treatment Technologies of Offshore Oil Spills

When an oil spills at sea is unavoidable, the department in charge of the marine environment will conduct scientific treatment. When treating, the governor must first determine the type of oil spills, referring to the existing oil fingerprint database is a fast and effective way to identify oil spills. After identifying the type of oil spills, take corresponding treatment technologies to resolve oil pollution. The treatment technologies for offshore oil spills are divided into three categories: physical treatment technologies, chemical treatment technologies, and biological treatment technologies.

4.1. Physical treatment

The physical treatment method refers to a method using physical means, such as using an oil fence to contain the spilled oil, then using mechanical equipment or sorbents to recover the spilled oil. The biggest advantage of this way is that it will not cause secondary pollution to the marine environment while the disadvantage is that it can only deal with thick oil spills.

4.1.1. Containment of oil spills

The purpose of controlling spilled oil is to prevent the leaked oil further diffusion and drift, ensure that it is controlled within a small range. At present, the most commonly used facility for controlling oil spills is oil fence, which will not cause further pollution to the ocean. There are many structures and forms of booms in the market. According to its structure, it can be divided into solid float oil boom, inflatable oil boom, external tension oil boom, double body oil boom, fireproof oil boom and shore beach oil boom. The structure of the conventional oil boom mainly includes three parts: a floating body, an oil shield body and a weight body. In addition, there are a reinforcing belt, a support body, a rope and a connecting member. The oil shield is upright in the water and plays the role of blocking oil. Its material is made of synthetic fiber cloth with surface treatment. At present, the most widely used are nylon cloth coated with polyvinyl chloride or coated with rubber. The weight body is located at the lower part of the oil retaining skirt body, so that the oil retaining skirt body is kept upright. Selecting different weight bodies can adjust the draught depth and the height above the water of the boom. The float floats on the water and provides buoyancy for the boom, preventing oil from crossing the upper part of the oil boom.

4.1.2. Recovery of oil spills

In order to prevent the enclosed oil spills from crossing the oil fence under the influence of wind and waves or other environmental factors, measures should be taken as soon as possible to recover the enclosed oil spills. Recovery of oil refers to taking measures to separate the spilled oil from the polluted area without changing the physical characteristics of oil to remove the spilled oil. There are various methods for oil spills recovery. The most commonly used are the following: oil skimmers, sorbents, and oil recovery vessels.

Oil skimmers are mechanical devices that recover marine oil spills while maintaining the physical and chemical characteristics of the oil spills at sea. It mainly relies on the flow characteristics of offshore oil spills, the density difference between oil and water and the absorption of sorbents to separate oil spills from water.

Sorbents refers to materials that can spill into the interior or adsorb on its surface. The method for recovering spilled oil by using sorbents has the advantages of safety in use, low price, convenient carrying and operation. However, the oil absorption is generally small, which is only suitable for the post-processing of small oil spills accidents or post-treatment of large oil spills accidents. For different oil spills, different adsorption materials should be selected. Some sorbents are suitable for adsorbing high viscosity spills, while others are suitable for adsorbing low viscosity spills.
A ship specially designed to recover oil spills and oil waste above the surface of water is called an oil recovery ship. According to the size of the hull, oil recovery ship can be divided into small ship, medium ship and large ship. The selection of an oil spills recovery vessel should take into account a number of factors, including the amount of oil, sea conditions, surrounding environment, economy, and operability of the equipment.

4.2. Chemical treatment

4.2.1. Combustion

The combustion method can handle a large area of oil spills in a short period of time, requires minimal logistics resources, and has low processing costs. However, the incineration process will also bring many other problems. Burning will generate a large amount of air pollutants (CO, SO₂, NOₓ) and a large amount of CO₂ particulate matter, which will be seriously damaged to the atmosphere if discharged. In addition, the incineration is also limited by many conditions. The oil slick to be incinerated must have a sufficient thickness (greater than 2 to 3 mm), because the water under the spills has strong heat transfer properties so that the spilled oil temperature will soon be lowered. Sufficient thickness is required to ensure that the heat generated by combustion is greater than the heat absorbed by the water in order to maintain continued combustion. It is also required that the spilled oil contain sufficient volatile components to facilitate ignition. Therefore, when dealing with oil spills at sea, a comprehensive analysis should be carried out before deciding to use combustion method, such as whether the conditions required for incineration, the effects on the environment must also be considered.

4.2.2. Dispersants

Dispersants are also called degreaser. They are mainly composed of a main agent and a solvent. The main agent is a non-ionic surfactant while the solvent is usually petroleum hydrocarbon. Dispersants are used to reduce the impact on the shoreline and birds and mammals live on the water surface, as well as to promote the biodegradation of oil. Surfactants used to formulate dispersants should have the following characteristics: good dispersibility to oil spills, good biodegradability, low toxicity to marine organisms, good compatibility with selected solvents, non-coagulation and precipitation at low temperatures. The main role of the dispersants is to combine the oil spills into fine oil droplets and prevent the small oil droplets from being combined, so that the oil spills is degraded by microorganisms. The advantages of dispersants treatment are: simple operation, quick results, and can still efficiently and quickly deal with large areas of oil spills when under severe sea conditions. However, due to chemical characteristics, their working efficiency is greatly reduced at low temperatures, and dispersion effects are also poor for oil films with a thickness more than 1 mm or high-viscosity spills (viscosities greater than 2000 cst). Because dispersants will cause secondary pollution to the marine environment, their use are strictly restricted. Nowadays, the competent authorities in many countries have made clear regulations on dispersants use guidelines, technical standards and management methods for product inspection and certification, and strictly control the use of dispersants through laws and regulations.

4.3. Biological treatment

The bioremediation is biological treatment method for degrading petroleum hydrocarbons by developing different kinds of microorganisms and then putting them into corresponding petroleum. The nutrients required for the metabolism of such microorganisms are obtained by degrading petroleum hydrocarbons. Oxygen, temperature and nutrient supply are the main factors affecting the rate of biodegradation, especially nitrogen and phosphorus compounds. Petroleum is a very complex mixture consisting of paraffins, aromatics, naphthenes, and some non-hydrocarbon compounds. Since each microorganism can only degrade the corresponding hydrocarbons, different types of microorganisms need to be invested. Studies have shown that different hydrocarbons in petroleum have
different degrees of difficulty in being decomposed, paraffins with medium chain length (C10 to C24) are most easily degraded, long chains have certain resistance to the decomposition of microorganisms, short chains are toxic to microorganisms and difficult to break down. In addition, chain hydrocarbons are easier to decompose than cyclic hydrocarbons, unsaturated hydrocarbons are easier to decompose than saturated hydrocarbons, straight chain hydrocarbons are easier to decompose than branched hydrocarbons, the more branches they have the more difficult to decompose, chain hydrocarbons with quaternary carbon atoms at the ends are also difficult to decompose. The use of microorganisms to treat spilled oil has the advantages of high efficiency, simple operation, safety, and no secondary pollution, especially for thin oil layers that are difficult to recover by mechanical devices. When the use of chemical agents is restricted, the biological treatment method has shown its incomparable superiority. The advantages of bioremediation have made this method widely used, but there are also some disadvantages as this new technology, which is mainly reflected in the high cost and difficulty in cultivating and preserving microorganisms.

The overall comparison of the above-discussed technologies is listed in Table 1.

| Technology/agent | When to use | Target Areas | Characteristics | Limiting factors | Oil types |
|------------------|-------------|--------------|-----------------|------------------|-----------|
| Booms, skimmers, recovery vessels | The first line of Defense during a response | Varies | Contains and Removes spilled product | Weather conditions; site accessibility | varies |
| Sorbents | Spill on land; to create a physical barrier; to immobilize small spills | Shorelines with recoverable oil | Low application rate; easy to recover | Access to deploy and retrieve products | Heavy, weathered or emulsified oils; not effective on viscous oils |
| Combustion | To quickly remove oil to prevent its spread to sensitive areas; reduce waste; limited access and recovery | Remote areas with land or water where oil is thick enough for an effective burn | Removal of free oil from the water; require certain oil thickness | Heavy, weathered or emulsified oils may not ignite; Wind can affect smoke; need air quality monitoring | Oil thickness required; Increases with oil weathering and heavy-component content |
| Dispersants | When dispersion has less impact than slicks that strand onshore or affect surface water resources | Open water | Products have to pass a dispersant | Low effectiveness with heavy, weathered, or emulsified oils | Any oil with a viscosity less than 20,000 cst |
| Bioremediation agents | After removal of gross contamination; when further oil removal will be destructive; when nutrients are limited | Where other cleanup methods would be destructive or ineffective; as a polishing tool for any size of spill | Treated samples Show oil degradation greater than control samples in lab tests; Site-specific | Nutrient availability; Temperature (>15.5°C); pH 7-8.5; limited moisture level; Surface area of oil | Less effective on heavy refined products and evaporative fraction |
5. Conclusion
With the development of offshore oil resources, the threat of oil pollution will become more serious in the future. All countries are facing a huge threat to marine pollution and oil spills during the process of oil extraction and storage will continue unabated, which will bring pressure and challenges to the research of marine ecological environment management technologies. From technical perspective, offshore oil spills treatment is a crossover and combination of multiple technologies. A single control measure is far from sufficient for an oil spills, it is necessary to combine multiple technologies to comprehensively control. Therefore, based on the prevention of offshore oil spills, new treatment technologies must be developed, comprehensive application technologies of physical, chemical, and biological also must be explored, which will solve the problems caused by marine oil leakage from the root cause and effect.

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