Odor-Treatment Technology for Recovered Hydrocarbons From Oily Waste in a Thermal-Desorption Unit

Jilei Fang, Xianghai Meng, Guoling Xu, Yong Yue, Peichao Cong, Chao Xiao, and **Wenhui Guo,** Yantai Jereh Oilfield Services Group

Summary

Oily waste, as the intrinsic byproduct of the oil and gas industry, is considered hazardous waste, and thermal-desorption units (TDUs) have been applied widely to process this waste under an environmentally sound protocol.

A TDU is used to separate hydrocarbons, water, and solids by indirect heating. In the process, the base oil and chemical additives are fractured and dissociated with the increasing temperature, resulting in a pungent odor from the recovered hydrocarbons. It is this odor that has restricted the reuse of the recovered hydrocarbons. After analysis, it is determined that the pungent odor is caused by the presence of sulfur and nitrogen compounds. Consequently, an odor-treatment system that is based on the catalytic cracking and preferential adsorption method has been developed and introduced into the TDU for the removal of the odor. The sulfur and nitrogen compounds are cracked into a broken-chain structure under the action of a catalyst, and then they are adsorbed selectively by adsorbing material. After treatment, the removal rate of total sulfur and total nitrogen reaches 93.74 and 98.41%, respectively, realizing the elimination of the pungent odor. Furthermore, the color of the recovered hydrocarbons fades away.

Currently, odor-treatment technology is applied directly in situ, where the oily cuttings are stored, and more than 1,300 bbl of acceptable hydrocarbons have been recovered. These recovered hydrocarbons meet all operating requirements, and have been reused for oil-based mud (OBM) or sales. Because of the operation, the recovered hydrocarbons could have a higher price for sales, which proves the process to be not only environmentally sound, but also valuable to the bottom line of the operator's production.

A TDU with odor-treatment system can bring technical and economic advantages to the user. Not only has the process proved to be very economical for recovered hydrocarbons, it is also preventive and can mitigate potential environmental liabilities.

Introduction

Oily waste, including oil-pit sludge, oily soil, OBM and oily cuttings (Bybee 2006), and tank-bottom sludge, is generated during the process of oil exploitation, transportation, refinement, and storage (Wei et al. 2015). The oily-waste pit represents an environmental liability for the operator, especially in terms of the presence of nondegradable hydrocarbons, which are extremely hazardous to the environment.

Conventional treatment methods for oily waste include landfill, incineration, and curing technology (Jiang et al. 2005). With increasingly demanding environmental standards, the conventional method has been unable to meet the environmental requirements. Consequently, environment-minded companies have taken substantive steps toward reducing their environmental footprints (Permata and McBride 2010) by use of several waste-treatment alternatives, including injection (Mkpaoro et al. 2015; Ntukidem et al. 2002), bioremediation (Ozumba and Benebo 2002), solidification stabilization (Segret et al. 2007), and thermal desorption. Although injection could dispose of the oily waste validly, its main issue is the lifetime of the injection well, which is limited to its application. The limitation of bioremediation is the slow process rate, requiring space and maintenance up to 1 year. With the solidification-stabilization method, there is a risk of potential leaching, and, in addition, the hydrocarbons cannot be recovered, resulting in waste of a useful resource. To maximize hydrocarbon recovery without noticeable impact on the environment, thermal desorption (Agha and Irrechukwu 2002), originating from the early 1990s (Gilpin 2014), is considered the optimal technology for future use (Seaton and Browning 2005) because it is environmentally clean and can be applied to varying levels of contamination (Hahn 1994). More importantly, the hydrocarbons can be recovered, reducing economic cost (Al-Suwaidi et al. 2004; Fang et al. 2007).

It is generally found, however, that the recovered hydrocarbons from thermal-desorption technology present a pungent odor, resulting from the presence of sulfur and nitrogen compounds. The odor has not only restricted seriously the reuse of recovered hydrocarbons, but has also threatened the environment. The aim of this paper is to present a TDU with an odor-treatment system for eliminating the pungent odor from recovered hydrocarbons.

Description of Processes

During the process of thermal desorption, the oily waste is treated by indirect heating in the thermal chamber. The high temperature causes oil and moisture gasification and separation from solids. After condensation, separation, and odor treatment, the pungent odor is eliminated from the recovered hydrocarbons, the recovered water and noncondensable gas are reused, and the exhaust gas satisfies the integrated emission standard of air pollutants. The entire process is depicted in **Fig. 1.**

Theory and Definitions

In the thermal-desorption process, the base oil and chemical additives are fractured into a series of sulfur and nitrogen compounds in the high-temperature condition, resulting in a pungent odor. The odor-treatment system in the TDU is used to remove the pungent odor from the recovered hydrocarbons. This system is based on a series of physical processes and chemical reactions. The chemical reaction of sulfur and nitrogen compounds in recovered hydrocarbons is disrupted by an oxidation reaction in the presence of an active site in the adsorbent and catalyst. The decayed sulfur and nitrogen compounds are adsorbed selectively on the internal channels of adsorbent. These chemical interactions, along with the physical adsorption, eliminate the pungent odor from the recovered hydrocarbons.

The adsorbent and catalyst provide approximately 280 to 300 m^2/g of specific area and have 5.4 silicon/aluminum (Si/Al). To

Original SPE manuscript received for review 12 August 2015. Revised manuscript received for review 21 August 2016. Paper (SPE 184399) peer approved 24 August 2016.

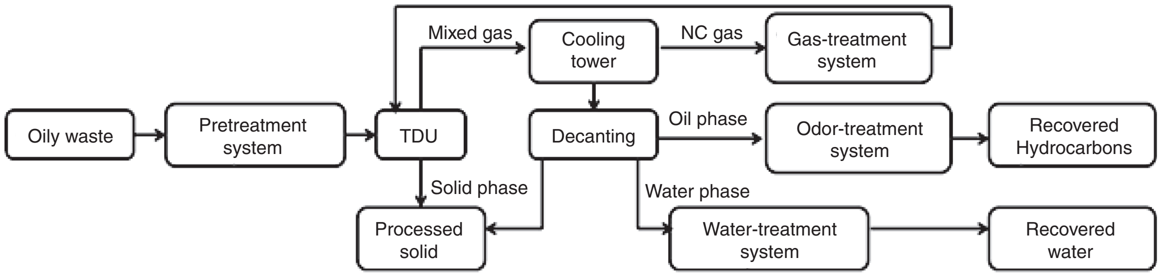

Fig. 1—The TDU process.

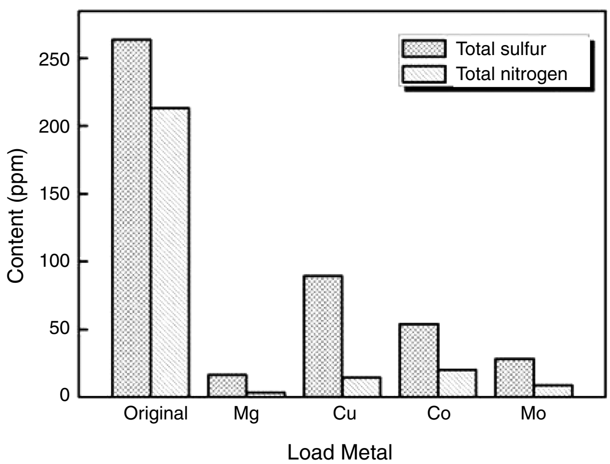

Fig. 2—Comparison of total sulfur and nitrogen in recovered hydrocarbons treated by different catalysts.

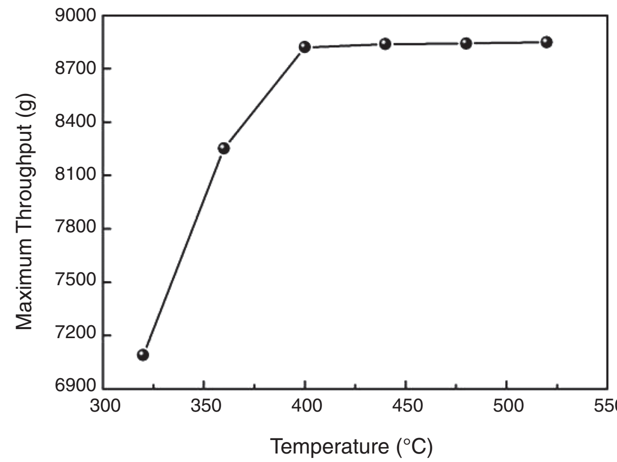

Fig. 3—Effect of temperature on the chemical reaction.

select the correct active site, different metals have been loaded in the adsorbent and catalyst. The total sulfur and nitrogen content of treated recovered hydrocarbons is shown in **Fig. 2.** It is found that loading magnesium (Mg) into the adsorbent and catalyst could provide a removal rate of 90% of total sulfur and nitrogen. As a result, the adsorbent and catalyst loaded with Mg is used in further research.

To optimize the processing conditions, a group of optimizing experiments was carried out, including the effect of temperature and water content. In the optimizing experiments, the maximum throughput of adsorbent and catalyst was used to reflect the effect while taking the 90% removal rate of total sulfur and nitrogen as the standard, and the dose of catalyst was determined at 20 g. The effect of temperature is shown in **Fig. 3.** It is found that the maximum throughput increases gradually, but dramatically with increasing temperature up to 400°C, but the increment becomes less dramatic as the temperature continues to increase, indicating that 400°C is the optimum temperature for the activity of the active site and for the increase in throughput of the adsorbent and catalyst. Accordingly, taking the energy consumption into consideration, the temperature is determined at 400°C for future experiments.

The chemical reaction is sensitive to water, and once the water is introduced, the ability of reaction and adsorption decreases. The dehydration and heating process is essential to achieving a fast and accurate reaction. The effect of water content in recovered hydrocarbon on the chemical reaction was determined and shown in **Fig. 4.** The results revealed that the maximum throughput decreases gradually with increasing water content, which leads to inactivation of the active site. When the water content was more than 2%, the maximum throughput decreased dramatically. Consequently, the water content should be determined to be less than 2%. From this optimizing experiment, when the water content was 0.5%, the ratio of adsorbents and catalysts to recovered hydrocarbons could reach 1:441, revealing the lifetime of adsorbents and catalysts.

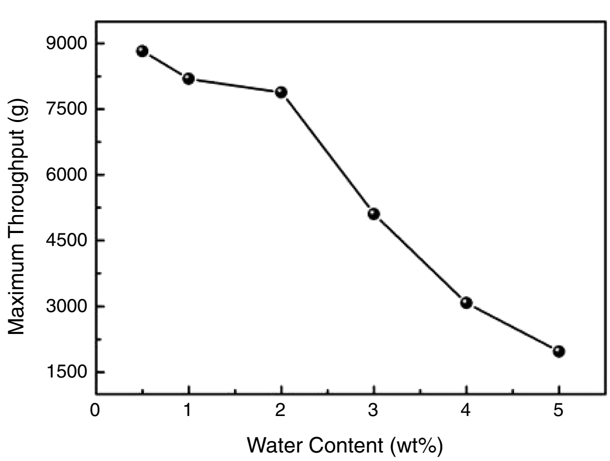

Fig. 4—Effect of water content on the chemical reaction.

Data and Results: Application of Process

The process of odor treatment in a TDU has been implemented successfully at the operator site by the contractor under a pilot project (shown in **Fig. 5**). In this project, the object is the oily cuttings (shown in **Fig. 6**), including oil (≈ 10 to 15%), water (≈ 10 to 15%), and solids (≈ 70 to 80%), and the operating temperature in the TDU is determined to be approximately 350°C. Over the term of the contract, approximately 2,000 tons of oily cuttings from the development process of shale gas in Sichuan (China) had been treated on-site, where the oily cuttings are generated. In the odor-treatment system, the Mg-loaded catalyst is applied, and the operating conditions are temperature of 400°C and water content of approximately 1 to 2%.

Fig. 5—Picture of the job site.

Fig. 6—Oily cuttings.

To date, approximately 1,300 bbl of workable recovered hydrocarbons have been generated. Treated by an odor-treatment system, the pungent odor from the recovered hydrocarbons has been eliminated and the color has also faded. The pungent odor was the result of the presence of sulfur and nitrogen compounds, such as mercaptan, sulfoether, thiophene, amine, benzpyrole, and carbazole, in the recovered hydrocarbons. In the odor-treatment system, the sulfur and nitrogen compounds are disrupted by the action of the active site in the adsorbent and catalyst, and then they are selectively adsorbed on the internal channels of the adsorbent. Compared with the recovered hydrocarbons without treatment, it was found that the removal rate of total sulfur in the treated recovered hydrocarbons was 93.74%,

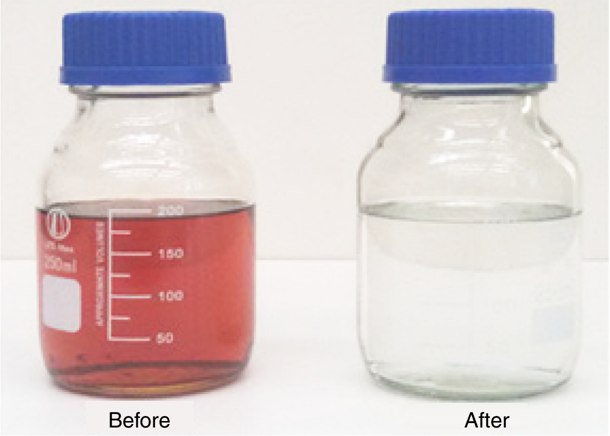

Fig. 7—Comparison of recovered hydrocarbons before and after treatment.

Item	Before (ppm)	After (ppm)	Removal Rate (%)
Total sulfur	263.7	16.50	93.74
Mercaptan	51.58	12.26	76.23
Sulfoether	202.22	4.24	97.90
Thiophene	9.90	0	100
Total nitrogen	213.20	3.40	98.41
Amine	61.74	3.40	94.49
Benzpyrole	3.62	0	100
Carbazole	147.84	0	100

Table 1—Comparison of sulfur and nitrogen compounds in recovered hydrocarbons.

and the total sulfur content was reduced to 16.50 from 263.7 ppm. Among sulfur compounds, the removal rate of mercaptan is the lowest at 76.23%, while sulfoether is 97.90% and thiophene is completely removed. As to the total nitrogen in the treated recovered hydrocarbons, the removal rate is higher and reaches 98.41%. The benzpyrole and carbazole are removed thoroughly, and the removal rate of amine could reach 94.49%. The comparison of sulfur and nitrogen compounds in recovered hydrocarbon is illustrated in **Table 1.** Simultaneously, the elimination of odor results in the color of recovered hydrocarbons fading. According to *ASTM D4007-11e1* (2011), the basic sediment and water of recovered hydrocarbons is less than 1%. The comparison of recovered hydrocarbons is shown in **Fig. 7.** Through statistics, the ratio of adsorbents and catalysts to recovered hydrocarbons could reach 1:350, revealing the lifetime of adsorbents and catalysts.

Subsequently, all the recovered hydrocarbons have been reused to prepare the OBM, which is proved to be not only environmentally sound, but also an additional value to the production operator's bottom line. The mud that is based on the recovered hydrocarbons, determined by China Nanhai Maikeba Mud, satisfies operating requirements. The oily cuttings, recovered hydrocarbons, processed solids, and recovered water are shown in **Fig. 8.** The TDU process could be applied directly in the field where the oily cuttings are produced, and can bring great technical and economic advantages to the user.

Benefit Analysis

The application of recovered hydrocarbons from oily waste by thermal desorption is limited by the presence of a pungent odor, failing in the true applications of the three Rs—reduce, reuse, and recycle. The recovered hydrocarbons treated by the odor-treatment system have been managed to prevent negative impact on human health and the environment. According to the preceding optimizing experiment, the disposal cost of the odor-treatment system is very low, with a low ratio of adsorbents and catalysts to recovered

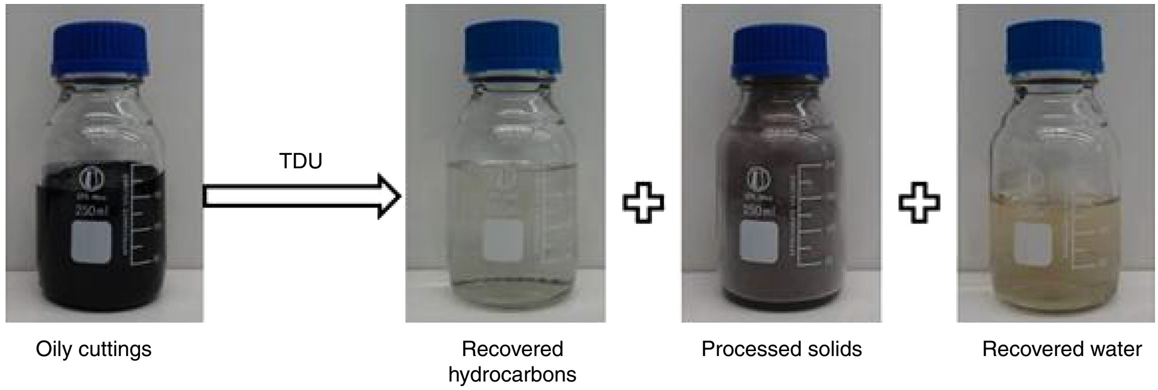

Fig. 8—Schematic of raw material.

hydrocarbons. To date, cost savings and revenue generated from oily-waste recycling are estimated at more than USD 100,000 per year for only a single well, which was calculated according to the output of oily cuttings, recovery rate of recovered hydrocarbons, and the price of base oil on the market.

Conclusions

Compared with the conventional process, a TDU with odor-treatment system has several advantages:

- Provides recovered hydrocarbons without pungent odor
- Removes environmental liability and potential hazards
- Yields substantial recovery of a main company product from a waste stream

The treatment of oily waste is a significant part in the process of energy exploitation and consumption. A TDU with odor-treatment system can be an economical solution to extracting the value of hydrocarbons trapped in the oily waste and to minimizing environmental liability. As a result, this technology has great potential, development possibilities, and merit for common application in future projects.

References

Agha, G. U. and Irrechukwu, D. O. 2002. Experiences in the Management of Drilling Fluids and the Regulatory Control of Associated Cuttings in the Nigerian Oil and Gas Industry. Presented at the SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production, Kuala Lumpur, 20–22 March. SPE-73932-MS. http://dx.doi.org/10.2118/73932-MS.

Al-Suwaidi, A., Hun, C., Marmash, F. et al. 2004. Comprehensive Solutions to Drilling Waste Management. Presented at the Abu Dhabi International Conference and Exhibition, Abu Dhabi, 10–13 October. SPE-88673-MS. http://dx.doi.org/10.2118/88673-MS.

ASTM D4007-11e1, Standard Test Method for Water and Sediment in Crude Oil by the Centrifuge Method (Laboratory Procedure). 2011. West Conshohocken, Pennsylvania: ASTM International. http://dx.doi.org/10.1520/D4007. (Superseded by *ASTM D4007–11, Standard Test Method for Water and Sediment in Crude Oil by the Centrifuge Method (Laboratory Procedure)*, 2016, http://dx.doi.org/10.1520/D4007-11R16.)

Bybee K. 2006. Effective Drilling-Waste Management Reduces Well-Construction Costs. *J Pet Technol* **58** (7): 77–78. SPE-0706-0077-JPT. http://dx.doi.org/10.2118/0706-0077-JPT.

Fang, C. C., Seaton, S., and Shumway, W. 2007. Enhanced Thermal Desorption Process Can Extend Life of Base Oil and Reduce Energy Costs. Presented at the E&P Environmental and Safety Conference, Galveston, Texas, USA, 5–7 March. SPE-106798-MS. http://dx.doi.org/10.2118/106798-MS.

Gilpin, C. A. 2014. Thermal Desorption as a Waste Treatment Option in the Gas Indusry. Presented at the SPE Middle East Health, Safety, Environment and Sustainable Development Conference and Exhibition, Doha, 22–24 September. SPE-170449-MS. http://dx.doi.org/10.2118/170449-MS.

Hahn, W. J. 1994. High-Temperature Reprocessing of Petroleum Oily Sludges. *SPE Prod & Fac* **9** (3): 179–182. SPE-25931-PA. http://dx.doi.org/10.2118/25931-PA.

Jiang, Y., Zhao, C., and Zhao, D. 2005. Characteristics of Oily Sludge and Several Treatment Methods. *Environmental Protection of Oil & Gas Fields* **15** (4): 38–41.

Mkpaoro, M. I. F., Okpokwasili, G. C., and Joel, O. F. 2015. A Review of Drill-Cuttings Treatment and Disposal Methods in Nigeria—The Gaps and Way Forward. Presented at the SPE Nigeria Annual International Conference and Exhibition, Lagos, Nigeria, 4–6 August. SPE-178325-MS. http://dx.doi.org/10.2118/178325-MS.

Ntukidem, J., Omonigho, R, and Anighoro, S. 2002. Thermal Desorption as an Alternative to Cutting Reinjection in Niger Delta Waste Management Operations. Presented at the SPE Annual Technical Conference and Exhibition, San Antonio, Texas, 29 September–2 October. SPE-77556-MS. http://dx.doi.org/10.2118/77556-MS.

Ozumba, C. I. and Benebo, T. E. T. 2002. Waste Recycling Initiatives in an Exploration and Production Company in Nigeria. Presented at the SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production, Kuala Lumpur, 20–22 March. SPE-73841-MS. http://dx.doi.org/10.2118/73841-MS.

Permata, E. and McBride, S. 2010. Regulatory Challenges of Drill Cuttings Waste Management in Indonesia. Presented at the SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production, Rio de Janeiro, 12–14 April. SPE-126738-MS. http://dx.doi.org/10.2118/126738-MS.

Seaton, S. and Browning W. K. 2005. Drilling Waste Management: Case Histories Demonstrate That Effective Drilling Waste Management Can Reduce Overall Well-Construction Costs. Presented at the SPE Annual Technical Conference and Exhibition, Dallas, 9–12 October. SPE-96775-MS. http://dx.doi.org/10.2118/96775-MS.

Segret, G., Kemala, P., Seaton, S. et al. 2007. Design and Construction of Drilling Waste Management Facility in Mahakam Delta, Indonesia. Presented at the International Petroleum Technology Conference, Dubai, 4–6 December. IPTC-11510-MS. http://dx.doi.org/10.2523/IPTC-11510-MS.

Wei, Y., Lv, L., Yang, Z. et al. 2015. Advances on Recycling Technique for Oily Sludge. *Oilfield Chemistry* **32** (1): 151–158.

Jilei Fang is the director of the Environmental Protection Technology Institute in the Jereh Group. He has been with the company for approximately 5 years. Fang's current interests include machine design and environmental technology, and he holds more than 30 patents.

Xianghai Meng is an engineer at the Environmental Protection Technology Institute in the Jereh Group. He has been with the company for approximately 3 years. Meng's current interests are in environmental technology, and he holds five patents.

Guoling Xu is an engineer at the Environmental Protection Technology Institute in the Jereh Group. She has been with the company for approximately 3 years. Xu's current interests are in environmental technology.

Yong Yue is the vice director of the Environmental Protection Technology Institute in the Jereh Group. He has been with the company for approximately 2 years. Yue's current interests are in environmental technology. He has authored or coauthored more than 30 technical papers and holds 10 patents. Yue holds a doctorate degree in environmental science and engineering from Beijing Normal University.

Peichao Cong is an engineer at the Environmental Protection Technology Institute in the Jereh Group. He has been with the company for approximately 4 years. Cong holds two patents, and he holds a master's degree in applied chemistry from the University of Science and Technology of Tianjin.

Chao Xiao is an engineer at the Environmental Protection Technology Institute in the Jereh Group. He has been with the company for approximately 4 years. Xiao holds two patents, and he holds a master's degree in applied chemistry from the University of Yantai.

Wenhui Guo is an engineer at the Environmental Protection Technology Institute in the Jereh Group. He has been with the company for approximately 5 years. Guo holds two patents, and he holds a master's degree in environmental science from the University of Ji'nan.