



Using disulfide oil as coke inhibitor to reduce environmental hazards in olefin heaters

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ABSTRACT

This paper describes the feasibility of replacing a sulfur-based additive with the waste by-product disulfide oil (DSO) in steam cracking for the production of olefin. The objective of adding this substance is to reduce coke formation, and consequently, prevent its formation on the inner walls of the reactor and heat exchanger. It is reported that dimethyl sulfide (DMDS) is a source of hydrogen sulfide, and it is hydrogen sulfide that minimizes coke formation, even though the mechanism is not clear. Disulfide oil is a waste material in gas refineries and a source for hydrogen sulfide production; therefore, it makes sense to evaluate its efficacy in minimizing CO production and coke formation during olefin production. Therefore, pilot plant runs were performed to evaluate its feasibility. By using disulfide oil, the total sulfur content of the pyrolysis gasoline will change and be equal to 26.89 mg/L for the unit with a capacity production of 18000 kg/hr. This action not only provides a low-price resource that inhibits coke deposition in olefin plants but also curtails the emission of hydrogen sulfide into the environment.

1. Introduction

The feedstock used for the cracking of hydrocarbons (from ethane to gasolines) and are important sources for olefin producing companies. Refinery production and petrochemical products are dependent on refinery feed. Naphtha is an ideal feed for olefin production and its composition affected the coking parameters [1]. The H-S energy band dissociation is equal to 91 kcal/mole which is less than its value for the C-H band in the ethane (101.1 kcal/mole), methane (104.99 kcal/mole) and propane (98.6 kcal/mole) molecules. The increase in coke formation during large-scale hydrocarbon cracking leads to a decrease in heat transfer and coils cross over as well as an increase in partial pressure. The process requires excess heat to compensate for the heat shortage due to the coke formation inside the transfer line exchanger and decoking process. The olefin selectivity decreases with more coke formation that has a negative economic effect [2-4]. Dimethyl Disulfide (DMDS) injection is traditionally one of

the most important routes to increase the olefin yield in refineries. It can also prevent the production of undesirable byproducts. When naphtha is used as the feedstock in crackers, the byproducts (e.g., carbon monoxide, carbon dioxide and coke) affect the wall and operation parameters of the crackers. This phenomenon causes an increase of partial pressure and a decrease in the heat transfer coefficient. With more increasing the time, coke accumulation forces the operator to stop the process in order to overhaul. Therefore, the crackers should be turned off for decoking [5,6]. In gas refineries in modern countries, mercaptan-containing substances are burned in the flaring system, which causes a lot of environmental hazards. One of these substances is disulfide oil (DSO), and its toxicity is well described. Disulfide oil vapor inhalation leads to health problems such as lung cancer, dizziness, drowsiness, etc. DSO and its related components affect humans, animals, plants, and aquatic life. When this substance burns or is barely heated, it produces some harmful gases such as carbon monoxide, carbon dioxide, aldehyde, and injurious

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oxides and sulfides, especially methyl mercaptans or radicals [7]. In refineries, the Meraux reaction is used to separate the mercaptans existing in the liquid gaseous, butane, propane, light naphtha and kerosene. DSO is the final product in the oxidation process of mercaptans. In the Meraux unit, NaOH is used as an extraction solution which is reused after recycling. Then, mercaptans are converted to DSO in the presence of oxygen and an alkaline solution (extracted solution). The DSO produced in the units is of no use. DSO is not a desired byproduct in gas refineries, and it is injected deep into the earth or burned in the flares which cause environmental pollution. Generally, the main part of DSO is formed from short chains of di alkyl disulfides. If DSO is not completely converted to H₂S, it increases the total sulfur content in gasoline, which in turn leads to serious environmental hazards. Refinery activities are the main source of DSO emission in the environment and ecosystems. To achieve this objective, appropriate technologies, namely steam cracking and fluid catalytic cracking, provide limited efficiency in olefin productions and generate a large amount of low-quality aromatics products and coke when they operate with liquid feeds. In this work, DSO is used as a coke inhibitor to reduce coke formation in the thermal crackers. This act provides a very cheap resource for replacing other coke inhibitors in olefin units and reduces sulfide gas emission into the environment. The use of a waste byproduct from a refinery process as a potential source of hydrogen sulfide to minimize coke formation during olefin production has not been reported before.

2. Materials and methods

2.1. Feedstocks

Dimethyl disulfide was purchased from the Lind Petrochemical Company (Germany). The disulfide oil was collected from the sweetening process at the Kangans City Gas Refinery (Asaluyeh, Iran) as a waste byproduct.

2.2. Measurement

The H₂S in stream were analyzed using gashouse chromatography (Borsig, Germany) according to the ASTM-D5453 test method for sulfur measurement. This procedure was applied to detect the sulfide concentration in the finished products. In all the tests, the total sulfur content was measured using hydrogen sulfide concentration detecting. The monoxide concentration in the final products was analyzed using a portable analyzer.

2.3. Crack Test

With a direct injection of DSO in the heater under the same condition for dimethyl disulfide, the resistance time causes a large number of problems such as an increase in the sulfide content of the byproducts (e.g., pyrolysis gasoil). To overcome these problems, a new and special unit was designed and installed before the crackers. After flowing through the reactor, hydrogen sulfide is obtained with a purity of 98%, which is injected directly into the reactor. Thus, the other sulfide-containing substances, mercaptans, etc. cannot enter or stay in the heaters. The scheme of the pilot designed for DSO conversion is presented at Figure 1.

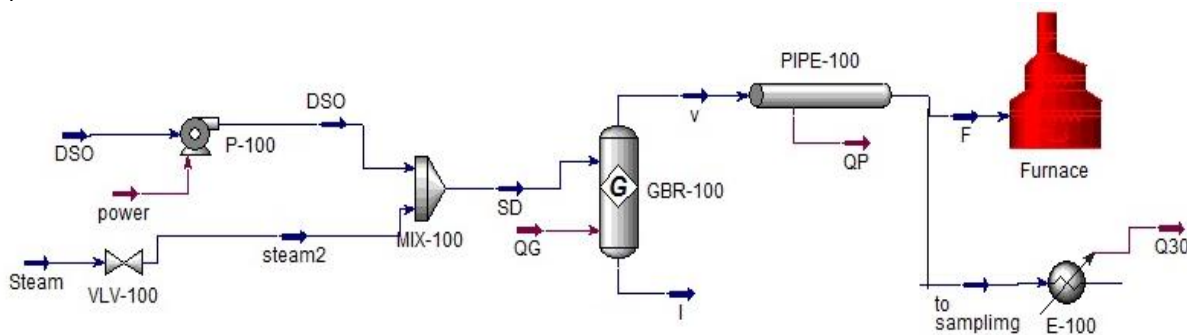


Fig. 1. Flow-diagram of designed reactor for disulfide oil conversion.

This pilot is made of Incolloy800 alloy (35Cr, 45Ni) and the size of the pipe is 24.31-33.41 mm ID. This grade was selected to adjust the tube stability in the process operation situation. Heat losses across the coil enables the direct estimation of the pressure, temperature and gradients of injection and products. The following list includes the reactor elements: double-pipe heat exchangers (ksp), pilot wall (grade 90 steel coil), dosing pump (ABB) (6 atm), 92 electric elements (=31 K.W), shell and tube devise (ABB), advance mixer (Alstom), self-tuning analyzer of input partial pressure (brawn), vapor loop mass meter with flange (sapag), vapor pneumatic pressure c.v (brawn), couplings (Yokogawa), mini PLC system (Masoneilan & Sapag),

instrumentation dsc system (Cossby), class 800 pressure s.v (Cossby), feedstock stop valve (Siemens), input manual valve (Yokogawa), and output manual c.v (Yokogawa). The DSO from the storage tanks was sent to the designed reactor using a pump (P-100) with a flow rate of 6000 g/h. and ambient temperature. This pump increased the feed pressure up to 6atm and sent it to a mixer (M-100). In other co-current regime (in the cracker unit), the required steam was generated at a pressure of 9 atm and 194 °C. The partial pressure was reduced to 6 atm into a valve (V-100) and mixed with the DSO stream in a MIX-100 mixer. The disulfide oil completely evaporated in the vicinity of the hot steam. The steam/ DSO mass ratio was kept at a constant value of

1.5. The mixed stream was transferred to the reactor (R-100) and warmed to complete decomposition at a temperature higher than 650 °C. The discharged gas volume in the effluent reactor was equal to 61330 mL/h, which was completely sent to the de Laval nozzles. All lines and electrical elements would be protected by a pressure-positive agent to ensure safety. Before the tests, this chamber was cleaned using a continuous stream of nitrogen with a flow rate of 200 mL/min.

2.4. Decoking procedure

In the decoking procedure, the furnace outlet temperature decreases to 820 °C at a rate not exceeding 50 Kg/h. This temperature is then kept constant. The dilution steam/hydrocarbon feed ratio control is disengaged, and the hydrocarbon feed valves are gradually closed. Next, there is a reduction in the hydrocarbon feed stepwise from 26 to 0 T/h. The DMDS or DSO injection has to be closed. Now the furnace is in standby condition. While closing the hydrocarbon feed valve, the furnace outlet temperature is held at 820 °C by reducing the fired duty. The heat release of the floor and side wall burners will automatically be reduced by the COT control. As soon as the feed flow falls to zero, the block valve upstream of the feed control valves has to be closed, and the feed lines have to be purged with process steam. Then, switch over to MP (Medium pressure steam) by first opening the valve in the MP-steam supply line, and finally close the valve at the process steam supply line to the furnace. Switch over from the process line to the decoking gas line (to the stack). When the temperature has stabilized at 820 °C, the switch to the decoking line can begin. When the cracked gas valve is completely closed, the LP (low pressure steam) normally injected for purging purposes will serve as the sealing medium to the valve. Subsequently, the furnace (pilot) will be decoked.

3. Results and discussion

3.1. Substitution of disulfide oil and environmental effects

The effects on the carbon monoxide production and sulfur concentrations on the final product injected with DSO were investigated. According to the datasheets and environmental laws, the amount of CO formed by each cracker should be less than 400 mg/L. It is assumed that carbon monoxide is produced solely from the gasification of coke. Therefore, the amount of carbon monoxide formation in the steam cracker units could be used as an indicator for detecting coke formation/deposition. Also, a high operating temperature is required to achieve the products with on-specification properties, especially when the monoxide concentration is too high. Thus, the influence of disulfide oil injection on the rates of carbon monoxide production should be well considered. Figure 2 shows the CO content in the effluent versus the DSO injection. As can be seen, during the cracking process, the amount of carbon monoxide produced decreases by increasing the amount of disulfide

oil injected up to 6 kg per hour. But with more DSO injected, the trend remains constant and seems that a steady-state has been established. This data is used to explain the direct coke gasification with steam and the removal of carbonaceous elements deposited during the steam reforming process. It is commonly accepted that the C ad atoms and CH_x groups on the surface are intermediates in the hydrocarbon steam reformers [4]. The high concentrations of monoxide production at the beginning of the process can be attributed to the catalytic activity of the cracker walls. When the metal particles of the reactor walls are covered with coke, they lose their activity. However, at the high temperatures the coke formation in the transfer line exchanger, is in accordance with the reports of Reyniers and Froment [8], the formation of the flat regain (steady-state) in Figure 2 is mostly due to hydrocarbon cracking. They reported that the coke deposition on the walls has a diminutive role in the production of monoxide.

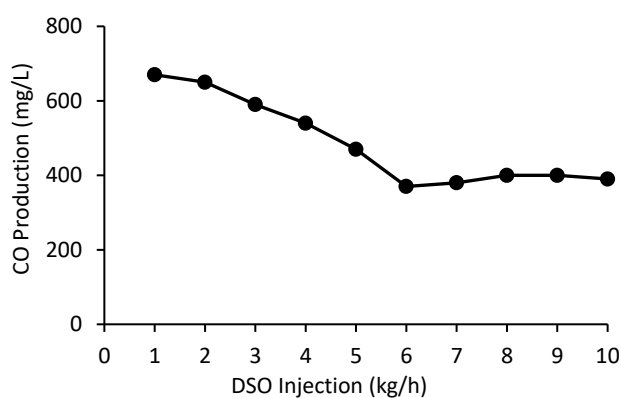
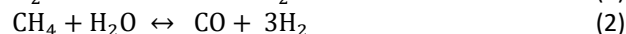


Fig. 2. The influence of DSO injection on the carbon monoxide production.

Since disulfide oil is completely converted to hydrogen sulfide before the injection, the amount of monoxide produced decreases with a steep slope. It shows/confirms that this pilot can effectively inject DSO or other sulfur-containing materials to the crackers. CO is formed in the steam reformers according to the following reactions:



By increasing the temperature, the equilibrium state of both chemical reactions declines and the reactions have more of a tendency towards increased carbon monoxide production. Hence, it can be expected that by increasing the H₂S concentration in Equation (1), due to Le Chatelier's principle, the chemical reaction obey the forward reaction; therefore, the amount of CO will be reduced. When DSO was selected as the inhibitor, a decrease in concentration of this substance produced with steep slope can be attributed to the complete conversion of this substance to hydrogen sulfide prior to injection it to furnaces (the conversion is done in the constructed pilot).

3.2. Gasoline sulfur content

Pyrolysis gasoline is one of the most important products in olefin refineries. Sulfur concentration in gasoline plays a critical role for use in downstream industries and environmental issues. The conversion of products is affected by the outlet temperature and the pressure inside the coils [10]. The total S-content of the pyrolysis gasoline changed and was equal to 25.89 mg/L when DSO was applied as a coke inhibitor at a reformer unit with a capacity of 18000 kg/hour. The total S-content of gasoline following the injection of disulfide oil varied from 20 to 100 mg/L. The total S-content for the produced gasoline from the unit versus the various amount of DSO injection is represented in Figure 3. As seen in Figure 3, with an increase in the amount of DSO injection, up to 6 kg, the amount of sulfur in the final product is constant and at its lowest value. With more increases in the DSO injection, the concentration of this substance increases significantly in the gasoline. This indicates that the surface saturation and the formation of a sulfide layer on the inner surface of the pipes are well formed. Therefore, it appears that DSO was successful in its role as a coke inhibitor. Also, it is well accepted that the sulfur highly affected the steam reforming reactions of the hydrocarbons [10]. The adsorption of the sulfur molecules from the gas phase by the metal sites of the wall occurs more rapidly than the adsorption of either the hydrocarbons or water [9]. The results show that this substitution can prevent the emission of millions of liters of sulfur oxides into the environment annually as well as providing economic savings.

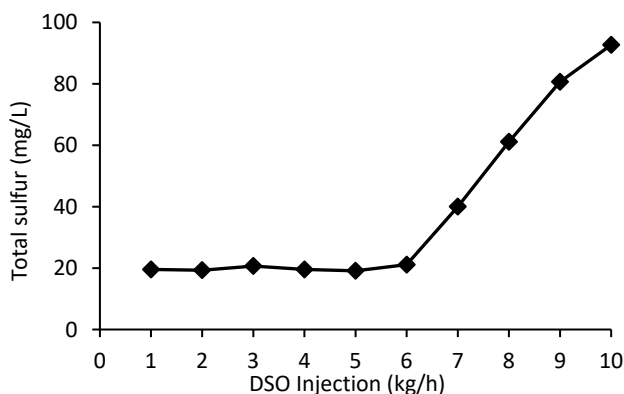


Fig. 3. Total sulfur content of pyrolysis gasoline produced from the unit.

4. Conclusions

As maintained by the literature, it was found that “disulfide oil” can be used to prevent coke formation at crackers of olefin units in refineries. This act not only provides a very inexpensive resource for coke inhibitors, but also holds back the emission of sulfur based gaseous into the environment. After constructing the equipment in pilot scale, the values of disulfide oil conversion to the gas were carefully calculated. Therefore, the amount of carbon monoxide

produced was considered as an indicator of catalyst poisoner and coke formation. The results attained from the injection of disulfide oil to crackers indicated that the carbon monoxide concentration remained in a standard value. The total S-content, which is an environmental contaminant and a component of gasoline, was regulated with disulfide oil. It was altered from 20 to 100 mg/L, which was agreeable.

References

- [1] Corma, A., Sauvanaud, L., Mathieu, Y., Al-Bogami, S., Bourane, A., Al-Ghrami, M. (2018). Direct crude oil cracking for producing chemicals: Thermal cracking modeling. *Fuel*, 211, 726-736.
- [2] Rahimi, N., Karimzadeh, R., Jazayeri, S. M., Nia, K. D. (2014). An empirical investigation of the influence of sulfur additives on the catalytic rate of coke deposition and CO formation in the steam cracking of LPG over Incoloy 600 and stainless steel. *Chemical engineering journal*, 238, 210-218.
- [3] Meyers, R. A., 2005, Meyers. Handbook of petrochemicals production processes. McGraw-Hill Prof Med/Tech.
- [4] Dhuyvetter, I., Reyniers, M. F., Froment, G. F., Marin, G. B., Viennet, D. (2001). The influence of dimethyl disulfide on naphtha steam cracking. *Industrial and engineering chemistry research*, 40(20), 4353-4362.
- [5] Crynes, B.L., Albright, L.F., Tan, L.F., “Thermal Cracking”, Encyclopedia of Physical Science and Technology, 3rd edition, 2002, Vol. 16, 613-626. Academic Press, New York.
- [6] Salari, D., Niaei, A., Shoja, M. R., Nabavi, R. (2010). Coke formation reduction in the steam cracking of naphtha on industrial alloy steels using sulfur-based inhibitors. *International journal of chemical reactor engineering*, 8(1) 1-20.
- [7] Ito, T., Miyaji, T., Nakagawa, T., Tomizuka, N. (2007). Degradation of dimethyl disulfide by *Pseudomonas fluorescens* strain 76. *Bioscience, biotechnology, and biochemistry*, 71(2), 366-370.
- [8] Reyniers, M. F. S., Froment, G. F. (1995). Influence of metal surface and sulfur addition on coke deposition in the thermal cracking of hydrocarbons. *Industrial and engineering chemistry research*, 34(3), 773-785.
- [9] Yuan, B., Li, J., Du, W., Qian, F. (2016). Study on co-cracking performance of different hydrocarbon mixture in a steam pyrolysis furnace. *Chinese journal of chemical engineering*, 24(9), 1252-1262.
- [10] Trimm, D. L., Turner, C. J. (1981). The pyrolysis of propane. II. Effect of hydrogen sulphide. *Journal of chemical technology and biotechnology*, 31(1), 285-289.