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### Original Research Article

## Modeling of the Hydrodesulfurization Process of Natural Gas Condensates

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#### ABSTRACT

Fossil fuels make up the bulk of the world's energy consumption today. One of these fuels is natural gas condensate, which is composed of various carbon compounds and is used as one of the main fuel sources. But these condensates also contain sulfur compounds such as hydrogen sulfide, thiols (citrale), and aromatic compounds that are considered environmental pollutants. Therefore, these sour hydrocarbon sources need to be refined to reduce the sulfur content. In this study, desulfurization of natural gas condensate extracted from the gas field of southern Iran and removal of disulfide oils produced in the South Par refinery was performed by hydrogen-desulfurization ion desulfurization ion with the help of hydrogen. For this simulation, the Aspen Plus software package was used. Unused hydrogen in the effluent is hydrated by washing with an amine solvent to reduce operating costs. Refined condensates are a mixture of complex hydrocarbon compounds called petroleum fractions classified according to their boiling point range. A multi-component distillation system is also simulated to produce optimal products. The cuts taken from the distillation section include boot, light naphtha, heavy naphtha, kerosene, and gas oil. This study aimed to investigate the number of sulfur compounds remaining in these hydrocarbon sections. The results of this experiment show that the final products are completely pure and free of sulfur compounds.

Keywords: Gas condensate; Disulfide oils; Sulfur compounds; Hydrophilic desulfurization

## Introduction

Due to the growing trend of energy consumption globally, there is a need to create new fuel sources and improve their quality[1]. Natural gas condensates contain complex hydrocarbon compounds and can be used as one of the main fuel sources. Condensation is the flow of liquid hydrocarbons present in natural gas reserves and sediment in the extracted gas. Therefore, these condensates, along with crude oil, can boost energy production in the oil industry. According to the IEA, the South Pars gas field, located in the Persian Gulf, has the largest gas source globally, shared between Iran and Qatar. It is estimated that this region has 51 trillion cubic meters of running natural gas and 7.9 billion cubic meters of gas condensate [2]. But the condensate extracted from this area is highly sour and contains 2000 ppmw of sulfur compounds. Sulfur in spent fuels has been the main cause of non-combustible pollutants. In addition to causing corrosion in various oil industry equipment, the presence of sulfur compounds produces toxic and dangerous sulfur dioxide gas when burned [3]. Usually, hydrocarbon products are not used directly after extraction from oil and gas wells, and operations are performed on them to remove impurities such as sulfur compounds, nitrogen-containing compounds, oxygenates, and metals to become products with the necessary standard and can be supplied to To be marketed[1,4]. These standards include environmental requirements, which are becoming increasingly stringent and limited. For example, the US Environmental Protection Agency set the maximum permissible amount of diesel incinerated sulfur compounds at 500 ppm in 2006, and the ppm has decreased by 15. There are similar environmental regulations in Europe that have forced the oil industry to reduce the sulfur content of spent fuels to 10 ppm since 2009. According to EuroV guidelines, the permissible sulfur level in various fuels is less than 10 ppm [5]. Sulfur in fossil fuels is divided into two groups of non-aromatic and aromatic compounds. The first group includes sulfides, disulfides, and mercaptans (thiols), and the second group includes thiophenes, benzothiophenes, dibenzothiophenes, and benzofluorenes. The first group is more reactive than the other sulfur compounds, while the second group is more difficult to desulfurize, especially benzothiophene and dibenzothiophene compounds. One way to reduce the sulfur in consumed fuels to the extent approved by international standards is desulfurization using dehydrogenation-sulfurization ions. This method eliminates both types of Sulfur compounds are very effective. In this method, a high-temperature reaction is carried out in the presence of a catalyst. In this process and detoxification, nitrogen and metal compounds are also destroyed,

and the deoxygenation process is performed [6-10]. This process has been selected for desulfurization of natural gas condensate due to the many advantages of hydrodesulfurization, such as reducing sulfur to less than 10 ppm, reducing environmental pollutants, extending the life of catalysts used, and simple operating conditions[11]. Research has also been done on the study and simulation of the hydrodesulfurization process. Studies on the hydrodesulfurization process simulation using Aspen HYSYS software to purify crude kerosene from compounds such as sulfur and nitrogen have been performed by Bilal[2]. Jimenez[5] Also used computer-aided modeling to investigate the processes of hydrodesulfurization, hydrodynamicnitrogenation, and hydrodramatization of vacuum oil and gas that occur simultaneously in industrial reactors[11]. The process of deep hydrodesulfurization is one of the main methods of desulfurization using hydrogen, which is performed under different operating conditions and in the presence of different catalysts to reduce the amount of sulfur[12].In addition to the hydrodesulfurization unit, a distillation system is required to separate the pure sections. Of course, the order of placement of these two units is also important. Gas condensate from the South Par region is sent to refineries to separate oil slices or sold on world markets. In either case, the high sulfur content in the condensate or a piece of sour oil can cause. It will cause damage the pipelines and equipment of downstream industries and increase the cost of their maintenance. In the present study, the initial design is done so that first the hydrodesulfurization unit and then the multi-component distillation system are located[13].One of the most important environmental problems of the South Pars refinery is the production of disulfide oils. Disulfide oils, especially dimethyl and diethyldisulfide, are inadvertently produced in large quantities in gas refineries[14]. There is currently no practical application for these materials. The disulfide oils produced are either injected deep into the earth, which pollutes the soil and groundwater or is incinerated, resulting in very severe air pollution in the area and produces Sulfur dioxide and carbonyl compounds. In both cases, there is serious damage to the environment. These compounds include more than 17 different types of disulfides and trisulfides with monoalkyl chains smaller than 1C. Disulfide oils are highly toxic and carcinogenic and adversely affect reproduction. Among the types of disulfide oils, dimethyl sulfide has the highest toxicity[15]. However, disulfide oils are very active in catalytic reactions in the presence of hydrogen and are easily converted to alkanes and hydrogen sulfide in the hydrodesulfurization process[16]. Therefore, this study aims to simulate a hydrodesulfurization unit and a distillation section in the South Pars refinery that refines

natural gas, condensates rich in sulfur, and produces clean and high fuel value fuel sections[17]. Also, due to the problems mentioned concerning disulfide oils in the refinery, in this simulation, a stream consisting of disulfide oils is injected into the gas condensate, which is sent as feed to the hydro-sulfurization unit, through which the condensate can also be Purified the gas, minimized its sulfur, and completely removed the disulfide oils from the South Pars refinery. The results of this simulation can be used in the construction of a new hydrodesulfurization unit for the purification of condensate from the nature of the South Pars region and the production of clean fuel sections. The main difference between this process and conventional hydrodesulfurization processes is in the simulated unit feed, a mixture of natural gas condensate and disulfide oils. In contrast, the feed of common processes is oil cuts such as naphtha and kerosene. The sulfur compounds in the final products of this simulation are expected to be very small[17-21].

### **Input feed features**

The characteristics of the natural gas condensates studied in this simulation, based on their actual boiling points at 0 ° C and 790 mmHg, are given in Table 1. The molecular mass and mass density of gas condensates are 120 and 756 kg/m<sup>3</sup>. Tables 2 and 3 also show the non-sulfur and sulfur compounds in the feed[1,22]. The feed of the hydrodesulfurization unit is a gas condensate mixed with a stream containing disulfide oils. Disulfide oils are soluble in ambient conditions (27 °C) and atmospheric pressure in the gaseous condensate. The boiling point and mass component of the two sulfur compounds of disulfide oils used in this study are shown in Table 4. Gas condensate flow and disulfide oil flow with a volume flow of 6360 and 47 cubic meters per day, respectively, maximum daily production of disulfide oils in the South Pars refinery is mixed and enters the inlet-sulfurization unit as the main feed according to it. Aspen Plus software is used to perform this simulation; the first step of the simulation is to define the input feed for the software[19-22]. A new file must be created, to begin with. All the available compounds and materials and the products of hydrodesulfurization reactions are selected from the compound section. The thermodynamic model of Chaosider, which is most compatible with existing processes and compounds, is selected[9]. Natural gas condensate contains very complex

compounds heavier than C6. Therefore, the properties of the compounds present in the condensate flow are determined based on their actual boiling point in the software tests section. Light compounds C2 to C5-n, which are pure compounds with low boiling points and present in the gaseous condensate, are also determined based on their mass component for the input feed. Finally, gas condensate flow and disulfide oil flow are generated in the simulation medium. The process flow diagram is shown in Figure 1[11].

**Table 1.** Specifications of natural gas condensates based on actual boiling point

Boiling point	Volume
15	5.18%
36.1	11.49%
150	53.24%
175	63.09%
215	73.41%
250	81.76%
275	87.01%
350	95.81%
360	100%

**Table 2.** Non-sulfur compounds in gas condensate

Non-sulfur compounds	weight percentage in gas condensate
Propane	0.3295%
Normal Botane	1.732%
Iso-Botane	0.7798%
Normal Pentane	0.0212%
Iso-Pentane	0.1602%
Water	0.008%
Hexane and heavier compounds	96.75%

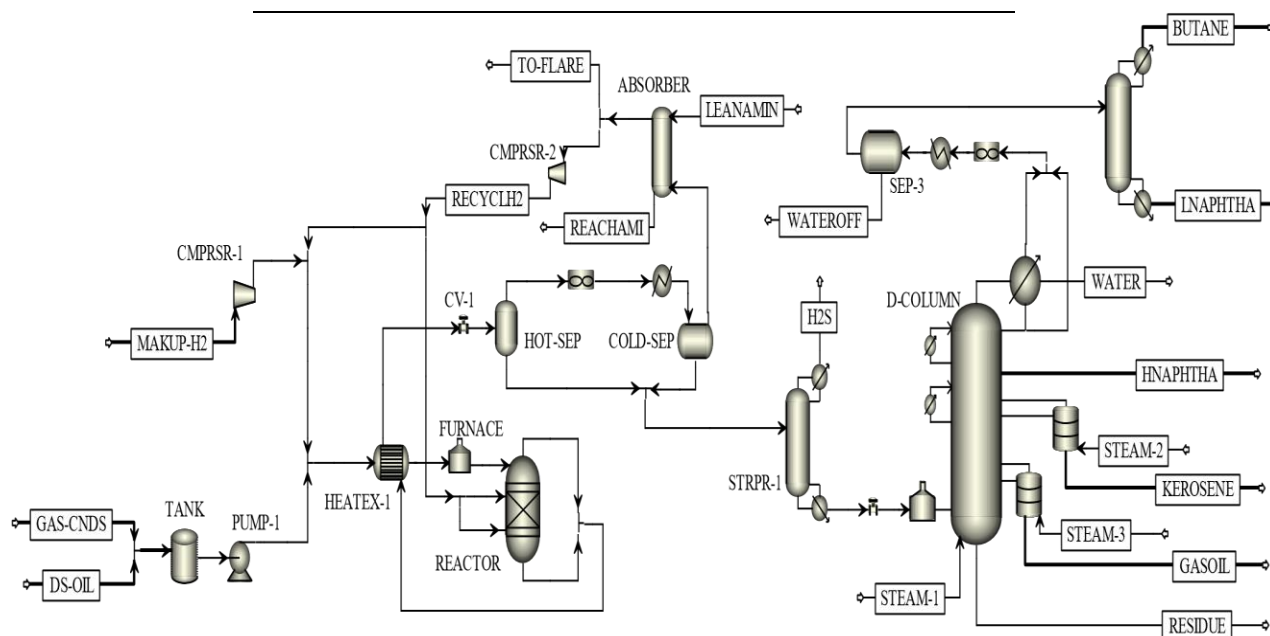
**Table 3.** Non-sulfur compounds in gas condensate

Sulfur compounds	Share
Methyl mercaptan	20
Ethyl mercaptan	350
ISO-propyl mercaptan	250

Tert-butylthiol	10
Normal-propyl mercaptan	100
Two-butyl mercaptan	210
ISO-butyl mercaptan	10
Normal-butyl mercaptan	100
Heavy sulfur compounds	570
Sulfides	300
Aryl sulfide	75
Benzothiophene	56
Benzonftotiofen	12
Dibenzothiophene	59
Total	2122

**Table 4.** Compounds in sulfide oil flow

Compound	Share%	Boiling point, C
Dimethyl disulfide	50%	110
Diethyl disulfide	50%	154



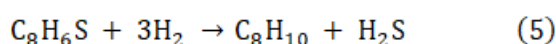
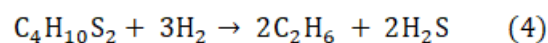
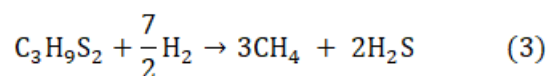
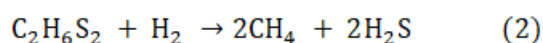
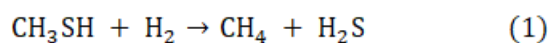
**Figure 1.** Flow diagram of the complete desulfurization process of gas condensate using hydrogen.

## Methods and Materials

## Hydrodesulfurization reaction

Hydrogen-assisted hydrodesulfurization or desulfurization is a catalytic process performed in refineries to remove sulfur compounds from fossil fuels. Most metals catalyze the hydrodesulfurization process, but the intermediate metals are more active. Ruthenium disulfide has the highest activity among catalysts, but usually, a relatively high dual combination of cobalt and molybdenum is used as the main catalyst in the process[7, 18]

The reaction occurs in a droplet bed reactor in which the direction of motion of the liquid phase is always from top to bottom, but the direction of motion of the gas phase can be from top to bottom or from bottom to top. This reactor is commonly used in hydrogenation reactions. The process temperature and operating pressures are 330 ° C and 4000 kpa, respectively. In this reactor, sulfur compounds are converted to hydrogen sulfide in the presence of hydrogen. All reactions are exothermic, and the reaction rate decreases as the length of the reactor increases. Some of the most important reactions that occur in this process are listed below[19, 20]:



Reactions 1 and 2 for mercaptans and reactions 3 and 4 are related to dimethyl disulfide and dimethyl disulfide, which are in the flow of disulfide oils with hydrogen, respectively. Also, reaction 5 is for benzothiophene[13-15].

## General description of the process

According to Figure 1, the flow of gas condensate with a flow rate of 200 ton/hr under ambient conditions (temperature 27 ° C and atmospheric pressure is mixed with the flow of disulfide oils at a flow rate of 2000 kg/hr and enters the process as the main feed. The feed flow pressure by the pump reaches 4900 kPa. Also, a compensating hydrogen flow with a flow rate of 170 kg/hr by the compressor reaches a pressure of 4650 kPa and is mixed with a stream of hydrogen recovered in the amine unit with a purity of 61% molar. The flow rate of recovered hydrogen is 16702 kg/hr. This flow is divided into two equal parts before being mixed with the compensatory hydrogen flow. As a cooling feed, a stream is divided into two equal parts and enters the hydrophilic reactor from two points between the substrates. The other stream is

mixed with compensating hydrogen by a mixer. A compressor is used to increase the pressure of the recovered hydrogen to 4650 kPa. The hydrogen mixed with the main feed is then mixed with the flow resulting from the combined feed[16-18]. There is a heat exchanger between the combined feed and the output products of the reactor to save energy. The hot fluid of this converter is the products leaving the reactor and the cold fluid of the combined feed. The heat exchanged in this exchanger is 39601 kW. The temperature of the combined feed reaches 272 ° C after passing through the heat exchanger. This current then enters the furnace to reach the required temperature of 330 ° C for the reaction in the reactor. The reactor's reactions are exothermic, and therefore a cooling stream of hydrogen is injected between the substrates. All reactions performed in the reactor are defined for the software. The rate of heat released in the reactor is 1984 kW[21]. After passing through the heat exchanger and reducing the temperature to 150 °C, the output products of the reactor pass through a pressure relief valve and reach a pressure of 1650 kPa. Then they enter the hot separator. In this separator, light compounds, which include 45 mol% hydrogens and 2.04 mol% hydrogen sulfide, come out of the separator at a temperature of 147 ° C and enter the cold separator. The temperature of this current decreases to 40 ° C in two stages before entering the second separator. First, it reaches a temperature of 105 °C using an air cooler. This current then enters a cooler, and its temperature is reduced to 40 °C[19-22].

A stream rich in hydrogen, also containing 5.6% by weight of hydrogen-sulfide, enters the blue base column using amines after leaving the top of the cold separator. It is separated from hydrogen. The amine current used with a flow rate of 44165 kg/hr includes 72.82% by weight of water, 27% by weight of diethanolamine, and 0.18% of carbon-oxide at a pressure of 1400 kPa and a temperature of 45 ° C. The refined hydrogen from the hydrogen sulfide is removed from the top of the column, and 1% of it is sent to the burner, and the rest is returned to the unit by the compressor. The effluent streams from the bottom of the hot separator and the cold separator, which contain heavy hydrocarbon compounds, are mixed and sent to the naked tower to remove residual hydrogen sulfide. The pressure of the stripping tower is about 1500 kPa. The steam flow from the condenser of this tower includes methane, ethane, hydrogen, and hydrogen sulfide compounds. The outlet stream from the bottom of the tower contains heavy hydrocarbons at a temperature of 225 ° C, which must be sent to the distillation section to separate the different sections. The nudity tower has 20 balance trays, a partial condenser, and a reboiler. Also, feed from tray 5 enters this tower. The current return ratio is 4.7, and the thermal load of the reboiler is 16180 kW[19, 22]. The outlet pressure from the bottom of the distillation tower is reduced to 400 kPa by the pressure relief valve before entering the distillation section. Then, using a furnace, its temperature reaches 310 ° C and is sent to the bottom of the distillation tower. High-pressure steam with 350 ° C and 1380 kPa pressure is injected down the distillation tower. The steam flow rate is 42 kg per cubic meter of the bottom product of the tower. The highest tray of the distillation tower is located at a temperature of 84 °



C, from which the output steam vapor enters the condenser and cools to a temperature of 74 ° C. The condensed water flow leaves the drum reflux. The first lateral flow is taken from a tray of 26 distillation towers containing heavy naphtha. This flow is sulfur-free. The second side stream from the distillation tower, taken from Tray 28, enters a kerosene side-naked device with ten trays. Steam with a temperature of 350 ° C and a pressure of 1380 kPa is injected as feed to the bottom of this nourisher. The output product from the bottom of this nourisher is kerosene. The third side stream is taken from the distillation tower from tray 26 and enters the gas oil desalination plant with eight trays. Steam with a temperature of 350 ° C and a pressure of 1380 kPa is injected as feed to the bottom of this nourisher[34]. The output product from the bottom of this stripper is gas oil. Finally, the remaining products, which contain heavy hydrocarbons, are removed from the bottom of the distillation tower. Heavy naphtha products, kerosene, residual gas oil, and condensate are pure and without sulfur compounds and stored in tanks. The tower has 30 balance trays and a partial condenser. The current return ratio is 16.02[1]. The flow of exhaust gas from the top of the drum reflux and the outlet fluid from the bottom of the drum tower reflux are mixed. This current then enters the separator to separate the remaining water after reducing the temperature by passing through the air conditioner and cooler. The dehydrated hydrocarbon stream is sent to the dehydration tower after the separator. The tower has 15 trays, a partial condenser, and a reboiler with a heat load of 54677 kW. It is also the return flow ratio, with a gaseous stream containing butane from above and a liquid stream containing light naphtha coming out from below. These products are free of sulfur compounds[2, 7].

## Results and Discussion

Aspen Plus software was used to simulate the complete desulfurization process of gas condensate and disulfide oils using hydrogen. Gas condensate is composed of many different compounds - these compounds have different boiling points and cover a wide temperature range. Each cut has a welding range that includes the primary boiling point and the second boiling point. Different welding ranges for different cuts are mentioned in the references. In this study, the boiling point ranges of different sections are defined based on the information extracted from the Chevron company site [8]. The boiling point range is entered in the oil specifications section to create different cuts in Aspen Plus software. The simulation results show that the distillation tower obtains five different sulfur-free sections of purified gas condensate. The simulation results are shown in Table 1.

To properly understand this process, two main performance indicators can be described. Hydrogen consumption is defined as the ratio of hydrogen required under normal conditions to react with all the sulfur compounds in the feed to the feed volume, which is 13 for this process. And the ratio of liquid products to feed, the mass flow rate of the lower products of the Aryansaz tower to the mass flow rate of the feed, is 61.

**Table 5.** Simulation Results

Flow specifications	butane	Recovered Hydrogen	disulfide oils	gas condensate
Mass flow rate, kg/hr	3135	16703	2001	2000100
Phase	Gas	Gas	Liquid	Liquid
Pressure, kPa	181	4650	641.32	101.32
Temperature, C°	17	161	48	26
Density, kg/m <sup>3</sup>	4.61	16.91	996	762
% By weight of sulfur	0	0	61	0.23
% By weight of hydrogen	0	9.3	0	0
% By weight of water	0	1	0	0.02
%By weight of light gases	98.6	64.3	0	3.1
% By weight of gas condensate	1.4	25.4	0	96.9
Flow specifications	Light oil	Heavy oil	Kerosene	Gas oil
Mass flow rate, kg/hr	35000	40880	83510	25664
Phase	Liquid	Liquid	Liquid	Liquid
Pressure, kPa	379	378	375	282
Temperature, C°	234	181	152	72
Density, kg/m <sup>3</sup>	668.36	659.1	595.4	617.9
% By weight of sulfur	0	0	0	0
% By weight of hydrogen	0	0	0	0
% By weight of water	0	0	0	0
% By weight of light gases	0	0	0.08	1.41
% By weight of gas condensate	100	100	99.9	98.5

## Conclusion

Due to the problems caused by sulfur compounds in fossil fuels, in this study, simulation of hydrogen desulfurization process from a natural gas condensate of South Pars gas field and the removal of disulfide oils produced in South Pars refinery, using Aspen software package. Plus done. This simulation consisted of two parts: desulfurization and distillation. In addition to

purifying gas condensate from sulfur compounds in this process, disulfide oils, which are one of the problems of the South Pars refinery, were also eliminated. Subsequently, a distillation tower consisting of two naked-makers and a destination tower was simulated to obtain different sections of the treated gas condensate. The simulation results show that the five sections obtained from the distillation section, including butane, light naphtha, heavy naphtha, kerosene, and gas oil, are free of sulfur compounds. This simulation can build a desulfurization unit in different phases of the South Pars refinery or as a background for further studies.

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