Economic and Environmental Approach to Acid Gas Disposal at the Eastern Desert using Modified Claus Process.

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ABSTRACT

When sour natural gases are sweetened with any suitable gas-sweetening process, the produced acid gases Hydrogen Sulfide and Carbon Dioxide must be further processed to dispose of the sulfur in the hydrogen sulfide. Disposing of this sour gas in a cost-effective and environmentally responsible manner represents a significant challenge. This paper discusses how to safely dispose of the acid gases produced from the Amine sweetening process in an economical method. The study aims the utilization these gases to produce a valuable product such as Elemental Sulfur which is the raw material for different industries. Although many sulfur recovery technologies are available for different conditions and applications, the Claus process is an essential and common method for recovering elemental sulfur from gaseous hydrogen sulfide and is frequently needed as part of gas desulfurization systems.

Simulation using HYSYS software has been done for the proposed sulfur recovery unit to produce sulfur from hydrogen sulfide with the lowest cost. The economic evaluation of the results from the simulations showed that the Claus unit would be economically accepted with a reasonable ROI in addition to the expected positive environmental impact of the study.

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1. INTRODUCTION

Sulfur is a valuable raw material that is present in the natural gas industry mainly as hydrogen sulfide (H_2S) and, in other fossil fuels, as sulfur-containing elements that are converted to hydrogen sulfide during different operations. The increase in sulfur volumes in waste gases along with the increasing environmental regulations drives up demand for recovered sulfur processes. The H_2S, along with some of the carbon dioxide (CO_2) present, is removed from the sour natural gas through different sweetening processes. The resulting acid gas stream from the sweetening unit is flared, incinerated, or fed to a sulfur recovery unit. [7,9]

There are many sulfur recovery technologies available for different conditions and applications such as Claus Process, Direct Oxidation, Liquid Redox, and H_2S Scavengers. The optimum selection of the sulfur extraction method depends mainly on the H_2S fraction in the inlet acid gas as shown in figure (1).

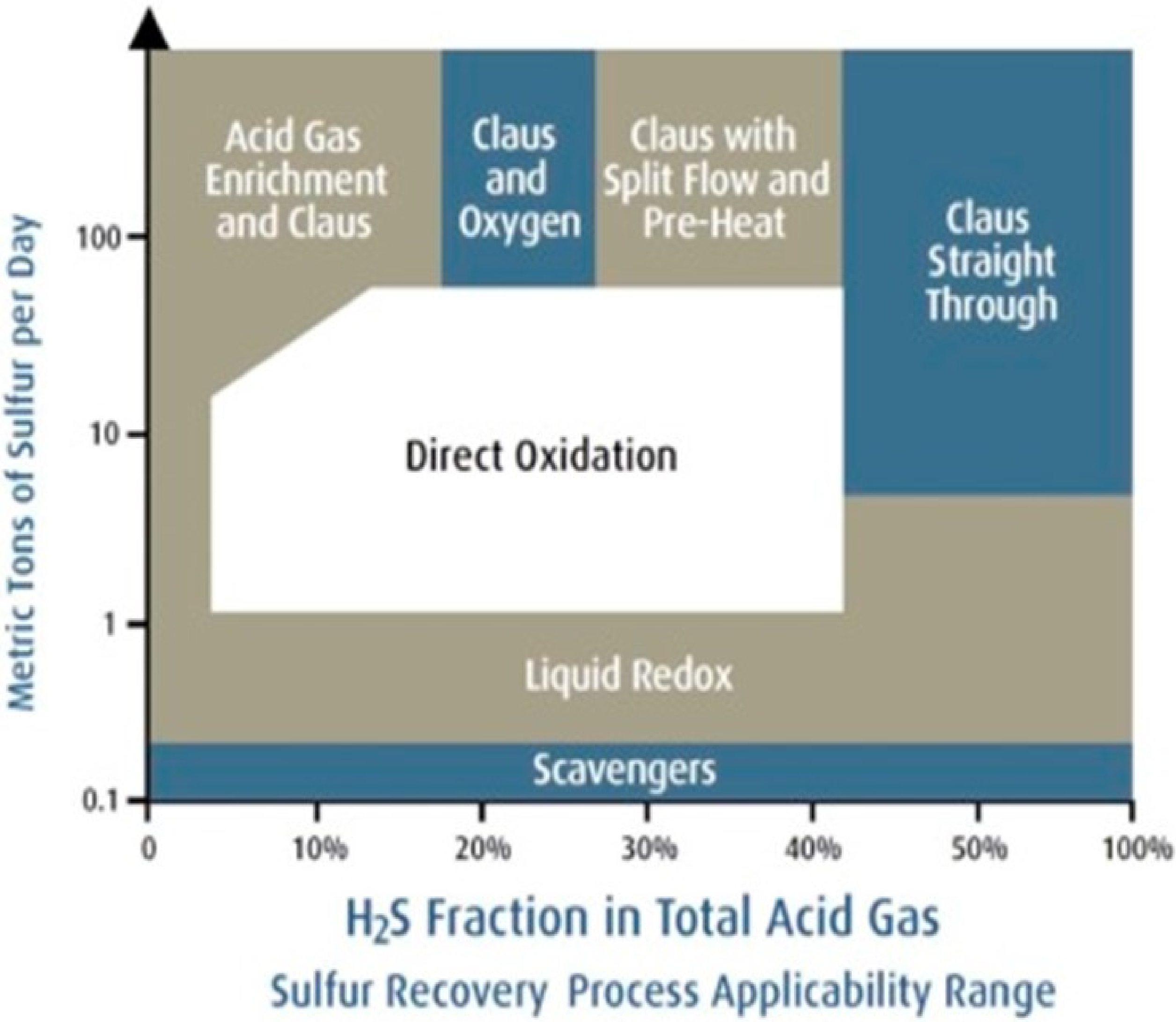

Figure (1): Sulfur Recovery process Applicability Range

In 1883, The Claus process was introduced by a German scientist called Carl Friedrich Claus. The early Claus process was very simple and consisted of only one step in which H_2S was reacted over a catalyst with oxygen in a single reactor to produce elemental sulfur beside the water.[5]

The efficiency of sulfur recovery of the early Claus process was low beside it was difficult to control the extremely exothermic reaction. In order to overcome the previous problems, a modification was developed later in which the overall process was separated into multi steps as shown in figure (2). [6]

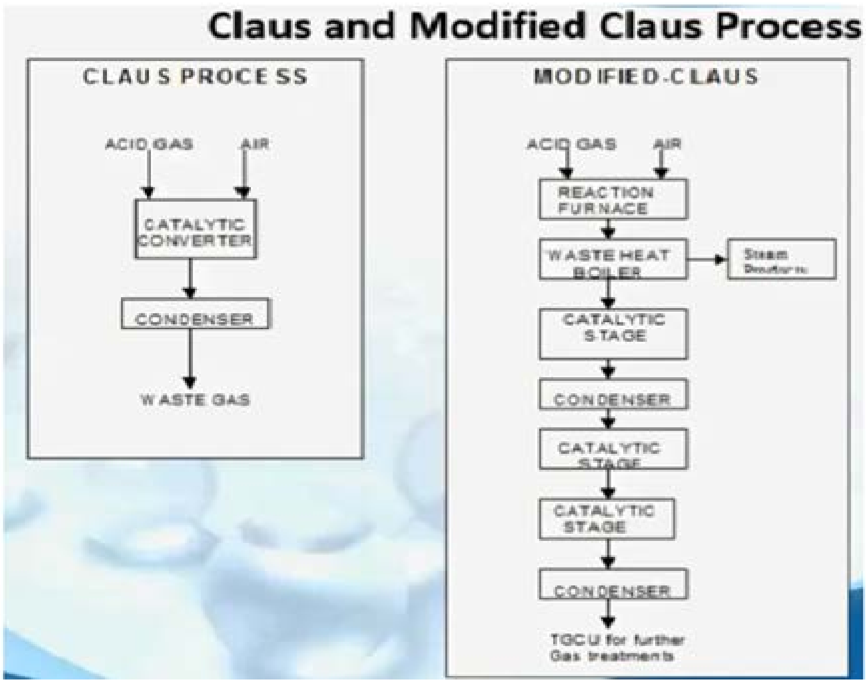

Figure (2): Claus and Modified Claus Process.

The modified Claus technology can be split into two primary operations, the Combustion Reaction section and the Catalytic reaction section. Chemical reactions in the process are staged and are as follows:

$H_2S+3/2O_2 \rightarrow SO_2+H_2O$ Combustion Reaction Section

$SO_2+2H_2S \rightarrow 3S+2H_2O$ Catalytic Stage

Figure (3) shows a simplified flow diagram of a Claus process cycle that contains three stages of catalytic reaction

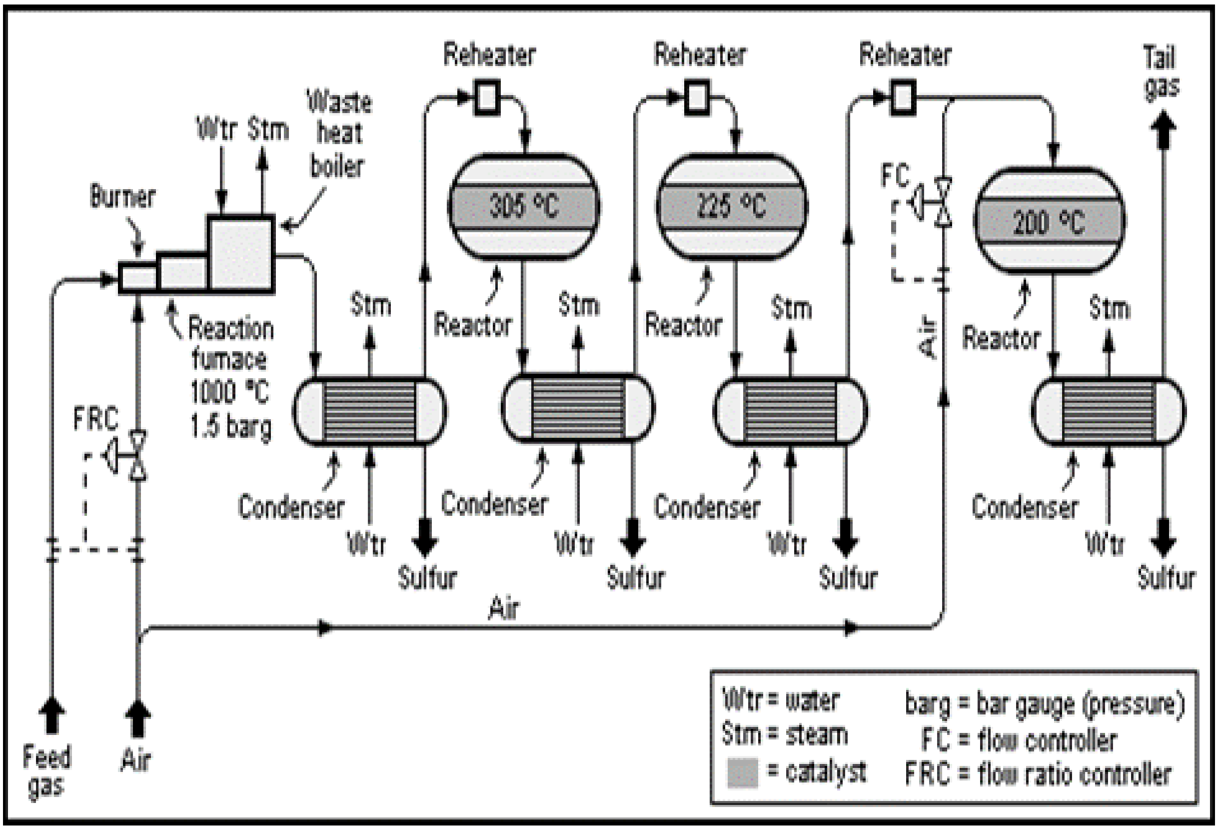

Figure 3. Flow Diagram of Claus Process

The first step in the Claus process is the combustion operation which is carried out to oxidize one-third of the H_2S to SO_2 at a pressure of 3-14 psig besides burning any mercaptans and hydrocarbons in the inlet stream. In most refinery Claus units, the combustion process is utilized also to oxidize ammonia and cyanides in the feed stream. In most cases, the thermal section produces 60 to 70% of the total amount of elemental sulfur produced in the whole process.[2,8]

The second step in the Claus cycle is the Catalytic Conversion stage; the primary function of this process is to promote the reaction of the remaining H_2S and SO_2 to extract elemental sulfur through a series of reactors. In most cases, the Claus process usually contains a series of two or three reactors. All Catalytic reactors must contain a catalyst, the common catalyst used in catalytic reactors is made of activated alumina with the chemical formula of (Al_2O_3). However, activated titania is also used as a catalyst to enhance sulfur recovery more than ordinary alumina but titania is an extremely costly material and can be 10-15 times the cost of activated alumina.[8]

Other operations in the Claus cycle include Sulfur Condenser Operation and Preheating Operation. Sulfur Condensers are utilized to condense sulfur vapors after each catalytic converter to increase the Claus reaction rate [10]. These condensers are typically designed for outlet temperatures of 330-360°F to produce condensed liquid sulfur with reasonably low viscosity and at a temperature above the sulfuric acid dew point. The final sulfur condenser outlet can be as low as 260 F.
Preheating Operation is needed to maintain the temperature of the process gas at the inlet of each catalytic converter higher than the expected outlet sulfur dew point, but As low as possible to maximize H_2S conversion. The temperature should also be high enough for complete hydrolysis of COS and CS_2 to H_2S and CO_2 as following [1]

$$COS + H_2O \rightarrow H_2S + CO_2$$

$$CS_2 + H_2O \rightarrow H_2S + CO_2$$

This paper outlines a proposal for the safe disposal of acid gases from Ras Gharib oil fields. The purpose of this study is to perform an economic study summarizing the profitability, revenues, and economics along with the expected environmental impact of treating and processing the acid gases produced from the amine sweetening unit in the Eastern Desert. A proposal of Two Stage Claus process is suggested to recover sulfur from the stream.
This research also discusses the main parameters affecting the recovery efficiency of the elemental sulfur through the process.

2. Methodology / Simulation study

This study discusses the utilization of the acid gases resulting from the Amine sweetening unit used to treat 15 MMSCFD of the sour gases produced from El-Hamd, Gharib, and Fanar in the Eastern Desert. The analysis of the acid gas stream which was made by a gas chromatograph is shown in table (1).

Table 1: Acid Gas Stream Composition

Methane	**0.0011**
Ethane	0.0007
Propane	0.0005
i-Butane	0.00
n-Butane	0.0001
i-Pentane	0.0306
n-Pentane	0.0361
Hexane	0.0354
heptane	0.0439
H_2S	0.6958
H2O	0.0759
$C0_2$	0.0799

The operating conditions of the Acid gas stream were measured using local gauges and an orifice plate flow meter; Table 2 shows the operating conditions of the feed.

Table 2: The operating conditions of the Acid gas stream

Pressure	15 psia
Temperature	41 C
Flow	2.247 MMSCFD
H2S Content	0.6958

The next step in the study is to simulate the proposed sulfur recovery unit by simulation software; HYSYS is a reliable and common software that can produce acceptable results with a high level of satisfaction and validity.
HYSYS V-9 with Sulsim Sulfur Recovery Model is used to simulate the Sulfur recovery unit to recover sulfur from the acid gas stream with the composition and the operating conditions shown in tables (1 and 2).

In the study, A proposal of Two Stage Claus process is suggested to recover sulfur from the stream. Due to the high percentage of H_2S in the stream, the Straight Through Claus process is utilized, the Process Flow Diagram of the proposal is shown in figure (4).

The simulation aims to optimize the conditions of the sulfur recovery unit to economically study the option of using the Claus unit to remove the sulfur compounds to comply with the environmental regulations at a reasonable cost.

Figure (4): Process Flow Diagram of the proposal

3. Results discussion

Sulfur recovery technologies are very wide. Common technologies such as the Claus Process, Direct Oxidation, Liquid Redox, and Scavengers are available for a variety of conditions and applications. The optimal process selection is primarily determined by the H_2S fraction in the inlet acid gas, as illustrated previously in figure (1).

The Acid Gas Stream from the regenerator in the amine sweetening unit which is the feed stream from the proposed Claus unit is rich in H_2S with a percentage of 0.6958 as shown in table (1). According to figure (3), the optimum desulfurization process is the Straight Through Claus process because the feed stream is rich in H_2S.

A proposal of Two Stage Claus process is suggested to recover sulfur from the stream. A simulation using Sulsim Sulfur Recovery in Aspen HYSYS is made for this proposal. Figure (5) shows the simulation case for the proposal.

Figure (5): Simulation of Proposed Sulfur Recovery Process

The proposed sulfur recovery cycle includes a reaction furnace, a waste heat exchanger, heat exchangers, condensers, and two catalytic converters. The following tables summarize the simulation results.

Table (3): Performance Summary of Conversion and Recovery percentages

	Reaction Furnace	Catalytic convertor 1	Catalytic convertor 2
Conversion (Unit) [%]	69.21	42.80	48.45
Conversion (Cumulative) [%]	69.21	82.39	90.92
Recovery (Unit) [%]	98.38	91.36	85.90
Recovery (Cumulative) [%]	68.09	81.15	89.54

Table (4): Performance Summary of Conversion and Recovery rates

	Reaction Furnace	Catalytic convertor 1	Catalytic convertor 2
Conversion (Unit) [LTD]	40.82	7.77	5.03
Conversion (Cumulative) [LTD]	40.82	48.59	53.62
Recovery (Unit) [LTD]	40.15	7.71	4.949
Recovery (Cumulative) [LTD]	40.15	47.86	52.81

The next table summarizes the operating conditions of the Reaction Furnace

Table (5): Operating Conditions of Reaction Furnace

Inlet Temp.	41 C
Outlet Temp.	1465 C
Operating Press.	15 psia

The conditions of the Preheaters in the cycle are shown in table (6)

Table (6): Operating Conditions of Preheaters

	Preheater 1	Preheater 2
Inlet Temp.	135 C	135 C
Outlet Temp.	270 C	210 C
Operating Press.	13 psia	12 psia

The next table summarizes the operating conditions of the Condensers

Table (7): Operating Conditions of Condensers

	Condenser 1	Condenser 2	Condenser 3
Inlet temp.	300 C	282 C	217 C
Outlet Temp.	135 C	135 C	135 C
Sulfur Produced	40 LTD	7.7 LTD	5 LTD

From the previous simulation, it's found that the Total Sulfur produced from that proposal is about 53 LTD.

The composition of the tail gas produced from the Claus unit is shown in table (8). It is obvious that the H_2S content decreased from 69.58 to 0.16 after the Claus process. The produced gas can be flared or injected into an underground reservoir without causing any environmental concerns.

Table (8): The composition of the Tail Gas Stream

Methane	**0.00**
Ethane	0.00
Propane	0.00
Butane	0.00
Pentane	0.00
N_2	0.6815
H_2	0.011
H_2S	0.0016
H_2O	0.1902
CO_2	0.0975
CO	0.0048
SO_2	0.0043
COS	0.001
Argon	0.0081

The main parameters affecting the conversion rate of the Claus cycle are Reactor temperature and oxygen Flowrate. The reactor temperate is inversely proportional to the conversion rate of the Sulfur. Figure (6) shows that the conversion rate increases at a lower temperature, however, the temperature should be held at Higher (25-30°F) than the expected sulfur dew point to prevent condensation of the vapor sulfur.

Fig (6): The Effect of Reactor Temperature

Most of the time, oxygen enrichment is used to increase the plant's throughput capacity because oxygen enrichment tends to maximize the consumption of H_2S gas into elemental sulfur in this process. However, oxygen enrichment should be used with care to avoid oxygen breakthroughs in the catalytic converters. Excess oxygen leads to further oxidizing of SO_2 to SO_3. This SO_3 then depletes the alumina catalyst in the reactors or reacts with water to produce sulphuric acid, which is corrosive to steel equipment. As illustrated in figure (8) Sulfur Conversion increases with airflow until it reaches the peak point and then decreases again with the increase in airflow.

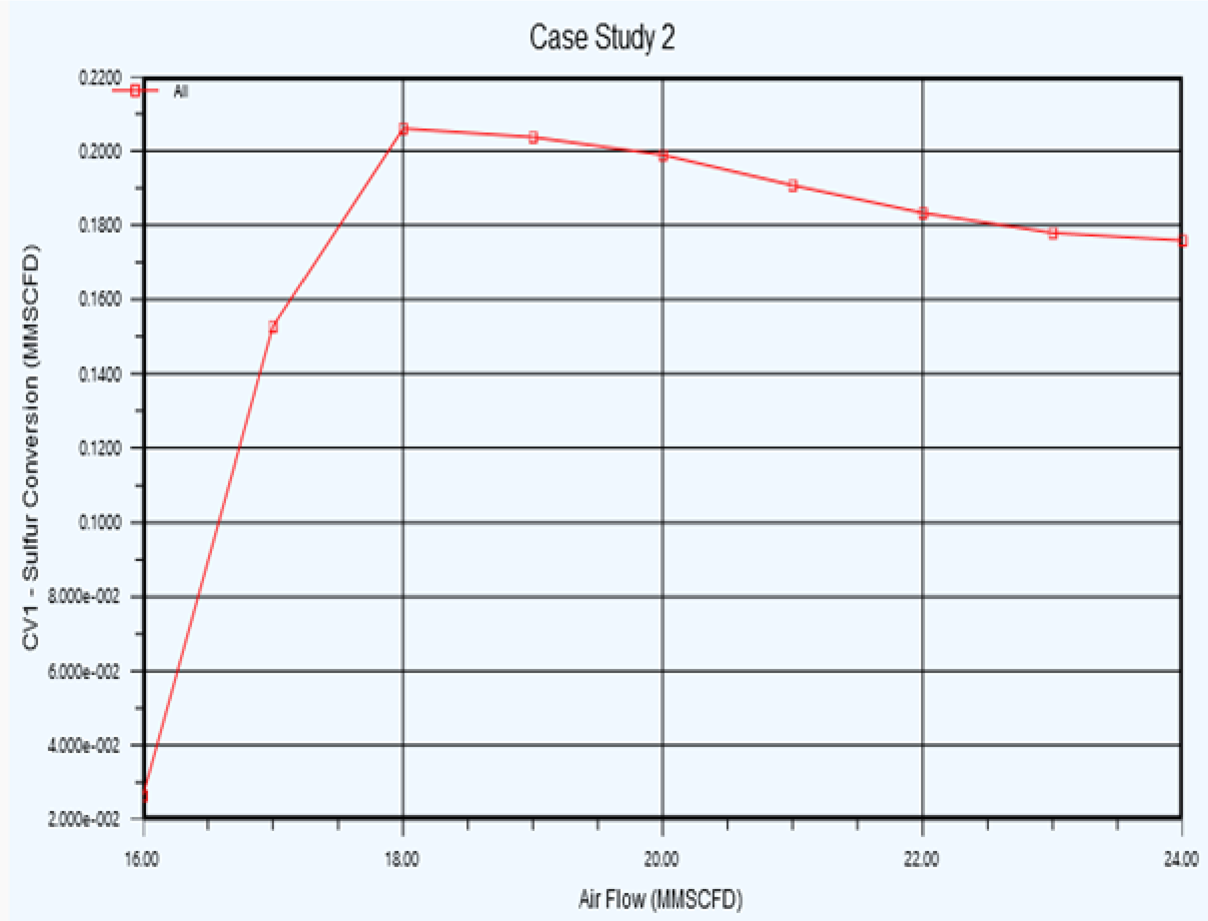

Fig (7): The Effect of Oxygen Flowrate

Compared to similar and equivalent projects, the average annual rental cost of a Claus unit is about 3,285,000 USD including operation and maintenance. Another important parameter that must be taken into consideration is the installation cost of the project, The cost of installation will be about 1,200,000 USD.

The raw material for the unit is acid gases from the amine sweetening unit, therefore, no expected cost for the raw material. Power is very vital for any project, next table illustrates the expected power requirement for the unit.

Table (9): The expected Power Requirement for Claus unit

Unit	Power
Condenser 1	1750 Kw
Condenser 2	1380 KW
Condenser 3	795 kW

On the other hand, sulfur's average price is about 285 USD/Ton and the total sulfur extracted from the process is about 53 LTD, therefore, the project is expected to make revenue in the second year while the ROI for the whole project is about 10% and the payback time is about 10 years which make the project is economically accepted.

Table (10) summarizes the economic details of the proposal.

Table (10): The Economic Summary of the Proposal

	First Year	Later Year
Power Cost	(2,292,200.00)	(2,292,200.00)
Rental Unit Cost	(3,102,500)	(3,102,500)
Rental Unit Installation Cost	(1,200,000)	0
Sulfur Price	5,503,265.60	5,503,265.60
Annual Profit	**(1,091,434.40) USD**	**108,565.60 USD**

4. Conclusion

Results showed that the Two-Stage Claus process can be used to safely dispose of the sulfur from the acid gas stream as the H_2S concentration decreased from 69.58 to 0.16 after the Claus process.

From an economic point of view, the Claus proposal is considered to be economically accepted according to the current Sulfur price and the total expected costs. along with the expected environmental impact of the proposal by the disposal of high sulfur content acid gases in a safe manner.

Nomenclature

MDEA	=	Methyl Diethanolamine
MMSCFD	=	Million Standard Cubic Feet per Day
MMBTU	=	Million British Thermal Unit
H_2S	=	Hydrogen Sulfide
COS	=	Carbonyl Sulfide
CS_2	=	Carbon Disulfide
PSIA	=	Pound per square inch absolute
KW	=	Kilowatt
CO_2	=	Carbon Dioxide
SO_2	=	Sulfur Dioxide
SO_3	=	**Sulfur Trioxide**

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