

CLAUS PROCESS

Manufacture of elemental Sulfur from Hydrogen Sulfide

Introduction: -

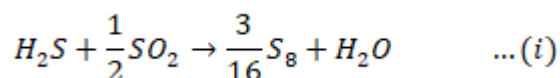
Claus process is the most common process used in the manufacturing of elemental Sulfur. The process is very useful to recover Sulfur in elemental in the petroleum refineries. The Claus process is the most significant gas desulfurizing process, recovering elemental sulfur from gaseous hydrogen sulfide. Hydrogen sulfide occurs in many gas wells. It is produced in bulk quantities in the desulfurization process of petroleum products where in the organic sulfur is trapped as hydrogen sulfide. It is sent to a Claus plant where the sulfur is recovered and a low grade steam is obtained. Hydrogen sulfide has been considered a liability which only occasionally turned out to be an asset depending on the international sulfur price. Now the claus process to obtain elemental sulfur has resulted in increase in the importance of hydrogen sulfide making it an asset¹.

The multi-step Claus process recovers sulfur from the gaseous hydrogen sulfide are also obtained from by-product gases containing hydrogen sulfide derived from refining crude oil and other industrial processes. The by-product gases mainly originate from physical and chemical gas treatment units (Selexol, Rectisol, Purisol and amine scrubbers) in refineries, natural gas processing plants and gasification or synthesis gas plants. These by-product gases may also contain hydrogen cyanide, hydrocarbons, sulfur dioxide or ammonia. The most direct process of obtaining hydrogen and sulfur from hydrogen sulfide is thermal decomposition, catalytically or non catalytically. However, the reaction is highly endothermic and the equilibrium conversion even at high temperatures is low (10%, 20% and 30% at 1143, 1283 and 1403K, respectively)¹.

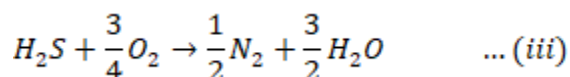
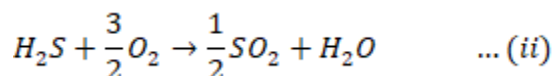
In this process H_2S is selectively oxidized to sulphur over $\text{TiO}_2/\text{SiO}_2$ catalysts². Claus process consist of two reactions; thermal oxidation and catalytic reaction that are discussed further. In order to provide a high selectivity to sulfur, reactions leading to SO need to be suppressed³.

Reactions: -

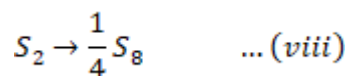
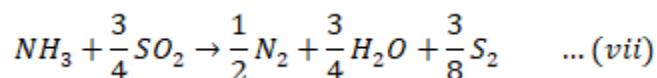
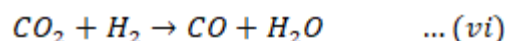
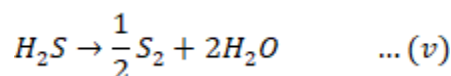
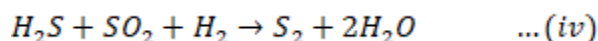
- Main Reaction:-



- Combustion reaction:-



- Side Reactions:-



Assumptions: -

1. All the reactions are considered as conversion reactions.
2. In RC-1501 B the reactions from (iv) to (viii) are considered as series reactions as there is no provision of Parallel reactions in DWSIM and conversion PFR are taken instead of a furnace because there is no provision of furnace in DWSIM.
3. Two different S₈ compounds were added into DWSIM database to match the stoichiometry. (Compound creator wizard was used to add two S₈ & S₂ compounds in DWSIM data base). Thermodynamic information of the created sulfur compounds were taken from literature.
4. Reaction (viii) is actually an equilibrium reaction and occurs after cooling in E 1504 but as there is no provision of such condition in DWSIM, it is assumed that this reaction occurs in RC-1501 B.
5. To maximize the Sulfur yield in downstream process (reactors) it is desired that only one third of the H₂S contained in the gases is oxidized to form a 2/1 ratio of H₂S to SO₂ in reaction (ii).

Brief Description: -*Raw material:*

Air (Oxygen), SWS off gas (H_2S , NH_3 , CO_2), AGR unit gas (H_2S , CO_2 , N_2).

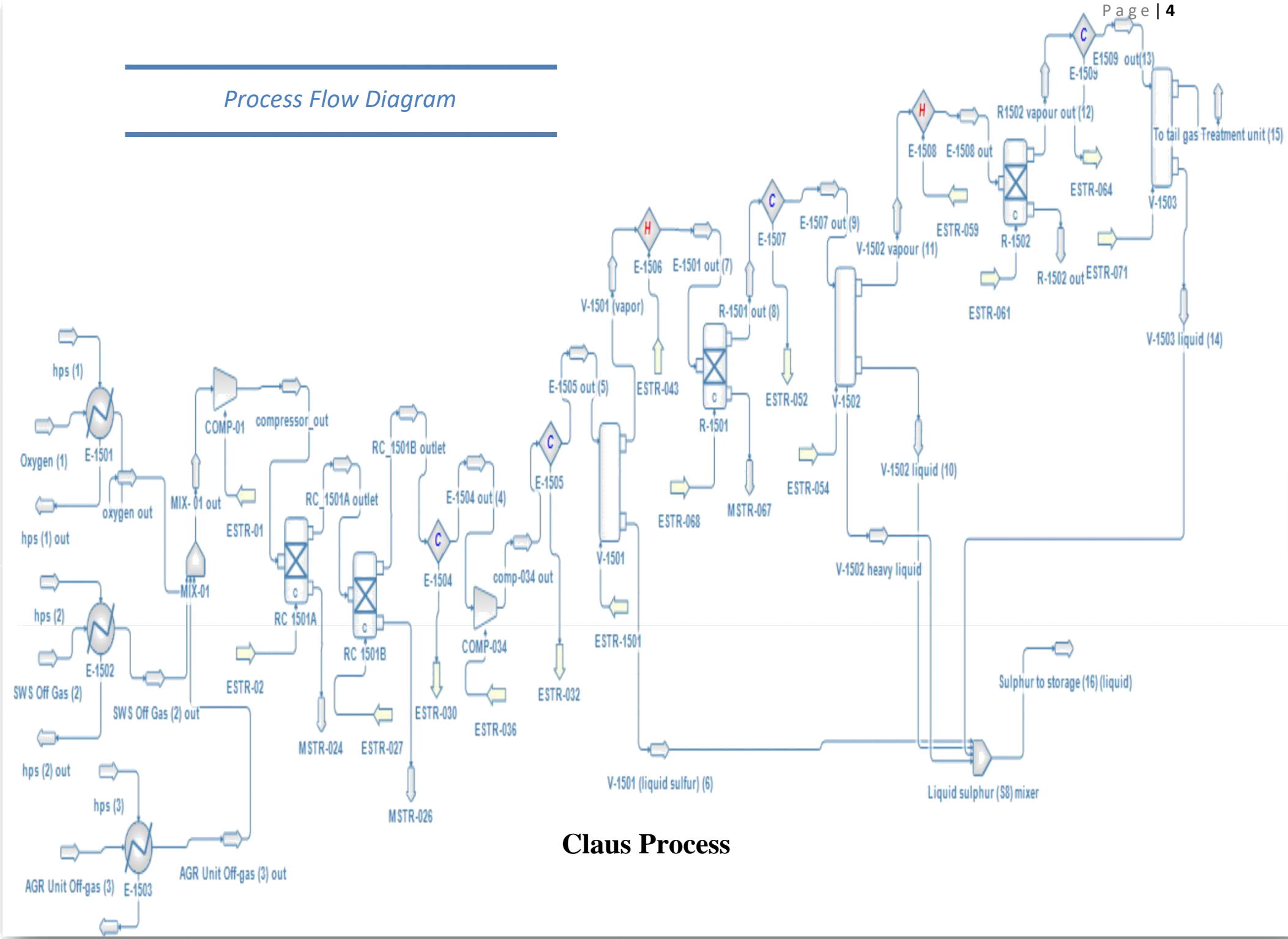
Product:

Sulfur in S_8 form and in liquid state.

All the streams Oxygen (1), SWS off gas (2), AGR unit off gas (3), are first heated in a shell and tube heat exchanger with process stream as high-pressure steam. These heated streams are then blended together and sent to the reactor RC-1501 A and followed by reactor RC-1501 B. In real process instead of using RC-1501 A and RC-1501 B reactors a single H-1501 reaction furnace is used but as there is no provision of furnace in DWSIM conversion reactors RC-1501 A and RC-1501 B are used⁴. In RC-1501A combustion reactions (ii) & (iii) occurs while reactions (iv) to (viii) occurs in RC-1501 B.

The outlet streams of the reactor RC-1501 B (RC_1501B outlet) is then sent to coolers E-1504 and E-1505 to drop the stream temperature to 195°C from 345°C . The stream E-1505 out (5) is then sent to V-1501 to separate liquid Sulfur from the mixture of gaseous products and unreacted reactants. The liquid stream obtained (viz V-1501 (liquid sulfur) (6)) is sent to storage. The stream V-1501 (vapor) after getting heated in E-1506 is then sent to an alternate series of reactors and R-1501 and R-1502 where reaction (i) takes place and separating vessel (v-1502 and V-1503) where liquid S_8 is separated from, reaction mixture. Then all the liquid sulfur streams are then mixed in mixer (Liquid sulfur (S_8) mixer) and sent to storage.

Process Flow Diagram



Claus Process

Flowsheet Description

The PFD of the Claus process is shown in Figure. In this report The Claus unit is designed such that it can process acid and sour-water gases generated in the operation of an integrated gasification combined cycle (IGCC) power plant⁵. It should be noted that elemental sulfur, in the operating temperature range of the Claus unit, can exist as S_2 and S_8 , among others. For the ease of simulation, only these two sulfur species will be considered. Acid gas, Stream 2, from an acid-gas removal unit and sour-water gas, Stream 3, from the sour-water stripper are preheated in E-1502 and E-1503, respectively, with high-pressure steam and sent to the reaction furnace, H-1501, for combustion. Preheated, enriched oxygen from an air separation unit (ASU) is used as the oxidizing agent in H-1501. Incomplete combustion of hydrogen sulfide to sulfur dioxide is carried out in the furnace. Since there is no provision of a furnace in DWSIM, we considered two conversion PFRs in series suggested in the literature⁴. Additionally, partial combustion of ammonia can also take place. It is desired that only one-third of the hydrogen sulfide contained in the gases be combusted to form a 2:1 ratio of hydrogen sulfide to sulfur dioxide. This 2:1 ratio of hydrogen sulfide to sulfur dioxide is required to maximize sulfur yield in the downstream reactors. Primary combustion reactions within H-1501 are given above. These highly exothermic reactions increase the temperature significantly (to about 1450°C) in H-1501. Several side reactions take place as shown above.

The hot process gas is then cooled in E-1504 to generate high-pressure steam and to quench the reactions taking place. At high operating temperatures, such as those in H-1501, sulfur exists primarily as S_2 . Due to the equilibrium shift, the primary sulfur species present at the outlet of E-1504 is S_8 . Further cooling is carried out in E-1505 by generating low-pressure steam. This cooled process gas is then sent to V-1501 to separate the liquid sulfur. The process gas is then sent to the first stage of a two-stage process. The process gas is heated in E-1506 with high-pressure steam before being sent to the reactor R-1501, where hydrogen sulfide and sulfur dioxide react in a 2/1 ratio to form elemental sulfur via Claus Reaction. The reactor effluent is then cooled by generating low-pressure steam in E-1507. The liquid sulfur is then removed in V-1502. The process gas is again preheated in E-1508 with high-pressure steam. The heated gas is sent to the second-stage catalytic reactor R-1502. The reactor effluent is cooled in E-1509 using cooling water to condense the formed sulfur. The process gas is then sent to a tail-gas treatment unit (not modelled here)⁴.

Below is the table for output values which we get after simulating the above process in DWSIM according to the above mentioned process flow diagram.

Output Table

Stream Number	1	2	3	4	5	6	7	8
Name of the stream	Oxygen	SWS off gas	AGR unit off gas	E-1504 out	E-1505 out	V-1501 (liquid Sulfur)	E-1501 out	R-1501 out
Temperature(°C)	32	120	50	345	195	195	195	314
Pressure(bar)	10	2.4	2.1	1.7	1.3	16	16	1.3
Vapor Fraction	1	1	1	1	1	0	1	1
Mass Flow(tonne/h)	3.01	2.2	14.4	19.6	196	3.857	15.743	15.743
Mole Flow(kmol/h)	94.7	85.9	388.1	528.13	408.07	44.46	610.95	610.7
Component	flow rates(kmol/h)							
Hydrogen Sulfide	0	23.9	158.62842	0.78	0.609	0	0.6	0.012
Sulfur dioxide	0	0	0	30.5	23.53	0.000045	23.53	23.23
Water	0	0	5.3421645	528.13	408.07	31.42	376.64	377.29
Carbon dioxide	0	16.9	173.93573	117.68	90.93	0.00017	90.93	90.93
Carbon monoxide	0	2.1	0	75.42	58.27	0.00011	58.27	58.27
Oxygen	90	0	0	0	0	0	0	0
Hydrogen	0	10.2	0	0	0	0	0	0
Nitrogen	4.7	1.3	31.299978	37.3	28.82	0.0005	28.82	28.82
Ammonia	0	31.6	7.8521445	39.5	30.52	0.225	30.29	30.29
S ₂	0	0	0	0	0	0	0	0
S ₈	0	0	0	18.9	14.65	12.81	1.83	1.94

Stream Number	9	10	11	12	13	14	15	16
Name of stream	E-1507 out	V-1502 liquid	V-1502 Vapor	V-1502 vapor out	E-1509 out	V -1503 liquid	To tail gas treatment unit	sulfur to storage
Temperature(°C)	175	108.25	175	234	160	160	160	170
Pressure(bar)	1.2	1.2	1.2	1	0.9	10	10	7.1
Vapor Fraction	1	0.33	0.99	0.99	0.99	0	0.99	0.017
Mass Flow(tonne/h)	15.743	0.00000012	15.743	15.743	15.743	1.29	14.45	5.149
Mole Flow(kmol/h)	610.73	0.000000926	610.76	610.76	610.73	47.66	563.09	92.13
Component	flowrates(kmol/h)							
Hydrogen Sulfide	0.012	2.23E-08	0.012	0.00024	0.00024	4.48E-10	0.0002	9.60E-10
Sulfur dioxide	23.2326	2.60E-08	23.23	23.22	23.22	4.27E-05	23.22	6.95E-08
Water	377.24	2.89E-07	377.24	377.25	377.25	4.55E+01	331.74	75.43
Carbon dioxide	90.93	2.72E-08	90.93	90.93	90.93	1.60E-04	90.92	2.70E-07
Carbon monoxide	58.27	2.65E-08	58.27	58.27	58.27	1.00E-04	58.27	1.73E-07
Oxygen	0	0	0	0	0	0	0	0
Hydrogen	0	0	0	0	0	0	0	0
Nitrogen	28.82	2.60E-08	28.82	28.82	28.82	5.29E-05	28.82	8.56E-08
Ammonia	30.29	8.02E-08	30.29	30.29	30.29	3.35E-01	29.96	0.45
S ₂	0	0	0	0	0	0	0	0
S ₈	1.94	4.31E-07	1.94	1.94	1.94	1.81E+00	0.12	14.63

(A) References:-

1. Engineering, P. Production of hydrogen and sulfur from hydrogen sulfide. **41**, 159–198 (1995).
2. Woo, S., Yeol, J. & Won, D. Selective oxidation of H₂S to elemental sulfur. **16**, 235–243 (1998).
3. Visser, L. M., Dillen, A. J. Van & Geus, J. W. SULFUR USING IRON OXIDE CATALYSTS ON VARIOUS SUPPORTS. **17**, 217–224 (1993).
4. Books, F. M. & Us, J. *Ebooks Chemical Engineering*.
5. Jones, D., Bhattacharyya, D., Turton, R. & Zitney, S. E. Rigorous Kinetic Modeling and Optimization Study of a Modified Claus Unit for an Integrated Gasification Combined Cycle (IGCC) Power Plant with CO₂ Capture. 2362–2375 (2012).

(B) References: -

1. Monnery, W. D., K. A. Hawboldt, A. Pollock, and W. Y. Svrcek, “New Experimental Data and Kinetic Rate Expression for the Claus Reaction,” Chemical Engineering Science 55 (2000): 5141–5148.
2. Hawboldt, K. A., “Kinetic Modeling of Key Reactions in the Modified Claus Plant Front End
3. Furnace,” Ph.D. thesis, Department of Chemical and Petroleum Engineering, University of Calgary, Canada, 1998.
4. Monnery, W. D., K. A. Hawboldt, A. E. Pollock, and W. Y. Svrcek, “Ammonia Pyrolysis and Oxidation in the Claus Furnace,” Ind. Eng. Chem. Res. 40 (2001): 144–151.
5. Perry, R. H., and D. W. Green, eds., Perry’s Chemical Engineers’ Handbook, 7th ed. (New York: McGraw-Hill, 1997).