While most analysts believe that there is enough crude oil (Figure 1) available to meet the energy requirements, the quality of crude to be supplied to the refinery will decline.

3.2 Trend of declining quality of crude

While shown to discover new sources of low sulfur crude (less than 1 wt% sulfur), these will compensate for the decrease of crudes with very low sulfur content, so the medium (containing 1-1.5 wt% sulfur) and high sulfur (greater than 1.5% sulfur) crude oils from Canada, Venezuela and the Middle East will meet the market demands. This trend is shown in Figure 2 [8].

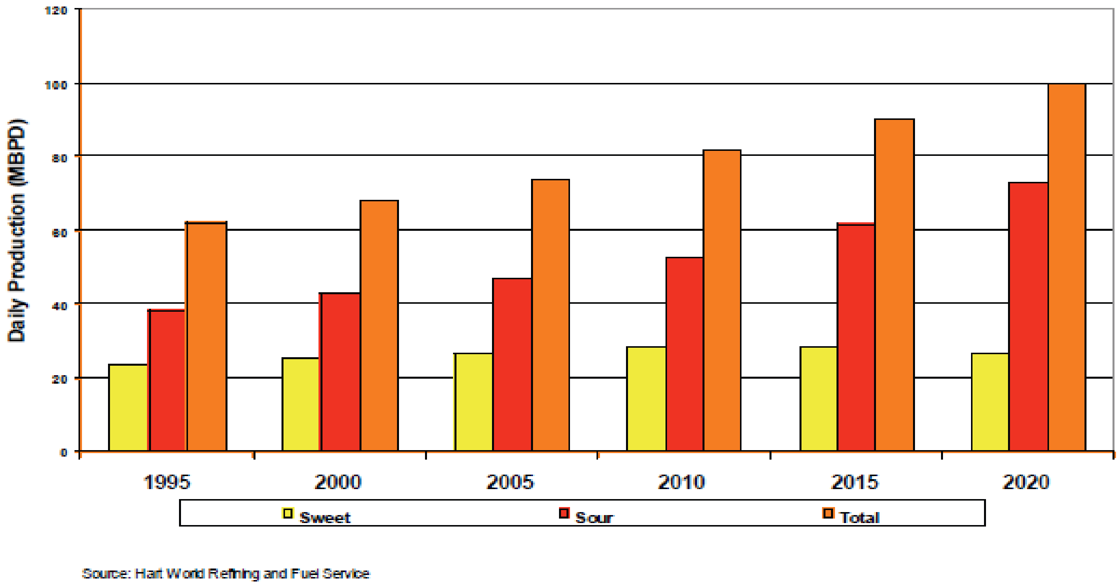

Figure 1: Global crude oil production [8]

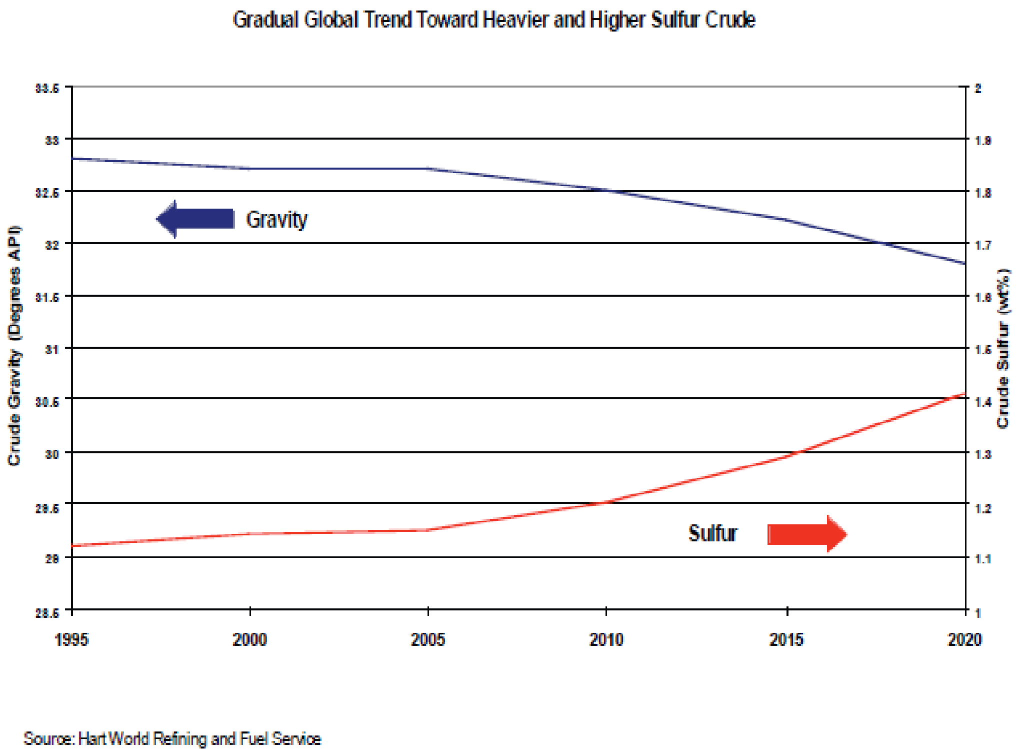

Figure 2: Trend of declining quality of crude [8].

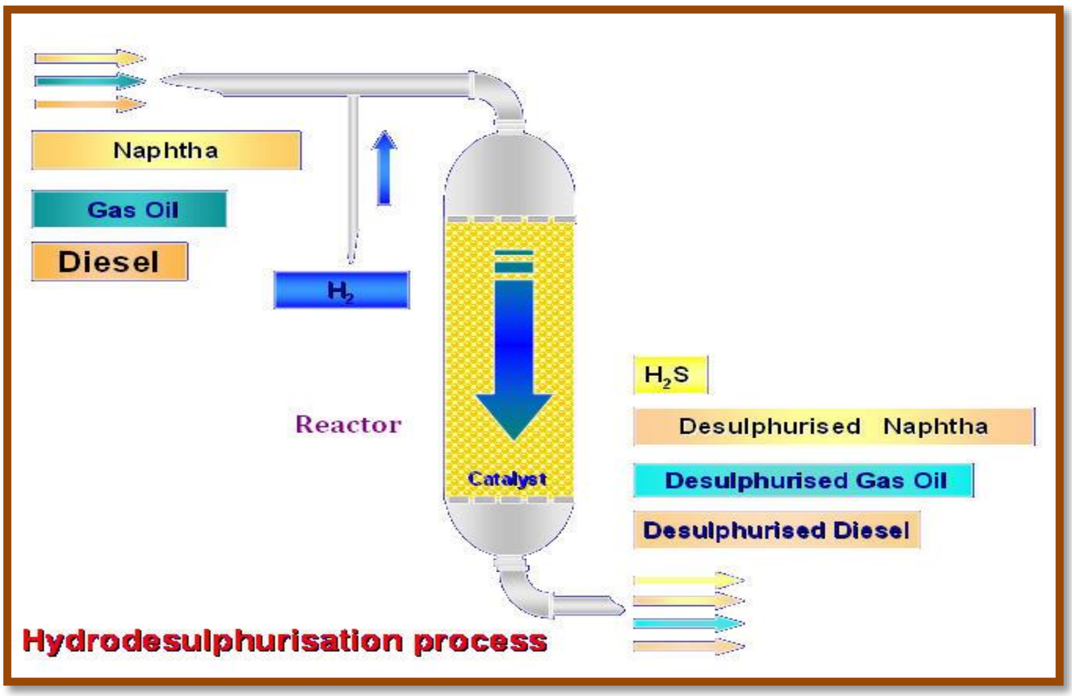

Figure 3: Simple schematic of the hydrodesulfurization process [10].

Figure 2 clearly shows the trend of decreasing quality. The quality of crude oil will progressively become heavier and with higher sulfur content.

3.3 Origin of acid gas-hydrogen sulfide

The hydrogenation processes (hydro-treating) of petroleum fractions play an important role in a refinery as it is the main method for reducing the sulfur content in fuels and for production of environmentally friendly fuels. By hydro-treating meant the addition of hydrogen in the fuel under controlled conditions of pressure (usually high) and temperature. Among the refinery hydro-treating processes important role has the hydrodesulphurization of fuels, especially this one of diesel. In the hydrodesulphurization process, the sulfur contained in the fuel, is converted to hydrogen sulfide eventually (Figure 3).

4. Method CLAUS-TAIL GAS Treatment

The produced during the desulfurization processes hydrogen sulfide is recovered by solvent amine (MDEA, MEA, etc.), in which it had selectively absorbed and routed for processing.In the refineries, the usual practice for the treatment of hydrogen sulfide is the Claus process, figure 4, where only the sulfur is recovered, while the hydrogen is lost as an oxidizable compound to water.

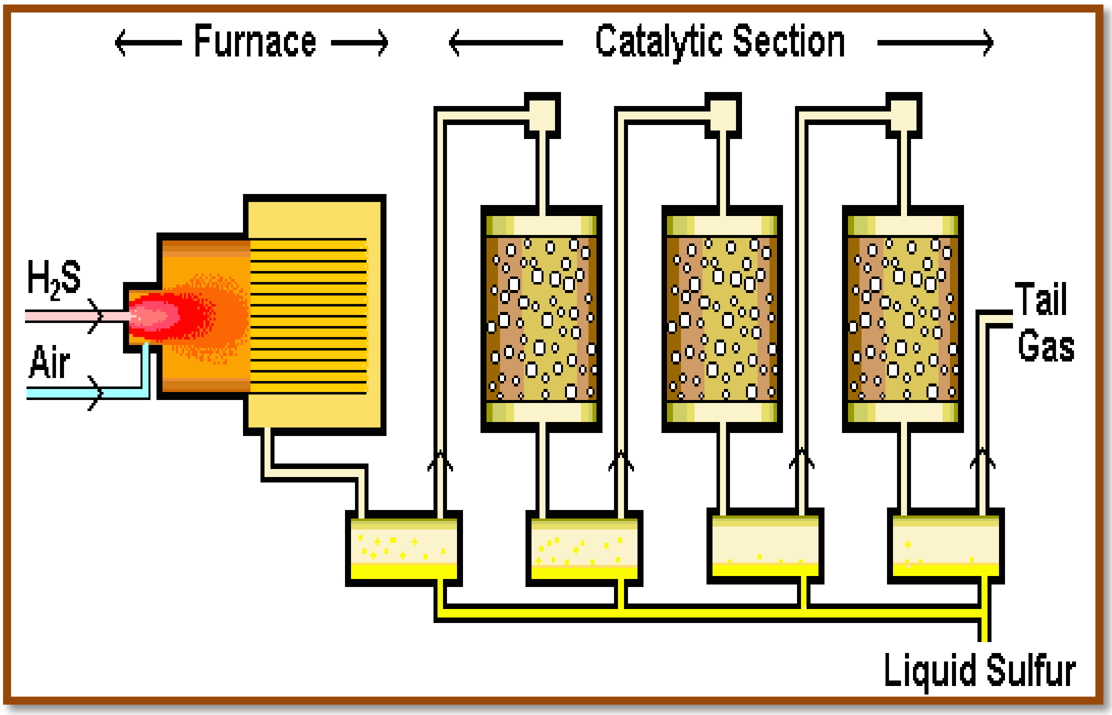

Figure 4: Typical arrangement of a Claus unit [6].

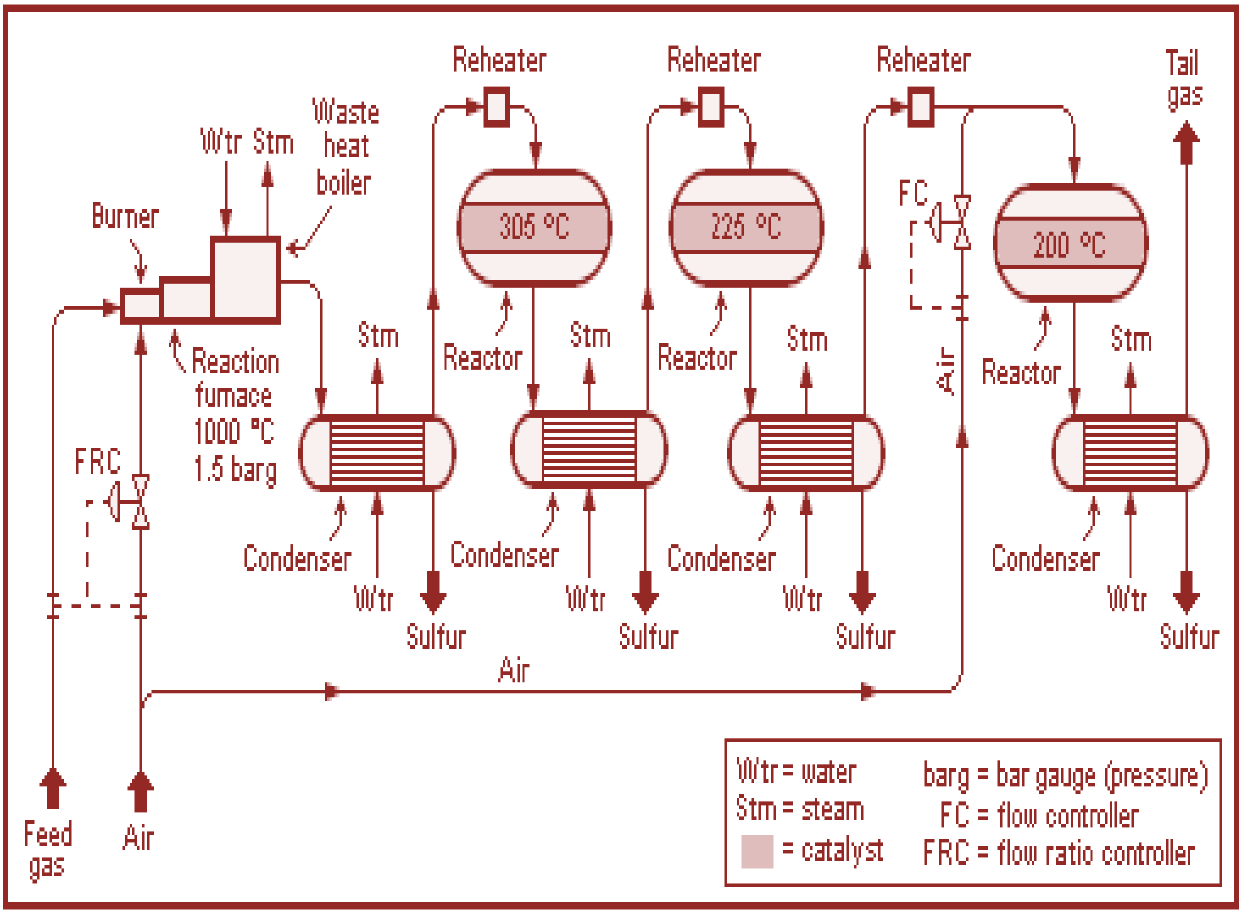

Figure 5: Typical Claus sulphur recovery unit.

In refineries, the Claus process is used to treat acid gas streams originated from hydrogen sulfide absorption with amines or sour water strippers ; it is based on the basic idea of oxidation of 1/3 of the hydrogen sulfide content in the acid gas to sulfur dioxide, which will react with the remaining 2/3 of the hydrogen sulfide to produce elemental sulfur and according to the following reactions:

$$H_2S + 3/2\ O_2 \longrightarrow SO_2 + H_2O + \text{heat} \quad (\text{oxidation}) \quad (1)$$

$$2H_2S + SO_2 \longrightarrow 3S + 2\ H_2O + \text{heat} \quad (\text{disproportionation}) \quad (2)$$

$$3\ H_2S + 3/2\ O_2 \longrightarrow 3S + 3\ H_2O \ (3) \quad (\text{total reaction}) \quad (3)$$

The reaction (1) is strongly exothermic and is accompanied by the equally strong exothermic second step (2) which is mainly catalyzed by alumina (Al_2O_3) [7 ,17].

A typical process flow diagram of the CLAUS method is given in Figure 5.

According to the principle of Le Chatelier, high yields achieved at low temperatures for exothermic reactions, while from a kinetic point of view, at low temperature, small reaction rates are obtained. For the simultaneous treatment of thermodynamic and kinetic limitations, the catalytic Claus reactors operate in the thermodynamic range of 200 to 350 °C, with conventional yields of up to 98% and space velocities of 800hr^{-1}.

The Claus reaction is auto-thermal and leads into clean energy production. The produced heat is of low quality due to the low operating temperatures of the unit. It is recovered by 80% and usually serves for the production of medium-pressure steam. The only commercial product of Claus units is the sulfur, while the hydrogen is lost in the form of water. To increase the recovery rate of sulfur, the hot gases from the CLAUS units are introduced into the reduction reactor with catalyst oxides of cobalt and molybdenum that are the tail gas treatment units(TGT).

The TGT units increase the overall sulfur recovery yield up to 99.9% , reducing the sulfur emissions from the refinery. For example if a refinery has a SRU, with capacity of 100t/d, with a two-stage Claus reactor emits about 5t/d. With the tail gas unit the emissions fall to 0.5t/d. The exhaust gases (tail gas) produced by the TGT units are burned in an incinerator in order to convert all sulfur compounds present in sulfur dioxide. The flue gas is released to the atmosphere via the stack [5]. Over 20 processes for Tail Gas Treatment Units have been developed to increase the recovery rate of sulfur from the produced refinery gas or from natural gas. The following table 2 shows the expected sulfur returns, the expected recoveries of extra sulfur, and the sulfur dioxide concentrations on a dry basis after the incinerator, in relation to the technologies applied. Based on the study below, in a period of 5 years, from 2009-2014, the world production of solid sulfur was determined to grow at an annual rate of 8%, reaching 67.1 Mt of sulfur (S) in 2014 (Figure 6). Significant increase in production was expected in East Asia, West Asia, Central Europe and Central Asia, North America. These five areas would contribute 85% to the net increase in production during the period 2009-

2014. Global consumption of elemental sulfur was projected to grow at an annual rate of 6 %, reaching 62.1 Mt of sulfur (S) in 2014. China was increasing the demand by 3.8 million tons/year and is the country that will significantly affect the consumption of elemental sulfur by the replacement of iron-pyrite. This increase in consumption was attributed to the increased demands in sulfuric acid used in the industry of acidic phosphate fertilizers and constant increasing use of sulfuric acid in metallurgy. If there was a slow recovery in demand and delays in the awarding of related projects of planned oil and gas, this could lead to potential annual surpluses by 2013, ranging from 3-4 Mt of sulfur (S)/year, equivalent to 5-8% of the total supply of sulfur [13].

Table 2. Expected overall sulphur recovery yield , the resulting additional recovered sulphur, and the SO_2 emissions(dry basis) after incineration [5].

Process	Expected sulphur recovery yield,%	Expected additional sulfur recovered, t/d	Expected SO_2 emissions (dry basis), mg/Nm^3
Claus	96.01	-	13652
SuperClaus	98.66	2.77	4631
Sulfreen	99.42	3.56	2010
Beavon	99 -99.9	-	-
CBA	99-99.5	3.65	1726
Clauspol	99.5-99.9		
Clauspol II	99.60	3.75	1382
SO_2 abatement	99.9		
Hydrosulfreen (1)	99.67	3.82	1066
DoxoSulfreen (2)	99.88	4.04	414
RAR	99.94	4.10	242
LO-CAT(3)	99.99	4.16	18
SCOT	99.5-99.99		

(1) Sulfreen reactors and hydrolysis section . (2) Sulfreen reactors, hydrolysis section and DoxoSulfreen reactors. (3) As LO-CAT II tail gas cannot be incinerated, sulfur is in the form of H_2S species.

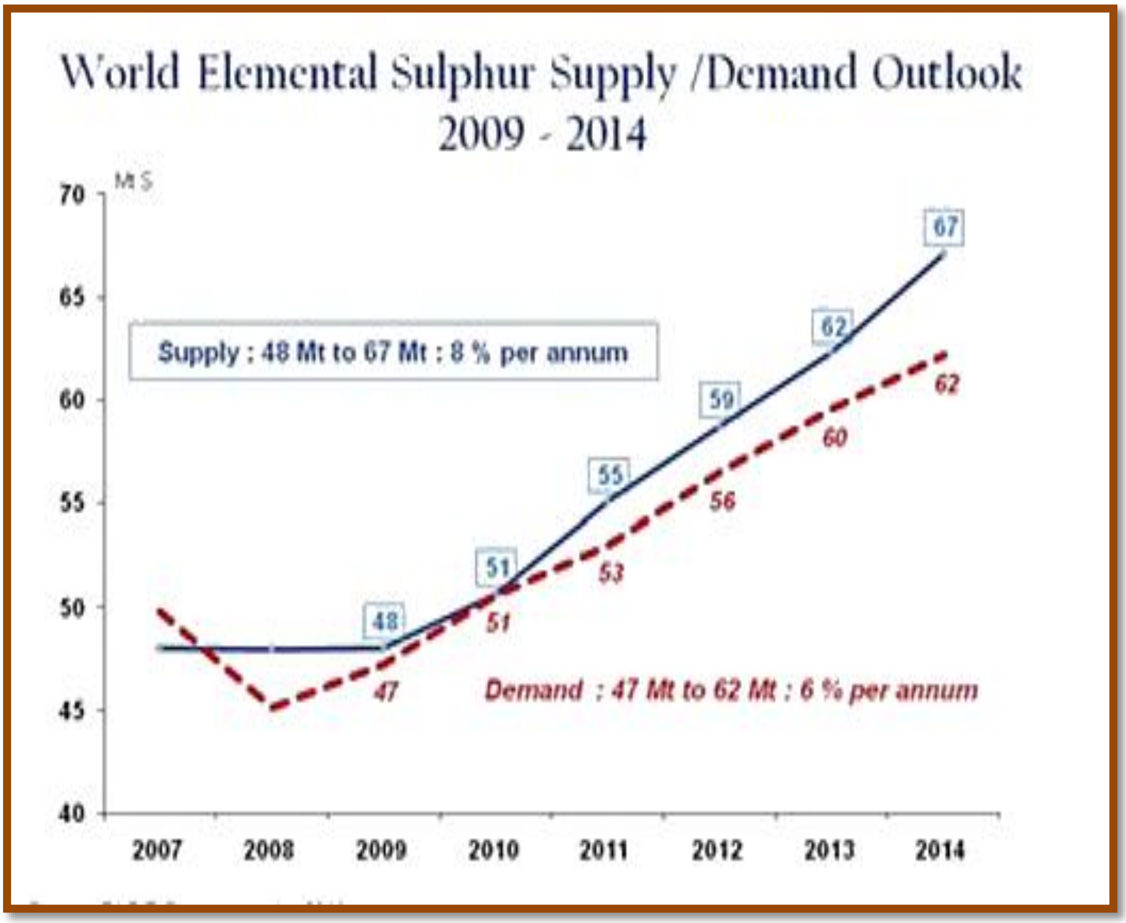

Figure 6. World Sulphur Supply / Demand Balance [13].

5. Conclusion

The global sulfur production is related to the production of elemental sulfur as a byproduct of petroleum refining processes (from sulfur recovery processes) and needs of sulfuric acid. The main process is the Claus sulfur recovery technique from the hydrogen sulfide component of crudes. China is portrayed as the main importer of elemental sulfur as a raw material in the production of sulfuric acid, which replaces the iron-pyrite in the domestic market; It is the country that will play a significant role in the petroleum refining and in the market of elemental sulfur. The production of elemental sulfur depends primarily on the Claus units, where elemental sulfur is recovered from the treatment of acid gas rich in hydrogen sulfide. Increasingly stringent environmental regulations on emissions of sulfur dioxide, require increasingly higher conversions, by focusing its studies on techniques to improve more and more in the yields of the Claus units.

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