Recovery of Elemental Sulfur and Treatment of the Tail Gases with the Claus Method: Application Study of Best Available Techniques for Pollution Prevention

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Abstract: In this article, we briefly present the current environmental legislation for the emissions of sulfur dioxide (SO_2) which is a strong gaseous polluter. Moreover, we present the new trends of the European legislation for the minimization of the environmental consequences during the course of the relative industrial processes. The description of the Claus catalytic process and its tail gases treatment units are presented, too. The article further consists from the description of the best available techniques and industrial practices for the reduction of the environmental consequences during the process of sulfur recovery with the Claus and other improved methods. The specific target is the minimization of the emissions of air pollutants in the atmosphere. Moreover, we present the trend and the applications of the global markets for the production and demand of elemental sulfur. We also refer to the pivotal role of the industries which produce fertilizers and sulfuric acid, as well as to the relative refineries which are the main suppliers and receivers of the produced elemental sulfur.

Keywords: Elemental Sulfur, Treatment of Tail Gases, Claus Method, Pollution Prevention.

1. Introduction

The release of pollutants into the atmosphere is due to both natural processes (volcanoes, biological activities, fires) and anthropogenic activities (industry, energy production, heating, etc.). The emissions from natural processes are very large; but the percentage of pollutants should not be considered negligible from anthropogenic activities since they are mainly concentrated in urban and industrial areas and many times their concentration exceeds the established limits. Acidification (pH: 4-4.6) is one of the essential phenomena due to atmospheric pollution, and in particular the presence of high concentrations of sulfur dioxide and nitrogen oxides; compounds which react with oxygen and water vapor in the atmosphere to form sulfuric acid and nitric acid, respectively, which in dry or wet deposition return to ground. The sun acts as a catalyst, increasing the rate of these reactions. Moreover, due to the fact that the fog consists of tiny droplets, it offers greater surface adsorption of SO_2 and NOx, than other forms of acid precipitation. It is known that acid rain has affected the cultural heritage of Greece, causing irreparable damage to important monuments such as karyatides. The phenomenon has assumed international dimensions because atmospheric pollution and acid rain do not recognize borders, and depend on the prevailing meteorological conditions facilitate the passage of pollutants from one country to another; e.g ., Norway receives five times more acid rain than it produces. The vast majority (over 90%) of sulfur compounds emitted from anthropogenic sources is found as sulfur dioxide. The coal holds a 60% contribution and the oil a 30% contribution in emissions of SO_2. The remaining 10% are attributed to burning pyrites, sulfur mineral etc. It has been estimated that more than 90% of SO_2 emitted from sources in the northern hemisphere [21,22,23].

The claim however, according to which the destruction of the environment is inevitable price of industrial development is untenable. Human ingenuity has the ability to overcome the negative effects that often accompany progress. The scientific research and the application of best available techniques have begun to offer their services to address the problems associated with the environment and most importantly began to form new ideas and rules that mark the path towards further progress and development. The economic and industrial development and environmental protection can serve the needs of humanity as a whole. The global economy coexists with global ecology. This can be seen by the new legislation introduced in several states and relating to the protection of the environment.

2. Study Details

2.1. Legislative Framework

The initial trend of environmental policy by adopting the polluter pays principle began to be replaced by the principle of environmental pollution prevention. Addressing environmental protection through European Directives is a collective responsibility of Member States of the European Union. The license to operate a manufacturing facility exists when the industry complies with environmental laws and regulations set by the state. In addition any investment in the environment or the proper design is combined with continuous and complete monitoring and intervention; it has designed to protect the environment throughout the course of the transport materials, storage, manufacturing, handling and disposal of products with parallel collection - treatment and disposal in the environment of sub-, byproducts and wastes [9].

Environmental Index

Times change and require the addition of new indicators, such as environmental and social indicators in order to measure correctly the progress of a society, the progress of a country. In this subject intensively working the European Commission, which believes that complementing GDP with additional accurate measurement criteria that reflect the concerns of the general public, will enable the convergence of EU policy to citizens' concerns. In this context the European Commission in a report, inter alia proposes to develop a comprehensive environmental action. The GDP and the percentages of unemployment and inflation are examples of such summary indicators. But they are not intended to reflect the situation on parameters such as the environment or the social inequalities.

Overall environmental index

As the Commission stated in its report, today there is not a comprehensive environmental indicator that can be used alongside GDP in policy discussions. Such a single measurement for the environment would promote a more balanced public debate on social goals and social progress. Among the possible relevant indicators are included the ecological footprint and the carbon footprint, but their scope is limited (the carbon footprint limited to the emissions of greenhouse gases). The ecological footprint does not consider certain effects, such as impacts on water. Nevertheless, the Commission tries it, among other indicators, for monitoring the development of the Thematic Strategy on the sustainable use of natural resources and Action Plan on Biological Diversity. As they have matured enough relevant indicators with complex data and methodologies, the Commission intends to present a trial version of an index on environmental pressure. This indicator will reflect pollution and other environmental damage within the territory of the EU, in order to assess the effects of environmental protection efforts. Any decline in the index would mean that progress exists on environmental protection.

The index will take into account the major axes of environmental policy:

- Climate change and energy use
- Nature and biodiversity
- Air pollution and health effects
- Water use and water pollution
- waste generation and resource use

Initially, the index will be published on an annual basis for the EU and the Member States, while the longer-term goal would be - if successful - to be published in parallel to GDP. It will be also published additional information on specific issues and related environmental targets at EU and Member State level in order to allow proper interpretation of the indicator.

Thanks to this indicator, along with GDP and social indicators, it is expected that people will be able to judge whether EU policies and national governments - and the efforts of individuals and companies - achieve the desired level of environmental protection and whether made progress in a balanced way to achieve social, economic and environmental objectives.

Beyond this overall indicator of environmental damage and pressures, it is also possible to develop overall environmental quality index, which indicates, for example, the number of EU citizens living in a healthy environment.

The Commission will endeavor to make the most topical environmental and social data in order to better inform decision-makers in the EU.

Satellites, automatic measurement stations and the Internet allow increasingly observing the environment in real time thanks to Directive INSPIRE (Directive 2007/2/EC) and through the GMES system ("Global Monitoring for Environment and Security") [9].

2.2 Directive 2004/35/EC of the European Parliament and of the Council of 21 April 2004 on Environmental Liability with Regard to the Prevention and Remedying of Environmental Damage

Directive 2000/35/EC included with Presidential Decree 148/2009 "Environmental responsibility for the prevention and remedying of environmental damage-harmonization with Directive 2000/35/EC of the

European Parliament and of the Council of 21 April as applicable" (Gazette 190/A/2009). The restoration of the environment to date in cases involving pollution causing the damage caused to persons and basic goods. Important components of the natural environment (such as plants, animals, habitats) and the impact on them of causing pollution were not included in rehabilitation efforts, as they were considered a public good for which no responsibility was recognized of the person who caused the damage. This lack, in terms of ownership and the cost of coverage, is regulated by Directive 2000/35/EC on environmental liability. The Directive introduces a scheme providing for the restoration of the environment where an operator cause pollution and is financially responsible for the damage and restoration of the environment and based on the principle "the polluter pays". Important role in the effective implementation of the Directive play stakeholders and Non-Governmental Organizations (NGOs) which carry legal interest. Under the Directive, environmental damage is a measurable adverse change in a natural resource, namely the damage being caused :

- to protected species and natural habitats, in which they live as referred to in Directive 79/409/EC and 92/43/EC
- to waters, resulting in the degradation of the ecological, chemical and / or quantitative condition
- to the ground, i.e., the challenge of any soil contamination that creates a significant risk of adverse effects on human health

The activities that may cause damage are the facilities for which authorization is provided under Directive 96/61; moreover each waste management process which includes the collection, storage, transportation, use and disposal of hazardous and non-hazardous wastes, the discharges to surface waters and groundwater, and the transport of dangerous or polluting goods, etc. [9].

2.3 Review of the Directive IPPC (IPPC)

The new directive is intended to address the shortcomings of current legislation on industrial emissions. There are seven overlapping directives covering similar activities with approximately 52,000 installations falling under the scope of the Directive on integrated pollution prevention and control (IPPC Directive). The main aim of the Directive is to increase the use of "best available techniques" (BAT) to ensure that industries use the most efficient cost techniques to achieve a high level of environmental protection. Because of the shortcomings of current legislation, BAT is not implemented in the EU to the extent required by the IPPC Directive. There are also inconsistencies between Member States in compliance with existing legislation and its enforcement, the complex legal framework carries unnecessary costs for industry. All these issues must be addressed in order to ensure a level playing field for industry, while offering higher levels of protection for the environment and human health. The Commission has investigated this issue thoroughly before proposing the new directive, as clearer and more coherent directive merging the IPPC Directive, and six sectored directives. This new Directive strengthens the application of BAT across the EU, particularly by restricting divergence from specific cases and placing greater emphasis on the justification of the terms of licenses.

The Directive sets stricter emission limits for certain industries in the EU, especially for large combustion plants where there has been insufficiently progressed in reducing pollution. It establishes minimum standards for environmental inspections of industrial installations and enables more effective permit reviews [9].

3. Sulfur Emissions to the Atmosphere from Refineries

3.1 Sulfur content (wt%) of selected crudes and their residues.

From the beginning, the refining of crude oil has been engaged in an ongoing effort to meet changing consumer demand for better and different products. Nowadays refineries produce a wide variety of products, among others, petrochemical raw materials and new environmentally friendly fuels using cutting edge technology. Globally, the percentage of sulfur in crude averages 1.25% wt, while in the markets there is crude with a sulfur content of 0.1% -6%, *see* Table 1. The sulfur content as shown in Table 1, is a key quality criterion of crude because of the complexity and cost of the refinery processes increases significantly with increasing the amount of sulfur in crude since the legislative framework imposes increasingly stringent legislative limits in both the content of sulfur in marketing fuels and in the emissions of sulfur dioxide into the atmosphere [19, 20].

Table 1: Sulfur content (wt%) of selected crudes and their residues [24,25].

Type, origin	Crude Oil	Atmospheric Residue
Ekofisk, Norway	0.1	0.3
Forties, Great Britain	0.3	0.6
Es-Sider, Libya	0.5	0.9
Alaska, USA	1.0	1.5
Wet Siberia, Russia	1.5	2.6
Isthmus, Mexico	1.6	3.0
Kuwait, Kuwait	2.5	3.8
Arabian Light , Saudi Arabia	1.7	3.0

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].

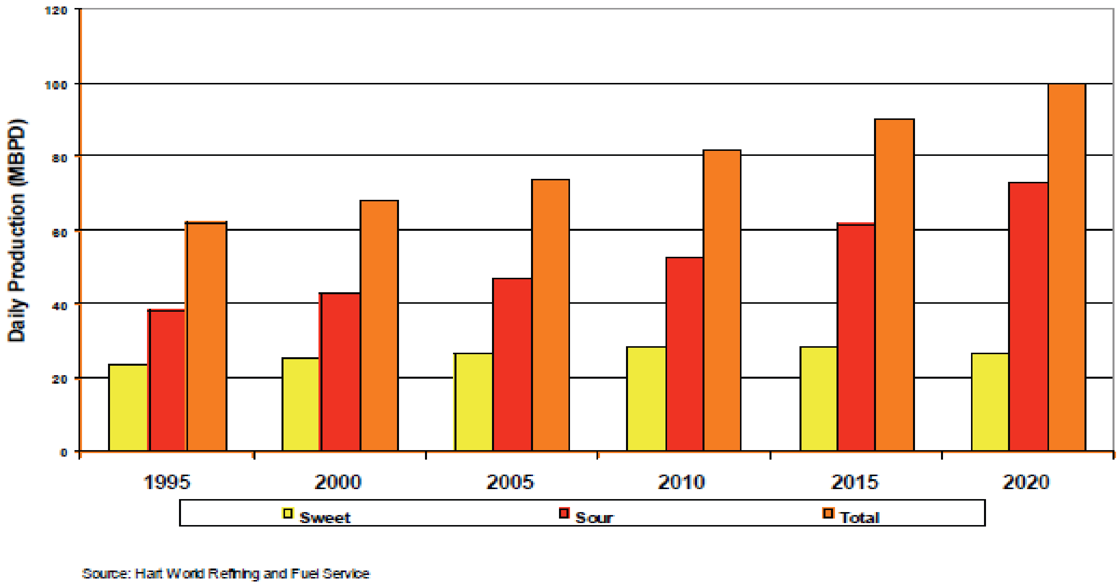

Figure 1: Global crude oil production [8]

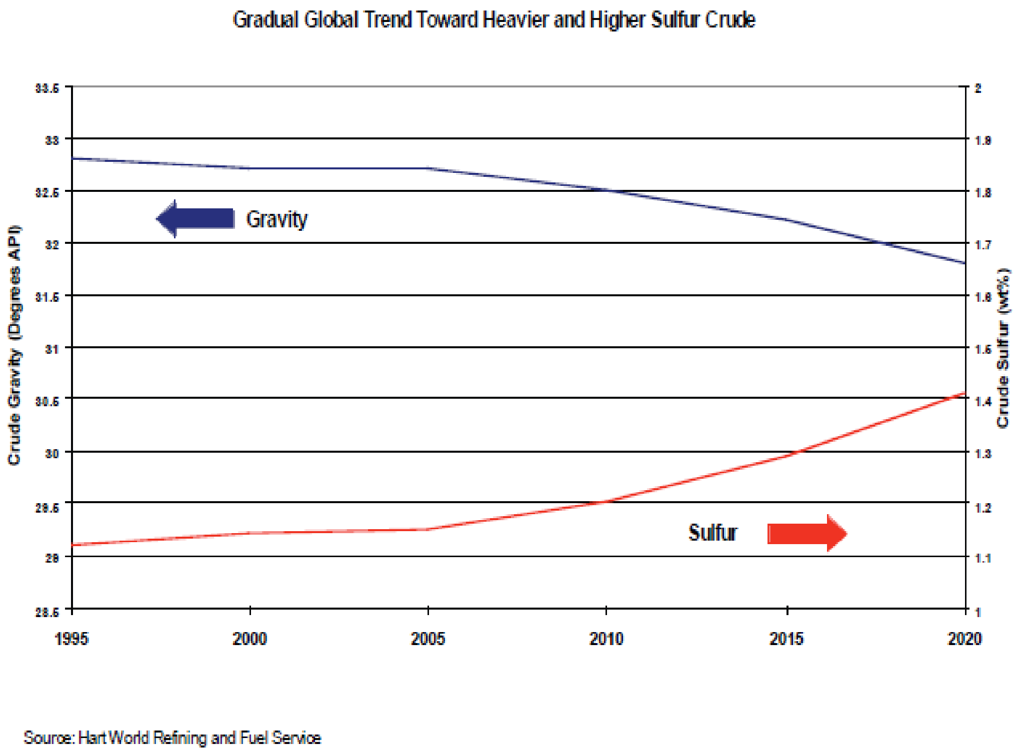

Figure 2: Trend of declining quality of crude [8].

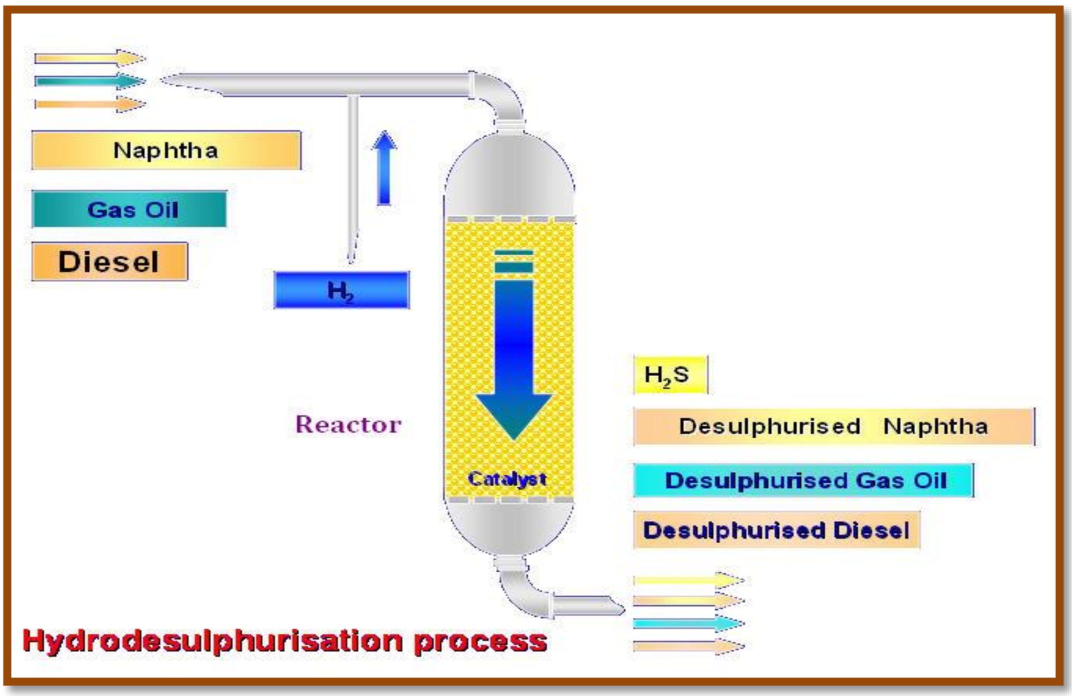

Figure 3: Simple schematic of the hydrodesulfurization process [10].

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.

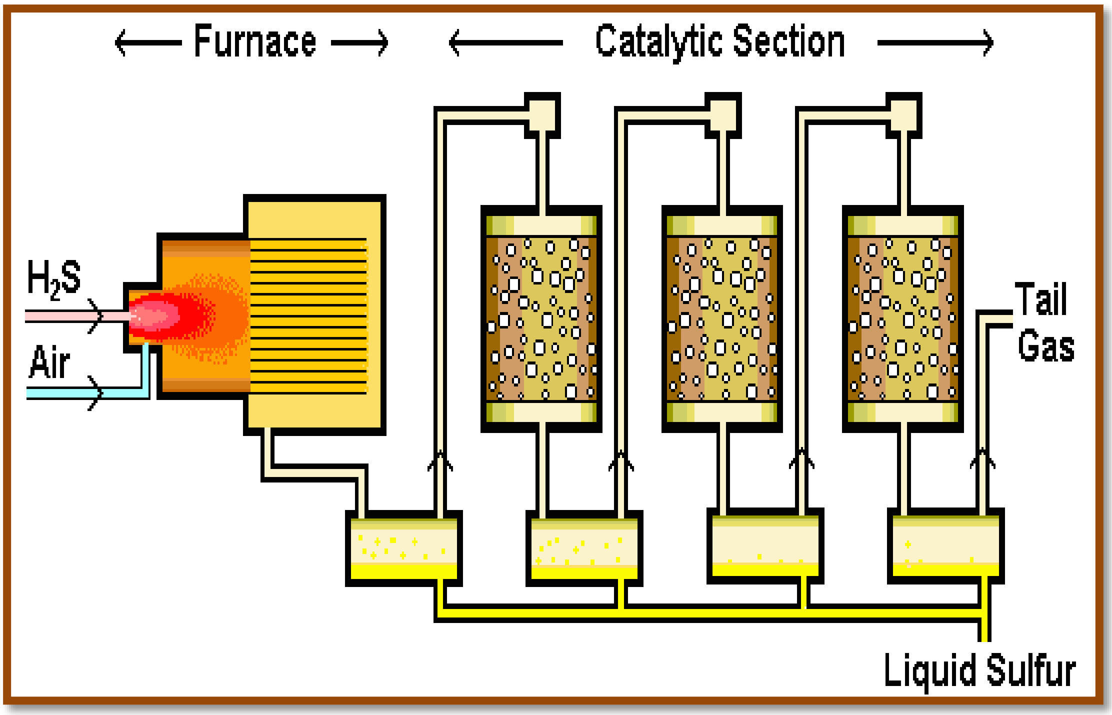

Figure 4: Typical arrangement of a Claus unit [6].

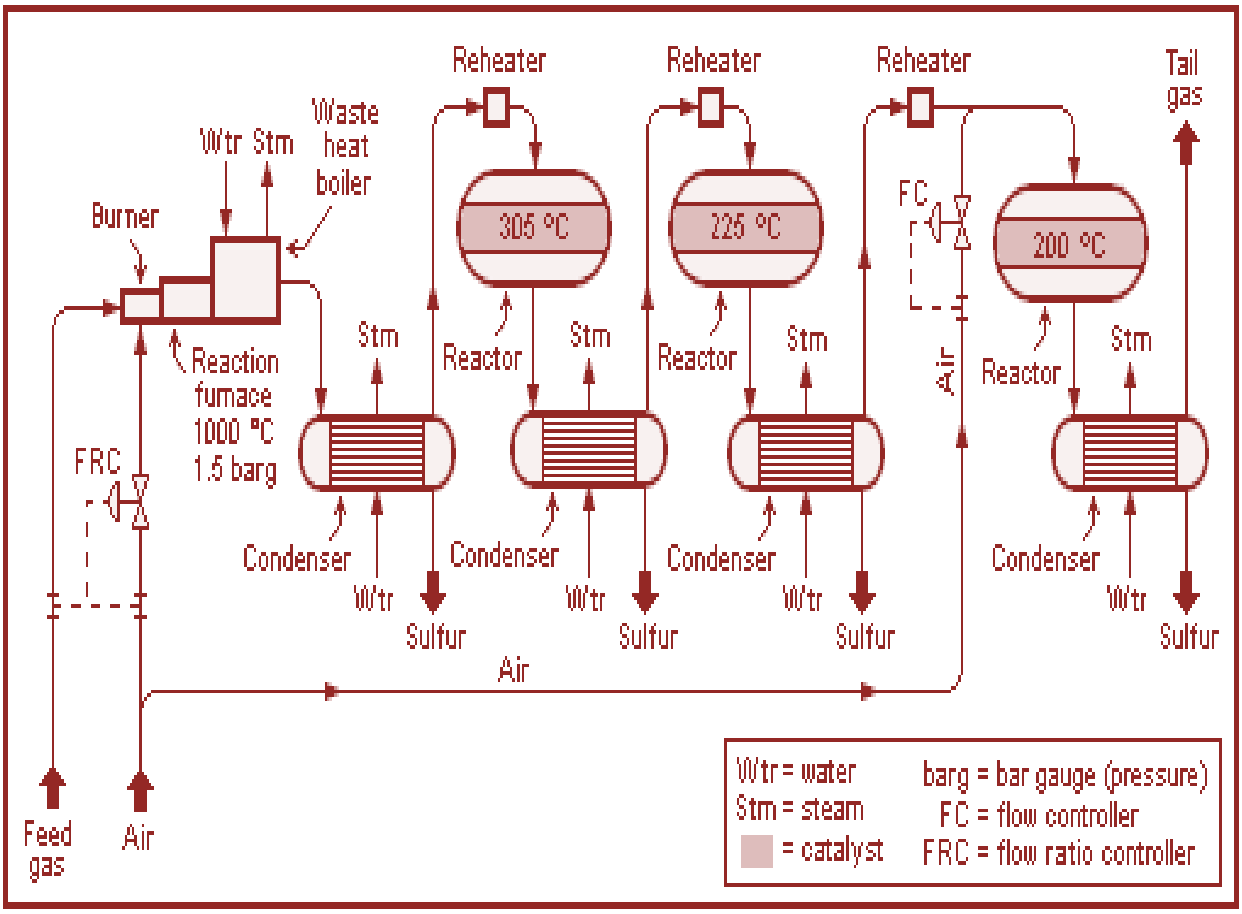

Figure 5: Typical Claus sulphur recovery unit.

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:

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

$2H_2S + SO_2 \longrightarrow 3S + 2\ H_2O$ + heat (disproportionation) (2)

$3\ H_2S + 3/2\ O_2 \longrightarrow 3S + 3\ H_2O$ (3) (total reaction) (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.

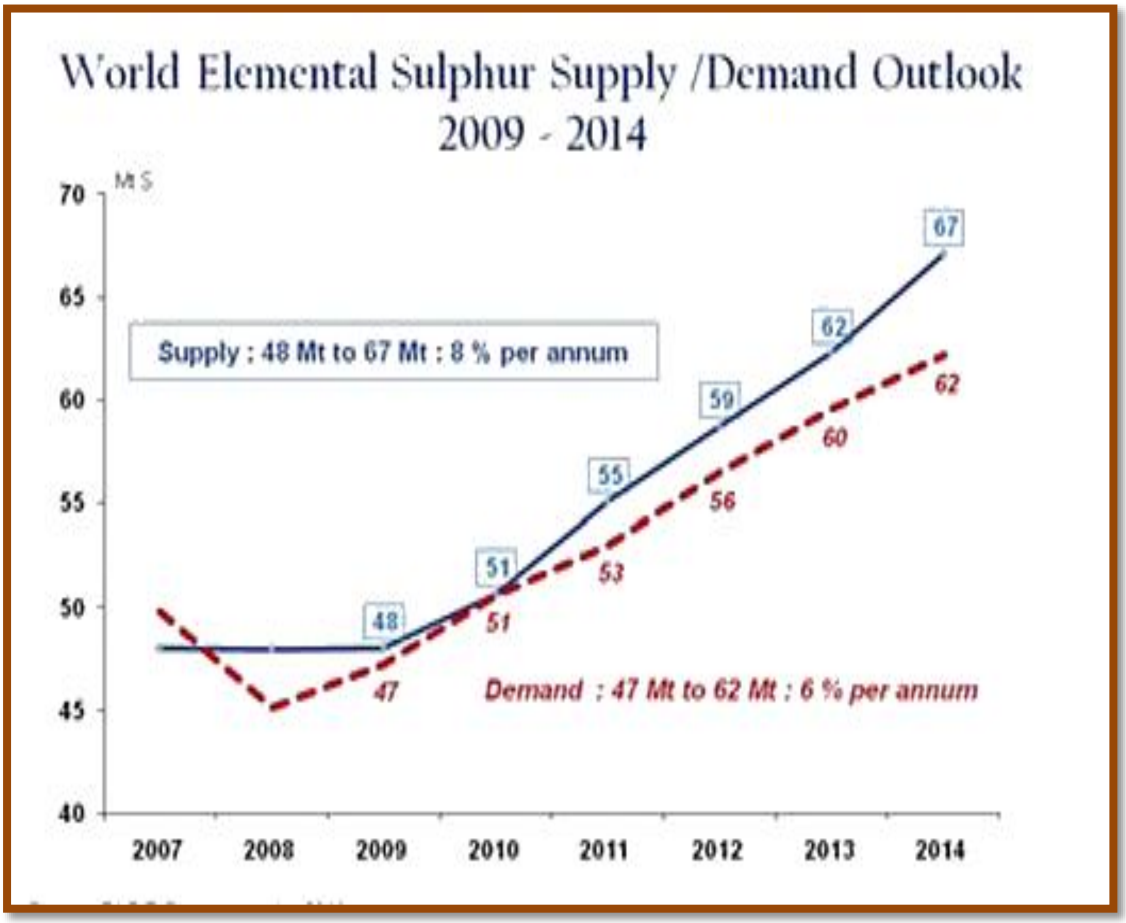

Figure 6. World Sulphur Supply / Demand Balance [13].

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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7. References

[1]. Dobbins R.A. 1979: Atmospheric Motion and Air Pollution, John Wiley and Sons.

[2]. Fox L. Donald, Boubel W.

Richard, Turner D. Bruce and Stern C. Arthur, 1992: Fundamentals of Air Pollution. Third Edition. Academic Press.

[3]. Godish Thad, 1991: Air Quality. Second Edition. Lewis Publishers INC., Chelsea, Michigan, U.S.A.

[4]. Manual on significance of tests for petroleum products-fifth edition . GeorgeV.Dyroff editor.

[5]. IPPC , BREF : Reference documents on best available techniques on mineral oil and gas refineries , February 2003.

[6]. Sulfur Recovery from Acid Gas Using the Claus Process and High Temperature Air Combustion (HiTAC) Technology, Am. J. Environ. Sci., 4 (5): 502-511, 2008.

[7]. Separating Impurities of Acid Gas from Hydrogen Sulfide by Using Adaptive Filter for Estimating of Claus Reaction Temperature by Neuron Networks, Gholam Ali Abdali , Amir Abolfazl Suratgar (Proceedings of the International MultiConference of Engineers and Computer Scientists 2009, Vol II, IMECS 2009, March 18 - 20, 2009, Hong Kong.

[8]. Solutions to Help Refiners Meet Clean Fuel and Environmental Challenges, Presented by Eric Ye at The Sulphur Institute's tenth biennial, international Sulphur Market Symposium, on April 4-6, 2006 in Beijing, China. Sulfur Institute : 1140 Connecticut Avenue, NW, Suite 612, Washington, DC 2006, USA, http://www.sulphurinsitute.org . Accessed: December 2012.

[9]. European Commission Environment. http://ec.europa.eu/environment Accessed: December 2012.

[10]. Ertc , Claus Technologies seminar , Brussels , March 12-14, 2008

[11]. European Commission Joint Research Center. http://ecb.jrc.ec.europa.eu Accessed: December 2012.

[12]. UNECE, United Nations Economic Commission for Europe. http://www.unece.org Accessed: December 2012.

[13]. Ministry of Energy and Climate Change. http://www.ypeka.gr Accessed: December 2012.

[14]. CONCAWE-the oil companies´ European association for environment, health, and safety in refining and distribution .http://www.concawe.be Accessed: December 2012.

[15]. International Fertilizer Industry Association (IFA), 28, rue Marbeuf – 75008 Paris – France, Fertilizer Outlook 2010 – 2014, Patrick Heffer and Michel Prud'homme, http:// www.fertilizer.org Accessed: December 2012.

[16]. http://www.unece.org/env/lrtap /multi_h1.htm Accessed: December 2012.

[17]. Stephen N. Massie, Business Manager, Gas Treating Catalysts Criterion Catalysts & Technologies LPSulfiding of Tail Gas Catalyst Proper Preparation of Tail Gas Hydrogenation Catalyst for Long and Active Life.

[18]. http://ec.europa.eu/environment

/air/transport/pdf/impacts_refineries.pdf Accessed: December 2012.

[19]. Science and technology of novel processes for deep desulfurization of oil refinery streams: review qI.V. Babich, J.A. Moulijn Faculty of Applied Sciences, Delft University of Technology, Delft ChemTech, Julianalaan 136, 2628 BL Delft, The Netherlands, available online 14 November 2002.

[20]. Global Trade and Fuels Assessment -Future Trends and Effects of Requiring Clean Fuels in the Marine Sector.

[21]. European Commission. 2009. Preserving our heritage, Improving our environment : Volume I 20 years of EU research into cultural heritage. European Research Area, Eur22050 EN, Edited by Michel Chapuis. http://ec.europa.eu/culture/documents/publications/20years_cultural_heritage_vol1_en.pdf Accessed: December 2012.

[22]. Asia-Pacific Cultural Centre for UNESCO(ACCU). 2004. Effects of Air Pollution on Cultural Properties: The Measuring of Air Pollution and the Protection of Cultural Properties in the Historic City of Nara, Japan. http://www.nara.accu.or.jp/elearning/2004/pollution.pdf Accessed: December 2012.

[23]. D. Melas, Atmospheric Pollution, Department of Physics, Aristotle University of Thessaloniki.

[24]. M.J. Avis and C.H. Birch. 2009. Impacts on the EU Refining Industry & Markets of Imo Specification Changes & Other Measures to Reduce the Sulphur Content of Certain Fuels. Prepared for: Directorate General Environment, 126p. http://ec.europa.eu/environment/air/transport/pdf/impacts_refineries.pdf. Accessed: December 2012.

[25]. Chemical laboratory of MOTOR OIL (HELLAS), CORINTHOS REFINERIES S..A.