Sustainability in the Sulphur Recovery Industry

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Introduction

With the growing awareness of the human footprint on our environment also comes the increasing drive to improve and change the way we produce energy and materials. The drive towards a circular economy is also supported by the Paris Agreement (Paris Agreement 2015) in which countries and governments have committed to reducing greenhouse-gas emissions. These developments spur ongoing innovation which also affects the Sulphur Recovery Industry. The main task at hand is: can we reduce or mitigate SO_2 emissions while at the same time adhere to a lower energy input and carbon footprint?

Sulphur recovery units are designed to convert highly toxic H_2S into elemental sulphur which is nowadays highly important to produce chemicals and fertilizer. In recent years there has been a trend for more stringent emission specifications with respect to unrecovered sulphur species in the form of SO_2. For many years the World Bank only funded projects where technologies capable of achieving less than 150 mg/Nm^3 of SO_2 in the stack were employed (World Bank Group 2016). With CO_2 starting to have a financial impact on operations via taxation and trading systems, questions can be raised such as to what extent a reduction of SO_2 emissions renders any benefit. This article seeks to discuss ongoing trends in the sulphur recovery industry as well as address the considerations which arise from the discussion on SO_2 and CO_2 emissions.

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Stringent Emissions

Since the industrial revolution, mankind has been responsible for an increase in SO_2 emissions. Impact on the environment through the formation of acid rain increased the awareness and technology development for sulphur recovery and saw a sharp decrease in SO_2 emissions from the 70's onwards. This peak in SO_2 emissions is clearly seen in Figure 1 after which the most significant reductions were achieved in North America and Europe (Ritchie 2019). Over time, the sulphur levels in fuel were reduced with the recent

Marpol V agreement the latest step change in SO_2 producing fuels. The trend in SO_2 emission reduction clearly has not stopped as is shown by the global anthropogenic SO_2 emissions curve. In Asia, SO_2 emissions are still rising but with growing awareness of the impact of air pollution on public health (World Health Organization 2016), a peak is to be expected. Particularly in urbanized areas with emissions from transport, industry and energy production, a trend towards more stringent emission regulations is apparent. This trend also drives the developments and innovations within the sulphur recovery industry.

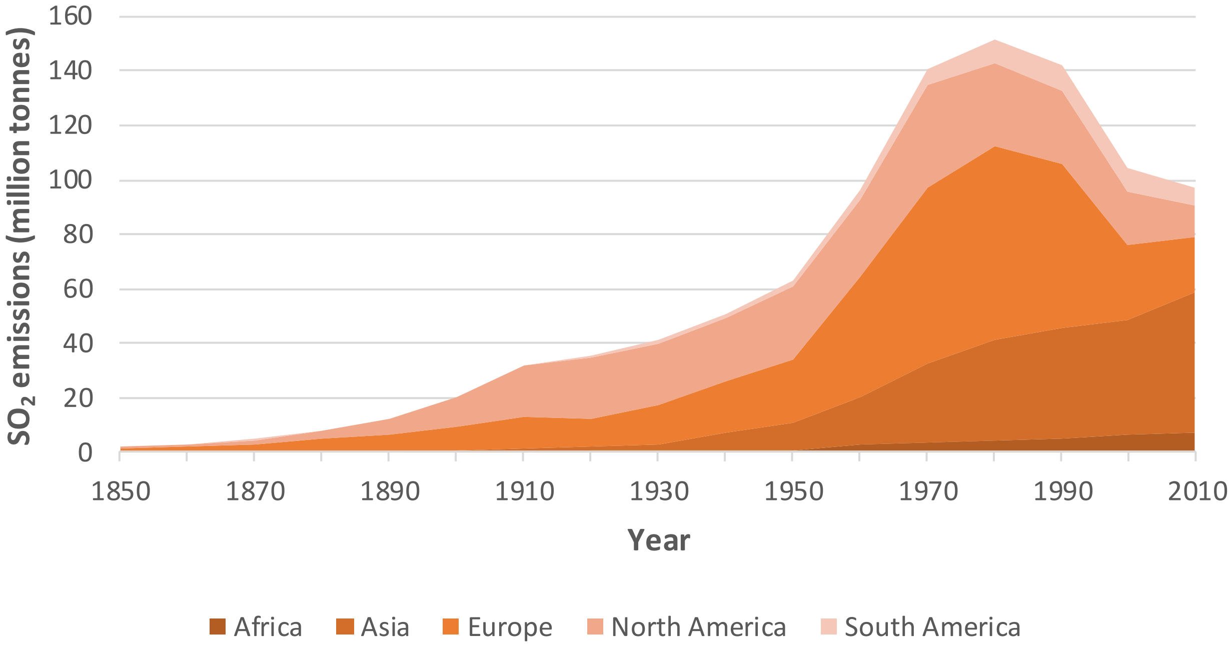

Figure 1. Anthropogenic global SO_2 emission per continent until 2010 (source: ourworldindata.org (Ritchie 2019)

Technology Improvements

In a lot of jurisdictions, Tail Gas Treatment Units (TGTU) are nowadays required to meet emission regulations. To further improve the performance of these technologies, new developments are continuously being rolled out. The development of new amine solvents with increased loading or with a reduced energy demand in the TGTU as well as improved catalysts are but a few examples.

These developments are mostly providing an economic benefit through reduced operational costs but are also examples of a reduction in energy and carbon footprint. A difference in performance level exists however when considering catalytic or amine-based TGTU options. The catalytic line-up with the highest sulphur recovery efficiency uses the selective oxidation of H_2S to S_x in the final reactor stage to overcome the Claus equilibrium. The SUPERCLAUS® and EUROCLAUS® processes are the top performing technologies and have been proven on large scale to be capable of meeting SRE levels of >99.6% (van Son, M. van Grinsven, R., Ghazal, K.S. 2017). The traditional difference in performance between amine based TGTU units as shown in **Error! Reference source not found.** which also indicates the costs advantage between the technologies.

At the Sulphur Conference 2018 in Gothenburg (Roelofs, T. 2018), a new generation of selective oxidation catalyst STRATACLAUS® was presented. With this catalyst the yield in the final reactor is improved as well as the higher performance during fluctuating operating conditions. When approaching 99.5% sulphur recovery efficiency in a catalytic SRU, a reduction of all remaining sulphur species becomes critical. The STRATACLAUS® catalyst is the first step which in combination with ongoing developments will result in a catalytic line-up capable of meeting 99.7% SRE on a continuous basis. This not only saves costs but also minimizes the installed footprint and therewith materials, transport and construction efforts.

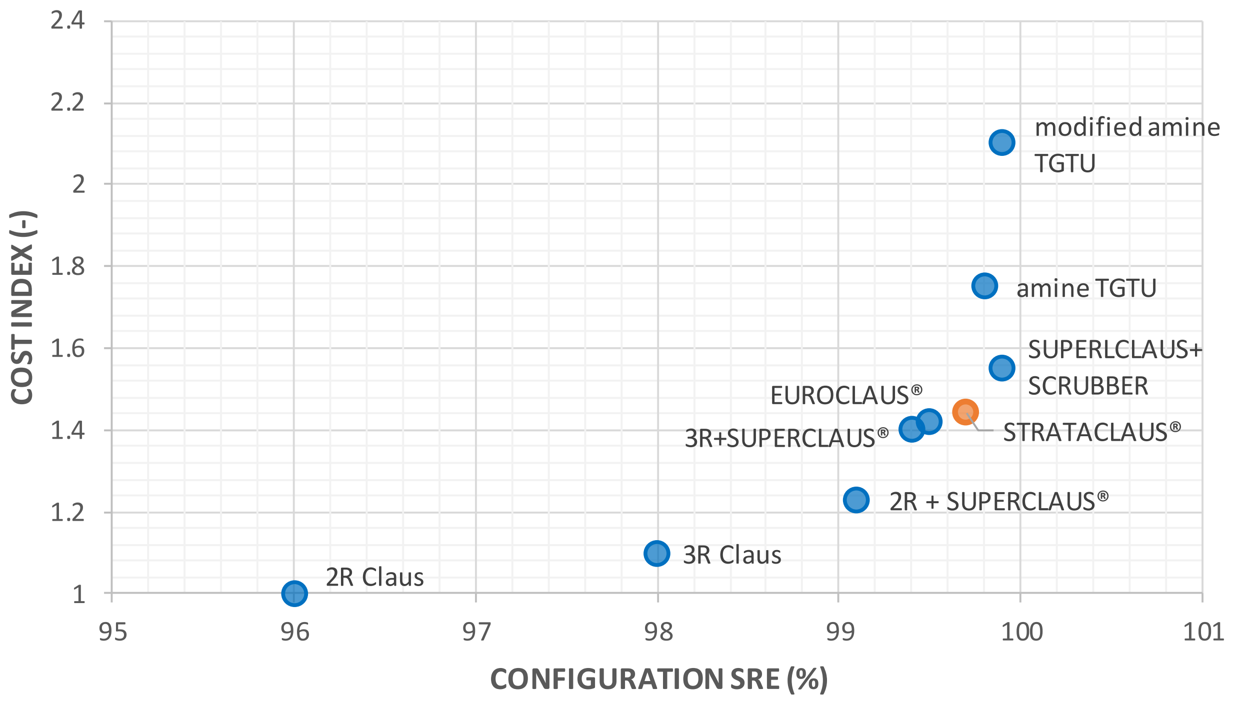

Figure 2. Cost Index Sulphur Recovery Technologies (source: Comprimo)

Effluent Streams

Effluent streams are of interest within sulphur recovery units as well. Small gas streams originating from different unit operation are oftentimes routed to the thermal oxidizer as they hold no economic value for further processing apart from heat generation. In case of a flash gas from a Gas Treatment Facility however, such a gas stream has the potential to contribute to the sulphur emissions of the plant. As the required sulphur recovery efficiency for many installations has increased over time so has the relative contribution of these streams and in some cases these gaseous effluent streams require additional processing to meet the emission regulations.

Other technologies to reduce SO_2 emissions such as scrubbers, produce a liquid stream which needs further processing (Roelofs 2019). For particular revamp situations where a reduction of SO_2 emissions is required, a scrubber offers economic and plot space benefit over an amine based TGTU. Comprimo uses caustic scrubbers to reduce post-combustion SO_2 emissions downstream of the SRU. The formed sodium sulphate brine solution can oftentimes be handled by local water treatment facilities. Alternatively, cooling crystallization can be employed where the formed sodium sulphate is separated as a dry product of industrial purity which can be used in e.g., the paper and pulp or detergent processes. The remaining water stream is recycled back to the scrubber reducing the water consumption of the system. This is a clear example of a waste stream that can be converted into a product stream that has a value to the client and a recycle closing the loop, thereby reducing the overall impact on the environment.

CO_2 Emissions – Pricing and Plant Economics

Governments in several countries are working on systems linking the economics of plant operations to the CO_2 emissions as a means of reaching the goals stated in the Paris Agreement (Plumer 2019). A well-known system in operation is the EU-ETS carbon trading system which works with a cap-and-trade system (Commission n.d.). In this system the total number of emissions allowances/emissions rights is reduced yearly, and companies can purchase yearly emissions rights for their operations. When exceeding the acquired emission allowances a penalty of €100 per tonne is due. As the majority of these emissions rights are auctioned, the price of emissions is balanced with the supply and demand. The year 2018 saw a sharp rise in CO_2 pricing from €7 to €21 per tonne as a result of a reducing the amount of emissions allowances (Market Insider n.d.) with an expected price of €50 per tonne by 2030. This ongoing trend has already triggered changes in investment strategies (Bauer 2018) and forces operators to rethink their operational costs. Notable economic regions with systems in place are the EU, Canada, China, Japan and some of the states in the USA. With ongoing effort to learn from past efforts development it is highly likely prices of CO_2 will affect also refineries and gas plants worldwide.

To visualize the impact of CO_2 pricing on operations of a plant, the impact of CO_2 pricing as function of sulphur recovery efficiency was studied for a European refinery and gas plant (Hennipman, J., Hanlon Kinsberg, K. 2019).

The Net Present Value (NPV) for differences in CO_2 price was investigated for the following cases:

- SRE = 99.5% using a EUROCLAUS® line-up
- SRE = 99.7% using a STRATACLAUS® line-up
- SRE = 99.8% using an amine based TGTU line-up (SCOT)

Apart from the direct pricing of CO_2 in the flue gas, the costs for all utilities were re-calculated based on their carbon footprint and corresponding price increase. Costs for the production of catalysts and chemicals was also taken into account.

In Figure 2 the impact of CO_2 pricing up to €50 per tonne on the NPV (20 years) for two SRU scenarios is shown. The impact on the refinery scenario is the lowest albeit significant at €50 per tonne. The direct costs for CO_2 in the flue gas accounts for 3% of the overall OPEX when a value of €20 per tonne is used. When the trading price is increased to €50 per tonne of CO_2, this number increases to 11%. As a sulphur recovery unit is typically a net energy producer (in the form of excess steam), an increase in CO_2 pricing will also bring about more value of this energy stream which balances with the increase in costs for electricity production. The net overall result is that the overall NPV for a typical refinery will be reduced but not significantly. The sensitivity for the different technologies with respect to CO_2 pricing is quite similar. Steam has a CO_2 equivalent value of 0.1 – 0.12 kg CO_2 per kg of steam. As all options in the refinery scenario produce steam the sensitivity towards CO_2 pricing is similar.

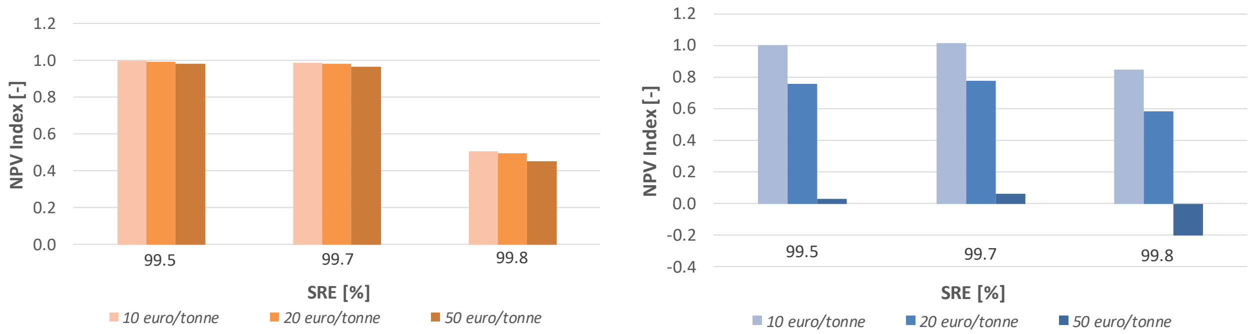

Figure 2: Impact of CO2 pricing on NPV – a) 115 T/D Refinery Scenario and b) 500 T/D Gas Plant (source: Comprimo)

The impact for a gas plant is far more visible and is largely determined by the CO_2 content of the flue gas in this scenario which are directly taxed by the CO_2 price. With a price of €50 per tonne a break-even point is reached when selecting a recovery efficiency of 99.5 – 99.7%. For the amine based TGTU a negative NPV is obtained at the higher CO_2 pricing level. This is a direct result of the increased power consumption and net steam consumption required for the regenerator reboiler. At a price of €10 per tonne, the direct cost for CO_2 accounts for 20% of the OPEX while at €50 per tonne it rises to 46% and starts to dictate the operational costs as is shown in Figure 3. The sensitivity of a gas plant with a higher-than-average CO_2 content in the feed is high and demands attention in the case CO_2 pricing is in effect.

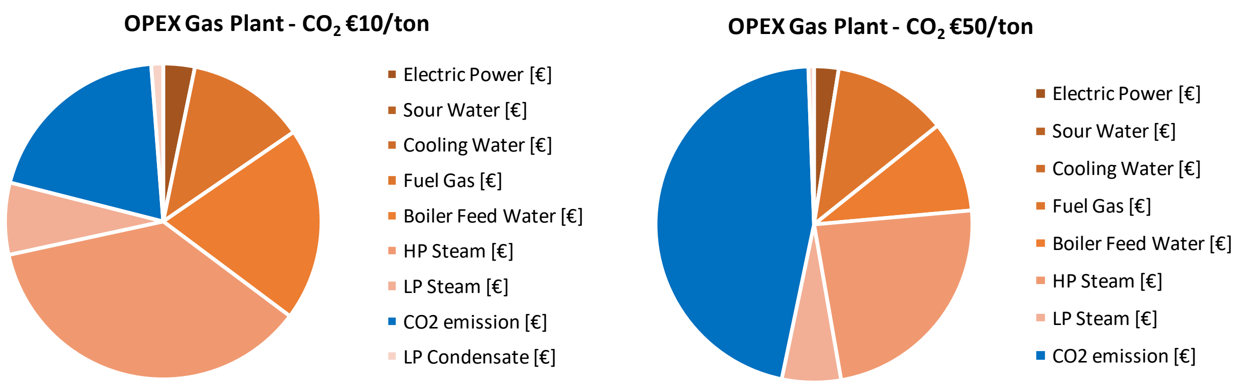

Figure 3: OPEX comparison Gas Plant Scenario for €10 and €50 per tonne of CO2 (source: Comprimo)

SO_2 or CO_2 reduction?

Slavens et al. *(Slavens 2018)* discussed the CO_2 footprint of different TGTU technologies and shows that CO_2 emissions rise exponentially with respect to the additionally recovered SO_2. Again, this prompts the question: why do we require such stringent SO_2 emissions specifications?

The health effects of CO_2 are known to occur at substantial levels ranging from headache and fast breathing until suffocation at high concentrations. The CO_2 emissions near petro-chemical installations is so low that these health impacts do not occur. The main concern with CO_2 is its impact on the global climate, the effects of which we are experiencing.

The health impacts of particulate matter, specifically urban areas, is a topic of high interest. Sizes <2.5µm can enter the finer parts of the lungs resulting in respiratory problems and related health effects (WHO 2005) (Awe 2015) . SO_2 has the potential to form particulate matter directly via reaction with other species as well as indirectly by formation of aerosols which in turn act as precursors for particulate matter. With capable technologies well established it is not hard to understand the drive towards lower SO_2 emissions.

Regardless, one can still raise the question, what are safe levels of SO_2 or particulate matter caused by SO_2? According to the World Health Organization a concentration of 20µg/m^3 is a safe level for a 24hr exposure (WHO 2005). The harbour of Rotterdam contains substantial petro-chemical facilities close to an urban environment. Reported ground level concentrations of SO_2 were 3.1 – 4.8µm/m^3 in 2018 as measured by DCMR, the official environmental protection agency for the Rijnmond area (DCMR 2019). Measurements were carried out near petro-chemical facilities as well as in the urban areas near roads and highways in Rotterdam. The reported values are much lower than safe exposure limits and the total ground level concentrations are still dropping as shown in Figure 4 (van den Elshout 2017). The 'background' SO_2 emissions are mainly related to North Sea shipping and external industrial activities. The Industry and Shipping SO_2 emissions are related to the local petro-chemical industry and shipping activities in the harbour area itself. A lower sulphur content in shipping fuel resulted in a reduction in both the Shipping SO_2 emissions in the harbour but also on the North Sea shown by a decrease in the Background emissions. The Industrial emissions have also been decreasing resulting in a net change of 60% with respect to 2005 with a total ground level SO_2 concentration of 5.5µg/m^3.

In addition, the particle size concentration PM_{10}, equivalent to particles smaller than 10 µm, was on average 20-24 µm/m^3 which is below the advised 40 µm/m^3. Some days were reported in which fine dust emissions exceeded the 50 µm/m^3. As fine dust has multiple sources, the direct relationship with SO_2 emissions is not present here. As the understanding of direct and indirect health effects of SO_2 has deepened, there has been a reduction in the accepted safe exposure concentration levels. Whether additional reductions in emissions will further benefit public health is still to be determined.

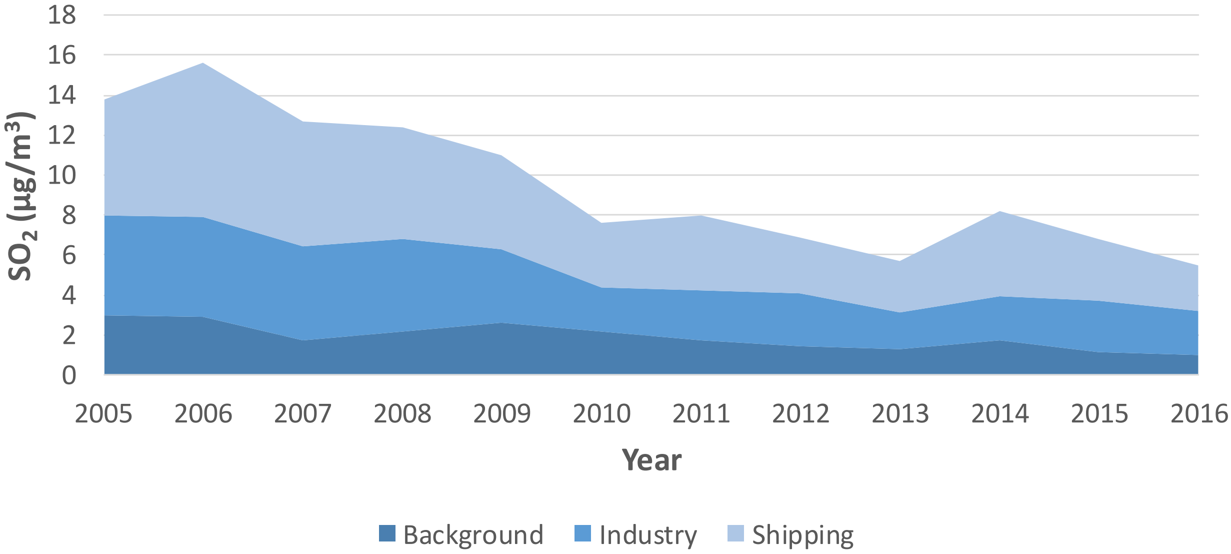

Figure 4: SO2 emissions in the Rotterdam harbour area

In Europe, new sulphur recovery units shall be designed to have a sulphur recovery efficiency of 99.5% (Barthe 2015). The average SRE of all SRUs in the Rotterdam area is unknown but it is interesting to observe that safe levels of SO_2 are obtained in an urban area right next to a high concentration of petro-chemical sites. If health effects are the main driver for (more) stringent SO_2 emissions, remote gas plants should not be required to have such high recovery efficiencies. This in turn would be beneficial for the utility and energy consumption as well as the overall carbon footprint of these facilities. Continuing with this rationale, then adhering to former World Bank emission standards increases not only the financial burden on the plant owner, from an investment and operational point of view but would also induce a higher carbon footprint. Based on the currently measured ground level SO_2 concentrations in the presented case study, there appears to be no basis for improving SO_2 emissions further. Therefore, the goals set in the Paris Agreement become harder to meet with more stringent SO_2 emission regulations.

Outlook

For the technology selection of sulphur recovery units, it seems there are more factors to be considered when evaluating options to reduce both SO_2 and CO_2 emissions. The question therefore is not so simple as to what the best means of is for reducing emissions. Simply applying the best available technology with the highest SO_2 recovery level or lowest CO_2 footprint can result in either residual SO_2 emissions or an increased carbon footprint. With the carbon taxation or trading systems regulatory authorities hold the key to driving the price of CO_2 with the aim of stimulating the development of a carbon-neutral economy. Via a case study it was shown that these developments will also affect the operational costs of sulphur recovery plants. As a result, the carbon-footprint starts becoming a selection parameter in the technology selection phase.

With increasing sulphur recovery efficiency, it was shown that the carbon footprint can strongly increase when pursuing the World Bank Standards (Slavens 2018). With the known effects of SO_2 on public health it is fair to say authorities would like to reduce emissions, particularly in urbanized areas. Safe levels of SO_2 concentrations however are met in urban areas with a large concentration of petro-chemical sites, with the harbour of Rotterdam scenario provided as an example. As such, ground level concentrations in many areas adhere to the WHO standards and therefore from a carbon footprint standpoint it appears that the overall net effect on the environment is negative when a further decrease in SO_2 emissions is mandated. These considerations illustrate the increasing complexity in emission regulations and technology selection facing policy makers and operating companies in the years to come.

Interested or have any questions? We're ready to help.

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