Assessment of air pollution control technologies to reduce SOx emission from thermal oxidizer for oil and gas industry

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Abstract. Many countries have put in place, various legislations that govern air emission limits/pollutants from the industries. The common pollutants being monitored are Sulphur Oxides (SOx), Nitrogen Oxides (NOx), Carbon Monoxide (CO), Carbon Dioxide (CO2), Volatile Organic Compounds (VOCs), particulate matters and dioxins. In Malaysia, the regulatory requirement aims to regulate emissions of air pollutants from industrial activities including oil and gas, power plants, waste fuel plants and asphalt mixing plants. One of the emission limits under Clean Air Regulation (CAR2014) is emission level for SOx should be less than 600 mg/m³ (reference condition at 3 % of O₂, 273 K, 101.3 kPa) whereby sum of SO₂ and SO₃ expressed as SOx. Excessive SOx emission can affect both health and the environment. Aligning with the regulation requirement, Group Technical Solution (GTS) under PETRONAS has embarked on assessment of technology solutions to meet the emission limit on SOx emission limit for thermal oxidizers which cover new and existing facilities. This paper describes on the work methodology and approach adopted during the assessment. The objective of the assessment is to determine the suitable process technology to reduce SOx emission in order to achieve the desired emission limit for flue gas at outlet stream of thermal oxidizer. Through evaluation was carried out based on proposal submission from various technology providers and Vendors. The selection criteria was developed and established. For existing thermal oxidizers, the assessment is more complex taking into consideration the nature of brownfield project and to ensure the proposed modification has minor impact to operability and maintainability of existing facilities. This study has successfully enabled identification of feasible process technologies such as Caustic Scrubber, Seawater Flue Gas Desulfurization and Ammonia based Desulfurization to meet the desired emission limit at thermal oxidizer outlet for Oil and Gas Industry and supporting environmental protection. The selected technology is varies based on plant/project specific requirement. Among main considerations are the by-product management, consumable and utility consumption as well as compatibility of the technology with existing plant on shutdown requirement.
1. Introduction
Many countries have put in place, various legislations that govern air emission limits/pollutants from the industries. The common pollutants being monitored are Sulphur Oxides (SOX), Nitrogen Oxides (NOX), Carbon Monoxide (CO), Carbon Dioxide (CO2), Volatile Organic Compounds (VOCs), particulate matters and dioxins. In Malaysia, the regulatory requirement aims to regulate emissions of air pollutants from industrial activities including oil and gas, power plants, waste fuel plants and asphalt mixing plants. One of the flue gas emission limits under Clean Air Regulation (CAR2014) is emission level at the thermal oxidizer exhaust stack for SOX should be less than 600 mg/m3 (reference condition at 3 % of O2, 273 K, 101.3 kPa), whereby sum of SO2 and SO3 expressed as SOX.

The function of the thermal oxidizer is to dispose-off acid gas from upstream unit to the atmosphere in an environmentally acceptable manner. This is achieved by combusting a mixture of fuel gas and the acid gas at high temperature of about 900 °C to decompose H2S and hydrocarbons including aromatics such as benzene, toluene and xylene. The flue gas emission shall meet the requirements of the Malaysian Laws as well as the requirements of Department of Environment (DOE).

SO2 is colourless gas with suffocating odour. It is very toxic and corrosive to the respiratory tract. Excessive SOX emission can affect both health and the environment. Short-term exposures to SO2 can harm the human respiratory system and make breathing difficult. People with asthma, especially children, are sensitive to these effects of SO2. At high concentrations, gaseous SOX can harm trees and plants by damaging vegetation and decreasing growth. SO2 and other sulfur oxides can contribute to acid rain which can harm sensitive ecosystems.

2. Background
Aligning with the regulation requirement, Group Technical Solution (GTS) under PETRONAS has embarked on assessment of technology solutions to meet the emission limit on SOX emission for thermal oxidizers which cover new and existing facilities. The objective of the assessment is to determine the suitable process technology and cost-effective solution to reduce SOX emission to achieve the desired emission limit for flue gas at outlet stream of new and existing thermal oxidizer.

3. Methodology
The methodology adopted for the study involved the following steps such as establishing the problem statement, reaching-out to the technology providers, technology selection, risk assessment and finally conclusion and recommendations.

The initial step was to establish the problem statement and the design requirement for the oxidizer including the emission limit. Then, the team reached out to the technology provider/vendors worldwide to identify the available process technologies. The technology provider refers to the inventor and provider of technology whereas vendors refer to the supplier of equipment product/service. The received technical proposals were consolidated and reviewed. Further questions were being clarified to ensure the proposal meeting the problem statement and design requirement.

Technology selection is performed using evaluation matrix based on technology selection criteria. Subsequently, Technology Risk Assessment was conducted to assess potential risk of adopting and implementing the technology. Finally based on the outcome of evaluation, team came-up with the conclusion and recommendations for the way forward. The methodology of work process for the study is illustrated in figure 1.
4. Findings
The available SOX Removal Technologies were divided into two categories which are pre-treatment and post-treatment technology to the thermal oxidizer. Pre-treatment is referring to reduction of H2S in sour gas prior entering the thermal oxidizer meanwhile post-treatment is referring to recover SO2 in the flue gas from thermal oxidizer stack. Regardless of the category, the objective is the same which is to achieve flue gas emission within the specified regulatory limit at the exhaust stack.
5. Technology Selection
The selection criteria were established based on the problem statement and objectives of the study. The following are among others the important categories considered in the technology screening and selection criteria.

| Categories                                  | Description of Selection Criteria                                      |
|---------------------------------------------|------------------------------------------------------------------------|
| Technology Performance                      | • Ability to meet emission limit                                      |
|                                             | • Utility consumption within plant limit                               |
|                                             | • Within provided plot space                                          |
| Coft-Effective                              | • Capital Expenditure (CAPEX)                                          |
|                                             | • Operational Expenditure (OPEX)                                      |
|                                             | • Life Cycle Cost (LCC)                                               |
| Technology Track Record                     | • Proven reference plant                                              |
| Technology Operability and Maintainability  | • Number of stream days                                               |
|                                             | • Turndown requirement                                                |
|                                             | • Turnaround interval requirement                                     |
| Impact on Health Safety and Environment (HSE)| • Compliance of effluent discharge to regulatory limit                |
|                                             | • Product handling/hazards                                            |

Based on the consolidated inputs of technologies, scoring was included into comparison table taking into account the assigned weightage for each criteria. The weightage was assigned based on the importance on the categories and its selection criteria elements. The scoring was given based on relative comparison between each technology against the minimum requirement which has been determined by the team, i.e, the required plot have to meet available plot size of 3800 m².

From the evaluation, ranking is done based on total score to select the most technical and economical feasible technology to be further studied in the next phase. Based on the study for acid gas treating plant, the identified suitable process technologies are summarized below.
Table 2. Summary of feasible desulfurization technologies.

| Technologies                        | Description                                                                                                                                 |
|--------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------|
| Caustic Scrubber                     | • Flue gas enters Caustic Scrubber unit and contact with circulating caustic solution (NaOH).                                                 |
|                                      | • Effluent is cooled down and sent to Effluent Treatment System.                                                                              |
| Seawater Flue Gas Desulfurization    | • Scrubbing of SO$_2$ in flue gas to SO$_3^{2-}$ by seawater and disengaging of Treated Gas and SO$_3^{2-}$ in Absorber  |
|                                      | • Oxidation of SO$_3^{2-}$ to SO$_4^{2-}$ at Oxidation Basin and seawater is discharged to sea.                                              |
| Ammonia based Desulfurization        | • SO$_2$ in flue gas is absorbed by ammonia and converted into ammonium sulfate.                                                            |
|                                      | • The ammonium sulfate solution is further processed to obtain ammonium sulfate product as fertilizer.                                       |

6. Risk Assessment
Technology Risk Assessment (TRA) was then carried out for the selected technology which met the minimum scoring requirement. The objectives of TRA are as to identify potential risks and operability issues related to the selection of the technology and to ensure adequate control measures are in place. The categories considered under TRA are:
• Performance
• Operability/Maintainability
• Readiness
• Hazards
• Implementation
Table 3. Example of TRA worksheet.

| Guide Word                       | Cause                                                                 | Consequence                                                                 | Recommendations                                                                 |
|---------------------------------|-----------------------------------------------------------------------|-----------------------------------------------------------------------------|--------------------------------------------------------------------------------|
| Feed gas quality                | 1. Varying feed gas composition (i.e., Hydrocarbon). 2. Presence of contamination in Ammonia. | 1. Potential slowdown and shutdown, resulting in SO₂ not meeting DOE specification. 2. Product not meeting specification. 3. Potential damage to equipment. | 1. To consult Technology Licensor about potential contaminants that will disrupt operation of the SO₂ removal technology unit. 2. To include the potential feed gas quality variation in the Basis of Design (BOD). |

Hazard studies, HSE case, Hazard and effect register

| Cause | Consequence | Recommendations |
|-------|-------------|-----------------|
| Lack of familiarity and awareness to manage ammonia leak/release due to newly introduced substance in existing facility | Potential LOPC, hazards to people and environment and asset damage. | 1. To conduct thorough HSE studies relevant to ammonia handling including the safeguard (e.g., people protection, emergency response etc.). 2. To include ammonia in relevant process safety and HSE documents (e.g., Hazard Effect Register) |

Based on the TRA review, recommendations were then provided to mitigate the risks of the technology under study. One of the identified concerns of applying ammonia based desulfurization technology in the natural gas liquefaction plant is the variation of feed gas composition (i.e., hydrocarbon) and presence of contaminant in ammonia solution. This can cause potential slowdown and shutdown of the unit and resulted the SO₂ may be exceed the limit. The recommendation is to include the potential flue gas quality range in the Basis of Design (BOD).

In addition, the other concern is lack of familiarization with handling, storing and Health Safety and Environment (HSE) management of newly introduced substances such as ammonia to existing facility. As part of the recommendation, it is suggested to conduct thorough HSE studies relevant to ammonia handling including the mitigation plans (e.g., people protection, emergency response etc.) during the next study phase.

7. Conclusion
Thorough evaluation was carried out based on proposal submission from various technology providers and vendors. The evaluation was performed based on the technology selection criteria and followed by technology risk assessment review. This evaluation study has successfully enabled identification of feasible process technologies such as Caustic Scrubber, Seawater Flue Gas Desulfurization and Ammonia based Desulfurization to meet the desired emission limit at thermal oxidizer outlet for Oil and Gas Industry and supporting environmental protection. The selected technology is varies based on plant/project specific requirement. Among main considerations are the by-product management.
limitation, consumable, utility availability and compatibility of the technology with existing plant on shutdown requirement.

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