Greenhouse Gas reduction Techniques in Petroleum Refinery

By- Atul Choudhari

Greenhouse gases are generated from various industrial processes. Though power generation is a known major contributor of the greenhouse gas (GHG) emissions, considerable amount of greenhouse gases are released from other energy intensive industries as well. The petroleum refining is one such energy intensive industry. The source of energy is mainly in form of fossil fuels which give rise to GHG upon combustion. Due to this, refining industry is considered as a significant source of greenhouse gas emissions. Apart from the direct fuel combustion, various refinery processes like fluid catalytic cracking unit (FCC), sulphur recovery plants, Hydrogen generation units, etc. also contribute to the GHG emissions. Waste gas flaring also adds to the overall emissions from petroleum refinery. This paper provides an overview of options available to track reduce GHG emissions.

Emission Sources:

The principal GHG includes Methane, Carbon dioxide and Nitrous oxide. There are also several tropospheric gases such as carbon monoxide (CO), NO_X, SO_X that can influence the climate and are considered as secondary sources contributing to the global warming. These gases are also air pollutants. The GHG emission sources from the refinery can be broadly classified under three categories as briefed below.

Direct Emission Sources: Direct emissions are resulted from sources such as Flares, Incinerators, various process units of the refinery (like FCC, Reformer, etc), and Fugitive losses. Hydrocarbon gases which cannot be recovered or recycled back to the process are sent to flare. Flare also serves as an important and critical safety system in the refinery. Apart from hydrocarbon flares, dedicated flares are generally provided for disposal of excess acid gases. These excess gases are burnt off in the flare producing CO_2, SO_X and NO_X.

Refinery fuel gas stream contains H_2S which is removed by using amine absorption/regeneration system. The H_2S rich sour/acid gas from the amine regenerators is used for recovery of elemental sulphur in a Claus sulphur recovery unit. The tail gases leaving the Claus unit are incinerated producing CO_2, SO_X and NO_X.

The cracking reactions in FCC reactor produces coke which gets deposited on the catalyst particles. Coke deactivates catalyst activity. Therefore, it is sent to the regenerator which burns this coke and returns regenerated catalyst back to the reactor. Due to the combustion process in the regenerator, GHG are emitted from FCC unit. Some of the other process units of the refinery like continuous catalytic reformers handle catalytic reactions in which the coke gets deposited slowly on the catalyst particles during the cracking reaction. The “catalyst coke” deposits are required to be burned-off to regain catalyst activity. This catalyst regeneration process produces CO_2, along with small amounts of N_2O.

Steam reforming deployed by the refineries to generate H_2, is another source for CO_2 generation. The light hydrocarbon feedstock (like methane, LPG or light naphtha) is subject to high-temperature steam reforming followed by water shift reaction, to maximize H_2 yield. In the process, carbon goes to CO_2.

In other types of losses, there are some legitimate losses e.g. breathing losses from storage tanks etc. The fugitive emissions occur due to leaks from pressurized system. The likely source of these leaks typically is from pump and compressor seals, valves, tank losses, etc.

Emissions due to fuel combustion in process furnaces: All refinery units require process heaters, e.g. crude and vacuum column heaters, coker heaters, reformer heaters etc. Process furnaces or fired heaters use variety of fuels to supply required heat duty. Commonly used fuel are natural gas, fuel gas (In-house), fuel oil, etc. The flue gas from combustion of these fuels generates mainly CO_2, SO_X, and NOX which is then discharged to atmosphere through stacks.

Emissions from utility generation units: Electricity is a common source used to drive process equipment such as pumps and compressors. Steam is one of the main sources of supplying heat to the process plant. Power and steam generation in refineries is through boilers and / or combined heat and power cycle. Generally, oil refineries prefer to generate their own power using internally generated fuel or other locally available fuel like natural gas, coal. These are major sources of GHG emissions from refinery.

Emission reduction and control techniques:

Figure 1 below suggests a broad roadmap to handle emissions. Based on the type of emission, the options are proposed to either control / reduce or to eliminate the emissions.

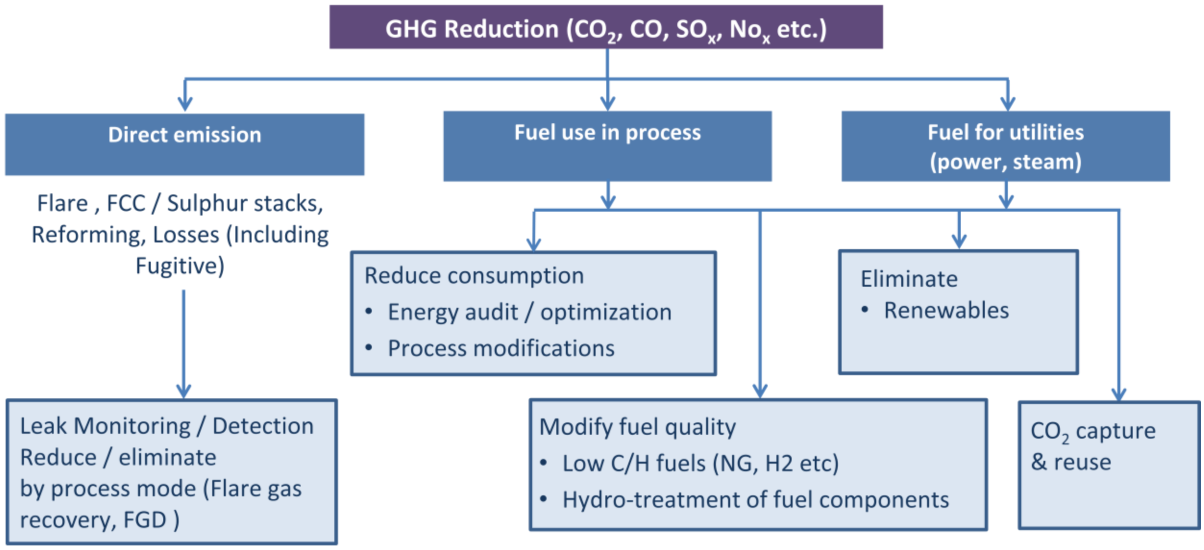

Figure 1: GHG reduction: Source and control methods

While, the emissions from direct emission sources can be reduced by implementing recovery systems such as flare gas recovery packages, the emission elimination methods may require employing a new process unit. For example - flue gas desulphurisation unit may be considered to eliminate SO_X emissions from refinery FCC unit.

Emissions due to fuel combustion can be reduced by reducing the fuel consumption itself through process optimization. Other means of reduction includes considerations of use of alternate fuel having low C/H ratio.

With certain limitations, efforts can be made to eliminate fossil fuel use as an energy source by considering renewable energy such as solar, wind, etc.

To eliminate CO_2 emissions from the power generation and also from various process stacks, suitable technology for CO_2 capture and its reuse can be implemented. Some of the major options are further discussed in section below:

Flaring and incineration:

Flares are critical for functioning of the refinery as it acts as final layer of protection in safety systems. All the emergency hydrocarbon containing streams from the various safety devices are disposed using flare. Any reduction in the quantity of waste gases flared will reduce the GHG emissions. Options for reduction of flare gases include implementation of flare gas recovery packages wherein releases of hydrocarbon gas to flare system are collected, compressed and recycled back to the fuel gas system. Existing flares can be monitored to improve combustion efficiency by controlling steam or air assist rates. Apart from the emergency relief streams, the off gases which cannot be recovered in the process are also sent to the flare. For such cases, refrigerated condensers can be considered to increase product recovery and reduce excess flare gas quantity. Recovery of hydrocarbons released to flare system normally has good economics as such materials fetch in no value, if flared.

The tail gases generated from sulphur recovery units have usually high concentrations of H_2S. These gases are disposed using incineration techniques. For complete combustion of H_2S, the incinerators must operate at a temperature of 650 ^{0}C or higher. It is necessary to maintain proper air-to-fuel ratio to eliminate pluming from the incinerator stack. Poor combustion efficiencies generally lead to the higher emissions. For emission monitoring, SO_2 analysers can be considered on the incinerator stack.

Process Improvements:

Process improvements are aimed to maximize the product yield at a minimum cost. Most of the process improvements program target for reduction in the energy consumption so as to increase profits. This objective also falls in line with aim of reducing GHG emissions. While fuel/products are obtained from crude oil processing, the carbon that cannot be incorporated in any of the product fuel streams will finally be emitted to atmosphere in form of CO_2. Newer developments in the processing technology provide process efficiency improvement opportunities. For example - New cracking catalysts help to increase conversion with reduction in overall energy consumption and aim at reduced coke formation. Another example is use of new membranes that are being developed to improve separation processes. Membranes are typically used for recovery of hydrogen from off gases. Hybrid technology using membrane plus distillation can be implemented for separation of close boiling propane and propylene streams at downstream of fluid catalytic cracker unit. Alternatively techniques like heat pump compression could be deployed for distillation of closely boiling components.

Use of modern day computer programs such as simulation, Pinch analysis and through use of advanced process control systems, refiners can evaluate opportunities for lowering energy demands which in turn help in reducing the GHG emissions.

Modify Fuel Quality:

Fuels containing lower carbon to hydrogen ratio (C/H) results in lower GHG emissions. Process heaters and furnaces often use in-house generated low value heavy end fuel oils as combustion fuel. Fuel oil has relatively higher C/H ratio than other alternate fuels such as LNG, LPG, fuel gas, hydrogen, etc. To meet the required energy input, combustion fuel can be selected so as to minimize overall GHG emissions from the refinery. Opportunities can be exploited to use low carbon fuels. However, the selection of fuel source remains very much a site specific choice as per fuel availability, logistics and associated economics.

Quality of the fuel can sometimes be modified by additional processing in order to minimize the GHG emissions. For example, the off gases generated from vacuum column overhead system are generally used as supplementary fuel in crude heater. Depending on the crude oil type, these off gases may contain significant amount of H_2S. Instead of combusting these sour gases directly in a process furnace; it can be first compressed and then treated with conventional alkanolamine absorption system for removal of H_2S. Sweet gas after amine treatment can then be sent to the crude heater for providing supplementary duty. The acid gases from amine generation column can be processed in Claus SRU for recovery of elemental sulphur. This way, the fuel type used in crude heater can be modified to reduce GHG emissions. Such measures also help in reducing air pollution.

Use of non-carbon-based energy sources- (Renewables):

Based on the advancements in technology, efforts are being made to reduce dependency on fossil fuel (Coal, Oil, and Gas) for meeting the energy demands on a large scale and in an economic manner. These energy sources are solar, wind, nuclear, hydroelectric, or geothermal energy. Demand for solar photovoltaic systems is growing rapidly. Floating PV solar and solar thermal could also be alternatives that could be evaluated. New technologies like deep sea gas hydrates are being developed. Natural gas obtained from coal bed methane is relatively clean source of alternate fuel. Refineries can exploit some of these locally available renewable options in future.

CO2 Capture and Reuse:

Technological options for capturing CO_2 include Adsorption, Absorption, and membrane systems. Molecular sieves can be used for adsorption of CO_2 from refinery streams. Solvent based chemical absorption is most widely used method for post combustion CO_2 capture. Membrane technology is still undergoing through a development and trial phase but it can be still used on selective streams. The biggest challenge in using CO_2 capture route is finding a suitable method for its reuse. Deep ocean storage is an expensive option. Captured CO_2 can be used for manufacturing of useful products or for enhanced recovery from oil & gas reservoirs.

Other Measures:

The fugitive emissions from the refinery can be controlled by an effective inspection and maintenance programs. The GHG emissions resulting from storage tanks emissions can be minimised by implementing vapour recovery systems. Storage tank type can be changed from the fixed roof tanks to the floating roof tanks. Secondary seals can be considered on existing floating roof tanks. Municipal wastes and biomass can be considered as a supplementary source for power generation.

Approach for GHG reduction:

A comprehensive, systematic and focussed approach is required for –

1. Establishing the base line of GHG emissions – it requires detailed hydrocarbon accounting and reconciliation of material / energy balances
2. Evaluation of various alternatives for GHG reductions
3. Quick benefit analysis of the options
4. Prioritization of opportunities
5. Detailing of shortlisted options for techno-economic feasibility
6. Implementation of the schemes
7. Confirmation of actual benefits and re-establishment of new base line

Concluding Remarks:

Petroleum refineries being energy intensive units are significant source of GHG emissions. These emissions can be reduced or sometimes eliminated through a systematic study effort and through scientific approach of implementing appropriate technology. Combinations of one or more methods as discussed above may help in reducing overall GHG from refineries.