SO₂ and CO₂ Emission Control from Refinery COGEN Units with Cansolv’s Capture & Recycling Systems

By

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ABSTRACT

As profitable outlets for high sulfur resids decline, additional options will need to be explored to maximize the value of smaller volumes of resid. Co-generation projects that generate power and steam for the refinery may be economically interesting.

Resid contains elevated amounts of sulfur as compared to sweet liquid fuels and its carbon impact is higher than for equivalent natural gas combustion systems. High sulfur resid fuels generate large quantities of SO₂ when combusted, that require removal by flue gas SO₂ scrubbing systems. Certain jurisdictions may require that carbon capture systems be applied to ensure that the carbon impact of the co-generation scheme is no worse than an equivalent project that uses natural gas as a fuel.

A CANSOLV SO₂ Scrubbing System is uniquely configured to control SO₂ emissions in the refinery, because it generates a pure stream of SO₂ that can be fed to the Sulfur Recovery Unit (SRU), to make elemental sulfur. The CANSOLV CO₂ Capture System can be effectively used in conjunction with the CANSOLV SO₂ Scrubbing System, because much of the energy consumed in the SO₂ Scrubbing System can be captured and cycled to the CO₂ Capture System, to reduce overall energy costs associated with the two capture systems.
Introduction

The refining industry faces greater supply side pressures to process more difficult crudes. Environmental initiatives are concurrently imposing additional limitations on the sulfur content of refinery product streams. Investment in bottom of the barrel hydrocracking or coking schemes can economically upgrade the value of large volumes of resid, but options are limited when smaller volumes of high sulfur materials must be accommodated. Co-generation projects may be economically justified, to consume modest quantities of high sulfur refinery product streams. These projects will require SO$_2$ scrubbing systems to prevent the sulfur in the fuel mix from escaping to atmosphere as SO$_2$. Additional regulations requiring the limitation of carbon emissions from these new co-gen projects, may also mandate that CO$_2$ capture systems be added.

A co-generation project may be of interest to the refinery for three reasons. First, co-generation projects can be designed to accommodate a wide range of fuels, from cycle oils to asphalt and coke. Secondly, on-site generation of power and steam reduces the refiner’s reliance on external, purchased balancing fuels. Finally, the versatile nature of the co-gen system to accept variable fuel qualities increases the refinery planner’s ability to fill the refinery crude slate with a wider range of crude and hence maximize his margins.

CANSOLV SO$_2$ Scrubbing – Regenerable vs Non Regenerable Systems

SO$_2$ Scrubbing can be accomplished with regenerable technologies that use an alkaline agent that reversibly absorbs and releases SO$_2$, or by non regenerable technologies that simply absorb the SO$_2$ until reagent is spent. Regenerable technologies have a higher capital cost and impose greater demands on plant utilities than non-regenerable systems. Non regenerable technologies have reduced capital costs as compared to regenerable systems, but become more expensive to operate as the quantity of SO$_2$ to be captured increases. When fuels are highly contaminated with sulfur, regenerable systems are often justified economically over their non regenerable counterparts.

Lime and limestone scrubbers are commonly used, non-regenerable systems. They require significant investment to prepare reagent and to dewater and dispose of gypsum byproduct. SO$_2$ Scrubbers that use NaOH (caustic soda) are also commonly used. A caustic scrubber requires little reagent preparation or byproduct management investment, since NaOH is sourced as a bulk liquid or easily dissolved solid. Its waste product, dilute aqueous sodium sulfate, is discharged to plant waste water treating systems.

Caustic systems have lower capital costs than other non-regenerable systems, because the reagent is purchased as a dry solid or concentrated liquid and wastes are easily absorbed in existing wastewater management systems. NaOH pricing can be volatile, however, because it is produced as a co-product in the manufacture of chlorine. Its price inversely tracks demand patterns for chlorine based chemical products such as vinyl chloride monomer, which is used to manufacture polyvinyl chloride plastics.
Sodium carbonate and sodium bicarbonate are less expensive alternatives to caustic and can often be substituted for caustic, but their cost is higher than for limestone or lime and they require greater investment in reagent preparation and management systems than for caustic scrubbing systems.

The regenerable CANSOLV SO₂ Scrubbing system, uses an alkaline agent, CANSOLV DS, to capture SO₂ and release it in pure form from a regenerator that removes the SO₂ from the solvent.

In the refinery, a pure stream of SO₂ from a regenerable system can often help de-bottleneck existing refinery Sulfur Recovery Units (SRU), that are often under pressure to convert greater quantities of H₂S to sulfur.

Regenerable systems have a higher capital cost than the non-regenerable systems since investment is required to regenerate the solvent and convert SO₂ to a marketable byproduct. Capital costs are offset by reduced operating costs, however in comparison to the non regenerable systems.

Case Study

A high level comparison was made between the CANSOLV and non regenerable system costs for a boiler being fired 35 t/hr (5,300 BPD) of vacuum resid, containing 4.6 wt% sulfur and 2.6 wt% sulfur.

![Figure 1 – Comparative Capital and Operating Costs – Cansolv vs Non Renerable Scrubbing Systems](image-url)
Figure 1 shows high level capital and operating cost comparisons for four SO$_2$ FGD technologies. The chart illustrates that the capital cost for the CANSOLV system is higher than for the non regenerable systems, but that its operating cost is lower. A second case comparing the costs of scrubbing 2.6% sulfur fuel are shown alongside the base case. The regenerable cost remains relatively unchanged, but the operating costs of the non-regenerable systems, dominated by reagent cost, drops proportionally to the amount of SO$_2$ in the flue gas.

Figure 2 shows the key elements of the CANSOLV SO$_2$ Scrubbing System.

- Flue gas is conditioned in an open spray Prescrubber. An optional flue gas cooler adjusts the flue gas temperature to appropriate conditions for the CANSOLV SO$_2$ Absorber.
- The SO$_2$ Absorber may be integral or separate from the Prescrubber. Gas is treated to remove SO$_2$ to the required threshold for environmental compliance.
- Flue gas leaving the SO$_2$ Scrubber may be post treated in a caustic scrubber to comply with very low SO$_2$ emission requirements or to precondition the gas for a future downstream CO$_2$ Capture system.
- Lean solvent is supplied from the SO$_2$ Regenerator
- Rich solvent flows to the SO$_2$ Regenerator
- Pure, water wet SO$_2$ flows to battery limits and on to byproduct processing systems.
- An Amine Purification Unit removes sulfate absorbed from the flue gas as SO$_3$ or generated via disproportionation in the CANSOLV System.
- TIC costs can range from $450/kW to $700/kW depending on industry and location
- Operating costs can range from $300/t SO$_2$ removed to $500/t depending on utility and capital cost charge assumptions.
CANSOLV CO₂ Capture System

The decision to burn liquid fuels requires an evaluation of the cost impact of increased CO₂ emissions on the facility.

Carbon taxes are now in place in many jurisdictions that charge a penalty for each ton of carbon emitted daily. Until government levies increase, CO₂ capture projects will be deferred in favor of payment of the relevant carbon tax, since CO₂ Carbon Capture and Sequestration (CCS) projects are currently estimated to cost considerably more than the penalties assessed for emission of CO₂. CO₂ Capture technologies are being developed and implemented in a handful of demonstration projects around the world and these projects will demonstrate the feasibility and cost of capturing CO₂ on a more accurate basis as they come on stream. Over the long run, capture technology costs are expected to drop as technology is demonstrated and improved.

CANSOLV Technologies has commercialized a CO₂ capture process that is currently in construction at two demonstration sites. Figure 3 shows the process flow diagram for these projects. The first demonstration project is planned for startup in 2011, while the second is planned for completion in 2015. The CANSOLV CO₂ Capture System is considered to be an “add on” technology to the CANSOLV SO₂ Scrubbing System technology described earlier.
Furthermore, the flow sheet of the SO₂ system can be adjusted to integrate with the CO₂ system and reduce energy consumption of the CO₂ system significantly.

Comparing this figure to Figure 2 – CANSOLV SO₂ Scrubbing System, it is seen that:

- Overhead heat from the SO₂ Scrubbing System SO₂ Regenerator is directed to the CO₂ regenerator through an SO₂ regenerator overhead mechanical vapor recompression (MVR) compressor.
- The CANSOLV CO₂ Scrubbing System is added
- The CO₂ Scrubbing System incorporates a lean solvent flash steam recycle MVR compressor to recover additional heat from lean CANSOLV CO₂ Absorbent

The integration scheme between the SO₂ Regenerator and the CO₂ Regenerator allow for the reduction of steam consumption by the CO₂ capture system. In effect, some of the steam fed to the CANSOLV SO₂ Scrubber can be used twice, while extra energy conservation measures are taken to ensure a net reduction in steam consumption by the CO₂ Capture system.

Figure 3 – Process Flow Diagram of the CANSOLV SO₂ and CO₂ Capture System

For the hypothetical case discussed above, the Prescrubber and SO₂ Scrubbing systems represent approximately 30% of the total cost of the SO₂ and CO₂ system. Approximately 900,000 t/year of CO₂ are captured as compared to 28,000 t/year of SO₂ in the 4.6% Sulfur in fuel case.

The capital and operating costs for the CO₂ system once again are driven by site specific considerations and must be evaluated on their own merit.
**Approach to a CO₂ Capture Project**

Fewer than 10 projects worldwide are currently in design and construction for CO₂ Carbon Capture and Sequestration (CCS) projects capturing CO₂ from boilers exceeding 150 MWe capacity.

Because few full scale CCS projects have been delivered to the power or refining industry to date, there is no firm data base in existence to support the capital cost projections of specific CO₂ capture projects. CCS technology vendors must therefore apply large contingency allocations to their budget estimates, to offset technological uncertainties. This can lead to excessive capital cost expectations and increase the risk of premature cancellation.

Until more projects are implemented and operated at large scale, detailed initial studies are required that are designed to improve project definition, reduce uncertainty and improve the quality of capital cost estimates.

At the current stage of CCS technology development, a four stage approach should be considered for a given project.

1) Perform high level CCS technology studies to develop a short list of technology vendors.
2) Select and purchase detailed Front End Engineering and Design (FEED) packages from multiple bidders. Demand firm turnkey prices for each capture system.
3) Select a single vendor from this group.
4) Proceed immediately to the EPC stage with the successful bidder and use his FEED package to form the basis for detailed design and final appropriation of funds.

Although the cost of acquiring multiple FEED packages early in the project increases costs during the development phase of the project, it delivered a number of tangible benefits:

- Optimization studies for each technology vendor can be performed prior to execution.
- A fixed price is obtained for the CCS systems that is based on a thoroughly developed design.
- Lower contingency allocations result from the fixed price basis and reduced capital risk results.
- The FEED stage of the project flows directly to the EPC stages of the project, reducing the overall project schedule.
Conclusions

CANSOLV SO$_2$ and CO$_2$ Scrubbing Systems can be used to allow a refiner to manage his bottom of the barrel stream more effectively.

The CANSOLV SO$_2$ Scrubbing System is most effective at high concentrations of sulfur in fuel and it can be effectively applied to treat flue gas to necessary specifications required for both atmospheric requirements and for a future, downstream CO$_2$ Capture system.

Energy consumed by the SO$_2$ scrubbing System can be directed to the CO$_2$ System, using a Mechanical Vapor Recompression system, cutting the operating cost of the CO$_2$ system significantly.

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