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Cracking carbon capture from oil refineries

Fluid catalytic cracking (FCC) units are one of the highest carbon dioxide (CO_2) emitting areas of an oil refinery. As a result they are a major focus for those taking on the challenge of developing next generation carbon capture technologies for use by the oil and gas industry. Ivano Miracca, head of the CO_2 Capture Project (CCP) Capture Team provides an overview of one such project that aims to capture up to 95% of FCC CO_2 emissions – potentially equating to some 20% to 30% of total CO_2 emissions from a typical refinery.

The oil and gas industry has been using carbon dioxide (CO_2) separation techniques for many years, with the resulting CO_2 streams used for a variety of purposes, including enhanced oil recovery (EOR). However, as the world looks for ways to tackle climate change, the industry needs to identify and develop next generation capture technologies that will allow this sector to economically capture and store CO_2 on an industrial-scale.

The CO_2 Capture Project (CCP) – a partnership of seven major energy companies: BP, Chevron, ConocoPhillips, Eni, Petrobras, Shell, Suncor and associate member EPRI – was formed in 2000 in a bid to advance the technologies that will underpin the deployment of industrial-scale CO_2 capture and storage (CCS). The CCP Capture Team, comprised of experts from the member companies, has been working to develop a suite of economically viable next generation technologies. Much of this work has focused on applications in three critical areas for the oil and gas industry – refining operations, steam production for heavy oil extraction and natural gas power generation. This has involved conducting research into reducing cost uncertainties and identifying the best options to take forward for field demonstration.

This work is now entering the critical phase of field demonstrations and it is the oil refinery scenario where the first of these is taking place. The target for this work is one of the highest emitting processes in a refinery – the fluid catalytic cracking (FCC) unit, which converts heavy, lower-value hydrocarbon feedstock into lighter, more valuable products. The demonstration, led by Petrobras, began in March 2011 at a large pilot-scale FCC unit at the company's research complex in Parana state, Brazil. The demonstration is expected to confirm the technical and economic viability of retrofitting such a unit to enable CO_2 capture through oxy-combustion. As a result, it is expected to bring closer to reality a cost-effective technology capable of capturing up to 95% of FCC CO_2 emissions, potentially equating to some 20% to 30% of total CO_2 emissions from a typical refinery.

Refinery emissions

Refineries are responsible for some 6% of total emissions of CO_2 from stationary sources worldwide (power stations account for more than 80%), amounting to 0.8bn t/y. The level of emissions from a single refinery depend on the specific process configuration and the mix of fuels used, but are broadly in the same range as emissions from a power station. For example, a world scale refinery processing 250,000 b/d of crude oil may emit between 4mn and 5mn t/y of CO_2, versus 3.5mn t/y generated by a 500-MW coal-fired power station. The carbon footprint of refineries is set to increase further as increasingly heavier oils are used as feedstock.

A typical refinery has a wide range of CO_2 emission sources, including fired heaters, boilers and process units, as well as several stacks emitting flue gas to the atmosphere. In this multi-source environment, two major emitters may be identified depending on the specific process scheme:

- The regenerator of the FCC unit.
- The hydrogen production unit (usually a steam reformer).

The combination of these two processes may account for up to 50% of CO_2. Therefore they are the main targets for a substantial reduction of greenhouse gas (GHG) emissions.

Generally, both pre-combustion and oxyfiring are better candidates than post-combustion to capture CO_2 in a refinery. While post-combustion would at least need one capture unit per stack, both pre-combustion and oxy-firing in theory could allow centralised capture, minimising concerns regarding plot space availability that are typical in a space-constrained refinery application. However, in the FCC unit of a refinery, pre-combustion is not applicable (see details of CCP techno-economic evaluation below).

Capture in the FCC unit

In the FCC unit, CO_2 is generated by combustion of the coke formed as a by-product in the reactor and adsorbed by the catalyst. This operation is necessary to restore catalyst activity and oxy-combustion is the only alternative to post-combustion. Air is replaced by pure oxygen, which is diluted with recycled CO_2, to maintain thermal balance and catalyst fluidisation. (See **Figure 1**).

The CCP conducted a techno-economic evaluation of oxyfiring and post-combustion amine absorption for CO_2 capture from the FCC regenerator. Both processes were able to achieve the required specifications and recovery level. Although the post-combustion option had a lower capital cost, the lower operational costs for oxyfiring delivered a much lower overall capture cost. This was also a consequence of the decision to use high purity oxygen, avoiding the need for final purification of CO_2 after capture. Since the FCC regenerator works at relatively high pressure, leakage of air into the system was not a concern.

Oxyfiring is thus considered by the CCP as a technology with high potential for FCC emissions capture, both for newbuilds and retrofitting to older units. However, a number of issues remain to be addressed – such as the possible corrosion of existing equipment, thermal balance, catalyst attrition and coke burn rate. As a result, the CCP and Petrobras set up an oxyfiring field demonstration at Petrobras' SIX testing facility in Parana state, Brazil, to test a number of assumptions and issues.

Project details

The main goals of the field demonstration project are to:

- Test start-up and shut-down procedures.
- Maintain stable operation of the FCC unit in oxy-combustion mode.
- Test different operational conditions and process configurations.
- Obtain reliable data for scale-up.

The demonstration started in March 2011 and results are expected this summer.*

The pilot FCC unit has the capacity to process up to 33 b/d of hydrocarbon feed (emitting 1 t/d of CO_2). It consists of an adiabatic riser, stripper and regenerator, which allows simulation of a commercial FCC unit, including the energy balance.

The retrofit of the unit for oxy-combustion operation involved the design, construction and installation of an oxygen supply system (OSS) and a CO_2 recycle system (CRS). Oxygen is stored in a liquid state and vapourised before injection in the regenerator. The CRS is skid mounted and includes catalyst fines removal, sulphur oxide (SO_x) removal, recycle compressor and a CO_2 temporary storage vessel.

Two different feedstocks will be tested in daily runs; testing operating variables, including feed flow-rate, solid loading to the cyclones, heat removal rate in the regenerator and SO_x abatement level in the recycle stream. A longer run in constant conditions will be carried out to verify any ageing effects on catalyst activity and reaction yields. The results will be used to define the scale-up path towards large-scale implementation of the technology and to update the technical/economical studies.

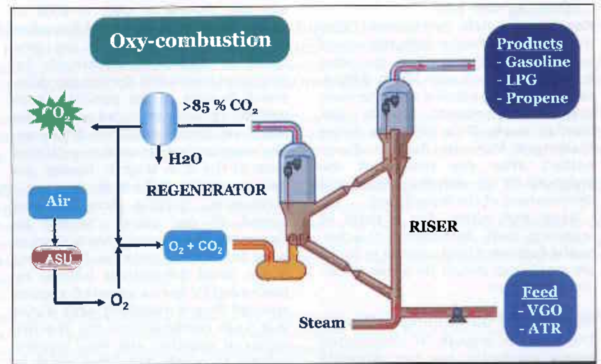

Figure 1: Capture process schematic (ASU = air separation unit)

**Petroleum Review* hopes to provide an update on the project in its December Future Refining and Bulk Storage supplement.*

CCS guidance and training at the EI

The Energy Institute (EI), together with the UK Health and Safety Executive, the Global CCS Institute and the Carbon Capture and Storage Association, has been working with industry to develop good practice for implementing CCS technology.

Coordinated as part of the EI Technical Work Programme, this work has involved a wide range of participants from across the oil and gas, power generation, industrial gases and engineering industries. To date, two guidance documents have been produced as a result of this cooperation: *Technical guidance on hazard analysis for onshore carbon capture installations and onshore pipelines* and *Good plant design and operation for onshore carbon capture installations and onshore pipelines*.

Building on this good practice, the EI, in association with Det Norske Veritas (DNV), has developed a two-day training course that provides an overview of the capture, transport and storage aspects of CCS and assesses the technical and safety requirements of each stage of the chain. Intended for engineers and technical personnel with an interest in carbon capture and storage, as well as project and commercial managers, the course provides an insight into the opportunities and risks involved in CCS. The course includes an introduction to the CCS chain and managing carbon dioxide (CO_2) stream risks, and covers capture concepts and technology, good plant design and operation, environmental and safety considerations, transportation, selection of storage sites and reservoirs, leak management, monitoring and performance targets.

Future technical research

Further EI CCS technical guidance is currently in development and the EI CCS Working Group has begun work on two key projects: 'Hazard analysis for offshore carbon capture platforms and offshore pipelines' and 'Failure rate data collection for CCS service equipment on capture installations'. The first project covers hazard and risk analysis, modelling techniques and application, as well as emergency procedures and requirements and practical examples.

Only minimal research has been completed regarding failure of equipment within CCS installations. The second EI-led CCS project aims to collect failure rate data and undertake statistical analysis of the failure modes of equipment used in CCS installations. Preliminary statistics and a report of findings will be issued, and analysis of the data will be used to identify areas of concern, and recommendations for inspections and maintenance. It is intended that these results will be presented in annual reports, including anonymous data on failure rate and modes for a range of CCS related equipment.

- If you would like to be involved in any future EI CCS technical projects, contact Martin Maeso, EI Technical Director, e: **mmaeso@energyinst.org**
- The next EI CCS course is planned for 4–5 October 2011. For more information about EI Training, contact e: **wsadler@energyinst.org**
- EI CCS technical guidance documents are freely available to download at **www.energypublishing.org**