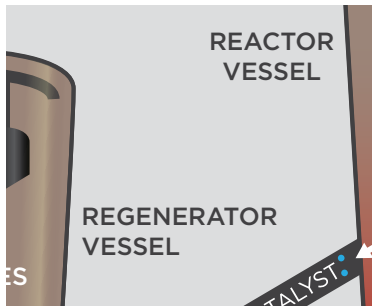# OXY-COMBUSTION TECHNOLOGY DEVELOPMENT FOR FLUID CATALYTIC CRACKERS (FCC) – LARGE PILOT SCALE DEMONSTRATION

Oxidant flow rate

B

- Air
- Recycle + O2

% vol

- CO2
- N2
- CO2

Kg/h

300.0
250.0
200.0
150.0
100.0
50.0
0.0

- Air
- Recycle + O2

Time

Time

H₂O

CO₂

REACTOR VESSEL

Regenerator dense phase temperature

Temperature °C

700
695
690
685
680
675
670

- Dense Phase T

17:16   18   19:12   20:09   21:07   22:04

Time

Excess O₂ **in flue gas**

B

6.5
5.5

- O2 (Online)

20:09   21:07   22:04   23:02

Time

OXY-COMBUSTION TECHNOLOGY DEVELOPMENT FOR FLUID CATALYTIC CRACKERS (FCC) – LARGE PILOT SCALE DEMONSTRATION

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ABSTRACT

The fluid catalytic cracking (FCC) process may represent as much as 30% of the total CO_2 emissions in a refinery. The oxy-combustion technology is a promising option to reduce these emissions and as part of the CO_2 Capture Project-Phase 3 (CCP3), Petrobras has retrofitted its large pilot scale FCC unit to demonstrate the technical viability of operating the unit at oxy-combustion conditions. The startup of the unit has shown that the transition from air to oxy is fast, however there must be a close monitoring of the excess O_2 in the flue gas as it may reach very low levels, taking the unit to a partial burn mode. Two extreme conditions were tested and called the same heat balance condition and same inerts flow rate condition. For the same heat balance, the O_2 content in the recycled gas mixture is around 29 %vol and there is minimum impact on unit operational conditions and product yields. For the same inerts rate, the O_2 content is close to 24 %vol and a higher overall feed conversion is observed due to a larger catalyst circulation. The oxy-combustion operation in this last condition allowed an increase of feed processing with very low changes in product slate. In all oxy tests, the CO_2 content in the flue gas showed values close to 95 %vol. Overall, the tests have demonstrated that it is technically viable to operate an FCC unit in the oxy-combustion mode.

About the CO$_2$ Capture Project (CCP)

The CCP was formed in 2000 to advance technologies and improve operational approaches to help make CCS a viable option for CO$_2$ mitigation. Today, this partnership of major energy companies is focused on delivering results from its demonstrations, field trials and studies. The group is made up of four teams; Capture, Storage, Policy & Incentives and Communications.

About the CCP Capture Team
The Capture Team is committed to developing technologies for reducing the cost of CO$_2$ Capture from the in-situ extraction of bitumen, oil, refining and natural gas power generation.

Please register on www.co2captureproject.org to receive updates on new project factsheets, technical papers and reports.

CO$_2$ Capture Project Phase Three participating organizations.

Contents

1. Introduction

The fluid catalytic cracking (FCC) process is one of the main sources of greenhouse gas emissions in the oil refining industry as an isolated source, equating to some 20-30% of total CO_2 emissions from a typical refinery. Capturing CO_2 from FCC flue-gas is therefore an important step in mitigating CO_2 emission of the refinery as a whole.

The conventional FCC process converts heavy oil fractions to lighter products such as liquid petroleum gas (LPG) and gasoline with the use of a cracking catalyst. During the reaction step, coke is also formed and deposited on the surface of the catalyst, which is then deactivated. To reestablish catalyst activity, the coke is burned in the regenerator with the use of air, thus forming CO_2, which is present in the flue-gas at typical concentrations of $10 - 20\%$ vol. at full combustion operation. The process works in a fluidized circulating bed type mechanism, with the catalyst circulating from the regenerator vessel to the reactor and back. The FCC unit is also thermally balanced, which means that the heat available from the burning of coke in the regenerator side accounts for the heat demand for feed vaporization and for the endothermic cracking reactions in the reactor side. One of the purposes of the catalyst is also to carry the heat released by the combustion of coke in the regenerator to the reaction side, so the amount of catalyst that circulates is dictated by this thermal balance. More information regarding the fluid catalytic cracking process may be found in the literature [1, 2].

Based on the characteristics of the FCC process, two possible ways to capture CO_2 from FCC units include post-combustion technologies, such as CO_2 absorption, as well as oxy-combustion. In a previous work [3], the oxy-combustion concept was shown to be a cost-effective alternative for CO_2 capture from FCC units and also pilot test results showed that this technology was ready to be taken to a larger scale. As part of the CO_2 Capture Project-Phase 3 (CCP3), Petrobras has retrofitted its large pilot scale FCC unit for operation at oxy-combustion conditions.

The main objectives of this work were to demonstrate the technical viability of operating an FCC unit in the oxy-combustion mode, to test the startup and shut down procedures and also to measure the impact of oxy-combustion operation in the main process variables and product yields.

2. Experimental

2.1. Test unit

The test unit has a capacity of processing up to 33 bbl/d of typical vacuum gasoil (VGO) feed, emitting around 1 ton/d of CO_2. Its scale, in terms of feed capacity, is close to 200 times larger than a conventional FCC pilot unit, but still 580 to 2000 times smaller than an industrial unit. Nevertheless, the size of the unit allows a very close approximation to an industrial unit, including the use of the same type of hardware found in industrial units, such as feed nozzles, regenerator two-stage cyclones, riser closed-coupled cyclones, structured packing stripper, use of lift and dispersion steam and an adiabatic system which assures a heat balanced unit. The adiabatic system allows the unit to respond in the same way as an industrial unit to changes in variables that affect the energy balance.

The reaction products from the unit are sent to a set of condensers where the liquid product is collected, weighted for material balance purposes and analyzed by GC SimDist (ASTM2887). The results are reported according to boiling range fractions: gasoline (C5-221 °C), light cycle oil - LCO (221°C-343 °C) and Bottoms (343+ °C). The gaseous products are quantified by a wet gas flowmeter and directed to the flare. The gas composition is determined by GC analysis and the results are reported as dry-gas (H_2, C1, C2, C2=), LPG (C3s and C4s) and gasoline in the gas phase (C5+), besides H_2S, CO_2 and N_2.

2.2. Unit retrofit

The unit has been retrofitted to allow operation in the oxy-combustion mode, with pure oxygen and a CO_2 recycle. The retrofit of the unit involved the design, construction and installation of an Oxygen Supply System (OSS) and a CO_2 Recycle System (CRS), as well as the integration of these systems with the pilot unit. There was also a need to develop and design a control strategy for start-up and continuous operation. Table 1 lists the major equipments installed while the general schematics showing the major equipments and system requirements for retrofitting the FCC pilot unit for oxy-combustion operation compared to air-fired operation are shown in Figure 1. Two full range CO_2 analyzers were installed at the flue gas line and also after the oxygen mixing point in the recycle stream (a new O_2 analyzer was also installed in this point).

2.3. Description of operation in oxy-combustion mode

During oxy-combustion operation, liquid oxygen stored in a tank is vaporized and used for the combustion of coke in replacement of air. In stable operation, the flue gas coming out of the regenerator consists mainly of carbon dioxide, water vapor and oxygen, with trace components of oxidized nitrogen (NOx) and sulfur (SOx) species. The gas is sent to the CO_2 recycle system, where it has particulate and SOx species removed in an alkaline washing tower (with structured packing) that uses a sodium hydroxide solution in counter flow. The pH of the alkaline solution is controlled between 7.5 and 8.5. The gas is sent to a second washing tower with structured packing that uses chilled water (at 10 °C) in counter flow to remove traces of sodium hydroxide and reduce the gas dew point. The gas than goes through a knock-out vessel with a demister and ultra fine solids filter before it is sent to be compressed. The cleaned gas is compressed from 0.2 bar g to around 11 bar g by a reciprocating, oil-free two stage compressor (model TZW70 supplied by Mehrer) and sent to a pressurized buffer tank. The CO_2 rich gas coming out of the tank is split into two streams, the majority of which is mixed with the pure oxygen (O_2 content ranging from 21 to 30 %vol) and directed back to the regenerator, while the remaining stream is vented to the atmosphere.

Table 1. Major equipments for Oxygen Supply and CO_2 Recycle systems

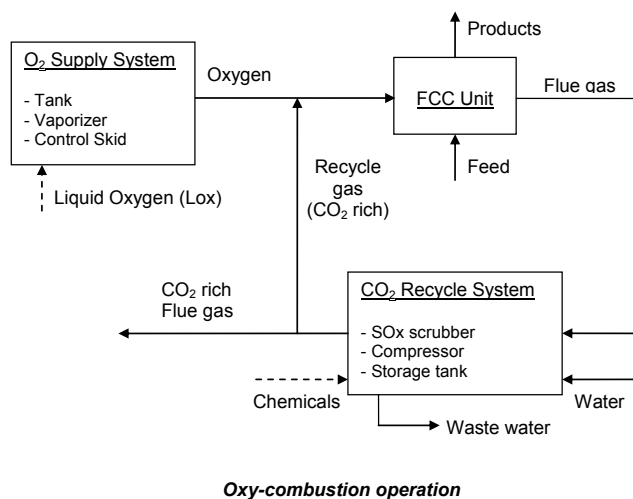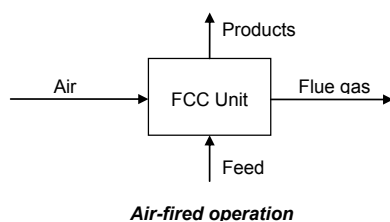|	Oxygen Supply System	CO_2 Recycle System
	Liquid O_2 tank	Catalyst fines and SOx removal unit
	Vaporizer system	Recycle compressor
Equipment List	Flow and pressure control skid	CO_2 storage tank
	Gaseous O_2 injector	Gas analyzers
	Piping	Piping

Fig. 1. Process Schematic of Air-Fired and Oxy- Combustion Operation

2.4. Test conditions

The operation in oxy-combustion may cause some impacts in the FCC unit, mainly due to different properties between nitrogen (present in air) and carbon dioxide (present in the recycle gas). Compared to N_2, CO_2 has a higher heat capacity (Cp) and specific gravity (ρ), which may affect the thermal balance of the unit and also catalyst fluidization and entrainment in the regenerator. Two of the conditions tested were planned to measure these impacts and they were called the same heat balance condition and the same volumetric flow rate condition.

In the same heat balance condition, the volumetric flow rate of recycled CO_2 would be only the amount sufficient to remove the same amount of heat from the regenerator as the nitrogen removes while in operation with air. Since CO_2 has a higher heat capacity compared to N_2, a smaller volumetric flow rate of CO_2 is needed to achieve this condition. This situation is illustrated in Figure 2. Since the oxygen demand remains the same (the amount of oxygen is that necessary to burn the coke), the lower volumetric flow rate of CO_2 during oxy-combustion implies that the recycle oxidant mixture will have a higher partial pressure of oxygen compared to air. Mass and energy balance calculations indicate that the oxygen partial pressure in this condition should be around 29 %vol. Since the heat balance of the FCC unit is not affected in this condition, the operating conditions are expected to remain the same, with minimum impact on products yields.

In the same volumetric flow rate condition, the volumetric flow rate of recycled CO2 would be exactly the same as that of N2 in air operation. Again, due to the larger heat capacity of CO2, the amount of heat removed from the regenerator would be greater compared to the operation with air (Figure 3). In this type of operation, the thermal balance of the unit is affected by the extra heat removed from the regenerator. In order to reestablish its thermal equilibrium, it is expected that the unit will increase catalyst circulation to account for the heat demand from the reaction side. In this new operating condition, it is expected that the catalyst to oil ration (CTO), which is the amount of catalyst per mass of feed, will increase and this may represent a gain in total feed conversion. However, due to the higher specific gravity of CO2, the total amount of solids entrainment is also expected to increase. This may affect the loss of catalyst fines through the regenerator.
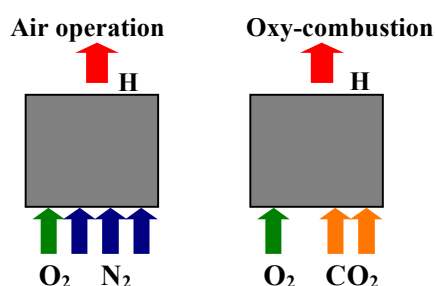

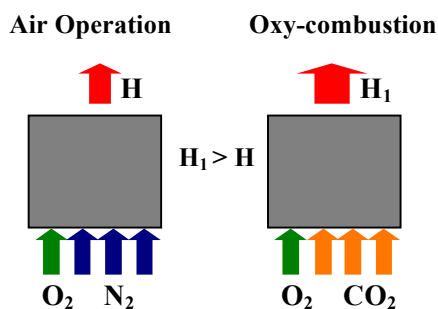Fig. 2. Oxy-combustion operation in the same heat balance condition

Fig. 3. Oxy-combustion operation in the same volumetric flow rate condition

3. Results and discussion

3.1. Plant startup

The objective of the startup phase was to perform short oxy-combustion trials to evaluate the operability of the entire system, identify possible limitations of the units and anticipate problems so that the tests could be carried-out.

The first startup trials targeted the same volumetric flow rate condition and therefore a 21% vol O_2 content in the recycled gas was initially established. Figure 4 shows the moment of transition between air operation and oxy-combustion in one of the trials and also the change in flue gas composition. For this trial, the full range CO_2 online analyzer was not fully operational and so gas samples were collected and analyzed by gas chromatography. The switch between air and oxy-combustion operation is very fast and simple, usually taking around 5 to 15 minutes. However, the transition from N_2 to CO_2 is gradual and may take up to four hours until stable oxy-combustion operation is achieved. Although the volumetric flow rate was held constant as the transition occurred, the mass flow rate of oxidant gas mixture (recycled gas + pure O_2) increased (Figure 4B) as a consequence of the change in gas composition since CO_2 has a higher molar weight than N_2.

Figure 5 shows the changes in some variables as the transition proceeded. The dense catalyst bed temperature in the regenerator (dense phase temperature) is mainly influenced by the amount of coke that is burned, the amount of heat that is removed (with the flue gas) and catalyst circulation. Since the CO_2 removes more heat from the regenerator than N_2, the dense phase temperature tends to decrease when the oxy-combustion operation is at the same volumetric flow rate condition (Figure 5A). As a consequence, the catalyst circulation increases to account for the heat demand in the reactor side, which remains the same as in air operation. The higher catalyst circulation results in a higher catalyst to oil ratio and consequentially in a higher feed conversion, which in turn increases the production of coke and also the O_2 demand in the regenerator side to burn the additional coke. Therefore, to maintain the full burn operation (when all coke is converted to CO_2), with the excess oxygen in flue gas at reasonable levels, a constant adjustment in the flow rate of the oxidant gas mixture must be made. Initially this was rather difficult to control and Figure 5B shows that the excess oxygen reached very low levels during the transition, possibly going to a partial burn mode (when some of the coke is converted to CO and not all the way to CO_2) at some points. Surely the difficulties aroused since this extra oxygen must be supplied by the recycled oxidant gas, and if a 21 vol% of O_2 is set for this stream (as it was initially made), the fall in dense phase temperature may be too large and affect the combustion kinetics and again contribute to move the regenerator into a partial burn condition. In fact, Figure 5A shows that the temperature drop was very intense up to half of the trial, when the temperature reached a value close to 675 °C. At this point, some measures were taken as an attempt to increase the regenerator temperature, such as the increase in oxidant inlet temperature, increase of feed temperature and flow rate (Figure 6). These measures did increase the dense phase temperature to some extent, however stable operation at a controlled and adequate excess O_2 level was only obtained after a slight oxygen enrichment was allowed by increasing only the pure oxygen flow rate, as shown by the times disclosed in Table 2 and Figure 5B.

This same effect was also observed in other trials and the slight oxygen enrichment was found to be necessary for stable operation in oxy-combustion mode. This new condition was therefore caller the same inerts volumetric flow rate condition, as only the volumetric flow rate of CO_2 would be the same as that of N_2 (in air operation), while the O_2 flow rate would need to be different.
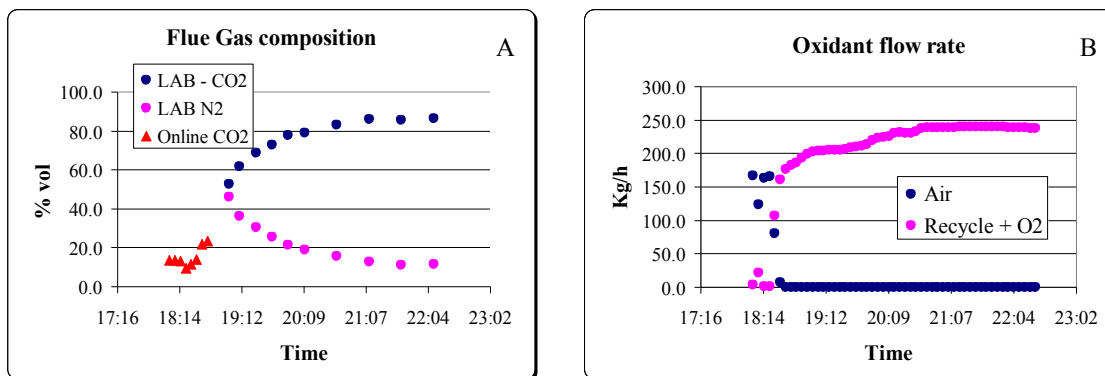
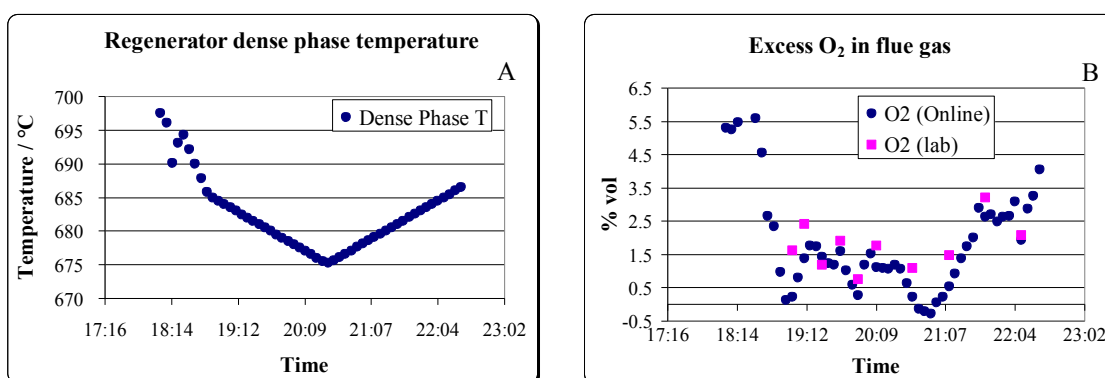Fig. 4. Transition from air to oxy-combustion operation

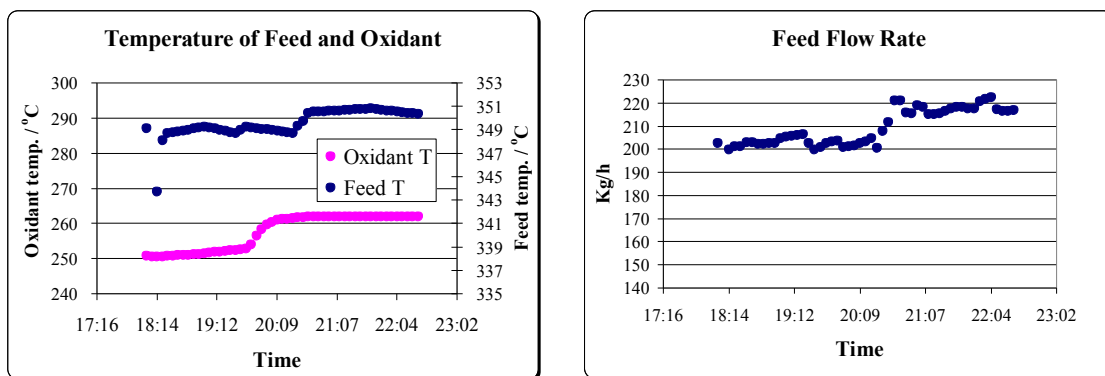Fig. 5. Changes in FCC dependent variables during transition from air to oxy-combustion operation

Fig. 6. Changes in FCC independent variables during transition from air to oxy-combustion operation

Table 2. Recycled oxidant gas mixture composition

	Time		
vol %	22:10	22:20	22:30
O_2	22.9	23.5	24.2
CO_2	67.5	67.0	66.2
N_2	9.6	9.6	9.6

3.2. Oxy-combustion tests

Several tests were made in the oxy-combustion mode at the same heat and same inerts flow rate conditions and compared to the operation with air. The values of some independent and dependent variables, as well as the flue gas composition for one series of tests are shown in Table 3, while the relative change in product yield and catalyst entrainment for the oxy cases compared to the base case are displayed in Table 4. All data shown represent the average value of a 2 hour period at stable conditions. For both oxy-combustion cases, the CO_2 content in flue gas achieved very high values, above 94%. The N_2 remaining in the flue gas is most likely to be from the use of instrument sealing gas in the reactor side and catalyst transfer line (standpipes), which in this specific unit is pure nitrogen and is carried over to the regenerator by the circulating catalyst. In industrial units, steam is used for this purpose and therefore the CO_2 content in flue gas is expected to be even higher.

For the same heat balance case, the amount of heat removed from the regenerator is supposed to be the same, and what characterizes this condition is an equal regenerator dense phase temperature on both air and oxy operation. To achieve this condition, the volumetric flow rate of CO_2 (inert gas) recycled back to the regenerator was 30% lower than the volumetric flow rate of N_2 in air operation and as a result, the O_2 content in the recycled gas was around 29 mol%. Since the thermal balance of the unit was not altered, the catalyst circulation and consequentially the catalyst to oil ratio remained the same. The impact on product yields was minimum, with little relative change compared to the base case. In addition, although the specific gravity of CO_2 is higher than N_2, the lower flow rate resulted in a 67% decrease in catalyst entrainment. Ultimately this represents a considerable decrease in solids loading to the regenerator cyclones.

Table 3. Values of independent and dependent variables for the oxy-combustion tests

Test condition	Air	Oxy	Oxy	Oxy
	Base case	Same heat	Same inert	Same inert/+Feed
Independent variable				
Reaction temperature, °C	540	540	540	540
Feed temperature, °C	350	349	348	350
Feed flow rate, kg/h	150	150	150	165
Air/oxidant temperature, °C	249	249	251	250
Excess O_2 in flue gas, mol%	2.7	2.6	2.5	3.1
Dependent variable				
Regenerator dense phase temp., °C	710	709	689	699
Catalyst to oil ratio (CTO)	6.7	6.8	7.9	7.2
%O_2 in oxidant gas, mol %	21	28.9	23.8	24.9
Inert vol. flow rate (m^3/h)	123	87	117	118
Flue gas composition, mol % (dry)				
CO_2	14.2	94.3	94.8	94.5
O_2	2.7	2.6	2.5	3.1
N_2	83.1	3.1	2.5	2.4
CO	0.00	0.06	0.11	0.01

To achieve the same inert volumetric flow rate condition, the amount of CO_2 recycled back to the regenerator was kept the same as the flow rate of N_2 in air. Due to the higher heat capacity of CO_2, the amount of heat removed from the regenerator is also higher and this was clearly characterized by a 20 °C drop in the dense phase temperature. As a result, the catalyst to oil ratio increased by 18% compared to the base case. The feed conversion and coke yield also increased, as expected (Table 4), and because of the higher coke production, the oxygen demand increased, thus explaining the O_2 content close to 24 mol% in the recycled gas. On the other hand, the solids entrainment increased almost 34% due to the higher specific gravity of CO_2. This ultimately shows that the amount of solids loaded to the internal regenerator cyclones increases in this condition and this may have a negative impact on the cyclones performance. Further testing is still needed to better understand this impact.

It is important to point that in this condition, the bottoms conversion increased by 15%, which is a remarkable result, as this may allow the FCC unit to operate with a higher feed rate or processing a lower quality (heavier) feed. For this condition the main products (LPG+gasoline) yields increased by almost 3.5 %, while it did not change for the same heat balance condition.

The results from these two extreme conditions (same heat and same inerts) indicate that it is possible to operate the unit at an intermediate oxy-combustion condition, where the amount of solids entrainment will be the same as in air operation, but the heat removed from the regenerator will still be slightly higher and the gains from an increased catalyst circulation may still be obtained.

An additional test condition was performed with a 10% feed flow rate increase and the results are also displayed in Tables 3 and 4. This test was designed to measure whether the gain in flexibility shown during operation in oxy-combustion at the same inerts condition, which was characterized by the drop in regenerator temperature and higher catalyst circulation, could allow an increase in feed throughput without impact on product slate. For this condition, the inerts volumetric flow rate was kept the same and the feed flow rate was increased. The results showed that with a 10% feed flow rate increase, there was still a lower regenerator temperature and higher circulation compared to air operation. Since the heat demand on the reactor side increased due to a larger amount of feed being processed, the coke production increased and so did the oxygen demand in the regenerator to bun the additional coke. As a result, the O_2 content in the oxidant gas mixture was higher than in the same inerts case (Table 3). The relative change in product yields compared to the air operation showed that there was still a slightly higher bottoms conversion with slightly higher gas and coke, although the main products (LPG+gasoline) yield was the same. When compared to the same inerts case, this condition shows an even higher solids entrainment as the total gas flow rate through the regenerator increases (higher O_2 flow rate) and also does the temperature, which changes the gas viscosity and superficial velocity. Nevertheless, this test has shown that it is possible to increase the feed throughput with low impact on product slate while operating an FCC unit in oxy-combustion mode. This may certainly contribute to lower the overall CO_2 capture cost for this technology.

Table 4. Relative change in product yields and catalyst entrainment

Test condition	% change relative to base case		
	Oxy Same heat	Oxy Same inert	Oxy Same inert/+Feed
Yields (mass basis)			
Dry gas	-1.9	-1.6	5.6
LPG	2.8	6.7	4.4
Gasoline	-0.8	2.4	-1.4
Gasoline + LPG	0.1	3.4	0.1
LCO	-1.4	-4.5	-2.2
Bottoms	-2.3	-14.9	-4.4
Coke	0.8	9.0	1.1
Conversion	1.0	4.9	1.7
Solids entrainment	-67.9	33.6	45.3

4. Conclusion

The Oxy-combustion demonstration tests in the large FCC pilot plant have shown that this technology is a technically viable option for CO_2 capture in industrial FCC plants.

Overall, the experience obtained showed that the shift from air to oxygen is relatively fast, taking, in average, from 5 to 15 minutes to be concluded. However, there must be a close monitoring of the excess O_2 in the flue gas after the transition takes place since it may reach very low levels as the CO_2 content in the recycle gas increases. To avoid a partial burn condition in the regenerator, there must be a constant adjustment of the O_2 flow rate during this transition. The starting dense phase temperature is an important variable for stable operation, especially for the same volumetric flow rate condition. As the gas is recycled, the regenerator temperature may significantly decrease due to the larger heat capacity of CO_2 compared to N_2, and therefore the coke burn rate may be affected. Whenever possible, the unit must be adjusted to start operation with a higher regenerator temperature.

To avoid an excessive drop in dense phase temperature, the targeted condition should not be that of the same volumetric flow rate, but rather the same inerts flow rate, which implies in a slight O_2 enrichment in the oxidant gas mixture during oxy-combustion operation. In this mode of operation, the O_2 content in the recycle oxidant mixture is typically between 23 - 24 %vol. Alternatively the unit may be operated in the same heat balance condition, where the amount of CO_2 recycled is just enough to keep the same heat removal from the regenerator. In this mode of operation, the O_2 content in the recycled oxidant gas mixture is close to 29 %vol. and the impact in the main operational variables of the unit, including product yields is minimum.

During oxy-combustion operation in the same inerts volumetric flow rate condition, the higher specific gravity of CO_2 increases the entrainment rates and thus the solids loading to the internal regenerator cyclones, which may have a negative impact on the cyclones performance. However, the drop in the regenerator dense phase temperature increases catalyst circulation, leading to an overall higher feed conversion, with a significant gain in bottoms conversion.

The gain in flexibity during operation in oxy-combustion at the same inerts condition, characterized by the drop in regenerator temperature and higher catalyst circulation, allowed an increase in feed throughput with very low impact on product slate and this certainly may contribute to lower the overall CO_2 capture cost for this technology.

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[3] Mello, L.F., Pimenta, R.D.M., Moure, G.T., Pravia, O.R.C., Gearhart, L., Milios, P.B., Melien, T., A technical and economical evaluation of CO_2 capture from FCC units. *Energy Procedia* 2009; **1**: 117-124.

CO₂ Capture Project®

CO₂ Capture Project Phase Three participating organizations