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## PART 2

# Post Combustion CO<sub>2</sub> Capture Captage de CO<sub>2</sub> en postcombustion

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# A Technical and Economical Evaluation of CO<sub>2</sub> Capture from Fluidized Catalytic Cracking (FCC) Flue Gas

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**Résumé — Évaluation technico-économique du captage du CO<sub>2</sub> présent dans les fumées d'une unité FCC (Fluidized Catalytic Cracking)** — Les contraintes environnementales actuelles relatives aux gaz à effet de serre et parmi eux le CO<sub>2</sub> vont devenir des challenges à relever à court terme. La pression sur l'industrie et par conséquent sur le raffinage afin de limiter et de gérer les émissions de CO<sub>2</sub> va vraisemblablement se renforcer dans les prochaines années.

L'industrie du raffinage contribue pour 2,7 % aux émissions totales de CO<sub>2</sub>. Le craquage catalytique en lit fluidisé (FCC) qui est l'un des procédés principaux du raffinage, représente à lui seul 20 % des émissions de CO<sub>2</sub> de la raffinerie. Sachant que ce type d'unité est présente dans une raffinerie sur deux, on comprend bien le défi à trouver des technologies afin d'en gérer les émissions.

Sur la base d'un cas industriel, les objectifs de cette étude sont de déterminer si la technologie HiCapt<sup>+</sup>, développée pour les centrales électriques, constitue une solution pertinente pour le domaine du raffinage et particulièrement pour le procédé FCC ainsi que d'évaluer le coût additionnel associé qui devra être supporté par les raffineurs.

**Abstract — A Technical and Economical Evaluation of CO<sub>2</sub> Capture from Fluidized Catalytic Cracking (FCC) Flue Gas** — Environmental issues, related to greenhouse gas and among them CO<sub>2</sub>, are becoming short term challenges. Pressure on industries and therefore on refining to limit and manage CO<sub>2</sub> emissions will be reinforced in next few years.

Refining industry is responsible for about 2.7% of global CO<sub>2</sub> emissions. Fluidized Catalytic Cracking unit (FCC), one of the main process in refining, represents by itself 20% of the refinery CO<sub>2</sub> emissions. As FCC unit is present in half of the refining schemes, it is challenging to find technologies to manage its emissions.

Based on an industrial case, the aims of the presented work are to determine if amine technology HiCapt<sup>+</sup>, developed for power plant, might be a relevant solution to manage FCC CO<sub>2</sub> emissions and to evaluate the additional cost to be supported by refiners.

## INTRODUCTION

Environmental issues and global warming effect are going to strengthen, in short and mid term, greenhouse gas limitations and among them CO<sub>2</sub> emissions. In Europe, pressure on industries have been reinforced, in the last few years by legislation and the two first stages of European Union Emission Trading System (EU ETS). Currently, the cost of a ton of CO<sub>2</sub> emission is quite low (6.5 euros/ton) and this is due to an excess of CO<sub>2</sub> quotas estimated at around 13%.

Stage three of EU ETS is going to be spread for 2013-2020 period. The main differences of this new stage compared to the previous ones will be a decrease of free quotas by 1.75% per year and an increase of no free CO<sub>2</sub> proportion with a final target in 2020 fixed at 70% of total quotas. It means that in 2020, CO<sub>2</sub> quotas will be limited by 21% compared to 2005 situation. In this context, refiners will have to reduce by around 10% their current CO<sub>2</sub> emissions or will have to buy quotas on CO<sub>2</sub> market.

As a reminder, refining industry is responsible for about 2.7% of global CO<sub>2</sub> emissions. The top five of most CO<sub>2</sub> emitters are the vacuum distillation unit (10%), the topping tower (15%), the utility production unit (17%), the steam methane reforming (in the range from 10 to 50% depending on refining scheme) and the Fluidized Catalytic Cracking Unit (FCCU) (20%).

In 2013, refining margins in Europe are low (less than 2 dollars per barrel). This new financial constraint related to CO<sub>2</sub> will be therefore negatively impact for refiners. This implies that there is a need for technological solutions in order to minimize CO<sub>2</sub> emissions for refining processes.

This is especially true for FCCU in the extent that it is one of the main CO<sub>2</sub> contributors and that coke production and combustion during regeneration step are required to run the unit. FCC process converts heavy oil fractions to lighter products such as Liquefied Petroleum Gas (LPG) and gasoline by means of a cracking catalyst. During the reaction step, coke is formed and deposited on the surface of the catalyst, which is then deactivated. To recover catalyst activity, coke is burnt in a regenerator with air and CO<sub>2</sub> is formed. FCC flue gas contain about 10-20% mol of CO<sub>2</sub> for example in full combustion mode. Heat produced in regeneration section is transferred through the catalyst in the reaction section to vaporize the feedstock and to reach the desired riser outlet temperature. The heat balance between regeneration section and reaction section is one of the key points of this process.

The capture of CO<sub>2</sub> from FCC flue gas is therefore a good way to reduce GHG emissions in refineries.

Post-combustion technologies such as CO<sub>2</sub> absorption may be used. The objective of this study is to evaluate the CO<sub>2</sub> capture from flue gas of an industrial FCC unit with available amine technology HiCapt<sup>+TM</sup> [1] developed by IFP Energies nouvelles and PROSERMAT. Feasibility and costs have been evaluated.

This work has been carried out within the FCC Alliance program developed by Total, Technip, Axens and IFP Energies nouvelles.

## 1 DESCRIPTION OF HICAPT+ AMINE PROCESS FOR CO<sub>2</sub> CAPTURE

Simplified process flow diagrams of HiCapt<sup>+TM</sup> process for CO<sub>2</sub> post-combustion capture and CO<sub>2</sub> compression are presented in Figure 1 and Figure 2.

Flue gas temperature at inlet of HiCapt<sup>+TM</sup> unit is around 50°C. In conventional schemes, a water quench tower is mandatory to cool down flue gas to 50°C. Flue gas enters the amine capture unit at atmospheric pressure. A blower is used to increase the pressure in order to compensate for the pressure drop through the absorber and to allow the evacuation of treated gas towards the stack.

Flue gas specifications at inlet of HiCapt<sup>+</sup> unit are provided in Table 1.

After the blower, the flue gas is introduced at the bottom of the absorber. This column uses a random or structured packing. The lean solvent is introduced at the top of the absorption section. The solvent is an aqueous solution of MonoEthanolAmine (MEA) at 40 wt%. The solvent and the flue gas flows circulate in counter-current manner through the packing. CO<sub>2</sub> present in flue gas diffuses through the solvent and reacts with MEA. The internal packing enhances mass transfer between the gas and liquid to ensure an optimum efficiency of the CO<sub>2</sub> capture. The absorption zone and the lean MEA flow rate are designed to reach a 90% CO<sub>2</sub> capture.

The decarbonised gas continues its rise through the washing section zone of the absorber, also equipped with packing. This section recovers the MEA and other organic compounds in the vapour (thermodynamic and mechanical entrainments) thanks to water washing at the top of the column. This zone reduces the amounts of degradation products and MEA contained in flue gas (volatile organic compounds, mainly NH<sub>3</sub>, MEA, etc.). Part of water extracted from washing zone is sent to the main solvent loop in order to keep a neutral water balance.

The decarbonised flue gas from the absorber is released to the atmosphere. The content of residual MEA is negligible.

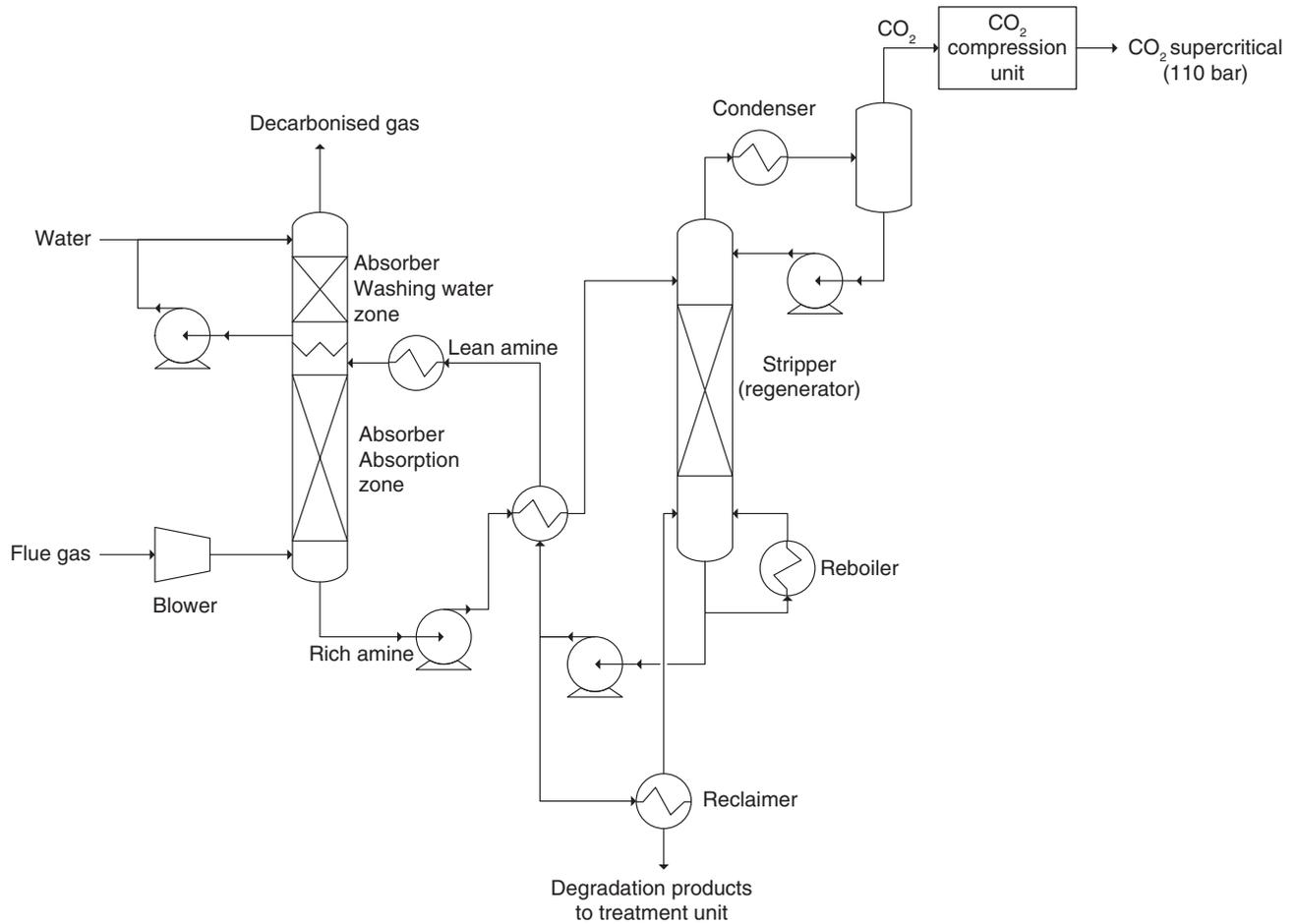


Figure 1  
Simplified process flow diagram of HiCapt<sup>+</sup> [1] process.

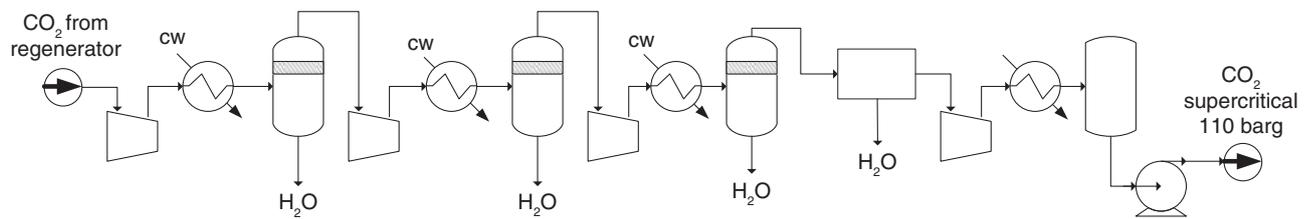


Figure 2  
CO<sub>2</sub> compression unit.

The solvent outlet at the bottom of absorber, highly loaded in CO<sub>2</sub>, is pumped and then preheated in the heat recovery exchanger, from 60°C to 100°C approximately, by the regenerated solvent coming from the bottom of the stripper (also called regenerator). The preheated solvent is introduced into the stripper, at a pressure between 1 and 2 bar approximately. The rich solvent circulates

through the packed column. In the bottom of a regenerator, a reboiler vaporizes a part of the solvent to provide the thermal energy necessary for regeneration.

The regenerated lean solvent is pumped towards the heat recovery exchanger for the preheating of the rich solvent. The temperature of the lean solvent decreases from 120°C to 70°C approximately. A second heat

TABLE 1  
Flue gas specifications for HiCapt<sup>+</sup>™

Component	Specification
SO <sub>2</sub>	< 10-20 mg/Nm <sup>3</sup>
NO <sub>2</sub>	< 15 mg/Nm <sup>3</sup>
NO <sub>x</sub>	< 200 mg/Nm <sup>3</sup>
Particulates	< 10 mg/Nm <sup>3</sup>

exchanger makes it possible to cool the lean solvent to around 50°C before storage and injection in the absorber.

The CO<sub>2</sub> recovered at the top of stripper, containing steam, is sent towards the condenser. The condensate returns towards the regeneration column and the CO<sub>2</sub> flow, with a purity greater than 99.9 mol% (except water content), is then conditioned for its transportation and injection. The conditioning phase needs several stages of compression/condensation and pumping to change CO<sub>2</sub> into a supercritical state at 110 barg, this pressure being able to vary according to specificities of each case.

Moreover, part of the regenerated solvent resulting from the regeneration column is sent towards a batch boiler. This equipment named “reclaimer” enables the vaporization of the solvent (H<sub>2</sub>O + MEA) to concentrate in an aqueous phase the degradation products (heat stable salt). These by-products are treated by an additional water treatment unit.

The degradation of the solvent is highly limited thanks to the addition of an inhibitor [2] of the reactions due to oxygen. The additive makes it possible to strongly decrease the ammonia emission and to reach the emissions specification at lower costs.

## 2 INDUSTRIAL FCC UNIT

### 2.1 FCC Unit Description

To evaluate the feasibility of CO<sub>2</sub> capture from FCC flue gas, an industrial case has been considered. The FCC unit evaluated in this study is located in Europe with processing capacity of 60 000 BPSD (Barrels Per Stream Day). For this case, FCC feed is an hydrotreated vacuum gas oil and the unit operates in maximum gasoline mode (gasoline yield around 51% of fresh feed).

An expander is installed on flue gas from the regenerator. This expander is coupled with the Main Air Blower (MAB). The flue gas at the expander outlet is sent to a waste heat boiler that cools the flue gas and generates a high pressure steam.

The flue gas at waste heat boiler outlet is sent to an ElectroStatic Precipitator (ESP) to reduce particulates content and then vented to the atmosphere through the stack.

The temperature of the flue gas at the outlet of ESP is around 250°C.

Wet gas or vapors from the main fractionator overhead reflux drum are compressed by the Wet Gas Compressor (WGC). The WGC is a two stage inter-cooled centrifugal machine generally driven by a steam turbine or by an electrical motor. The wet gas compressor of the industrial FCC unit considered for this study is driven by an electrical motor.

### 2.2 FCC Flue Gas Characteristics

The properties of the FCC flue gas are given after heat recovery in a waste heat boiler and after the electrostatic precipitator. This composition is comparable with values provided by [3].

Flue gas properties are presented in Table 2.

Despite the presence of an electrostatic precipitator, the content of particulates in flue gas is too high for HiCapt<sup>+</sup>™ process (Tab. 1, 2). Deeper SO<sub>2</sub> and NO<sub>x</sub> removals from FCC flue gas are also required for HiCapt<sup>+</sup>™ process (Tab. 1, 2).

### 2.3 CO<sub>2</sub> Balance of FCC Unit

A simplified CO<sub>2</sub> balance of FCC unit (Tab. 3) has been estimated considering the three main contributors which are:

- coke combustion;

TABLE 2  
FCC flue gas characteristics

Pressure	0.04	barg
Temperature	250	°C
Composition		
N <sub>2</sub>	77.5	mol%
CO <sub>2</sub>	17.7	mol%
H <sub>2</sub> O	3.6	mol%
O <sub>2</sub>	1.2	mol%
SO <sub>2</sub>	134	mg/Nm <sup>3</sup>
NO <sub>x</sub>	118	mg/Nm <sup>3</sup>
CO	15	mg/Nm <sup>3</sup>
Particulates	30	mg/Nm <sup>3</sup>

- electricity consumption for wet gas compressor and main air blower;
- steam balance (consumption – production).

### 3 CO<sub>2</sub> CAPTURE FROM FCC FLUE GAS WITH HICAPT™ AMINE PROCESS

#### 3.1 FCC Flue Gas Pre-Treatment before CO<sub>2</sub> Capture

SO<sub>2</sub> and NO<sub>x</sub> removal technologies were investigated. Two different technologies for SO<sub>2</sub> and NO<sub>x</sub> removals, wet and dry scrubbers, were proposed. In both cases, the temperature of FCC flue gas is 250°C.

#### 3.1.1 Wet Scrubber Technology (Fig. 3)

In this case, the gas treatment consists of dust capture by electrostatic precipitator at 250°C, then a catalytic DeNO<sub>x</sub> scrubber at 250°C with injection of ammonia solution (NH<sub>4</sub>OH) 25 wt%. The DeSO<sub>x</sub> washing section (with caustic soda) reduces the SO<sub>2</sub> concentration at 10 mg/Nm<sup>3</sup>. The DeSO<sub>x</sub> unit works at low temperature (about 50°C). This technology is mature. The electrofilter is mandatory according to the wet scrubber supplier.

#### 3.1.2 Dry Scrubber Technology (Fig. 4)

In case dry scrubber is used, an inlet temperature of 200°C is recommended based on the reactant used

TABLE 3  
Simplified CO<sub>2</sub> balance of FCC unit

	Value	CO <sub>2</sub> emission factor	CO <sub>2</sub> eq (t/h)
Coke combustion	18.4 t/h	3.4 t CO <sub>2</sub> eq/t of coke	62.9
Electricity consumption for MAB and WGC	6.1 MW	148 g CO <sub>2</sub> eq/MJ of electricity <sup>(1)</sup>	3.3
Steam balance (consumption – production)	-47.8 MW	72 g CO <sub>2</sub> eq/MJ of steam <sup>(2)</sup>	-12.4
Total			53.8

<sup>(1)</sup> Corresponding to world average (2004),

<sup>(2)</sup> Corresponding to steam production in a boiler with typical refinery fuels.

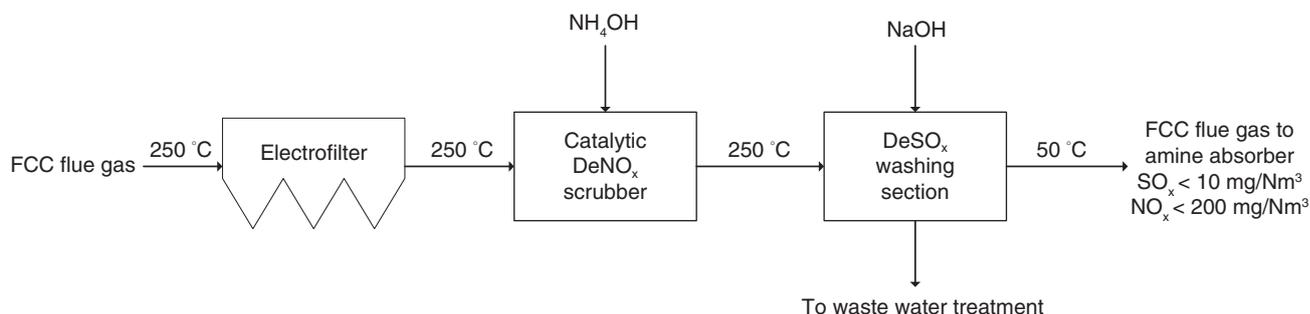


Figure 3

Wet scrubber technology.

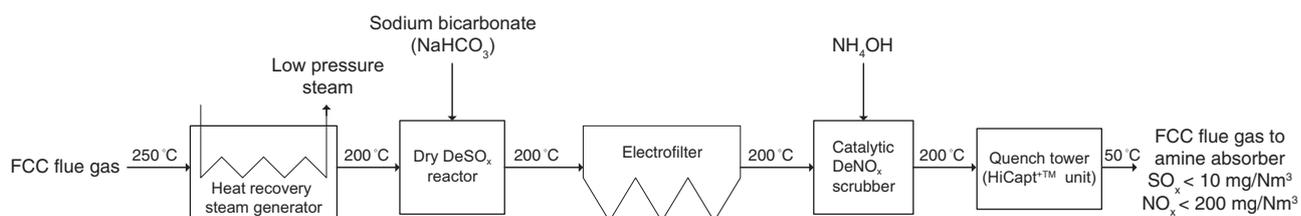


Figure 4

Dry scrubber technology.

(sodium bicarbonate  $\text{NaHCO}_3$ ) and the  $\text{DeSO}_x$  scrubber dry reactor. The gas treatment requires a cyclone to protect the electrofilter. After the electrofilter, the  $\text{DeNO}_x$  scrubber works at  $200^\circ\text{C}$  adding  $\text{NH}_4\text{OH}$ . This technology works at  $200^\circ\text{C}$  and it is necessary to reduce the temperature from  $250^\circ\text{C}$  to  $200^\circ\text{C}$  before the dry  $\text{DeSO}_x$  reactor. Heat recovery on FCC flue gas can be implemented to recover heat from  $250^\circ\text{C}$  to  $200^\circ\text{C}$ . 6.3 t/h of Low Pressure (LP) steam can be generated. In the case of dry scrubber, the quench tower at the amine capture section is required to cool down the flue gas from  $200^\circ\text{C}$  to  $50^\circ\text{C}$ . This technology is considered more complex than the wet scrubber solution.

### 3.2 Impact of Pre-Treatment on $\text{CO}_2$ Capture

The design of the amine unit is independent of the  $\text{DeSO}_x/\text{DeNO}_x$  technology. The gas composition before  $\text{DeSO}_x/\text{DeNO}_x$  unit implies that it is undersaturated at  $50^\circ\text{C}$  and requires make-up water to reach a neutral water balance in the process battery limits.

For a wet scrubber technology, the make-up water comes from the  $\text{DeSO}_x$  washing tower. In this case, the flue gas could be injected directly at the bottom of the absorber.

For a dry scrubber technology, a quench tower is required before the absorber, to decrease the temperature from  $200^\circ\text{C}$  to  $50^\circ\text{C}$ . The water saturation occurs in this equipment and the make-up is added to the water cooling loop directly.

### 3.3 Utilities for Flue Gas Pre-Treatment and $\text{CO}_2$ Capture

The list of utilities used for pre-treatment and  $\text{CO}_2$  capture and compression is indicated in Table 4.

TABLE 4  
Chemicals and utilities balance for HiCapt<sup>+</sup> process

Caustic soda
Sodium bicarbonate (for dry scrubber case only)
Ammonia aqueous
MEA
Anti-oxidation additive
Electricity
LP steam
Cooling water

The main contributors of HiCapt<sup>+</sup> operating cost are low pressure steam (3 GJ/t of captured  $\text{CO}_2$ ), electricity and cooling water.

### 3.4 $\text{CO}_2$ Balance of FCC Unit with HiCapt<sup>+</sup> Process

As for the reference case, a simplified  $\text{CO}_2$  balance has been performed for FCC unit but at that time a more severe flue gas post treatment and the  $\text{CO}_2$  capture on flue gas were considered.

This  $\text{CO}_2$  balance has been estimated to 14.1 t  $\text{CO}_2\text{eq/h}$  that is to say a reduction of 74% of  $\text{CO}_2$  emissions of the reference case.

As an FCC unit represents around 20% of refinery total  $\text{CO}_2$  emissions, HiCapt<sup>+</sup> association with an FCC unit will remove more than 14% the refinery emissions and therefore much more than the required target of 10% as presented in the introduction.

Nevertheless, the cost associated with this significant GHG emission reduction has to be evaluated.

### 3.5 Economical Evaluation of $\text{CO}_2$ Capture with HiCapt<sup>+</sup> Process

The following section presents investment and operating cost estimates considering the wet scrubber technology for  $\text{DeSO}_x/\text{DeNO}_x$ .

#### 3.5.1 Investment Cost Estimation

ISBL (InSide Battery Limit) cost of FCC unit has been estimated without and with  $\text{CO}_2$  capture on flue gas. Results are presented in Table 5.

#### 3.5.2 Operating Cost Estimation

HiCapt<sup>+</sup> shows energy consumption between 3.1 to 3.3 GJ to reduce  $\text{CO}_2$  emissions by one ton. This places HiCapt<sup>+</sup> among the most currently effective process technologies. A techno-economic evaluation of HiCapt<sup>+</sup> compared to 30 wt% MEA process shows a reduction of around 15% in the cost of  $\text{CO}_2$  captured [1].

Operating cost of an FCC unit has been estimated with and without the  $\text{CO}_2$  capture system on flue gas. Operating cost includes utilities, chemicals and catalyst

TABLE 5  
ISBL cost

	FCC unit without $\text{CO}_2$ capture	FCC unit with $\text{CO}_2$ capture
ISBL (MS)	Base	Base $\times$ 1.25

TABLE 6  
Operating cost

	FCC unit without CO <sub>2</sub> capture	FCC unit with CO <sub>2</sub> capture
Operating cost	Base + CO <sub>2</sub> penalty of 75 \$/t CO <sub>2</sub> avoided	Base

costs. Results are presented in Table 6. A penalty at 75 €/t of CO<sub>2</sub> avoided must be compared with the cost of CO<sub>2</sub> avoided in a refinery. In a recent study [4], the cost of CO<sub>2</sub> capture lies in the range of 40-263 €/t CO<sub>2</sub>-refinery-avoided. Process integration between the capture process and the refinery is a key point to reduce costs, for example using excess heat or combined with heat pumps.

As presented in CO<sub>2</sub> balance, one of the main contributors to CO<sub>2</sub> in FCCU is the compressors and especially the wet gas compressor. In order to go further in FCC CO<sub>2</sub> reduction, it is therefore interesting to investigate and evaluate solutions to reduce utilities required for this compressor.

### 3.6 Impact of Wet Gas Compressor Driver

Generally, wet gas compressors are driven by condensing steam turbines or electric motors as in the reference

case considered previously. In condensing steam turbines, exhaust steam is in a partially condensed state (vapor fraction near 90%) and at a pressure well below atmospheric. Exhaust steam is then condensed with water (Fig. 5).

When steam is preferred to drive the wet gas compressor and when HiCapt<sup>+</sup>™ process is used for CO<sub>2</sub> capture, it is interesting to use a back-pressure steam turbine instead of a condensing steam turbine. The back-pressure steam turbine will consume more high pressure steam but low pressure steam at turbine outlet can be used directly in HiCapt<sup>+</sup>™ process for amine regeneration (Fig. 6).

The back-pressure steam turbine has the advantage to reduce the consumption of the cooling water of the process. A water condenser for vacuum steam condensation is no more needed. The flow rate of cooling water to condense vacuum steam is always very high.

The variation of operating cost and GHG emissions for the system “WGC + amine regeneration” is indicated in Table 7 compared to a total condensing steam turbine.

The back-pressure turbine is therefore a relevant solution to limit CO<sub>2</sub> emissions if there is a specific need of LP steam as it is when amine capture is implemented.

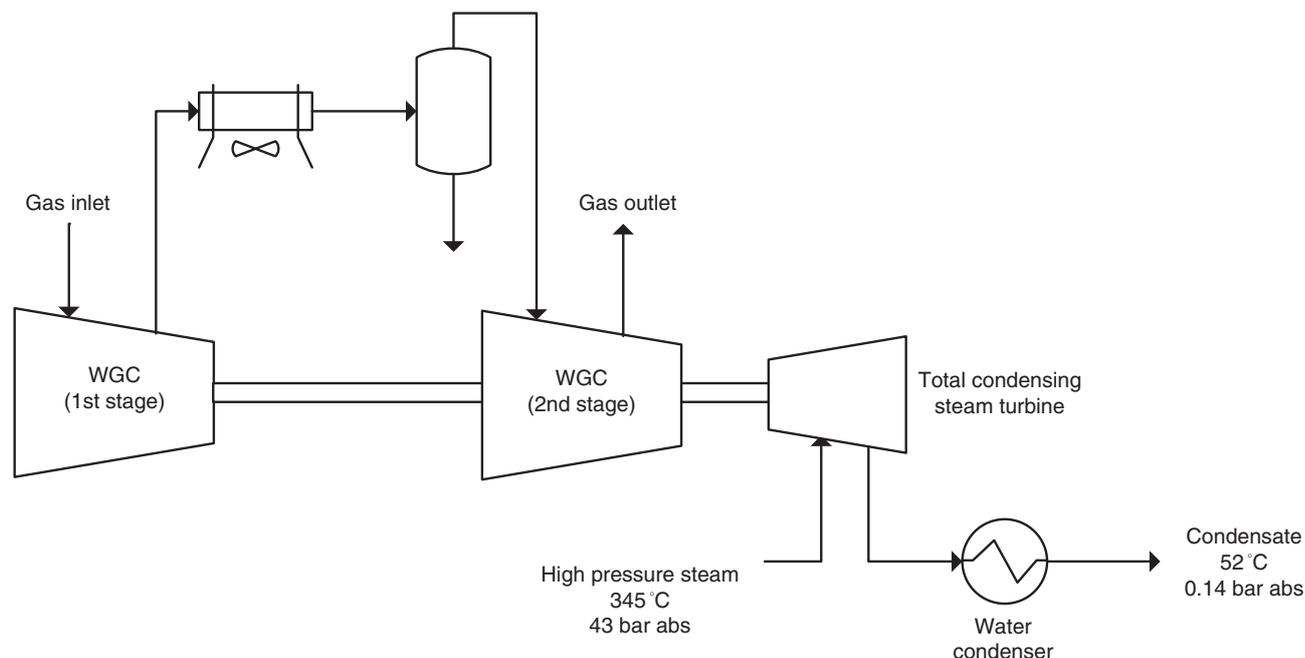


Figure 5

Wet gas compressor driven by a condensing steam turbine.

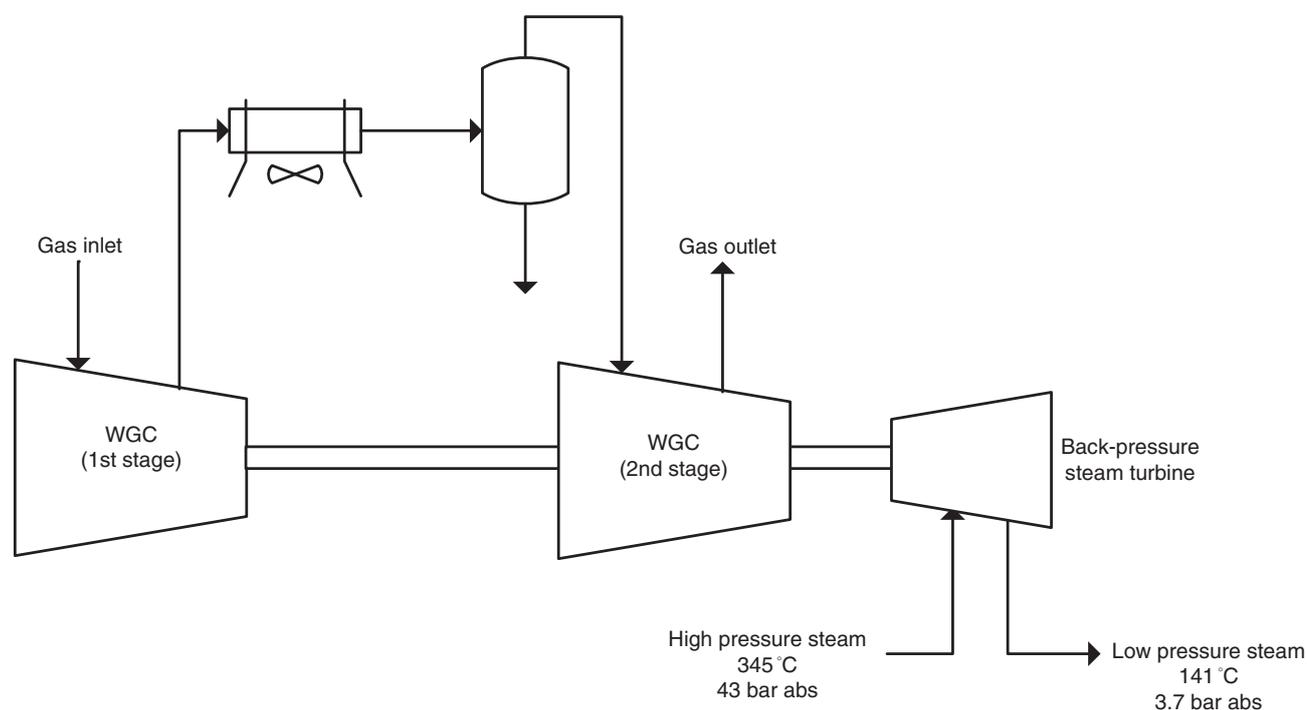


Figure 6

Wet gas compressor driven by a back-pressure steam turbine (HP → LP steam).

TABLE 7  
Comparison of operating cost and GHG emissions for total condensing and back-pressure steam turbine

WGC driver type	Total condensing steam turbine	Back-pressure steam turbine (HP → LP steam)
HP steam for WGC driver	Base	Base + 41 t/h
Cooling water for WGC driver	Base	0
LP steam for amine regeneration	Base	Base – 87 t/h
Operating cost <sup>(1)</sup>	Base	Base – 4.8 M\$/year
GHG emissions <sup>(2)</sup>	Base	Base – 7.3 t CO <sub>2</sub> eq/h

<sup>(1)</sup> Considering following costs: HP steam = 22 \$/t, LP steam = 15 \$/t, Cooling water = 0.08 \$/m<sup>3</sup>;

<sup>(2)</sup> Considering following GHG emission factors: HP steam = 221 kg CO<sub>2</sub>eq/t, LP steam = 183 kg CO<sub>2</sub>eq/t, Cooling water = 0.188 kg CO<sub>2</sub>eq/m<sup>3</sup>.

## CONCLUSIONS

The presented work enables to conclude that HiCapt<sup>+TM</sup> process is a relevant technology to manage CO<sub>2</sub> in FCC flue gas. In a technical point of view, FCC Flue gas can be treated in HiCapt<sup>+TM</sup> process because HiCapt<sup>+TM</sup> inlet specifications can be easily reached. Based on a representative industrial case, it was evaluated that 74% of CO<sub>2</sub> emitted in FCC can be captured and this corresponds to a reduction of more than 14% of the total CO<sub>2</sub> emitted in the refinery.

In an economical point of view, an amine capture unit leads to an additional cost estimated at around 25% which is significant but relatively limited. The impact on operating cost is fully in accordance with the one for power plant for which HiCapt<sup>+TM</sup> process was developed. As amine capture requires LP steam, back pressure turbine for wet gas compressor is an effective option which leads to additional CO<sub>2</sub> gains. In conclusion, HiCapt<sup>+TM</sup> process is therefore a possible solution to reduce CO<sub>2</sub> emissions for refining processes and especially for FCC.

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