

MEMBRANE CAPTURE OF CO₂ FROM REFINERY EMISSIONS

FIELD OF THE INVENTION

This invention relates to the reduction of CO₂ emissions from a Fluid Catalytic
5 Cracker (FCC) regenerator via membrane capture of CO₂.

BACKGROUND OF THE INVENTION

One of the biggest point-sources of CO₂ emissions in a refinery is the FCC (Fluid
Catalytic Cracker) regenerator offgas. In the FCC regenerator, spent catalyst is regenerated
by burning the coke with air at high temperature. An FCC with 390 tonne/day coke will yield
10 emissions of 0.46 million tonnes/year (MMTPA) of CO₂ when burned with air based on 20%
excess O₂. The flue gas from a FCC regenerator is hot, dilute in CO₂, and at low-pressure
which renders separation and recovery of the CO₂ challenging. One known-art process for
capturing CO₂ is based on amine absorption using solvents such as Fluor Econamine FG, 30
wt.% monoethanolamine (MEA), and Mitsubishi Heavy Industry's KS-1. The flue gas is
15 first cooled to a suitable temperature such as 50C, and then compressed in a blower to
overcome the pressure drop from the downstream equipment. The gas then goes through an
amine plant, which comprises an amine absorber (not shown) for removing the CO₂ and an
amine regenerator (not shown) for recovering the CO₂ from the solvent. The amine plant
reduces the direct CO₂ emissions from the FCC unit down to 0.08 MMTPA, however, since
20 power and steam are needed to circulate and regenerate the solvent, indirect emissions of
0.10 MMTPA are incurred. The net avoided CO₂ emissions are thus 0.26 MMTPA. One of
the disadvantages of the amine process is that the process equipment and footprint are
significant, which often translate to high capital costs. High steam consumption leads to high
operating costs and high indirect CO₂ emissions from the steam boilers.
25 A method for capturing CO₂ without high steam consumption and lower indirect
CO₂ emissions is therefore desired.

SUMMARY OF THE INVENTION

Herein is disclosed a method for CO₂ capture from refinery exhaust emissions or flue
gas using crossflow and sweep-based membranes in series.
30 A further embodiment is a method of lowering the input of energy required to capture
CO₂ from an FCC regenerator using select membranes.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG 1 is a diagram of FCC emissions.

FIG 2 is a diagram of a process for capturing CO₂ known in the art based on amine absorption.

FIG 3 and FIG 4 show how a membrane process may be integrated with a FCC regenerator.

5 **FIG 5** is another embodiment in the process where a lower sweep gas flowrate is used while a higher amount of fresh air is used for the FCC regenerator to achieve 20% excess O₂.

FIG 6 is a diagram of an alternative embodiment of the membrane configuration wherein the polishing membrane is eliminated.

10 **DETAILED DESCRIPTION OF THE INVENTION**

Herein is a further embodiment for CO₂ capture from a FCC wherein a membrane process may be integrated with a FCC regenerator (FIG 3 & FIG 4).

Embodiments of the invention as described herein pertain to refinery-based combustion systems and flue gas treatment systems which incorporate sweep-based
15 membrane separation units to control carbon dioxide emissions from combustion processes and streams.

An embodiment of the invention is a method for capturing CO₂ produced from a FCC regenerator flue gas comprising, (1) cooling and compression of the flue gas to overcome the pressure drop in equipment downstream of the FCC regenerator; (2) operating
20 a crossflow membrane at vacuum permeate pressure to remove the bulk of the CO₂, followed by a membrane which operates with a counter-current air sweep on the permeate side to further reduce the CO₂ amount; (3) two stage compression of permeate from the crossflow membrane using vacuum pumps and then in 3 stages of compression to 48 bar; (4) liquefying the CO₂ using a CO₂ liquefaction unit that liquefies CO₂ out the bottom and
25 produces a CO₂-rich vapor which is sent to a high-pressure polishing membrane; (5) recycling the permeate of the polishing membrane to the liquefaction unit feed while the retentate is recycled to the crossflow membrane feed.

Another embodiment of the invention (as seen in FIG 3) is cooling and compression of the flue gas to overcome the pressure drop in equipment downstream of the FCC regenerator.
30 The difference with the amine process is twofold: (1) there is no steam import required, and (2) a portion of the combustion air for the FCC is replaced by a CO₂-enriched, oxygen-depleted air sweep. The air sweep flowrate is adjusted to ensure the same % excess oxygen as the uncontrolled FCC. The direct emissions of the membrane process is 0.08 MMTPA.

Indirect emissions from 23 MW of power import is 0.08 MMTPA, which results in an avoidance of $0.46 - 0.08 - 0.08 = 0.30$ MMTPA, which is 15% better than the amine case.

FIG 4 shows more detail of how to arrange the membrane flowsheet.

Previous efforts to remove CO₂ from a flue gas comprise removal in two stages in series and may be based exclusively on spiral-wound membranes which have inherently less packing efficiency and thus will necessarily take up more space in a refinery operation compared to using hollow-fiber membranes. Therefore, an embodiment of the invention is the use of a crossflow membrane which operates at vacuum permeate pressure, 0.1 to 0.2 bar, to remove the bulk of the CO₂, followed by a hollow-fiber module which operates with a counter-current air sweep on the permeate side to further reduce the CO₂ amount. The permeate from the crossflow membrane is compressed in 2 stages using vacuum pumps and then in 3 stages of compression to 48 bar. A CO₂ liquefaction unit operating at 7C liquefies CO₂ out the bottoms and produces a CO₂-rich vapor which is sent to a high-pressure polishing membrane. The permeate of the polishing membrane is recycled to the liquefaction unit feed while the retentate is recycled to the crossflow membrane feed. The sweep stream has enriched CO₂ but slightly depleted O₂ is combined with combustion air in the FCC regenerator.

An embodiment of the membrane configuration is elimination of the polishing membrane (FIG 6). The overhead of the CO₂ condenser is recycled back to the feed of the crossflow membrane. Because the crossflow membrane is processing a much higher %CO₂ compared to the process in Figures 4, the overall CO₂ recovery is worse and permeate compression requirements are higher.

Permeance is directly related to the thickness of the membrane and will characterize the gas transport through the membrane. Permeance is an important parameter when comparing the separation suitability of membranes for mixed gases. A practical unit often used is gas permeation unit (GPU). The membranes for the crossflow, air sweep, and polishing steps are all preferably polymeric, hollow-fiber membranes with CO₂ permeance of > 1000 GPU and CO₂/N₂ selectivity of 25 to 50 and O₂/N₂ selectivity of 5 to 10. The polymeric materials may be any known in the art provided they can achieve this separation performance under both wet flue gas conditions and in the high-pressure polishing conditions. For example, the crossflow membrane may have high GPU and selectivity for CO₂, while the sweep membrane has high GPU and selectivity for CO₂, and low O₂/N₂

selectivity and the polishing membrane operates at 45 bar and 7C – low to modest CO₂/N₂ selectivity but high CO₂ permeance and high durability.

The hollow fiber membranes may be selected from those known to one of skill in the art selected from the consisting of polypropylene, polyethylene, polytetrafluoroethylene, polyvinylidene difluoride, polysulfone, PEBAX, PDMS, polyimide, carbon molecular sieve, graphene oxide, mixed matrix – comprising zeolites and or metal organic frameworks and polyetherimide based membranes.

An FCC combustor will have different operating parameters with regard to temperature, pressure and excess O₂ when compared to other combustion sources. As such, a preferred embodiment of the invention, seen in FIG. 4, wherein the flue gas from FCC containing CO₂ is fed to a crossflow membrane for feed into a sweep membrane or to a vacuum pump with CO₂ compression, condensation and feed to a polishing membrane, results in the largest amount of avoided CO₂ emissions.

Table 1 summarizes a comparison of the various embodiments. The process with the highest avoided CO₂ emissions is Figure 4, utilizing a high air sweep and polishing membrane. The process with the lowest power requirement is Figure 5, utilizing a low air sweep and polishing membrane.

Table 1

	Uncontrolled FCC	Membrane Case 1 – high sweep	Membrane Case 2 – low sweep	Membrane Case 3 – no polishing
Combustion Air (kgmol/hr)	6873	847	6250	847
Sweep Air (kgmol/hr)	0	6475	1000	6475
Total Air (kgmol/hr) to FCC	6873	7322	7250	7322
CO ₂ direct emissions (MMTPA)	0.46	0.08	0.17	0.15
CO ₂ indirect emissions (MMTPA)	0	0.08	0.05	0.11
Total CO ₂ emissions (MMTPA)	0.46	0.16	0.22	0.26
Power Import (MW)	0	23	14	28.5
Total membrane surface area (m ²)	0	100,796	100,796	98,320
CO ₂ liquid product (>95 mol% purity, 151 bar)	0	0.39	0.30	0.33

WHAT IS CLAIMED IS:

1. A method for capturing CO₂ produced from a FCC regenerator flue gas comprising,
(1) cooling and compression of the flue gas to overcome the pressure drop in equipment
downstream of the FCC regenerator; (2) operating a crossflow membrane at vacuum
5 permeate pressure to remove the bulk of the CO₂, followed by a membrane which operates
with a counter-current air sweep on the permeate side to further reduce the CO₂ amount; (3)
two stage compression of permeate from the crossflow membrane using vacuum pumps and
then in 3 stages of compression to 48 bar; (4) liquefying the CO₂ using a CO₂ liquefaction
unit that liquefies CO₂ out the bottom and produces a CO₂-rich vapor which is sent to a
10 high-pressure polishing membrane; (5) recycling the permeate of the polishing membrane to
the liquefaction unit feed while the retentate is recycled to the crossflow membrane feed.
2. The method of claim 1 wherein the crossflow membrane and polishing membrane are
hollow fiber membranes selected from the group consisting of polypropylene, polyethylene,
15 polytetrafluoroethylene, polyvinylidene difluoride, polysulfone, PEBAX, PDMS, polyimide,
carbon molecular sieve, graphene oxide, mixed matrix, zeolites, metal organic frameworks
and polyetherimide.
3. The method of claim 2 wherein the vacuum permeate pressure is 0.1 to 0.2 bar.
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4. The method of claim 3 wherein the liquefaction unit is operating at 7 °C to liquefy the
CO₂.