

# Purification Methods for Captured CO<sub>2</sub> from Petroleum Coke Oxy-Combustion Power Plants

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## **Abstract:**

We present eco-technoeconomic analyses of four processes, including two novel designs, for the purification of captured CO<sub>2</sub> from flue gas for a petroleum coke (petcoke) oxy-combustion power plant operated with carbon capture and sequestration (CCS). A base case petcoke oxy-combustion design obtained from a previous study consisting of flue gas water removal using condensation was used in this study. Other purification processes evaluated consist of a cryogenic distillation petcoke oxy-combustion with CCS, an oxygen deficient petcoke oxy-combustion with CCS and a catalytic dehydration petcoke oxy-combustion via hydrogen conversion with CCS. An eco-technoeconomic analysis considering greenhouse gas (GHG) emissions, levelized cost of electricity (LCOE), thermal efficiency and CO<sub>2</sub> product purity to meet pipe-line specifications, was conducted on all purification candidates. This revealed that base case design did not meet the CO<sub>2</sub> pipeline specifications. The highest LCOE was attributed to the cryogenic distillation design, although it produces the purest CO<sub>2</sub> product compared to all other designs. The oxygen-deficient design has the lowest LCOE and GHG emission, proving to be a desirable candidate, however further re-search is required to determine the feasibility associated with the incomplete combustion of fuels. The catalytic de-oxygenation design appears to be a middle ground between the latter two designs, with a lower LCOE than the cryogenic design and a higher purity CO<sub>2</sub> product compared to the oxygen deficient design. In brief, this study presents and performs eco-technoeconomic analyses of four candidates for the purification of captured CO<sub>2</sub> from petcoke oxy-combustion power plants while respecting pipeline specifications, the first of its kind to do so.

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# Purification Methods for Captured CO<sub>2</sub> from Petroleum Coke Oxy-Combustion Power Plants

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## ABSTRACT

We present eco-technoeconomic analyses of four processes, including two novel designs, for the purification of captured CO<sub>2</sub> from flue gas for a petroleum coke (petcoke) oxy-combustion power plant operated with carbon capture and sequestration (CCS). A base case petcoke oxy-combustion design obtained from a previous study consisting of flue gas water removal using condensation was used in this study. Other purification processes evaluated consist of a cryogenic distillation petcoke oxy-combustion with CCS, an oxygen deficient petcoke oxy-combustion with CCS and a catalytic dehydration petcoke oxy-combustion via hydrogen conversion with CCS. An eco-technoeconomic analysis considering greenhouse gas (GHG) emissions, levelized cost of electricity (LCOE), thermal efficiency and CO<sub>2</sub> product purity to meet pipeline specifications, was conducted on all purification candidates. This revealed that base case design did not meet the CO<sub>2</sub> pipeline specifications. The highest LCOE was attributed to the cryogenic distillation design, although it produces the purest CO<sub>2</sub> product compared to all other designs. The oxygen-deficient design has the lowest LCOE and GHG emission, proving to be a desirable candidate, however further research is required to determine the feasibility associated with the incomplete combustion of fuels. The catalytic deoxygenation design appears to be a middle ground between the latter two designs, with a lower LCOE than the cryogenic design and a higher purity CO<sub>2</sub> product compared to the oxygen deficient design. In brief, this study presents and performs eco-technoeconomic analyses of four candidates for the purification of captured CO<sub>2</sub> from petcoke oxy-combustion power plants while respecting pipeline specifications, the first of its kind to do so.

**Keywords:** petroleum coke, eco-technoeconomic analysis, captured CO<sub>2</sub>, oxy-combustion

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## INTRODUCTION

Oxy-combustion consists of burning fuels in the presence of oxygen at very high concentrations and recirculating the flue gas to produce a flue gas largely composed of CO<sub>2</sub> at a high temperature. The purified CO<sub>2</sub> product is then fed into pipelines and sent to CO<sub>2</sub> sequestration sites to be used for various purposes, namely enhanced oil recovery, etc. An important concern in the transportation of the captured CO<sub>2</sub> is the oxygen specification of the pipeline, which if overlooked, could have detrimental effects on these pipelines. However, in investigating recent studies, it was determined that many fail to consider the oxygen specification of pipelines. By doing so, they generate inaccurate eco-technoeconomic analysis studies which underestimates costs and environmental impacts as well as overshoots the plant's performance and efficiency.

This study considers four designs for the purification of captured CO<sub>2</sub> from a petroleum coke (petcoke) oxy-combustion power plant operated with carbon capture and

sequestration (CCS). These four designs are a base case petcoke oxy-combustion with CCS, a cryogenic distillation petcoke oxy-combustion with CCS, an oxygen deficient petcoke oxy-combustion with CCS and a catalytic dehydration petcoke oxy-combustion with CCS. The Kinder Morgan pipeline specifications which indicate a maximum oxygen level of 10 ppm, among other component specifications, will be used as a guideline to avoid pipeline corrosion [1].

Readers are referred to [2] for full details.

## METHODS

The purification methods presented are evaluated at a net power output of 550 MWe. All the following designs were simulated using Aspen Plus V10 using the Peng-Robinson with the Boston-Mathias alpha function (PR-BM) property package. However, the property package used to simulate the steam/power generation, CO<sub>2</sub> capture and compression including CO<sub>2</sub>-H<sub>2</sub>O separation, and the CO<sub>2</sub> dehydration via

TEG absorption were Predictive Redlich-Soave (PSRK), STEAMNBS and HYSGLYCO respectively. The properties of the delayed petcoke are displayed in Table 1 was modeled as a solid non-conventional substance pseudo-component.

Aspen Plus APV100 Pure-36 databases were used to model the conventional chemicals while the non-conventional substance pseudo-component model was used for the delayed petcoke, with properties shown in Table 1.

**Table 1:** Delayed petcoke properties.

Delayed coke	
HHV (MJ/kg)	34.7
Ultimate analysis (wt % dry)	
C	84.9
H	3.9
N	1.3
S	6
Cl	0
Ash	3.1
O (diff)	0.8
Proximate analysis (wt %)	
Moisture	1.8
Volatile matter	11.9
Fixed Carbon	83.3
Ash	3

### Base case oxy-combustion

This design and corresponding model is the base case oxy-combustion model from a previous study [3]. Petcoke is crushed and mixed with water to form a petcoke slurry which is then combusted in the oxycombustor in the presence of high purity oxygen, obtained from the air separation unit (ASU), at stoichiometric ratio to obtain the flue gas. A heat recovery steam generator (HRSG) is used to generate electricity from steam at different pressures using a steam cycle accompanied by a cooling tower. Flue gas desulfurization (FGD) utilizing a limestone slurry is also employed in this process to treat the flue gas as a result of the formation of sulfur compounds within the oxycombustor. Following FGD, the flue gas is cooled to 21°C and fed through a cascade of flash drums operating at decreasing pressures to remove water at 99 mol% purity resulting in minimal losses. It is at this point that the following designs will differ from the base case, as the flue gas will undergo further methods of purification. In this case, the flue gas exiting the flash cascade at 9 bar, now largely composed of CO<sub>2</sub> along with minor impurities, is compressed to pipeline conditions of 153 bar. This design, however, does not meet the Kinder Morgan O<sub>2</sub> specifications, therefore it is rejected as a possible purification method. Further details about this design are presented in prior work [3].

### Cryogenic distillation purification oxy-combustion

The cryogenic distillation purification model was also acquired from a previous study [3]. This process differs from the base case following the flue gas' exit from the cascade of flash drums at 21°C and 9 bar. The impure CO<sub>2</sub> is compressed to 30 bar and cooled to 9°C using a series of heat exchangers, which

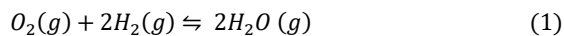
minimizes the duty requirements prior to distillation. The impure CO<sub>2</sub> is then fed into a cryogenic distillation column with the desired bottoms output of 10 ppm of oxygen. It is important to note that a greater CO<sub>2</sub> recovery is limited by a greater energy cost, of which a lower energy cost was favoured. Therefore, only 95% CO<sub>2</sub> capture was achieved due to losses with the oxygen distillate stream that was vented into the atmosphere. Further details about this design are presented in prior work [3].

### Oxygen deficient oxy-combustion

This design follows a similar structure as the base case design, however it utilizes less oxygen within the oxycombustor, rather than using oxygen at a stoichiometric ratio, to meet the Kinder Morgan pipeline requirement of 10 ppm. Chemical equilibrium was assumed when simulating this design. Alternatively, sub-equilibrium conditions would ensue a greater amount of uncombusted gas in the product as well as lower efficiencies.

### Catalytic de-oxygenation oxy-combustion

Another novel design presented in this study is CO<sub>2</sub> purification via catalytic de-oxygenation, presented in Figure 1. The impure CO<sub>2</sub> obtained at 21°C and 9 bar from the flash drum cascade is heated to 150°C and is fed into a de-oxygenation reactor with a hydrogen inlet. The excess oxygen (above 10 ppm) will catalytically react with hydrogen to form water, as shown in Equation 1. A study conducted by Deshpande et al. presented a catalyst (Ce<sub>0.83</sub>Ti<sub>0.15</sub>Pd<sub>0.02</sub>O<sub>2-δ</sub>) that can achieve a 97% hydrogen conversion at 150°C and atmospheric pressure [4]. Therefore, this reaction was assumed to achieve 97% conversion of hydrogen with this catalyst while operating at 9 bar, since a greater pressure would push the reaction forward. A design specification was used to modify the inlet hydrogen flow rate to allow an outlet concentration of O<sub>2</sub> below 10 ppm within the impure CO<sub>2</sub> gas. This reaction produces a large amount of water, which in turn exceeds the Kinder Morgan specification of 690 ppm and requires further treatment for water removal [1]. The stream is then cooled to 35°C and fed into a flash drum to knock out 99.9 mol% water, however since it still exceeds the pipeline requirements, it is compressed to 41 bar using a multistage compressor with intercoolers and enters the TEG dehydration cycle.



The TEG dehydration cycle in Figure 2 allows for the removal of excess water in the stream. This dehydration cycle utilizes TEG since it acts as a drying agent on account of its high affinity for water. Impure CO<sub>2</sub> at 41 bar and 35°C enters the bottom of absorption column in which TEG at the same conditions is fed at the top to strip the CO<sub>2</sub> of water. In this column, the TEG absorbs the water from the water rich gas to become rich TEG, exiting from the bottom of the column, and dry gas, exiting from the top. The CO<sub>2</sub> recovered from the top is greater than 98% pure. The water-rich TEG undergoes further processing to recover and recycle TEG, avoiding additional material costs. A valve is used to decompress the water-rich TEG and it enters a flash drum to separate any accompanying gases, containing high purity CO<sub>2</sub>. These gases are compressed to match the conditions of the CO<sub>2</sub> product from the

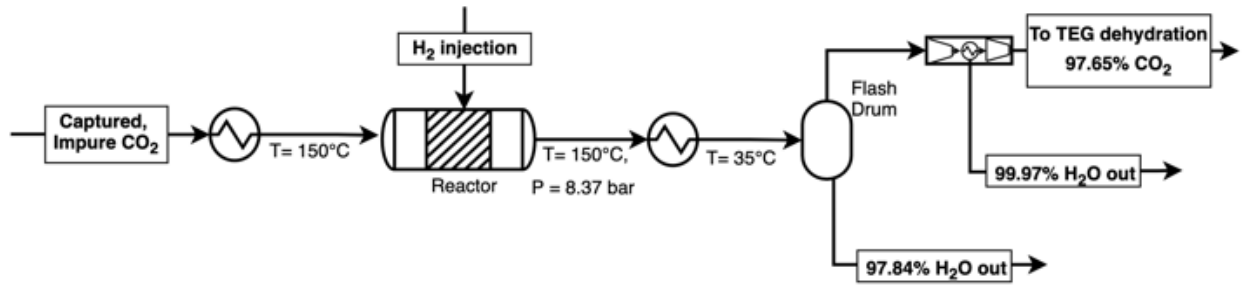


Figure 1: Process flow diagram for the catalytic de-oxygenation of captured CO<sub>2</sub>.

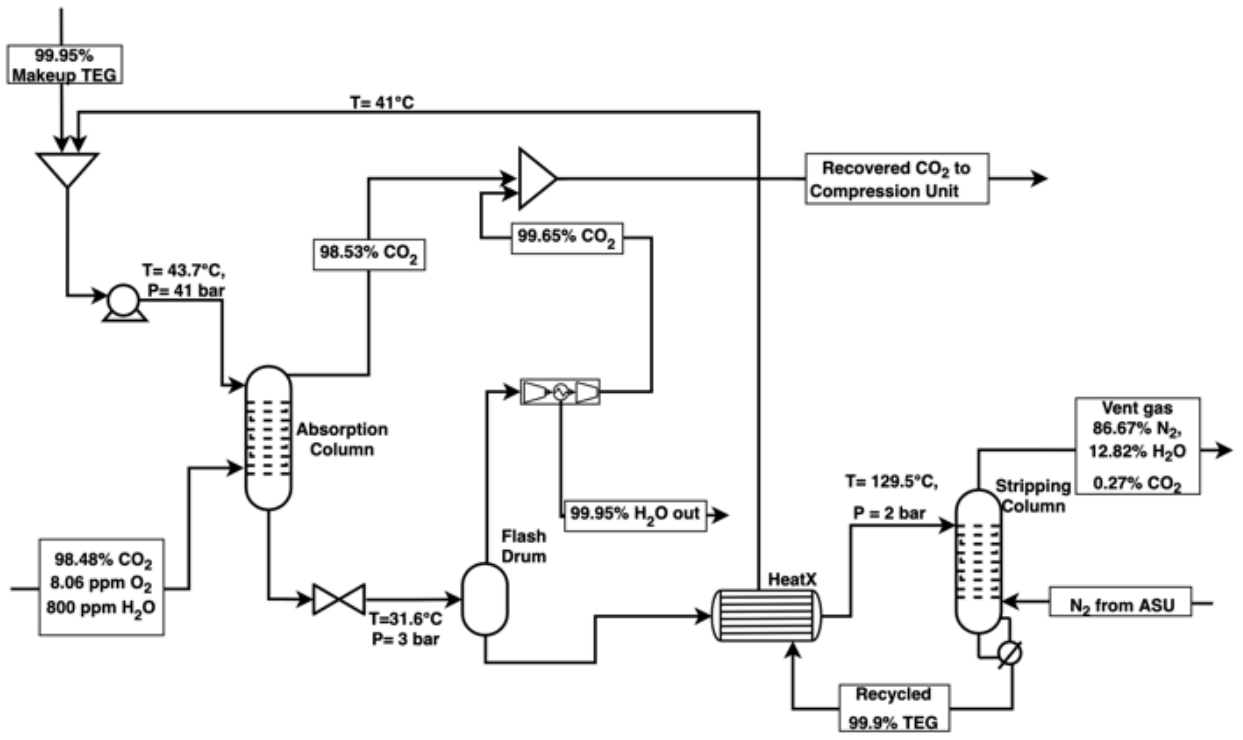


Figure 2: Process flow diagram for the TEG dehydration cycle of the captured CO<sub>2</sub>.

absorber using a multistage compressor with interstage cooling, with which they will be mixed, and they are further compressed to pipeline conditions of 153 bar.

The water-rich TEG is then heated and enters the top of a stripping column while nitrogen, recovered from the ASU, is fed into the bottom as a stripping gas. The stripping column has a reboiler that operates at a boilup ratio of 0.8 but it does not have a condenser. The distillate exiting the top of the column is vented to the atmosphere since it is largely made up of nitrogen and water. The lean TEG obtained from the bottom of the column is 99.9% pure, it is cooled and pumped to 41 bar to be recycled back to the system. A makeup TEG stream is used to account for minor TEG losses within the cycle.

## RESULTS

The performance of all four designs were evaluated for a net power of 550MW and the results are displayed in Table 2.

The total power generation is highest for the cryogenic distillation design compared to the others, due to its higher

parasitic load which requires a more power generation to attain 550MW. The cryogenic distillation design also has a higher direct GHG emission compared to other designs on account of the CO<sub>2</sub> lost in the distillate vent gases, as previously mentioned, which in turn reduces its CO<sub>2</sub> sequestration ratio. The oxygen deficient and catalytic de-oxygenation designs exhibit nearly 100% CO<sub>2</sub> capture and fewer emissions, and subsequently have a higher sequestration ratio and lower direct GHG emissions. However, the catalytic de-oxygenation design has significantly higher indirect GHG emissions compared to the other designs, which is associated with the assumption that the hydrogen used in the de-oxygenation reactor was obtained from a steam methane reforming process operated without CCS [5]. Hence, the emissions from this process must be accounted for. Altogether, the latter design has the highest total GHG emissions.

Table 3 presents the product stream conditions for all four designs. As previously mentioned, the base case design

**Table 2:** Performance summary of each purification design.

Parameters	Base case	Cryogenic distillation	Oxygen deficient	Catalytic de-oxygenation
CCS Enabled	Yes	Yes	Yes	Yes
Petcoke feed rate (tonne/h)	183.5	193.3	192.6	185.6
Petcoke feed capacity (MWHHV)	1769	1863	1856	1789
Total power generated (MW)	733	772	735	742
Total parasitic load (MW)	183	221	185	192
Net power output (mW)	550	550	550	550
Heat rate (MJHHV/MWh)	11,577	12,196	12,150	11,712
Thermal Efficiency (%HHV)	31.1	29.5	29.6	30.7
Direct GHG Emissions (kgCO <sub>2</sub> eq/MWh)	0.46	54.7	0.49	0.46
Indirect GHG Emissions (kgCO <sub>2</sub> eq/MWh)	0.17	0.18	0.18	57.4
Total GHG Emissions (kgCO <sub>2</sub> eq/MWh)	0.63	54.9	0.66	57.9
CO <sub>2</sub> sequestered (tonne/h)	596	567	600	582
CO <sub>2</sub> sequestered ratio (tonne CO <sub>2</sub> /tonne petcoke)	3.25	2.93	3.12	3.14

**Table 3:** Composition of captured CO<sub>2</sub> stream for each purification design.

	Kinder Morgan Pipeline Spec	Base case	Cryogenic distillation	Oxygen deficient	Catalytic de-oxygenation
CCS Enabled		Yes	Yes	Yes	Yes
Meets pipeline Spec?		No	Yes	Yes	Yes
H <sub>2</sub> O	690 ppm	337 ppm	401 ppm	337 ppm	314 ppm
CO <sub>2</sub>	>95%	95.1%	99.9%	97.6%	98.5%
H <sub>2</sub> S	10-200 ppm	trace	trace	trace	trace
CO	no spec	trace	trace	1.00%	trace
C <sub>x</sub> H <sub>y</sub>	<5%	trace	trace	trace	trace
H <sub>2</sub> , N <sub>2</sub> , Ar	<4%	1.34%	0.44 ppm	1.37%	1.4%
O <sub>2</sub>	<10ppm	3.49%	9.40 ppm	9.41 ppm	8.06 ppm
NO <sub>2</sub>	no spec	0.28 ppm	0.31 ppm	0.12 ppm	0.27 ppm
N <sub>2</sub> O	no spec	0.01 ppm	0.01 ppm	0.01 ppm	0.01 ppm
SO <sub>2</sub>	no spec	305 ppm	338 ppm	317 ppm	316 ppm
SO <sub>3</sub>	no spec	0.72 ppm	0.80 ppm	0.47 ppm	0.72 ppm

**Table 4:** LCOE of each purification design with/without carbon tax and T&S.

	Base case	Cryogenic distillation	Oxygen deficient	Catalytic de-oxygenation
CCS Enabled	Yes	Yes	Yes	Yes
LCOE w/o carbon tax and w/o T&S	90.94	102.8	92.28	97.67
LCOE w/o carbon tax and with T&S	104.7	115.9	105.8	110.9
LCOE with carbon tax and w/o T&S	90.96	105.5	92.31	97.69
LCOE with carbon tax and with T&S	104.8	118.7	105.9	111

does not meet the pipeline requirements and it has been rejected. The cryogenic distillation design provides the highest product CO<sub>2</sub> purity compared to all other purification methods, making it a desirable design for when CO<sub>2</sub> purity is essential. Higher concentrations of unconverted fuels, such as CO and H<sub>2</sub>, in the product stream of the oxygen deficient design is attributed to its incomplete combustion in the presence of oxygen below the stoichiometric ratio. These components are still within their respective specifications, and therefore this design remains satisfactory.

Table 4 presents the levelized cost of electricity (LCOE) for all four plant designs with the varying constraints of carbon

tax and transportation and storage (T&S). Omitting both constraints, the base case design has the lowest LCOE followed by the oxygen deficient, catalytic de-oxygenation and the cryogenic distillation, which is the highest. When T&S is considered, the designs with the highest capture rates observe a more significant LCOE increase compared to the design with the lowest capture rate, cryogenic distillation. If a carbon tax of \$50 per tonne of CO<sub>2</sub>eq is applied without T&S, the cryogenic distillation design is greatly impacted due to its loss of CO<sub>2</sub> with vent gases. Applying both the carbon tax and the T&S cost indicated that the highest LCOE belongs to the cryogenic

distillation design followed by the catalytic de-oxygenation, oxygen deficient and base case, in decreasing LCOE order.

## CONCLUSIONS

Although the base case design was the most efficient and cost-effective design, it did not meet the oxygen limit pipeline requirements and was excluded from the rest of the analysis. While the oxygen deficient design showed promising efficiencies, LCOE and total GHG emissions, the assumption that chemical equilibrium was attained under incomplete combustion must be evaluated to determine if these results are feasible at an industrial scale. The cryogenic distillation design achieves a very high final CO<sub>2</sub> purity, but has the highest LCOE compared to all the designs. This design would be advantageous if the product purity was of the utmost importance, such as the product would be sold for example. Finally, the catalytic de-oxygenation design was determined to be the most efficient design and has a lower LCOE than the cryogenic distillation design, while maintaining a high purity CO<sub>2</sub> product. However, it has higher indirect GHG emission associated with the H<sub>2</sub> injection within the de-oxygenation reactor. In brief, the three viable designs been presented in this study have their own trade-offs. Further details regarding the results of this study are presented in a manuscript pending publication [2].

Future work would entail the investigation of other purifications, such as catalytic methane oxidation, that would avoid any trade-offs to reduce GHG emissions, maintain a low LCOE and meet pipeline requirements.

## ACKNOWLEDGEMENTS

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