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CO_2 capture processes: Novel approach to benchmarking and evaluation of improvement potentials

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Abstract

A consistent and transparent benchmarking methodology is required for comparison and ranking of different technologies for CO_2 capture, and also for evaluation of different means of integrating novel capture process units into power cycles. A novel benchmarking methodology is presented in this work where the difference between the thermodynamic maximum and the technology limited efficiencies quantifies the theoretical improvement potential and is a benchmark for the process. Additionally, the source(s) of this difference in efficiency can point to possible future directions for technology development. . The benchmarking methodology is applied to the three CO_2 capture routes – post-combustion, pre-combustion and oxy-combustion – using simplifying assumptions and with fuels of varying HC ratios. The first step of the benchmarking methodology is defining ideal reversible processes for CO_2 capture with no detailed process information. This enables determination of a consistent thermodynamic maximum efficiency of processes. Results show that apart from methane as fuel, where post-combustion has the lowest thermodynamics limited efficiency penalty, pre-combustion process routes have the lowest thermodynamics limited efficiency penalty, followed by post-combustion and then oxy-combustion. These results should not be seen as an attempt to rank the different capture routes, but rather as the thermodynamic limit for technological improvements.

Keywords: CO_2 *capture, Benchmarking, Maximum thermodynamic efficiency*

1. Introduction

Capture of CO_2 from fossil fuelled power plants is generally seen as one of several potential measures to reduce greenhouse gas emissions to the atmosphere, thus combating global warming [1]. The technologies for CO_2 capture from power plants can be divided into three groups (or capture routes): post-combustion, oxy-combustion and pre-combustion capture. In order to enable the separation of CO_2 from a standard power plant without CO_2 capture, process units with different levels of novelty are integrated in

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the power cycle. Examples of such units are cryogenic air separation, CO_2 absorption using physical or chemical solvents, membrane reactors and chemical looping reactors. The introduction of these novel process units introduces an energy penalty. In this context it is vital to apply a consistent and transparent benchmarking methodology in order to compare and possibly rank different technologies for CO_2 capture and the different means of integrating the required novel process units into power cycles. A requisite benchmarking will then provide a snapshot of the performance of different novel processes, related to a well-defined reference process.

Earlier efforts on benchmarking of power cycles with CO_2 capture have compared different capture processes, where an essential part of the methodology has been to perform process simulations that determine first-law thermal efficiency and CO_2 emissions [2,3]. The sensitivity of the power cycle efficiency with respect to technological developments has also been studied [4]. The earlier cited works on benchmarking present first law efficiencies for comparing different process routes for CO_2 capture given a consistent benchmarking framework (list of component and process stream specifications) and variations thereof. While these comparisons were based on thermodynamic efficiencies, no further insight into the limitations of further process development can be gained from the benchmarking process.

1.1. Thermodynamic basis for benchmarking

For a process with a specified energy output, it is evident that schemes that require lower energy input will be more efficient, and consequently, research tends to focus on identifying ways to improve efficiency.

The three efficiency categories that can be specified for a process are:

1. Thermodynamics limited: This is a scheme that requires the thermodynamically lowest possible energy input to produce the specified energy output. The resulting efficiency is the "ideal" efficiency which is the thermodynamic maximum attainable for such a process. This efficiency can never be achieved in practice since it requires perfectly reversible processes, but it provides a thermodynamic benchmark or target for process design.
2. Technology limited: Limitations, technological and those inherent in unit operations, prevent achieving the thermodynamic maximum efficiency. The first law efficiency attainable by employing state-of-the-art technology can be thought of as a technology limited efficiency, which is typically compared in different benchmarking studies such as in [2].
3. Economics limited: While the technology limited efficiency is achievable, it may not necessarily be practical. Latest technologies are almost always associated with a premium which make utilizing them, economically infeasible. Thus the economics limited efficiency is the efficiency of a process using technology that results in it being commercially viable.

Power plants with CO_2 capture can be benchmarked with respect to the three above-mentioned efficiencies. It must be noted that while the thermodynamic limited efficiency is fixed for a given process, the technology limited and economics limited efficiencies are subject to change over time.

The difference between the thermodynamic maximum and the technology limited efficiencies quantifies the theoretical improvement potential and is a benchmark for the process. Additionally, the source(s) of this difference in efficiency can point to possible future direction for technology development. The first step, however, is to evaluate the theoretical maximum efficiency of a process.

There have been efforts to benchmark processes with respect to the maximum possible efficiency to present the available scope for improvement for post-combustion [5] and oxy-combustion processes [6]. In the former case, with post-combustion capture [5], work requirements for amine-based CO_2 capture using existing and projected technologies were compared to the theoretical minimum work requirement while in the latter, oxy-combustion capture [6], the minimum theoretical work requirements of the air separation process and the CO_2 purification unit were used to motivate innovative and efficient designs for the process. While these evaluations are simple for post-combustion and oxy-combustion processes (with either no or fixed recycle), it is not straightforward for more complicated pre-combustion processes.

It is argued by the present authors that the origin of the difference between the thermodynamics limited efficiency and the technology limited efficiency constitutes an additional source of information for benchmarking studies, which merits further attention. The purpose of the present paper is therefore first to introduce a novel systematic methodology for thermodynamic benchmarking of power cycles with CO_2 capture and then focus on the introductory step of evaluating the thermodynamic maximum efficiency.

2. Systematic methodology for benchmarking of power plants with CO_2 capture

The concept of benchmarking in the literature for CO_2 capture processes has been used to compare the efficiencies and provide a ranking of the different processes. The purpose of developing a novel systematic methodology for benchmarking is that in addition to ranking, the procedure provides further information on potentials for improvement. The ultimate goal is to increase the understanding of power plants with CO_2 capture, to identify the most promising capture technologies and to pinpoint what technology improvements should be most beneficial to pursue.

The approach consists of applying engineering thermodynamics to increase the understanding of the fundamental losses imposed on a power cycle when introducing CO_2 capture. The first step in the methodology is to evaluate the maximum efficiency limited by thermodynamics. This limit is achieved by defining an ideal (reversible) process.

A set of non-idealities in the form of technological limitations are added systematically in series to go from the thermodynamics limited to the technology limited cases. The difference between the thermodynamics limited and technology limited efficiencies can thus be attributed to the different sets of irreversibilities and quantified. This is represented visually in Figure 1.

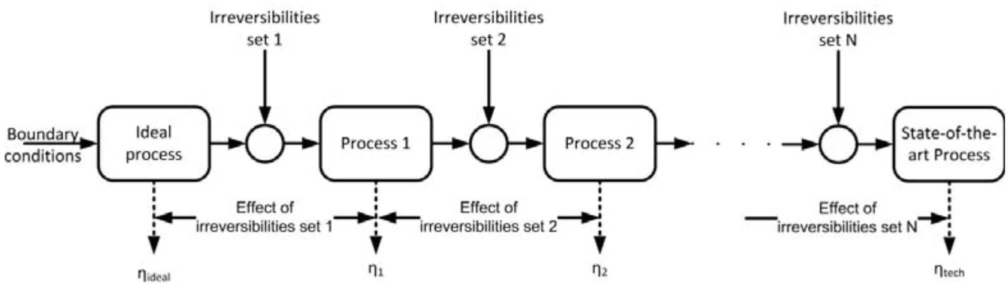

Figure 1: Representation of the systematic methodology for benchmarking of CO_2 capture processes

The remainder of the paper focuses on the definition and evaluation of the thermodynamics limited case and preliminary benchmarking calculations for the three process routes (post-, oxyfuel- and pre-combustion) and a range of fuels.

3. Design of ideal processes for benchmarking purposes

To achieve thermodynamic maximum efficiency requires the process to be thermodynamically feasible and second law analysis requires the process to be reversible. Ideal (reversible) processes for the three

CO_2 capture routes are defined and are thereafter employed to determine the thermodynamic maximum efficiency. Figure 2 shows the process block diagrams of the reference case and the three capture routes.

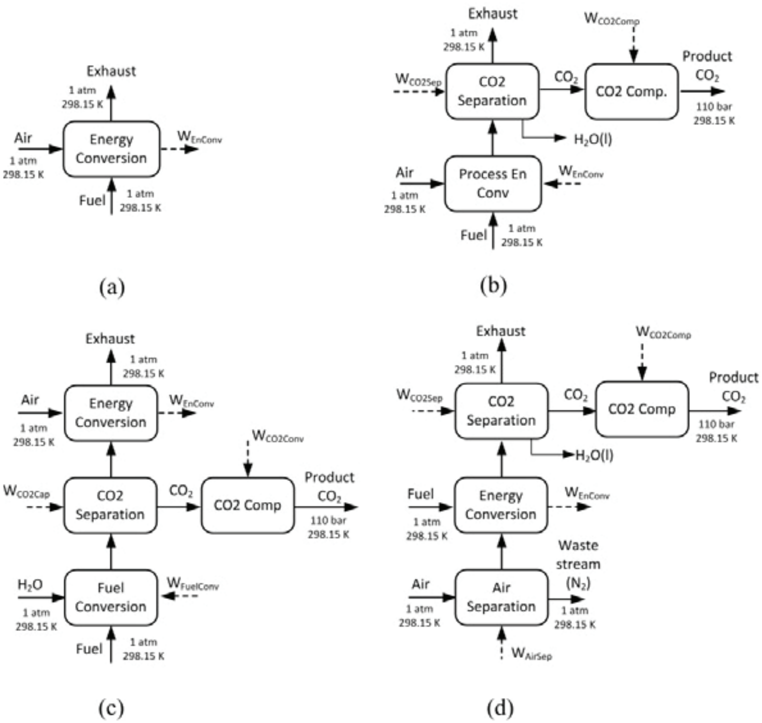

Figure 2: Process block diagrams for (a) the reference case without CO_2 capture (b) post-combustion capture process (c) pre-combustion capture process, and (d) oxy-combustion capture process

3.1. Methodology description

The minimum work required for capturing 100% CO_2 at 100% purity is referred to as the *minimum capture work target*, and should be determined without defining any details of the configurations of the unit operations involved. The conceptual design of such processes is done by considering the reversible process unit (which could be any of those illustrated in the boxes in Figure 2) defined by a set of inputs and outputs. This is done to ensure no bias when evaluating the targets. Since ideal reversible processes are considered, the calculations are independent of the different possible process layouts and specifications for any capture route. More specifically, this approach means that for instance in post-combustion capture, no consideration of solvent or capture unit performance is included.

Process molar balance is specified based on the inputs and products for the process unit under consideration. This defines the process unit and provides the basis for subsequent calculations.

With the molar balance, the energy balance can be performed without any further detailed knowledge of the process and gives the maximum amount of energy output or the minimum amount of energy required by the process. For processes under consideration in this work, the kinetic and potential energy contributions are assumed to be zero.

The maximum work produced (or minimum work consumed) by a process has been shown to be related to the change in Gibbs energy, assuming the inputs and outputs of the process are pure components at standard condition [7]. This can be evaluated using the standard Gibbs energy of formation. However, it must be noted that in this work, emphasis is on CO_2 separation, and hence assuming pure component streams is not relevant. Thus an exergy analysis is performed. Taking all energy input or output to the process in terms of equivalent shaft work, the ideal work targets for the process is the difference between the input and output exergy flows.

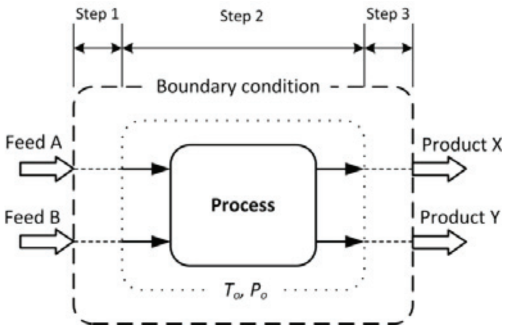

Figure 3: Steps in the conversion of raw materials to products

The conversion of raw materials to products can be considered to occur in 3 steps for any of the processes in. This is shown in Figure 3.

Step 1. Feeds/raw materials are taken from process conditions at the boundary limit to standard reference conditions T_o, P_o. (Relevant for e.g. pressurized CH_4)

Step 2. Raw materials are transformed to products at T_o, P_o.

Step 3. Products are taken from T_o, P_o to their respective boundary limits. (Relevant for e.g. CO_2 compression)

Molar, energy and exergy balances for each of the three steps are performed. The balances for Steps 1 and 3 are straightforward as no chemical reactions occur. All reactants and products to and from Step 2 where the transformation (chemical reaction, separation or compression) takes place are at standard reference conditions (298.15 K and 1 atm). The energy aspect of Step 2 can be evaluated as the enthalpy change of the process (ΔH), which at standard condition is evaluated using the standard heats of formation.

Three basic reversible process units are applied with this approach; energy conversion in chemical reactors, separation, and CO_2 compression. The combination of the processes will differ for the three different capture routes shown in Figure 2.

4. Benchmarking methodology applied to ideal CO_2 capture processes

This section presents the comparison of the three CO_2 capture routes (post-combustion, pre-combustion and oxyfuel-combustion) with four fuels with different HC ratio, using the modeling methodology described in Section 3. The input parameters used in this work are listed in Table 1. The fuels used are methane, natural gas (EBTF specifications [8]), coal (EBTF specifications [8]) and carbon.

The gross process output, i.e. the shaft work generated from the energy conversion process (Energy Conv), the gross plant power output, is kept constant (400 MW) for all cases.

Table 1Assumptions used in the benchmarking analysis

Parameter	Value
Gross power plant output	400 MW
CO_2 product purity	100%
CO_2 product pressure	110 bar
CO_2 capture ratio	100%
O_2 product purity (from ASU)	100%

4.1. Efficiency measures

In order for a benchmarking to be possible one or more suitable efficiency measures are required. As mentioned in the introduction, first-law efficiency is predominantly used as the basis of comparing different processes with CO_2 capture that are modeled with a framework set up to reflect operation of realistic power plants. First law efficiency is applied also in the present work, since it is believed to give fundamental information about the behavior of the ideal processes studied, i.e. it gives the first-law thermodynamic maximum efficiency for the three CO_2 capture routes and the reference process without CO_2 capture. First-law efficiency (η_{HHV}) is defined, in this work, as the net shaft work output from the process as a percentage of the total fuel thermal energy input in terms of its higher heating value (HHV). HHV is used for defining the thermal energy input to the process as the combustor exhaust stream includes partly condensed water at standard conditions. Using the lower heating value (LHV), as is common in literature, could lead to efficiencies greater than 100%. Another suitable efficiency measure is one of the many exergy efficiencies defined in the literature, the net shaft work as a percentage of the fuel exergy input to the process (rational efficiency - η_R)

A commonly used parameter to compare CO_2 capture processes is efficiency penalty, π. This is defined to be the difference in efficiency for a reference power plant without CO_2 capture and a power plant with CO_2 capture using the same fuel. In this paper, the efficiency penalty is considered both for first law efficiency and rational efficiency. The minimum capture work target is obtained by subtracting from the 400 MW energy conversion process the work required by all other processes (Figure 2b–d).

4.2. CH_4 fuel

Table 2 gives the performance metrics of the reference case and the three capture routes with CH_4 as fuel. The results show that the post-combustion process, under ideal reversible conditions, has the lowest efficiency penalty of 1.8 % points compared to oxy-combustion with 2.1 % points and pre-combustion with 2.4 % points. In the post combustion process route, the share of the energy penalty is equally split between the CO_2 separation and compression units. For the oxy-combustion case, the air separation unit contributes the most to the energy penalty followed by CO_2 compression. The CO_2 separation penalty is very low in this case. In the pre-combustion route, the fuel conversion process unit contributes to the bulk of the penalty.

4.3. Effect of HC ratio

Figure 4 shows the efficiency penalties of the three capture routes for fuels of varying HC ratio. The general trend is that the efficiency penalty increases with decreasing HC ratio. This is not the case for the pre-combustion route when going from methane to natural gas (NG) as fuel, where there is a significant decrease in efficiency penalty. The work target for fuel conversion decreases significantly, while the CO_2 capture and compression work targets increase slightly.

The pre-combustion process route has the lowest efficiency penalty with NG as fuel. Post-combustion process route lies slightly higher and oxy-combustion has the largest efficiency penalty. However, with decreasing HC ratio, the relative difference of efficiency penalty between the process routes decreases, tending to the same value for C.

Table 1: Overall performance metrics for the reference case and three capture routes with CH_4 as fuel

		Reference	Post-comb	Pre-comb	Oxy-comb
Fuel flow (kg/s)		7.9	7.9	6.9	7.8
Fuel thermal energy, HHV (MWth)		438	438	382	436
Fuel Exergy, (MW)		409	409	357	407
W_s- Energy Conversion (MW)		400	400	400	400
Minimum capture work targets	W_s - CO_2 separation (MW)	-	3.8	2.7	0.8
	W_s - CO_2 compression (MW)	-	4.0	3.5	3.9
	W_s - Fuel Conversion (MW)	-	-	53.5	-
	W_s - Air Separation (MW)	-	-	-	5.9
Net shaft work (MW)		400	392.2	340.3	389.4
η_{HHV} (%)		91.4	89.6	89.0	89.3
η_R (%)		97.9	96.0	95.4	95.6
π_{HHV} (% points)		-	1.8	2.4	2.1
π_R (% points)		-	1.9	2.5	2.3

5. Conclusions

The paper presents the fundamentals for a novel benchmarking methodology where the difference between the thermodynamics limited efficiency and technology limited efficiency is used for benchmarking processes and identifying potentials for process improvements. The first step in this methodology is evaluating the thermodynamics limited efficiency where ideal reversible processes for CO_2 capture are defined with no detailed process information. Maximum thermodynamic efficiencies (energy- and exergy-related) were calculated, and minimum capture work targets were determined.

The methodology was applied to benchmark ideal CO_2 capture process routes with four fuels of differing HC ratio. The efficiency penalties are in the range 1.8-3.6 % points In comparison, capture penalties for real power processes have been shown to be in the range of 8–15 percentage points, which indicates that there should be room for technology improvements, while keeping in mind that regardless of technology development some irreversibilities will always be unavoidable.

The benchmarking methodology presented in this paper will be further developed and the minimum capture work targets are expected to provide useful insights in situations where efforts should be made to reduce irreversibilities in real power processes for CO_2 capture. The minimum capture work targets calculated in the present paper show the quantity of work that is lost in different parts of ideal (reversible) power processes due to the introduction of CO_2 capture.

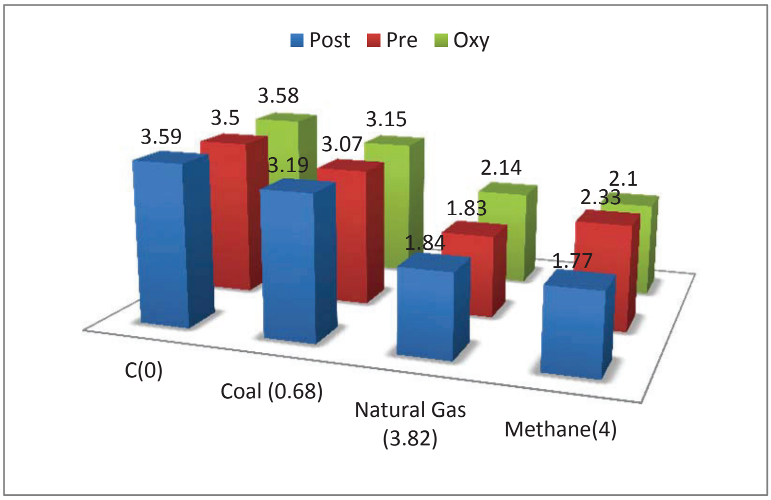

Figure 4: Efficiency penalty (in % points) for the three capture routes with fuels of different HC ratio

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