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STEAM CYCLE OPTIONS FOR CAPTURE-READY POWER PLANTS, RETROFITS AND FLEXIBLE OPERATION WITH POST-COMBUSTION CO_2 CAPTURE

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A rock pile ceases to be a rock pile the moment a single man contemplates it, bearing within him the image of a cathedral.

Antoine de Saint Exupéry

Abstract

The energy penalty for post-combustion carbon dioxide capture from fossil-fired power plants can be greatly reduced - independently of the intrinsic heat of regeneration of the solvent used - by effective thermodynamic integration with the power cycle. Yet expected changes in electricity generation mix and the current immaturity of post-combustion capture technology are likely to make effective thermodynamic integration throughout the operating life of such plants a challenging objective to achieve because of a requirement for extensive part-load operation and also for matching to future technology improvements. Most previous published studies have, however, focused on base-load operation of the power cycle and the carbon dioxide capture plant and with the assumption of a fixed technology.

For carbon dioxide capture-ready plants the characteristics of the capture plant are also not known when the plant is designed. The plant must operate initially without capture at a similar efficiency to 'standard' plants to be competitive. Capture-ready plants then also need to be able to be retrofitted with unknown improved solvents and to be capable of integration with a range of future solvents.

This study shows that future upgradability for post-combustion capture systems can be facilitated by appropriate steam turbine and steam cycle designs. In addition fossil-fired power plants with post-combustion capture may need to be able to operate throughout their load range with the capture unit by-passed, or with intermediate solvent storage to avoid the additional emissions occurring when the absorption column is by-passed. Steam cycles with flexible steam turbines can be adequately designed to accommodate for part-load operation with these novel operating conditions and with rapid ramp rates.

Several approaches for effective capture-ready pulverised coal and natural gas plants are also described. These achieve identical performance before retrofit to a conventional plant with the same steam conditions, but have the potential to perform well after capture retrofit with a wide range of solvents, at the expense of only a small efficiency penalty compared to hypothetical plants built with perfect foreknowledge of the solvent energy requirements. For existing plants that were not made capture-ready, and provided sufficient space is available and other physical limits are not too constraining, ways to achieve effective thermodynamic integration are also discussed.

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Nomenclature

ABC	Ammonium Bicarbonate
AC	Ammonium Carbonate
ALA	Alanine
AMP	Aminomethylpropanol
CCGT	Combine Cycle Gas Turbine
CCR	CO_2 Capture Ready
CCS	Carbon Capture and Storage
CO_2	Carbon dioxide
COP	Conference of Party
CSLF	Carbon Sequestration Leadership Forum
DEA	Diethanolamine
DEFRA	Department for Environment, Food and Rural Affairs
DGA	Diglycolamine
DIPA	Methyldiethanolamine
DMMEA	Dimethylmono-ethanolamine
DOE	Department of Energy
EOP	Electricity Output Penalty
ESP	Electrostatic Precipitation
FCO	Foreign Commonwealth Office
FGD	Flue Gas Desulphurisation
GCV	Gross Calorific Value
GHG	Greenhouse Gas
GtC	Gigatonnes of Carbon
HP	High Pressure
HRSG	Heat Recovery Steam Generator

IEA	International Energy Agency
IEAGHG	International Energy Agency Greenhouse Gas
IP	Intermediate Pressure
IPCC	International Panel on Climate Change
KEPCO	Kansai Electric Power Company
KS1	MHI Proprietary Solvent
KS2	MHI Proprietary Solvent
LHV	Low Heating Value
LP	Low Pressure
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MHI	Mitsubishi Heavy Industries
NETL	National Energy Technology Laboratory
NGCC	Natural Gas Combine Cycle
NH_3	Ammonia
NO_2	Nitrous Dioxide
NO_X	Nitrous Oxides
NZEC	Near Zero Emission on Coal
PeF	Power Equivalent Factor
PZ	Piperazine
SCR	Selective Catalytic Reduction
SO_x	Sulphur oxide (SO_2 and SO_3)
SRES	Special Report on Emission Scenarios
TAR	Third Assessment Report
UNFCCC	United Nations Framework Convention on Climate Change
VLE	Vapour-Liquid Equilibrium

1. Introduction

1.1 Motivations for Carbon Capture and Storage: Carbon in the ground

Carbon capture and storage (CCS) is the operation of removing carbon dioxide (CO_2) emissions from the use of fossil fuels, and subsequently transporting and storing it in deep geological formations to isolate it from the atmosphere. It was proposed as part of a portfolio of technology options for climate change mitigation as early as 1985 (Steinberg, 1985).

Fossil-fuel reserves will not limit carbon emissions to the atmosphere during the 21st century to levels that are expected to avoid dangerous climate change, as pointed out in Figure 1-1. Proven conventional oil, gas and coal reserves - on the left hand side of the diagram - contain far more carbon than the limits on cumulative carbon emissions associated with stabilising atmospheric greenhouse gases at the levels recommended by the International Panel on Climate Change (IPCC) - on the right hand side of the diagram. A tentative target for stabilisation between 450 ppm of CO_2 equivalent and 550 ppm of CO_2 equivalent – between the WRE 450 and WRE 550 scenarios - ,is, at the time of writing, commonly accepted to avoid the worst effects of climate change (IPCC 2007) and potentially limit global temperature rise to 2 degrees Celsius. Recently, the Conference of the Parties (COP) of the United Nations Framework Convention on Climate Change (UNFCCC) considered the possibility of strengthening further the long-term goal for temperature rises to 1.5 degrees Celsius (COP 15, 2009). Nevertheless, cumulative carbon emission limits over the next century, matters more than global levels of carbon emissions in 2050 and beyond and greenhouse gas atmospheric concentrations (Allen et al., 2009).

Additional evidence highlights the need for early action to peak global carbon emissions as early as possible (Committee on Climate Change, 2008). For example, emissions trajectories, peaking in 2028 with an annual reduction rate of total CO_2 emissions of 3% per annum, give a 50% probability of limiting global average warming to 2.5°C this century, and a 21% probability of exceeding a severely dangerous 3ºC, as indicated in Figure 1-2 and Figure 1-3. In contrast, emissions trajectories, peaking in 2016 at a 3% reduction rate per annum or above, give a 50% probability to limit global average warming to 2.1ºC and 2.2ºC with reductions at respectively 3% and 4% per year, as indicated in Figure 1-4 and Figure 1-5. Probabilities of exceeding 2°C by 2100 are 63% and 56% respectively. Additionally, the Committee on Climate Change advocates that global net CO_2 emissions from fossil fuels must ultimately achieve near zero levels for a significant period of time, possibly indefinitely, if dangerous climate change with serious negative impacts on human activities is to be avoided.

In parallel, the IEA World Energy Outlook 2009 forecasts that fossil fuels will remain a significant source of energy for the global economy for several decades while the net CO_2 emissions from large emerging economies, relying heavily on coal as a primary energy source, will increase over the same period of time (IEA, 2009).

Leaving fossil fuel in the ground at the expense of economic development is probably not a politically-acceptable option for developing countries, while energy security without fossil fuel is a concern worldwide within the very short timescales required for action on climate change.

One way of reconciling global climate change ambitions with economic development and energy security is to decouple the use of fossil fuel from CO_2 emissions through the use of Carbon Capture and Storage (CCS), and leave the carbon from fossil fuel based energy as carbon dioxide safely stored in deep geological formations.

An obvious application for CCS is power generation, where power plant flue gases form large point sources of CO_2. The International Energy Agency (IEA) suggests, for example, an interim target of 240 GW of installed CCS capacity by 2030 as part of a mitigation programme to maintain long-term atmospheric greenhouse gas concentrations on a pathway to atmospheric concentration around 450ppm CO_2eq (IEA 2009).

In the UK, the Committee on Climate Change recommends that average specific emissions from electricity generation must fall rapidly to below 100 gCO_2/kWh by 2030, and further down to 50 g CO_2 per kWh by 2050 (Committee on Climate Change, 2009), as illustrated in Figure 1-6. This is compared to a current system average level of around 500 gCO_2 per kWh. Unabated emissions at full load are around 350-500 gCO_2 per kWh for gas plants and 750-1000 gCO_2 per kWh for coal plants without CCS. Although coal has received all the attention so far, this highlights the fact that climate change mitigation to avoid dangerous levels of global mean temperature rise cannot be achieved without a deployment of CCS on natural gas combined cycle gas turbine (CCGT) plants too.

1.2 Post-combustion capture systems with liquid solvents

CO_2 capture techniques were historically developed in the oil and gas industry to treat acid and sour gas and are also used to deliver CO_2 for applications such as soda ash production, liquid CO_2 and dry ice preparation, beverages and in urea production (IPCC 2005). Concepts for capturing CO_2 from fossil power generation for climate change mitigation have been developed more recently and there are now three basic systems, as illustrated in Figure 1-7. Post-combustion carbon dioxide capture from power plant flue gases is the focus of this thesis. Because of the overwhelming preponderance of pulverised coal and natural gas combined cycle power plants, post-combustion capture is likely to have a definite role for retrofit CCS applications and also appears to be a strong contender for new-build CCS plants (IEAGHG, 2006a).

Capturing CO_2 from flue gas is essentially a gas separation process and several alternative separation methods can be used such as chemical absorption, physical absorption, membrane technologies, and cryogenic separation. Capture efficiency, energy consumption, process economy and other technical and operational issues are the judging criteria to assess these technologies. Chemical absorption processes are currently the state-of-the-art technology to capture carbon dioxide from power generation applications.

These technologies make use of the reversible nature of the chemical reaction of a weak base, typically an amine, with a weak acid - carbon dioxide - and of the inherent selectivity of the reaction with respect to the majority of the rest of the (non-acidic) flue gas components. CO_2 can be absorbed by many basic sorbents - including alkali carbonate, aqueous ammonia, and alkanolamines – normally with water as the solvent carrier to create appropriate aqueous solvents. The bond between sorbent molecules and CO_2 is `strong' enough to offer a fast and effective removal of most of the $CO_2$ in one stage of absorption and `weak' enough for the two molecules to be separated through a temperature swing at moderate temperatures (100-150ºC). One of the main causes for the high regeneration energy requirement associated with post-combustion capture is the regeneration of the solvent and attention needs to be paid on how the solvent is regenerated.

The selectivity of the aqueous solvent towards acid gases makes the control of impurities and minor components in the flue gas critical. The types of solvents used for CO_2 absorption tend also to have a high selectivity towards the other acid gases included in flue gas such as oxides of sulphur (SO_x) and nitrogen (principally NO_2), which form heat-stable salts and thus consume the solvent. These components have to be removed before the gas enters the CO_2 absorber. Some solvents are also sensitive to oxidation and to thermal degradation when they are heated for regeneration.

1.2.1 The process for post-combustion capture

Chemical absorption processes operating at atmospheric pressures are usually employed to separate CO_2 from the flue gas before it is discharged to the atmosphere. They are likely to be added after other flue gas treatment processes - Selective Catalytic Reduction (SCR) for nitrous oxide removal, ElectroStatic Precipitation (ESP) or baghouse filter for particulates, and Flue Gas Desulphurisation (FGD) for sulphur oxides.

A typical post-combustion capture plant is composed of three stages as represented in Figure 1-8. In the first stage, CO_2 is removed from the flue gas through direct contact absorption by the solvent in a packed 'scrubber' column. Before entering the absorber both the flue gas and the solvent are cooled to around 40-60ºC for most amines, a trade-off between solvent reaction rates and solvent CO_2 capacity. Flue gas passes through a direct contact cooler to reduce to temperatures where the chemistry of absorption is most efficient. The CO_2 'rich' solvent leaves at the bottom of the column and is heated up against CO_2 'lean' solvent in the cross-flow heat exchanger before entering the stripper. A water wash section at the top of the absorber column removes any droplets of solvent that get carried-over with the rest of the flue gas and also balances any water evaporation in the system.

In the second stage, the chemical bond between the solvent and the CO_2 is broken by heating in the 'stripper', to give a 'temperature swing' cycle between absorption and desorption. The heat necessary for solvent regeneration is provided in a reboiler at the bottom of the column. The total amount of heat required is commonly referred to as the *reboiler heat duty* and is essentially the sum of the energy used for:

- Sensible heat: the energy required to cover the temperature difference between the incoming rich solvent and the outgoing lean solvent
- Heat of absorption: reversing the absorption reaction by breaking the chemical bond between the CO_2 and the absorbent
- Latent heat: vaporising water to establish an operating CO_2 partial pressure and using steam as the stripping gas to carry the CO_2 to the top of the column

After leaving the top of the stripper column (possibly after another water wash) the mixture of CO_2 and water vapour is cooled down. The condensed water is returned to the stripper while the CO_2 is compressed in the third stage (not included in Figure 1-8) to a dense phase fluid at a pressure suitable for transport to a geological storage site, typically 110 bar. The remaining water condensate

is gradually removed as part of the compression process. At the bottom of the stripper the lean solvent is recycled back to the scrubber column through the cross flow heat exchanger followed by further cooling before re-entering the absorber column. In addition to stripping the CO_2, a reclaiming operation is conducted periodically to recover amine by decomposing heat stable salts created by flue gas impurities and oxygen and to dispose of degradation products.

Post-combustion CO_2 capture systems for flue gas from 'conventional' power plants operate close to atmospheric pressure, which result in:

- Large volume of flue gas to be treated and so large equipment sizes.
- Low CO_2 partial pressure, which has an effect on the driving force for the chemical reaction in the absorber. For this reason flue gas from coal plants, which contains 10-15% of CO_2 are more favourable for chemical absorption than flue gas from natural gas combined cycle (NGCC) plants with CO_2 content of around 4% (and a high oxygen content). NGCC post-combustion capture could, however, be significantly helped by flue gas recycling.

Additionally, specific challenges to gas plants may arise. Tolerance to oxygen could prove to be an issue with some specific solvents developed for absorption on coal plant flue gases. These specific solvents may need to be replaced by specific solvents with lower oxidative degradation rates.

Potentially high levels of solvent contamination by sulphur oxides may occur when sulphur-containing liquid fuels are used for supplementary firing. This may necessitate bypassing the capture system since NGCC plants would typically not be fitted with the high-efficiency FGD units required for oil- and coal-fired power plants with CO_2 capture.

Plume visibility at the top of the flue gas stack may also need to be addressed in some jurisdictions. Scrubbed flue gases at the absorber exit leave saturated with water and have to be reheated to avoid plume formation under some conditions (especially still, cold weather). In coal plants this may be done using a rotary air heater at the inlet to the flue gas desulphurization (FGD) units. Air heaters are not currently employed on NGCC units, however, and would be relatively large because of the high excess air levels and hence flue gas volumes. Operation and maintenance of this additional equipment would also be a new feature for NGCC stations, although some operators might be familiar with them from coal plant experience.

The energy intensive aspects of post-combustion CO_2 capture processes are the supply of heat for solvent regeneration and shaft power for CO_2 compression and ancillary equipment, such as flue gas blowers and solvent circulation pumps. The most efficient way to provide heat to the solvent reboiler is to use steam taken from an intermediate point in the expansion stage of the power cycle.

This steam is then no longer available for further electrical power production and an associated decrease in steam cycle power output is observed. Low-grade heat is available in the capture and compression units and can be used in the steam turbine island for boiler condensate feed water heating. The steam previously extracted for condensate heating from the low pressure turbine is now available for power generation, which minimises the drop in power output.

1.2.2 Process selection parameters

The key parameters when determining the technical and economic operation of a CO_2 absorption system are (IPCC 2005):

- Flue gas flow rate - The flue gas flow rate will determine the size of the absorber and the absorber and its packing represents a major part of the overall cost.
- CO_2 content in flue gas - Since flue gas is usually at atmospheric pressure, the partial pressure of CO_2 will be as low as 3-15 kPa. Under these low CO_2 partial pressure conditions, aqueous amines (chemical solvents) are the most suitable absorption solvents (Kohl and Nielsen, 1997).
- CO_2 removal level - In practice, typical CO_2 recoveries are between 80% and 95%. The exact recovery choice may be an economic trade-off, a higher recovery will lead to a taller absorption column, higher energy penalties and hence increased costs, or could be a specified minimum level (as very high overall emission reduction targets, i.e. 80% by 2050, are adopted). The economic cost of emitting CO_2, possibly a carbon price, can in any case be expected to increase over time.
- Solvent flow rate - The solvent flow rate will determine the size of most equipment apart from the absorber. For a given solvent, the flow rate will be fixed by the previous parameters and also the chosen CO_2 concentrations within the lean and the rich solutions.
- Cooling requirement - Cooling is needed to bring the flue gas and solvent temperatures down to temperature levels required for efficient absorption of CO_2. Also, the product from the stripper will require cooling to recover water from the stripping process for recycling.
- Energy requirement - The energy required is the sum of the thermal energy needed to regenerate the solvents, plus the electrical energy required to operate liquid pumps, flue gas blowers or fans and compress the CO_2 recovered to the final pressure required for transport and storage, typically above 100 bar. A dedicated methodology to assess the performance of power generation applications is proposed in Chapter 2 and specific considerations for these applications are discussed.

Additional parameters are:

- Purity of CO_2 achieved – CO_2 transport may require low levels of impurities to avoid corrosion issues for pipeline and ship transport, although this is typically not a major issue for post-combustion absorption processes.
- Volatility of the solvent – in order to reduce carry-over losses in the absorber.
- Degradation rate in order to reduce solvent losses. Oxidative degradation typically occurs in the absorber caused by excess oxygen in the flue gas, while thermal degradation occurs in the desorber, mostly in the solvent reboiler.
- Corrosiveness of the sorbent – additional capital costs may be required if stainless steel components have to be used, although work, on the use of coatings and alternative materials, e.g. for concrete absorption column, is also taking place to reduce construction costs. Due to concerns about corrosion and mixture viscosity, dilute solutions are used, which in return increases the energy requirement of the process for solvent regeneration.

1.2.3 Potential for retrofit and capture-readiness

Because post-combustion capture systems are added downstream of the normal combustion and flue gas cleaning process, they do not modify the base plant to any great extent. Therefore the contribution of post-combustion capture technology to the deployment of CCS by retrofitting existing plants, as part of a global strategy for implementing CO_2 emissions reductions, could potentially be significant.

While a demonstration programme for CCS technologies is put in place over the next decade it is critical that fossil power plants (and other large CO_2 point sources) constructed now and in the future are built as `CO_2 capture-ready' (CCR) so that they can be retrofitted with capture without unnecessary difficulties (See IEAGHG (2007a), co-authored by the candidate). The economic and operating life of coal plant projects is long enough to guarantee that a large fraction of the electricity generation in emerging economies with a fast build-rate of coal plants will in 2030 (and beyond) come from plants built in the next decade, as illustrated in Figure 1-9. The characteristics of post-combustion capture systems can be exploited for capture-readiness of both coal and gas plants.

1.3 Objectives and Outline

Post-combustion capture systems for power generation applications specifically need to consider effective thermodynamic integration between the flue gas scrubbing systems and the power plant steam cycle to guarantee good energetic and economic performance. The significant amount of heat required for solvent regeneration is most efficiently provided by condensing steam extracted from the power cycle. Gibbins et al. (2004) proposes six rules for thermodynamic integration with the power cycle, of new-build plants as follows:

1. Add heat to the steam cycle at as high a temperature as possible (i.e. be prepared to use best available steam conditions if commercially justified).
2. Reject heat from the steam cycle, in the steam extracted for solvent regeneration, at as low a temperature as possible.
3. Produce as much electricity as possible from any additional fuel used, consistent with rejecting heat at the required temperature for solvent regeneration.
4. Make use of waste heat from CO_2 capture and compression in the steam cycle.
5. Use the latest solvent developments
6. Exploit the inherent flexibility of post-combustion capture

The following solvent-specific characteristics are also important:

- The thermal energy of regeneration of the solvent specifies the quantity of heat to be taken from the steam cycle
- The temperature of regeneration of the solvent specifies the steam extraction pressure and thus has an effect on the power loss. On the solvent side of the reboiler it determines the desorber pressure – for a specific solvent - and, in return, the compression power requirement
- The temperature available for heat recovery for feed water heating is directly related to the temperature of regeneration
- The vapour-liquid equilibrium of the solvent-CO_2 system at desorber conditions determines the suction pressure at the compression inlet, and thus the power requirement.

Most published studies, undertaken before this work, have focused on base-load operation of both the power cycle and the carbon dioxide capture plant. Expected changes in electricity generation mix and the current immaturity of capture technology are, however, likely to make effective thermodynamic integration throughout the entire economic life of fossil plants a more challenging objective to achieve because of a requirement for extensive part-load operation and also for matching to future technology improvements.

Furthermore, for CO_2 capture-ready plants the characteristics of the capture plant are not known at the time of commissioning. The plant must operate for a long period without capture and at a similar efficiency to 'standard' plant to guarantee a good economic return. As with plants built with capture from the outset, capture-ready plants also need to be able to use improved solvents and therefore need to be capable of integration with a range of future solvents.

Finally, the inherent flexibility of post-combustion capture can be exploited by retrofitted units - and possibly some new-build units with post-combustion capture – to operate with the capture unit by-passed to boost their power output if/when required, or with intermediate solvent storage to avoid the additional emissions occurring when the absorption column is by-passed.

The scope of work presented in this thesis is related to the rules for thermodynamic integration proposed above. It is organised as follows:

- Chapter 2 reviews the existing literature on the thermodynamic integration of power systems with post-combustion capture and discussed the rationale for CO_2 capture-ready power plants. The existing literature on chemical solvent developments and their potential future developments is then reviewed.
- Chapter 3 examines steam cycle options for capture-ready designs for pulverised coal and natural gas power plants. Design principles are also established to exploit the inherent flexibility of post-combustion capture systems for capture-readiness and used to compare the capture-ready options on the basis of capital costs, operability and performance with and without capture.
- Chapter 4 considers site-specific parameters of pulverised coal plants that were not intended to be retrofitted with post-combustion capture. It shows that the efficiency penalty associated with capture is independent of the base plant efficiency. Steam cycle retrofit options for effective thermodynamic of existing units are assessed and the effect of fuel composition on the efficiency penalty is evaluated.

- Chapter 5 proposes a methodology for a rigorous assessment of solvent characteristics based on thermodynamic integration with the power system and the compression system. The capture-ready steam cycle options of Chapter 3 are assessed on the basis of their potential for future solvent upgrade.
- Chapter 6 presents flexible modes of operation for post-combustion capture systems, including part-load, voluntary by-pass of the capture unit and solvent storage schemes, and their consequences for the operation of the turbine system.
- Finally, conclusions and recommendations for future work are suggested.

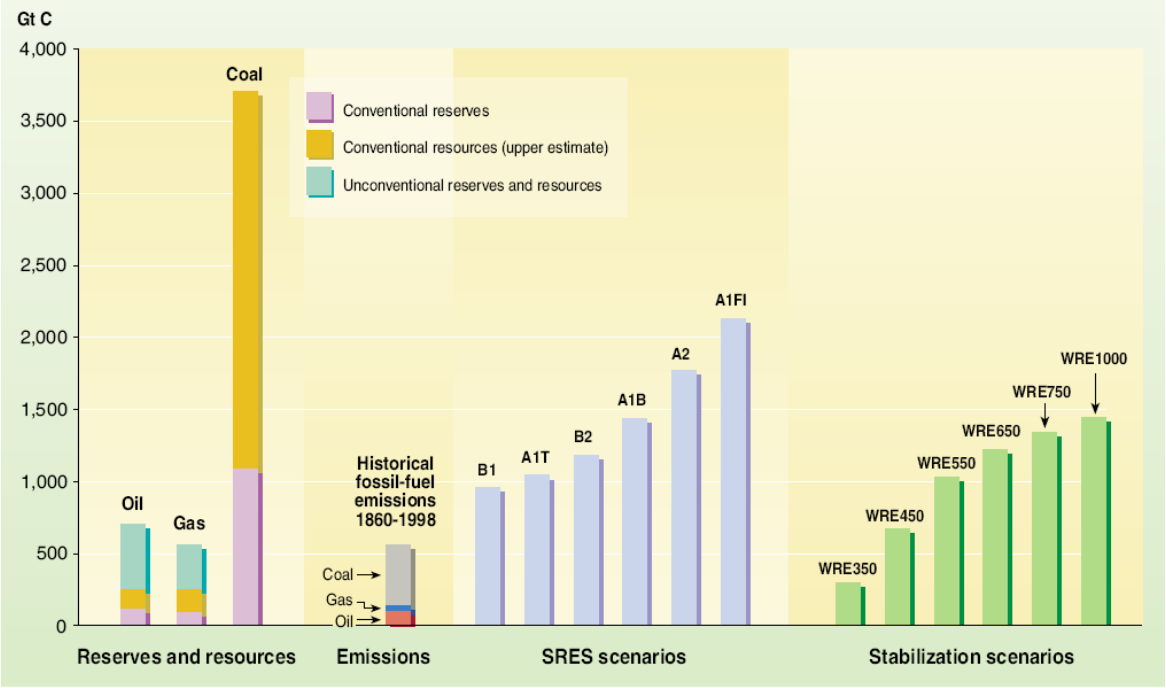


Figure 1-1: Carbon in fossil-fuel reserves and resources compared with historical fossil-fuel emissions and with cumulative carbon emissions.
A range of SRES (Special Report Emission Scenarios) scenario and TAR (Third Assessment Report) stabilisation scenarios until the year 2100 are shown on the right hand side. Unconventional oil and gas includes tar sands, shale oil, other heavy oil, coal bed methane, deep geopressured gas, gas in aquifers, etc. Gas hydrates (clathrates) that amount to an estimated 12,000 Gt C are not shown. Source IPCC (2001)

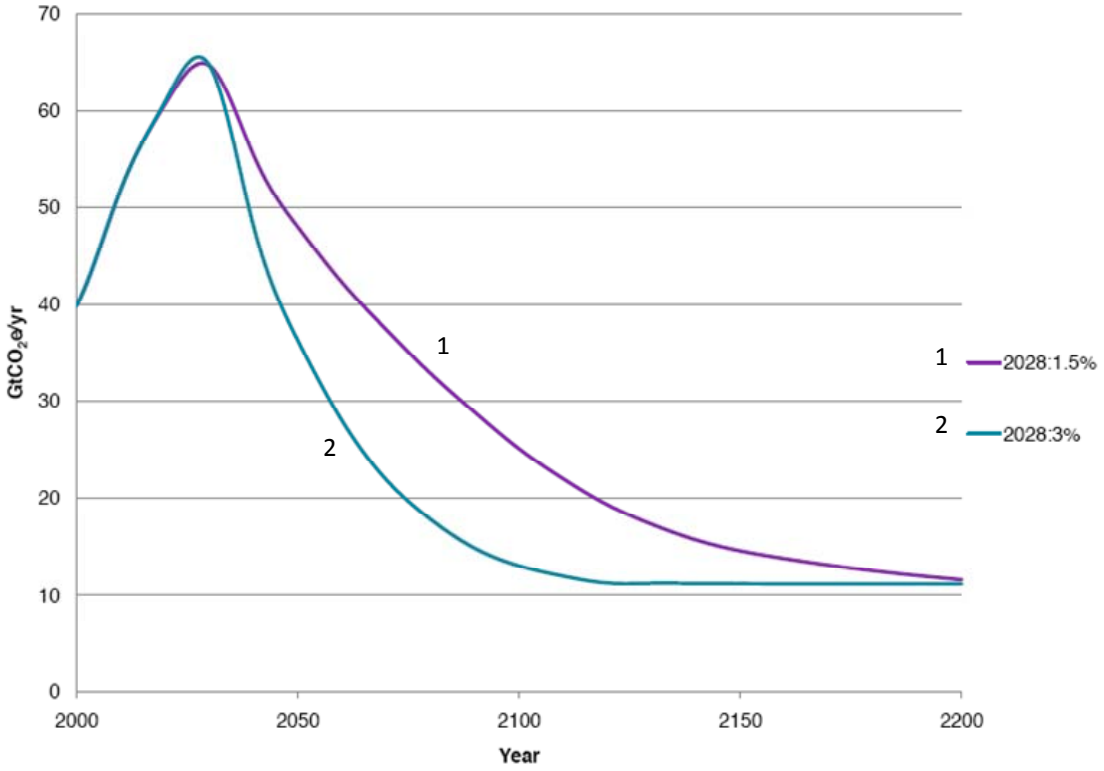


Figure 1-2: Scenario for global GHG emissions reduction trajectories peaking in 2028 with a 1.5% and 3% rates of total CO_2 emissions per annum, from Committee on Climate Change (2008)

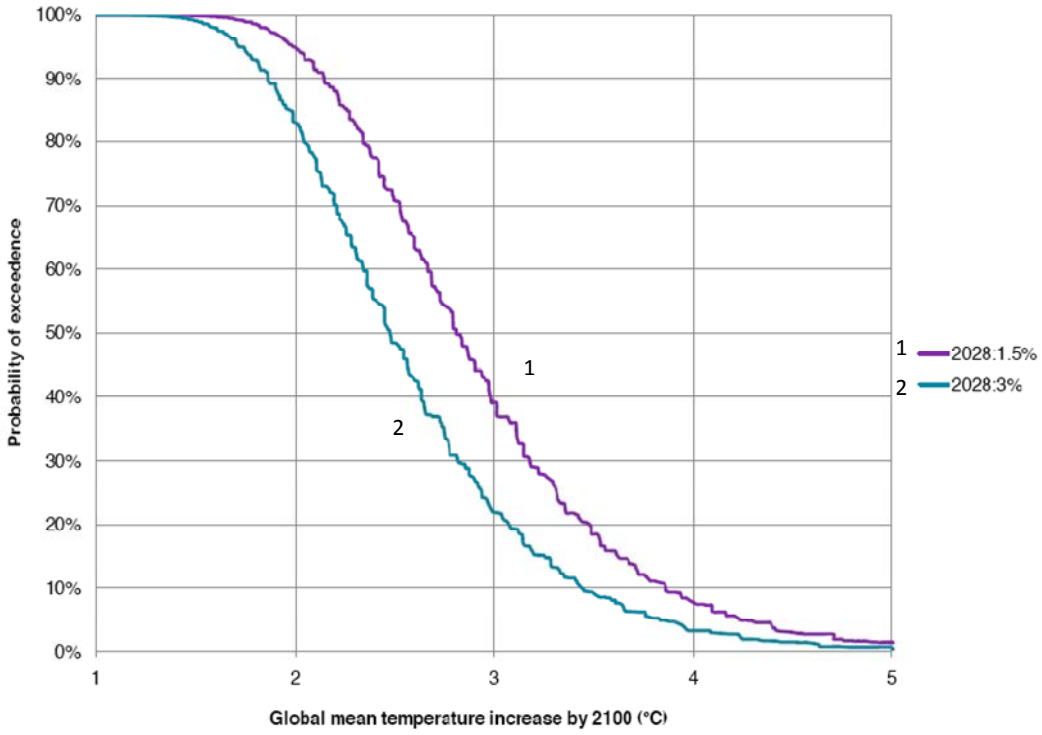


Figure 1-3: Probabilities of exceeding a given global mean temperature increase by 2100 for emissions trajectories peaking in 2028, from (Committee on Climate Change, 2008)

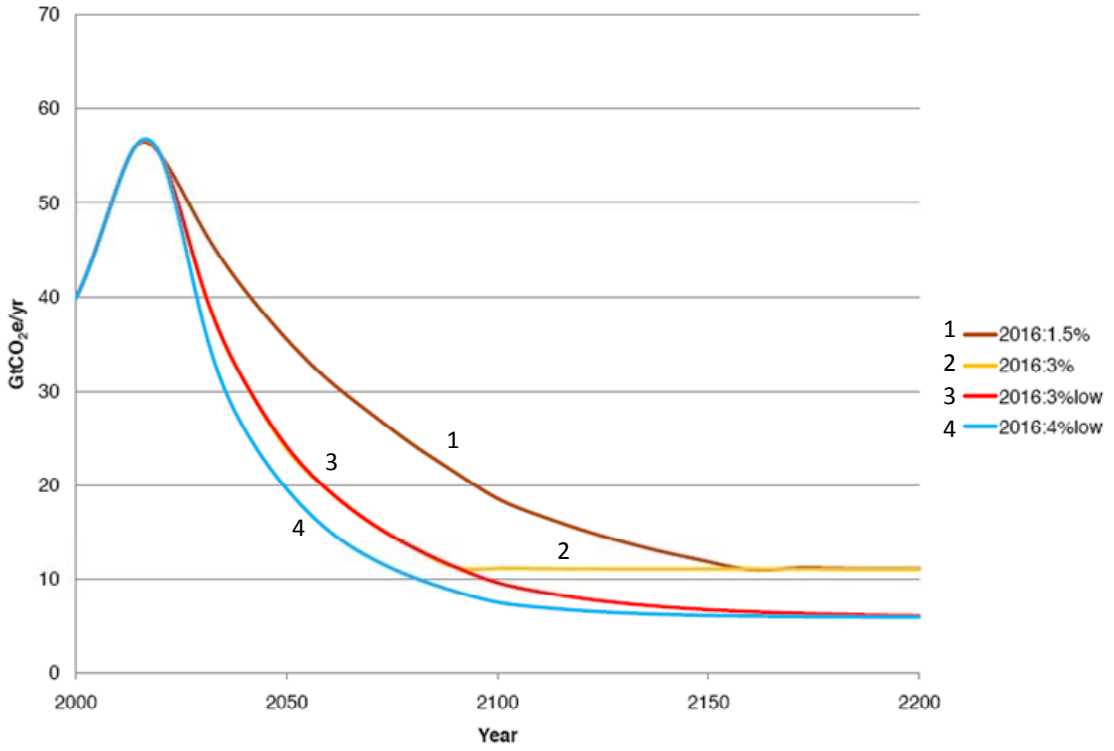


Figure 1-4: Global emissions reduction trajectories peaking in 2016

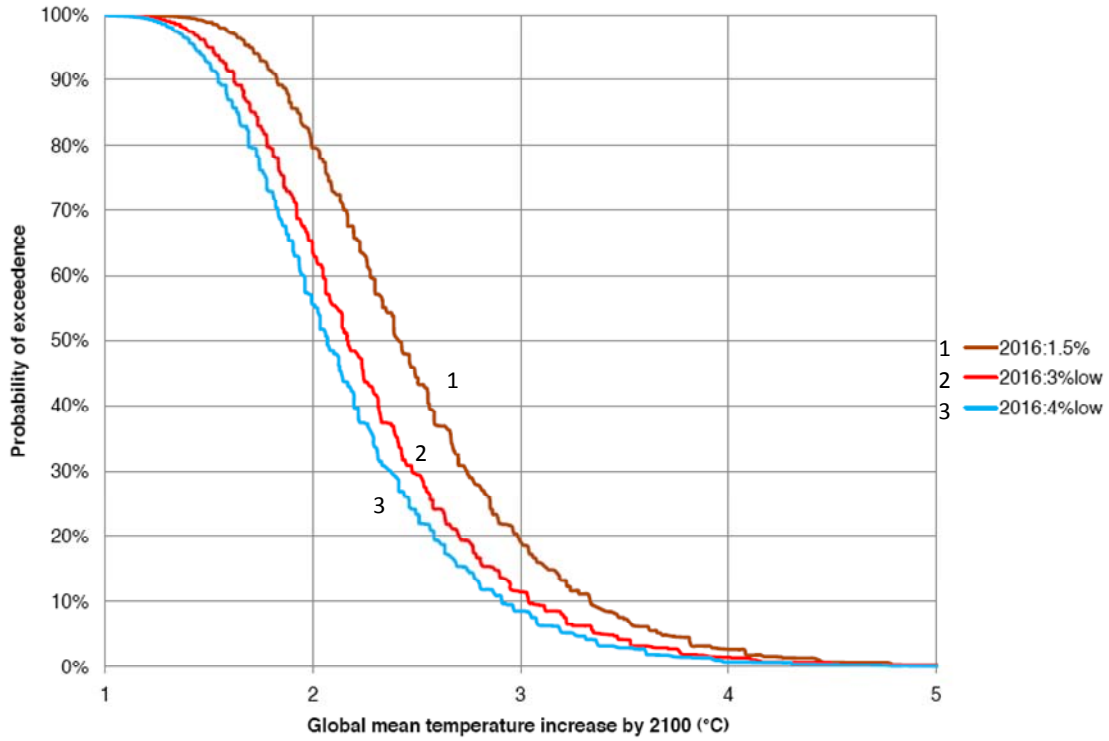


Figure 1-5: Probabilities of exceeding a given global mean temperature increase by 2100 for emissions trajectories peaking in 2016

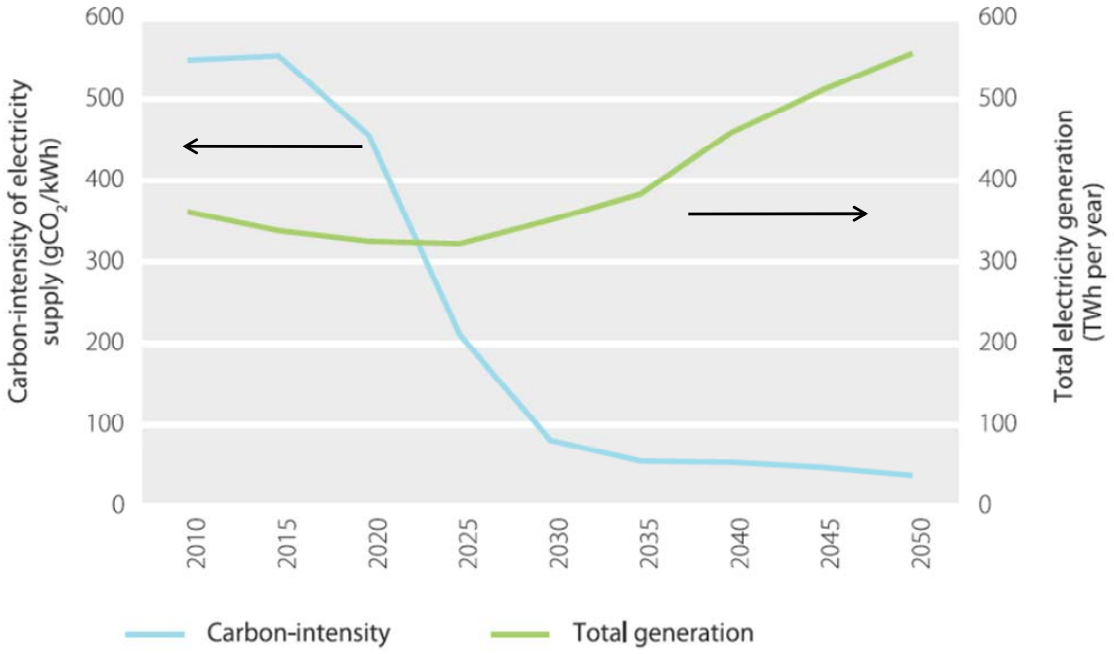


Figure 1-6: Committee for Climate Change (2009) - Declining carbon-intensity and increasing generation of electricity to 2050

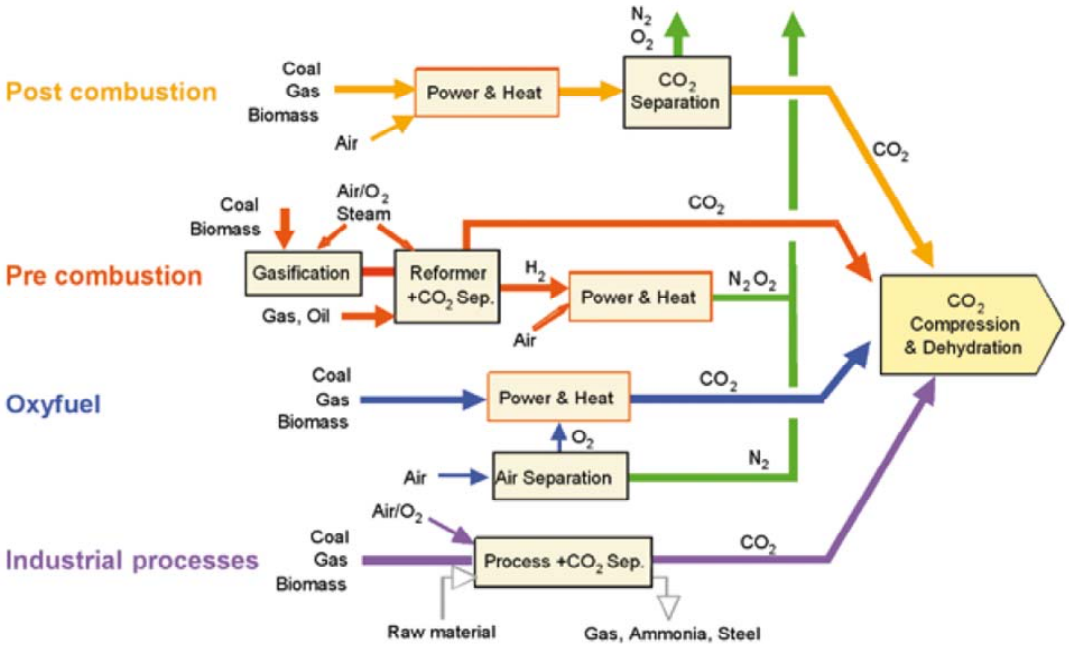


Figure 1-7: CO_2 capture systems

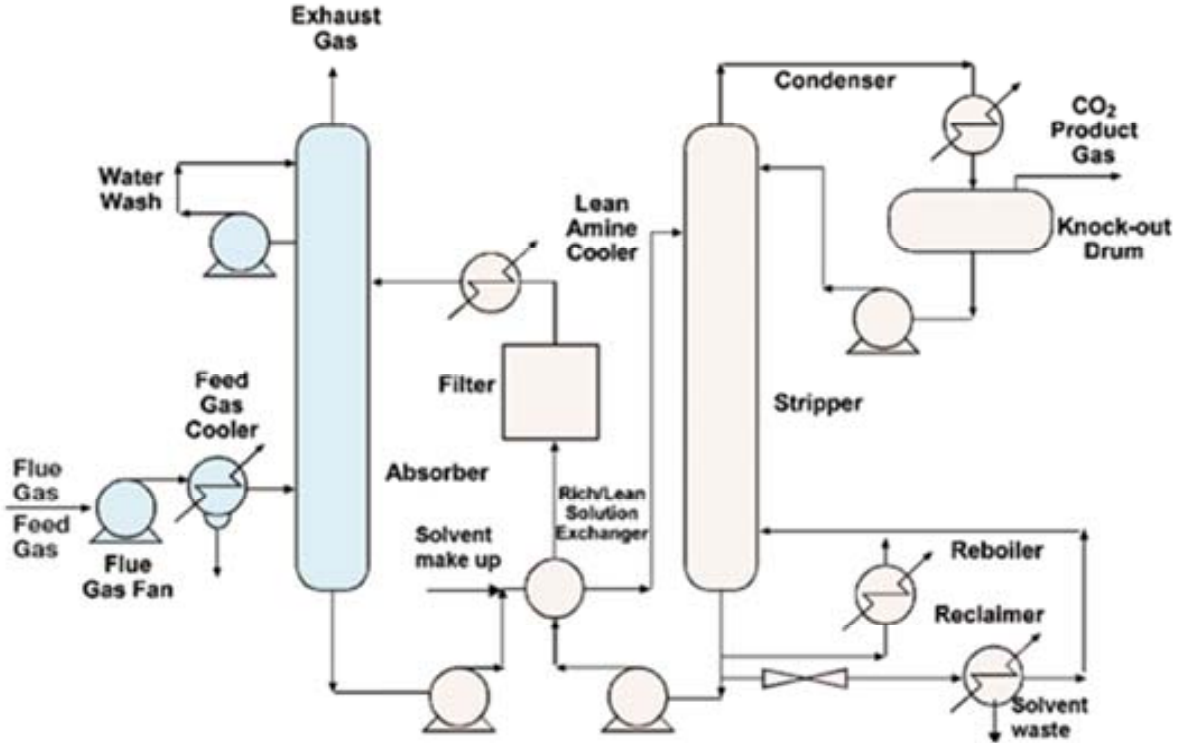


Figure 1-8: Process flow diagram for CO_2 recovery from flue gas by chemical absorption, from IPCC (2005)

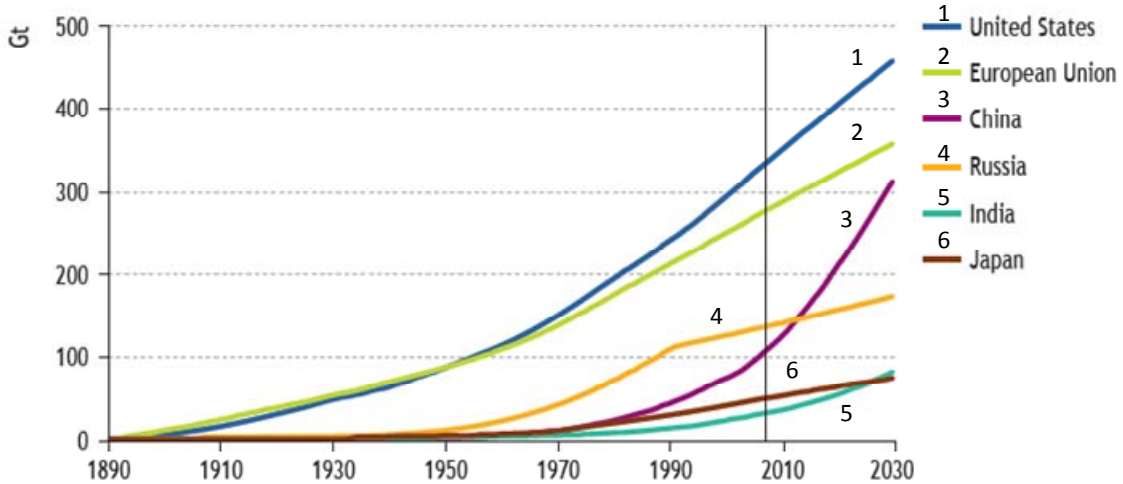


Figure 1-9: National cumulative energy-related CO_2 emissions since 1890 in the reference case of IEA (2009), Source: Marland et al. (2006)

2 Post-combustion capture in power generation with liquid solvents

2.1 Energy requirements for post-combustion capture and thermodynamic integration

Overall the total energy requirement for solvent-based post-combustion capture systems is a mix of thermal heat for solvent regeneration and electrical energy for CO_2 compression and ancillary equipment, such as circulating pumps and flue gas fans. In power generation applications, heat is usually expected to be extracted from the power cycle and carried by the latent heat of saturated steam that is condensed in the solvent reboiler. In addition some of the heat available in the capture plant and in the compression train may also be recovered by steam cycles that would otherwise use low-pressure steam extraction for condensate water heating (i.e. pulverised coal power plants but not combined cycle gas turbine plants). Therefore, a specific methodology is needed for power generation application in order to assess the performance of the capture system on a consistent basis.

2.1.1 Electricity output penalty

The overall energy requirement for post-combustion capture is commonly indicated in two ways. Some studies report it as a fractional fall in the total electricity output from the plant (e.g. a 20% drop in output from the plant), others, as a percentage point drop in the overall thermal efficiency of the plant (e.g. a 9 percentage point efficiency penalty – so the fall in electricity output per unit of fuel energy input). The latter is the more representative metric since the overall energy requirement is independent of the base plant efficiency, as will be shown in Chapter 4. Thus, although the fraction of the total output lost for CO_2 capture and compression in low efficiency plants is greater than in high efficiency plants, the absolute loss of output is the same. The efficiency penalty is, however, affected by fuel composition since the amount of CO_2 generated by combustion per unit of useful thermal energy, and hence the total energy requirement for capture and compression, varies depending on the ratio of carbon content to heating value.

The methodology proposed here allows the performance to be assessed independently of the fuel composition by concentrating rather on the intrinsic performance of the post-combustion capture systems for comparison.

This alternative metric is the electricity output penalty (EOP) per unit of CO_2 captured and compressed on a mass basis. It is composed of the sum of the loss of generator power output incurred by steam extraction and the power requirement for compression and ancillary equipments, divided by the absolute mass flow of compressed CO_2 exiting the plant boundaries, as follows:

$$\text{EOP} = (\text{Loss of generator output} + \text{Compression \& ancillary power}) / \text{CO2 mass flow} \quad (1)$$

Electricity output penalty (EOP)	(kWhe/tCO2)
Loss of generator output	(kW)
Compression & ancillary power	(kW)
CO2 mass flow	(tCO2/hr)

The electricity output penalty relates to the efficiency drop of the power plant as follows:

$$\text{Efficiency penalty} = \text{Fuel specific emissions} * \text{Electricity Output Penalty} \quad (2)$$

Efficiency penalty	(MWhe/MWhth)
Fuel specific emissions	(kgCO2/MWhth)
Electricity Output Penalty	(kWhe/tCO2)

The loss of power output of the turbines due to steam extraction can favourably be traded-off against a reduced energy requirement for compression. For example, solvents delivering a high pressure of CO_2 during the regeneration part of the process can, in some cases, outperform solvents with lower temperature of regeneration, by reducing compression requirements, despite rejecting heat from the steam cycle at a higher pressure.

A modified version of Gibbins' second rule is proposed to account for that effect, by emphasising the need to maximise net plant output.

Originally:

2. Reject heat from the steam cycle, in the steam extracted for solvent regeneration, at as low a temperature as possible.

Modified:

2. Reject heat from the steam cycle, in the steam extracted for solvent regeneration, at a temperature *as close as possible to the temperature of regeneration of the solvent*. *Optimise solvent temperature of regeneration to minimise the sum of the overall electricity output of the capture system and the compression system*.

2.1.2 Performance improvement by effective process integration

Effective thermodynamic integration between the power plant and the capture and compression system contributes to reducing significantly the electricity output penalty. An early description of the principles was given by Mimura et al. (1995) and Mimura et al. (1997) and these have been developed since (Gibbins and Crane, 2004a). State-of-the-art integration is, for example, implemented in a comprehensive study undertaken for the International Energy Agency Greenhouse Gas (IEAGHG) R&D Programme (IEAGHG, 2004). Steam is extracted from the crossover pipe between the intermediate pressure (IP) and low pressure (LP) turbine to reject heat at a temperature as close as possible to the temperature of regeneration of the solvent. The reboiler condensate returns to the power cycle at a temperature as close as possible to the boiler condensate, as opposed to returning to the power cycle condenser. Boiler condensate leaving the power cycle condenser is heated using low-grade heat from the compressor intercoolers and from the reflux condenser at the top of the desorber, as outlined in Figure 2-1.

Earlier Singh et al. (2003) proposed the addition to the pulverised coal boiler of a separate natural gas ancillary boiler to provide steam for solvent regeneration, breaking the first rule of Gibbins et al. by burning natural gas at a relatively low temperature. Unsurprisingly, they report higher cost of abatement for post-combustion capture. Separate ancillary boilers have more recently been proposed for natural gas plants retrofits in the UK, as discussed in more detail in Chapter 3.

Since 2004 a number of studies (Ciferno et al., 2007; Xu et al., 2007; Oexmann et al., 2008; Romeo et al., 2008a; Romeo et al., 2008b; Just et al., 2009; Korkmaz et al., 2009; Kuemmritz et al., 2009; Heischkamp et al., 2009; Linnenberg et al., 2009; Oexmann et al., 2009; Panesar et al., 2009; Pfaff et al., 2009; Romeo et al., 2009;) have been published in the area of thermodynamic integration with no significant achievement in terms of performance improvement, with the exception of joint patents from Mitsubishi Heavy Industries (MHI) and the Kansai Electric Power Company (KEPCO). Kamijo et al. (2006) proposed reheating semi-lean solvent taken from the desorber by heat exchange with relatively low temperature flue gas (128ºC-150ºC) exiting the plant boiler. Ijima et al. (2006) proposed multiple steam extraction from the LP turbine with different pressures to provide heat to the solvent reboiler and to the semi-lean solvent extracted in the middle of the desorption column, as in shown in Figure 2-2.

A review of the electricity output penalty of early industry studies for pulverised coal plants (2000-2004) and their respective levels of thermodynamic integration is provided in Table 2-Table 2-1. It illustrates the potential improvement arising from effective thermodynamic integration, showing that the overall electricity output penalty of post-combustion capture has reduced from 410-470 kWh/tCO_2 to 260-310 kWh/tCO_2 with current state-of-the-art solvents. This improvement is illustrated particularly well by two of the studies in Table 2-1 that were carried out on the same plant. Ciferno et al. (2007) is a follow-on study of Bozutto et al. (2001) of Unit 5 at Conesville, Ohio, USA, and shows a significant reduction in the overall electricity output penalty compared to Bozutto et al. Yet Ciferno et al. still report a higher electricity output penalty than the most recent studies. Although none of the integration rules of Gibbins et al. for new-build CCS plants are broken in this study, the turbine retrofit still offers potential for significant improvement. A critique of Ciferno et al.'s thermodynamic integration is provided in more detail in Chapter 4, followed by an addition to the integration rules, specific to retrofit projects.

2.1.3 Thermodynamic integration under varying operating conditions and uncertainty

Until recently, thermodynamic integration studies have been mostly limited to base-load operation of both the power cycle and the carbon dioxide capture plant. But with expected changes in electricity generation mix with the introduction of low-carbon power generation - inflexible nuclear plants and intermittent renewable sources, such as wind turbines - thermodynamic integration under an extensive range of operating loads has become critical. It has been covered by relatively limited number of studies (Möller et al., 2007; Lucquiaud et al., 2008; Linnenberg and Kather, 2009) and is further discussed in Chapter 6.

A staged deployment of CCS and the requirement to build new fossil power plants as CO_2 capture-ready (CCR) plants make thermodynamic integration even more challenging. Effective thermodynamic integration must be achieved throughout the whole operating life of fossil plants. The integration of the power cycle before capture is fitted must thus not preclude effective thermodynamic integration with capture. The fact that the characteristics of the capture plant are not known at the time of commissioning and the current immaturity of capture technology require plant developers to design systems under uncertain conditions.

2.2 CO_2 capture-ready plants

2.2.1 The rationale for CO_2 capture-ready (CCR) plants

Rapid global deployment of carbon capture and storage (CCS) requires a two-track approach. CCS needs to be deployed at scale as quickly as possible and other plants, if built without CCS, need to be built CO_2 capture ready (CCR) before they are subsequently retrofitted. In particular, coal plants are likely to continue to be built in large numbers in developing countries. CCS is not an immediate option for all or most of these plants, but it would be feasible to make large numbers of them CCR for subsequent retrofit of flue gas scrubbing systems for post-combustion capture.

Emerging economies such as China, India, and South Africa are heavily reliant on expanding their coal-based power generation and, anecdotal evidence suggests, are not likely to implement CCS on the coal plants they build until it has been deployed in developed countries. Particularly, in these rapidly developing countries, where alternative energy sources are likely to, at best, only reduce the rate of growth in coal use somewhat, building new fossil power plants carbon capture ready (CCR) is likely to be the only approach that can reduce the risk of carbon lock-in, a '*persistent market and policy failures that can inhibit the diffusion of carbon-saving technologies despite their apparent environmental and economic advantages'* (Unruh, 2002).

At company level, making plants CCR also gives plant developers the option to fit capture in the future to protect the value of their investment against potential future increases in CO_2 emission pricing or a regulatory requirement for CCS. Plants not designed to be capture ready may still be able to be retrofitted with capture equipment and connected to CO_2 storage, but at an increased cost (Gibbins et al., 2006). They may also be 'capture impossible'; it would be cheaper to knock them down and start again, possibly in a new location, rather than attempt to implement capture.

2.2.2 Historic development of CO_2 capture-readiness

The term capture-ready was initially associated with Integrated Gasification Combined Cycle plants (IGCC), where coal is gasified to produce syngas burnt into a combined cycle for electricity generation. Capture-ready discussions in the literature, especially in the USA, were often confined to IGCC plant (with an implicit assumption that capture could not be retrofitted to other types of power plant, principally pulverised coal units, or that no special provisions were needed to make such combustion units capture-ready). This emphasis on IGCC plants was apparently based on the expectation that a capture process could easily be added with a shift reactor without modifying the existing base plant.

Sekar et al. (2005) argued notably that the choice of a base generation technology - between IGCC and PC, is itself a capture-ready decision, since they viewed IGCC as being a more cost-effective platform for long-term capture and this view was also implicit in US energy policy at the time (DOE, 2007).

Rutkowski et al. (2003) studied the options of retrofitting capture to an oversized IGCC system and compared it to an un-modified 'pre-investment' IGCC plant, using a quench gasifier. Efficiencies with and without capture were predicted to be the same for all options. They showed that the capture-ready plant with the oversized gasifier had specific investment costs approximately 5% higher than a standard plant without capture, and once capture was fitted approximately 5% lower than a standard IGCC plant built with capture from the outset. Griffiths and Scott (2003) proposed a specific design for a capture-ready IGCC which incorporates a shift reactor from the outset operated both without and with capture, and showed that the capture IGCC system compared to purpose-built conventional systems have a slightly lower efficiency before capture, corresponding to an extra 5% fuel use, and approximately 2% higher specific capital costs with capture. Since then several studies using option valuation techniques[1](Sekar, 2005; Bohm, 2006; Bohm et al., 2007; Liang et al., 2009) have highlighted the absence of economic drivers to make large pre-investment for capture-ready designs worthwhile and pointed out that, beyond space and access, significant capital pre-investments do not appear to be justified by the cost reductions that can be achieved when capture is added. Proposals for capture-ready designs for IGCC plants seem to have since largely been abandoned, with the growing expectation that most IGCC plants that are built will have capture from

[1] Option valuation techniques are methods developed in finance to help the decision-making of investment under uncertainty

the outset (e.g. the Powerfuel Project at Hatfield, UK (Powerfuel, 2009) and the BP and Rio Tinto project at Kern County, California (Hydrogen Energy, 2009)).

2.2.3 Recent developments on CO_2 capture readiness

At the 2005 G8 Gleneagles summit it was agreed that the participants should adopt a plan of action on climate change that included working "to accelerate the development and commercialization of Carbon Capture and Storage technology by… inviting the IEA to work with the CSLF to study definitions, costs, and scope for 'capture ready' plant and consider economic incentives…". In response to the G8 communiqué the IEAGHG R&D Programme prepared a comprehensive report (IEAGHG, 2007a – co-authored by the candidate) where the essential criteria for CCR fossil plants were largely resolved. It identified technical approaches for pulverised coal plants to be made capture ready for post-combustion capture or oxy-combustion, and in particular, the major requirements for CCR plants regardless of the CCS technology chosen for the retrofit, which are principally

- a study of options for CO_2 capture retrofit and potential pre-investments;
- inclusion of sufficient space and access for the additional facilities that would be required;
- identification of reasonable route(s) to storage of CO_2.

In 2008 the US Department of Energy (DOE) National Energy Technology Laboratory (NETL) published a comprehensive study on CCR coal plants looking at pre-combustion capture and post-combustion capture options for respectively IGCC plants and pulverised coal plants, including a list of major equipment required to build a CCR plant (Ciferno et al., 2008). Unfortunately, this study was predicated on the assumption that the net power output of the plant had to be maintained after retrofit. This approach, based on perceived requirements in some markets in the United States at the time, impacted significantly on the economic performance and technical design of the plant and inevitably required specific pre-investments to be made. This failure to consider alternatives where investments to cover capture energy penalties are made at the time of retrofit contradicts the work of Sekar (2005), Bohm (2006), Bohm et al. (2007) and Liang et al. (2009) and is unlikely to be a suitable approach for CCR design in most markets.

In contrast, the IEAGHG study (IEAGHG, 2007a) showed that it is more appropriate to define and implement CCR plants so that a loss in the continuous maximum power output of the plant is acceptable when it is fitted with CCS. If additional power is required to substitute for lost capacity

when CCS is retrofitted then new capacity built at the time of retrofit can be specifically designed for the prevailing requirements and appropriately incorporate the latest technological improvements. If this approach is followed, initial pre-investment requirements can amount to less than 1% of the total capital cost for post-combustion capture systems, which was subsequently confirmed in a study commissioned by the FCO and DEFRA investigating the potential for CCR plants in India (Napier-Moore et al., 2008).

In 2009 Carbon capture readiness was enforced by an EU Directive (EU, 2009) equipped with CCS facilities during their operational lifetimes. In the UK, the Department of Energy and Climate Change released CCR guidelines for plant developers seeking planning consent (DECC, 2009), although new (NGCC) plants given planning consent during 2007 and 2008 were, however, also required by the UK government to be built as CCR despite the absence of such a regulatory guide.

2.2.4 Steam cycle considerations for CO_2 capture-ready fossil power plants

Despite major developments with regards to capture-readiness over the last couple of years the technical literature on the thermodynamic integration of CCR plants for post-combustion capture is limited, to the candidate's knowledge, to two industry studies (Xu et al., 2007; Panesar et al., 2009), a patent on a specific steam turbine design by ALSTOM (Lord and Hemsley, 2009) and to two peer-reviewed articles authored by the candidate on CCR requirements for pulverised coal plants and natural gas plants (Lucquiaud and Gibbins, 2009; Lucquiaud et al., 2009). Lord and Hemsley propose to configure the intermediate pressure (IP) turbine for post-modification for operation with post-combustion capture. In its initial configuration the turbine rotor and casing are each longer than is necessary to accommodate all turbine stages. When capture is retrofitted the turbine is modified to include at least one further stage and increase steam expansion down to the pressure required for the post-combustion capture process. Lord and Hemsley's approach achieves good thermodynamic integration with and without capture, but does so at the expense of locking-in the IP turbine outlet pressure with capture at a time when the immaturity of post-combustion capture system technology uncertainty still prevails. To address this limitation the following section discusses possible future solvent developments while Chapter 5 specifically examines steam turbine configurations for upgradeable post-combustion capture applications.

2.3 State-of-the-art amine based solvents and their potential future developments

2.3.1 Monoethanolamine: the reference solvent

The most widely sorbents used for acid gas treatment are alkanolamines, including aqueous monoethanolamine (MEA), diglycolamine (DGA), diethanolamine (DEA), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA).

Monoethanolamine (MEA) is the most widely studied for post-combustion CO_2 capture from power plant flue gas and is often used as the reference solvent for performance comparison. It is relatively reactive and thus able to achieve a high volume of acid gas removal at a fast rate. The chemical equilibrium between aqueous MEA and CO_2 can be written with the following equilibrium equations where R is - C_2H_4OH and R' is –H for MEA:

$$2\,H_2O \quad <\text{-----}> \quad H_3O^+ + OH^- \qquad (3)$$

$$CO_2 + 2\,H_2O \quad <\text{-----}> \quad H_3O^+ + HCO_3^- \qquad (4)$$

$$HCO_3^- + H_2O \quad <\text{-----}> \quad H_3O^+ + CO_3^{2-} \qquad (5)$$

$$H_3O^+ + RR'NH \quad <\text{-----}> \quad RR'NH_2^+ + H_2O \qquad (6)$$

$$RR'NH + HCO_3^- \quad <\text{-----}> \quad RR'NCOO^- + H_2O \qquad (7)$$

Two moles of MEA are needed to absorb one mole of CO_2. The reactions are reversible and the direction of the equilibriums is temperature dependent. The kinetic of reaction (7) is relatively fast and the $RR'NCOO^-$ species formed, a carbamate ion, is relatively stable. Thus, in the region of 0.02-0.48 mol of CO_2 per mol of amine the reaction of CO_2 with aqueous MEA can be approximated by a single chemical equilibrium reaction (Gabrielsen 2005):

$$2RR'NH + CO_2\,(aq.) \quad <\text{-----}> \quad RR'NH_2^+ + RR'NCOO^- \qquad (8)$$

It should be noted that the precise nature of the mechanism has been the subject of debate (Aboudheir et al., 2003, da Silva and Svendsen, 2003, 2004, 2006, 2007).

2.3.2 Potential for performance improvement

The development of better sorbents with lower overall regeneration energy requirement was identified as the highest priority R&D objective according to an expert elicitation carried out by Rao and Rubin (2006). Alternative solvents to MEA are being actively researched to reduce the overall costs of post-combustion capture systems. This effort often focuses on the reduction of operating costs and, in particular, on developing solvents with a lower thermal energy of regeneration in the expectation that this will reduce the energy penalty of post-combustion captures systems. This assumption is not necessarily true, however, for solvents with a lower thermal energy of regeneration but increased compression energy requirements. The temperature of regeneration therefore also matters and the updated second rule for thermodynamic integration with the power cycle and the compression system must prevail, i.e. the overall electricity output must be minimised. This section reviews the alternative solvents to MEA proposed in the literature while Chapter 5 proposes a rigorous methodology to assess their performance in an integrated power plant system.

The thermal energy of regeneration of solvents can be broken down into three principal parts, as pointed out earlier:

- Sensible heat: the energy required to cover the temperature difference between the incoming rich solvent and the outgoing lean solvent
- Heat of absorption: reversing the absorption reaction by breaking the chemical bond between the CO_2 and the sorbent
- Latent heat: vaporising water to establish an operating CO_2 partial pressure and use steam as the stripping gas to carry the CO_2 to the top of the column

Typical values for MEA are approximately 50% of the overall energy of regeneration for sensible heat, 25% for the heat of absorption and 25% for steam stripping/ latent heat (Ciferno et al, 2005). These values differ from one solvent to another and are only given as an illustrative example.

Work has been undertaken to optimise each of these components. Alie et al. (2005) and Abu-Zahra et al. (2007) performed a parametric study of a MEA CO_2 absorption process.A significant finding was that the thermal energy requirement for regeneration of MEA decreased with increasing lean loading until a minimum was reached. The optimum loading to minimise the thermal energy of regeneration of the solvent was found to be around 0.32–0.33 mol CO_2/mol MEA for a coal power plant with 90% CO_2 removal and a 30 wt% MEA solution (Abu Zahra et al., 2007). Plaza et al. (2010) found that, when the a counterfactual is included to account for the loss of output due to steam extraction and for the energy necessary for compressing CO_2, the optimum lean loading for 30%wt

MEA shifts to a higher loading around 0.41 mol CO_2/mol MEA. The methodology of Plaza et al. (2010) is discussed in more details in Chapter 5.

Corrosion inhibitors for reduction of solvent sensible heat

Corrosion is typically the limiting factor for MEA concentrations. Concentrations up to 30 wt% MEA for aqueous solutions are currently reported, although Aboudheir et al. (2001) reported pilot plant studies on MEA systems at ultra-high concentration, up to 54 % on a mass basis. Higher carrying CO_2 capacity with increased concentration of the solvent reduces the required solution circulation and, therefore, the sensible heat for the temperature swing.

Recently, Carette et al. (2009) proposed advanced corrosion inhibitors, which allow the capture unit to operate with a solvent concentration up to 40% on a weight basis, and thus reduce the amount of water to heat up between the absorber and the stripper, and thus reduce the specific heat component. This leads to a reduction of thermal energy of regeneration from 3.2 GJ/tCO_2 to 3GJ/tCO_2 without changing the reboiler temperature (Lemaire and Raynal, 2009).

Tertiary amine reaction – increased solvent capacity

The maximum CO_2 loading capacity of MEA is, based on stoichiometry, about 0.5 mol of CO_2 per mol of amine. Tertiary alkanolamines have a maximum loading capacity of 1 mol of CO_2 per mol of amine and have been proposed as alternative chemical absorbents. Unlike primary amines and secondary amines, tertiary amines such as MDEA cannot form carbamate ions because they lack an atom of hydrogen attached to the nitrogen. Instead they form bicarbonate ions in a reaction in which water acts as a homogeneous catalyst, which can be written as follows, where R_3N is the molecule of MDEA

$$CO_2 + R_3N + H_2O \text{ <-----> } HCO_3^- + R_3NH^+ \quad (9)$$

MDEA has an equilibrium CO_2 loading capacity that approaches 1 mol CO_2/mol amine. This advantage is offset by a slower rate of absorption though. Similarly, mildly hindered amines mainly absorb CO_2 as bicarbonate, not carbamate, so their absorption capacity approaches 1 mole for each mole of CO_2.

Another example of a solvent with an increased capacity is a proprietary solvent developed by Kansai Electric Power Company (KEPCO) and Mitsubishi Heavy Industries (MHI). The KS-1 solvent is a sterically hindered amine which can achieve loading as high as 1 mol of CO_2 per mol of amine (Mimura et al., 1995). It has been developed jointly with specific equipment such as the proprietary packing KP1 and specific process integration to reduce the energy requirement of the CO_2 capture

process by 20% compared to MEA as stated in (Yagi et al., 2004; Yagi et al., 2006). The regeneration of the KS-1 solvent can be carried out at low pressures and temperatures of 110–120°C, the levels of formations of heat stable salts that cannot be recovered in the reclaiming process are low and KS-1 is also reported to exhibit corrosion levels 25 to 30 times lower than inhibited MEA (Mimura et al., 1995). Mimura et al. (1997) described the other proprietary solvent developed by MHI and KEPCO: KS-2. The performance in terms of energy requirement is similar to KS-1. The corrosion and degradation rates are also comparable to KS-1. KS-2 offers a better efficiency than KS-1 for low CO_2 content flue gas and is, therefore, more suitable for applications for CO_2 absorption from the combustion of natural gas.

Aqueous piperazine

Piperazine (PZ) is a di-amine with two molecules of nitrogen available for CO_2 absorption. The absorption of CO_2 into PZ has been studied in depth by Bishnoi (2000), Ermatchkov (2003, 2006), Derks (2006). They investigated reaction kinetics, mass transfer, and CO_2 solubility. Later, Hilliard (2008) suggested that the concentrations used in these studies for CO_2 solubility in aqueous solutions, from 0.2 and 0.6 mol/m^3, were too low for industrial applications. Notably, Hilliard showed that piperazine loaded with CO_2 becomes more soluble in water. Recently Freeman et al. (2010) carried out an extensive analysis of aqueous piperazine with new experimental data on viscosity, reaction rates (two times faster than MEA), and thermal stability (adequate up to 150ºC). The thermal heat of regeneration is reported to be 10% lower than MEA.

Ammonia

Ammonia wet-scrubbing was originally developed for flue gas desulphurisation, to reduce SOx levels in flue gas from combustion gases (e.g. Bai et al., 1994). CO_2 presents similarities with SO_2 but is a less strong acid. Ammonia reacts with CO_2 via different mechanisms as represented below

$NH_3(aq)$	+	$H_2O(l)$	+	$CO_2(g)$	<----->	NH_4HCO_3 (aq.)	(10)
$2NH_3(aq)$	+	$H_2O(l)$	+	$CO_2(g$	<----->	$(NH_4)_2CO_3$ (aq.)	(11)
$(NH_4)_2CO_3$ (aq.)	+	H2O (l)	+	CO_2 (g)	<----->	2 NH_4HCO_3 (aq.)	(12)

Yeh et al. (2005) reports the enthalpy of absorption for the 3 reactions, respectively

$$\Delta H_{rx} = 15.25 \text{ kcal/mol} \quad (13)$$

$$\Delta H_{rx} = 24.1 \text{ kcal/mol} \quad (14)$$

$$\Delta H_{rx} = 6.4 \text{ kcal/mol} \quad (15)$$

For comparison the enthalpy of absorption of 30%wt MEA is 82kJ/mol, 19.6 kcal/mol (Mc Cann et al., 2008)

Ammonia-based absorption has a number of other advantages over amine-based systems (Figueroa et al., 2008), such as:

- the potential for high CO_2 capacity,
- lack of degradation during absorption/regeneration
- tolerance to oxygen in the flue gas
- low cost, and
- potential for regeneration at high temperatures and hence pressures.

Some concerns exist with ammonia wet-scrubbing, notably that the flue gas must be cooled to enhance the CO_2 solubility and minimise ammonia vapour emissions from the absorber (see the Chilled Ammonia Process below). Additionally, ammonia carryover in the CO_2 during regeneration at elevated temperatures may require an additional water-wash at the top of the stripper.

You et al. (2008) proposed to add different amine-containing hydroxyl groups (OH-) to reduce the volatility of aqueous ammonia (NH_3). The additives also slightly increased the removal efficiency. These results were attributed to the interactions between ammonia, its additives and CO_2 via hydrogen bonding.

The Chilled Ammonia Process

The CO_2 capture process using chilled ammonia is a post-combustion process that has been patented in 2006 by ALSTOM (Gal, 2006). It involves absorbing the carbon dioxide from the flue gas of a power plant at low temperature (0–20 °C) using aqueous ammonia as the solvent. In this temperature range precipitation occurs in the absorber, which requires specific process equipment to handle a slurry at the outlet of the absorber. The desorption is made at high temperature (100–200 °C). This process uses the same absorption chemistry as the aqueous system described above, but differs in

that a slurry of aqueous ammonium carbonate (AC) and ammonium bicarbonate (ABC) and solid ABC is circulated to capture CO_2, which increases the CO_2 carrying capacity. The absorption process operates at temperatures around 5-10ºC to limit the ammonia slip in the flue gas leaving the absorber. The flue gas is cooled before absorption using chilled water, which constitutes an additional use of ancillary power, and a series of direct contact coolers. Darde et al. (2009) published a preliminary independent assessment of the capture process.

Other alternative absorbents

Rochelle (2000) outlined the different types of amine solvents, which could be used for CO_2 capture. These include:

- simple alkanolamines;
- primary – monoethanolamine (MEA) - $(C_2H_4OH)NH_2$;
- secondary – methylmonoethanolamine (MMEA), diethanolamine (DEA) – $(C_2H_4OH)_2NH$;
- tertiary – dimethylmonoethanolamine (DMMEA), methyldiethanolamine (MDEA);
- hindered amines;
- mildly hindered primary – alanine (ALA);
- moderately hindered – aminomethylpropanol (AMP);
- cyclic diamines – piperazine.

The heat of absorption of these chemical absorbents is determined by the overall reaction path, and includes (McCann et al., 2008):

- Hydration of CO_2 in the solution, which for water is around 25% of the binding energy in case of MEA (~20 kJ/mol CO_2).
- Carbamate formation depending on the amine which is around 15% of the binding energy in case of MEA (~10 kJ/mol CO_2).
- Protonation of the amine which contributes around 60% of the binding energy in the case of MEA (~50 kJ/mol CO_2).

The literature on chemical absorbents aiming at outperforming current state-of-the arts solvents is extensive. The properties of numerous amines, ionic liquids, amino-acid salts and enzymes additives have been investigated, as indicated in Table 2-2. Solvents blends, developed to tune the characteristics of solvents, have completed this large effort. The emphasis for solvent development,

was, however, initially put on high removal rate following 'historical' requirements for the gas treating industry. Discussions were often confined to the heat of absorption of the solvent with an implicit assumption that a low heat of absorption would imply a low thermal heat of regeneration, and by extension lower overall energy requirements. The contribution of the heat of absorption to the overall thermal energy of regeneration is still currently subject to debate. For example Feron (2010) argues that reducing the binding energy results in a lower energy of regeneration of the solvent. This contradicts previous work by Oyenekan (2007), however, who demonstrated that for a given stripper operating pressure there is an optimum heat of reaction to lower the solvent energy of regeneration, and by extension the reboiler duty. The optimum is attained when reduction in solvent capacity are compensated by reduction in the steam stripping component of the energy of regeneration.

In reality, as chapter 5 shows, minimising the overall EOP of a specific solvent necessitates adequate process integration and a lower reboiler duty does not necessary lead to a lower electricity output penalty (EOP).

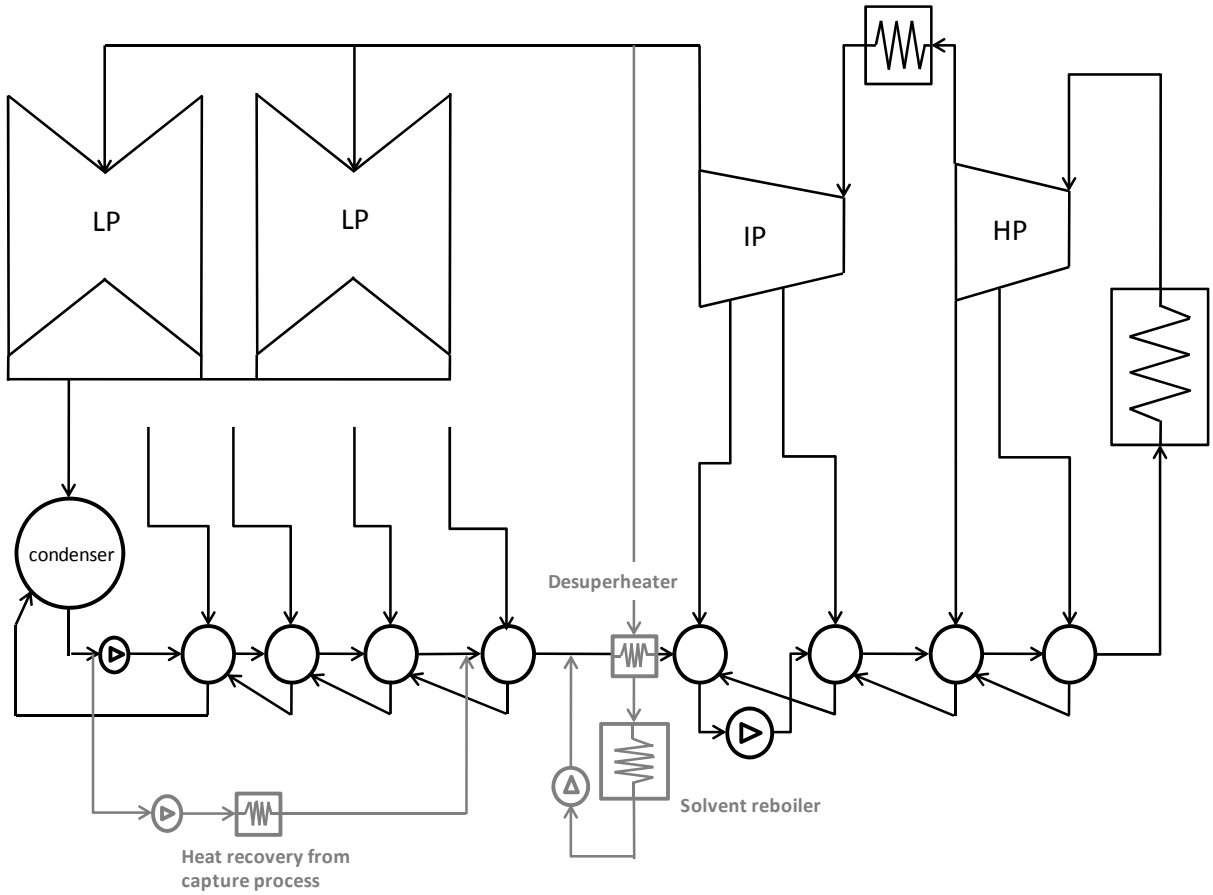


Figure 2-1: Principles for thermodynamic integration between the steam cycle of a new-build pulverised coal unit and the capture process

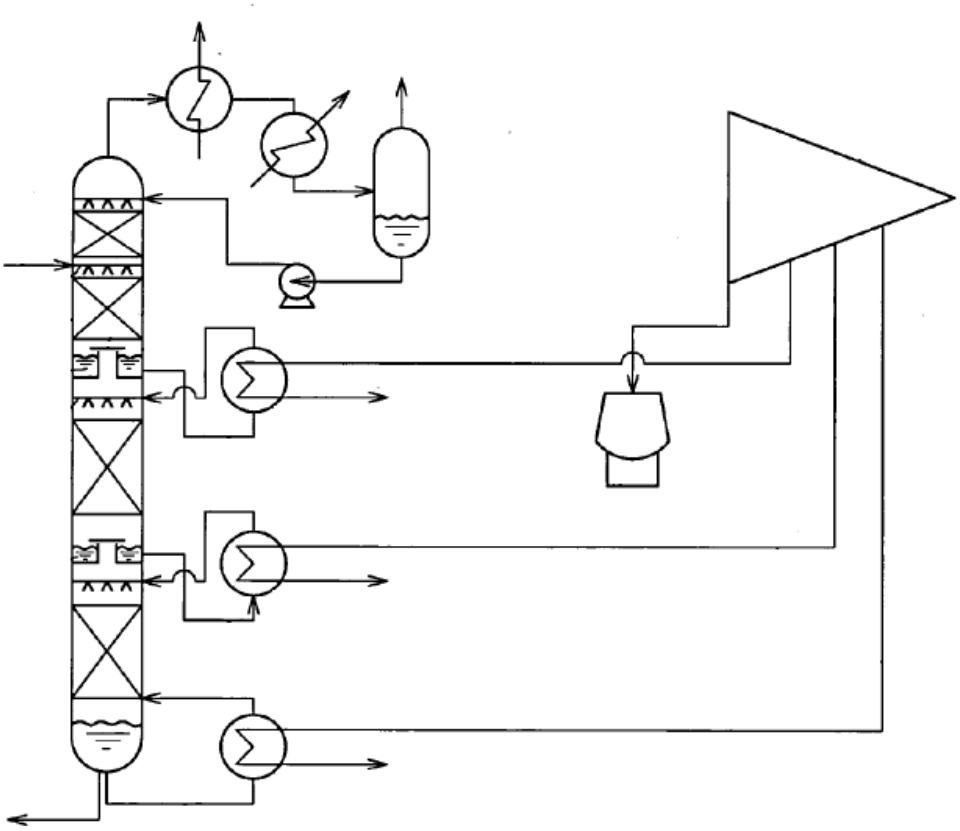


Figure 2-2: Schematic diagram for multiple steam extraction for solvent regeneration, from Ijima et al. (2006)

Table 2-1: Comparison of the electricity output penalty of industry studies to illustrate the benefits of thermodynamic integration

	Owens et al. (2000)	Owens et al. (2000)	Bozutto et al. (2001)	Parsons et al. (2002)	IEAGHG (2004, Fluor)	IEAGHG (2004, MHI)	Ciferno et al. (2007)[2]	Xu et al. (2007)	Xu et al. (2007)	Panesar et al. (2009)
	Supercritical new-build	Ultra-supercritical new-build	Subcritical Retrofit	Subcritical New-build	Ultra-Supercritical New-build	Ultra-Supercritical New-build	Subcritical Retrofit	Supercritical New- Build	Supercritical Retrofit	Ultra-Supercritical Retrofit[3]
Solvent	MEA	MEA	MEA	MEA	MEA	KS1	MEA	KS1	KS1	MEA
Thermal heat of regeneration ($GJth/tCO_2$)	3.8	3.8	5.4	4	3.24	3.2	3.6			3.2
Steam cycle EOP (kWh/tCO_2)	345.8	345.8	339.4	227.3	153	134.6	229.9	171.5	161.6	156.9
Steam extraction pressure (bara)	5.2	5.2	4.5	2.4	3.6	3.6	4.5	4	4	3.6
Reboiler condensate return to condenser	YES	YES	YES	YES	NO	NO	NO	NO	NO	NO
Heat recovery into power cycle	NO	NO	NO	NO	YES	YES	YES	YES	YES	YES
Ancillary power EOP (kWh/tCO_2)	66.5	69.2	132.8	134.8	128.5	122.4	119.7	141.1	143.5	109.6
CO_2 delivery pressure (bar)	83	83	139	103	110	110	139	140	140	110
Overall EOP (kWh/tCO_2)	412.293	415.018	472.2	362.1	281.5	257	349.6	312.6	305	266.5

[2] Please note that Bozutto et al (2001) and Ciferno et al (2007) apply to the same plant at Conesville Unit 5, Ohio, USA. Ciferno et al (2007) is discussed further in Chapter 4

[3] Advanced boiler turbine retrofit and CO_2 capture retrofit

Table 2-2: Review of potential solvents for post-combustion capture

Alternative chemical absorbents in aqueous solutions	
AMP	Yeh et al. (2001), Aroonwilas and Veawab (2004)
DEA	Murrieta-Guevara et al. (1998), Veawab et al. (2003), Aroonwilas and Veawab (2004)
DIPA	Aroonwilas and Veawab (2004)
MDEA	Veawab et al. (2003), Aroonwilas and Veawab (2004), Kim et al. (2006)
AEEA	Kim et al. (2006), Ma'mun et al. (2006), Ma'mun et al. (2007),
DGA	Al-Juaied and Rochelle (2006)
DETA	Hartono et al. (2008)
Demixing amine solvents	Raynal et al. (2008)
Sodium carbonate (Na_2CO_3)	Knuutila et al. (2009a), Knuutila et al. (2010a), Knuutila et al. (2010b)
Amino-acid salts	Van Holst et al. (2009)
Ionic liquids	Anderson et al. (2006), Wappel et al. (2010)
Blends of chemical absorbents in aqueous solutions	
MEA/PZ	Dang and Rochelle (2003), Oyenekan (2007)
PZ/K_2CO_3	Oyenekan (2007), Oexmann et al. (2008), Oyenekan and Rochelle (2008)
PZ/MDEA	Xu et al. (1998), Liu et al. (1999), Zhang et al. (2001), Bishnoi and Rochelle (2002a, 2002b), Zhang et al. (2003), Oyenekan (2007), Derks et al. (2010)
MEA/MDEA	Aroonwillas et al. (2004), Idem et al. (2006), Van Loo (2007)
MEA/AMP	Aroonwillas (2004), Sakwattanapong et al. (2009)
DEA/AMP	Murrieta-Guevara et al. (1998)
DEA/MDEA	Murrieta-Guevara et al. (1998)
PZ/AMP	Seo and Hong (2000), Sun et al. (2005)
Enzymes additives to amines	
Enzymes additives	Fradette and Ceperkovic (2008)

3 Capture-ready steam turbines

[The next two sections are an edited and extended version of an article co-authored by the applicant in Lucquiaud and Gibbins (2009)]

When considering building a plant as capture-ready for post-combustion capture the design of the steam cycle is of critical importance for effective thermodynamic integration of the capture equipment with the power cycle. Regulatory and technology-related uncertainties, however, make effective thermodynamic integration throughout the whole operating life of fossil plants a challenging objective to achieve. The characteristics of the capture system are likely to be unknown at the time of commissioning whilst the plant must operate for an undetermined period without capture. These pre-requisites must be taken into account when designing steam turbines for CO_2 capture-ready plants.

This chapter examines options for capture-ready steam turbines. Base-load operation is considered and perfect foreknowledge of the solvent characteristics is assumed throughout this chapter. As with plants built with capture from the outset, capture-ready plants need, however, to be able to use improved solvents and to operate at part load and also with the capture unit by-passed. Chapter 5 and Chapter 6 complement the approach in this chapter by investigating, respectively, the critical issues of future-proof upgrading flexibility for a range of possible future solvents and operational flexibility with post-combustion capture.

3.1 General principles for the design of capture-ready steam turbines

In addition to the general requirements for CCR plants outlined in Chapter 2, amine-based processes specifically require

- Changes to the flue gas desulphurization (FGD) equipment design so that high levels of sulfur oxide removal can be achieved. Some developers may prefer to add a polishing unit after a previously installed FGD process during the CO_2 capture retrofit.

- Making the steam cycle 'capture friendly' so as to be able to supply the required amount of steam for the capture system, at the pressure corresponding to the required saturation temperature for thermal regeneration of the solvent (allowing for pressure losses and temperature drops in the system).

For the purpose of comparing turbine options ideal CCR plant principles are introduced below[4]. They represent the limit for performance when the post-combustion capture plant is matched exactly to the steam cycle at the design load for the plant, and could also be used to compare post-combustion capture to other CCS technologies. It is worth noting, however, that in practice, in order to achieve satisfactory operability, such close matching to ideality may not be desirable.

Ideal CCR plant principles

1. The efficiency of a CCR plant before capture is fitted should be the same as the efficiency of a state-of-the-art standard plant designed with no consideration of capture ready principles.

2. The efficiency of a retrofitted CCR plant should be the same as a new plant built with CCS from the start – and with the same steam conditions – at the time when the retrofit occurs.

3. There should be no up-front additional costs for a CCR plant compared with a state-of-the-art standard plant.

4. The retrofitted power plant should have the ability to operate without capture.

5. The CCR plant should allow for future technology developments and when the capture technology is upgraded the retrofitted plant should have the same efficiency as a CCS plant – with the same steam conditions – built with perfect foreknowledge of what the upgrade technology would be.[5]

[4] They were first proposed in (Gibbins et al (2006) co-authored by the candidate.
[5]The consequences of this principle on the design of steam turbines for post-combustion capture are analysed in more details in Chapter 5 and are not included in this chapter

In reality, it is impossible to meet all of these ideal principles simultaneously and some trade-offs will have to be made by plant developers and manufacturers when designing CCR plants. Since economics depends critically on unknown parameters, such as time to fit capture, future fuel, CO_2 prices, etc., the approach adopted here is to implement CCR plants with only minimal essential up-front capital cost options, with an acceptable loss in the maximum power output of the plant when it is fitted with CCS, and with little or no effect on plant performance prior to retrofit. Otherwise, it is possible that CCR plants would be dispatched less frequently and recovery of the initial capital in the first part of the plant's life – critical due to the time value of money – would be more difficult. Utilities therefore face no need to resolve the uncertainty surrounding the timescale for a retrofit in order to justify any generation revenue losses. The timescale would be important if the additional plant costs have to be justified and the tradeoffs in this case have been examined using option-valuation techniques (Sekar, 2005; Bohm et al., 2007, Liang 2009). In other jurisdictions the need to be CCR is now a licensing requirement (See for the UK: DECC, 2009) and essential CCR costs must be borne in any case.

3.2 Capture-ready steam turbines for pulverised coal plants

This section proposes three steam turbines configurations, specific to pulverised coal plants, and assesses their respective merits against the above principles. Schematic diagrams are outlined in Figure 3-1 and the corresponding steam expansion pathways are represented in Mollier (enthalpy/entropy) diagrams in Figure 3-2. The concepts were first proposed in Gibbins et al. (2006) and IEAGHG (2007a) – both co-authored by the candidate. The floating IP/LP pressure was subsequently applied in Xu et al. (2007) and the throttled LP turbine option in Panesar et al. (2009), two industry studies funded by UK the Department of Business, Enterprise and Regulatory Reform and the UK Department of Energy and Climate Change.

3.2.1 Capture-ready steam turbine options

Clutched LP turbine

The steam cycle is conceived so that one of the LP turbines is attached to the main turbine shaft by a clutch system. Clutch systems are commercially available and used in the operation of the steam cycle of natural gas plants (Neeves and de Arcangelis, 2009). When the plant is retrofitted the turbine is unclutched and taken out of service for capture operation. The steam flow required for solvent regeneration exactly matches the inlet steam flow of the removed cylinder. The crossover pressure between the intermediate and the low pressure turbine (the IP/LP crossover) is set to provide condensing steam at the desired value for solvent regeneration when the plant is retrofitted. Adding capture to the plant leaves the operating conditions of the turbine unchanged, given that the remaining LP turbine cylinders operate at their design conditions, as is shown on a Mollier Diagram in Figure 3-2(a). It can be seen on the diagram that the dryness fraction of the LP turbine is reduced with capture by 1.1% point, from 89.6% to 88.5%. This is a consequence of the reduction of the condenser pressure with increased cooling capacity in the main condenser of the plant, which is discussed in more details in the next section. Unless exactly 66, 50, or 33 per cent flow is required, different-sized LP cylinders would be necessary. For the system to operate without losses the regeneration steam flow has to be predicted accurately. In practice, this is unlikely to be the case due to the uncertainty surrounding future developments in post-combustion capture systems. The clutch system also adds additional initial costs and complexity with no immediate benefit before retrofit, although provision to remove an LP rotor and replace it with a lay shaft is likely to require minimal up-front costs. This latter option may be most attractive for systems with three LP cylinders, which can subsequently accommodate steam extraction rates of 33 per cent, or somewhat higher with modest throttling. In this case, steam extraction rate above design conditions requires the addition of the valve to maintain the IP/LP crossover pressure, as discussed in the throttled LP turbine option below.

Throttled LP turbine

Like the clutched LP turbine the IP/LP crossover pressure is set at the desired value for a specific solvent regeneration temperature. Space is allocated for a throttling valve downstream of the steam off-take tee. When capture is retrofitted and steam extracted at the IP/LP crossover, the LP turbine inlet is throttled using the valve to maintain the crossover pressure, as shown in on the Mollier diagram in Figure 3-2(b). This creates a loss, represented by the horizontal line on the Mollier diagram, when the steam is expanded in the valve by reducing pressure at the expense of an

increase in entropy. Given that the outlet pressure of the LP turbine is set by the cooling temperature, and in this case limits the enthalpy drop, the LP turbine is effectively derated. This counteracts the drop in dryness fraction resulting from a drop in condenser pressure. Consequently, the dryness fraction is relatively constant when capture is added, varying from 89.6% to 89.5%. The throttled LP turbine configuration is able to accommodate large variations in steam demand – although only at pressures around or below the initial value. Up-front costs for such a capture ready steam cycle are, however, minimal, with the principle additional items being a tee-piece with a flange for a suitably sized steam off-take to be connected at the IP/LP crossover and a spool piece for the throttling valve (or a spool piece for both).

Floating IP/LP crossover pressure

Unlike the previous option, the extraction pressure is not controlled by a throttle valve but rather determined by the amount of steam extracted. This system eliminates the losses in the valve when the plant operates at base load. The initial IP/LP crossover pressure is set so that, when the predicted amount of steam is extracted for solvent regeneration, it falls to the required value as shown on the Mollier Diagram in Figure 3-2(c). Arrangements for future steam extraction are illustrated in Figure 3-3 and Figure 3-4 for this configuration, although similar to arrangements for the two other options. The IP cylinder must be capable of accommodating both the reduced exit pressure and increased stage loadings with capture (i.e. the axial thrust changes for single flow units, increased blade bending moments) and possibly also flow restrictions. This may be done by suitably designing the last stages of the IP turbine from the outset so that the capture conditions can be sustained without any changes, thus avoiding the need to open up the cylinder and make any modifications. Alternatively, the IP turbine can be modified as part of the conversion to better match its new operating conditions. In both cases a slight loss in IP cylinder efficiency occurs with capture, although this is likely to be within normal design variations.[6] The change in steam flow and pressure ratio across the LP turbine also modifies the operating conditions of the LP turbine and reduces its efficiency. It can be seen on the respective Mollier diagram that these irreversibilities increases the entropy at the outlet of the LP turbine, which counteracts the drop in dryness fraction resulting from the increased in cooling capacity. With capture the dryness fraction drops by 0.8% point to 88.8%.

[6] Chapter 4 examines further the consequences of turbine stage loadings, modification of the steam velocity triangle in the turbine rotor and isentropic efficiency change on the overall turbine isentropic efficiency at reduced IP exhaust pressure conditions. It shows that the absolute change in overall turbine isentropic efficiency with steam extraction is limited to 2% point and discusses possible blade design strategies.

As with the clutched LP design, the best performance with capture is obtained if the extraction steam flow with capture is 'guessed' correctly but, unlike the clutched LP, both higher and lower steam extraction flows can be accommodated if valves are used downstream of the extraction tee or in the extraction line, respectively. More precise matching to the actual capture steam flow might be accomplished by appropriate modifications to the IP turbine. Furthermore, this option also increases the amount of superheat available in the extracted steam at reduced extraction flows, which can advantageously be used for feed water condensate heating instead of spraying reboiler condensate to desuperheat the solvent reboiler steam.

For this option, the principle additional items requiring up-front costs are the reinforcement of the last IP turbine blades to tolerate pressure and temperature variations at the IP/LP crossover, a tee and a flange for a suitably sized steam off-take to be connected.

3.2.2 Modelling approach

A model of the power cycle of a pulverised coal plant was implemented for each of the capture-ready steam turbine options. in gPROMs[7], based on previous work in MathCad[8] published in (Lucquiaud and Gibbins, 2009). The model parameters are based on published industrial experience (Babcock and Wilcock Company, 1992; Cotton, 1994) in conjunction with existing '1997 steam' property libraries (Gibbins, 2003). The model was validated against proprietary industrial data, which are not available for public distribution and were used for a study carried out for the IEA Greenhouse Gas R&D Programme (IEAGHG, 2004). Results with and without capture are consistent with those from the steam cycle used by ALSTOM for the study. The model was also validated against a similar steam cycle model developed in GateCycle[9] - commercial software developed by GE. Additional details on the assumptions and the implementation of the steam turbine model are given in Appendix A.

For the capture case the energy requirements (probably high by future standards) for solvent regeneration are based on the Fluor's Econamine FG CO_2 capture technology from the same study, which uses a 30 wt% aqueous MEA solvent. An optimization routine using the steam cycle Rankine

[7] http://www.psenterprise.com/gproms/
[8] http://www.ptc.com/products/mathcad/
[9] http://www.gepower.com/prod_serv/products/oc/en/opt_diagsw/gatecycle.htm

efficiency as the objective function and steam pressures for feed water heating as variables was implemented. The original fixed design point analysis with CO_2 capture in the IEA GHG reference study was then extended to represent a retrofit with post-combustion capture.

The analysis is based on a power plant with supercritical steam conditions (290 bar/600ºC/620ºC). The steam cycle before capture is fitted, shown in Figure 3-5, includes one high pressure (HP), one intermediate pressure (IP), two low pressure (LP) cylinders, three HP feedwater heaters, a deaerator taking steam from the IP turbine, and four LP condensate heaters.

The clutched LP turbine and the throttled LP turbine have an IP/LP crossover set at 3.6 bar to allow regeneration of the MEA based solvent chosen at 120ºC, once a pressure drop of 0.5 bar in the extraction line and a temperature difference of 15 K in the solvent reboiler are taken into account. Turbine efficiencies, steam flows and pressures for boiler regenerative condensate heating and the boiler input to the steam cycle are identical, allowing each configuration to have the same power output before capture is fitted for the purpose of comparability. The floating pressure system has a higher IP/LP crossover pressure before capture is fitted.

When capture is retrofitted, the lower steam flow-rate through the LP turbine reduces the cooling duty of the condenser. If the cooling water flow is maintained, additional cooling capacity becomes available and the resulting effect is a reduction of the condenser pressure. In contrast the total heating load for the plant increases since the overall plant efficiency decreases and more heat has to be rejected from the capture process for flue gas and solvent cooling, and CO_2 compressor intercooling. In some cases, water constraints may restrain the cooling capacity of certain plants. This could counterbalance the previous effect by raising the steam cycle condenser pressure. Optimised water usage could, however, give priority to the steam cycle condenser for best available cooling water temperature over the capture unit requirements. For the purposes of this comparison, and in the absence of the necessary site-specific and capture technology information, it has been assumed that cooling water supply is not constrained and that the condenser pressure drops with capture. This has the advantage of a higher enthalpy drop across the LP turbine, and higher pressure ratio across the LP turbine that would otherwise occur, resulting in a smaller reduction in the turbine isentropic efficiency. This tends to increase the overall power output. It should be noted that this can only be achieved provided that the LP turbine can sustained periods of operation with a reduced outlet dryness fraction, notably for the clutched LP turbine and floating crossover pressure options. Typical sustainable values are of the order of 88% and above (Cotton, 1994) to avoid rapid erosion of the very last stages of blades of the LP turbine caused by repeated shocks with water droplets. If the dryness fraction were to drop below this value, reblading the last stages of the LP turbine may be

necessary during the first prolonged outage of the plant. Alternatively the condenser cooling capacity could be controlled to avoid such operating conditions. Finally, it is assumed that, when capture is retrofitted, the low pressure feed water heater train is kept in service and at temperature by passing through 10% of its initial mass flow, in order to improve the time response for the plant to return to maximum power output when required and to avoid any possible corrosion issues.

Clutched LP turbine

This option is shown with further detail in Figure 3-6. The IP/LP crossover is equipped with an extraction valve. Once the unwanted LP turbine rotor has been removed, the extraction line is connected to the IP/LP crossover. Low-grade heat available in the capture plant and the compression train is recovered by a train of heat exchangers and used to heat up 90% of the condensate flow leaving the condenser outlet. The condensate returns to the steam cycle after the 3rd feed water heater. The 4th feed water heater now operates at reduced load and maintains the condensate temperature at the deaerator inlet to ensure efficient removal of any inert gas dissolved in the condensate.

Throttled LP turbine

The retrofitted configuration is shown in Figure 3-7. The IP/LP crossover is equipped with an extraction valve for the solvent reboiler extraction pipe. Low-grade heat available in the capture plant and the compression train is recovered by a train of heat exchangers and used to heat up the condensate at the condenser outlet, using a similar arrangement to the clutched LP turbine retrofit. Once valves have been fitted at the LP turbine inlets, steam is extracted for capture

Floating IP/LP crossover pressure

This option is shown in Figure 3-8. Similar arrangements are used for boiler condensate heating and steam extraction. The IP turbine exhaust pressure is initially set to 5.8 bar and drops to 3.6 bar when the required amount of steam is extracted.

3.2.3 Retrofit with the design solvent

This section evaluates the performance of the turbine options under base-load operation conditions for the technology – amine-based capture – and for the solvent chosen at the time of the retrofit feasibility study: a temperature of regeneration of 120ºC and an energy of regeneration of 3.2 GJ/tCO_2. In other words, it is assumed that the steam flow rate for solvent regeneration has been predicted correctly. The respective performances of each option, before and after a retrofit with capture, are shown in Table 3-1.

First CCR principle

The efficiency without capture of each of the turbine options is identical to the efficiency of a standard plant with identical steam conditions and so meets the first principle of capture-ready design.

Second CCR principle

As far as the second principle is concerned, each of the turbine options benefits from an oversized condenser surface compared to the reference case with capture, which is assumed to have, for consistency, a condenser pressure identical to the reference case without capture. Steam extracted for capture is condensed in the reboiler and returns to the steam cycle after the feed water heating train, by-passing the condenser, to improve thermodynamic integration. Provided that the same cooling water flow is maintained when capture is added, the cooling water leaving the condenser is colder than in the reference case without capture. Neglecting increased air leakage into the condenser at part-load, then conduction solely drives the heat transfer on the steam side of the condenser. The approach temperature at the pinch then tends to reduce, which contributes to reducing further the condensing steam temperature and therefore the condenser pressure, as illustrated in Figure 3-9. This improves the plant efficiency by lengthening the total enthalpy drop in the LP turbine and increasing its power output. Thus, each of the turbine options has a higher efficiency with capture than the reference case with capture.

The clutched LP turbine option, in which the turbine and steam flows are exactly matched, naturally gives the best performance with capture in this case. At equivalent condenser pressure, the efficiency would obviously be identical to the reference case with capture. The throttled LP turbine

option has an oversized LP turbine with capture and suffers a higher electricity output penalty due to the throttling losses required to maintain the crossover pressure. The floating LP pressure achieves intermediate performance; it has no throttling losses (in the ideal case, when designed for the exact steam extraction rate) but the higher IP stage loadings give reduced overall IP cylinder efficiency even if the performances of most stages are not significantly reduced at the changed operating conditions (See Chapter 4).

When capture is fitted the absolute leaving losses at the outlet of the LP turbine - expressed in MW_e - decreases although the specific exit losses - expressed in kJ/kg of steam - increases. Reblading the last stage of the LP turbine can help to recover some of lost kinetic energy and provide additional power. It is worth noting that the new blading should avoid, if possible, excessive exit losses when the plant returns to its initial output since the drivers for this operating mode are likely to be a higher value on power.

Table 3-2 compares the turbine options based on the four three capture-ready design principles and shows the required additional investments required for each option, based on estimates from the IEAGHG study (IEAGHG, 2007a), and from a Mott MacDonald study on CCR plants in India for the throttled LP turbine and the floating IP/LP crossover pressure option (Napier-Moore et al., 2008).

Third CCR principle

It is estimated that the clutched LP turbine option would require a higher up-front investment, of the order of 3 per cent of the total capital costs of the plant, whereas the two other options both require less than 1 per cent additional capital. Liang et al. (2009) have evaluated the economics of these retrofit options in the Chinese context, which corresponds to an analysis of the third principle of capture-ready design. Their study suggests that, despite 3 per cent being a relatively small increase, the higher up-front investment for the clutched LP turbine cannot be justified by the time value of the option of retrofitting capture but that the two other options could be economically viable. Once the initial investment has been made in a clutched LP turbine there is, however, a higher probability of the plant being retrofitted with CCS compared with the two other options due to its assumed better performance when CCS is added – although the performance over the plant lifetime will probably be relatively worse in the likely event of solvent improvements.

Fourth CCR principle

The fourth principle to consider is operation without capture. Bypass systems for the capture equipment are likely to be necessary to manage unplanned situations where there is an unexpected outage of the capture plant or downstream pipeline or storage. A bypass could also be for operating flexibility, i.e. used on a voluntary basis to generate additional power, up to the output of the plant before retrofitting, at critical times to support electricity network stability or when electricity selling prices are high.

In reality, without even considering upgrading flexibility – the fifth principle - it is impossible to meet the first four principles simultaneously, and this analysis shows that some trade-offs will have to be made by plant developers and manufacturers when designing CCR plants. This is especially true for the first generations of post-combustion capture systems since these plants are likely to operate with a range of different solvents throughout their economic lives, and in jurisdictions relying on a competitive electricity market, to compete against more recent plants, which will have benefited from the lessons learned from operating these older plants. Chapter 5 provides a more detailed analysis of the design of steam turbines for advanced solvents.

3.3 Capture-ready steam turbines for natural gas combined cycle plants

[This section is an extended version of a journal article co-authored by the applicant in Lucquiaud et al. (2009). Preliminary results were presented in Gibbins et al. (2009)]

Several technology options could be used for capture-readiness of NGCC plants. In the short to medium term, two approaches are most likely to be considered. These are (a) designing the plant to be suitable for retrofit with post-combustion capture and (b) choosing gas turbines that could (with burner modification/replacement) be upgraded to burn hydrogen produced with a pre-combustion CO_2 capture system (or from a non-fossil fuel source). Hydrogen from fossil fuel could be produced via a coal gasifier (or possibly a natural gas reformer) equipped with CCS either on the same site as the combined cycle, if space adjacent to the plant and for access to critical parts of the plant is available, or located at a remote site and then transported to the combined cycle plant, probably by pipeline (IEAGHG, 2005a). Lower costs are, however, reported for gas plants with post-combustion capture (IEAGHG, 2005a). It is worth noting, however, that making a plant CCR for post-combustion does not preclude from also making the plant CCR for pre-combustion capture.

The approach presented in the previous section, that no major penalties in the costs of CCR plants and performance prior to retrofit should be considered, is critical for NGCC plants since they are likely to be retrofitted later than coal plants, due to the higher expected CO_2 price requirements to fund CCS (Davison, 2007). As shown in the schematic diagram of a NGCC plant with post-combustion capture, provided in Figure 3-10, the gas turbine is left unchanged and continues under normal operation when capture is retrofitted. The main additional measures that would need to be taken specifically for NGCC plants with flue gas wet scrubbing, in addition to the general criteria for CCR plants, are as follows.

- Design the steam cycle and the heat recovery steam generator (HRSG) so that before retrofit the plant achieves identical performance to a ‘standard’ non-CCR plant.
- Make the steam cycle ‘capture friendly’ so as to be able to supply any steam required for thermal regeneration of the capture solvent with the minimum loss of plant performance.
- Make the HRSG ‘capture friendly’ to accommodate modified conditions in condensate stream return coming from the retrofitted steam cycle.

Figure 3-11 shows further details of the gas turbine, the heat recovery steam generator and the combined steam cycle of a unit without capture where the IP and LP turbines are in separate cylinders with crossover pipes (this term understood to include also possible cross-under pipes) between them. In this case the condensing steam for solvent regeneration is extracted from the IP/LP crossover and is then desuperheated using a spray with condensate from the solvent reboiler. A stand alone HP turbine with a combined IP/LP cylinder is another common design option, with consequences for future retrofits with post-combustion capture. In this latter configuration access for steam extraction from the IP/LP crossover can be a difficult challenge. An alternative retrofit and capture-ready design approach for this case is also discussed below.

3.3.1 Capture-ready steam turbine options

This section examines the retrofit of several steam cycle configurations of natural gas combined cycle plants, shown in Figure 3-12, and assesses their performance with capture compared to a reference plant without capture. Arrangements to set the value of the IP/LP crossover pressure to match the temperature of the solvent reboiler are similar to those described in the previous section. This section considers alternative capture-ready configurations, for which the IP/LP crossover is higher than the minimum pressure necessary for solvent regeneration (either because of a desire to use an existing design, or to give a margin to accommodate new solvents) and discusses possible additional measures, which can be taken at the time of retrofit, to guarantee effective thermodynamic integration with capture. To avoid future confusion it should be noted that, amongst the retrofit options proposed in Figure 3-12, some of these retrofit options are worth pursuing for capture-ready design – option a), b) and c) - while others are proposed for illustrative purposes in order to highlight the consequences of poor thermodynamic integration with capture – option d), e).

a) Replacement of the LP turbine cylinder

In this retrofit option the existing LP steam turbine is replaced by a new LP turbine cylinder when capture is retrofitted, as shown in Figure 3-13. The design steam flow for the new turbine exactly matches the flow available once steam has been extracted for the CO_2 capture system. This option involves additional capital costs compared to a standard retrofit, but gives the option to retrofit the plant with a system that is similar in performance to a new-build NGCC power plant with post-combustion capture. It can be seen as the reference case with capture for other capture-ready design and retrofit options in terms of performance with capture - and conversely also a worst case scenario for operating and upgrading flexibility since the LP turbine is sized for capture operation only.

b) Pass-out back-pressure turbine from reheater outlet

Access for steam extraction at the LP inlet may prove to be difficult for configurations with a combined IP/LP cylinder and hence no IP/LP crossover. In this case the only access point for large amounts of extraction is at the reheater outlet[10], for steam at a higher pressure and temperature, and again space needs to be provided to do this, with a spool piece at the front of the IP turbine. The pressure and temperature conditions are obviously unsuitable for use directly for solvent regeneration, while both the IP and LP turbine now operates at reduced flow, which modifies the pressure ratio across the IP and LP turbine and decreases their absolute pressures. This modifies the blade velocity triangles and reduces the overall turbine efficiency. (See Appendix B for more details). To match steam conditions to the IP/LP cylinder and the capture plant a tailored design pass-out back pressure turbine comprising two distinct groups of blades, as shown in Figure 3-14, is fitted. It takes the entire mass flow of steam at the reheater outlet and expands it down to the new reduced IP turbine inlet pressure. The required amount of steam for capture is expanded in the second group of blades of the additional turbine, whilst the remaining flow is expanded across the IP and LP turbine. A third group of blades gives the option of keeping the LP superheater operating when capture is fitted and avoiding the losses that would occur if the steam available at the LP superheater outlet had to be throttled down to the new LP turbine inlet pressure. Instead the steam available expands, from the LP superheater pressure down to the reboiler pressure, in the last stages of the pass-out back-pressure turbine and generates power. Provisions for steam extraction, reinforcement of foundations and space for the additional turbine (and generator, if not clutched to the main generator) have to be considered for capture-readiness.

[10] Space for steam extraction is also available at the reheater inlet, but would affect heat transfer downstream in the flue gas path and would necessitate costly modifications of the HRSG too.

c) Retrofit with two back-pressure turbines

This option, shown in Figure 3-15, also gives the advantage to power plant developers to free the steam turbine design from IP/LP crossover pressure limitations without consequences for the performance with capture, provided that the pressure is set above future expected requirements for solvent regeneration. A back-pressure turbine is fitted in the steam extraction line to generate power while reducing the steam pressure to the desired value in the reboiler, while a second back-pressure turbine is fitted before the steam enters the LP turbine, which would otherwise be throttled, to provide additional power. The principal additional items for CCR consideration involves providing space and reinforcing the foundations of the turbine hall at the location of the back-pressure turbines (and their dedicated generator if required, or provide provision for connection via a clutch) and a spool piece in the IP/LP crossover for a tee to facilitate steam extraction.

3.3.2 Alternative configuration investigated

This section provides a discussion of possible alternative retrofit options, which despite meeting the first principle of capture-ready design[11] should be ruled out for capture-ready combined steam cycle design on the grounds of poor performance with capture – second principle - or high levels of technical complexity – third principle.

d) Retrofit with two throttle valves

In this retrofit option the LP turbine is left unchanged. Consequently the reduced steam flow through the LP turbine results in a lower inlet pressure. To maintain the design exit pressures for the IP turbine and the LP evaporator pressure it is necessary to throttle the LP inlet downstream of the extraction point, e.g. using the butterfly valve shown in Figure 3-16. A second valve is added in the solvent extraction line to expand the steam down to the pressure corresponding to the desired reboiler saturation temperature, once pressure drops and temperature difference in the reboiler have been taken into account. The principal additional items for CCR consideration are a spool piece in the IP/LP crossover for a tee and the throttling valves. The performance with capture is poor due

[11] The efficiency of a CCR plant before capture is fitted should be the same as the efficiency of a state-of-the-art standard plant designed with no consideration of capture ready principles.

to the losses occurring through the two valves. This option, however, does offer the advantages of minimising the outage to retrofit the plant since, if space has been provided to allow construction activities while the plant is in normal operation, the final connection of the valve and the additional pipes at the crossover and the LP evaporator can probably be achieved during a short planned maintenance outage.

e) Retrofit with a separate ancillary boiler

This option leaves the steam turbines unchanged and instead uses a separate ancillary boiler to provide the heat necessary for solvent regeneration. It has, however, been considered in several occasions on the grounds that it does not entitle any modifications to the steam turbines[12] and retains most of the electrical output from the plant (only the additional ancillary power is lost). The drawback of using a separate boiler to provide the energy for solvent regeneration is straightforward, however. Great efforts have been deployed to improve the efficiency of NGCC plants up to 55-60% LHV level because it makes economic sense to do so. The calorific value of natural gas is used at very high temperatures in the gas turbine, then high pressure, high temperature steam is raised from the gas turbine exhaust. Most of the energy coming from the fuel is used and low grade heat is rejected in the gas turbine exhaust at around 80-100ºC and in the steam cycle condenser at around 30ºC. Providing energy for solvent regeneration by extracting low pressure steam from the turbines repeats the above, only differing in the temperature of condensation. The steam required for capture is condensed in the solvent reboiler at 100ºC to perhaps 150ºC depending on the solvent used. In contrast, separate ancillary boilers do not make use of the full potential of the fuel calorific value. They turn the energy in the gas to heat at this same low reboiler temperature, missing out all the opportunity to extract higher-grade electrical energy. Performance at base-load is reported in the next section.

[12] This design approach has notably been recently proposed for NGCC plants seeking permitting in the UK. It strongly relies on the belief by some that CCS will not be fitted on NGCC plants before their capital costs have been paid back and can be considered as a 'least-hassle' answer to recent regulations on capture-readiness.

f) Retrofit with a separate ancillary boiler – and an optional back-pressure turbine

With a separate ancillary boiler the generator rated capacity constrains the amount of power that can be exported to the grid. The net power output of the plant is, however, still reduced because, as noted above, additional ancillary power has to be provided for the capture plant and CO_2 compression. If the boiler is used to generate superheated steam at a higher pressure, which is then expanded through a back-pressure turbine upstream of the reboiler, additional power is available for ancillary consumption. The plant then operates with the same net output to the grid before and after capture is fitted. This option, shown in Figure 3-17, still extracts less electrical energy per unit of gas than feasible in a gas turbine attached to a combined cycle and suffers from an additional electricity efficiency penalty compared to steam turbine retrofits. Performance at base-load is reported in the next section.

g) Floating IP/LP crossover pressure

Another retrofit option similar to the floating pressure system proposed for capture-ready steam turbines has been investigated, but has not been considered further in this analysis on the basis that a change in pressure at the IP/LP crossover would affect the heat transfer regime of several heat exchangers in the HRSG – the LP economizer, the LP evaporator, the IP economizer, and the HP economizer – and would require an intensive additional investment as a CCR pre-investment, which contradicts the 3rd principle of capture-ready design that only low-cost pre-investment should be considered. This option has been ruled out for further analysis but could be considered for units, which operates with capture from the outset.

3.3.3 Modelling approach

The system modelled is based on the gas plant cases of the same IEAGHG study (IEAGHG, 2004). The ancillary power for CO_2 capture and compression are based on the Fluor Econoamine FG Plus case. As previously noted this is, however, expected to be a 'worst case' compared to best available technology in 2009 and beyond, and so there is an expectation that this is a maximum value for a range of possible future steam extraction rates. Two type GE9351 FA gas turbines with a gross output of 260MW$_e$ each are followed by two HRSG units and a single steam turbine set. The steam cycle is a sub-critical (125/27/5.3 bar) triple pressure reheat cycle. The IP steam is superheated up to

the maximum superheat temperature possible (560 ◦C) by an additional tube bundle located in the gas path in parallel with the high pressure (HP) superheater. When CO_2 capture is retrofitted to the plant, the gas turbine performance remains unaffected, since there is no direct connection between the gas turbines and the capture plant[13]. The scope of modelling work has, therefore, been limited to the capture- ready features of the HRSG and the steam cycle. Mass flows and heat exchanger duties in the HRSG remain approximately unchanged except for the LP economizer duty, which is reduced due to the lower LP turbine mass flow. For each of the steam turbine options the turbines have been modelled as in Appendix B. As previously discussed, it is assumed that additional cooling water is available for the requirements of capture and compression and that the condenser pressure drops when the mass flow of steam is reduced.

3.3.4 Comparison of performance for the design solvent

The respective performance of the capture-ready steam cycle configurations is shown in Table 3-3, and discussed below. Additional performance metrics – other than the electricity output penalty output - are introduced for a rigorous comparison of the two separate ancillary boiler options. Their performance and the non-capture ready configurations with the two throttling valves are shown in Table 3-4. Table 3-5 summarises important parameters while additional details are given in Appendix C.

Plant efficiency before capture – first CCR principle

All the options examined have the same LHV efficiency as the reference plant before capture is fitted.

Plant efficiency with capture – Second CCR principle

The three capture-ready retrofit options achieve similar performance with capture, around 48.2% LHV, an electricity output penalty of approximately 403 kWh/tCO_2.

The retrofit option where the LP turbine is replaced has a similar configuration to a new-build unit not designed for flexible operation, although performance is slightly improved compared to a new-build plant with capture and the same steam conditions due to favourable condenser pressures

[13] The provision of a flue gas blower to overcome the absorber pressure drop ensures that the gas turbine back pressure is not modified when capture is added and that its output is not modified.

when LP steam flows are reduced. A small reduction of power output, 0.5MW, is observed for the retrofit with two back-pressure turbines taking steam at the IP/LP crossover. Additional power generated through the reduction of the condenser pressure compensates for the reduction in the LP turbine isentropic efficiency – of the order of 1.5-2 percentage points - due to the change of pressure ratio.

The pass-out back-pressure turbine retrofit reduces power output further, by approximately 0.9MW, compared to the LP replacement option. Since almost half of the initial IP turbine inlet mass flow now expands in the second group of stages of the pass-out turbine, the IP turbine inlet pressure drops from 27 bar to 13.6 bar. As a result, both the IP and the LP pressure turbine operate in a mode equivalent to sliding pressure operation, i.e. at reduced flow and a similar pressure ratio. The IP turbine efficiency is not affected by the change of operating conditions. Like the previous option the LP turbine isentropic efficiency reduces by 1.5-2 percentage points, since expansion in the last stages is 'forced' by the outlet pressure.

The lower condenser pressure compensates for the additional losses to some extent because there is a second positive feedback in lowering the condenser pressure. The LP turbine operates closer to its initial pressure ratio and helps to maintain a velocity triangle close to design conditions in the last stages and therefore the stage isentropic efficiency.

This effect is illustrated in Figure 3-18 for the retrofit with two back-pressure turbines, where the LP turbine output and the relative change of pressure ratio across the turbine are plotted as a function of the turbine outlet pressure, showing that there is an almost inverse linear relationship between the turbine pressure ratio and the turbine output. Variations in the LP turbine isentropic efficiency, and, in particular, the stage efficiency for the last row of blades, indicated in Figure 3-19, shows that the last stage of the turbine in particular is affected by the outlet pressure. For these three options part of the LP economizer has to be bypassed to avoid 'steaming' when capture is added. The inclusion of an LP economizer gas bypass (or economiser section isolation) to accommodate the reduced duty is also a possible capture ready feature and should avoid time-consuming modifications to, or replacement of, the LP economizer. It is, however, an optional pre-investment that can be considered in making a capture ready investment decision at the original design stage, rather than being an essential requirement.

Performance of alternative retrofit options

The retrofit with two valves inevitably suffers from high throttling losses, accounting for 1 percentage point reduction in LHV efficiency, an additional electricity output penalty of 55 kWh/tCO_2.

The two retrofit options with a separate ancillary boiler leave the steam cycle unchanged but increase the gas consumption of the plant. For the purpose of comparison alternative performance metrics need to be introduced.

First, the gas usage per tonne of CO_2 abated is a useful metric to quantify the additional gas consumption of the separate ancillary boiler options over the abatement. It is defined as the difference between the gas consumption per unit of electricity with and without CCS, over the difference of specific CO_2 emissions, as follows:

$$\frac{\mathrm{MW_{th}/MW_e\ with\ CCS} - \mathrm{MW_{th}/MW_e\ without\ CCS}}{\mathrm{kg\ CO_2\ /MWh_e\ without\ CCS} - \mathrm{kg\ CO_2\ /MWh_e\ with\ CCS}} \quad (16)$$

The gas usage of the separate ancillary boiler retrofit option increases to 1.82 MWh_{th}/tCO_2 abated. When a back pressure turbine is added to generate power from the steam raised in the additional boiler, it is still increases 1.50 MWh_{th}/tCO_2 abated, compared to 0.87-0.88 MWh_{th}/tCO_2 for the previous three capture-ready retrofit options.

A second useful performance metric is the equivalent electricity output penalty, defined as the difference in power output if the same amount of gas were burnt into a reference plant without capture, over the difference in CO_2 emissions, as below.

$$\mathrm{EOP_{eq}} = \frac{\mathrm{Q_B^R} * \eta - \mathrm{W}}{\mathrm{E} - \mathrm{E^R}} \quad (17)$$

$\mathrm{EOP_{eq}}$	kWh/tCO_2	Equivalent electricity output penalty of capture and compression
Q_B^R	MW_{th}	Gas input with capture
η	-	LHV efficiency of NGCC plant without capture
W	MW_e	Net power output of NGCC plant without capture
E	kg/s	CO_2 emissions without capture
E^R	kg/s	CO_2 emissions with capture

The equivalent electricity output penalty more than doubles to 890.7 kWh/tCO_2 with the separate ancillary boiler alone, compared to 403 kWh/tCO_2 for the capture-ready options. The addition of a back-pressure turbine generates additional power, which matches the additional ancillary power requirement, and slightly reduces the electricity output penalty to 822 kWh/tCO_2.

This clearly shows that retrofitting a separate ancillary boiler to a NGCC plant is, not only, not as thermally efficient as an integrated retrofit extracting steam from the combined cycle for solvent regeneration, but is also likely to increase the impact of natural gas price volatility on future costs of generation. Such retrofit options should thus be disregarded for capture-readiness and consideration to the steam cycle design should be given instead.

Additional costs for capture-ready options – Third CCR principle

Minimal upfront investments are likely to be required for the options a), b and c). Provision of space, reinforcement of the turbine hall foundation at the location of the back-pressure turbines and the generator , provision for a flange at the extraction crossover are all likely to be 'lost in the noise' of normal variations of capital cost. Up-front investment can be expected to be of the same order or lower than those of capture-ready steam turbines for pulverised coal plants, i.e. less than 1%.

It should be noted that the replacement of the LP turbine and the provision for a back-pressure turbines with a separate generator are likely to require additional capital costs at the time of retrofit compared to fitting two smaller back-pressure turbines with a smaller generator.

Operation without capture

Operation at full load without capture for a retrofit where the LP turbine is replaced appears to be challenging since the new LP turbine cannot accept any additional steam flow that would be available at the IP/LP crossover pressure when the capture system is not operating. Alternatives might be for the gas turbine to be operated at part load or, if an HRSG bypass damper was installed, it might be possible to reduce steam evaporation rates accordingly. For options b) and c) the additional back-pressure turbine can simply be by-passed to return to operation without capture.

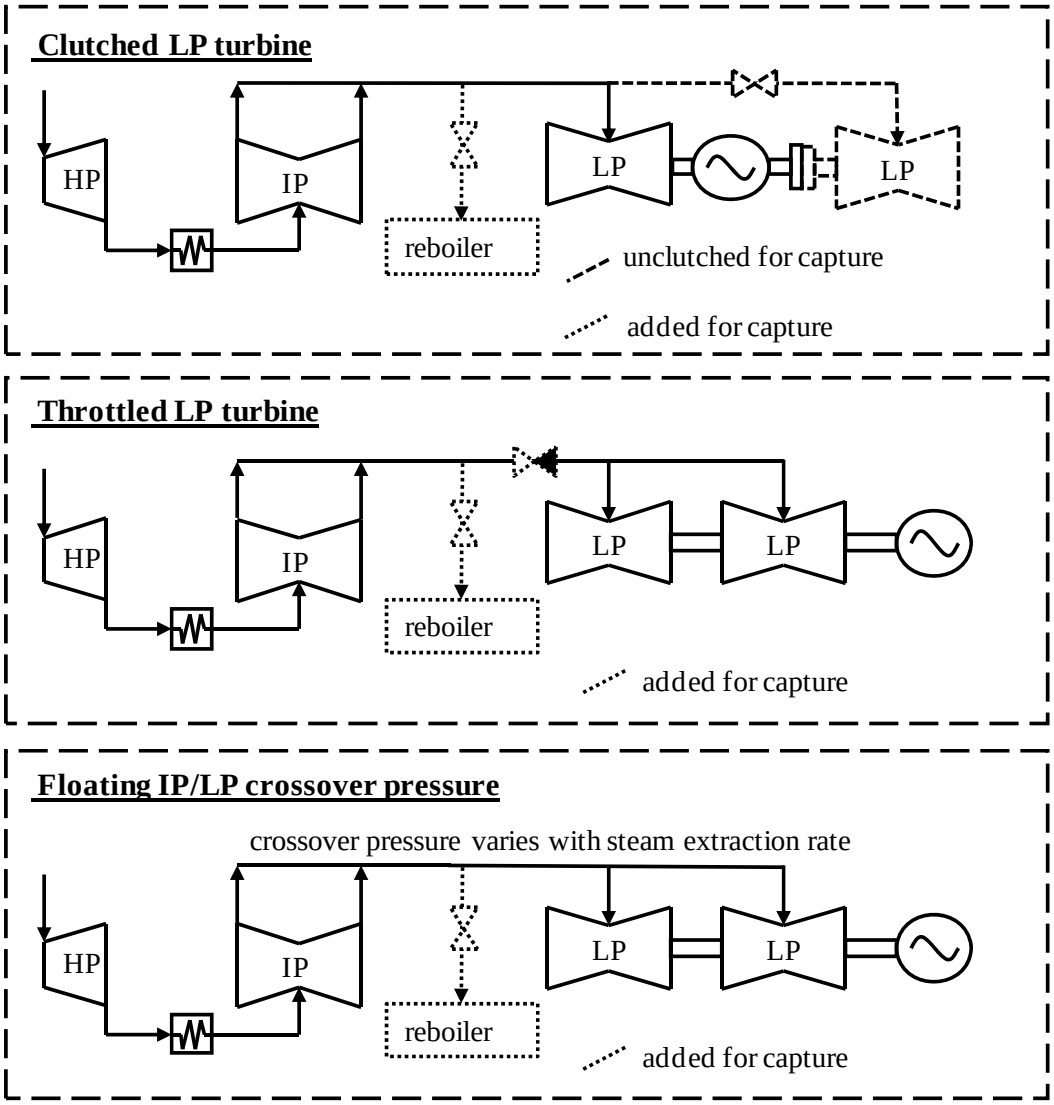


Figure 3-1: Outline of capture-ready steam turbine options for pulverised coal plants

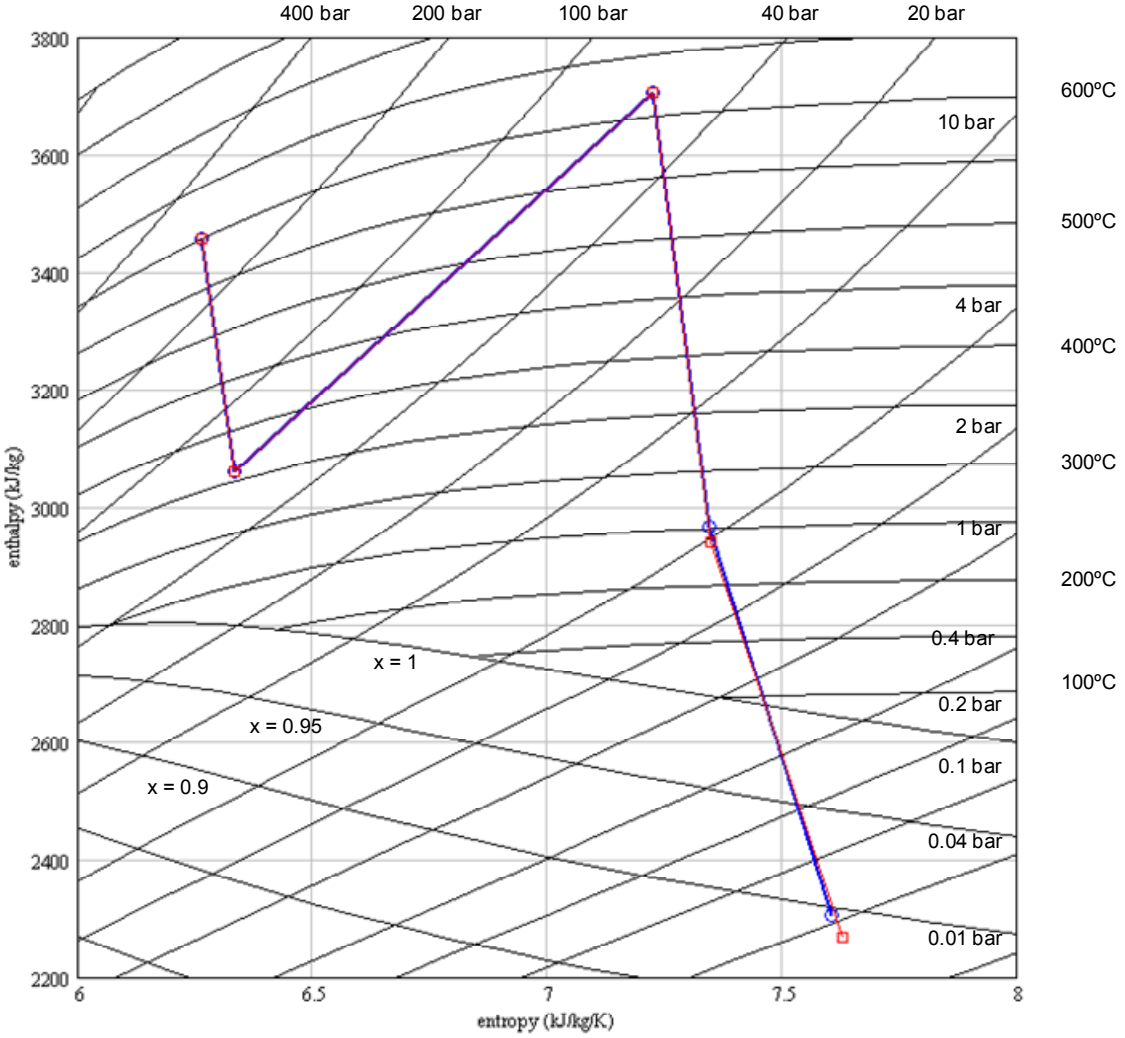


Figure 3-2a: Mollier diagrams for capture-ready steam cycle option with clutched LP turbine
O before capture, □ with capture

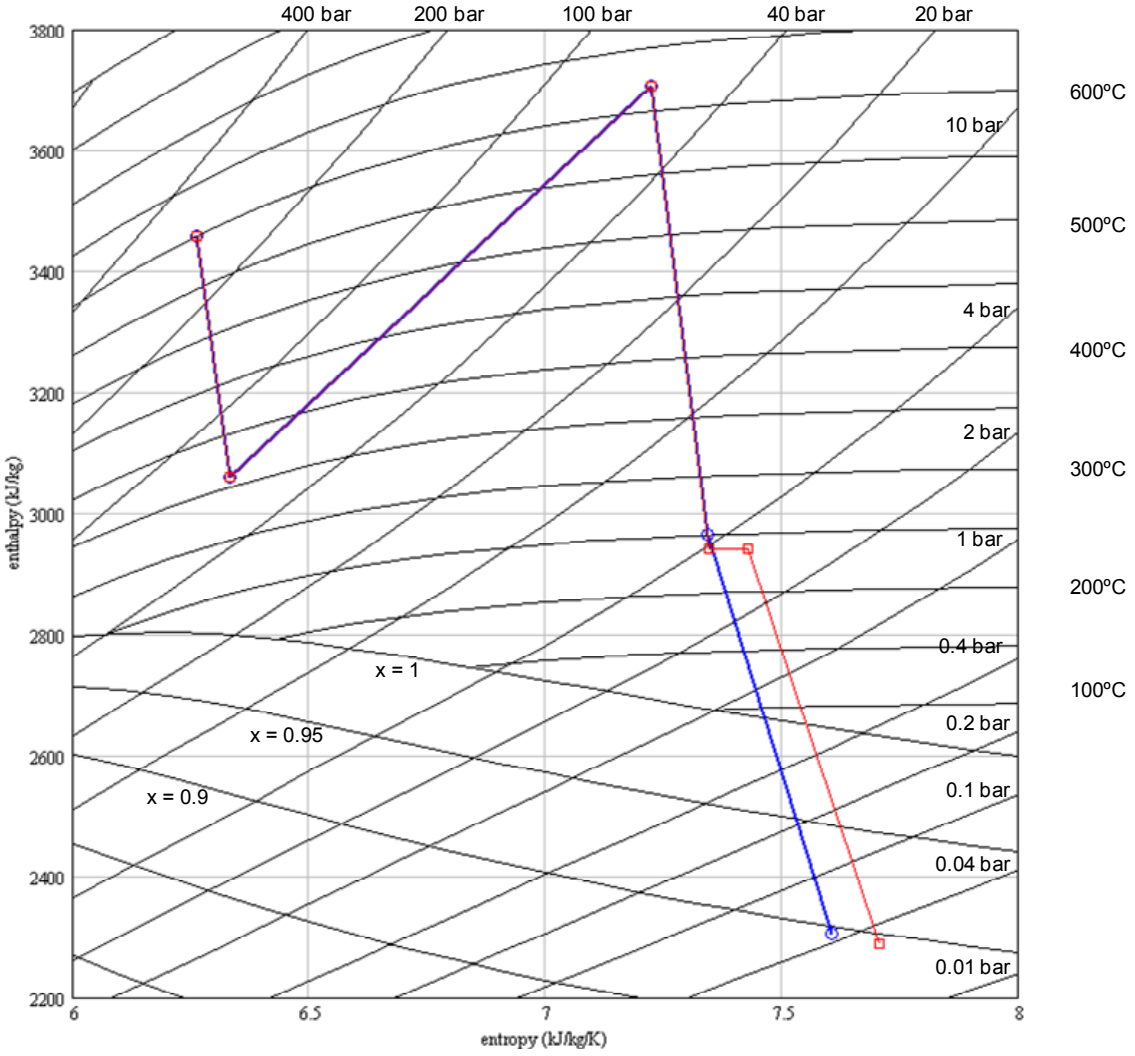


Figure 3-2b: Mollier diagrams for capture-ready steam cycle option with throttled LP turbine
O before capture, □ with capture

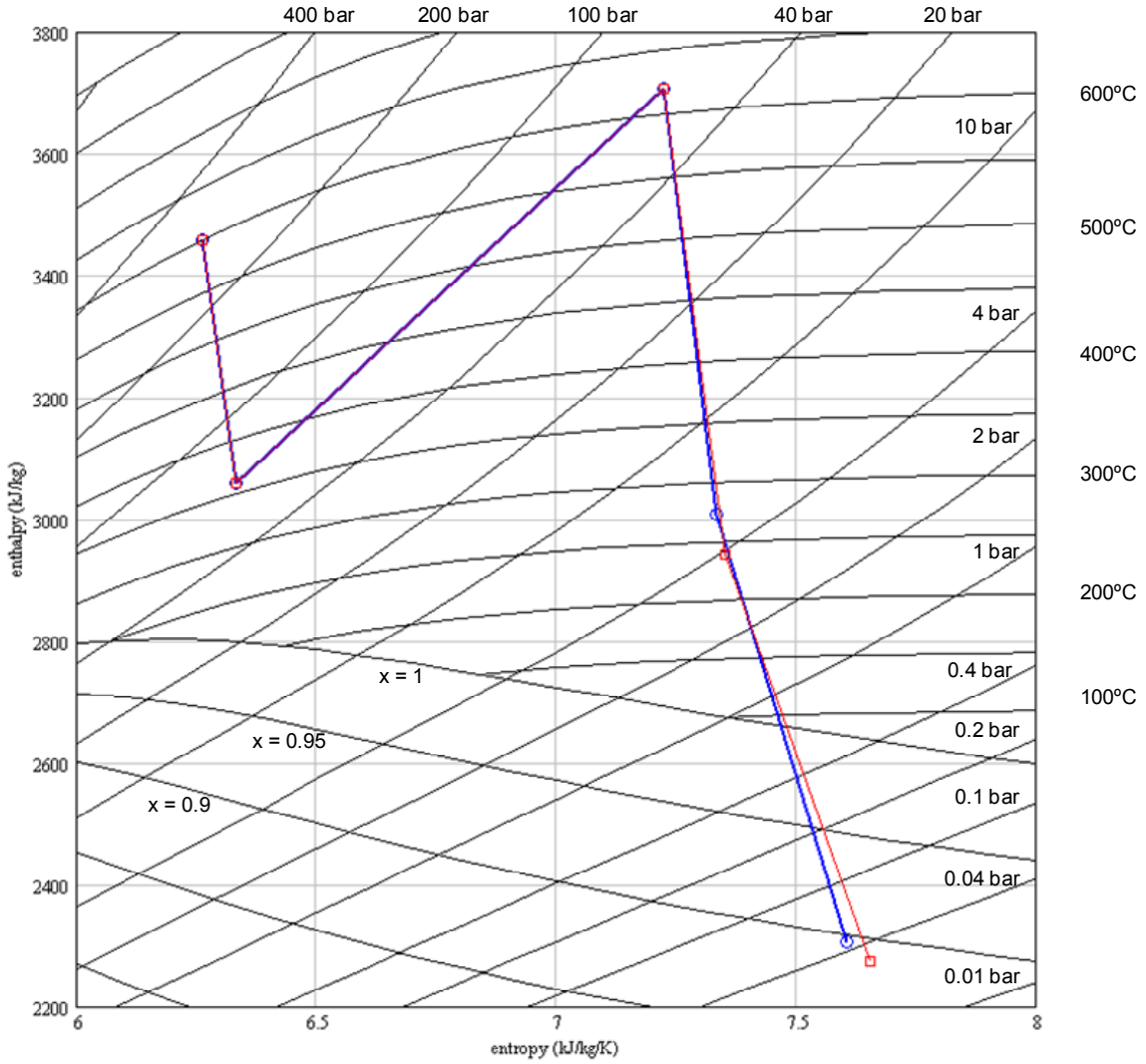


Figure 3-2c: Mollier diagrams for capture-ready steam cycle option with throttled LP turbine
O before capture, □ with capture

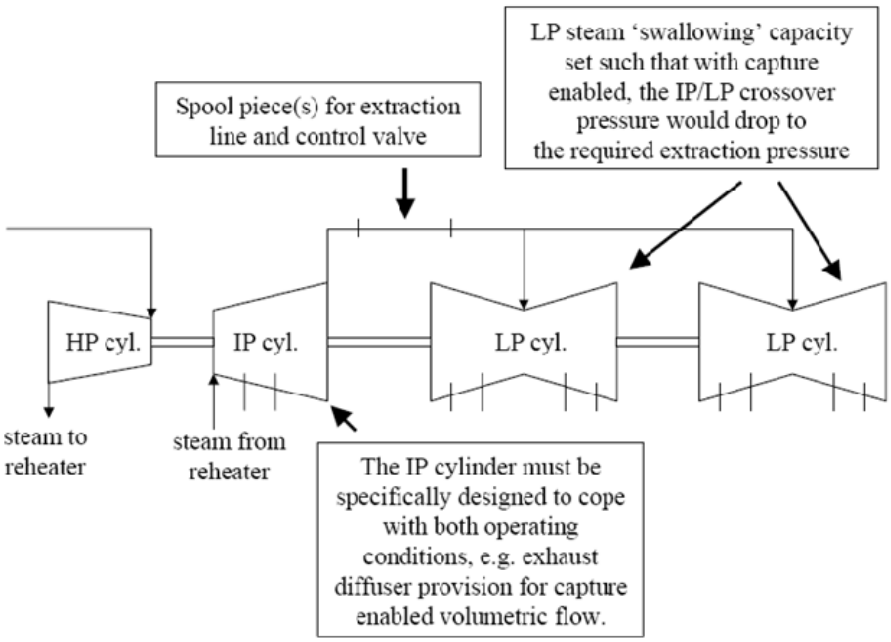


Figure 3-3: Capture-ready arrangements for subsequent steam extraction at the IP/LP crossover for a floating IP/LP crossover pressure system, from Gibbins et al. (2006)

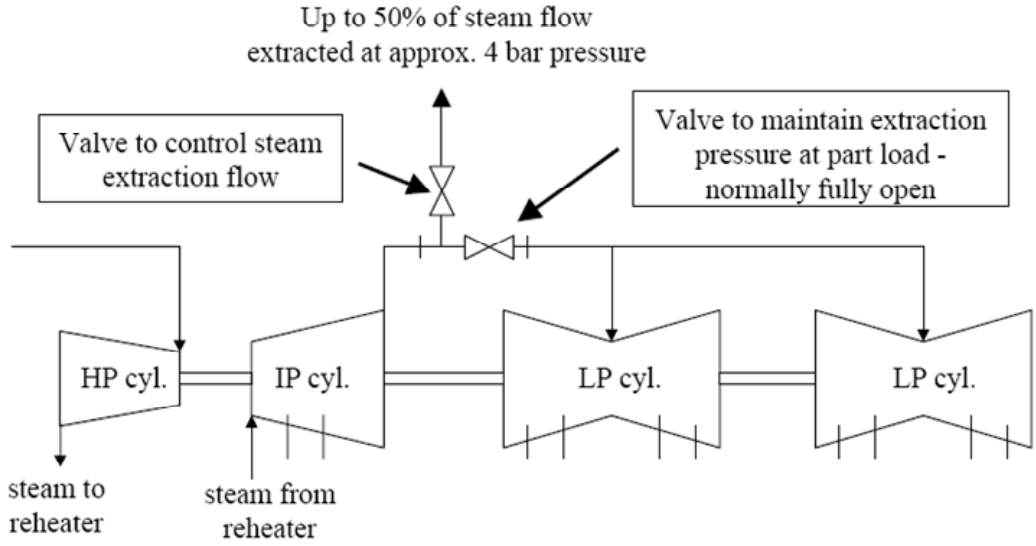


Figure 3-4: Retrofit arrangements for steam extraction at the IP/LP crossover, from Gibbins et al. (2006)

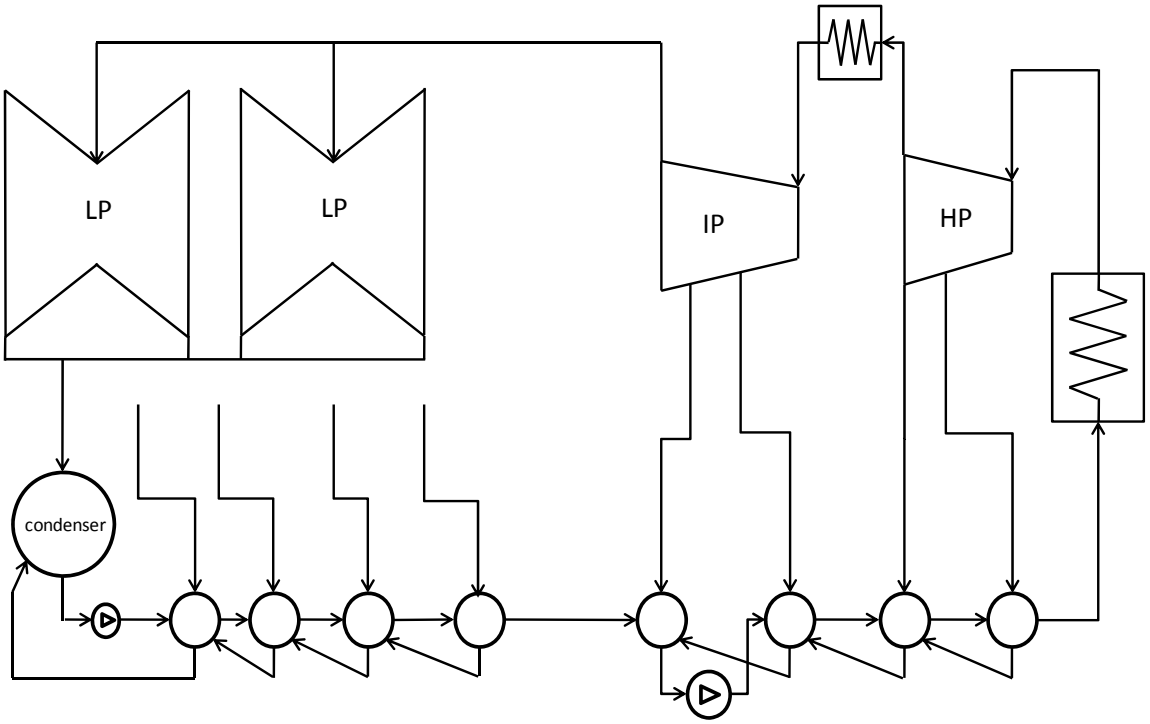


Figure 3-5: Capture-ready steam cycle diagram - Reference case (shaft and generator not shown)

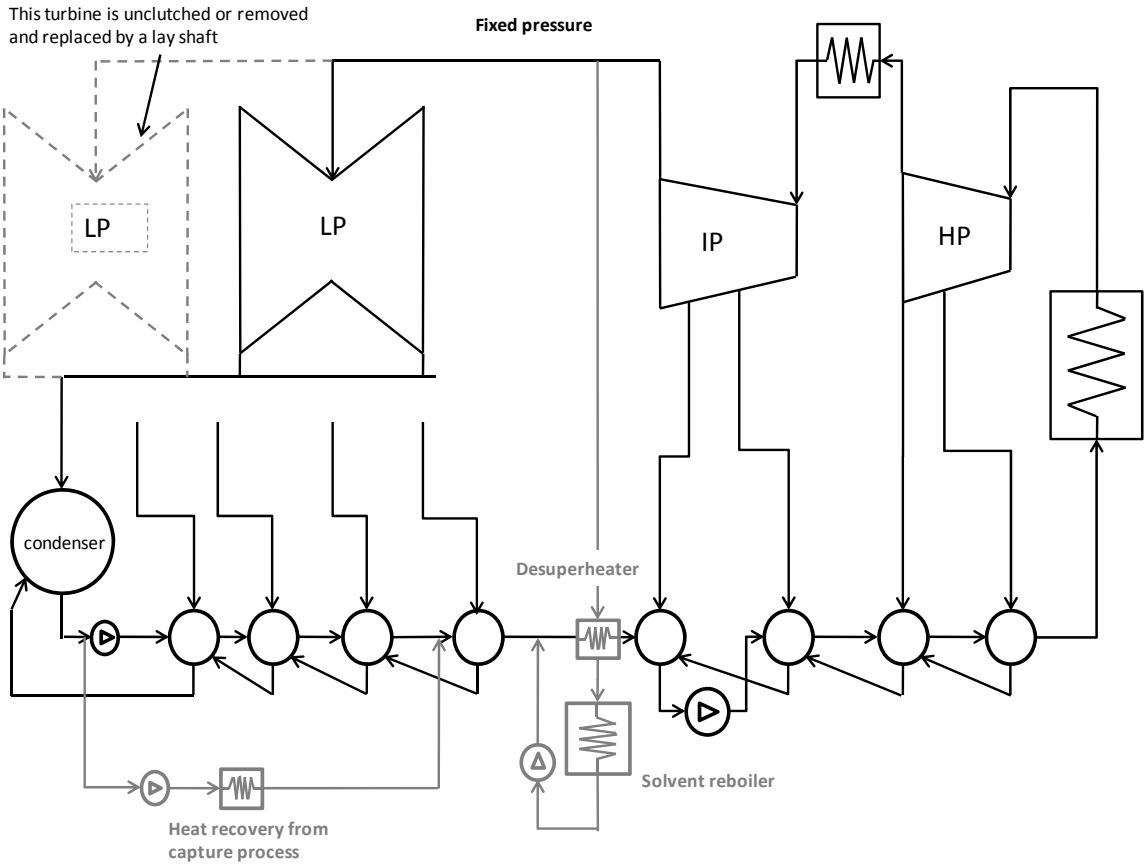


Figure 3-6: Retrofit of the clutched LP turbine option

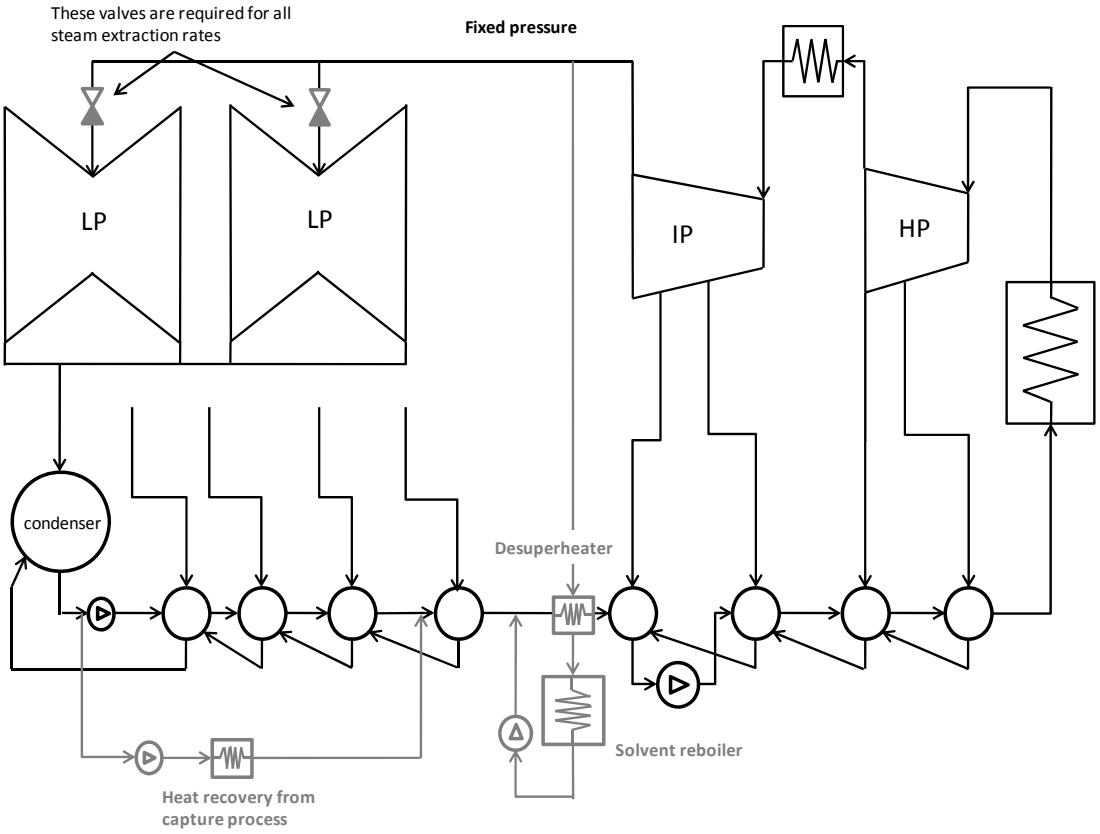


Figure 3-7: Retrofit of the throttled LP turbine option

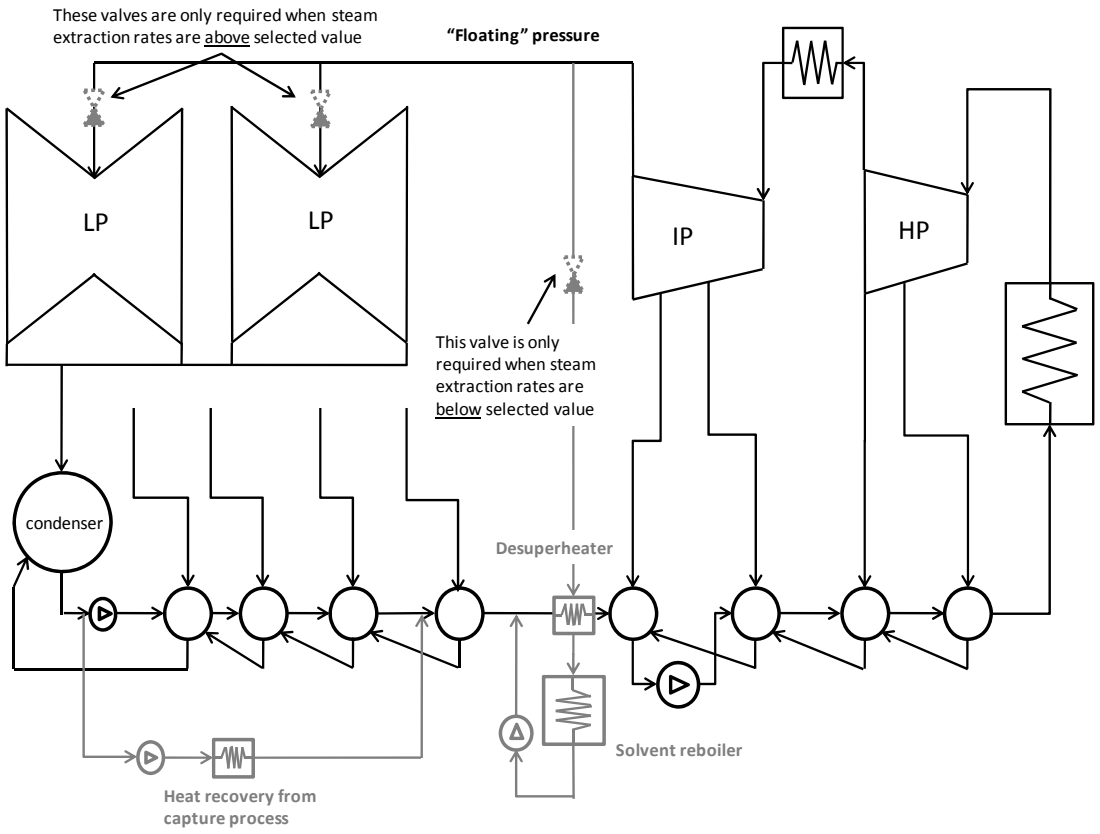


Figure 3-8: Retrofit of the floating IP/LP crossover pressure option

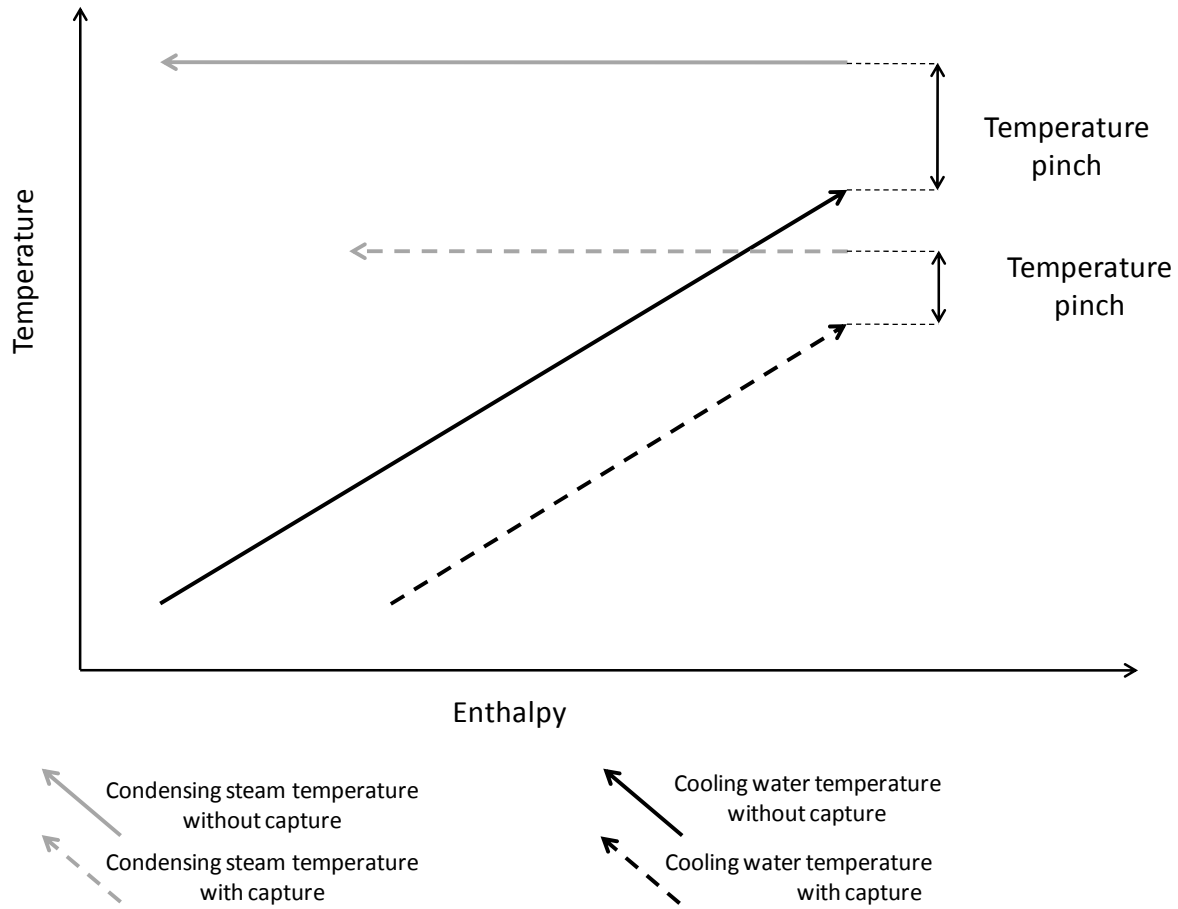


Figure 3-9: Illustrative T-h pinch diagram of condenser heat transfer

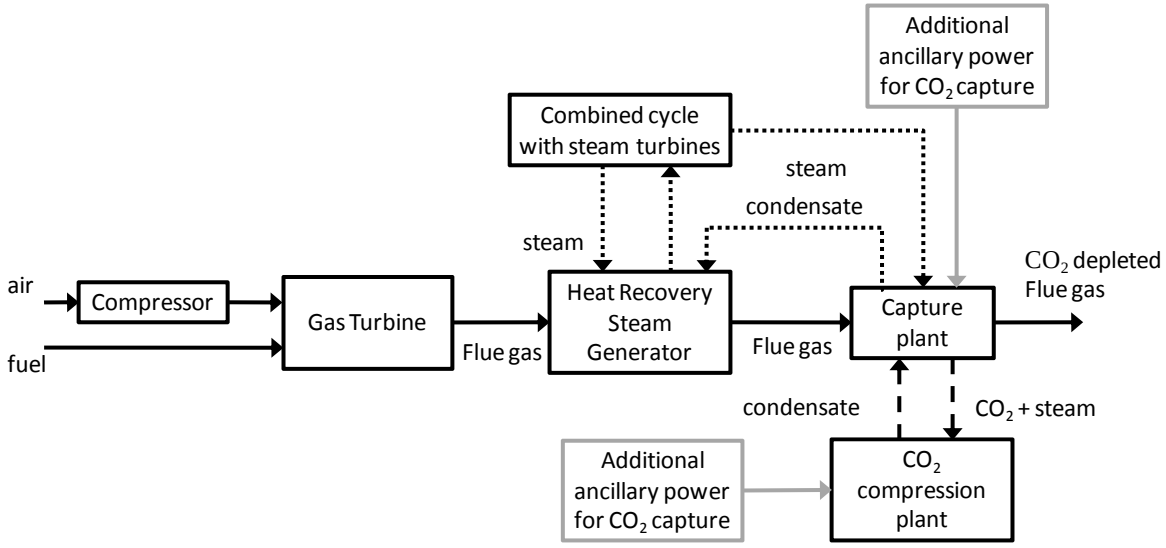


Figure 3-10: Schematic process flow diagram of a NGCC plant with post-combustion capture

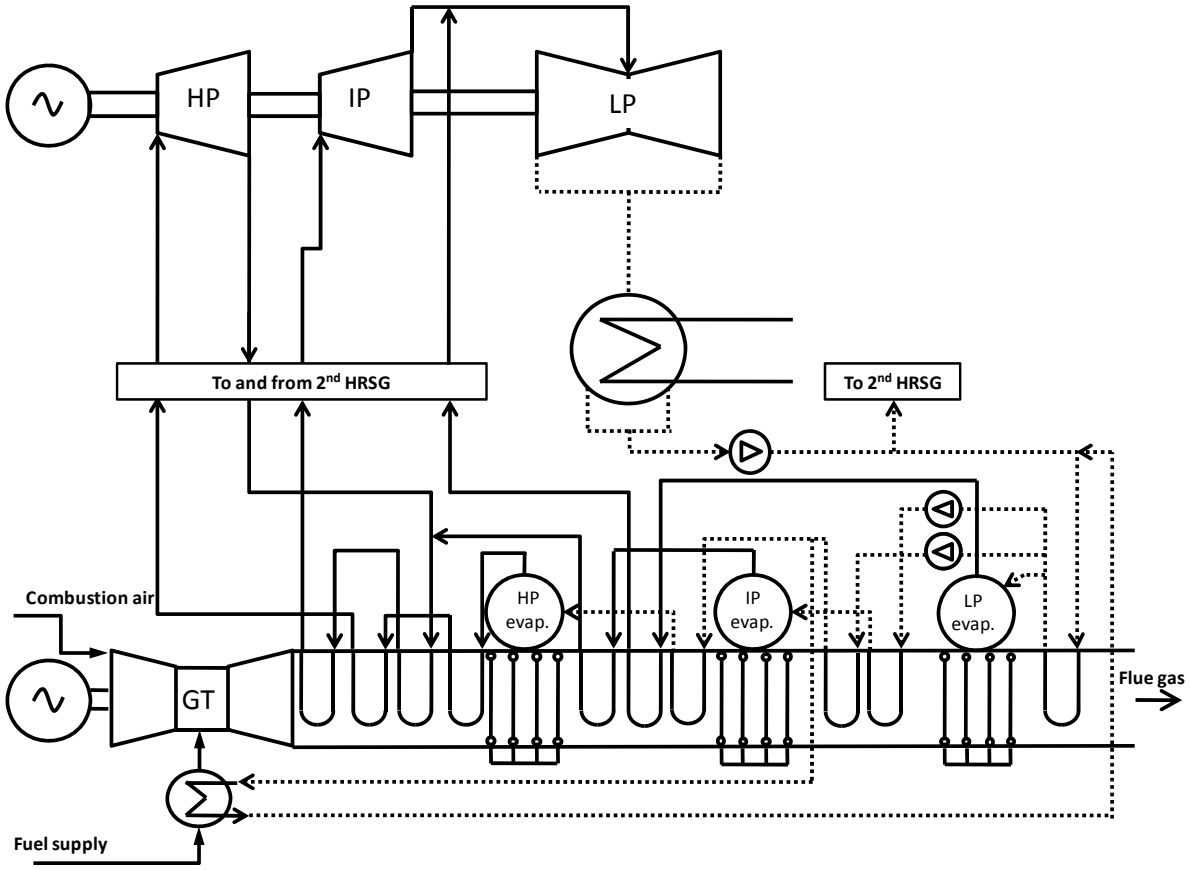


Figure 3-11: Process flow diagram of a natural gas combined cycle plant without capture, adapted from (IEAGHG, 2004)

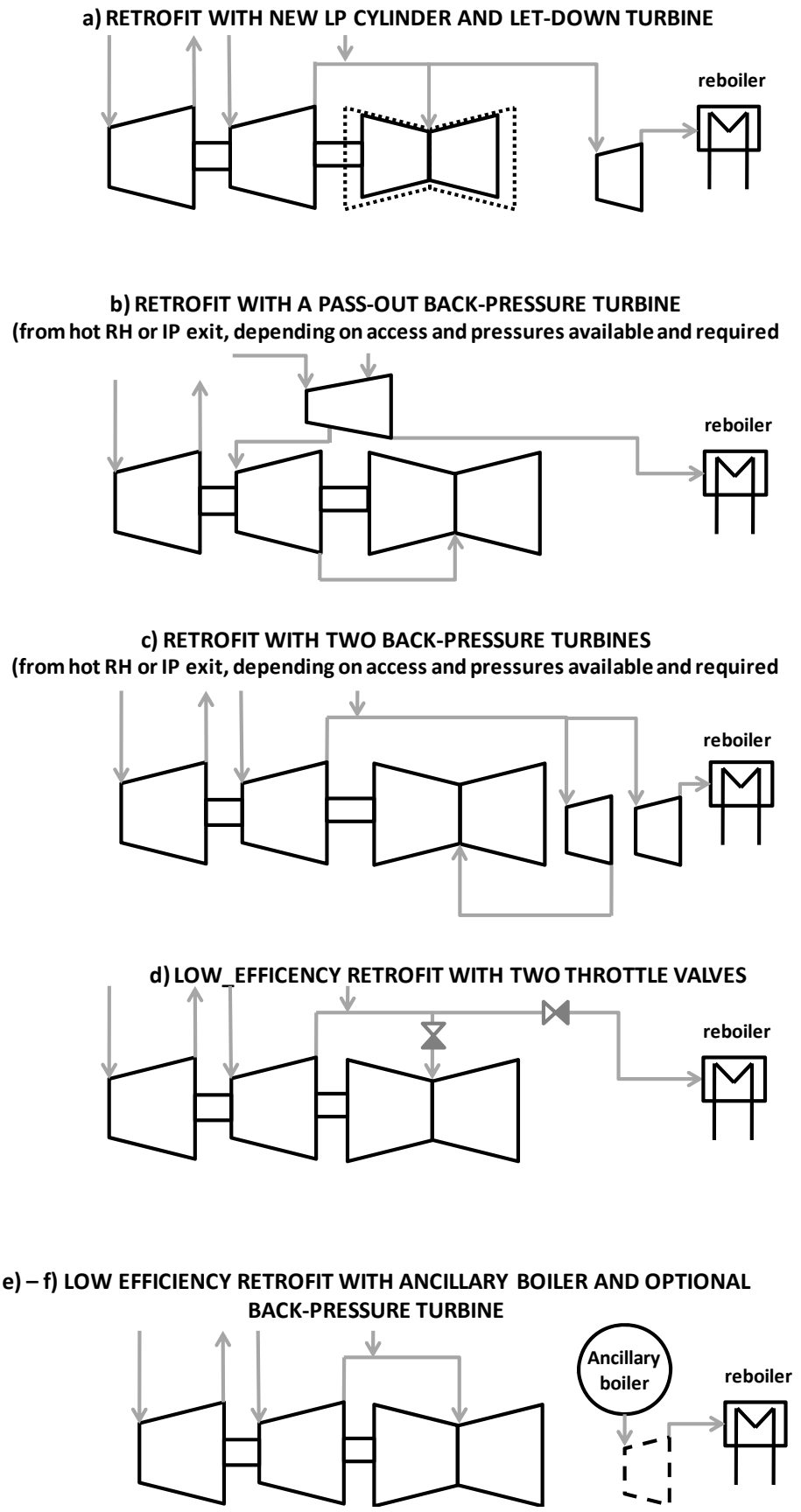


Figure 3-12: Retrofit options for natural gas combined-cycle plants (generator not shown)

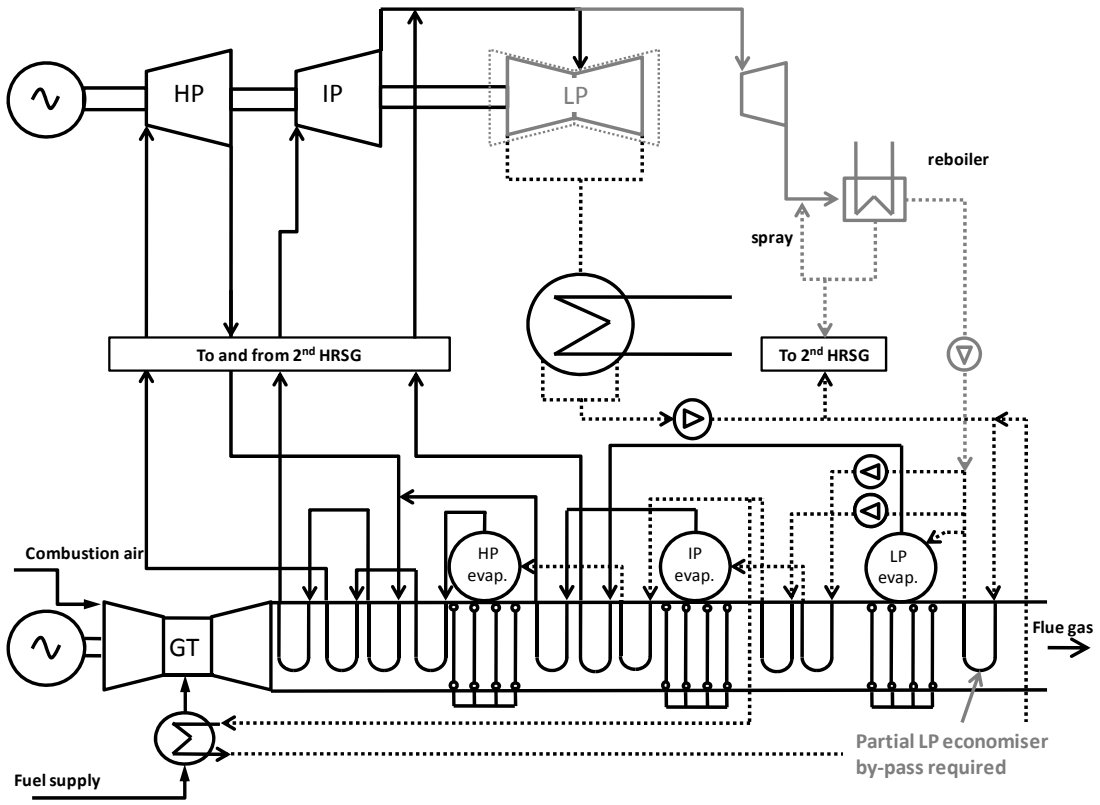


Figure 3-13: Retrofit of a natural gas combined cycle plant by replacing the low pressure turbine and the addition of a back-pressure turbine in the solvent extraction line

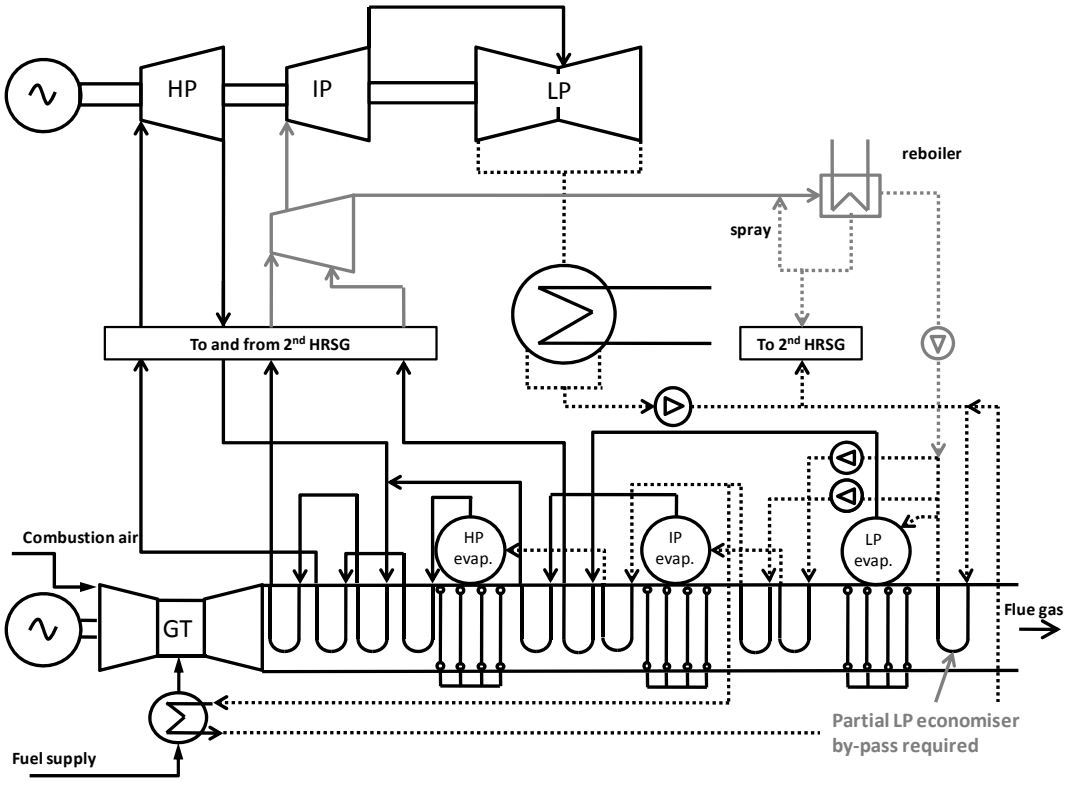


Figure 3-14: Retrofit of a natural gas combined cycle plant with the addition of a tailored design pass-out back-pressure turbine at the reheater outlet

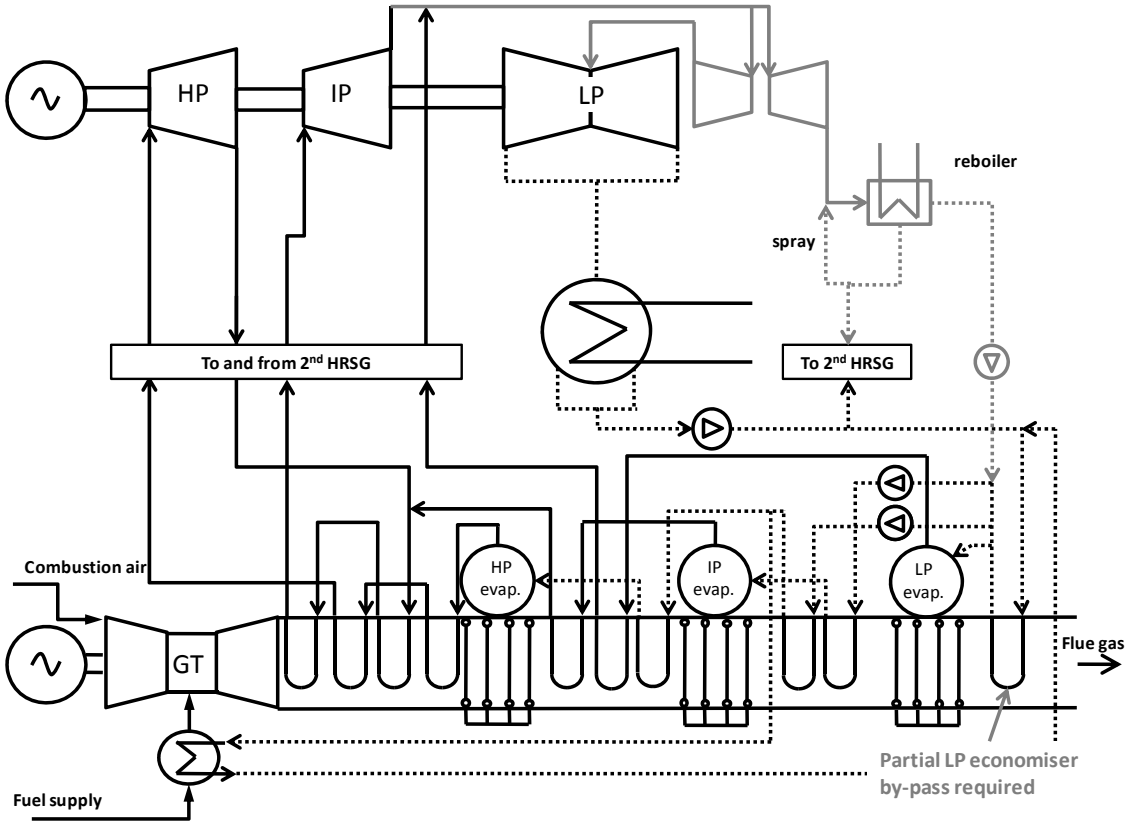


Figure 3-15: Retrofit of a natural gas combined cycle plant with the addition of two back-pressure turbines

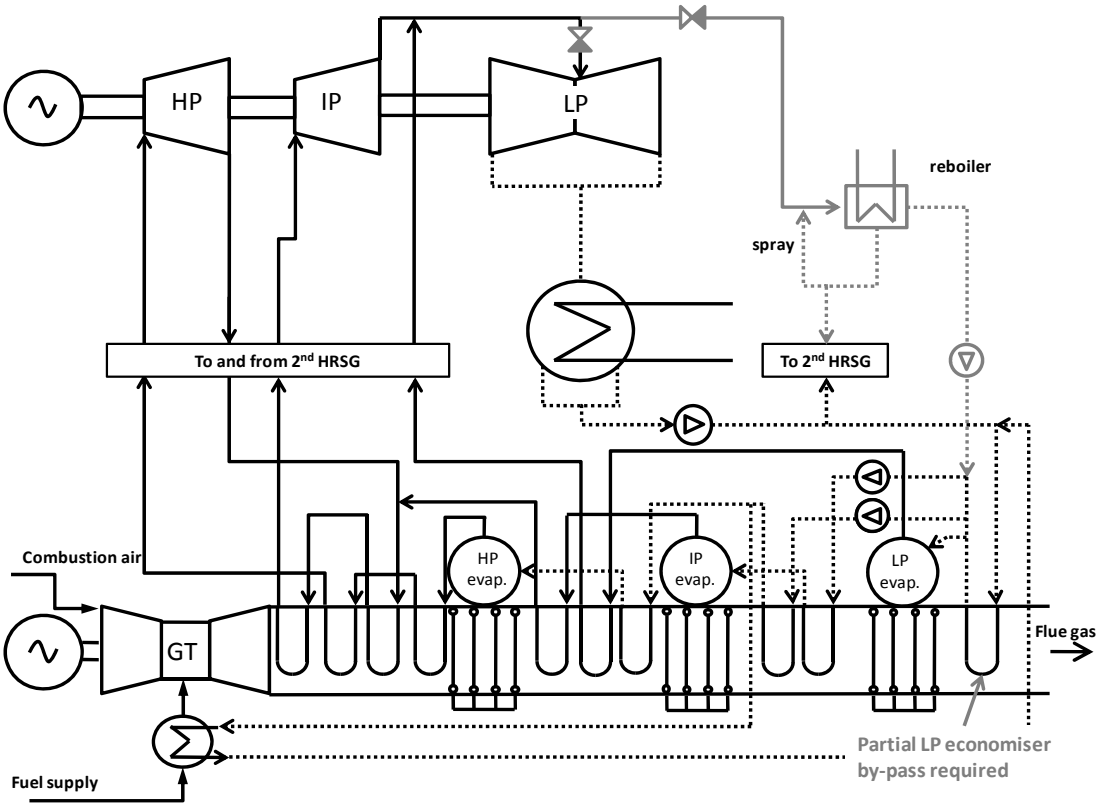


Figure 3-16: Retrofit of a natural gas combined cycle plant with two throttling valves

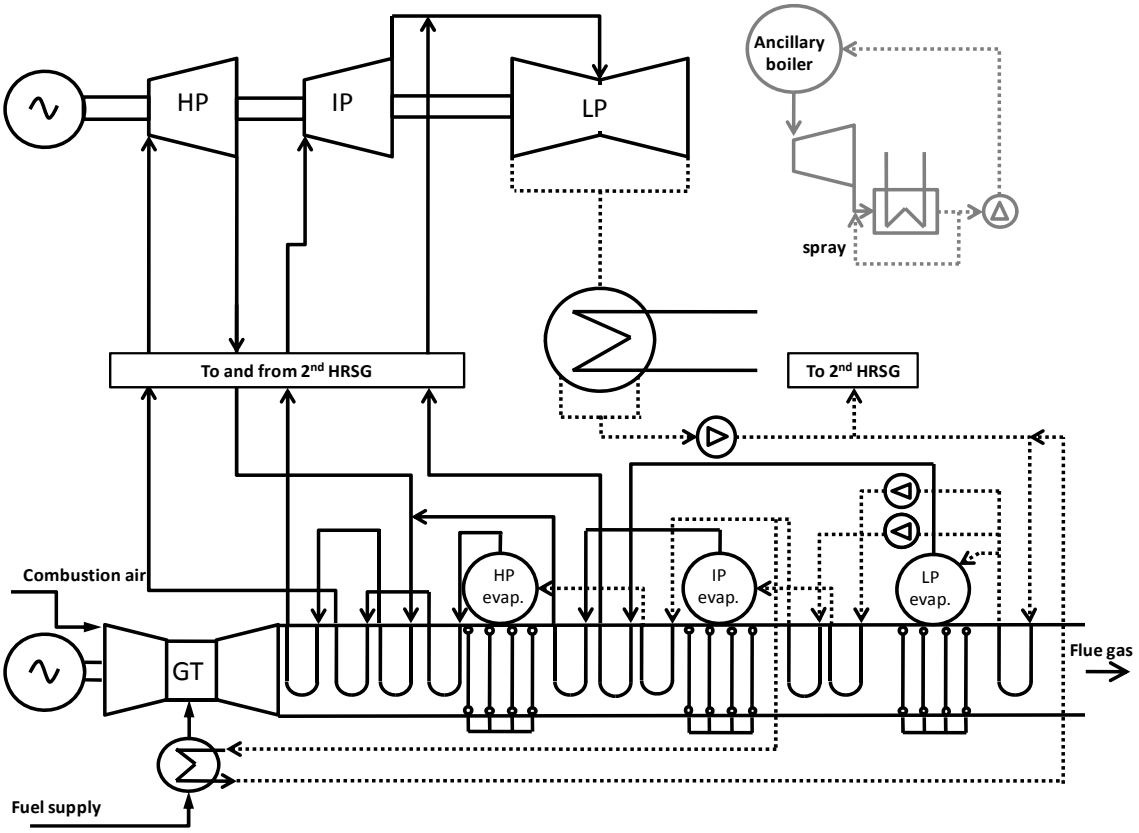


Figure 3-17: Retrofit of a natural gas combined cycle plant with a low efficiency separate ancillary boiler and back-pressure turbine system

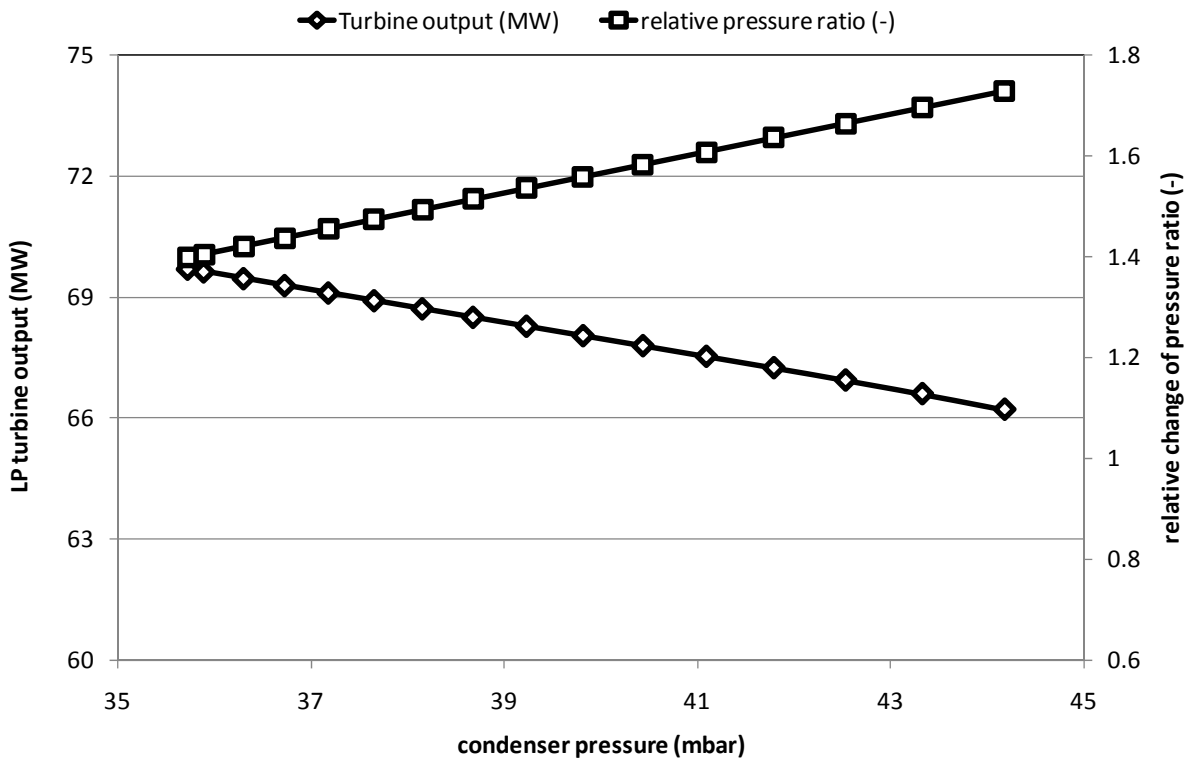


Figure 3-18: Variations of LP turbine output with the condenser pressure of a two back-pressure turbine retrofit

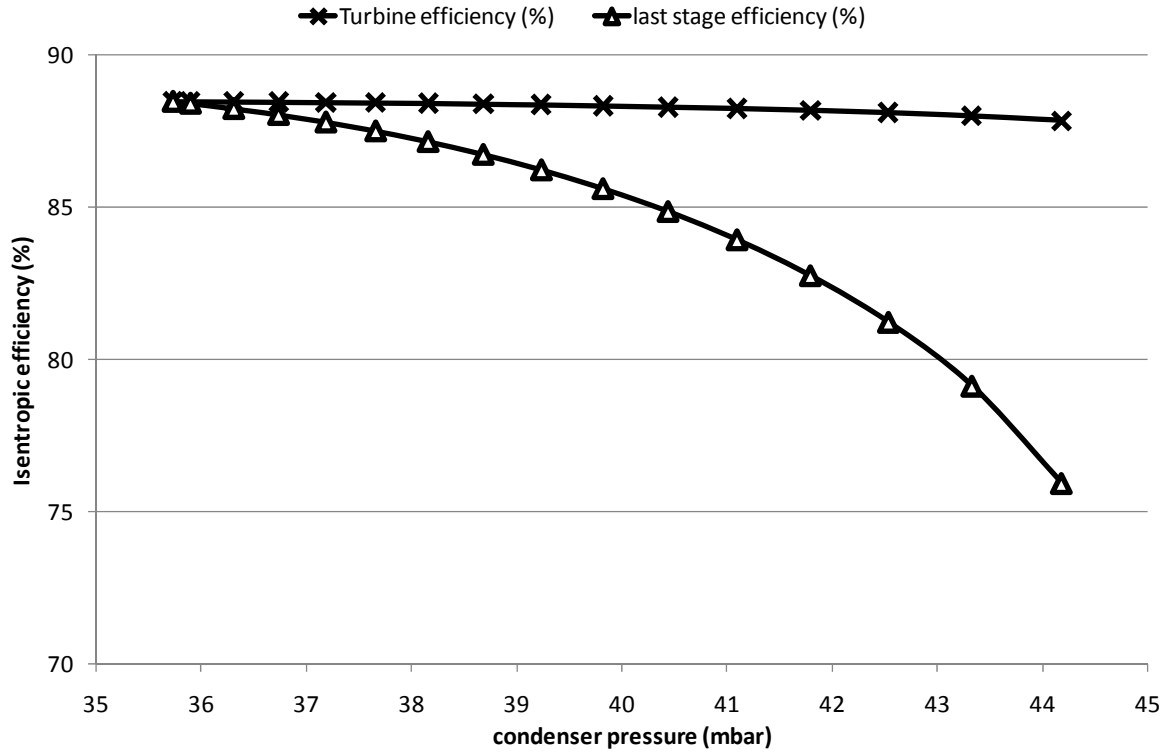


Figure 3-19: Variations of the LP turbine efficiency with condenser pressure of a two back pressure turbine retrofit

Table 3-1: Comparison of the performance of coal retrofit options

	New plant w/o CCS	New plant with CCS	Clutched LP turbine	Floating pressure	Throttled LP turbine
Fuel input (MW_{th})	1752.6	1752.4	1752.6	1752.0	1752.6
Performance without capture					
Efficiency w/o CCS (% LHV)	44.3	X	44.3	44.3	44.3
Gross Power output (MW)	850	X	850	850	850
Ancillary power for boiler and turbine island (MW)	74.3	X	74.3	74.2	74.3
Net power output (MW)	775.7	X	775.7	775.8	775.7
condenser pressure (mbar)	50	X	50	50	50
Performance with capture					
Efficiency w CCS (% LHV)	X	34.64	35.17	35.06	34.86
Gross Power output (MW)	X	758.6	768.1	765.9	762.6
Ancillary power for boiler and turbine island (MW)	X	74.2	74.3	74.2	74.3
Ancillary power for capture and compression (MW)	X	77.4	77.4	77.3	77.4
Net power output (MW)	X	607.0	616.4	614.3	610.9
condenser pressure (mbar)	X	50	35	35	36
Performance metric					
Electricity output penalty (kWh/tCO_2)	X	327.1	308.8	313.1	319.5

Table 3-2: Partial assessment of capture-ready steam turbine retrofit options based on ideal the first three capture-ready principles

	Clutched LP turbine retrofit	Floating crossover pressure retrofit	Throttled LP turbine retrofit
1st principle: Penalty performance before retrofit (% LHV)	0	0	0
2nd principle: Penalty performance with capture[14] (% LHV)	-0.6	-0.4	-0.2
Change in electricity output penalty compared to new-build unit (kWh_e/tCO_2)	-18.3	-14.0	-7.6
3rd principle: Additional capital costs (%) IEAGHG (2007a) Napier-Moore et al. (2008)	 2.89 < 1%	 0.74 <1%	0.41

[14] The reference plant is built with post-combustion capture from the outset. Its cooling system is sized for operation with capture

Table 3-3: Performance of capture-ready steam turbine options for NGCC plants

	Base case no capture	LP turbine replacement	Two back pressure turbine retrofit	Pass-out turbine retrofit
Performance without capture				
Gas input (MW_{th})	1396.0	1396.0	1396.0	1396.0
Net power output (MW_e)	773.6	773.6	773.6	773.6
Efficiency (% LHV)	55.4	55.4	55.4	55.4
Performance with capture				
Gas input (MW_{th})	1396.0	1396.0	1396.0	1396.0
Gas turbine gross output (MW_e)	520	520	520	520
Steam cycle gross output (MW_e)	277.6	230.9	230.4	230.0
Gross power output (MW_e)	797.6	750.9	750.4	750.0
Ancillary power (MW_e)	24.0	78.0	78.0	78.0
Net power output with capture (MW_e)	773.6	672.9	672.4	672.0
Efficiency with capture (% LHV)	55.4	48.2	48.2	48.1
CO_2 emissions				
CO_2 emissions (kg/s)	81.7	12.3	12.3	12.3
CO_2 emissions (g/kWh)	368.7	58.8	58.8	58.8
CO_2 Capture rate	0.00	0.85	0.85	0.85
Performance metrics				
Gas usage per tonne abated (MWh_{th}/tCO_2)	0	0.87	0.88	0.88
Electricity output penalty (kWh/tCO_2)	0	403.1	405.0	406.6

Table 3-4: Performance of low-efficiency NGCC retrofit options

	Two valve retrofit	Ancillary boiler	Ancillary boiler and turbine
Performance without capture			
Gas input (MW_{th})	1396.0	1396.0	1396.0
Net power output (Mw_e)	773.6	773.6	773.6
Efficiency (% LHV)	55.4	55.4	55.4
Performance with capture			
Gas input (MW_{th})	1396.0	1660.3	1750.0
Gas turbine gross output (MW_e)	520	520	520
Steam cycle gross output (MW_e)	217.1	277.6	351.4
Gross power output (MW_e)	737.1	797.6	871.4
Ancillary power (MW_e)	78.0	92.8	97.8
Net power output (Mw_e)	659.1	704.9	773.6
Efficiency (% LHV)	47.2	42.5	44.2
CO_2 emissions			
CO_2 emissions (kg/s)	12.3	14.6	15.4
CO_2 emissions (g/kWh)	59.8	65.8	63.5
CO_2 Capture rate	0.85	0.85	0.85
Performance metrics			
Gas usage per tonne abated (MWh_{th}/tCO_2)	1.01	1.82	1.50
Equivalent electricity output penalty (kWh/tCO_2)	458.0	890.7	822.0

Table 3-5: Parameters for NGCC retrofits

Solvent energy of regeneration (GJ/tCO_2)	3.2
Fuel specific emissions (kg/MWh)	210.7
Specific ancillary power for power generation (kW_e/MW_{th})	17.2
Specific ancillary for power and compression (kWh/tCO_2)	216
Generator efficiency (%)	97.6

4 Options for retrofitting existing pulverised coal plants with post-combustion capture

[This Chapter is an edited and extended version of an article co-authored by the applicant and submitted for publication (Lucquiaud and Gibbins, 2010)]

Existing coal-fired power plants were not designed to be retrofitted with post-combustion capture (PCC) and have tended to be disregarded as suitable candidates for carbon capture and storage on the grounds that such a retrofit would be uneconomical. Although beyond the scope of this thesis similar arguments are often made for retrofit with oxyfuel combustion. Low plant efficiency with capture and hence poor economic performance compared to new-build projects are often cited as critical barriers to capture retrofit.

There also appears to be some confusion in the literature whether the energy requirement per tonne of CO_2 capture is higher for low efficiency plant, or not. One solution to this, which has been suggested, is to increase the efficiency of the base plant by rebuilding the boiler and turbine to ultra-supercritical steam conditions, e.g. Panesar et al. (2009). Provided that the boiler turbine retrofit can be accomplished cheaply this could be a cost effective option (Gibbins and Crane, 2004b). This option is not considered further in this chapter and only power plant retrofit with post-combustion capture, but without any boiler or turbine modifications, are envisaged

With capture ready plants, as in Chapter 3, the power cycle is designed to be able to accommodate a future retrofit with CO_2 capture, which is not be the case for most existing plants. The proposed methods for steam supply and heat recovery for integrating retrofitted capture systems with the power plant steam cycle, which are possible with capture ready plants, may, in some cases, incur excessive energy penalties. Alternative approaches can achieve effective thermodynamic integration between the capture and compression plant and the power cycle of a retrofitted unit, and hence efficiency penalties close to those of new-build or capture ready plants, for a wide range of steam cycles (although other restrictions, such as space limitations, may still apply).

4.1 The case for retrofitting existing units

Investment decisions in new-build coal capacity seem to have become, at the time of writing, an unsolvable jigsaw. This can be explained by a combination of factors (Specker et al., 2009): accelerated investment in energy efficiency, the expectation of a reduced electricity demand in the short term, uncertainty about capital costs, reduced availability of financing, and uncertainties with regards to future CO_2 emissions policies that have contributed to delaying or cancelling several coal-based power projects. National and local public opposition to coal in some countries has also considerably delayed, and in some cases, blocked the permitting process of coal-fired units, notably in the United States (Hildebrand, 2009). In these countries the emphasis for the decarbonisation of electricity generation, and the deployment of CCS, has shifted towards retrofitting existing units. Post-combustion capture technologies can play an important role in the deployment of CCS within the existing fossil generation fleet because as 'end of pipe solutions' they are unlikely to require extensive modification to retrofitted plants, and as a result could be the main options deployable for a fast-track emission mitigation strategy. Many technical and economic factors could, however, affect the practical feasibility of retrofitting capture to an existing pulverised coal power plant. Most of these are site specific: access to CO_2 storage, space on site and within the plant to add capture equipment, the future life of the plant, the performance of the existing pollution control equipment. The nature of the electricity and carbon markets in which the plant operates should also be considered for the replacement power induced by loss of output. Technical barriers to retrofit projects are discussed in (IEA GHG, 2007a) (co-authored by the candidate) and so, for conciseness are not discussed here.

4.2 Thermodynamic analysis of the efficiency penalty of power plant retrofits

The extent to which the non-site-specific base power plant efficiency, and in particular the peak steam temperature and pressure used in the plant - rather than other site specific factors also affecting plant efficiency such as ambient temperature, cooling method, coal properties, duty cycle - affects retrofit economics is a topic of concern. In particular there is a question of differentiation between the large number of plants built with steam conditions around the effective limits for sub-critical boiler technology, 150-175 bar and 540ºC, which can achieve efficiencies in the range of 36-39% LHV, and the later supercritical steam plants with pressures of 250 bar or higher and steam temperatures of 550ºC to 600ºC with current boiler materials, which reach efficiencies between 40 and 46%. In the future even higher efficiency with 700ºC steam temperatures achieved by changes in boiler and high pressure steam turbine materials may be built, as shown in Figure 4-1.

The following thermodynamic analysis evaluates the effect of the base-plant efficiency on the efficiency penalty for post-combustion capture combined with both subcritical and supercritical plants.

An energy balance for a coal-fired plant retrofitted with post-combustion capture is provided in Figure 4-2. The power cycle receives an amount of heat, Q_B, from the boiler provided by combustion of the fuel. The energy inputs to the boiler are LHV and $W_{A,}$ respectively the total calorific value of the fuel and the ancillary power for boiler machinery, and the LOSSES term includes principally stack losses and heat losses from the boiler and pipework. Boiler efficiencies are potentially the same for both sub-critical and supercritical steam plants, so it can be assumed that the same amount of heat per unit of fuel burnt, and hence per unit of CO_2 captured, is transferred to the steam cycle for both, although at a higher average temperature for the latter. The power cycle generates mechanical work W_T and rejects heat Q_C through the condenser; it can be assumed that these together sum to Q_B since other losses are small. When the plant is retrofitted with capture additional heat, Q_{CAP}, is taken from the power cycle and transferred to the capture unit for regeneration of the solvent, along with the ancillary power W_A^R for the capture unit ancillary machinery. It should be noted that Q_{CAP} is the net heat provided for solvent regeneration, allowing for heat recovered in the capture unit for use in the steam cycle (typically for condensate heating).

The efficiency of the plant η and η^R, respectively without capture and when the plant is retrofitted, can be expressed as follows:

$$\eta = \frac{W_T - W_A}{LHV} \quad (18)$$

$$\eta^R = \frac{W_T^R - W_A - W_A^R}{LHV} \quad (19)$$

The efficiency penalty for capture is then:

$$\eta - \eta^R = \frac{W_T - W_T^R + W_A^R}{LHV} \quad (20)$$

Where:

Superscript	R	retrofitted plant
η	-	Plant efficiency based on fuel low heating value
W_T	MW_e	Mechanical work output
W_A	MW_e	Ancillary power
LHV	MW_{th}	Fuel energy input based on low heating value

The loss of mechanical work output caused by steam extraction from the power cycle can alternatively be written as:

$$W_T - W_T^R = Q_B - Q_C - Q_B + Q_C^R + Q_{CAP} \quad (21)$$

$$W_T - W_T^R = Q_{CAP} - (Q_C - Q_C^R) \quad (22)$$

$$W_T - W_T^R = Q_{CAP} - (\dot{m}_C * (h_{steam} - h_{liq}) - \dot{m}_C^R * (h_{steam}^R - h_{liq}^R)) \quad (23)$$

$$W_T - W_T^R = Q_{CAP} + \dot{m}_C * \left[(h_{steam}^R - h_{steam}) - (h_{liq}^R - h_{liq})\right] - (\dot{m}_C - \dot{m}_C^R) * (h_{steam}^R - h_{liq}^R) \quad (24)$$

Where:

Superscript	R	retrofitted plant
Q_B	MW_{th}	heat input from boiler to steam cycle
Q_C	MW_{th}	heat rejected by the condenser
Q_{CAP}	MW_{th}	Net heat taken from the power cycle for regeneration of the solvent
$\dot{m}_C$	kg/s	steam cycle condenser steam flow without capture
h_{steam}	MJ/kg	stagnation enthalpy per unit of mass of steam at low pressure turbine outlet
h_{liq}	MJ/kg	stagnation enthalpy per unit of mass of condensate at condenser outlet

The efficiency penalty can be written as the sum of two terms. The first one depends solely on the performance of the post-combustion capture system, while the second one is specific to the plant configuration

$$\eta - \eta^{R} = \frac{Q_{CAP} + W_{A}^{R}}{LHV} + \frac{+\dot{m}_{C} * \left[\left(h_{steam}^{R} - h_{steam}\right) - \left(h_{liq}^{R} - h_{liq}\right)\right] - \left(\dot{m}_{C} - \dot{m}_{C}^{R}\right) * \left(h_{steam}^{R} - h_{liq}^{R}\right)}{LHV} \quad (25)$$

For the purpose of comparing a sub-critical and supercritical plant the following parameters can be assumed to be identical, since they are site specific factors not intrinsically related to the steam conditions.

- Coal properties, specifically calorific value and the quantity of carbon dioxide produced per unit heat
- Boiler efficiencies, so that the amount of heat transferred to the power cycle Q_B is the same
- By extension these two assumptions imply that the fuel specific emissions are the same
- Ambient conditions, cooling systems and low pressure turbine exit dryness fraction, so that condenser pressure is the same
- Steam extraction pressure at the point it leaves the steam cycle and low-grade heat use for condensate heating

- Capture unit design and operation, so that the output penalty per mass of CO_2 captured are identical

Therefore for both units the amount of heat extracted from the steam cycle Q_{CAP} and the ancillary power for capture $W_A{}^R$ for the same fuel input are the same. The efficiency penalty, in terms of percentage points of efficiency lost, for the sub-critical and the supercritical plants is then identical, except for any variation in the value of the second term:

$$\dot{m}_C * \left[\left(h^R_{steam} - h_{steam}\right) - \left(h^R_{liq} - h_{liq}\right)\right] - \left(\dot{m}_C - \dot{m}^R_C\right) * \left(h^R_{steam} - h^R_{liq}\right) \quad (26)$$

Provided that the same condenser pressure and exit dryness fraction for the low pressure turbine are used, then steam and condensate enthalpies h_{steam} and h_{liq}in the condenser are identical for sub- and supercritical units without capture. If an equally efficient method of integration is employed for capture retrofit to the sub-critical and the supercritical plant[15], the reduction in steam flow to the condenser, $\dot{m}_C - \dot{m}^R_C$, is the same for both types of plants. The difference in the efficiency penalty is, thus, only a function of the condenser mass flow without capture, $\dot{m}_C$, and the (possibly) changed steam enthalpies in the condenser h^R_{steam} and h^R_{liq}.

For the same boiler heat input to the power cycle a subcritical plant produces less power without capture, rejects more heat through the condenser and therefore has a higher condenser mass flow without capture, $\dot{m}_C$, than a supercritical plant. This higher original mass flow means that the relative change in the mass flow through the condenser $\frac{(\dot{m}_C - \dot{m}^R_C)}{\dot{m}_C}$ is smaller for the subcritical plant, which directly affects the extent to which the condenser pressure drops with capture. If the cooling water flow is maintained, a lower drop in condenser pressure for the subcritical plant is observed, and hence a slightly higher values for h^R_{steam} and h^R_{liq} than for the supercritical plant. On the other hand a smaller relative change of the mass flow through the LP turbine results in a smaller drop in the isentropic efficiency of the LP turbine of a subcritical plant. This would make h^R_{steam} and h^R_{liq}lower than for a supercritical plant for a given condenser pressure, which tends to counteract the previous effect.

Additionally, it can be shown that the magnitude of this second term is relatively small. Values for h^R_{steam} and h_{steam} are of the order of 2300-2320 kJ/kg and for $h_{liq}$and h^R_{liq} of the order of 120-160 kJ/kg, with likely relative changes of the order of 30 kJ/kg for both h_{steam} and h_{liq} , when capture is

[15] The next section discusses steam turbine retrofit options to achieve that objective.

added. Because the effects of steam extraction on condenser pressure counteracts between sub- and supercritical plants, the difference in the magnitude of the enthalpy changes is, thus, likely to be limited to 5 kJ/kg maximum. A 600MW_e retrofitted unit operating with capture has a condenser mass flow of the order of 250-300kg/s, once approximately 50% of the low pressure turbine flow is extracted. Variations in condenser pressure between sub- and supercritical plants, thus, account for a difference in power generated of maximum 1-1.5 MW_e.

A similar analysis can be made on the sensitivity to boiler efficiency, which was previously assumed to be constant. If we now consider the case of a plant with a high boiler efficiency and a plant with a low boiler efficiency, but with the same steam cycle efficiency, a similar counter effect on the low pressure turbine output occurs. With a more efficient boiler the steam cycle generates more power through a higher steam flow, and hence a higher low pressure turbine and condenser steam flow $\dot{m}_C$. When steam is extracted for capture, the lower reduction in the isentropic efficiency of the low pressure turbine – beneficial for the overall plant output - counterbalances the lower drop in condenser pressure – detrimental for power output. In addition, it should be noted that overall boiler efficiencies do not vary much between sub- and supercritical units.

Therefore, to a very close approximation, this analysis shows that the plant steam conditions, and by extension the plant efficiency, has no significant direct effect on the efficiency penalty of a capture retrofit, but rather depends on site specific considerations, e.g. the condenser heat transfer surface or the low pressure turbine efficiency profile at reduced flow. The effects of site-specific parameters are likely to be small compared to the influence of the capture system characteristics and can only be evaluated on an individual basis.

4.3 Steam turbine retrofits for post-combustion capture

The integration of post-combustion capture systems with the steam cycle for new-build plants at base load has been studied extensively, as pointed out in Chapter 2, with the aim of reducing the energy penalty independently of the specific solvent regeneration energy requirements. Neither of the approaches proposed are, however, likely to be practicable for many of the existing fleet of coal-fired plants, which have a wide range of IP turbine exit pressures. For example, a US Department of Energy study (Ciferno et al., 2007) examined the site-specific retrofit of a coal-fired unit based at Conesville, Ohio, USA, with an IP turbine outlet pressure of 13.4 bar, i.e. considerably higher than the pressure required for the MEA solvent used. A requirement to maintain the capacity for operation with the capture plant by-passed to permit the maximum generator output to be obtained, meant that *'permanent modifications [to the turbines and generator] were not possible*'. The study also assumed that the IP/LP crossover pressure would not be reduced, on the basis that "*the exhaust section of the IP turbine and the existing blading would not be able to withstand this increased mechanical loading*" (although no further details on the high cycle endurance fatigue or tensile strength of the IP blades were given). The LP turbine inlet was throttled to maintain the IP turbine outlet pressure, and the steam extracted was expanded down through a back pressure turbine, before leaving the steam turbine hall to go to the solvent reboiler.

A schematic diagram of the Conesville retrofit, with the addition of a desuperheating feed water heater in the steam extraction line instead of a spray desuperheater, for consistency with the rest of the work presented here, is provided in Figure 4-3. Throttling losses in the LP inlet valve inevitably resulted in an electricity output penalty higher than for a capture plant in which throttling would not be required. In addition, (Ciferno et al., 2007) also report a higher delivery pressure for the steam leaving the boundaries of the steam cycle to the capture plant – 4.5 bar instead of 3.6 bar -, which contributes to increasing further the electricity output penalty. A higher pressure such as this could be a consequence of the remote location of the capture plant from the turbine island, with increased pressure drop in the connecting pipes, but could also result from a decision to reduce the size of the solvent reboiler to unnecessarily favour capital expenditure at the expense of a higher electricity output penalty. Comparative results from other studies for new-build plants and retrofits of capture-ready units, where the IP turbine outlet pressure was selected to be at a lower pressure,

are provided in Table 4-1.The retrofit option proposed by (Ciferno et al., 2007) increases significantly the electricity output penalty of CO_2 capture.

This highlights the need to update the third rule for thermodynamic integration proposed by Gibbins et al. for new-build plants with post-combustion capture, and previously updated in Chapter 2, as follows.

Originally:

3. Produce as much electricity as possible from any additional fuel used, consistent with rejecting heat at the required temperature for solvent regeneration.

Updated:

3. Produce as much electricity as possible *from the power cycle (i.e. be prepared to use additional turbines for retrofit projects if commercially justified)* and from any additional fuel used, consistent with rejecting heat at the required temperature for solvent regeneration.

The gPROMs model of the power cycle described in Chapter 3 has been extended to examine the performance of alternative steam turbine options for the retrofit of the steam cycle of an existing unit, following the updated integration rule above. Flexibility is provided within the model to represent a range of IP turbine outlet pressure and solvent heat of regeneration. For consistency, it is assumed that the boiler efficiency and the ancillary power of the CO_2 compression train are constant for each configuration. In this example a supercritical pulverised coal boiler delivers steam at respectively 242bar and 565ºC at the HP turbine inlet and 42.1 bar and 566ºC at the IP turbine inlet, based on the existing configuration - without capture - of the steam cycle of a Chinese pulverised coal unit provided within the NZEC project[16]. The IP turbine outlet pressure is initially set to 11.1 bar.

When the plant is retrofitted and operates with capture, the LP condensate heaters are retained and receive 10% of their design mass flow to keep them at temperature so that they can be used to facilitate rapid changes in capture levels and power output. Additional parameters are given in Appendix D. For this illustrative study the solvent regeneration temperature is assumed to be 120ºC, the temperature difference in the reboiler is 15K and the pressure drop across the connecting pipe from the turbine island to the solvent reboiler is 0.5 bar. A sensitivity analysis of these values is presented in later in this Chapter.

[16] The joint UK-China Near Zero Emissions Coal (NZEC) initiative, http://www.nzec.info/en/

Effective thermodynamic integration of the turbine with the capture process implies that as much power as possible is recovered from both the extracted steam going to the reboiler and the remaining steam entering the LP turbine. This should not, however, compromise the ability of the retrofitted plant to return to operation with maximum generation output. For example, for a given solvent and IP turbine outlet pressure it might be possible to recover the maximum mechanical work available in the steam leaving the IP turbine by converting one of a pair of LP cylinders to back pressure operation by removing a suitable number of LP stages so that steam from that cylinder could go to the reboiler instead of to a conventional condenser. But this permanent modification would lock the plant into operation with capture if full output was to be achieved and also allow only limited changes in the solvent.

Retrofits aiming for solvent upgradability, flexible capture and maximum efficiency should seek to maintain the full original steam swallowing capacity of the LP turbine (for upgradability and flexibility), but not use throttling valves to restrict the steam flow through the LP when capture is retrofitted (for maximum efficiency). One option for achieving this is shown in Figure 4-4 where two let-down back-pressure turbines are fitted in the extraction line and between the LP and IP turbine. The back pressure turbine at the inlet of the LP turbine is by-passed without capture. At intermediate capture levels between 0 and 90% capture both additional turbines are partially by-passed.

A second option is shown in Figure 4-5. In this case, additional steam expansion happens in the very last stages of the IP turbine while the LP turbine swallowing capacity is left unchanged. The supply pressure to the reboiler is not controlled by a valve but rather by the amount of steam extracted at the IP outlet. The crossover pressure is directly related to the mass flow entering the LP turbine and approximated in this analysis by the Stodola ellipse law (Stodola, 1927; see Appendix B). At intermediate capture levels the pressure floats between the 90% capture and no capture values and the back pressure turbine in the reboiler line is throttled. Without capture the steam cycle returns to an operating regime similar to the conditions before retrofit. The concept is somewhat similar to the floating IP outlet pressure system examined for capture-ready steam turbines in Chapter 3, with the addition of a back pressure turbine expanding the steam extracted from the new IP/LP crossover pressure to the reboiler pressure.

The change of pressure ratio across the IP turbine changes the enthalpy drop per stage, increases the steam inlet velocity relative to the blade, modifies the velocity triangle in the rotor and therefore reduces the isentropic efficiency of the IP stages. Bending moments and other mechanical stress on the blades and the end thrust on the IP turbine are all also increased.

Figure 4-6 shows a comparison of the electricity output penalty for base-load operation between the two options above and a retrofit using a throttle valve to reduce the flow through the LP turbine, as in (Ciferno et al., 2007), for a range of initial (before capture) IP turbine outlet pressures, and both with and without heat recovery from the capture and compression units.

With a valve at the LP turbine inlet and the addition of a back-pressure turbine in the extraction line the electricity output penalty (EOP) accounts for approximately 310-315 kWh/tCO_2, and is higher for elevated crossover pressures. This indicates that higher throttling losses occur with elevated crossover pressures, although the effect is relatively small compared to the absolute value of the EOP. They account for a increase of 33-38 kWh/tCO_2 compared to the option with two back-pressure turbines, which has a constant EOP of approximately 277 kWh/tCO_2 across the range of IP turbine outlet pressures. Finally the floating pressure system with a back pressure turbine provides a constant EOP of the order of 280-285 kWh/tCO_2 for IP/LP crossover pressures above 7 bar. The difference with the retrofit with two back-pressure turbines is principally due to modifications of the HP feed water heating system. As the outlet pressure of the IP turbine drops the pressure of the deaerator tapping point is reduced too. The deaerator then has to be fed from a higher pressure tapping point, as pointed out in Figure 4-5, which leads to a less efficient operation of the HP feed water heating system. For IP/LP crossover pressures below 7 bar the IP outlet pressure drops down to the reboiler supply pressure before the required amount of steam is extracted and hence some amount of throttling at the LP turbine inlet has to occur to maintain the reboiler steam pressure. The performance is then obviously intermediate between that of the un-throttled and the throttled systems.

4.4 Site-specific parameters

Selected sites may be suitable for an effective steam turbine retrofit depending on parameters such as space, access and scope for foundations in the turbine hall or other locations (e.g. along the steam line to the reboiler) to support the additional pieces of equipment. Different site-specific parameters may, however, not be critical 'showstoppers', but would rather affect the technical and/or economic aspects of retrofit projects. Some of them are discussed below.

4.4.1 Sensitivity to reboiler heat transfer and steam connecting pipe pressure drop

On the steam side of the reboiler condensing steam transfers the energy for solvent regeneration. The latent heat available is a function of the steam temperature and thus of the solvent temperature once the temperature difference across the heat transfer surface of the reboiler has been taken into account. Any marginal reduction in the temperature difference across the reboiler therefore reduces the required pressure for the extracted steam to achieve a given solvent temperature, as illustrated in Figure 4-7 (a). Any marginal reduction in the steam extraction pressure results in an increase of the power plant output and in a reduction of the electricity output penalty. Similarly, a reduction in the pressure losses of the pipe taking steam from the steam cycle to the solvent reboiler reduces the EOP. The effect of increasing the steam extraction pressure is shown in Figure 4-7 (b) for the steam cycle used in this example. For the pressure drop used in the connecting pipe of this example - 0.5 bar - the EOP is increased by 9 kWh/tCO_2, compared to a hypothetical case with no pressure drop. This suggests there is a case for a cost-benefit analysis of the implementation of an effective heat supply for the reboiler and a minimisation of the pressure losses across the pipe connecting the IP/LP crossover to the solvent reboiler. In the case of retrofit projects, where it may be difficult to locate the whole capture plant close to the steam turbine, the possibility of locating just the solvent stripper close to the turbine island could also be considered. Additional pumping power to circulate the solvent between the absorber and the stripper, and the cost of additional solvent inventory would have to be balanced against the extra power output (and solvent storage) obtained.

4.4.2 Sensitivity to fuel composition

The energy required for post-combustion capture is directly proportional to the amount of CO_2 captured, when expressed in lost electrical output per tonne of CO_2 captured, and is independent of the base plant efficiency. When considering a possible retrofit project, the amount of CO_2 that must be captured to achieve a standard emission level (in kg CO_2 per MWh electrical output) obviously then depends on the plant efficiency, but it is an equally good use of energy to capture the emissions of a subcritical and a supercritical plant. In contrast, coal composition has a direct effect on the total amount of CO_2 generated in the flue gas per unit of energy transmitted to the power cycle, and thus on the electricity output penalty of CO_2 capture. The ratio between the fuel heating value and the carbon content and the moisture content notably matter.

Dulong's formula is one of the best known, and the most extensively used, method to predict a coal calorific capacity as a function of its composition (Lowry, 1963).

$$\mathrm{GCV} = 14554 * \mathrm{C} + 62028 * \left(\mathrm{H} - \frac{\mathrm{O}}{8}\right) + 4050 * \mathrm{S} \tag{27}$$

Where

GCV	BTU/lb	Gross calorific value of the fuel
C	%	Fuel carbon content on a dry matter free mass basis (ultimate analysis)
H	%	Hydrogen carbon content on a dry matter free mass basis (ultimate analysis)
O	%	Oxygen carbon content on a dry matter free mass basis (ultimate analysis)
S	%	Sulphur carbon content on a dry matter free mass basis (ultimate analysis)

In this formula, the oxygen of the coal is assumed to be associated with hydrogen in the proper ratio to form water, the excess hydrogen being available for combustion together with the carbon and the sulphur.

Based on lower heating value – i.e. with water in the combustion products in a gaseous state - a fuel's specific CO_2 emissions (i.e. $kgCO_2/MWh$) can be expressed as,

$$E = \frac{C * (1 - H2O - ash) * {}^{M_{CO2}}/_{M_C}}{(GCV * {}^{2.326}/_{1000} - H * {}^{M_{H2O}}/_{M_H} * \Delta h_{lat}) * (1 - H2O - ashh) - H2O * \Delta h_{lat}} \quad (28)$$

Where

E	kg CO_2/MWh	Fuel specific emissions on a LHV basis
H_2O	%	Water content on mass basis (proximate analysis)
ash	%	Ash content (proximate analysis)
M_{CO2}	kg/mol	Molar mass of carbon dioxide, 44.01
M_C	kg/mol	Molar mass of carbon, 12.01
M_{H2O}	kg/mol	Molar mass of water, 18.016
M_H	kg/mol	Molar mass of hydrogen, 2.016
Δh_{lat}	MW_{th}/kg	Latent heat of vaporisation of water, 2.442

Based on the UK Seyler Coal Chart in Figure 4-8 (Lowry, 1963), from which information about typical coal composition are extracted, a sensitivity analysis of the specific emissions of a range of different coals is shown in Figure 4-9 and Figure 4-10 for three moisture contents, of respectively 0%, 25% and 50% on a mineral matter free basis, assuming that

- carbon content varies from 70 to 85%,
- hydrogen content is constant at 5% mass basis over this carbon range
- sulphur and nitrogen contents are neglected
- the oxygen content is then found by difference

Since boiler efficiency has only a marginal effect on the efficiency penalty of post-combustion capture, and since the purpose here is to compare existing power plants suitable for a retrofit, it can be assumed that the combustion of each type of coal represented here occurs at the best combustion and heat transfer conditions possible.

Figure 4-9 and Figure 4-10 show the effect of moisture on fuel specific emissions is not linear; the higher the carbon content, the weaker the effect of moisture. An increase of 2.5-3.5% in specific emissions is observed at 25% moisture over the carbon content considered compared to the hypothetical dry coal with 85% carbon and no moisture. At 50% moisture carbon content has a stronger effect. Specific fuel emissions increases from an additional 8% at 85% carbon content, compared to the range of base coal with no moisture, to 11% at 75% carbon content. As far as ash is concerned, specific emissions increases marginally with the ash content; a change of the order to 0.4-0.6% maximum is observed when the ash content varies from 0% to 30% over the range of carbon content and 10% moisture, as shown in Figure 4-11. It should be noted that the ash content is not reported here in a standard manner and that the ash content changes the ratio between the moisture and the dry ash free coal. Nonetheless, this does not affect the validity of the results showing that the influence of the ash content is negligible.

Figure 4-12 illustrates the efficiency penalty of post-combustion capture - expressed in percentage point of LHV power plant efficiency, and shows that carbon and moisture content can drastically change the efficiency of post-combustion capture. The reference case is a coal containing 85% carbon, no moisture and no ash in a plant with an electricity output penalty of 300 kWh/tCO_2 plant for capture and compression. The efficiency penalty, expressed in percentage point LHV, of post-combustion capture increases by 0.8 to 1.1 percentage point, depending on the moisture content, when the carbon content decreases from 85% to 70. It increases by another 0.5 to 0.8% percentage point when the moisture content changes from 25% to 50%. Future improvements in post-combustion capture are, however, likely to reduce the dependence of the efficiency penalty on the coal composition.

The analysis shows that the composition of the coal used, and the boiler design, is an important parameter when comparing two potential retrofit sites, or when selecting between different coals for the same plant. The type of coal burnt has a strong effect on the overall efficiency penalty of CCS.

4.4.3 IP turbine considerations for floating pressure systems

In the floating IP outlet pressure system, shown in Figure 4-5, the changes for the IP turbine are:

- an increase of the end thrust for each expansion cylinder due to the change of pressure ratio across the turbine, and
- an increase of the mechanical stress on the blades.

Design strategies to mitigate the consequences of these changes are discussed below.

Changed IP turbine end thrust: For single flow IP turbines, either a stand-alone cylinder design or a combined HP-IP cylinder design, modifications to the balancing pistons could be necessary to adapt to the new operating conditions.

In contrast, the end thrust on each side of double-flow IP cylinders should balance out and modifications of the balancing pistons should not be necessary.

Mechanical strength of the IP blades

The increase in the mechanical stress on the blades of the IP turbine of the present retrofit configuration is illustrated in Figure 4-13. For this illustrative analysis the turbine is composed of 8 impulse stages made of hypothetical turbine blades, which can sustain any levels of mechanical stress. (See Appendix B for more details). The changes in isentropic efficiency and stage loading, i.e. the chages in mechanical stress, are plotted for each stage following the turbine expansion. For this configuration the IP exhaust pressure is initially set to 11.1 bar and drops to 5.5 bar at 90% capture. The overall effect on the turbine efficiency is of the order of a 1.9-2 percentage point drop in cylinder isentropic efficiency, mostly due to a drop in isentropic efficiency resulting from a modification of the steam velocity triangle occurring in the last few stages. The analysis also suggests that floating pressure systems are likely to be constrained by the mechanical stresses on the blades of the very last stage of the IP turbine. Strategies to increase the bending modulus of these blades will thus directly enhance the benefits of floating pressure systems if throttling losses would otherwise be incurred. Possible strategies for specific blade design are discussed below:

- Since the bending stress on the blade is limited by the high cycle fatigue strength of the material used, which in turn is proportional to the tensile strength for common turbine materials, upgrading the alloy used in IP blades is an obvious option.
- The induced stresses could also be reduced, within the constraints of the casing and the geometry of the stator of the IP turbine, by reblading with thicker blades capable of withstanding a higher bending load but, because of the thicker aerofoil cross-section, with a small penalty in efficiency.

Reduction of the output penalty of capture achieved by increasing the mechanical strength of the last blades of the IP turbine are shown in Figure 4-14, contrasted against a case where an upper limit on the mechanical strength has been applied to a floating pressure system with a crossover pressure of 11.1 bar without capture. In this analysis, a constant amount of CO_2 is captured whilst a limit is set on the relative increase of mechanical stress that can be sustained by the last blade of the IP turbine. When capture is fitted, steam extraction gradually increases while IP turbine exhaust pressure falls until the limit on the blade is attained. If more steam needs to be extracted, the extraction is then controlled by throttling the LP turbine inlet until the required capture level is obtained. (The modelling follows the approach presented in Appendix B).

Without increasing the mechanical strength of the final IP stage the amount of throttling in the valve before the LP turbine is of the order of 5.4 bar. A 50% increase in mechanical strength reduces the pressure drop across the valve to 2.4 bar and reduces the electricity output penalty by 15 kWh/ tCO_2, and further by 26 kWh/ tCO_2 for a 100% increase in the allowable bending stress of the last IP turbine blades.

4.4.4 Boiler feed pump turbine

Many existing steam cycles are equipped with a turbine-driven main boiler feed pump taking steam from the IP/LP crossover pipe, which requires some consideration when capture is retrofitted. In particular, a retrofit with a floating IP turbine exhaust pressure reduces the inlet pressure and thus the power output of that turbine, requiring it to be supplemented or replaced by an electric drive boiler feed pump. It is important that the boiler feed pump turbine is not removed, however, to allow the plant to return to maximum generator output when the solvent reboiler is by-passed.

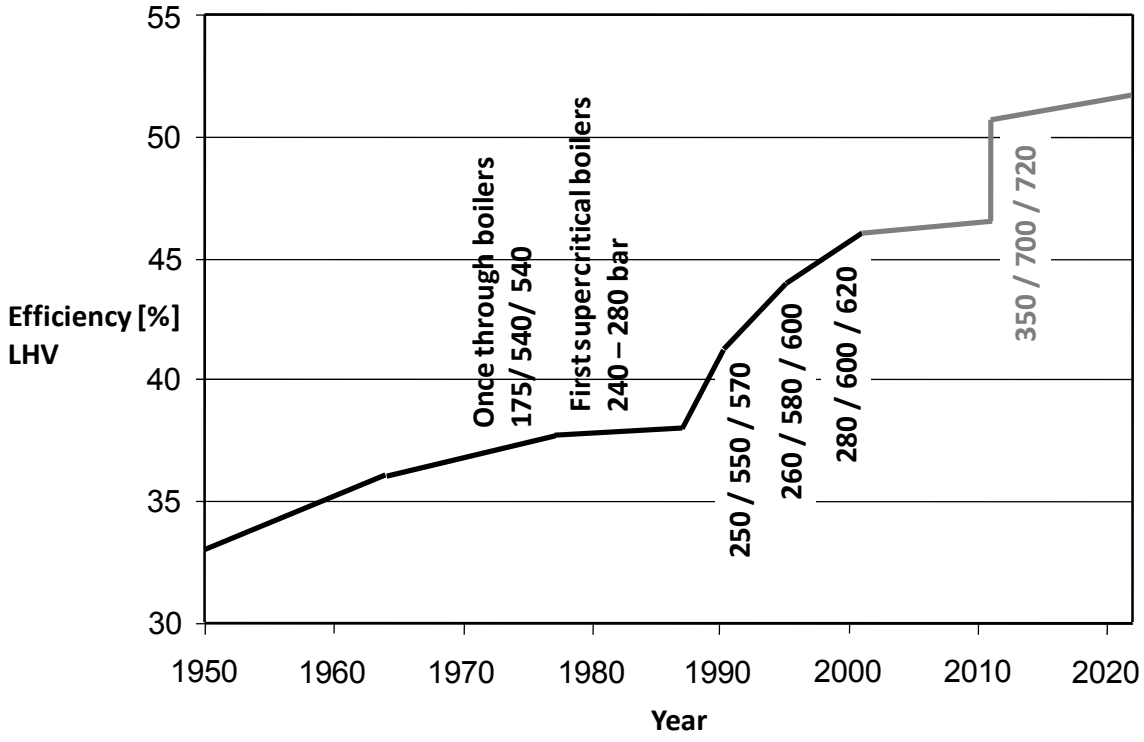


Figure 4-1: Development in EU steam plant efficiency – Steam conditions are shown as HP inlet pressure (bar)/temperature (°C)/reheat temperature (°C) – Adapted from (Epple, 2004)

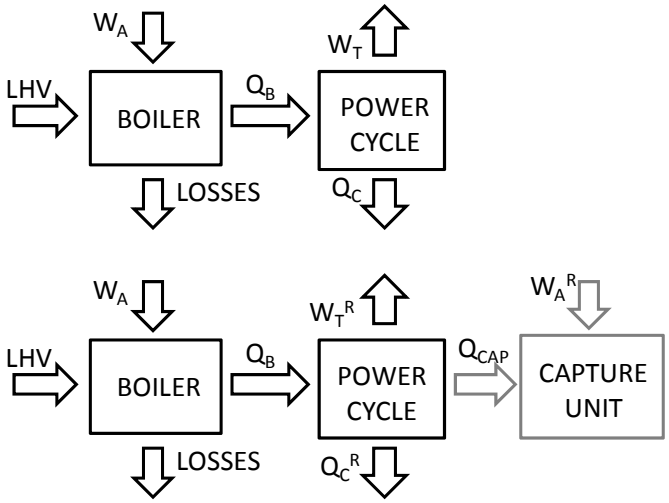


Figure 4-2: 1st law analysis of a power cycle without (upper) and with (lower) capture retrofitted

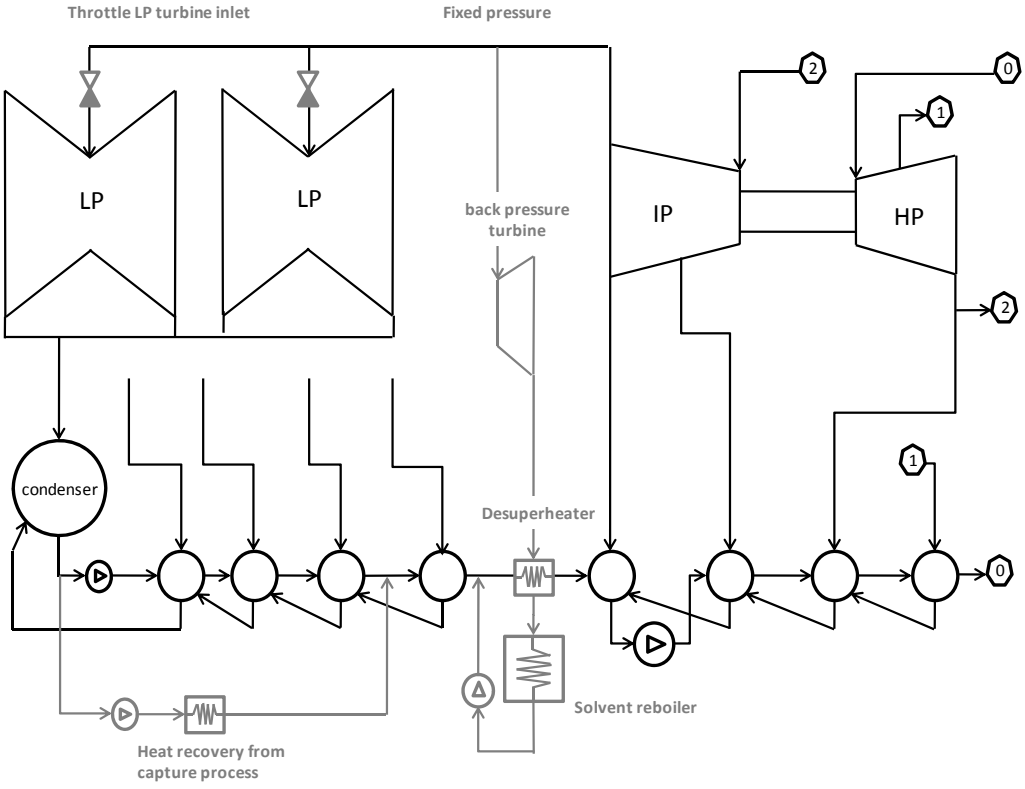


Figure 4-3: Steam turbine retrofit with a fixed crossover pressure and a single back-pressure turbine

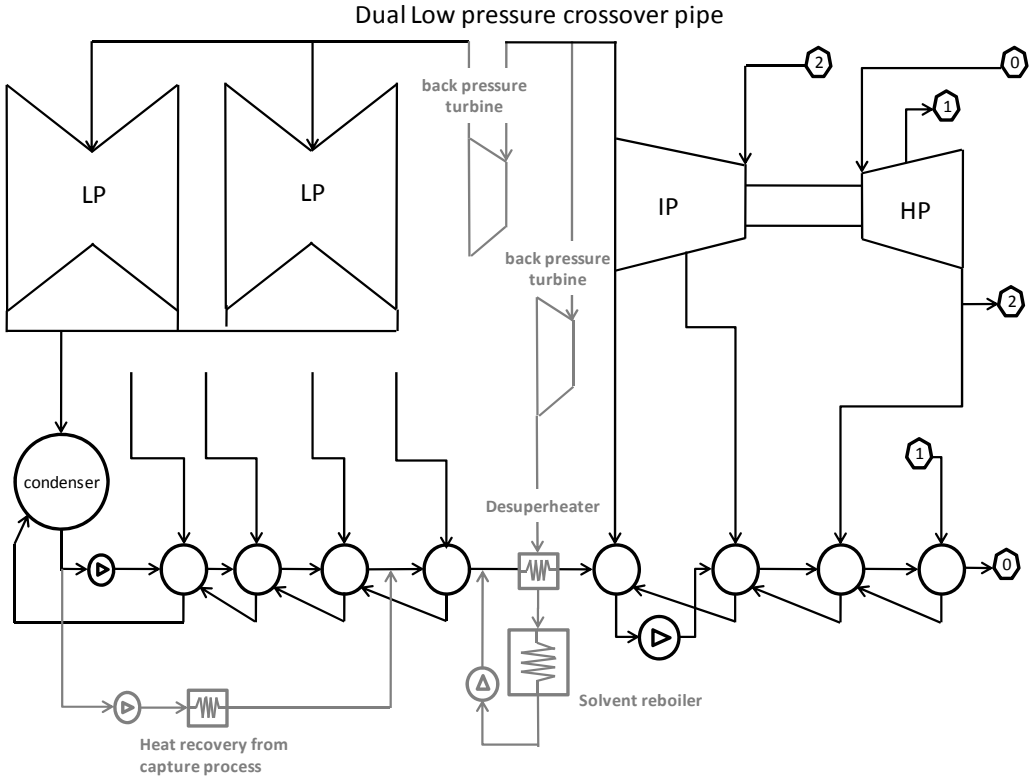


Figure 4-4: Steam turbine retrofit with a fixed intermediate pressure turbine outlet and two let-down back-pressure turbines

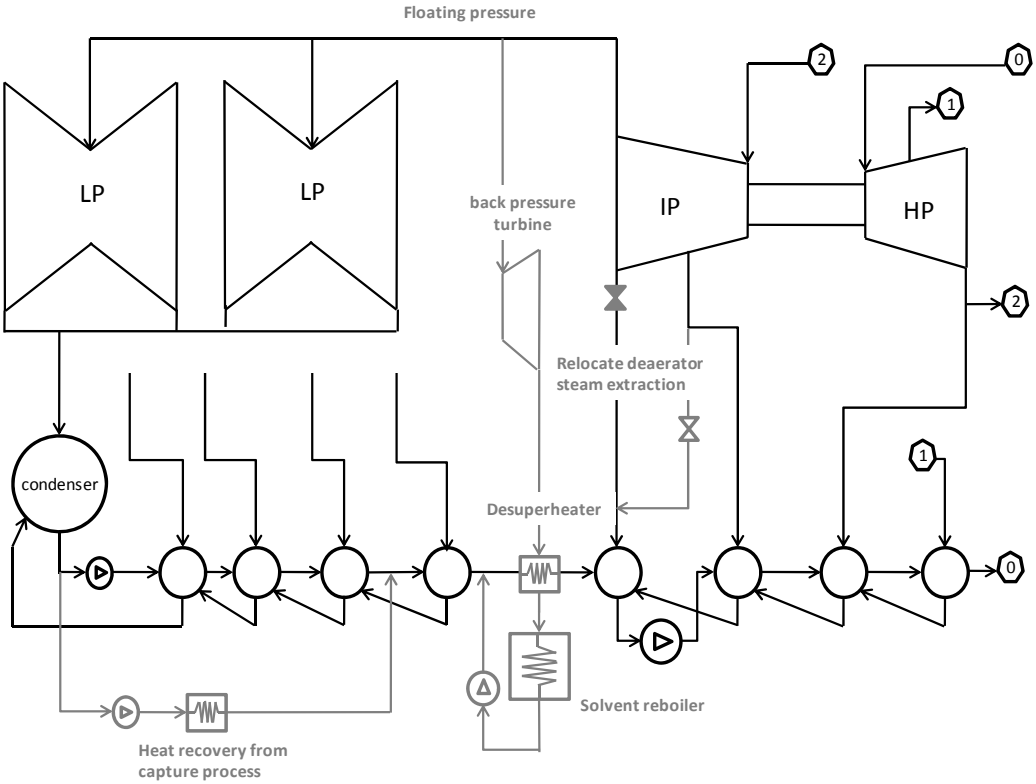


Figure 4-5: Steam turbine retrofit with a floating intermediate pressure turbine outlet and a let-down back pressure turbine

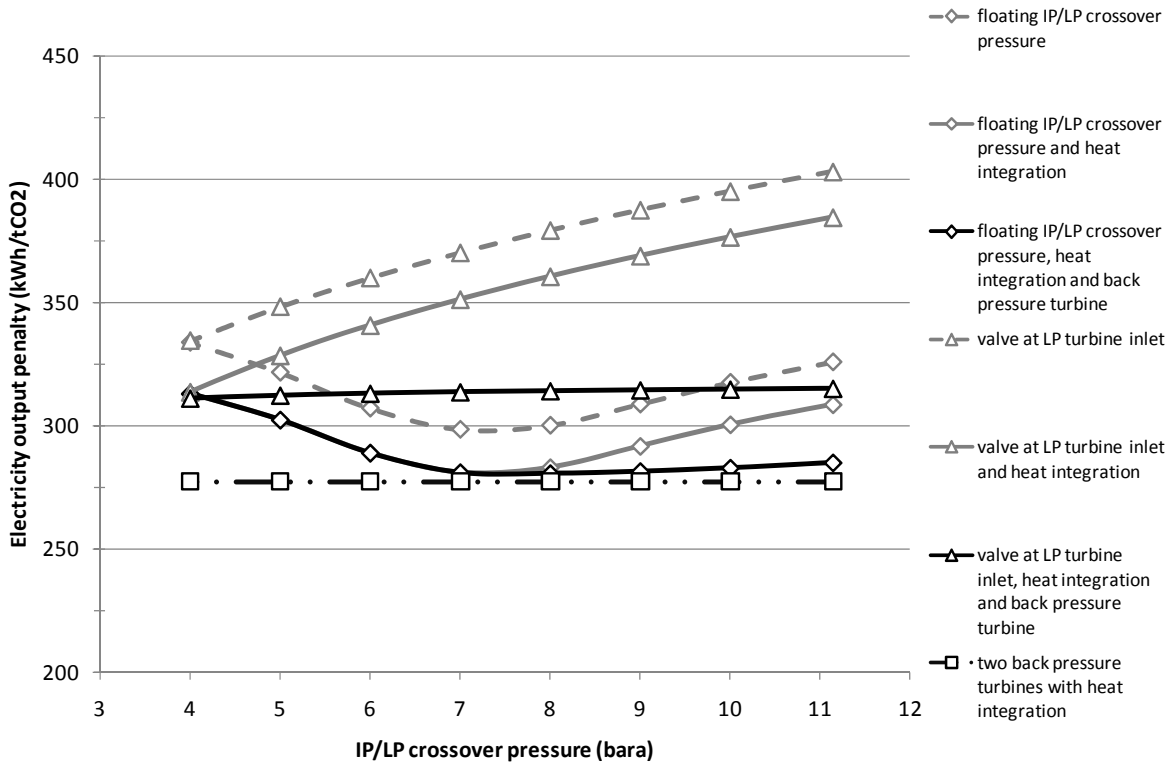


Figure 4-6: Comparison of the electricity output penalty of steam turbine retrofit options for a range of steam cycle configurations

90% capture rate – 125 kWh/tCO_2 electricity output penalty for ancillary and compression power – solvent heat of regeneration of 3.2 GJ/tCO_2 – 94% boiler thermal efficiency

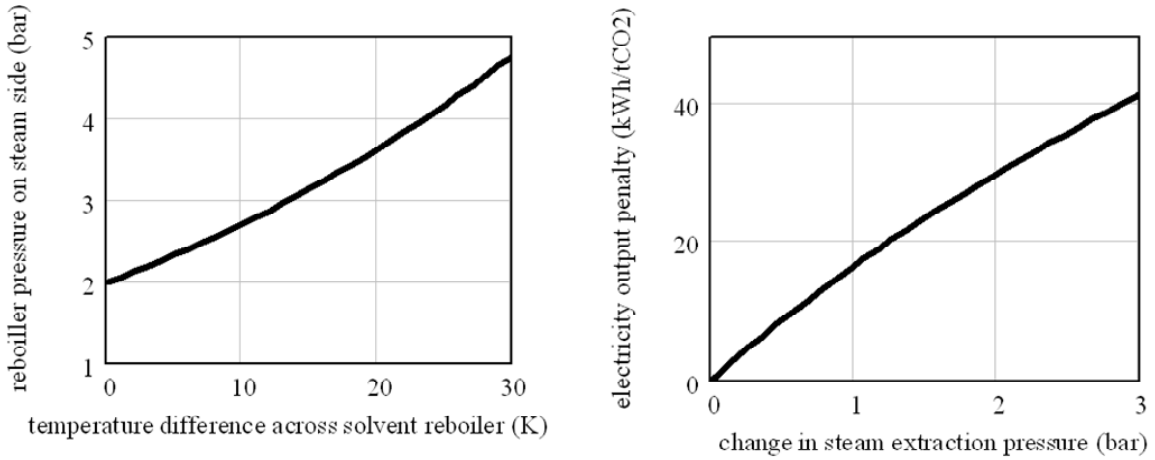


Figure 4-7: (a) - LHS - Effect of temperature difference across solvent reboiler on steam side pressure - (b) – RHS - Effect of steam extraction pressure on electricity output penalty

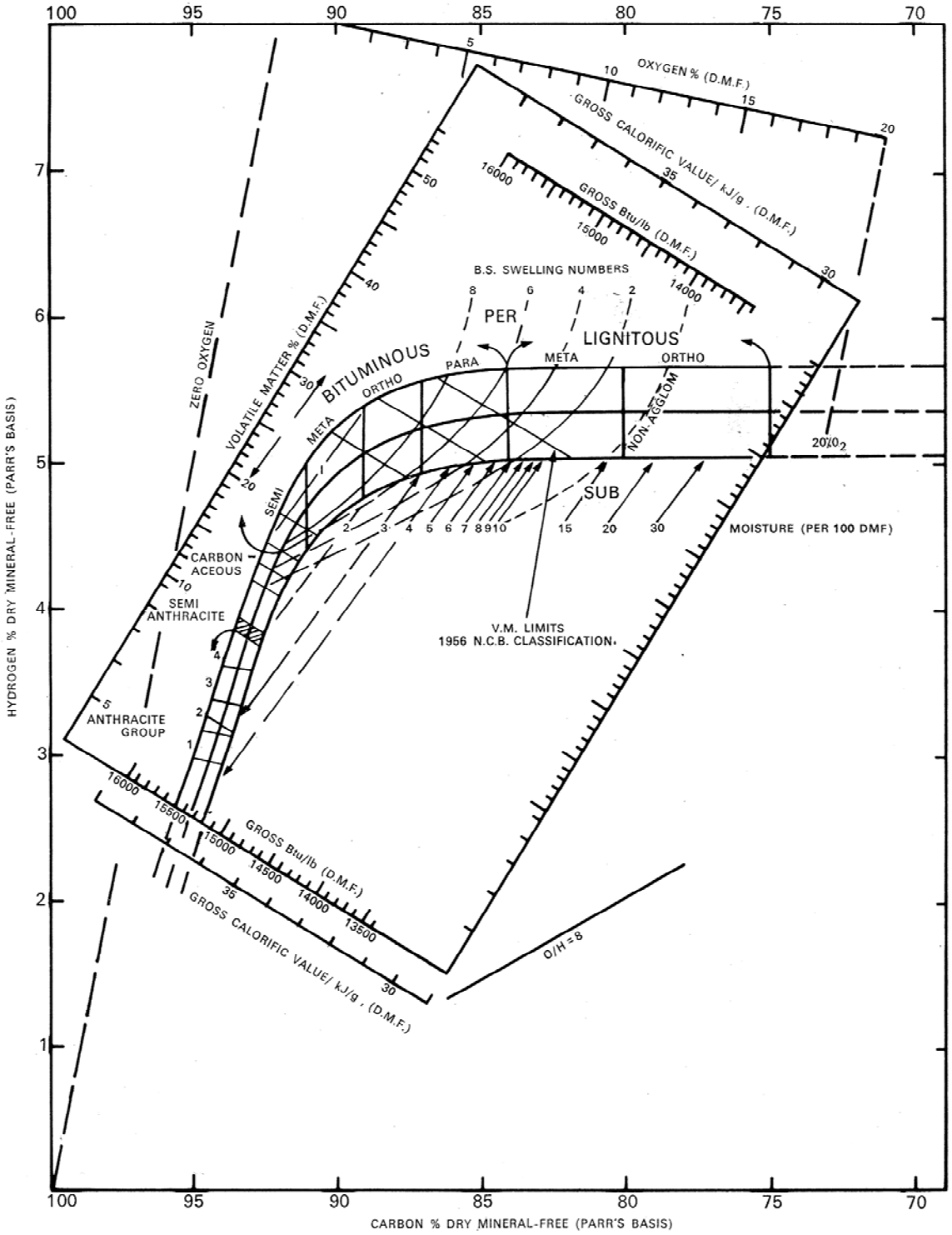


Figure 4-8: Seyler's coal chart

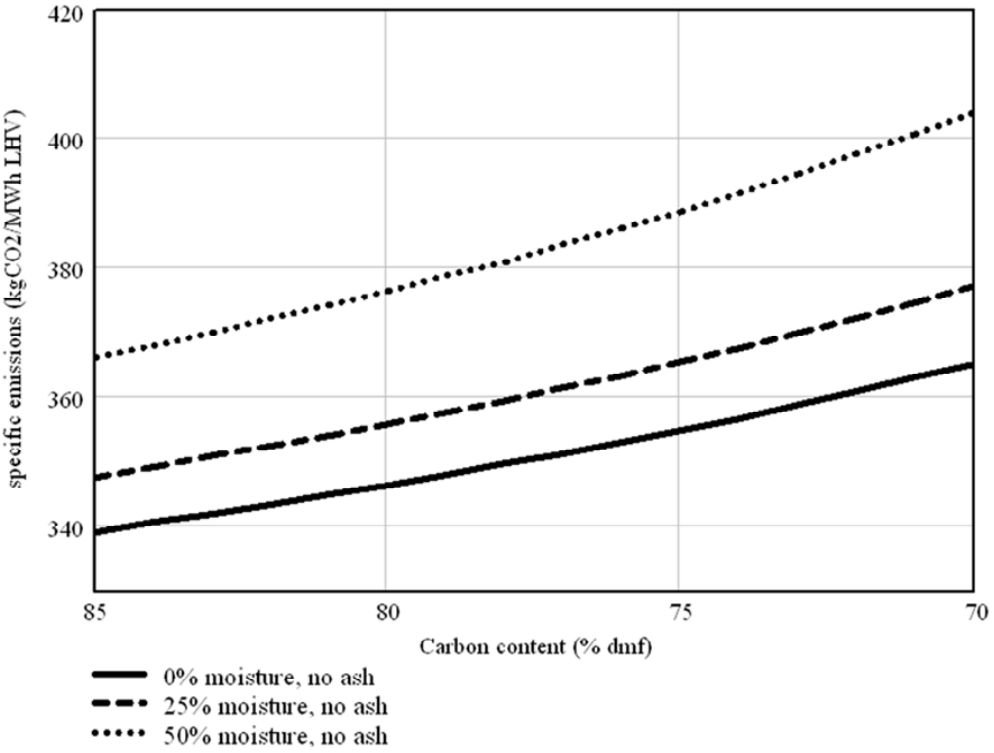


Figure 4-9: Specific CO_2 emissions of coal as a function of carbon and moisture content

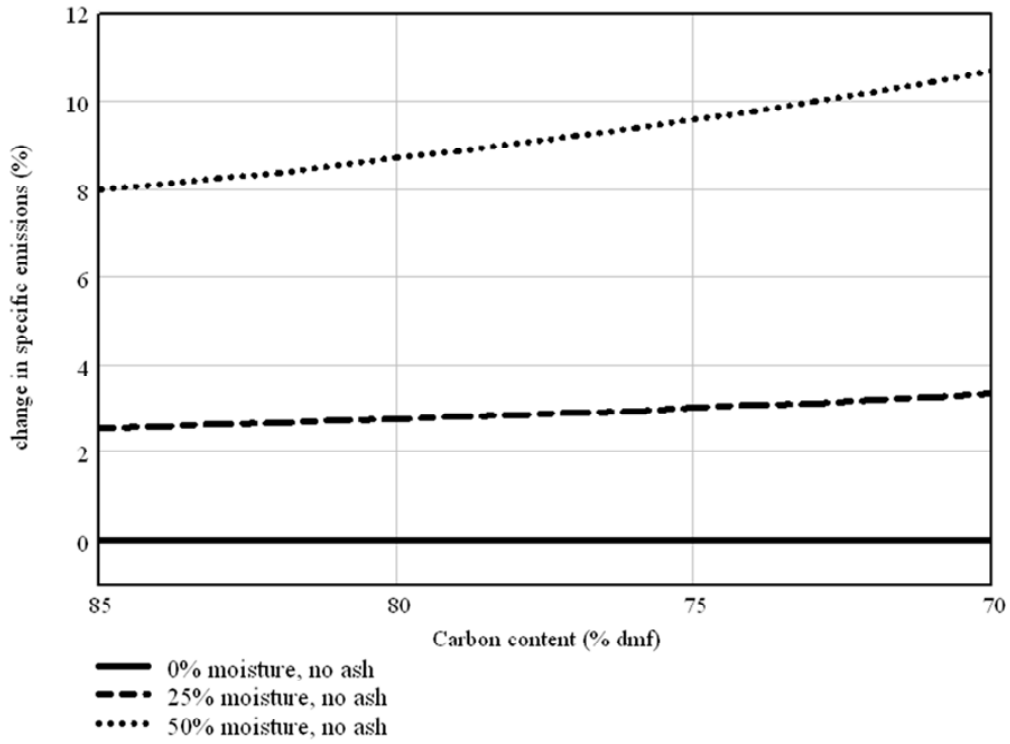


Figure 4-10: Variation in the specific emissions of coal with moisture content over a range of carbon contents

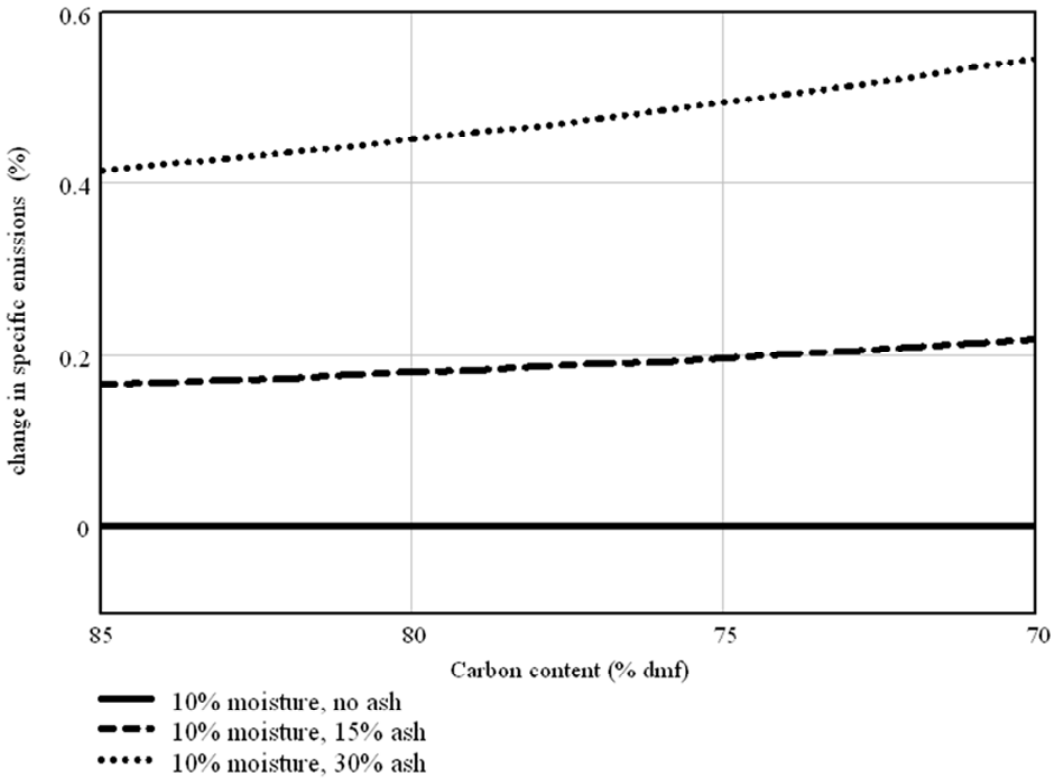


Figure 4-11: Variations of the specific emissions of coal with ash content

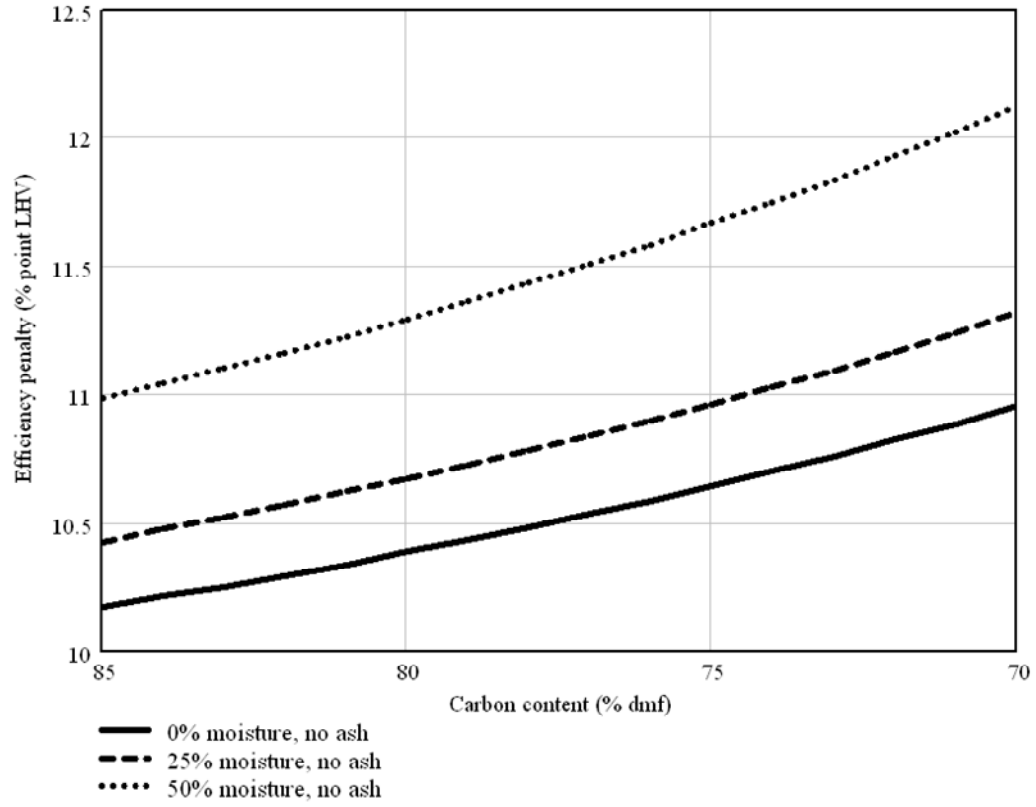


Figure 4-12: Variation in the efficiency penalty of post-combustion capture with coal type
Base case: Coal with 85% C, 0% moisture content and no ash. Electricity output penalty for capture and compression of 300 kWh/tCO_2

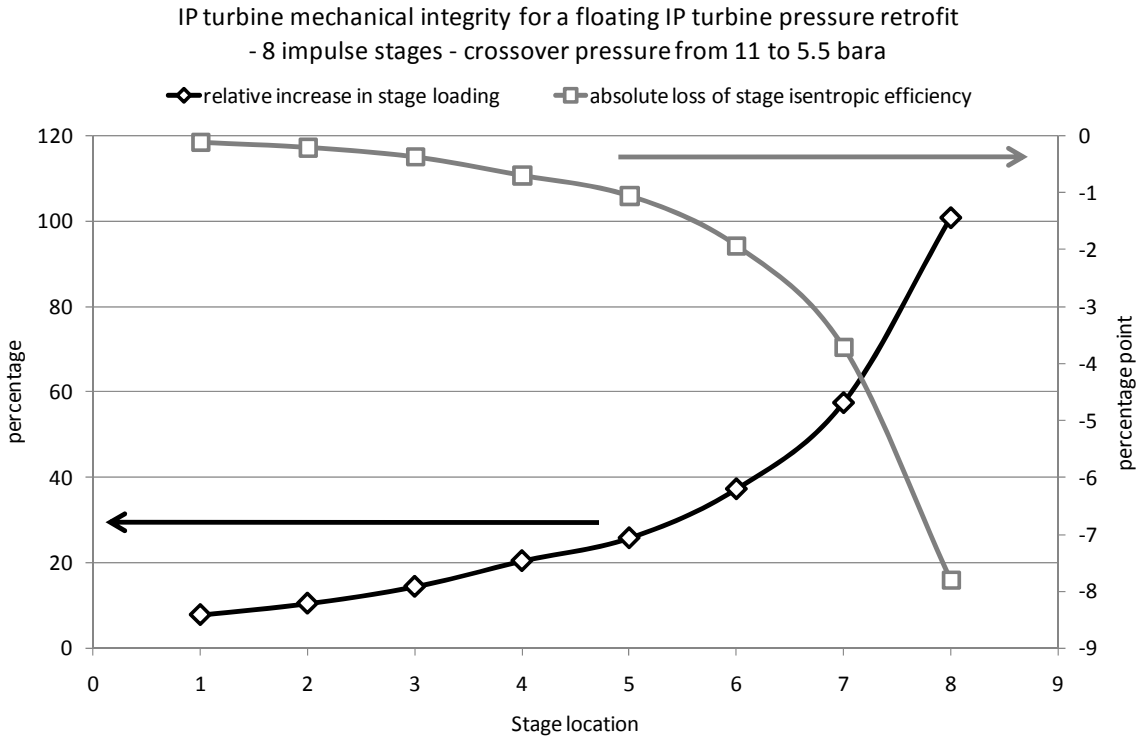


Figure 4-13: Change in isentropic efficiency and mechanical loading on each blade of an impulse IP turbine for a floating pressure with CO_2 capture

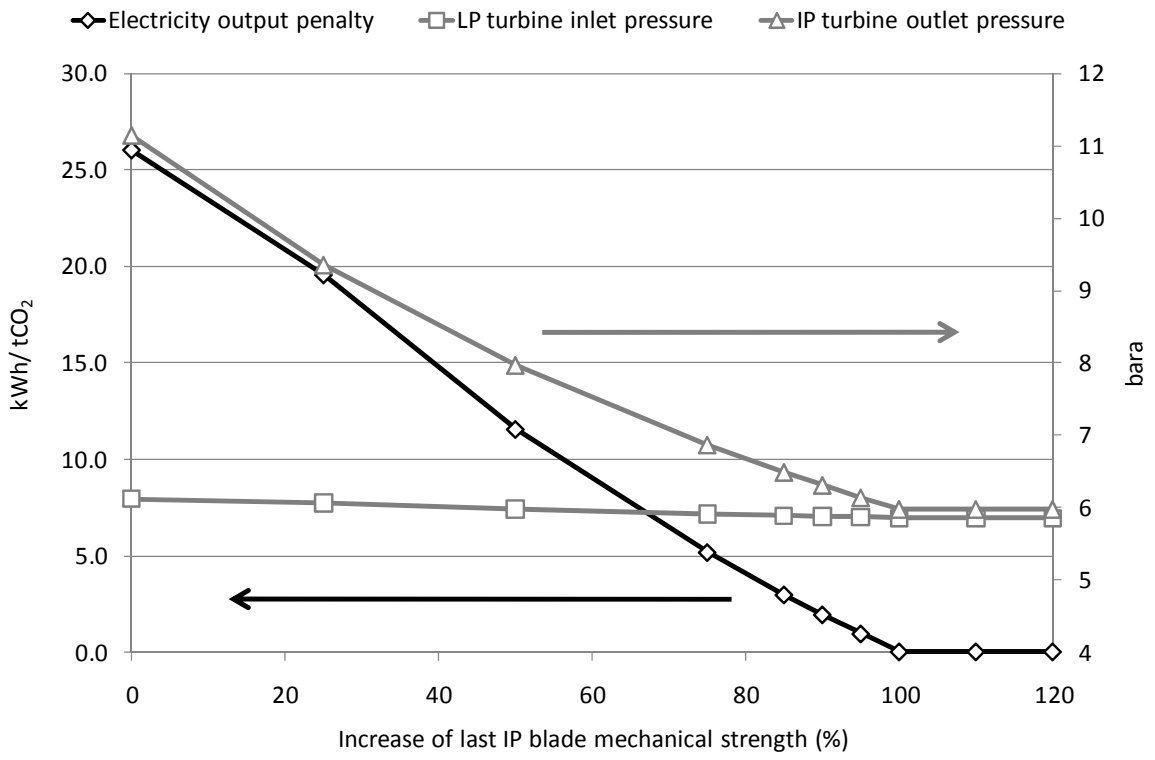


Figure 4-14: Reduction in electricity output penalty of a floating IP outlet pressure system with a reinforcement of the IP turbine last stage blades

Table 4-1: Comparison of the electricity output penalty of industry studies on retrofits

Source	IEA GHG PH4/33 - MHI case	IEA GHG PH4/33 – Fluor case	DTI 407 – Fluor	Ciferno et al. (2007) MEA case	Ciferno et al. (2007) future solvent case
Solvent heat of regeneration (GJ_{th}/tCO_2)	3.2	3.24	3.24	3.6	2.8
Reboiler steam supply pressure (bara)	3.24	3.24	3.24	4.5	4.5
Electricity output penalty (kWh/tCO_2)	257	281.5	266.5	349.6	308.6
Ancillary power electricity output penalty (kWh/tCO_2)	122.4	128.5	109.6	119.7	119.7
Steam cycle electricity output penalty (kWh/tCO_2)	134.6	153	156.9	229.9	189.0

5 Steam turbine configurations for upgradeable post-combustion capture applications

5.1 Background

Amine capture systems proposed for post-combustion capture have historically been developed in the oil and gas industry. These units are financed and operated under a different business model to that expected for typical fossil fuel power generation with CCS. They are typically operated for acid gas cleanup for natural gas, at pressures above atmospheric in an oxygen deprived environment, where higher levels of CO_2 removal are favoured over low energy consumption, and the CO_2 is subsequently vented.

The emphasis in power generation is somewhat different. The flue gas treated has a much higher oxygen content and a lower partial pressure of CO_2. In addition, low energy consumption for solvent regeneration is a key factor, but also needs to be traded off against ancillary power consumption for capture and compression to the delivery pressure for CO_2 transport in determining the cost of electricity generation. Improvement in post-combustion capture is the focus of an intensive research effort at academic and industry level. Reduction of the energy requirement for solvent regeneration is notably an area, which has received, and currently receives much attention (IEAGHG, 2005b, 2006b, 2007b, 2008, 2009). This effort splits between incremental improvements in currently proposed solvents and the development of different chemical absorbents for alternative solvent compositions. For example better corrosion inhibitors allow higher solvent concentration and reduce the specific heat component of solvent regeneration (Carette et al., 2009; Sexton, 2008). Alternative solvents, such as CO_2-binding ionic liquids or amine acid-salts, are also being developed and will be operated in similar ways to current flue gas wet scrubbing amine systems (See for example Heldebrant et al., 2009; Van Holt et al., 2009; Marsh et al., 2009; Wappel et al., 2010). Finally new technologies with a radically different process for treating the flue gas are also under investigation (See Figueroa et al., 2008) for a review of the US DOE funded project in that area).

There are a considerable number of potential scenarios, which could be investigated when considering the development of carbon capture technologies and the type of plants fitted. In this chapter, the approach is limited to post-combustion capture systems using flue gas wet scrubbing with an aqueous solvent, although some of the conclusions can be extrapolated to other technologies. The type of plants chosen is limited to the first generation of power plants, for which the option of fitting post-combustion capture has been envisaged. In a broad sense this includes CO_2 capture-ready (CCR) units designed on the basis of current state-of-the-art solvents, and demonstration units, built as part of the first or second tranches of large-scale demonstration projects, which in some cases may only be capturing a fraction of the total emissions of the plant, say of the order of 40-50%. On current expectations these plants might be built from now until roughly 2025.

Once CCR units are constructed and commissioned they are likely to have to compete with units built later, as capture-ready and then retrofitted, or with CCS from the outset. These plants will benefit from lessons learned and improvements of the first tranches of demonstration units, and are thus likely to achieve a lower marginal cost of generation using a less energy intensive solvent. Likewise first and second tranche demonstration units, which may be attached to a power generation asset to be paid back over 25 years or more, are also likely to have eventually to compete against units built later with the latest solvents available at the time. In order to reduce the overall long-term cost of implementing CCS, it is therefore important that the first generation of CCS plants is then not locked into either the level of performance that is assumed in current conceptual capture retrofit studies when they are designed for capture-ready plants, or the actual level of capture and performance during the first years of operation for first of a kind large scale units. Instead these plants should be designed with the ability to take advantage of improvements in the technology and to use more advanced solvents. This last requirement could be particularly relevant for CCR natural gas combined cycle plants since current proposals, e.g. the Queen's Speech on the 2010 Energy Bill (Queen's Speech, 2009), suggest that policy developments in the UK - and possibly in most jurisdictions - are likely to encourage the deployment of CCS on coal-based generation first, but that CCS on gas plants may be required at large scale by 2030, as proposed by the Committee on Climate Change (Committee on Climate Change, 2009).

Under an aggressive technology development and deployment programme for CCS, it is possible that the steam turbines of capture-ready fossil-fired units may be required to operate with steam extraction rates that vary from current values to zero in order to accommodate future capture

systems, the latter if CCS develops through a different technology pathway than thermally cycled solvents, e.g. if gas separation membranes and pressure swing absorption close to atmospheric pressure level became available[17].

5.2 Possible future solvent developments

5.2.1 Review of the existing methodology for assessing solvents

The intensive research effort currently undertaken to reduce the specific thermal energy for solvent regeneration shows some limitations in the way performance is evaluated. Consideration of integration between the compression process and the power cycle is often either ignored or assessed in a non-satisfactory way when comparing solvents. This section comprises a sensitivity analysis of solvent parameters with a direct impact on the overall electricity output penalty of the capture system. It aims to provide an insight into how future solvents may develop in the future

When assessing the energetic performance of a given solvent it is important to take into account several factors, which contribute to the overall electricity output penalty. The following factors need to be assessed simultaneously and on a consistent basis:

- Thermal energy of regeneration of the solvent,
- Loss of output of the turbines due to steam withdrawal for solvent regeneration,
- Recovery of low-grade heat available in the capture plant to replace regenerative feed water heating, and
- Ancillary power requirement for pumps and CO_2 compressors.

The existing literature on the subject either falls short of one or several of the former factors, or lacks a rigorous thermodynamic assessment of their impact on power generation. A majority of studies only limit their analysis to solvent thermal energy of regeneration.

Abu Zahra et al. (2007) undertake a parametric study to determine the minimal energy of regeneration of 30%wt MEA. It considered neither the loss of output of the power cycle as a function of the reboiler temperature, and thus the steam extraction pressure, nor the potential in the energy required for CO_2 compression by increasing the reboiler temperature and therefore the first compressor suction pressure. Similarly Dave et al. (2009) compares the performance of 30%wt MEA

[17] Zero extraction rates will also be required for fault conditions and possibly for intermittent output 'boosts' when capture is stopped or solvent storage is used, as discussed in Chapter 6

and ammonia without accounting for the effect of temperature of regeneration on the compression system and on the power cycle.

In (Göttlicher, 2004) eight amine solvents and a potassium carbonate based solvent are compared. Compression is not included and all solvents are regenerated at the same temperature, notably the non-amine based potassium carbonate solvent. A first-order thermodynamic analysis was used to estimate the mechanical work equivalent of steam extracted for solvent regeneration, and thus to evaluate the loss of power output of the low pressure steam turbine. The relevance of the Equivalence Factor α proposed by Göttlicher suffers, however, from some imprecision.

$$\alpha = \frac{\mathrm{h}(\mathrm{p_Z}, \mathrm{T_Z}) - \mathrm{h}(\mathrm{p_{COND}}, \mathrm{x_{COND}}) + \eta_{\mathrm{el}} * (\mathrm{h'}(\mathrm{p_Z}) - \mathrm{h'}(\mathrm{p_{COND}}))}{\mathrm{m_Z} * \mathrm{h}(\mathrm{p_Z}, \mathrm{T_Z})} \quad (29)$$

Where

α	-	Equivalence Factor
h	kJ/kg	Enthalpy as a function of pressure and temperature
h'	kJ/kg	Enthalpy at saturation as a function of pressure
m_Z	kg/s	Mass flow of steam extracted
p_Z	bar	Pressure of steam extracted
T_Z	K	Temperature of steam extracted
p_{COND}	bar	Condenser pressure
x_{COND}	-	Low pressure turbine exit dryness fraction
η_{el}	-	Efficiency of the low pressure part of the steam cycle

First, the mechanical work equivalent of the low pressure turbine is calculated by the difference $h(p_Z, T_Z) - h(p_{COND}, x_{COND})$and should by multiplied by the turbine isentropic efficiency. Second, the efficiency of the low pressure part of the steam cycle with capture, which includes the LP turbine, the main condenser and the feed water heating system, is admittedly a function of T_Z, but also, as previously explained, a function of the solvent used through the amount of heat available for feed water heating.

Integration studies into a supercritical coal-fired power plant in (Aroonwillas and Veawab, 2007; Aroonwillas and Veawab 2009) compare amine blends of MEA-MDEA and MEA-AMP to 30%wt MEA, but do not include the compression system. The performance of the AMP-MEA blend is thus overestimated compared to MEA reference case since the reduced reboiler temperature of the blend – 103ºC – will increase compression energy requirements compared to the reference case eboiler temperature - 110ºC.

Oyenekan (2007) compares the performance of seven different solvents by evaluating the equivalent mechanical work to the total energy required for CO_2 stripping, as follow:

$$\mathrm{W_{eq}} = \mathrm{W_{pump}} + 0.75 * \mathrm{Q} * \frac{(\mathrm{T_{reb}} + 10) - 313}{\mathrm{T_{reb}} + 10} + \mathrm{W_{comp}} \qquad (30)$$

Where

$\mathrm{W_{eq}}$	W	Total equivalent mechanical work
W_{pump}	W	Pump work
Q	W	Energy required for stripping in reboiler
T_{reb}	K	Reboiler temperature
W_{comp}	W	Compression work

This simplistic approach does not account for feed water heating using low grade heat available in the absorption and compression process, and uses a simple Carnot efficiency multiplied by an approximate ‘Carnot factor’ of 0.75 to relate the energy for stripping to the loss of output of the steam cycle, which only provides a first order approximation of the ‘value’ of steam extracted for solvent regeneration. It can only be used to provide trends and no absolute value. Furthermore, the 0.75 factor is a function of the steam extraction temperature, and thus of the amount of superheat available in the steam before it enters the reboiler. Oyenekan’s approach was also subsequently used by Van Wagener in (Plaza et al., 2010; Freeman et al., 2010).

Oexmann et al. (2008) uses a similar method but undertakes a sensitivity analysis of what is the fudge factor in (Oyenekan, 2007) and expresses it as a function of pressure or as a function of steam saturation temperature., based on a separate power plant model. They obtain a good agreement of 0.5% for temperatures comprised between 131º and 155ºC but without considering the potential for heat integration.

Recently, Feron explored the potential for improvement of the energy performance of coal fired power plant with post-combustion capture, in (Feron, 2010). For different generations of chemical absorbents, Feron estimates thermal energy requirements for regeneration. His results are reproduced in Table 5-1 for clarity. G1 applies to chemical absorbent developed for acid gas treating, G2 to current state-of-the-art solvents, G3 and G4 to potential future solvents. He then uses a power equivalent factor (PeF) to relate the amount of steam needed for the reboiler duty to the energy output reduction, as illustrated in Table 5-2. Feron predicts that the PeF of future capture system can be reduced by 25% from 0.20 to 0.15 on the grounds that, in current systems 'a significant portion of the heat requirement of the liquid absorbent process is (…) still recoverable as it leaves the regenerator as steam and its heat of condensation can be used'; and that 'because of the large amounts (of low grade heat available) its re-use in the power station (for feed water heating) might be (currently) limited' compared to future systems (2009:p.7). The first part of his analysis is correct but the second is questionable when scrutinised.

Recently, Feron (2010) discussed the potential for improvement of the energy performance of coal fired power plant with post-combustion capture based on the assumption that future generations of chemical absorbents would have progressively lower thermal energy requirements for regeneration. The estimates are shown in Table 5-1: G1 applies to chemical absorbents developed for acid gas treating, G2 to current state-of-the-art solvents developed for power generation, G3 and G4 to potential future solvents (it is worth noting that if higher capture levels are required in the future then this might offset any such performance gain at current capture levels (i.e. ~90%)).

Feron used a power equivalent factor (PeF) to relate the amount of steam needed for the reboiler duty to the overall electricity output penalty for coal fired power plants, also shown in Table 5-2. This factor is defined as "the ratio of incremental power reduction to incremental heat output when extracting steam" by Bolland and Undrum (2003), with values shown in Figure 5-1 for steam extraction from the steam turbine of a combined cycle plant. Feron predicted that in future capture system α can be reduced by 25% of its current value, from 0.20 to 0.15, on the grounds that, in current systems '*a significant portion of the heat requirement of the liquid absorbent process is (…)*

still recoverable as it leaves the regenerator as steam and its heat of condensation can be used'; and that '*because of the large amounts (of low grade heat available) its re-use in the power station (for feed water heating) might be (currently) limited' compared to future systems*.

The first part of this analysis is correct but the second needs to be examined, since for post-combustion capture from coal plant the value of α will be dependent on the heat requirements of the solvent as well as the temperature at which the heat is required. This is because in coal plant steam cycles, unlike combined cycle steam cycles in the work of Bolland and Undrum (2003), relatively large amounts of steam are extracted for the turbine for condensate and feed water heating. With properly-integrated post-combustion capture systems some of this steam extraction can be replaced by recovered heat, but the effect of this is determined by the amount and quality of heat available for recovery in the steam cycle and also the scope for a given steam cycle to use recovered heat. For a given mass flow rate of captured CO_2, the amount and temperature of heat available in the reflux condenser (if fitted) and the compressor intercoolers is related to solvent properties through the compressor pressure ratio, the compression path used, and the temperature and moisture content of the CO_2 leaving the desorption stage. All of these factors, except the compression path, are dependent on the solvent properties. Moreover, there will be a tendency for improved solvents with lower heat requirements and/or lower compression work requirements to have less heat available for recovery through a reduction of the contribution to thermal energy requirement of steam stripping, as shown in Table 5-1.

Thermodynamic integration of the amine capture plant and the compression system with the power cycle of a new–build pulverised coal plants was carried out by Romeo et al. (2008a). Their study included a sensitivity analysis of solvent thermal energy of regeneration from 4.2 to 1.6 GJ/tCO_2, but was limited to a constant solvent regeneration temperature, and thus did not consider solvent thermal stability as an important parameter for thermodynamic integration nor, by inference, allow for variation in desorber pressure as an important factor in overall solvent system performance.

Finally, Ciferno et al. (2007) shows a case with a future solvent with a thermal energy of regeneration reduced from 3.6 to 2.8 GJ/tCO_2 using a rigorous integration study with the power cycle and the compression train. Their analysis is, however, limited to a case where the reboiler temperature does not change.

5.2.2 Thermodynamic integration for solvent assessment

Compression of the carbon dioxide is required for transport and safe geological storage and accounts for a significant part of the overall electricity output penalty. The compression process rejects heat at temperatures above the coldest heat sink of the power cycle i.e. the main condenser. To provide a consistent basis for comparison solvents need to be assessed by accounting for the effect of using the low grade heat available to replace boiler condensate feedwater heating.

In an ideal case the minimum energy requirement for compression equals the difference in enthalpy between the inlet and the outlet minus the difference in entropy between the inlet and the outlet multiplied by a reference. It can be calculated using the difference in Gibbs Energy between the suction and the discharge of the compression system. The Gibbs Energy is given by

$$\mathrm{G} = \frac{\mathrm{H} - \mathrm{T} * \mathrm{S}}{\mathrm{M}_{\mathrm{CO2}} * 3.6} \tag{31}$$

where

T	K	Temperature, 313K
G	kWh/tCO_2	Gibbs Energy. Calculated using ideal gas properties in Multiflash[18]. At outlet: 10606.4J/mol at 110 bar and 313K. At inlet: -24.7J/mol at 1 bar and 313K.
H	J/mol	Enthalpy
S	J/mol/K	Entropy
M_{CO2}	g/mol	Molar mass of CO_2:44.02 g/mol

[18] www.infochemuk.com

In the case of the isothermal compression of an ideal gas the inlet and outlet enthalpies are equal and the mechanical work –P*dV can be calculated from the first law of thermodynamics as

$$W = \frac{R * T * \ln\left({}^{P1}/_{P0}\right)}{M_{CO2} * 3.6} \quad (32)$$

where

W	kWh/tCO_2	Mechanical work
R	J/mol/K	Universal gas constant: 8.3145
P1	bar	Discharge pressure: 110
P0	bar	Suction pressure: 1
M_{CO2}	g/mol	Molar mass of CO_2: 44.02

Figure 5-2 shows the minimum energy requirement to compress carbon dioxide from 1 bar at 313K to 110 bar at the same temperature, based on the Gibbs Energy (Equation 31) and isothermal compression of an ideal gas (Equation 32). The overall energy requirement is of the order of 70 and 80kWh/tCO_2 for, respectively, the Gibbs Energy and the ideal gas assumption, compared to 90-110kWh/tCO_2 for 'real 'compression systems. To a first approximation using these relatively crude assumptions, it can be seen that approximately two thirds of the compression work is used to increase the CO_2 pressure to 20 bar. For 'real' compression systems it accounts potentially for half of the compression work, i.e. 15 to 20% of the total electricity output penalty. This illustrates well the fact that the suction pressure of the compression system is a critical parameter for an overall assessment of a specific post-combustion capture system. A more detailed compression model is discussed in the next section to pursue this analysis further.

Solvents with favourable vapour-liquid equilibrium (VLE) to deliver a higher partial pressure of CO_2 in the desorber can potentially significantly reduce the compression work, and higher loss of output in the power cycle could be justified to achieve favourable trade-offs. When assessing various solvents it is also important to consider the effect of thermal compression during the temperature swing

between the absorber and the desorber. Solvents capable of tolerating higher temperatures before thermal degradation allow operating the desorber/reboiler system at higher temperatures, increasing the partial pressure of both CO_2 and water, and thus the overall pressure. Again trade-offs with the loss of output of the turbine could be justified, if steam was extracted at a higher pressure for a more thermally stable solvent operating at higher desorber temperatures.

5.2.3 Relationship between solvent thermal stability and partial pressure of CO_2

Oyenekan and Rochelle (2006) points out the relationship between the temperature swing of the process and the enthalpy of absorption of the solvent. The rationales are explained in details in Oexmann and Kather (2008). Assuming that the mixture is ideal, the Van't Hoff equation relates the change in temperature of the solvent to the change in equilibrium constant, expressed here as pressure, given the standard enthalpy change for the process. It can be written as

$$\frac{\mathrm{d}\ln \mathrm{P_{CO2}}}{\mathrm{d}\frac{1}{\mathrm{T}}} = -\frac{\Delta \mathrm{Habs}}{\mathrm{R}} \tag{33}$$

Where

P_{CO2}	Bar	Partial pressure of carbon dioxide
R	J/mol/K	Universal gas constant: 8.3145
T	K	Temperature
$\Delta Habs$	J/mol/K	Enthalpy of absorption of carbon dioxide

Assuming that, to a first order approximation, the standard enthalpy change is relatively constant over the temperature swing and the change of solvent loading, it is possible to relate the ratio of partial pressure of CO_2 in the absorber and in the desorber to the temperature swing of the process

$$\frac{P_{CO2}^{des}}{P_{CO2}^{abs}} = \exp\left(\frac{-\Delta Habs}{R} * \left(\frac{1}{T_{des}} - \frac{1}{T_{abs}}\right)\right) \quad (34)$$

Where

Superscript	des	Desorber
Superscript	abs	absorber

Oyenekan and Rochelle (2006) indicates that, for a given temperature swing, say 80ºC, solvents with high enthalpy of absorption will deliver a higher partial pressure of CO_2, and by extension a higher total desorber pressure. They refer to it as thermal compression of carbon dioxide.

The Van't Hoff equation also shows that increased solvent thermal stability produces the same effect. The changes between partial pressure of CO_2 and desorber temperature are highly non-linear as indicated by equation (37), so that thermally stable solvents with a relatively low enthalpy of absorption can possibly benefit from thermal compression. This needs to be quantified rigorously with a model including the loss of output of the power cycle due to steam extraction, a the potential for integration between the capture unit and the power cycle accordingly to the solvent regeneration temperature, and a dedicated compression model.

5.2.4 Methodology for solvent assessment: An integrated approach

Typical examples of solvents needing to be assessed on a rigorous basis compared to 30%wt MEA are ionic liquids, piperazine and ammonia based solvents. Wappel et al. (2010) have proposed to regenerate the former at 110ºC with a partial pressure of CO_2 at the top of the desorber for the optimised solvent loading reported, of the order of 0.3-0.4 bar, compared to 1.1 bar for MEA. On the other hand, piperazine and ammonia solvents have a lower thermal energy of regeneration but are regenerated at a higher temperature. Ammonia-based solvents can be regenerated between 100 and 200ºC (Gal, 2006) while piperazine-based solvents are thermally stable up to 150ºC (Freeman et al., 2010).

This and the two previous sections illustrate the need for a rigorous methodology to assess process conditions specific to solvent properties. An integrated power plant, solvent, compression system was developed for that purpose. The steam cycle model for pulverised coal plants of Chapter 3 was modified to conduct a sensitivity analysis of sixteen solvents with a range of thermal energy from 3.5 to 2.6 GJ/tCO_2 and a range of reboiler operating temperature from 90ºC to 180ºC. The enthalpy drop and the number of turbine stages of the IP and the LP turbine was adjusted to set the IP/LP crossover pressure to match the temperature required on the solvent side of the reboiler. For consistency the generator output without capture is identical for each case. Figure 5-3 shows the steam turbine configuration adopted for solvents with a temperature equal or above 120ºC on the solvent side of the reboiler. For reboiler temperatures of 150ºC and 180ºC it was necessary to relocate the steam tapping point feeding the deaerator upstream, since the reboiler condensate with capture is hotter than the water outlet temperature of the last LP turbine feedwater heater when the steam cycle is operated without capture.

Solvents with a temperature of 90ºC required a different turbine arrangement. In practice the condensate heating arrangement would need to be modified for these solvents by replacing one of the LP turbine feed water heaters and move it upstream to the IP turbine. Instead, the extracted steam for solvent regeneration was expanded in an additional back-pressure turbine, as shown in Figure 5-4, so that steam was entering the reboiler at as low a pressure as possible. The addition of the back-pressure turbine allowed consistency with the reference case without capture. After the expansion in the back-pressure turbine the steam extracted did not contain enough superheat to justify a desuperheating feed water heater and this was replaced by a reboiler condensate spray.

In addition to the steam cycle model five adiabatic compressors, their respective intercoolers and the stripper reflux condensers were modelled to work out the temperature and the amount of heat available for each configuration, to replace the LP turbine feed water heating arrangement with capture. The stripping steam, carried away with the carbon dioxide at the top of the desorber, is gradually removed in the reflux condenser and in the compressor intercoolers. The compression arrangement is illustrated in Figure 5-5.

Solvent volatility was neglected so that the gas mixture leaving the desorber is only composed of water and carbon dioxide. Although this de facto limits the analysis to low volatility solvents, behaving relatively closely to an ideal mixture, the methodology could be extended to other solvents with available vapour liquid equilibrium data. Modelling assumptions for thermodynamic integration and temperatures available for heat recovery are given respectively in Table 3-3 and Table 3-4. It should be noted that the composition of the mixture at the inlet of the first compressor is only

determined by the temperature of the cooling medium, i.e. either the power cycle condensate or water available in the main plant cooling system.

Variations of the loss of output of the steam cycle, expressed as electricity output penalty are shown as a function of solvent thermal energy and temperature of regeneration in Figure 5-6, and presented as the difference in output, expressed in kWh/tCO2, with a reference solvent with similar characteristics to 30%wt MEA, i.e. 3.2GJ/tCO_2 required at 120ºC. It can notably be seen that the power output of the power cycle, and hence the electricity output penalty (EOP), is a strong function of the reboiler operating temperature. For example, solvents with a thermal energy of regeneration of 3.5 GJ/tCO_2, higher than the reference solvent, but requiring the extraction of steam at a lower pressure to deliver 90ºC on the solvent side of the reboiler, reduce the EOP of the power cycle by 15 kWh/tCO_2. On the contrary solvents with a lower thermal energy of regeneration but operating with a higher reboiler temperature can increase the EOP of the power cycle, e.g. by 20 kWh/tCO_2 for a 2.9GJ/tCO_2 solvent regenerated at 180ºC.

To complete the analysis the pressure at the top of the desorber equally needs to be considered to calculate the power requirement of compression, and add them to the loss of output of the steam cycle to estimate the overall EOP of a specific solvent. Oexmann et al. (2008) shows that the minimum efficiency penalty possible for 30%wt MEA is achieved with a desorber total pressure of 2.1 bar at regeneration temperature of 120ºC, for the specific plant configuration they studied[19]. The reference solvent was assumed to be identically operated with its total pressure set t0 2.1 bar. It should be noted that the total pressure in the desorber is composed of the sum of the contribution of the partial pressure of carbon dioxide and water.

The energy requirements for a mixture of CO_2 and water at 2.1 bar compressed up to 20 bar are shown in Figure 5-7. This illustrates the potential trade-offs between power for compression and loss of output in the steam cycle for solvent selection as the contribution of the electricity output penalty of the steam cycle can be compensated by a reduction of the compression energy requirement resulting from solvents with favourable vapour-liquid equilibrium.

To facilitate solvent selection the desorber total pressure of each of the sixteen solvents considered in this sensitivity analysis was reverse-engineered to calculate a break-even pressure. This break-even pressure can be seen as a hypothetical total desorber pressure for which the overall electricity

[19] This was optimised rigorously by considering compression work and the loss of output of the turbines, although their results cannot be extended for a different feed water heating system and beyond the limited temperature range they considered – 131ºC to 155ºC.

output penalty is equivalent to the reference solvent, assuming that the ancillary power for solvent circulation in the capture unit is independent of the type of solvent. For example, solvents with a lower contribution to the electricity output penalty in the power cycle have a break-even pressure lower than the reference solvent, and vice versa. In fact, the metric for solvent comparison becomes the break-even pressure, shown in Figure 5-8. Each of the solvents needs to operate with a total desorber pressure above its break-even pressure to outperform the reference solvent.

The methodology proposed allows a rapid comparison of solvents against 30% wt MEA as a function of their thermal stability, desorber total pressure and thermal energy of regeneration. It also shows that the emphasis on thermal energy of regeneration in the existing chemical engineering literature is misleading. The current research effort should assess potential solvents not on the sole basis of thermal energy of regeneration, but use a rigorous methodology taking into account the power cycle and the compression system, for which the reboiler temperature is a key issue.

5.3 Steam turbine design for future-proof upgradability

Steam turbine approaches to capture retrofit should offer flexibility to allow for solvent upgrading as well achieving a low electricity output penalty at a selected design point (or averaged over a design range). More flexible arrangements for steam extraction help avoid the risk of a retrofitted plant turning into a stranded asset after a period of technology change when less energy intensive solvents with potentially a different temperature of regeneration are likely to become available.

The fifth principles for the design of CO_2 capture-ready (CCR) plant previously proposed in Chapter 3 is now being considered. It is repeated below for clarity

> A CCR plant should allow for future technology developments and when the capture technology is upgraded the retrofitted plant should have the same efficiency as a CCS plant – with the same steam conditions – built with perfect foreknowledge of what the upgrade technology would be.

Capture-ready steam turbines can be designed for a given steam extraction rate at the IP/LP crossover pipe to provide the right amount of heat for a specific solvent. Although it is impossible to design a capture-ready steam cycle with an ideal efficiency for a range of solvents, it is feasible to design steam cycles that achieve performance close to the ideal for a given range of solvents. Future performance of solvents remains, by definition, unknown but reasonable options in the design of the steam cycle can handle a wide range of uncertainty.

5.3.1 Upgrade with same reboiler operating temperature

The methodology in this section uses the model developed for pulverised coal plants in Chapter 3 to provide an illustrative example of the risk facing power plant developers with an inflexible steam turbine system that locks the plant into specific levels of performance despite incremental improvements to the technology, which other plants built later (or with flexible steam cycles) benefit from.

The steam turbine model is extended to account for a range of steam flow rates, representing a range of solvent thermal energy of regeneration from 3.2 to 2.6 GJ/tCO_2. It is assumed that each of the capture-ready options is initially retrofitted with a solvent which requires 3.2 GJ/tCO_2 of heat at 120 ºC. The process and/or the solvent are subsequently upgraded to reduce the thermal energy of regeneration and the upgrade does not modify the reboiler operating temperature. For amines, the operating limit on the reboiler temperature is typically set by thermal degradation of the solvent, and a compromise between low degradation and the overall energy requirement has to be made (Oexmann et al., 2008; Freeman et al., 2010).

In practice, improvements in the capture and compression process could be achieved to reduce the thermal energy requirement in the reboiler, and therefore the steam extraction rate from the turbines, without changing the solvent by advanced thermodynamic integration. Some examples from (Leites, 1998; Leites et al., 2003; the Fluor Econamine process in IEAGHG, 2004; Ijima et al., 2007; Oyenekan and Rochelle, 2007; Ijima, 2008; Shaw, 2009; Ziaii et al., 2009) are listed below as illustrative examples.

- Lower approach temperatures in the cross heat exchanger reduce the sensible heat needed for the solvent thermal swing between the absorber and the stripper.
- Intercooling the absorber to limit the temperature increase in the column, reduce irreversibilities and the overall thermal energy requirement.
- Split flow solvent loops, where semi-lean solvent from the desorber return to the absorber at mid-column, to reduce irreversibilities in the absorber.
- Flash regeneration of the solvent before the desorber and a multiple flash system in lieu of the desorber.
- The incorporation of the cross heat exchanger partly in the stripper section and absorber to achieve the same effect

- Flash of the reboiler outlet followed by vapour recompression of the gas phase back into the desorber
- Vapour compression of the desorber overhead
- Multipressure stripping and integration with CO_2 compressors

As post-combustion capture is gradually deployed further process integration advances from 'learning by doing' can be expected to reduce the overall energy requirement.

Alternatively, it is possible to reduce the sensible heat of the thermal swing by increasing solvent concentration. Aqueous MEA concentrations are usually limited by corrosion effects. Carette et al. (2009) propose advanced corrosion inhibitors, which allow increasing concentration up to 40%wt, and reduce the energy requirement down to approximately 3GJ/tCO_2 without changing the reboiler temperature (Lemaire and Raynal, 2009). Similar advances with less widely used solvents than MEA are obviously also possible.

Finally, a replacement of the initial solvent by another less energy intensive (possibly amine-based, but anyway having similar characteristics) solvent with analogous thermal degradation properties, and thus a similar reboiler operating temperature, is obviously possible and could lead to similar scenario of solvent upgrade. This could be the case if a 30 wt% aqueous MEA solvent was upgraded with a blend of MEA and AMP, as suggested by (Aroonwilas and Veawab, 2009)[20].

The performance of the throttled LP turbine option and the floating IP/LP crossover pressure option are shown in Figure 5-9 and compared against a range of reference plants. Each of the reference plants are assumed to have been purposely built and respectively optimised at a notional design point for a specific solvent thermal energy of regeneration. The analysis in Chapter 3 showed that it is possible to significantly improve the performance of retrofitted plants compared to new-build units, if the site cooling capacity is not limited by water constraints, by making use of the lowest temperature available to lower the condenser pressure of the steam cycle and increase its power output. The retrofitted capture-ready plants outperformed the new-build plant with the same solvent, which was operated at a higher condenser pressure. The cooling overcapacity – with capture - of retrofitted capture-ready units is justified by the performance of the system before

[20] Aroonwilas and Veawab (2009) show that blends of MEA-AMP have lower steam requirements that 30%wt MEA. Their methodology includes neither CO2 compression, nor the VLE of the MEA-AMP at stripper conditions. It should be noted that MEA-AMP blends would not necessarily have a lower overall energy penalty than MEA. These blends are mentioned here as a potential illustrative example only.

steam is extracted for capture. A techno-economic analysis for a new-build plant with the same cooling medium available, e.g. sea water, would not necessary lead to oversizing the plant cooling system. But, for consistency, the reference plants benefit here from the same cooling capacity as the retrofitted units in this analysis, allowing a generalisation of the results to sites with water constraints.

Clutched LP turbine retrofit upgrade

The clutched LP turbine retrofit has no potential for upgrade since the additional LP steam flow available cannot be handled by the remaining turbine cylinder. As the performance of the reference plants improve when thermal energy requirement reduces, the difference between the retrofitted clutched option and the best available plant increases gradually. In practice, the risk for the plant owner is that the plant can potentially move down in the dispatch merit order, be dispatched less frequently, and possibly either start competing with peaking plants or become obsolete in advance of the complete depreciation of its capital, therefore becoming a stranded asset.

Unlike the clutched LP turbine, both the throttled LP turbine retrofit and the floating IP/LP crossover retrofit have the potential to reduce their electricity output penalty and improve their performance when less energy intensive solvents and /or process improvements become available.

Throttled LP turbine retrofit upgrade

As the solvent energy requirement decreases more steam is available for power generation in the LP turbine. The throttling losses at the LP turbine inlet gradually decreases and the electricity penalty output of that option tends to get closer to the best available plant.

Floating IP/LP crossover pressure retrofit upgrade

Like the former option, this capture-ready option has the potential to reduce its electricity output penalty. The difference with the best available plant is relatively constant for the range of solvent studied, and always lower than the throttled LP turbine retrofit. As more steam becomes available for power generation in the LP turbine the IP/LP crossover pressure floats towards a higher pressure. A valve then becomes necessary in the extraction line, as shown in Figure 3-8, to avoid overheating the solvent in the reboiler by maintaining the pressure of condensation of the steam.

Hybrid capture-ready retrofits

Capture-ready power plant developers may want to design the steam turbines to achieve a minimum electricity output penalty at a given steam extraction rate that is lower than state-of-the art solvents at the time of commissioning of the plant. By doing so they may anticipate future solvent requirements for plants that are unlikely to be retrofitted soon enough to be sure of using currently-available solvents. A hybrid design can offer the flexibility required to achieve good performance over a specific range of steam extraction rates, by setting the IP/LP crossover pressure between the value of a full floating pressure system and the value of a throttled LP turbine system. Figure 5-10 illustrates the performance of a hybrid system - optimised for a solvent requiring 2.9 GJ/tCO_2- over a range of solvents regenerated at 120ºC with the thermal energy of regeneration varying from 3.6 GJ/tCO_2 down to 2.6 GJ/tCO_2[21]. Its performance is compared to three capture-ready retrofits, similar to those previously discussed, but designed to be initially retrofitted with a solvent requiring 3.6GJ/tCO_2.

When capture is added using this solvent the IP/LP crossover pressure drops down to the required pressure for capture, similarly to the floating pressure retrofit. The LP turbine then needs to be throttled, although throttling losses are obviously smaller than for a throttled LP turbine retrofit upgrade. As solvent thermal energy decreases, throttling losses gradually reduce to zero when the solvent energy requirement reaches 2.9 GJ/tCO_2. The LP turbine inlet pressure is then equal to the crossover pressure and corresponds to the pressure required for steam extraction. Further reduction in solvent thermal energy increases the pressure at the IP/LP crossover and the LP turbine inlet. At this stage a valve has to be used in the steam extraction line to the reboiler. The system overall performance still improves, but the difference with best available plants increases.

The hybrid system offers a good compromise and achieves better performance than both options over the range of solvents considered. Any upgrade from the initial solvent/process at 3.6 GJ/tCO_2 leading to a reduction of thermal energy requirement solvent below 3.3 GJ/tCO_2 makes the hybrid option the most efficient of the capture ready options.

[21] Note that the power cycle model is as per Lucquiaud and Gibbins (2009a). Results do not match those of Figure 5-9 due to different initial assumptions, provided in Appendix E

5.3.2 Upgrade for a lower reboiler temperature

Future post-combustion capture systems may operate at a lower reboiler temperature, with possibly higher thermal energy requirements, provided that solvents with favourable trade-offs between the loss of output and the compression energy requirements are obtained, as shown previously.

Extracted steam may be throttled down the new steam condensing pressure, or perhaps expended through an additional back-pressure turbine if space is available and it is otherwise technically feasible and economically justified. If higher amounts of steam were required it would then become necessary to maintain the IP/LP crossover pressure – and thus the reboiler temperature - by throttling at the LP turbine inlet and reducing its inlet pressure.

5.3.3 Upgrade for a higher reboiler temperature

Unlike the clutched and the throttled LP turbine options, the temperature for solvent regeneration with a floating IP/LP crossover pressure is not limited to its design value. With this system the steam extraction pressure is a function of the steam extraction rate, and so can be the reboiler temperature. Abu Zahra et al. (2007) show that solvent thermal energy requirement is a strong function of the reboiler temperature, as indicated in Table 5-5. The floating pressure system thus offers some potential for incremental improvement over the less upgradeable options. For example, if steam extraction rates are reduced by a third the reboiler temperature can be increase by approximately 5K. For a solvent with a higher temperature of regeneration this system could potentially outperform less flexible options by allowing the reboiler/stripper system to operate closer to its optimum temperature/pressure.

5.4 Capture-ready design for radically different solvents

5.4.1 Capture-ready steam turbines for pulverised coal plants using radically different capture solvents

In a plant that is purpose-built to operate with capture it might be thought that the best approach is to set the LP crossover pipe pressure so as to provide steam at the required reboiler pressure (i.e. allowing for pressure drops in the connecting pipes and the temperature difference for heat transfer in the reboiler) and to size the LP cylinder(s) and condenser(s) to take only the remaining flow when the capture plant is operated (e.g. IEAGHG, 2004). In practice, however, this would lock in the supply steam pressure, and to some extent the steam extraction rate to a range of flows equal or higher than the initial value. A more flexible approach for capture-ready steam turbines has been proposed, where the LP cylinder is capable of taking the full steam flow with an initial (non-capture) IP cylinder outlet pressure set so that, when steam is extracted, the pressure falls to the required value. The range of feasible maximum steam supply pressures is, however, limited and a radically different approach may be required for capture-ready steam turbines in some jurisdictions where CCS deployments can be expected to occur after the technology has been demonstrated and improved somewhere else. In that situation time increases uncertainty and the spectrum of potential solvents and processes widens. Committing the plant to a specific steam supply pressure or a limited range of supply pressure, even with a floating pressure system, may not be advisable. Power plant developers may want to design steam turbines with the options of fitting radically different solvents. In an era of technology change this can prove to be hedge against technology developments, which are by nature difficult to predict.

Chapter 4 showed that existing coal units can be retrofitted efficiently, independently of the value of the IP/LP crossover pressure, by fitting two back-pressure turbines taking steam from the IP/LP crossover and expanding it down to the reduced LP turbine inlet pressure and down to the required reboiler pressure respectively. With the provision of space, and the reinforcement of foundations at appropriate locations, in the turbine island or in its vicinity, it is possible to design steam turbines as capture-ready for almost any reboiler steam supply pressure, provided that IP outlet pressure exceeds the reboiler pressure once pressure drops are taken into account.

Piperazine-based and ammonia-based solvents are two examples of promising alternatives to current amine solvents, which are more thermally stable and would require higher IP/LP crossover pressure than most amine-based solvents. As mentioned above, these two chemical absorbents can

be used in aqueous solvents regenerated at temperatures as high as 150ºC (Freeman et al., 2010) and 200ºC (Gal, 2007) respectively. Figure 5-11 illustrates the potential IP/LP crossover pressures for solvent regeneration temperatures ranging from 90ºC to 200ºC and shows that setting the IP/LP crossover pressure has to be set as high as 22 bar to offer the potential to provide practically any reboiler operating temperature. This obviously may have some implications with regards to the capital costs of the steam turbines. Current design trends seem to favour lower IP/LP crossover pressure, which may not be suitable for solvent upgradability; the rationale being the reduction of the total number of turbine stages in the IP and the LP cylinders, by favouring steam expansion in the IP cylinder over the multiple LP turbine cylinders. The magnitude of the additional capital costs incurred by setting the crossover pressure to an elevated value is, however, likely to be small compared to the overall cost of the plant, and therefore may be justifiable as a capture-ready measure with a good return on investment, as suggested in (Bohm et al., 2007).

5.4.2 Capture-ready steam turbines for natural gas combined cycle plants for radically different solvents

Gas power plant developers also face technology uncertainty with regards to post-combustion capture. Process developments specific to this type of plant are likely to occur as the technology is deployed on a wider scale. The design parameters are different from coal plant applications that may be deployed earlier, notably in that carbon dioxide and oxygen concentrations in the flue gas are somewhat different, e.g. around 4% carbon dioxide for gas vs. 12-15% for coal. One way to address the low concentration of CO_2 in the flue gas, and accelerate kinetics in the absorption column and reduce the amount of flue to be treated and hence capital costs, is to recycle flue gas from the outlet of the heat recovery steam generator to the gas turbine compressor inlet via a cooler (IEAGHG 2000a; IEAGHG, 2000b). Flame stabilisation in the combustion chamber or possibly compressor performance may be the limiting factor on the extent to which this can be undertaken. These process developments are, however, unlikely to critically modify the regeneration part of the capture process.

As is the case for coal plants, there is a risk that natural gas plant developers will also see their plants become obsolete if the capture-ready steam turbines of the combined cycle lock the plant into a specific level of steam extraction pressure, and by extension performance. Like the clutched LP turbine option for coal, the alternative option of making provision for a replacement of the LP turbine cylinder of the combined cycle when capture is retrofitted still locks the turbines into a specific steam extraction rate – or possibly higher values by throttling at the LP turbine inlet – and a

specific supply steam pressure since the new LP turbine does not have the necessary steam swallowing capacity to absorb additional steam. Options with additional back-pressure turbines have the capability to provide a range of solvent temperature of regeneration and avoid committing too early to a specific solvent, and thus meet the fifth capture-ready principle.

5.4.3 Summary of key considerations for capture-readiness and future-proof upgradability

Table 5-6 expands on the findings of Chapter 3 and summarises the key aspects of capture-ready steam turbines design for both coal and gas plants, including the potential for future-proof upgradability. It shows that the options with the lowest electricity output penalty for the initial solvent design are at risk of becoming obsolete if 'better' solvents with a higher temperature of regeneration (and hence probably lower compression work requirements) are developed and become the industry norm. For coal plants the floating pressure option has the lowest electricity output penalty for a range of solvents, as pointed out in Figure 5-9. As far as gas plants are concerned, it is possible to design capture-ready systems, which do not commit steam turbine developers to select a specific solvent through the choice of the IP/LP crossover pressure. This leaves the option of fitting a wide range of potential solvents by specifically adjusting the design of the additional back-pressure turbine(s) at the time of retrofit.

5.4.4 Upgrading new-build units built with CCS from the outset

Reducing the energy requirement of post-combustion capture systems on a retrofitted unit allows the generator output to be increased through more power in the LP turbine with the additional steam available. Since the generator, LP turbines and condenser have been derated by adding capture the potential to do so exists at no additional cost.

New-build fossil plants built with CCS from the outset, if sized for a given generator output with capture, obviously do not have spare power export capacity. When it comes to technology development power plant developers are left with a challenging investment decision on whether or not to oversize critical components in order to protect the plant from future technology obsolescence. Real-option analysis, beyond the scope of this thesis, could provide valuable insights in this typical situation of decision-making under uncertainty. The next section investigates power plant operating flexibility, showing that the value of being able to supply additional export power is not only limited to upgradability, but extends to the ancillary services and additional modes of

operation arising from the inherent flexibility of post-combustion capture systems. As such it suggests that associated operating profits should also be included in real-option analysis investigating the value of oversized export facility.

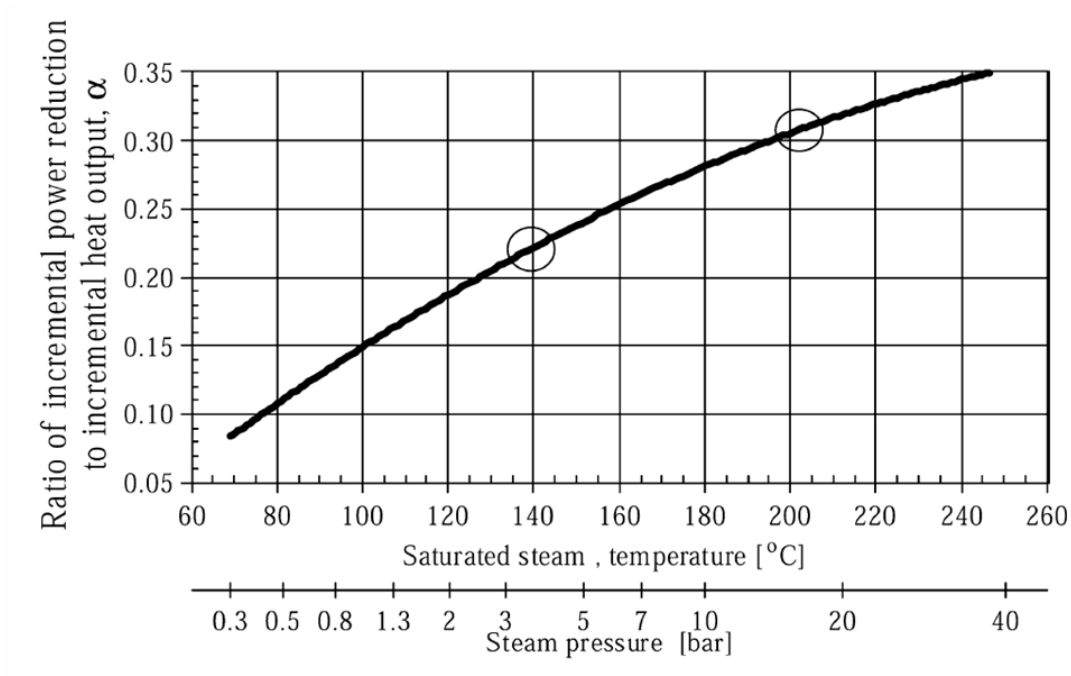


Figure 5-1: The ratio (α) of incremental power reduction to incremental heat output when extracting steam at given pressures from a steam turbine, from (Bolland and Undrum 2003)
The calculations are made for a large high-efficiency CC with triple-pressure reheat steam cycle with a condenser pressure of 0.04 bar. The extracted steam is spray desuperheated in order to deliver saturated steam at all pressures. The condensate return temperature is held constant at 70ºC.

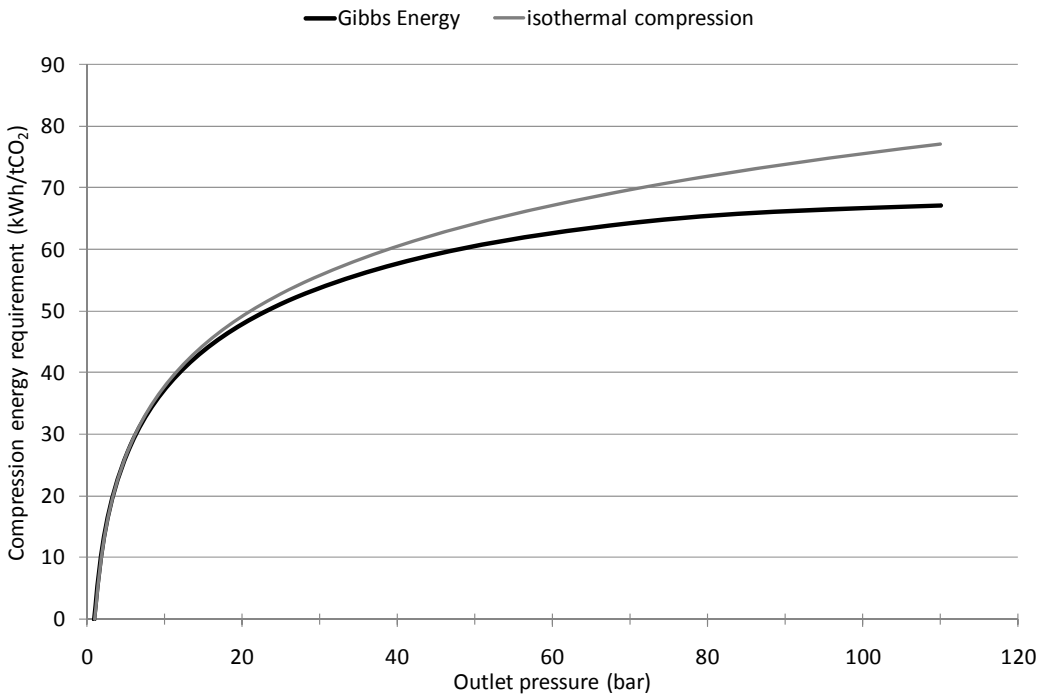


Figure 5-2: Minimum energy requirement for the compression of carbon dioxide from 1 bar at 313K to 110 bar

Isothermal compression based on ideal gas assumption. Gibbs Energy based on Multiflash properties.

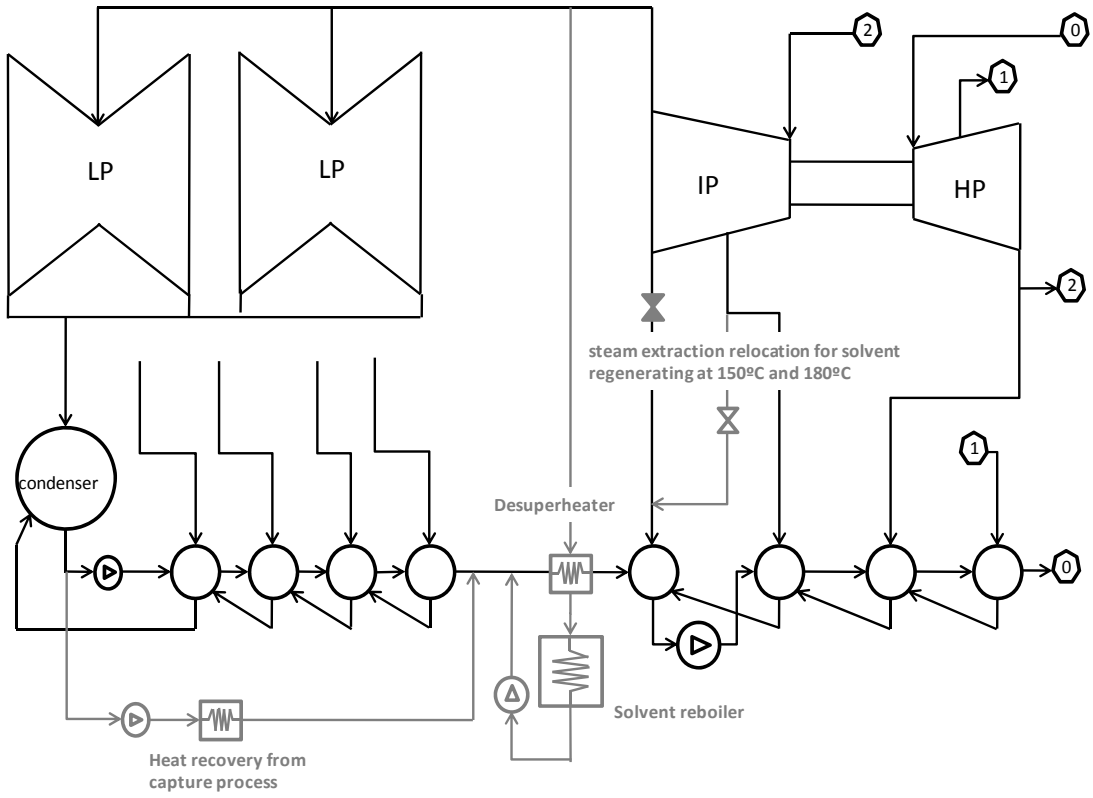


Figure 5-3: Steam cycle configuration for solvents regenerated at 120ºC, 150ºC and 180 ºC

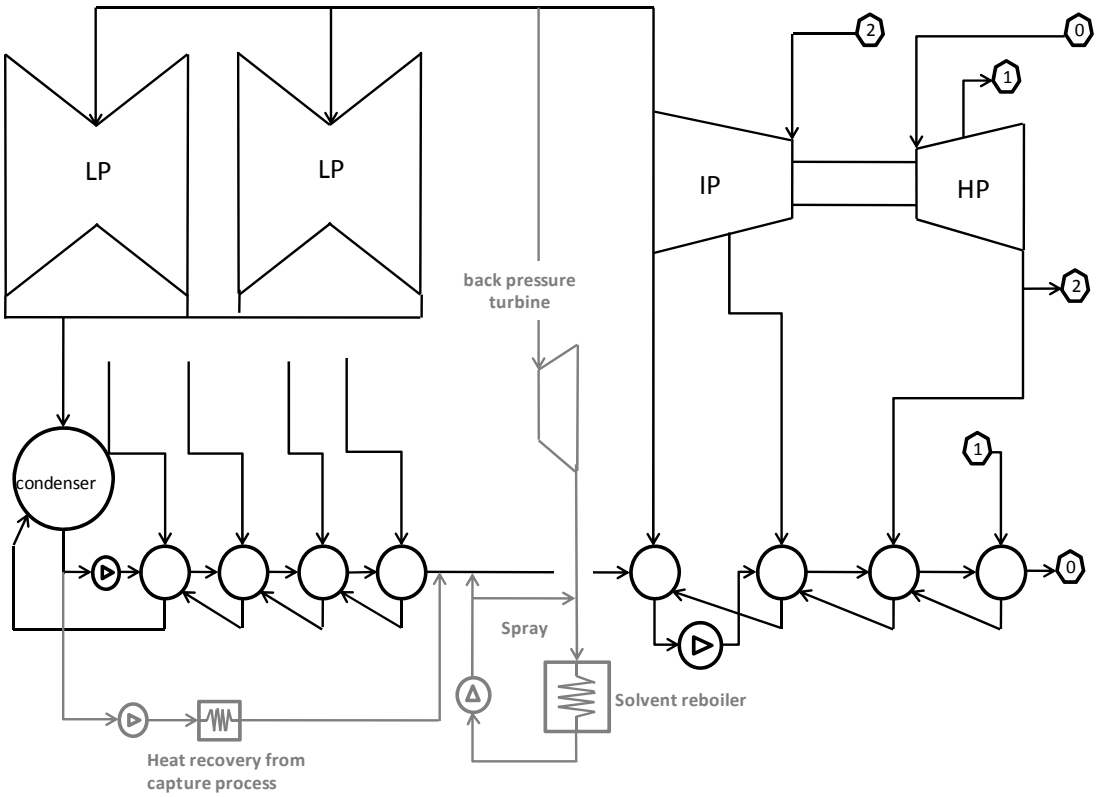


Figure 5-4: Steam cycle configuration for solvents regenerated at 90ºC

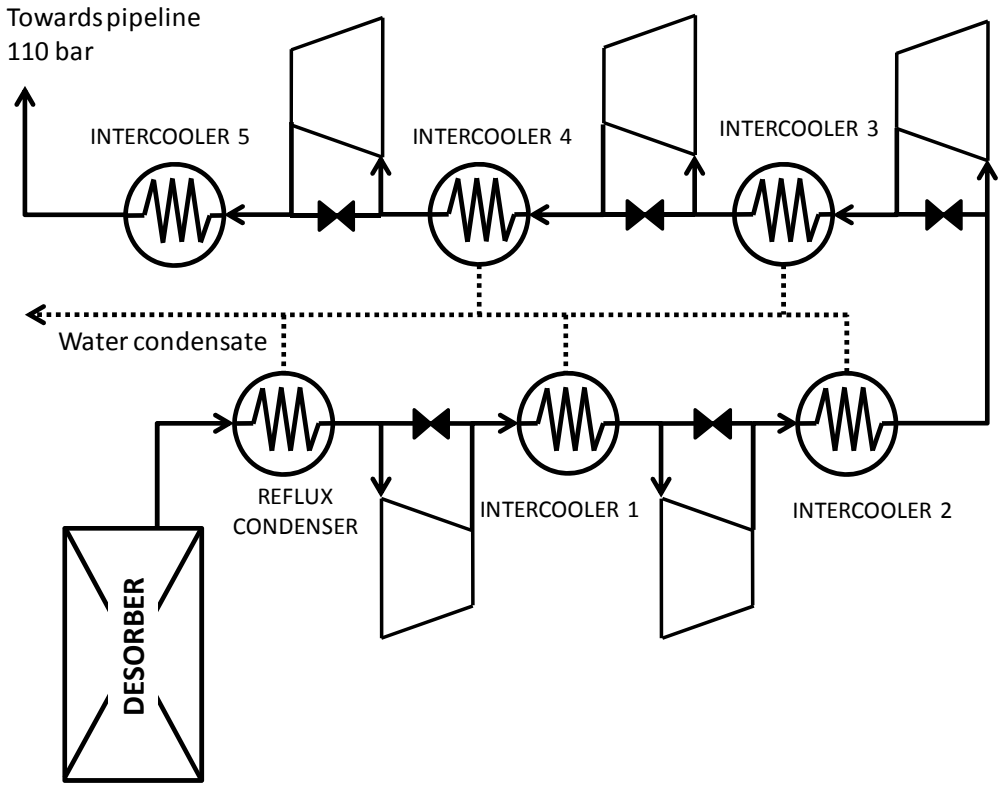


Figure 5-5: Schematic diagram of desorber reflux condenser and CO_2 compression and drying train

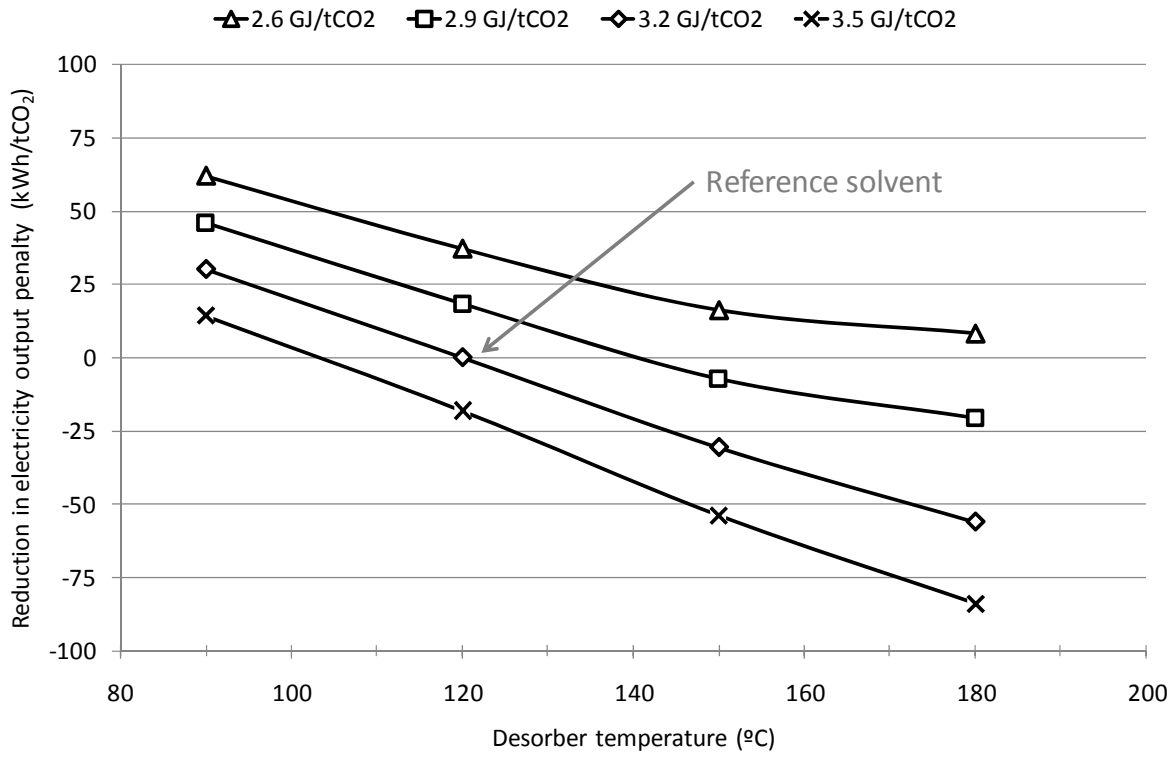


Figure 5-6: Changes in electricity output penalty for a range of solvent as a function of solvent thermal energy of regeneration and regeneration temperature.

Reference solvent performance: 3.2 GJ/tCO_2 at 120ºC. Boiler efficiency, fuel composition and generator output without capture identical for each case. The IP/LP crossover pressure is set by the desorber temperature, except for solvent regenerated at 90ºC, for which a back-pressure turbine is fitted in the steam extraction line and the feed water heater desuperheater replaced by a spray. The deaerator steam extraction is relocated upstream in the steam expansion path when capture is fitted for desorber temperature of 150ºC and 180ºC. Thermodynamic integration parameters are provided in Table 5-3 and Table 5-4 for each solvent

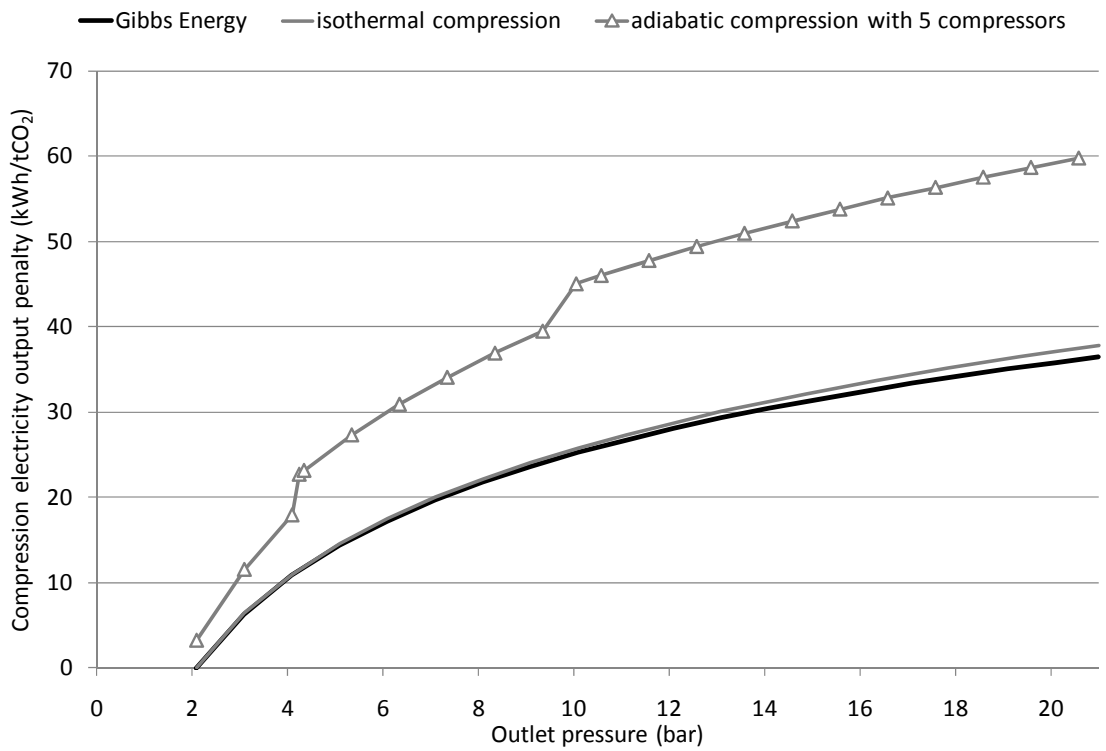


Figure 5-7: Electricity output penalty for compression of the reference solvent up to 20 bar.
Inlet suction pressure is 2.1 bar. Compression system parameters as per Table 5-3.

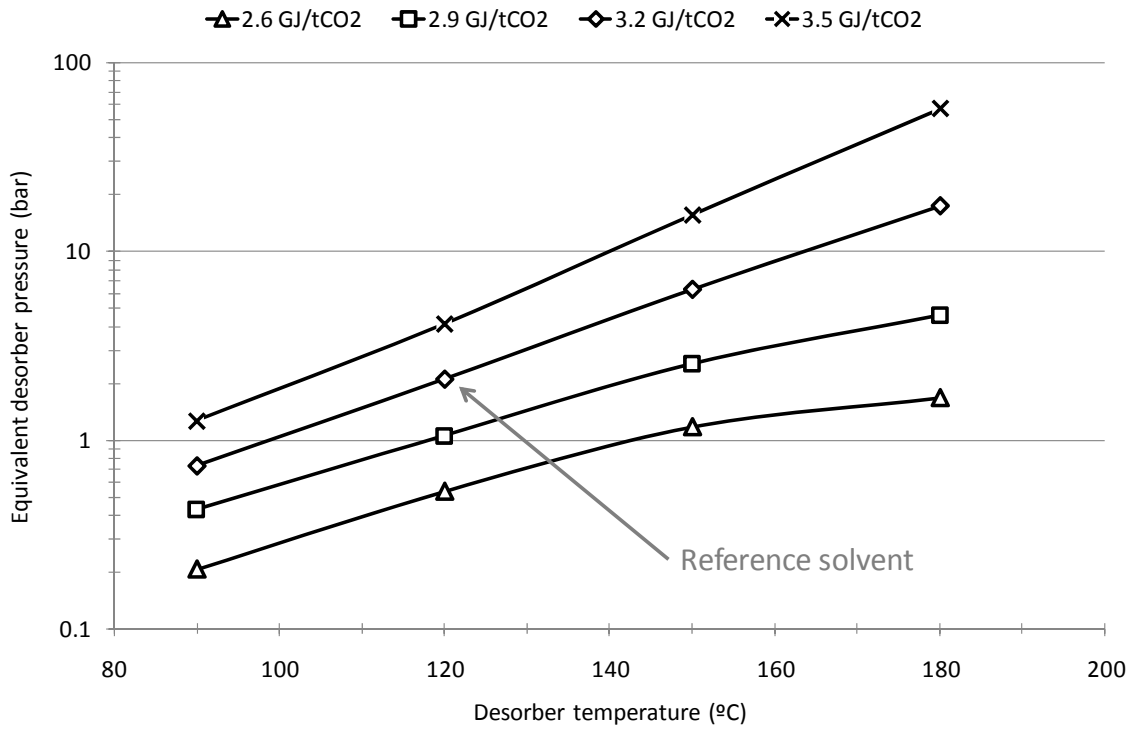


Figure 5-8: Break-even desorber pressure for the range of solvents selected.
If the total desorber pressure of a solvent is above the break-even pressure, the sum of the contribution to the overall electricity output penalty of the power cycle and the compression train are lower than the overall electricity output penalty of the reference solvent.
Reference solvent performance: 3.2 GJ/tCO_2 at 120ºC. Ancillary power for solvent circulation etc. is assumed to be identical. Compression system parameters as per Table 3-3.

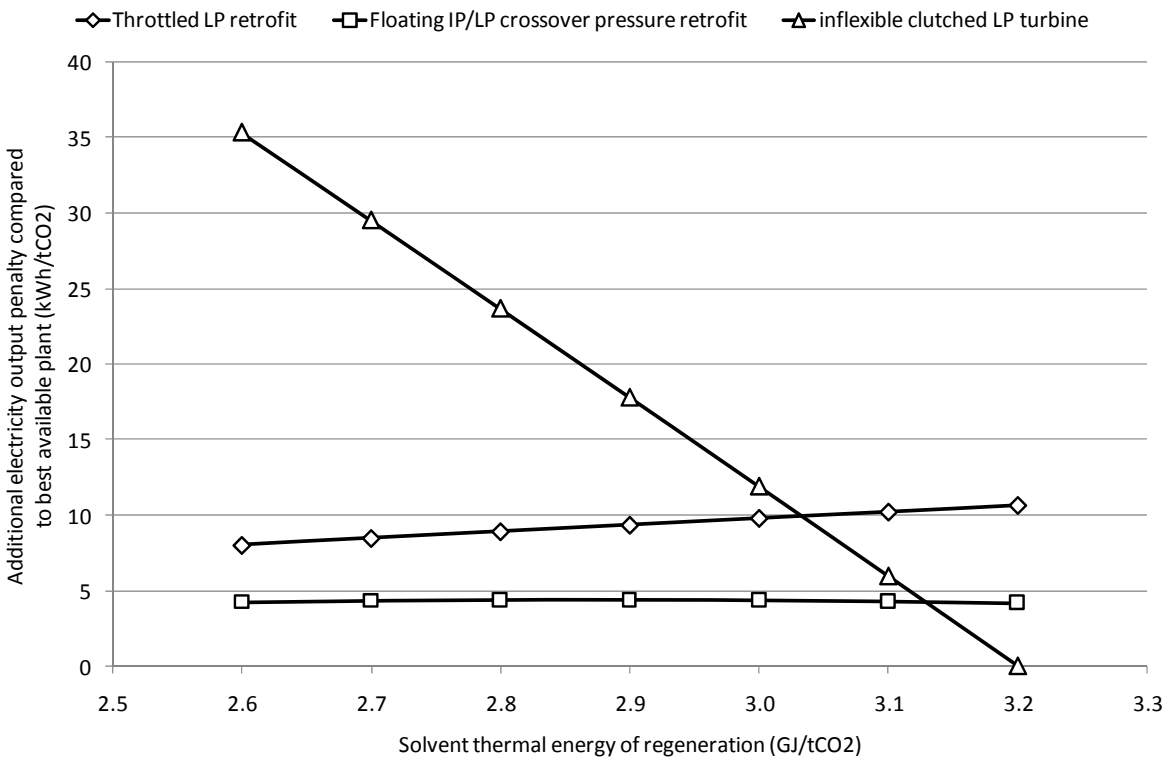


Figure 5-9: Sensitivity analysis of solvent thermal energy of regeneration requirement on the performance of retrofitted capture-ready coal plants initially designed for 3.2 GJ/tCO_2.
The best available plant is one built for each specific thermal energy of regeneration and having the same cooling capacity as the retrofitted capture-ready options. Solvent temperature of regeneration: 120ºC.
Each retrofitted plant is initially fitted with the 3.2 GJ/tCO_2 solvent and is then subsequently upgraded with a less energy intensive solvent.

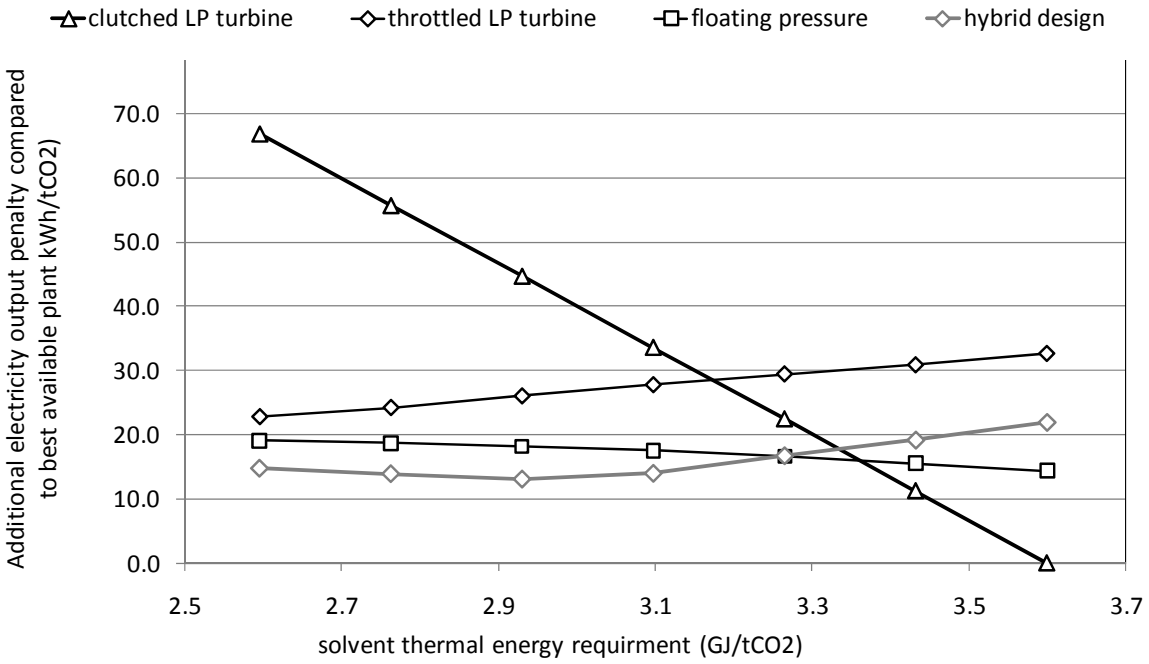


Figure 5-10: Comparison of the performance of a hybrid capture-ready system for a range of thermal energy of regeneration requirement. Adapted from (Lucquiaud and Gibbins, 2009)

The best available plant is one built for each specific thermal energy of regeneration and having the same cooling capacity as the retrofitted capture-ready options. Solvent temperature of regeneration: 120ºC.

Each retrofitted plant is initially fitted with the 3.6 GJ/tCO_2 solvent and is then subsequently upgraded with a less energy-intensive solvent. The hybrid design is optimised for 2.9 GJ/tCO_2

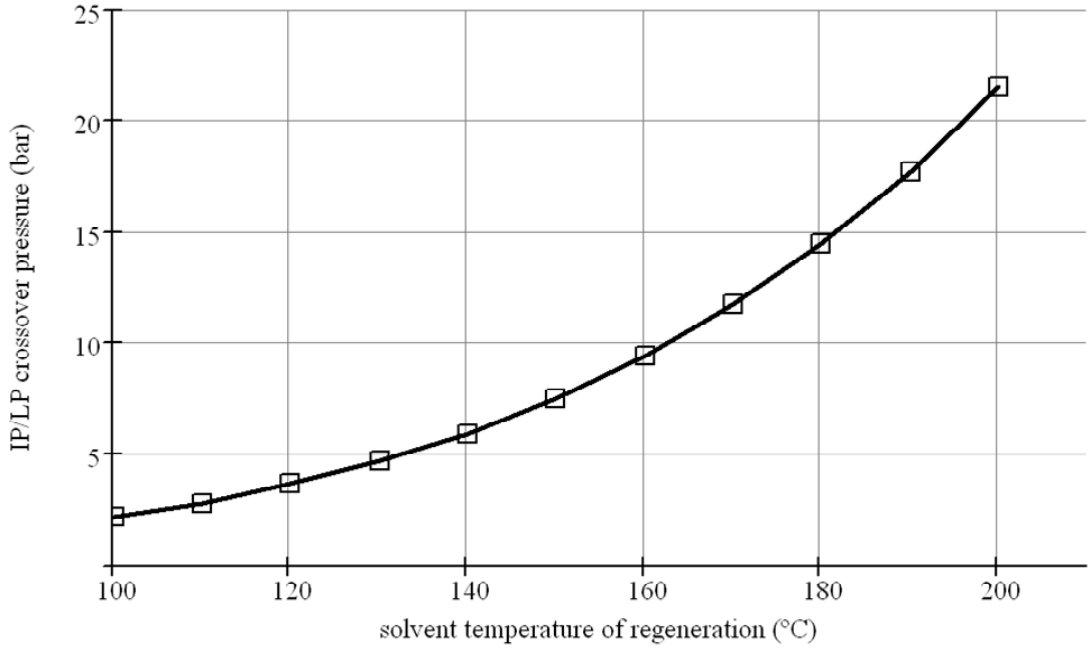


Figure 5-11: Range of potential steam extraction pressures required for post-combustion capture

Assumed reboiler approach temperature: 15K; pressure drop from crossover to reboiler: 0.5 bar.

Table 5-1: Estimated thermal energy requirement for regeneration of liquid absorbents, from Feron (2010)

Absorption process development status	G1	G2	G3	G4
Binding Energy(MJ/kmol CO_2)	80	70	55	30
Cross heat exchanger approach temperature (K)	15	10	5	3
Solvent flow (m^3/tCO_2)	20	10	8	4
Reflux ratio (tH_2O/tCO_2)	0.7	0.6	0.4	0.1
Thermal energy (GJ/tCO_2)	4.56	3.31	2.29	0.95
Contribution CO_2 binding (GJ/tCO_2)	1.82	1.59	1.25	0.68
Contribution solvent heating (GJ/tCO_2)	1.20	0.40	0.16	0.05
Contribution steam stripping (GJ/tCO_2)	1.54	1.32	0.88	0.22

Table 5-2: Estimated improvement in thermal integration of absorption process with power system, from Feron (2010)

Status power plant technology	G1	G2	G3	G4
Power plant thermal efficiency (%)	0.35	0.41	0.46	0.50
Thermal Energy (GJ/tCO_2)	4.56	3.31	2.29	0.95
Power equivalent factor	0.25	0.20	0.15	0.15
Electricity output penalty (kWh/tCO_2)	317	184	95	40

Table 5-3: Parameters for thermodynamic integration between power cycle and CO_2 compression/drying process

Reference case solvent thermal energy	3.2GJ/tCO_2
Reference case desorber temperature	120ºC
Reference case generator output	754.5 MW
Mass flow of CO_2 captured	143 kg/s
Capture rate	90 %
Gas mixture composition	CO_2 and water. Solvent volatility is neglected.
Thermodynamic properties	LKS equation of state and Redlich-Kwong for pure component (based on Multiflash[22])
Compressor outlet temperature	140ºC
Compressor efficiency	85%
Solvent reboiler approach temperature	15ºC
Hot side cross heat exchanger temperature difference	15ºC
Intercooler approach temperature (cold side)	15ºC
Intercooler approach temperature (hot side)	20ºC
Intercooler and reflux condenser pressure drop	15% of inlet pressure

[22] http://www.infochemuk.com/

Table 5-4: Thermodynamic integration between steam cycle and CO_2 compression/drying process

Solvent temperature of regeneration (ºC)	90	120	150	180
Steam temperature on reboiler hot side (ºC)	105	135	165	195
Temperature at the top of the stripper (ºC)	75	105	135	165
Available temperature for heat recovery reflux condenser(ºC)	60	90	120	150
Available temperature for heat recovery Compressor intercoolers (ºC)	120	120	120	120

Note: For each case the temperature of the condensate returning to the power cycle is maximised depending on the heat and temperature available

Table 5-5: Solvent thermal energy of regeneration of 30%wt MEA for a range of reboiler temperature, from Abu Zahra et al. (2007)

Stripper pressure (bar)	Stripper temperature (ºC)	Thermal energy of regeneration (GJ/tCO_2)
0.9	108	4.87
1.2	114	4.24
1.5	120	3.89
1.8	124	3.68
2.1	128	3.56

Table 5-6: Assessment of CCR design principles for capture-ready coal and gas steam turbines

CAPTURE-READY STEAM TURBINES FOR COAL PLANTS				
	Clutched LP turbine option	Floating IP/LP crossover pressure option	Throttled LP turbine option	Two back-pressure turbine option
Main specific capture-ready design actions	Size clutched LP cylinder for predicted steam extraction rate. Set crossover pressure for predicted reboiler temperature	Set crossover pressure to fall to predicted value when capture is added	Set IP/LP crossover pressure for predicted reboiler temperature	Set crossover pressure to maximum expected temperature. Space and foundations reinforcement for turbines
Penalty before capture	None	None	None	None
Performance with capture	Reference	+ 4.3 kWh/tCO_2	+ 10.7 kWh/tCO_2	As reference
extra CAPEX before retrofit	+ 2.89% (IEAGHG 2007a)	+0.7% (IEAGHG 2007a), < 1% (Napier-Moore et al., 2008)	+0.4% (IEAGHG 2007a), <1% (Napier-Moore et al., 2008)	Likely to be < 1%
extra CAPEX with capture	None	None	None	Cost of back-pressure turbines
Upgradability for higher temperature solvents	NO	YES to a limited extent	NO	YES. Almost any solvent upgrade is possible
Upgradability for same or lower temperature solvents	YES	YES	YES	YES
CAPTURE-READY STEAM TURBINES FOR NATURAL GAS CONBINED CYCLE PLANTS				
	LP turbine replacement		Two back-pressure turbine option	Pass-out back-pressure turbine option
Main specific capture-ready design actions	Provision for cylinder replacement Set IP/LP crossover pressure for predicted reboiler temperature		Set crossover pressure to maximum expected temperature. Space and foundations reinforcement for turbines	Space and foundations reinforcement for turbines
Penalty before capture	None		None	None
Performance with capture	Reference		+ 1.9 kWh/tCO_2	+ 3.3 kWh/tCO_2
extra CAPEX before retrofit	Likely to be < 1%		Likely to be < 1%	Likely to be < 1%
extra CAPEX with capture	New LP turbine cylinder		Cost of back-pressure turbines	Cost of pass-out back-pressure turbine
Retrofit with higher temperature solvents	NO		Tailored-design retrofitted turbine	Tailored-design retrofitted turbine
Retrofit with same or lower temperature solvents	YES		Tailored-design retrofitted turbine	Tailored- design retrofitted turbine

6 Steam turbines for flexible operation of post-combustion capture systems

6.1 Background

The inherent nature of electricity necessitates a permanent balance between generation and demand in electricity systems. This has obvious implications for the operation of power plants, and more specifically for fossil-fired plants, which play an important role in electricity networks as mid-merit plants that can respond relatively quickly to changes in supply and demand. As a consequence, they are required to operate over a wide output range to maintain the quality and security of electricity supply of the electricity network. A detailed description of the different operating regimes for power plant is provided by (Gross et al., 2006), and is illustrated in Figure 6-1.

The capacity to vary the steam extraction levels from the power cycle of fossil power plants to adjust both capture levels, possibly down to zero for some period of time, and power output is thus a valuable option to:

- maintain the output of the power plant in case of a failure either in the CO_2 capture, transport or storage part of the system,
- increase/decrease power output to meet grid code requirements
- generate revenue in response to price signals in the electricity trade short-term market.

Because the contribution of CO_2 emissions to the radiative forcing of the energy balance of the atmosphere can be aggregated over very long periods, of the order of decades at least, (IPCC, 2007) a temporary by-pass of the capture system still achieves perfect environmental integrity. Until the necessity of near zero emissions – and possibly negative emissions - in power generation triggers high levels of capture (i.e. approaching 100%) in the whole electricity sector so that all plants must be fitted with capture and operated all the time, these approaches offer a valuable option to maintain network quality and security of supply.

As CO_2 emissions limits increase and/or carbon price increases alternative methods can be employed to avoid a fraction or the totality of the energy penalty associated with CO_2 capture during critical periods for network stability, or during periods of peak electricity price, without increasing overall CO_2 emissions (Gibbins and Crane, 2004a). When operating fossil power plants fuel costs, and by extension all operating expenditures, do not equate directly to the selling price for electricity. Being

able to choose when to take the energy and, hence, financial penalty for CO_2 capture may have a great effect on the energy component of CO_2 capture costs, but depends entirely on the electricity market conditions. These alternative methods rely on the intermediate storage of solvent, between the absorber and the scrubber column of the post-combustion capture process, as illustrated in Figure 6-2, to decouple the absorption from the energy intensive part of the process, composed of regeneration of the solvent and CO_2 compression. Lean solvent flows from a storage tank to the absorber column, bonds with carbon dioxide in the flue gas and is then stored in a second tank while the steam used for solvent regeneration is now available for additional power generation in the low pressure turbine of the steam cycle. The compression system can also be turned off to increase further the generator output. Regeneration of the rich solvent stored occurs later, in addition to standard regeneration under normal operating conditions, and at that time then temporarily decreases the electricity output of the plant, typically at times where demand, and hence electricity selling price, are low.

The value of voluntary capture by-pass and solvent storage options is intrinsic to the electricity system in which the plant operates, and consists of the value of the ancillary services provided to the grid. In other words, it either consists of the value of the ancillary service contract between the plant owner/ operator and the grid operator, or it consists of the profit made over the complete storage and additional regeneration cycle due to the differential between electricity generation costs and electricity selling price, once the value of CO_2 emissions have been externalised.

This chapter proposes an evaluation of new operating modes at part-load for flexible operation with post-combustion capture proposed by Gibbins and Crane (2004a) and Chalmers and Gibbins (2007) on the basis that plants have sufficient power export capacity, either through their pre-existing capability before capture is fitted, or by an investment decision for plants built with capture from the outset. Steam cycle operating options for voluntary absorber by-pass and solvent storage schemes are proposed. Although the analysis is here limited to coal plants, it can also be generalised to gas plant operation.

6.2 Part-load and transient operation

Part-load operation of fossil power plants plays an important role in maintaining the quality of supply in electricity systems. The existing literature on the part-load performance of fossil plants with post-combustion capture is relatively recent and, as far as the candidate is aware, is limited to a small number of publications.

Möller et al. (2007) investigate the off-design performance of NGCC plants with CO_2 capture. The part-load model of the CO_2 capture system is limited to pressure drop correlations through the absorber, a constant regeneration temperature and a constant heat demand for the MEA solvent while the solvent circulation rate is varied. More recently, Linnenberg and Kather (2009) evaluated the performance of a pulverised coal plant at part-load. They notably show that at part-load the increase in air ratio for combustion in the boiler lowers CO_2 concentrations in the flue gas while oxygen concentration rises. The amine plant is modelled and optimised in ASPEN - independently - of the power cycle and the desorber is operated at constant pressure by maintain the IP/LP crossover pressure with a throttling valve at the LP turbine inlet. This last assumption in particular can be challenged. Since the amine plant has been optimised independently of the power cycle the optimum operating mode at part-load is likely to have been missed since there certainly is a trade-off between heat demand and throttling losses in the power cycle. In addition, modification of the reboiler heat transfer regime and reduction of the pressure drop in the extraction line with less steam demand - beneficial for part-load operation - have not been taken into account. These adjustments have a significant influence on the electricity output penalty of the steam cycle, as discussed in Chapter 4 and in section 6.2.2.

In another integration study Pfaff et al. (2009) propose to throttle the LP turbine inlet at base-load to reduce throttling losses at part-load and maintain the reboiler pressure. This assumption can again be challenged. Profits in power generation arise from the difference in the cost of generation and the value of electricity, i.e. in this case the selling price. There is a strong case to maximise profits through efficiency, and thus output, at times where demand and selling price are high. When plants operate at part-load this is typically the consequence of large amounts of power generated at a lower selling price, and thus inefficiencies matter less.

6.2.1 Part-load operation control philosophy

With post-combustion capture the steam turbines are operated at nominal load so that the pressure requirements on the steam side of the reboiler are met. When the boiler load reduces, pressures in the steam cycle drop to reduce the plant power output. There are several ways to control fossil fuel power plant at part-load.

- Fixed boiler pressure control: This method was the first one in use. The steam pressure in the boiler is maintained and a valve at the HP turbine inlet is used to reduce the pressure along the turbine steam expansion path. Valve control induces significant losses in the valve and reductions of the turbine efficiencies, due to large changes of their pressure ratio, but provides fast dynamic response (Cotton, 1994), as illustrated in Figure 6-3.
- Sliding pressure control: The boiler pressure in a once-through boiler (typically supercritical) is reduced by controlling the discharge pressure of the boiler feed pump. This method allows faster start-up procedures (Vitalis, 2006) and by eliminating the valve and maintaining the pressure ratio across the turbine ameliorates plant efficiency at part-load (Cotton, 1994).
- Partial-arc admission: A set of valves control the admission of steam to the turbine nozzles across the circumference or arc of the HP turbine rotor. Sequential closure of the control valves at part-load reduces the mass flow - hence the turbine power output – and lowers losses since only a fraction of the inlet mass flow is throttled.

In practice, plants tend to use both boiler control philosophy (Vitalis, 2006) to trade-off between fast start-up, fast dynamic response at full load and part-load efficiency. Partial-arc admission is a turbine control philosophy, which can be combined with both boiler control method (Silvestri, 1989; Vitalis and Hunt, 2005) to improve further part-load efficiency.

6.2.2 Existing options for power output enhancement

Coal plants

Traditionally pulverised coal plants have relied on the thermal energy stored in the steam drum[23] of sub-critical boilers to temporarily rapidly accommodate small changes in load. Power output is augmented by flashing the saturated water available in the drum into the steam turbines. As boiler technology developed towards once-through supercritical boilers, the evaporation phase of the heat transfer between the boiler water/steam and the flue gas disappeared and steam drums are no longer needed. As a consequence, supercritical plants have a rather limited capacity for thermal energy storage. This has led to some concerns in the power industry, notably in the UK where practical experience of supercritical plants operation is limited, with regards to compliance to a frequency ramp of 0.5Hz over 10 seconds in the UK Grid Code requirement (National Grid, 2009).

Gas plants

Several options are currently being used to temporarily increase the power output of NGCC plants.

The injection of steam or water at the end of the combustor is typically used for NOx abatement but also increases the gas turbine mass flow and hence power output. Additionally, steam or water can be injected at the end of the compressor discharge casing of the gas turbine as well as the combustor. The reduction in firing temperatures is then counterbalanced by higher transfer heat rates to the first stage turbine blades due to the additional heat capacity of water in the flue gas. Typical increases in total power output are of the order of 5-6% for a reduction of heat rate of approximately 5% (Jones and Jacobs, 2002).

Steam turbine output can equally be augmented by 40% independently of the gas turbine - for a net power plant output increase of 15 % - by supplementary firing of natural gas in the heat recovery steam generator (HRSG), at the expense of increased capital cost for oversized components and higher temperature materials (Jones and Jacobs, 2002). Additional generation of steam in the HRSG requires controlling the steam cycle pressures, usually by throttling the HP turbine inlet or by sliding-pressure operation, which leads to a reduction in the plant efficiency. Supplementary firing

[23] Steam drums are large cylindrical vessels located at the top of the boiler in which saturated steam is separated from the steam-water mixture leaving the evaporator tubes and the water is returned to the evaporator.

obviously increases CO_2 concentrations in the flue gas and the amount of CO_2 generated, as well as reducing the power plant efficiency.

Future electricity markets with a large wind, hence intermittent, power component will require that the capability of fossil plants for part-load and transient operation is, at least, maintained, and most likely improved. Unpredictable changes in supply, and thus in fossil power demand then become much more common so it is likely that 'unprepared' ramp rates - i.e. where plants are not standing by with long advance notice to meet a foreseen increase in demand - have to be improved.

6.2.3 Flexible and part-load operation with post-combustion capture

[This section is an edited and extended version of Lucquiaud et al. (2008)]

The analysis presented here is an extension of the pulverised coal plant steam cycle model of Chapter 3 for part-load operation, with the inclusion of the compression system for heat recovery. The plant is a capture-ready retrofit with a floating IP/LP crossover pressure and the ability to return to its initial output. Sliding pressure control is selected as the boiler control philosophy for better part-load performance. The boiler firing load is limited within a range of 70% to 100% of its nominal load so that the solvent regeneration temperature can kept constant. Solvent circulation is adjusted to the flue gas flow rate and complemented by a partial solvent by-pass line, shown in Figure 6-2, taking rich solvent at the outlet of the absorber back to the inlet to keep the liquid gas ratio constant in the desorber. The heat requirement, is then taken as proportional to the amount of CO_2 captured, as shown in (Ziaii et al., 2009). The solvent by-pass line can also maintain stable gas and liquid distribution within the absorber if necessary. Important parameters are given in Table 6-1. The need to provide steam to the solvent reboiler at the required pressure influences the way the steam cycle is operated. In this case it has been assumed that the temperature on the solvent side of the reboiler is maintained and steam is throttled into a valve before entering the LP turbine inlet. Yet two beneficial effects help limiting throttling losses at part-load. First, conduction is the main resistance for heat transfer in the solvent reboiler as both fluids go through a phase change. As less CO_2 needs to be captured at reduced boiler load, the temperature difference across the reboiler steam tubes walls reduces in proportion to the reboiler heat duty. Second, smaller pressure losses in the

extraction line occur with reduced mass flow. This leads to significant savings in the electricity output penalty of the steam cycle at part-load, as was previously highlighted in Chapter 4.

The following analysis illustrates how the flexibility of the floating pressure steam turbine system and the flexibility of the post-combustion capture system can complement part-load operation of the boiler. Controlled variations of the electricity output penalty of the capture and compression system can rapidly increase or decrease the overall plant electricity output, and ameliorate the transient capability of the plant. Several operating modes of the capture and compression system are possible. Their impacts on the operation of the steam turbines are illustrated in Figure 6-4. Figure 6-5 illustrates the plant performance over the range of boiler load considered and with the different modes of operation for the post-combustion capture system, as listed below and described in the subsequent paragraphs:

a) Part-load operation with reduced boiler firing load and 90% capture
b) Voluntary absorber by-pass
c) Solvent storage
d) Additional solvent regeneration

a) Part-load operation with reduced boiler firing load and 90% capture

Plant operators can choose to keep a constant capture level when the boiler firing rate is reduced in order to maintain plant net emissions, in gCO_2 per MWh, at their base-load value. As mentioned previously the LP turbine is then throttled to maintain the reboiler temperature.

b) Voluntary absorber by-pass

As also noted, it is possible to partially, or fully, recover the energy penalty of post-combustion capture, within the limits of the plant generator export capacity, by diverting steam back to the LP turbine and turning off the capture and compression system. Reduced steam extraction rates increases the crossover pressure and it may be necessary to throttle the extraction to avoid overheating the solvent.

The LP turbine response to rapid changes in mass flow from modulation of the steam extraction rate to the reboiler is fast, of the order of tens of seconds. This gives an opportunity for frequency responsive spinning reserve, as illustrated in Figure 6-1, and thus to replace the thermal energy storage of sub-critical plants. The ramp rate of the compressors is of the order of 6%/min (Panesar et al., 2009), i.e. tens of minutes to shut down, and can be used for load following, supplemental and replacement reserve. This additional dynamic flexibility can obviously be added to the boiler ramp

rate, and so it can be expected that future fossil plants fitted with post-combustion capture may be more flexible than current, non-capture systems.

c) Solvent storage

Solvent storage can lower the value of the lost electricity output of CO_2 capture by shifting the loss from periods of high electricity selling prices to periods of low electricity selling prices on a routine basis. It can provide peak load capacity and offer nearly the same electricity output boost benefits (with the exception that the ancillary power for the flue gas blower at the front of the absorber and solvent circulating pumps cannot be recovered) as voluntary absorber by-passing, but avoids additional CO_2 emissions by maintaining lean solvent flow to the absorber.

d) Additional solvent regeneration

Solvent that has previously been stored needs to be regenerated, in addition to the requirement for regeneration of solvent to meet the current operating needs. When the boiler firing load is reduced, there is spare capacity in the regeneration and compression system that can be exploited without necessitating additional investment. Solvent storage and additional solvent regeneration can be combined to give fast control for sustained periods of time of the electricity output in an analogous way to the combination of boiler sliding pressure with turbine partial-arc admission. Plant output can be reduced further by regenerating additional solvent at times where the plant is operated at part-load, i.e. most often at periods of low electricity selling price. The emphasis shifts from delivering the maximum power to buffering between electricity supply and demand, and varying operating strategy to maximise revenues. Regenerating additional solvent during those periods of low operating profits creates the potential for more valuable additional power output at critical times. Haines and Davison (2009) showed that the profitability of solvent storage schemes can pay back the additional capital charge of solvent inventory and storage tanks under different price scenarios, and that profitability increases with storage capacity up to a certain limit. It should be noted, however, that the existing literature assessing the real value of power plant flexibility with absorber by-pass and solvent storage in future electricity markets with CCS is still in its infancy. In general, though, other studies in that area (Chalmers et al., 2009[24]; Alie, 2009; Ziaii et al., 2009) tend to justify the general principles for flexibility.

[24] Co-authored by the candidate

Equally, investments to oversize the solvent reboiler and the compression system, omitted in Haines and Davison (2009), can further increase solvent regeneration levels and accelerate the time to complete regeneration of the stored rich solvent. Aggressive levels of additional solvent regeneration can lower the net revenue loss of the regeneration part of the solvent storage/regeneration cycle (Chalmers and Gibbins, 2007).

The limiting factors for solvent regeneration arise from the operation of the steam cycle deaerator and the minimum mass flow of the LP turbine. At high levels of solvent regeneration it is necessary to increase the pressure of the steam supplied to the deaerator by withdrawing steam upstream. As far as the LP turbine is concerned, a minimum mass flow (typically 10% of the design flow) needs to pass through the LP turbine to cool down the blades and avoid overheating by churning.

So far, the value of potential ancillary service contracts for flexible fossil plants has not been studied. Ancillary services could potentially complement fossil power plant revenues in the future as electricity markets are expected to tend towards having a larger fraction of intermittent renewable energy. State-of-the -art supercritical plants are currently capable of ramp rates in the region of 4% output/min over the entire range of the boiler load (Blum, 2008). Rapid variations of LP turbine output through closure of the valve in the extraction line and opening the throttling valve upstream of the LP turbine could increase plant output by approximately 22% within tens of seconds - compared to the electricity output at full boiler load and a 90% capture level. The ancillary power for compressors, solvent circulating pumps, flue gas blower etc. can also be avoided within minutes, adding another 10% to the electricity net output. This can potentially be done at any boiler load between minimum stable generation and boiler maximum firing load, independently of the boiler ramp rate.

Fossil plants with capture systems that were designed to support faster dynamic response could, in the future, provide similar services to unabated peaking power plants, but without additional CO_2 emissions. For example, if the plant were operated at 70% boiler load and at a 100% additional solvent regeneration rate generating 310 MW_e whilst backing-up wind power capacity, the electricity output could be increased rapidly within tens of seconds to 410 MW_e by stopping additional solvent regeneration and return to solvent regeneration levels equivalent to 90% capture level. The plant output could be increased further to 490 MW_e within another tens of seconds by switching to solvent storage with steam extraction rates reduced to zero, allowing for the boiler load and the compression train to gradually catch up.

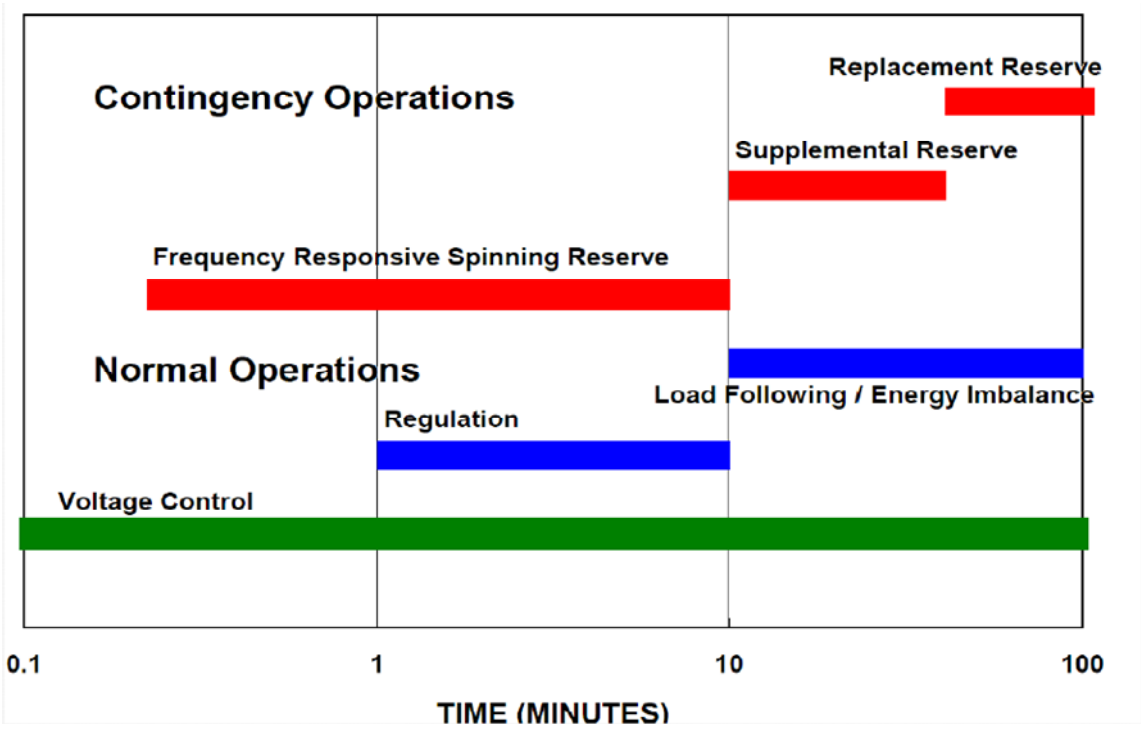


Figure 6-1: Response time requirements of different ancillary services to electricity network (from Kirby et al., 2006)

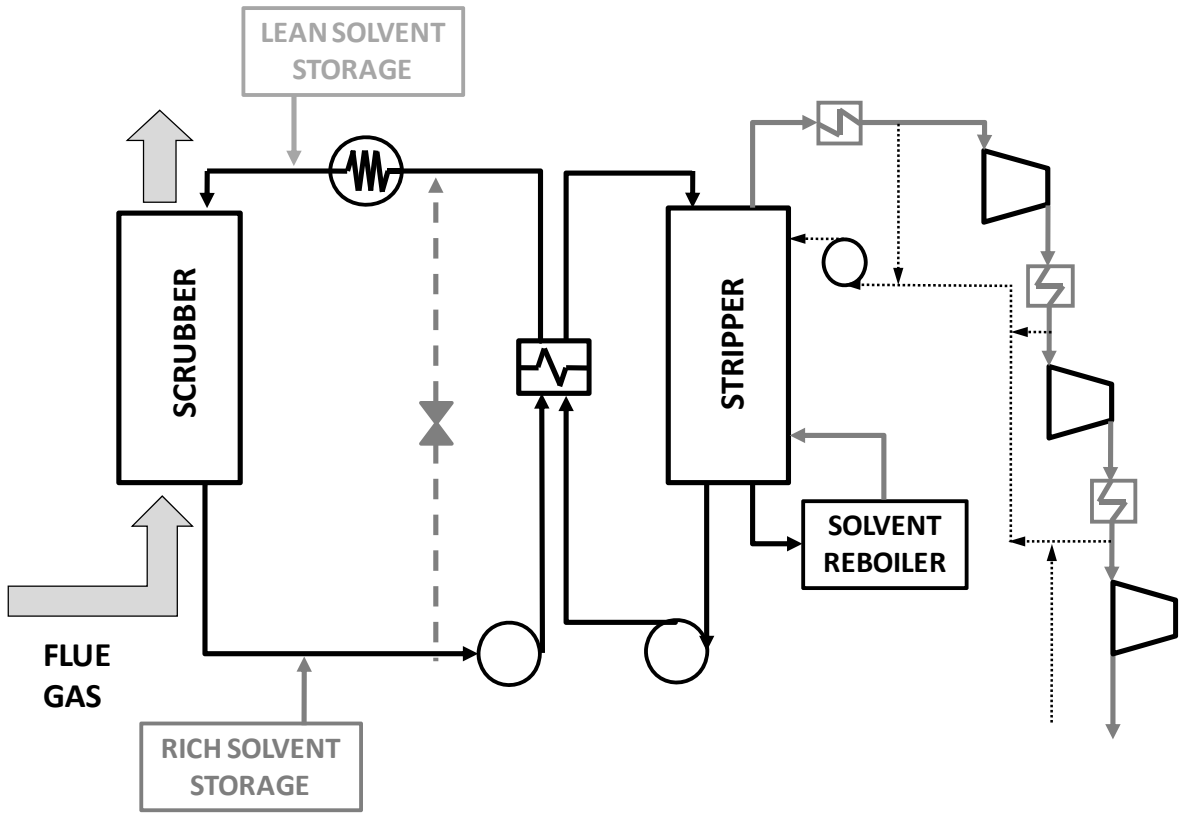


Figure 6-2: Illustrative principles of a solvent storage system

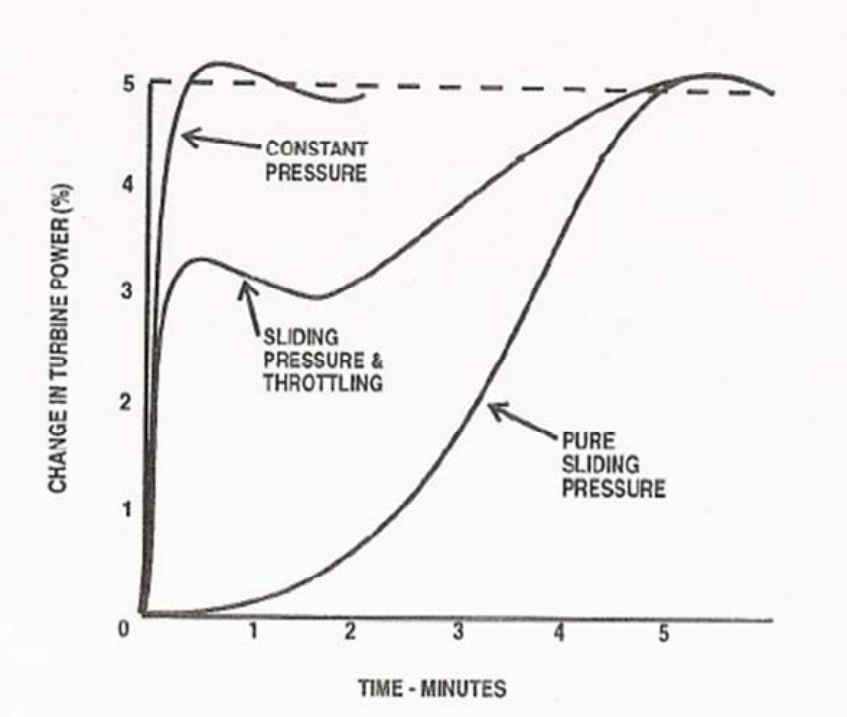


Figure 6-3: Change in power turbine response time for fixed and sliding pressure operation from Cotton (1994)

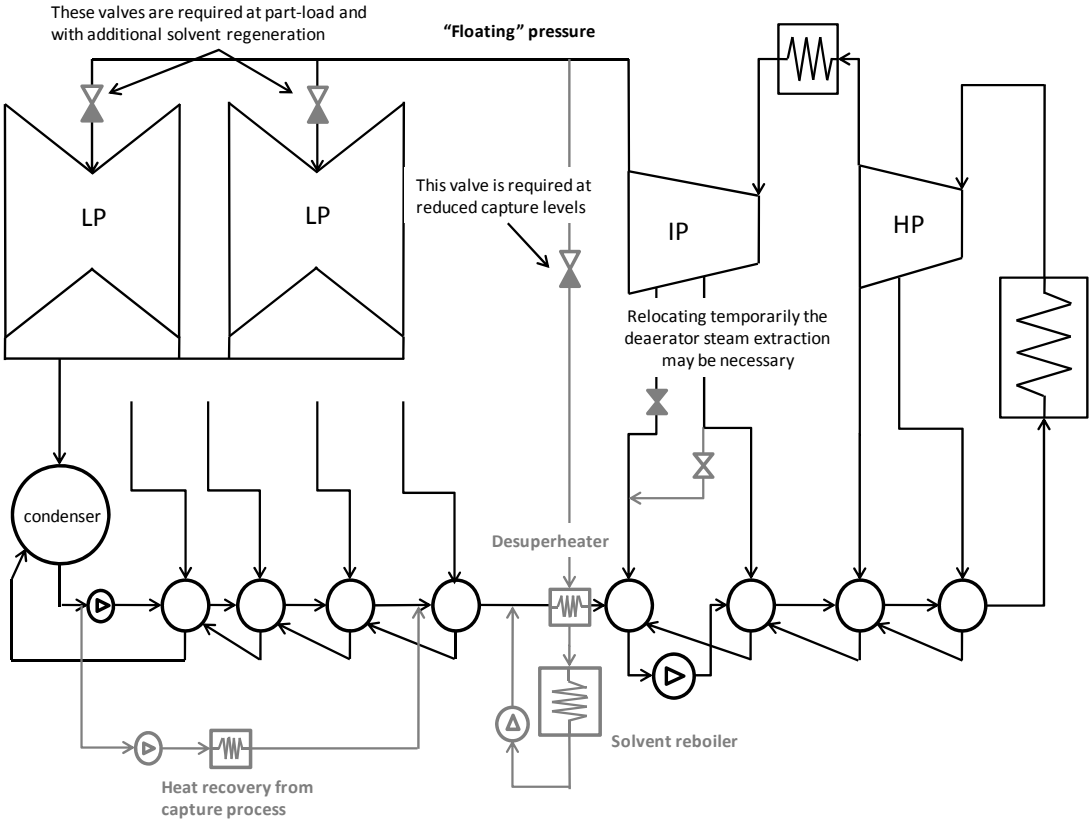


Figure 6-4: Part-load operation of the steam turbines with flexible capture

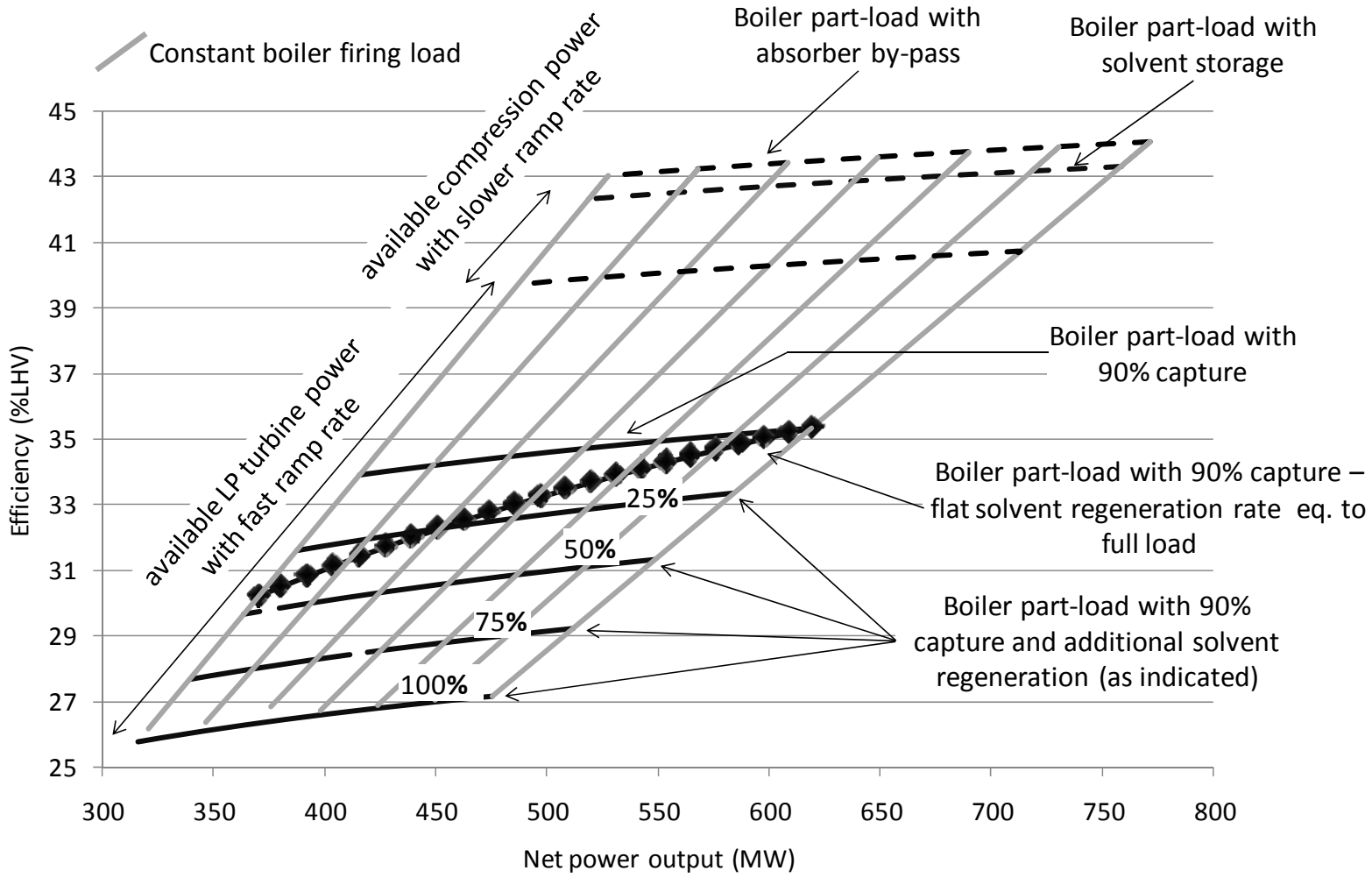


Figure 6-5: Plant part-load performance with flexible operation of the capture system

Table 6-1: Assumptions for part-load operation

Boiler firing load	70-100%	Main reheat and superheater outlet temperatures are maintained at their design load value
Boiler efficiency	94%	Constant across the boiler load range. Constant temperatures at main reheat and superheater outlet
Fuel specific emissions	327 kg/MWh_{th}	As per Chapter 3
Plant control philosophy	Sliding pressure	
Steam turbine design	Floating IP/LP crossover pressure	Valves at LP turbine inlet and in steam extraction line. Possibility to relocate deaerator steam extraction
Capture levels	Variable	90% maximum
Solvent thermal heat of regeneration	3.2 GJ/tCO_2	Kept constant by maintaining the liquid/gas ratio in the desorber
Ancillary power for capture unit	25 kWh/tCO_2	Proportional to the amount of CO_2 captured
Ancillary power for compression	115 kWh/tCO_2	Proportional to the amount of CO_2 captured

7 Conclusions

7.1 Thesis overview

Fossil-fuel reserves are large enough for cumulative carbon emissions to the atmosphere during the 21st century to reach a level that is expected to give a high risk of dangerous climate change (IPCC, 2001). Leaving fossil fuel in the ground at the expense of economic development is probably not a politically-acceptable option for developing countries, while energy security without fossil fuel is a concern worldwide within the very short timescales required for action on climate change. Carbon Capture and Storage (CCS) enables the use of fossil fuels to be decoupled from their associated CO_2 emissions.

Rapid deployment of CCS in power generation requires a two-track approach. Firstly, CCS needs to be developed at scale as quickly as possible, possibly through a staged deployment with subsidised large-scale demonstration projects first, followed by pre-commercial CCS power plants using the lessons learned from these first-of-a kind demonstration projects. In the meantime other plants, if built without CCS, need to be built CO_2 capture ready (CCR): a design concept to ensure that they can be retrofitted, at an acceptable cost, when the capture technology has been demonstrated at the required scale. Although coal has received all the attention so far, CCS on gas power plants may be required sooner than some studies would suggest (Pöyry, 2009) for gas-reliant developed countries such as the UK (Committee on Climate Change, 2009). In 2009 an EU directive enforced carbon capture readiness for new fossil fired power stations above 300MW_e (EU, 2009), including both coal and gas plants. In the UK, the Department of Energy and Climate Change recently released CCR guidelines for new plants (DECC, 2009) while new gas plants given planning consent during 2007 and 2008 were already required to be built as CCR.

Post-combustion CO_2 capture techniques with liquid solvents were historically developed in the oil and gas industry for acid gas removal, with an emphasis on very high levels of removal and operation at constant load.

These techniques now need to be optimised for a different business model where :

- the CO_2 is no longer vented,
- solvents encounter an oxidising environment,
- high levels of capture are still expected, but with an economic balance required on the maximum extent of CO_2 removal,
- the focus is on maximising the plant electrical power output with capture rather than minimising the heat (steam) requirement of the capture system.

Furthermore, because fossil-fired power plants are operated in integrated electricity grids, and because they are required to provide a flexible electricity output to accommodate daily variation of electricity demand and supply, there is some concern that the quality and security of supply from these plants will be affected with CCS. Therefore, they need novel modes of operation matching the flexibility expected of fossil-fired power plant in future electricity systems.

This thesis focuses on each of the two-track approach necessary for a large scale deployment of post-combustion CO_2 capture, on the flexibility of post-combustion capture and develops options for the effective thermodynamic integration of the steam cycles of both pulverised coal and natural gas plants with the post-combustion capture system.

With regards to the first track, this thesis shows that existing coal-fired power plants, which have tended to be disregarded for CCS retrofits, can be suitable candidates for demonstration and pre-commercial projects. The peak steam temperature and pressure have no intrinsic impact on the performance of the capture system. The electricity output penalty for abating the CO_2 emissions of existing low-efficiency plants is, thus, similar to that of more efficient new-build plants, provided that effective thermodynamic integration of the steam cycle and the capture systems is achieved with an appropriate steam turbine retrofit. As a consequence, this widens the choice of retrofit sites beyond what has sometimes hitherto been considered to be the case and makes it easier to identify favourable site-specific conditions, such as ready access to geological storage and adequate on-site space.

As far as the second track is concerned, this thesis shows that pulverised coal plants and natural gas combined cycle plants can be built as CO_2 capture ready (CCR) for post-combustion capture, provided that their power cycle has been designed adequately. Effective thermodynamic integration before capture is fitted, and once the plant is retrofitted, can be achieved at an additional cost of less than 1% of their total capital costs, and for a range of future solvents. The steam cycle can also

be built to suit a range of capture technology and operating requirements throughout the whole operating life of CCR plants. This limits the technology risks related to the relative immaturity of post-combustion capture by allowing CCR plants to change and upgrade their solvent as state-of-the-art capture techniques develop with demonstration and pre-commercial projects.

Finally, most studies on thermodynamic integration have been, so far, limited to base-load operation. This thesis extends the analysis of post-combustion capture systems to part-load operation and identifies specific steam cycles designs for flexible operation of the capture system. It examines novel steam cycle operating regimes where

- the capture system is by-passed at critical periods of time to recover the electricity output penalty of CCS.
- interim storage of solvent and delayed regeneration shifts the electricity output penalty, and thus the financial penalty of CCS, from periods of high operating profit to periods of low operating profit
- rapid transitions between power plant loads are possible by adjusting the levels of solvent storage and regeneration

7.2 Summary of findings

This section provides a summary of the most significant observations from each chapter and draws some conclusions on the design of steam turbines for post-combustion capture.

Effective thermodynamic integration for new-build and retrofits

The methodology proposed in this thesis is to evaluate the performance of a capture system on the basis of the electricity output penalty, as defined below, independently of the fuel composition.

Efficiency penalty = Fuel specific emissions * Electricity Output Penalty

Efficiency penalty	(MWh_e/MW_{th}) or (% point)
Fuel specific emissions	($kgCO_2/MWh_{th}$)
Electricity Output Penalty	(kWh_e/tCO_2)

Six rules for effective thermodynamic integration of the capture and compression system with the power cycle are established. They are based on initial suggestions by Gibbins et al. (2004), which have been updated (see italics) accordingly to the findings of this study.

1. *For new build projects*, add heat to the steam cycle at as high a temperature as possible (i.e. be prepared to use best available steam conditions if commercially justified). *For retrofits to existing plants, though, the penalty per tonne of CO_2 emissions avoided is independent of the steam conditions.*
2. Reject heat from the steam cycle, in the steam extracted for solvent regeneration, at a temperature *as close as possible to the temperature of regeneration of the solvent. Optimise solvent temperature of regeneration to minimise the sum of the overall electricity output of the capture system and the compression system.*
3. Produce as much electricity as possible *from the power cycle (i.e. be prepared to use additional turbines for retrofit projects if commercially justified)* and from any additional fuel used, consistent with rejecting heat at the required temperature for solvent regeneration.
4. Make use of waste heat from CO_2 capture and compression in the steam cycle.
5. *Anticipate* the use of the latest solvent developments *throughout the whole operating life of the plant.*
6. Exploit the inherent flexibility of post-combustion capture *to a) shift the financial penalty of capture from high to low operating profit periods of time, and b) accelerate ramp rate during transient operation if necessary*

For state-of-the-art solvent and state-of-the-art thermodynamic integration at the time of writing the electricity output penalty of post-combustion capture is of the order of 257-312 kWh/tCO_2 for pulverised coal plants, and of the order of 400-405kWh/tCO2 for natural gas combined cycle plants.

Assessment of solvent developments

The focus on solvent development on the sole basis of a low thermal heat of regeneration is misleading. Solvent performance needs to be assessed on a rigorous basis, maximising the plant net electrical power output with capture rather than minimising the heat (steam) requirement of the capture system. This requires a simultaneous focus on:

- Thermal energy of regeneration
- Thermal stability, which determines the reboiler operating temperature, and by extension a) the 'value' of the steam extracted for solvent regeneration, b) the maximum temperature available for heat recovery for boiler condensate heating
- Vapour-liquid-equilibrium under desorber conditions, which determines the electricity output penalty of the compression system
- Solvent loading capacity, which determines the electricity output penalty of the ancillary power of the capture process

Design principles for capture-ready steam turbines

Ideal design principles for CO_2 capture-ready plant are established.

1. The efficiency of a CCR plant before capture is fitted should be the same as the efficiency of a state-of-the-art standard plant designed with no consideration of capture ready principles.

2. The efficiency of a retrofitted CCR plant should be the same as a new plant built with CCS from the start – and with the same steam conditions – at the time when the retrofit occurs.

3. There should be no up-front additional costs for a CCR plant compared with a state-of-the-art standard plant.

4. The retrofitted power plant should have the ability to operate without capture.

5. The CCR plant should allow for future technology developments and when the capture technology is upgraded the retrofitted plant should have the same efficiency as a CCS plant – with the same steam conditions – built with perfect foreknowledge of what the upgrade technology would be.

It should be noted that close and simultaneous matching of these principles may not be desirable in practice in order to achieve satisfactory operability, and that trade-offs between principles may be necessary to minimise costs throughout the plant operating life.

- Several studies (Sekar, 2005; Bohm et al., 2007; Liang et al., 2009) highlighted the absence of strong economic drivers to make large pre-investment for capture-ready designs worthwhile and pointed out that, beyond space and access, significant capital pre-investments do not appear to be justified by the cost reductions that can be achieved when capture is added. Because of the time value of money only minimal essential up-front capital cost options, with an acceptable loss in the maximum power output of the plant when it is fitted with CCS, and with little or no effect on plant performance prior to retrofit are acceptable.
- The timing of a retrofit determines the approach to upgradability. In order to limit technology risks it may be acceptable to:
    - trade-off performance with capture against solvent upgradability for plants, which are likely to be retrofitted relatively 'early', such as coal plants in developed countries
    - avoid committing the plant 'too early' to a range of temperature of regeneration by specifically designing the steam cycle with an elevated pressure for steam extraction, and subsequently retrofit with tailored-design back-pressure turbines if necessary. This approach may be justified for gas plants in developed countries, and coal plants in emerging economies that do not yet have a new build CCS programme.

Steam cycle options for upgradeable capture-ready pulverised coal plants

It is possible to achieve ideal performance both before and after retrofit with a clutched turbine retrofit option, provided the solvent is known in advance. This approach requires, however, significantly higher up-front costs in the order of 3 per cent additional capital costs. Further it might have difficulty in switching rapidly to operation without the capture plant in case of an unexpected outage of the CO_2 capture unit, and in taking advantage of any improvements in solvent regeneration energy requirements. Economic analysis (Liang et al., 2009) also suggests that the option value of retrofitting capture is not sufficient to justify the additional investment in a clutched LP turbine.

A throttled LP turbine retrofit option and a floating IP/LP crossover pressure turbine options require less than 1 per cent additional total capital cost at the expense of a small electricity output penalty, in the range of 4-10 kWh/tCO_2 when capture is retrofitted (compared with the clutched turbine retrofit option that is retrofitted with the expected solvent). Both the throttled and floating options, or a hybrid mixture of the two, have significant potential to perform well for a wide range of solvent energy requirements. Hence, they are able to cope with the inevitable uncertainties with respect to future capture system developments. The performance of the throttled LP turbine option can, however, only be improved with solvents that have a similar, or lower, temperature of regeneration. The floating pressure option can be upgraded, to some extent, with solvents with a lower or higher temperature of regeneration.

A fourth option, with an elevated IP/LP crossover pressure and a retrofit with two back-pressure turbines, avoids committing the plant too early to a specific range for the temperature of regeneration, at the expense of additional capital costs for the two turbines when the plant is retrofitted.

Steam cycle options for upgradeable capture-ready natural gas combined cycle plants

Retrofit options with a separate ancillary boiler are thermodynamically inefficient and can more than double the fuel consumption penalty per unit CO_2 abated compared to retrofit with steam extraction from the power cycle.

A CCR steam cycle option with provision for two back-pressure turbines withdrawing steam from an elevated steam pressure IP/LP crossover, and a CCR steam cycle option with a tailored-design pass-out back-pressure turbine withdrawing steam at the reheater outlet require limited additional initial capital cost for capture-readiness, at the expense of a minimal electricity output penalty, in the range of 2-4 kWh/tCO_2 when capture is retrofitted (compared with replacement of the LP turbine cylinder).

Because of the technology immaturity of post-combustion capture and since, in most countries, CCR gas plants are likely to be retrofitted after demonstration and pre-commercial projects are implemented on coal plants, these two options may allow for retrofit with radically different improved solvents.

Steam cycle options for retrofitting existing coal units

Low efficiency pulverised coal plants can achieve good performance with capture, at an electricity output penalty similar to new-build units, through effective thermodynamic integration with appropriate steam turbine retrofit solutions, largely irrespective of the initial steam cycle design. Two steam turbine retrofits are proposed, both of which allow good operability, a return to maximum power output when needed and are also suitable for subsequent modification to take advantage of solvent improvements:

- the addition of back-pressure turbines at the LP turbine inlet and in the steam extraction line, where throttling losses would normally occur, and/or
- the reblading of the very last stages of the intermediate pressure turbine of the power cycle.

The efficiency penalty is independent of the steam peak pressure and temperature, but will be affected by site-specific parameters, such as the cooling system and the composition of the coal burnt – notably carbon and moisture contents. Additionally, having adequate space and access on site will help to reduce the capital costs of retrofit projects, while location and access to geological storage will obviously affect the feasibility and the overall costs of transport and geological storage.

Steam cycle options for operating flexibility

This thesis presents the operating envelope of a pulverised coal plant with post-combustion capture, under different boiler firing load and a range of capture levels, solvent storage and additional regeneration. It highlights that appropriate steam cycle design and operation is critical for flexible operation of the capture system. The inherent flexibility of the capture system and of the steam cycle can be used to significantly accelerate the overall ramp rates of the plant. The loss of electricity output due to steam extraction can be recovered within tens of seconds by rapidly diverting steam from the solvent reboiler to the low pressure turbine, and vice-versa, without additional CO_2 emissions with a solvent storage scheme.

7.3 Limitations and recommendations for future work

Time was not available within the scope of this study to address all the issues of post-combustion capture that have been raised. The following discusses some of the limitations of the work presented here and possible future programmes of work to address them.

(a) There are a number of possible permutations combining the concepts for capture-ready steam turbines presented in this thesis. In practice, plant developers may develop steam cycle with hybrid systems featuring several of the characteristics of the basic concept presented here. For example, the implications of clutched turbine systems combined with a floating IP/LP crossover pressure for satisfactory part-load operation have not been explored.

(b) Part-load performance of the power plant/capture and compression system has been assessed over a limited range of boiler firing rates (70-100%). A rate-based model of the capture process, integrated with power cycle and compression train models, would allow the following studies:

- Evaluate performance down to minimal stable generation, by evaluating trade-offs between throttling losses in the steam cycle and variations of the thermal energy of regeneration of the solvent and compression power at reduced reboiler temperatures.
- Identify specific design strategies to mitigate changes in flue gas volumes, liquid/gas ratios in the columns, temperature profiles, etc.
- Explore the consequences of solvent storage; the effect of additional regeneration with partial absorber by-pass on the operation of the absorber, the desorber and compressors need to be explored.
- Identify critical pieces of equipment for future solvent upgrade, such as the absorber, the first compressor stage etc.

(c) The financial implications of solvent storage schemes and voluntary absorber by-pass need to be assessed under conditions that may prevail in future carbon-constrained electricity markets. Preliminary studies (Chalmers and Gibbins, 2007; Haines and Davison, 2009) have estimated their value and potential benefits, but have reached limited conclusions since the implications for power plant operability and the need to oversize the plant power export capacity, i.e. generator, condenser and low pressure turbine, have not been accounted for new-build projects.

(d) Power plants are subjected to volatility in electricity markets, daily changes in ambient conditions, coal composition, operating parameters, and are capable of adjusting their output quickly. On the other hand, achieving stable operating conditions in the post-combustion capture system may take of the order of hours (Ziaii, 2009), because of relatively long circulation times – of the order of 15-30min - between the absorber and the desorber. Further work is needed to develop dynamic models for transient operation of the capture system and account for the different ramp rates of various parts of the integrated process. Operating regimes where the capture system response is lagging behind the power cycle need to be characterised, and strategies for effective operation of the post-combustion capture system, taking into account the tradeoffs possible with the electricity output penalty, need to be developed.

(e) Site specific factors need to be factored in to gain a greater understanding of project-specific costs under varying geographic and market conditions. For example, concerns have been raised about the water usage of post-combustion capture systems using wet cooling towers in water-deprived geographic areas. Further work on optimisation of the overall cooling system, possibly by trading priority for low temperature cooling between solvent requirements at the absorber inlet, the power cycle condenser and the compression intercoolers, is necessary to optimise overall cooling requirements and minimise overall water loss, including from the absorber tower.

(f) The addition of post-combustion capture to power systems changes the potential for thermodynamic optimisation of the overall system. Capture and compression reject heat at temperatures above ambient conditions. Novel systems with heat pumps and bottoming cycles may be able to take advantage of these heat sources. In addition, solar thermal power could be employed for solvent regeneration and boiler condensate feed water heating, and integrated with a solvent storage system to smooth daily variations of solar energy.

(g) Finally, further work is needed to fully characterise solvents for power plant applications in addition to 'standard' VLE and other thermodynamic properties, notably:

- Environmental impacts of the solvent and volatile degradation products (affecting absorber design and operation),
- Thermal stability (affecting reboiler temperatures),
- Corrosion issues and compatibility with materials (solvent concentrations and possibly temperatures),
- Costs of solvent manufacturing (affecting solvent storage costs).

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Appendix A: Description of the implementation of steam cycle model in gPROMs for pulverised coal capture-ready plant modelling

gPROMS is an equation-oriented modelling system used for building, validating and executing first-principles models within a flowsheeting framework. System cycle models are constructed in gPROMS by writing down the fundamental thermodynamic equations that govern the process, given below.

Turbine expansion line modelling

For a given turbine the steam expansion is modelled as a stated number of consecutive expansions, representing the consecutive turbine stages. It is assumed that the isentropic stage efficiency is identical for each stage of a given turbine. This implies that the geometry of each stages is identical, a current design practice.

Steam is extracted for feed water heating at the end of the expansion of a turbine stage, taking into account stage reheat factors.

Under wet conditions in the LP turbine, “Baumann’s rule” is followed assuming of a 1% reduction in stage efficiency for 1% of wetness (Kearton 1944)

Exit losses at LP turbine outlet

The blade angle of the last stage of the LP turbine needs to be determined without steam extraction in order to calculate the change in exit losses when steam extraction rate for solvent regeneration varies. The procedure is described below:

LP steam turbines are double flow axial turbines with backward blades. Neglecting the swirl of the steam flow exiting the LP turbine, the steam is assumed to leave the rotor parallel to the turbine shaft. The velocity triangle can then be determined (See Appendix 2 for a more detailed discussion of velocity triangles), based on the frequency of the grid (50 Hz here) and the the hub to tip of the last blade, given in Table A1.

Feed water heaters

Feed water heaters are modelled by performing an enthalpy balance between the steam taken from the turbine and the boiler feed water flow. The steam flow is calculated by iteration so that the two following constraints are respected:

- the temperature difference between the “hot” condensate and the steam saturation temperature is fixed
- the temperature difference between the “cold” condensate and the steam leaving the heat exchanger is fixed

The respective values for HP and LP feed water heater temperature differences are given in Table A1.

Condenser heat exchange

A model of the heat transfer exchange in model was implemented for operation at reduced steam flow rate, when steam is extracted for capture. Steam is condensing on one side of the condenser, therefore it is reasonable to assume that conduction is the main driver of heat exchange in the condenser. Typical values for cooling water mass flow, inlet and outlet temperature taken from Babcock & Wilcox Company (1992) were used to calculate the condenser cooling load on the water side and the heat transfer coefficient in $kg*m^2/(s^3*K)$.

Solvent reboiler heat exchange

In the solvent reboiler the steam extracted condenses while the solvent boils on the other side. Conduction is the main driver for heat transfer.

Steam extraction pressure optimisation

gPROMS multi-parameter optimisation solvers were used to maximise the gross power output of the steam cycle against the steam extraction pressure for feed water heating.

Table A1: parameters of pulverised coal plant capture-ready steam cycle model

COAL PROPERTIES	
Fuel specific emission ($kgCO_2/MWh_{th}$)	327
BOILER PARAMETERS	
Boiler efficiency (%)	94
Main steam outlet pressure (bar)	290
Main steam outlet temperature (K)	873.15
Main steam outlet mass flow (kg/s)	625.1
Reheater temperature outlet (K)	839.15
Main steam pressure drop (bar)	35
Reheater pressure drop (bar)	4.5
GENERATOR	
Generator efficiency (%)	98.8
Generator output without capture (MW)	850
TURBINES	
HP turbine	
Steam extraction pressure and enthalpy (bar – kJ/kg)	85.79 – 3126.82; 64.5 – 3060.1
Outlet pressure and enthalpy (bar – kJ/kg)	64.5 – 3060.1
IP turbine	
Steam extraction pressure and enthalpy (bar – kJ/kg)	21.8 - 3374.0; 12.7 - 3220.9
Outlet pressure and enthalpy (bar – kJ/kg)	4.4 - 2965.8
Number of turbine stages	27
Degree of reaction of turbine stages	50%
Enthalpy drop per stage before capture (kJ/kg)	25.8
Isentropic stage efficiency before capture (%)	90
LP turbine	
Steam extraction pressure and enthalpy (bar – kJ/kg)	3.1 - 2895.1; 1.25 - 2730.2; 0.41 - 2565.3; 0.16 - 2447.5
Outlet pressure and enthalpy (bar – kJ/kg)	0.045 - 2306.2
Number of turbine stages	29
Degree of reaction of turbine stages	50%
Enthalpy drop per stage before capture (kJ/kg)	24.24
Isentropic stage efficiency before capture (%)	90

Number of LP cylinders	2
Steam exit velocity (m/s)	200
Last stage hub to tip ratio	2.11
Last stage steam outlet angle to rotor axis (º)	0
CONDENSER	
Approach temperature (ºC)	3
Sea water cooling temperature (ºC)	15
FEED WATER HEATING SYSTEM	
Deaerator	
Steam pressure drop (fraction of inlet steam pressure)	0.06
Low pressure feed water heaters	
Steam pressure drop (fraction of inlet steam pressure)	0.02
Pressure drop on water side (bar)	2.5
Temperature difference at water inlet (K)	8
Temperature difference at water outlet (K)	3
High pressure feed water heaters	
Steam pressure drop (fraction of inlet steam pressure)	0.02
Pressure drop on water side (bar)	2.5
Temperature difference at water inlet (K)	3
Temperature difference at water outlet (K)	-1.5 (water is hotter than steam saturation temperature)
PUMPS	
Boiler feed pump efficiency	0.85
Condenser outlet pump efficiency	0.75
Reboiler condensate pump efficiency	0.75
REBOILER	
Steam pressure drop (fraction of inlet steam pressure)	0.05
Pressure drop across extraction line (bar)	0.5
Solvent heat of regeneration (kJ/kgCO2)	3.2
Capture level (%)	90
HEAT RECOVERY SYSTEM FROM CAPTURE AND COMPRESSION UNITS	
Condensate outlet temperature (K)	393.15
Pressure drop (bar)	2.5
Fraction of condenser mass flow through heat exchanger	0.9

ANCILLARY POWER	
Ancillary power for power generation (kW_e/MW_{th})	42.3

Table A2: Comparison between gPROMS model and GATECYCLE for the steam cycle of Figure 3-11

HP turbine parameters	
mass flow (kg/s)	158.1
Pressure inlet/outlet (bar)	125/31.85
Temperature inlet/outlet (ºC)	550/346.85
IP turbine parameters	
mass flow (kg/s)	177.74
Pressure inlet/outlet (bar)	25/5.29
Temperature inlet/outlet (ºC)	560/327.11
LP turbine parameters	
mass flow (kg/s)	200.3
Pressure inlet/outlet (bar)	5.29/0.05
Temperature inlet (ºC) – Enthalpy outlet (kJ/kg)	323.12 – 2411.3
Exit velocity (m/s)	271.71
Gross work output (MW)	
GATECYCLE	276.65
gPROMS	276.65

Appendix B: Turbine stage modelling

This appendix provides background information and the equations necessary for the modelling of steam turbine stages under off-design conditions with a reduced mass flow or a modified pressure ratio.

Definition of the velocity triangle

The expansion into a steam turbine happens through consecutives axial stages. Each turbine stage comprises two rows of blades: a row of fixed guide vanes or nozzles, the stator row, mounted in the casing, which converts potential energy into kinetic energy, and a row of moving blades or buckets, the rotor row, attached to the turbine rotor, which converts kinetic energy into mechanical work. Steam enters the stator with an absolute velocity c_1 at an angle α_1 and accelerates to an absolute velocity c_2 at an angle α_2, as shown in Figure A1. The rotor inlet *relative* velocity w_2, at angle β_2, is found by subtracting, vectorially, the blade speed U from the absolute velocity c_2. The relative flow within the rotor accelerates to velocity w_3 at an angle β_3 at rotor outlet; the corresponding absolute flow (c_3, α_3) is obtained by adding, vectorially, the blade speed U to the relative velocity w_3.

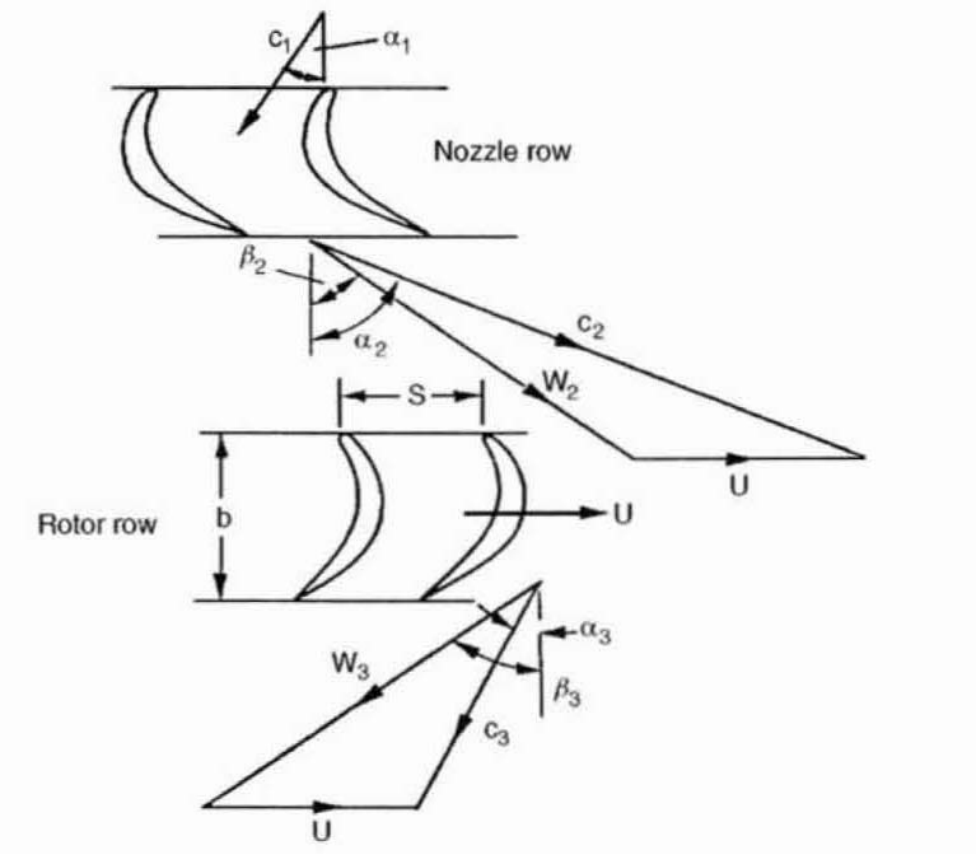


Figure A1: Steam velocity triangle in a turbine stage, Source Dixon (1966)

Degree of reaction

The classification of different types of axial turbine is described by the degree of reaction. Several definitions for the degree of reaction are available. In this work the definition adopted is the ratio between the static enthalpy drop in the rotor to the static enthalpy drop in the stage.

$$R = \frac{h_2 - h_3}{h_1 - h_3} \tag{A1}$$

R	-	Degree of reaction
c_2	m/s	Steam absolute velocity at rotor inlet
h_1	kJ/kg	Steam static enthalpy at stator inlet
h_2	kJ/kg	Steam static enthalpy at stator outlet
h_3	kJ/kg	Steam static enthalpy at rotor outlet

The degree of reaction is, in effect, a statement of the stage flow geometry

Steam velocity at rotor inlet

The steam velocity C_2 at the rotor inlet is related to the degree of reaction, as follows

$$c_2 = \sqrt{2 * (1 - R) * (h_1 - h_3)} \tag{A2}$$

R	-	Degree of reaction
c_2	m/s	Steam absolute velocity at rotor inlet
h_1	kJ/kg	Steam static enthalpy at stator inlet
h_3	kJ/kg	Steam static enthalpy at rotor outlet

Stage adiabatic efficiency

The stage efficiency is, in this work, the *total-to-static isentropic* efficiency η_{ts} of the two rows of blades and is defined as the ratio between

- the actual mechanical work output of the stage, generated by a change in momentum and enthalpy of the steam in the stage, and
- the mechanical work that would be generated if the steam expansion were reversible, i.e. if no entropy was created, when operating to the same outlet pressure

It can be approximated by

$$\eta_{ts} = \frac{h_1 - h_3}{h_1 - h_{3ss} + \frac{1}{2} * c_3^2} \quad \text{(A3)}$$

η_{ts}	-	Total-to-static isentropic efficiency
h_1	kJ/kg	Steam static enthalpy at stator inlet
h_3	kJ/kg	Steam static enthalpy at rotor outlet
h_{3ss}	kJ/kg	Steam static enthalpy at rotor outlet after isentropic expansion in the rotor and the stator
c_3	m/s	Steam absolute velocity at rotor outlet

Relation between stage loading and stage efficiency

The loading of a turbine stage, defined as the ratio between the rotating blade velocity U and the steam velocity at the outlet of the stator C_2, can be related to the total-to-static efficiency, as follows:

a) Zero reaction stage

For a zero reaction stage the stage total-to-static efficiency is given as (Dixon, 1966)

$$\eta_{ts} = 4 * \frac{U}{c_2} * (\sin\alpha_2 - \frac{U}{c_2}) \quad \text{(A4)}$$

η_{ts}	-	Total-to-static isentropic efficiency
U	m/s	Rotor radial velocity
c_2	m/s	Steam velocity at stator outlet
α_2	rad	Steam velocity angle at rotor inlet (measured from the axial direction)

The maximum value of the efficiency is attained when

$$\frac{d\eta_{ts}}{d(\frac{U}{c_2})} = 0 \quad \text{(A5)}$$

i.e. when the stage loading is related to the steam rotor inlet angle α_2 by

$$\frac{U}{c_2} = \frac{\sin\alpha_2}{2} \quad \text{(A6)}$$

b) 50% reaction stage

For a 50% reaction stage the total-to-static efficiency is (Dixon, 1966),

$$\eta_{ts} = \frac{U}{c_2} * (2\sin\alpha_2 - \frac{U}{c_2}) \quad \text{(A7)}$$

The maximum value is attained when

$$\frac{U}{c_2} = \sin\alpha_2 \quad \text{(A8)}$$

Enthalpy drop per stage

Steam turbine design common practice is to design turbine stages for a constant change in stagnation enthalpy at every radius (Wilson and Korakianitis, 1998).

Flow characteristics

One of the earliest attempts to assess the flow variation of a multistage turbine is credited to Stodola (1927), who formulated the "ellipse law". This expression has been used for many years in steam turbine practice to predict steam turbine behaviour under different conditions (Cotton, 1994). It relates the mass flow of turbine stages to their pressure ratio, and inlet temperature

$$m * \frac{\sqrt{T_0}}{p_0} = k * \left(1 - (\frac{p_1}{p_0})^2\right)^{1/2} \quad \text{(A9)}$$

m	kg/s	Stage inlet mass flow
T_0	K	Stage inlet temperature
p_0	Pa	Stage inlet pressure
P_1	Pa	Stage outlet pressure
k	$kg*K^{1/2}*Pa^{-1}$	Stage swallowing capacity

Appendix C: Summary of parameters for natural gas capture-ready plant modelling

POWER PLANT ASSUMPTIONS	
Fuel input (MW_{th})	1396
Ancillary power for power generation (kW_e/MW_{th})	17.2
Gas turbine electrical output (MW_e)	520
Capture level (%)	85
Fuel specific emissions ($kgCO_2/MWh_{th}$)	210.7
Electricity output penalty for ancillary and compression power (kWh/tCO_2)	216
Solvent thermal energy of regeneration (GJ/tCO_2)	3.2
Generator efficiency (%)	97.6
HEAT RECOVERY STEAM GENERATOR	
HP SUPERHEATER	
outlet pressure (bar)	125
outlet temperature (ºC)	550
outlet temperature mass flow (kg/s)	158.1
IP SUPERHEATER	
outlet pressure (bar)	27
outlet temperature (ºC)	560
outlet temperature mass flow (kg/s)	177.7
LP SUPERHEATER	
outlet pressure (bar)	5.3
outlet temperature (ºC)	288
outlet temperature mass flow (kg/s)	20.4
HP/IP GLAND LEAKAGE	
outlet pressure (bar)	125
outlet temperature (ºC)	550
outlet temperature mass flow (kg/s)	2.1
TURBINES	
HP TURBINE	
outlet pressure (bar)	31.85

outlet temperature (ºC)	347.5
IP TURBINE	
Number of stages	15
Degree of reaction	50%
Enthalpy drop per stage (kJ/kg)	31.55
Stage isentropic efficiency without capture (%)	89.7
LP TURBINE	
Number of stages	15
Degree of reaction	50%
Enthalpy drop per stage (kJ/kg)	49.07
Stage isentropic efficiency without capture (%)	89
Number of LP cylinders	1
Steam exit velocity (m/s)	271.7
Last stage blade length (m)	1
Last stage steam outlet angle to rotor axis (º)	0
BACK PRESSURE TURBINE	
Isentropic efficiency of each group of stages (%)	90
CONDENSER	
Approach temperature (ºC)	3
Sea water cooling temperature (ºC)	15
REBOILER	
Steam pressure (bar)	3.24
Pressure drop across extraction pipe (bar)	0.26

Appendix D: Summary of parameters for Chapter 4 steam cycle retrofit model

COAL PROPERTIES	
Fuel specific emission ($kgCO_2/MWh_{th}$)	340
BOILER PARAMETERS	
Boiler efficiency (%)	94
Main steam outlet pressure (bar)	242
Main steam outlet temperature (ºC)	565
Main steam outlet mass flow (kg/s)	548.9
Reheater temperature outlet (ºC)	566
Main steam pressure drop (bar)	60
Reheater pressure drop (bar)	4.68
GENERATOR	
Generator efficiency (%)	98.8
TURBINES	
HP TURBINE	
Steam extraction pressure and enthalpy (bar – kJ/kg)	65.28 – 3077; 46.78 – 3004
Outlet pressure and enthalpy (bar – kJ/kg)	46.78 - 3004
IP TURBINE	
Number of turbine stages	8
Degree of reaction of turbine stages	0
Enthalpy drop per stage before capture (kJ/kg)	53.1, 53.1, 53.1, 53.1, 46.1, 46.1, 46.1, 46.1
Isentropic stage efficiency before capture (%)	89.2, 89.2, 89.2, 89.2, 90.2, 90.2, 90.2, 90.2
IP/LP crossover pressure loss (fraction of inlet steam pressure)	0.98
LP TURBINE	
Steam extraction pressure and enthalpy (bar – kJ/kg)	4.6 – 2989.6; 1.2 – 2735.8; 0.53 – 2609.5; 0.23 – 2516.9

Number of LP cylinders	2
Last stage exhaust area (m^2)	7.518
Last stage blade length (m)	0.9055
Last stage steam outlet angle to rotor axis (º)	0
BACK PRESSURE TURBINE	
Isentropic efficiency (%)	90
CONDENSER	
Pressure (bar)	0.1013
Inlet steam enthalpy (kJ/kg)	2430.9
FEED WATER HEATING SYSTEM	
DEAERATOR	
Steam pressure drop (fraction of inlet steam pressure)	0.05
LOW PRESSURE FEED WATER HEATERS	
Steam pressure drop (fraction of inlet steam pressure)	0.05
Pressure drop on water side (bar)	1.6
Temperature difference at water inlet (K)	5.5
Temperature difference at water outlet (K)	2.8
HIGH PRESSURE FEED WATER HEATERS	
Steam pressure drop (fraction of inlet steam pressure)	0.03
Pressure drop on water side (bar)	3.5
Temperature difference at water inlet (K)	5.6
Temperature difference at water outlet (K)	0
PUMPS	
Boiler feed pump efficiency	0.85
Condenser outlet pump efficiency	0.8
Reboiler condensate pump efficiency	0.8
REBOILER	
Steam pressure drop (fraction of inlet steam pressure)	0.05
Solvent heat of regeneration (kJ/kgCO2)	3.2
Steam pressure (bar)	3.24
Capture level (%)	90

HEAT RECOVERY SYSTEM FROM CAPTURE AND COMPRESSION UNITS	
Condensate outlet temperature (K)	393.15
Pressure drop (bar)	1.6
Fraction of condenser mass flow through heat exchanger	0.9
ANCILLARY POWER	
Ancillary power for power generation (kW_e/MW_{th})	42.3
Ancillary power for capture and compression (kWh/tCO_2)	125

Appendix E: Summary of parameters of steam cycle model from Lucquiaud and Gibbins (2009)

COAL PROPERTIES		
Fuel low heating calorific value (MJ/kg)	25.87	
Fuel composition – proximate analysis	Coal dry and ash free	78.3%
	Ash	9.5%
	Moisture	12.2%
Fuel composition – ultimate analysis	Carbon	82.5%
	Hydrogen	5.6%
	Oxygen	9.0%
	Nitrogen	1.8%
	Sulphur	1.1%
	Chlorine	0.03%
BOILER PARAMETERS		
Boiler efficiency (%)	94	
Main steam outlet pressure (bar)	290	
Main steam outlet temperature (ºC)	620	
Reheater temperature outlet (ºC)	620	
Main steam pressure drop (bar)	60	
Reheater pressure drop (bar)	4.5	
Boiler condensate inlet temperature (ºC)	300	
GENERATOR		
Generator efficiency (%)	98.8	
TURBINES		
HP turbine		
Inlet/Outlet pressure (bar)	290/64.5	
Isentropic efficiency (including inlet valve losses) (%)	90	
Number of stages	6	
IP turbine		
Inlet/Outlet pressure (bar)	60/6.7	
Isentropic efficiency (including inlet valve losses) (%)	93	
Number of stages	10	

Idealised expansion line	
Inlet/Outlet pressure (bar)	6.7/3.6
Isentropic efficiency (including inlet valve losses) (%)	92
Number of stages	12
LP turbine	
Inlet/Outlet pressure (bar)	3.6/40mbar
Isentropic efficiency (including inlet valve losses) (%)	91
Number of stages	10
Steam exit velocity (m/s)	250
Last stage hub to tip ratio	2.11
FEED WATER HEATING SYSTEM	
Deaerator	
Steam pressure drop (fraction of inlet steam pressure)	0.06
Low pressure feed water heaters	
Steam pressure drop (fraction of inlet steam pressure)	0.02
Pressure drop on water side (bar)	2.5
Temperature difference at water inlet (K)	8K with subcooler; otherwise steam leaves at saturation temperature
Temperature difference at water outlet (K)	3
High pressure feed water heaters	
Steam pressure drop (fraction of inlet steam pressure)	0.02
Pressure drop on water side (bar)	2
Temperature difference at water inlet (K)	3
Temperature difference at water outlet (K)	-1.5 (water exhaust hotter than steam saturation temperature)
PUMPS	
Boiler feed pump efficiency	0.85
Other pump efficiency	0.75

REBOILER	
Steam pressure drop (fraction of inlet steam pressure)	0.10
Solvent heat of regeneration (kJ/kgCO2)	3.6
Steam pressure (bar)	3.6
Capture level (%)	90
HEAT RECOVERY SYSTEM FROM CAPTURE AND COMPRESSION UNITS	
Condensate outlet temperature (K)	393.15
Pressure drop (bar)	2
Fraction of condenser mass flow through heat exchanger	100

List of publications

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Gibbins, J., Lucquiaud, M., Chalmers, C., Popa-Bosoaga, A., Edwards,R. (2009) Capture readiness: CCGT owners needn't feel left out, *Modern Power Systems*, December 2009