

# **Pre-combustion decarbonisation in IGCC: Abatement of both steam requirement and CO<sub>2</sub> emissions**

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## Abstract

This paper presents the results of system assessments that were conducted to compare conventional and advanced water-gas-shift reaction section in Integrated Gasification Combined Cycles (IGCC) with pre-combustion CO<sub>2</sub> capture. The advanced shift reactor section comprises four staged reactors with distributed syngas and quench water addition in between the reactors. This advanced reactor section reduces the steam requirement of the shift reaction up to 70% at approximately 85% CO<sub>2</sub> capture, in comparison with conventional shift reactor sections.

## Introduction

Clean coal conversion in terms of coal gasification and pre-combustion CO<sub>2</sub> capture gained increased interest in the recent past. However, the implementation of the CO<sub>2</sub> capture section in Integrated Gasification Combined Cycles (IGCC) forms a challenge in pursuit of commercial application of CO<sub>2</sub> capture and storage.

The most important barrier for large-scale application is the loss in electric efficiency that is related to CO<sub>2</sub> capture. This loss comprises the reduced Lower Heating Value (LHV) of the synthesis gas caused by carrying out the water-gas-shift reaction, as well as the energy consumption for CO<sub>2</sub> separation and compression. These losses are -to a large extent- governed by the relative amount of CO<sub>2</sub> captured. Decreasing the steam requirement for the water-gas-shift (WGS) reactor section in the CO<sub>2</sub> capture section provides the likeliest option to reduce the efficiency penalty. Moreover, reduction of the steam requirement enhances the operational flexibility of the integral IGCC including CO<sub>2</sub> capture, thus allowing speculation on the CO<sub>2</sub> market. Figure 1 displays an IGCC with pre-combustion CO<sub>2</sub> capture as well as the causes for the loss in electric efficiency.

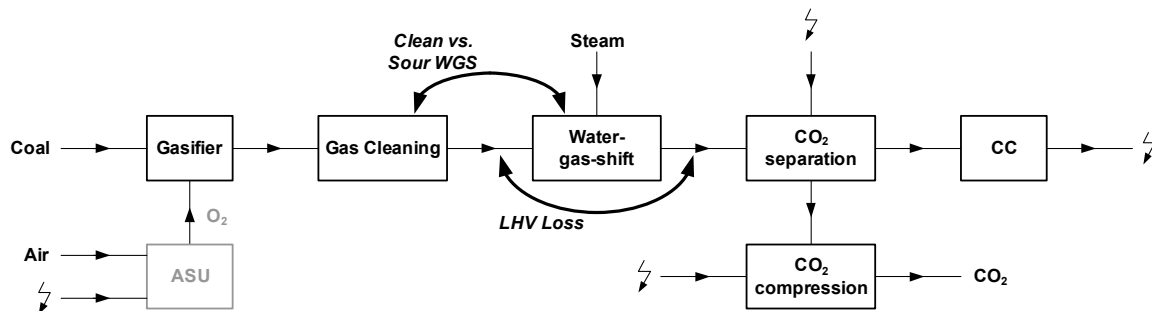


Figure 1 Integrated Gasification Combined Cycle (IGCC) with pre-combustion CO<sub>2</sub> capture

This assessment focuses on the application of entrained flow coal gasification, since the relatively low amount of impurities allows application of sour water-gas-shift catalysts downstream of the venturi particulate scrubber. Entrained flow gasifiers are categorised by coal pressurisation method: dry-fed where coal is pressurised with gas (often nitrogen) and slurry-fed where coal is mixed with water and pressurised [1]. Dry-fed gasification allows implementation of both sour and clean shift. Slurry-fed gasification is better suited for sour shift due to the high moisture content in the syngas; application of clean shift would result in condensation of the water content prior to the desulphurisation section that is operated at ambient temperature. Table 1 displays the gas composition and conditions at the inlet of the shift section for the three options described above.

**Table 1** Gas composition and conditions at inlet shift section for dry- and slurry-fed entrained flow coal gasification

Gas composition [mol%]	Dry-fed gasification after gas cleaning (clean shift)	Dry-fed gasification after venturi scrubber (sour shift)	Slurry-fed gasification after venturi scrubber (sour shift)
H <sub>2</sub>	31.3	28.2	27.5
CO	60.5	54.5	38.4
H <sub>2</sub> O	0.3	9.1	20.0
CO <sub>2</sub>	2.9	3.8	12.0
CH <sub>4</sub>	0.0	0.0	0.1
N <sub>2</sub>	3.8	3.4	1.5
Ar	1.1	1.0	0.1
H <sub>2</sub> S	10 – 20 ppm	0.13	0.11
Temperature [°C]	40	180	210
Pressure [bara]	28	28	40

## Conventional Shift Reactor Section

The water-gas-shift reaction was discovered over two centuries ago and nowadays serves in various chemical processes, such as ammonia production and Fischer-Tropsch synthesis [2]. The equilibrium reaction converts carbon monoxide into hydrogen and carbon dioxide and is moderately exothermic.

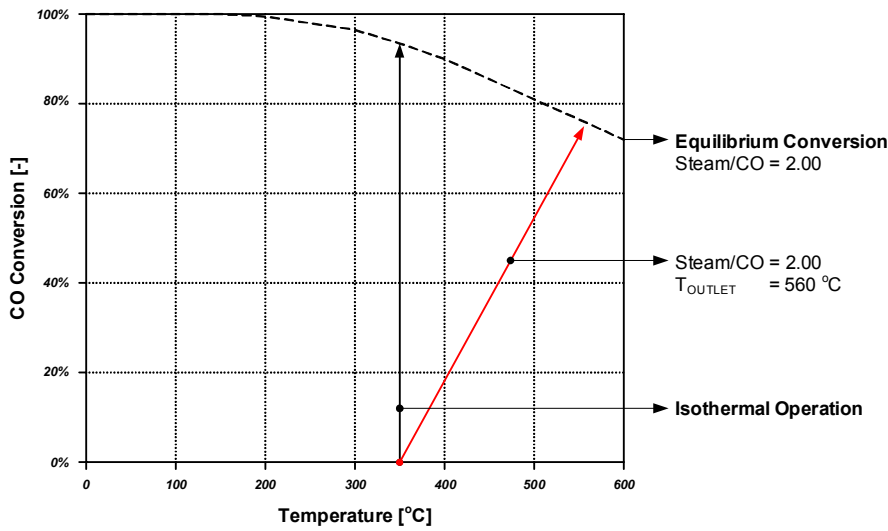


Several types of shift catalysts are commercially available and widely applied in practice, the three most important being [3]:

- High-temperature shift catalyst  
Active component: Fe<sub>3</sub>O<sub>4</sub> with Cr<sub>2</sub>O<sub>3</sub> as stabiliser  
Operating conditions: 350 – 500 °C; sulphur content syngas < 100 ppm
- Low-temperature shift catalysts  
Active component: Cu supported by ZnO and Al<sub>2</sub>O<sub>3</sub>  
Operating conditions: 185 – 275 °C; sulphur content syngas < 0.1 ppm
- Sour shift catalysts  
Active component: Sulphided Co and Mo (CoMoS)  
Operating conditions: 250 – 500 °C; sulphur content syngas > 300 ppm

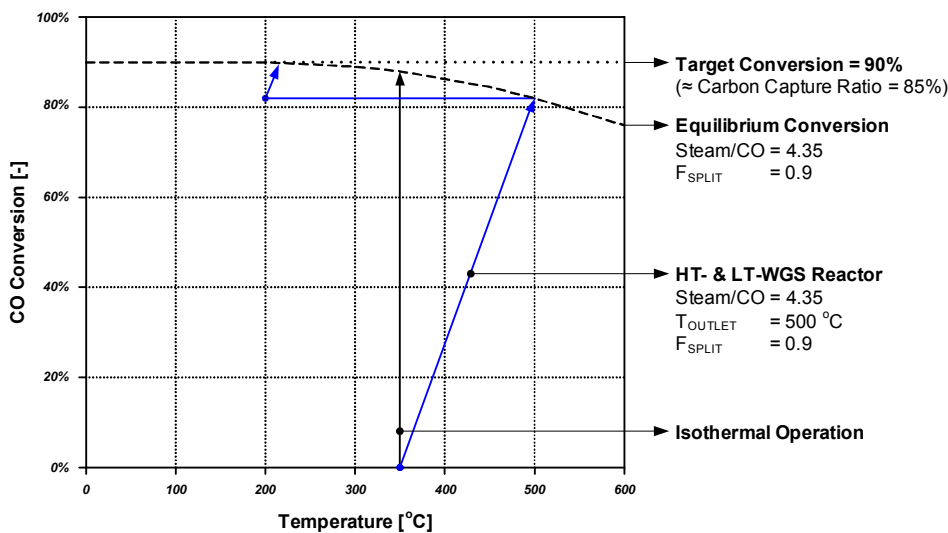
The minimum steam/carbon monoxide ratio is 2, to avoid carbon deposition at the catalyst surface and formation of larger hydrocarbon molecules. The high- and low-temperature shift catalysts are often operated in sequence, where the high-temperature catalysts convert the bulk of carbon monoxide and low-temperature shift catalyst realise CO-conversion up to ppm levels at the reactor outlet. The shift reaction is equilibrium limited, which implies that the extent of CO-conversion is dependent on the temperature in the shift reactor. Figure 2 provides the equilibrium conversion in a high-temperature shift reactor as function of the temperature, with the syngas composition obtained from a dry-fed gasifier downstream of the gas cleaning section (see Table 1). Application of the minimum steam/CO-ratio of 2 results in an outlet temperature of 560 °C, which results in irreversible deactivation of the catalyst by sintering. Isothermal operation would result in the highest obtainable CO-conversion; in this case the shift reactor generates saturated steam from boiler feed water. However, the design of isothermal shift

reactors is complex and catalyst replacement is difficult, therefore this reactor configuration was not considered during the presented assessments.



**Figure 2** Equilibrium conversion at steam/CO ratio of 2 (dry-fed gasification, clean high-temperature shift reactor)

Increasing the steam supply results in a lower outlet temperature of the high-temperature shift reactor; this is demonstrated in Figure 3. The common layout for the shift section with a target CO-conversion of 90% usually applies a high- and low-temperature shift reactor in sequence where approximately 10% of the syngas feed stream is bypassed over both reactors. The syngas bypass results in reduction of the steam consumption, since the CO-conversion in low-temperature shift reactor is less affected by equilibrium limitations which results in an outlet CO-slip at ppm level. The target CO-conversion of 90% corresponds to a CO<sub>2</sub> capture ratio of approximately 85%.



**Figure 3** Equilibrium conversion at steam/CO ratio of 4.35 (dry-fed gasification, clean high- and low-temperature shift reactor in sequence, 10% bypass)

## Advanced Shift Reactor Section

The previous Paragraph illustrated that the steam requirement of shift reactors is significantly larger than the stoichiometrically required amount of steam for CO-conversion, because of catalyst requirements regarding the minimum inlet steam/CO-ratio and maximum outlet temperatures. A qualitative assessment (using strategies by [4]) of an optimum shift reactor section implemented in an IGCC indicates that staged injection of synthesis gas and quench water between reactors could reduce the steam requirement. Moreover, the carbon monoxide conversion is enhanced by staged addition of reactants as well as the corresponding temperature quenches. The application of high-temperature or sour shift catalysts is desirable; these allow retrofit application since desulphurisation sections are not affected by additional purity demands. As mentioned before these catalysts are commercially available and are applied on a broad industrial scale.

Figure 4 displays the layout of the advanced shift reactor section. Syngas is split and directed to the four reactors; the first split stream is preheated (if required) and mixed with intermediate pressure (IP) steam. The steam/CO-ratio at the first reactor is equal to that of the HT-& LT-shift section case, however only a fraction of the syngas feed stream is fed to the first reactor which results in a significant decrease of the absolute steam consumption. After the first reactor, the heat released by the shift reaction is quenched with water, then mixed with the second split stream and subsequently lead to the second shift reactor. This sequence is repeated prior to the third and fourth reactor. The outlet of the fourth reactor can be applied to preheat the first split stream or to generate additional IP steam. The heat available at the outlet of the shift section will be reduced compared to a conventional shift section. However the quenches are expected to result in a more significant advantage: the addition of water, being both a coolant and reactant ultimately leading to a lower initial steam requirement. The temperature increase in the fourth reactor is moderate (less than 20 K) in all cases, which indicates that the CO-conversion is in close proximity of the equilibrium conversion. Therefore the design of the advanced shift reactor section is limited to four shift reactors.

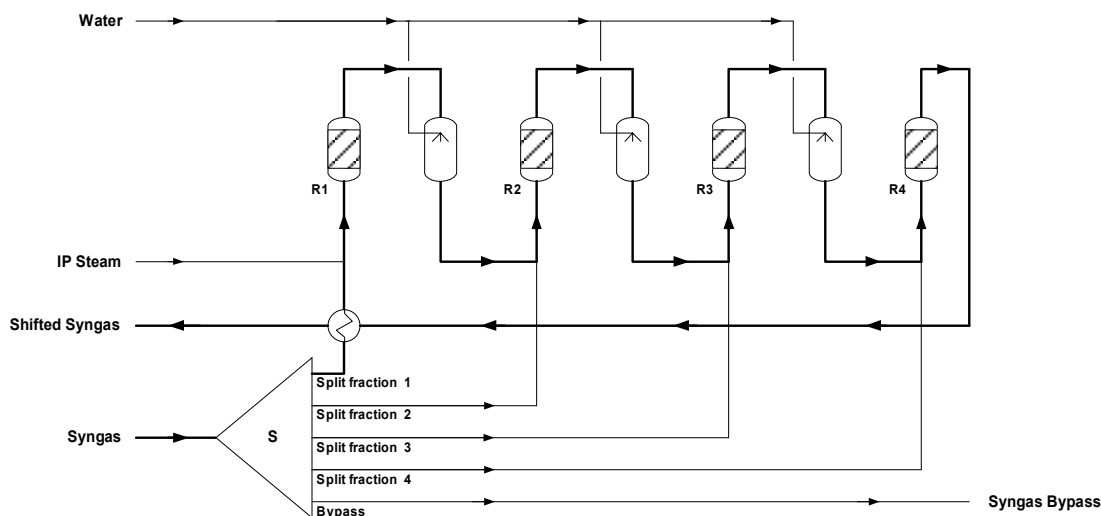


Figure 4 Advanced shift reactor layout

## Analysis

The IGCC's with CO-conversion, CO<sub>2</sub> separation and liquefaction were analysed using AspenPlus, which was expanded with the add-on tool 'Exercom.' The latter provides the exergy content (chemical, physical, mixing and total exergy) per flow sheet stream. Exergy defines the potential for power conversion of process streams with respect to a given environment [5]; exergy analysis of a process

therefore identifies the opportunities to reduce losses. Sensitivity analyses provided the steam requirement and exergy analysis; the following parameters were varied during the sensitivity analyses:

1. Split fractions 1-4 and bypass: 0 – 1
2. Water quenches: 0 – 50 kg/s
3. Capacity preheater: 0 – 20 MW<sub>th</sub>

The most important assumptions with respect to the system assessments are:

- Coal type: Eastern Australia (‘Wambo’)
- Inlet pressure shift section (dry-fed gasification): 28 bar
- Inlet pressure shift section (slurry-fed gasification): 40 bar
- Rated output without CO<sub>2</sub> capture: 500 MW<sub>e</sub>
- H-class turbine technology ready for syngas application [6]
- Equilibrium approach shift reactors: 10 K
- CO<sub>2</sub> separation by Selexol
- CO<sub>2</sub> compression and liquefaction: 110 bara

## Results and Discussion

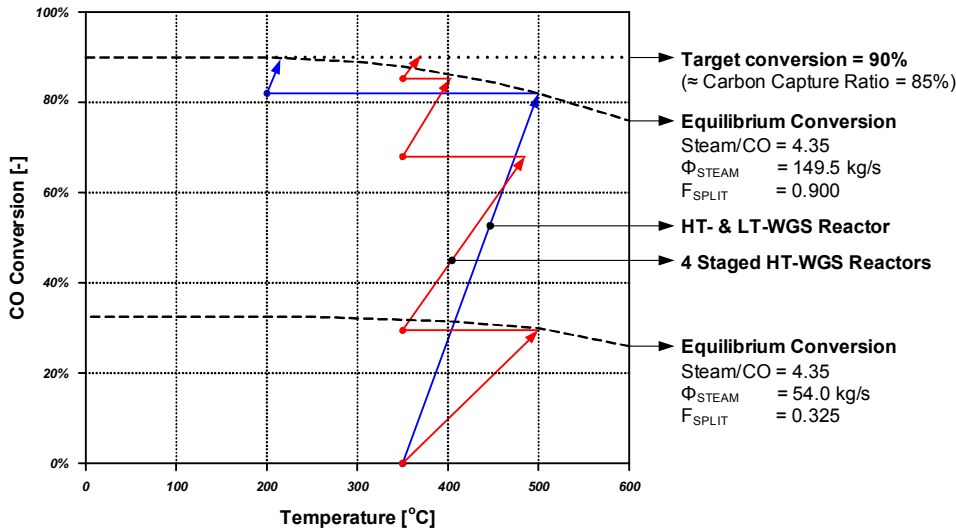
The results of the sensitivity analyses demonstrate that implementation of the advanced shift section leads to significant reductions of the steam requirement compared to conventional shift sections, as displayed in Table 2. The efficiency penalties at a CO-conversion of 90% (approx. 85% carbon capture) illustrate that application of sour shift catalysts over clean shift catalysts is more advantageous. This is ascribed to the lower inlet temperature of the sour shift reactors (250 instead of 350 °C), which is favourable for the equilibrium conversion. The efficiency penalties are approaching the upper limits of the ranges specified in [7].

**Table 2** Efficiency penalties conventional and advanced WGS sections at 90% CO-conversion

	Efficiency w/o capture (LHV) [%]	Efficiency Penalty Steam Requirement [% pts.]	Total Efficiency Penalty [% pts.]	Efficiency with Carbon Capture [%]	Specific Loss [MJ <sub>e</sub> /kg CO <sub>2</sub> ]
Dry-fed IGCC & Conventional Clean WGS	47.4	11.5	14.7	32.7	1.75
Dry-fed IGCC & Advanced Clean WGS	47.4	4.0	9.4	37.9	1.12
Dry-fed IGCC & Conventional Sour WGS	47.4	3.7	9.5	37.9	1.11
Dry-fed IGCC & Advanced Sour WGS	47.4	1.4	7.4	40.0	0.87
Slurry-fed IGCC & Conventional Sour WGS	42.8	2.7	8.4	34.3	0.98
Slurry-fed IGCC & Advanced Sour WGS	42.8	0.8	6.6	36.2	0.77

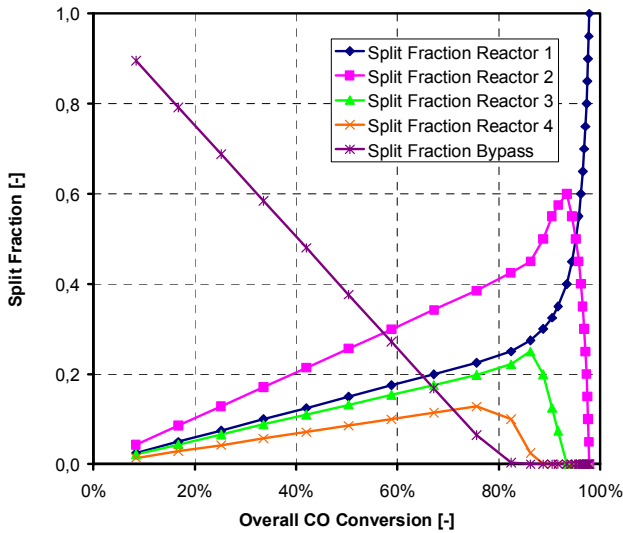
Only the results of the ‘dry-fed gasification with advanced clean shift section’ case are discussed in-depth on the following pages, in order to provide a comprehensible overview. The results of the two advanced sour shift cases provide similar trends, as displayed in Figure 9 where the most important results of the assessments are summarised. Figure 5 depicts the CO-conversion as function of the temperature for the conventional (see Figure 3) and advanced clean shift section, downstream of dry-fed gasification. The steam requirement for the advanced section is approximately three times lower than that of the conventional section. The steam/CO-ratio remains 4.35 at the inlet of the first reactor in the

advanced section, however only 32.5% of the syngas feed stream is fed to this reactor. Moreover, the final outlet temperature approaches the inlet temperature of 350 °C, indicating elevated CO-conversion.

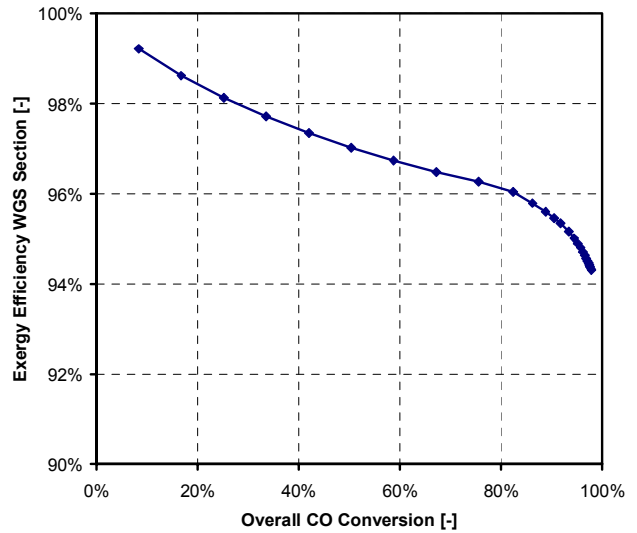


**Figure 5** CO-conversion as function of temperature (dry-fed gasification, conventional and advanced clean shift reactor section)

The optimum split fractions of the feed stream as function of the CO-conversion are displayed in Figure 6. The split fractions of the first, second and third reactor feed stream at a desired CO-conversion of 90% amount 0.325, 0.550 and 0.125, respectively. The exergy efficiency as function of the overall CO-conversion is displayed in Figure 7. The decline up to 80% CO-conversion is non-linear, which is attributable to the water quenches (increased heat production leads to increased water addition, which results in a higher CO-conversion at relatively lower steam consumptions thus higher exergy efficiencies). Above 80% CO-conversion the exergy efficiency declines significantly, since large surpluses of steam are required to further increase the CO-conversion.



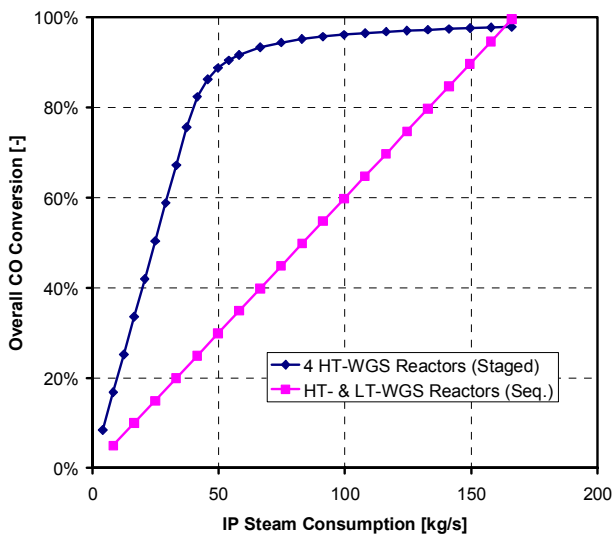
**Figure 6** Optimum split fractions as function of desired overall CO-conversion (dry-fed gasification, advanced clean WGS section)



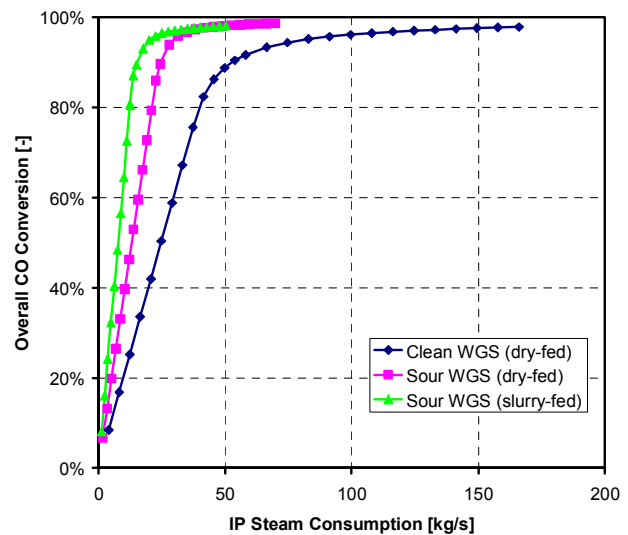
**Figure 7** Exergy efficiency as function of desired overall CO-conversion (dry-fed gasification, advanced clean WGS section)

The steam requirement of the advanced shift section is significantly reduced compared with the conventional shift section, when a CO-conversion up to approximately 90% is pursued as depicted in Figure 8. Application of a staged configuration for hydrogen production as proposed by [8] seems undesirable, since the CO-conversion above 90% is only slightly affected while the steam requirement increases significantly. However, this could provide an opportunity for application of a Sorption Enhanced Water Gas Shift (SEWGS) reactor [9]. The SEWGS reactor is filled with high-temperature shift catalyst and CO<sub>2</sub> adsorbent pellets. Very low CO<sub>2</sub> partial pressures are achieved, which enhances the shift reaction without increasing the steam requirement.

Figure 9 displays the CO-conversion as function of the steam requirement for all three advanced shift sections. The clean shift section downstream of dry-fed gasification has the largest steam requirement, since the reactor inlet temperature is higher (350 vs. 250 °C for sour shift reactor sections). Furthermore, the water content of the syngas is also relatively low at the outlet of the desulphurisation section. The steam requirement for the sour shift section downstream of slurry-fed gasification is lower than downstream of dry-fed gasification, which is also attributable to the relatively higher water content in the syngas obtained from slurry-fed gasification.



**Figure 8** Overall CO-conversion as function of intermediate pressure steam consumption (dry-fed gasification, conventional and advanced clean WGS section)



**Figure 9** Overall-CO conversion as function of intermediate pressure steam consumption for three advanced WGS sections

## Conclusions and Future Work

The results of the system assessments demonstrate that the implementation of advanced shift reactor sections results in reductions of the steam requirement up to 70% at a carbon capture ratio of 85%, when compared with conventional shift reactor sections. The advanced reactor section appears particularly suitable for CO<sub>2</sub> capture and storage up to carbon capture ratios of approximately 90%, but offers no advantages when pure hydrogen production is envisioned, since hydrogen production still requires large quantities of steam to enhance the CO-conversion close to 100%. The application of sour shift catalysts results in lower efficiency penalties than high-temperature clean shift catalysts in IGCC's with pre-combustion CO<sub>2</sub> capture. This is attributable to the high moisture content downstream of the venturi scrubber as well as the lower inlet temperature in sour shift reactors. The application of a SEWGS reactor in combination with advanced shift reactor section to obtain close to 100% CO-conversion, without significantly increasing the steam consumption, will be investigated in the near future.



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