GHGT-12

Water-gas shift (WGS) operation of pre-combustion CO$_2$ capture pilot plant at the Buggenum IGCC

H.A.J. van Dijk[a]*, K. Damen[b], M. Makkee[c], C. Trapp[d]

[a] *Energy research Centre of the Netherlands (ECN), Sustainable Process Technology, Westerduinweg 3, 1755 LE, Petten, The Netherlands*
[b] *Vattenfall, Engineering and R&D, Hoekenrode, 1102 BR, Amsterdam,The Netherlands*
[c] *Delft University of Technology, Catalysis Engineering, Julianalaan 136, 2628 BL, Delft, The Netherlands*
[d] *Delft University of Technology, Propulsion and Power, P.O. Box 5058, 2600 GB, Delft, The Netherlands*

Abstract

In the Nuon/Vattenfall CO$_2$ Catch-up project, a pre-combustion CO$_2$ capture pilot plant was built and operated at the Buggenum IGCC power plant, the Netherlands. The pilot consist of sweet water-gas shift, physical CO$_2$ absorption and CO$_2$ compression. The technology performance was verified and validated models were obtained. This paper describes the validation of a WGS reactor model and the excellent catalyst resistance to carbiding at steam/CO=1.5 mol·mol^{-1} testing. Model-based optimization shows that compared to conventional operation at steam/CO=2.65, applying steam/CO=1.5 leads to a 10% lower CO$_2$ capture penalty of 1155 MJ$_{electric}$·t$_{CO2}$$^{-1}$, albeit at a decreased optimum CO$_2$ capture efficiency of 78.5% versus 87.5%.

Keywords: Pre-combustion CO$_2$ capture ; pilot plant ; WGS section ; reactor model ; lowered steam/CO ratio ; optimization

1. Introduction

In 2005, Nuon/Vattenfall started the development of a multi-fuel Integrated Gasification Combined Cycle (IGCC) power plant, the so-called Magnum project, in Eemshaven, The Netherlands. The original concept for Magnum was to construct the gasification section first, with the option to install the pre-combustion CO$_2$ capture unit afterwards ("capture ready retrofit"). The envisioned pre-combustion CO$_2$ capture section would consist of a water-gas shift

* Corresponding author. Tel.: +31-88-515-4259; fax: +31-88-515-8489.
E-mail address: h.vandijk@ecn.nl

(WGS) section to convert CO into CO_2 and H_2 by reaction with steam, CO_2 removal by physical absorption and CO_2 compression. A sweet shift by FeCr-based catalysts was chosen rather than a sour shift by CoMo-based catalysts due to its compatibility for easy CO_2 capture retrofit and the ability to bypass the shift and CO_2 absorption unit (e.g. when CO_2 capture is not economically viable).

This pre-combustion CO_2 capture scheme combines processes that are proven in the chemical industry, such as WGS and bulk CO_2 removal with solvents, yet in different configurations. The syngas composition from coal (and biomass) gasification in power applications differs considerably from the syngas resulting from reforming natural gas or heavy oil residues for chemicals production, for which most experience exists [1]. Single-stage entrained flow coal gasification using oxygen as oxidant [2] produces a dry syngas with a CO content as high as 60% and a H_2/CO ratio as low as 0.5. Moreover, in coal power plants less stringent desulphurization is commonly applied compared to the chemical industry, leading to exposure of the FeCr-based WGS catalyst to typically 20 ppm inorganic sulfur. The mode of operation in the power sector also differs from the chemical industry in the sense that the load of the WGS and CO_2 capture unit should follow the ramping of the power plant. Moreover, the WGS section is not designed for maximum H_2 yield but rather to minimize the CO_2 capture penalty. Therefore, Nuon/Vattenfall decided to demonstrate and optimize the pre-combustion CO_2 capture concept at a small scale first before full-scale commercial application at the Magnum plant could be considered. This resulted in the initiation of the so-called CO_2 Catch-up project in 2008, with the objective to demonstrate pre-combustion CO_2 capture at a pilot plant in Buggenum, The Netherlands, in order to verify the technology performance and to generate validated models and operational experience.

This paper describes the lessons learned from the operation of the WGS section in the Buggenum pilot plant.

Nomenclature

K_{eq}	equilibrium constant of the WGS reaction
p_i	partial pressure of component i in bar
R	gas constant
r_{WGS}	WGS reaction rate in $mol \cdot kg^{-1} \cdot s^{-1}$
T	temperature in K

---

2. Pilot plant lay-out

The Buggenum pilot-plant layout is schematically represented in Figure 1 [3], while a photo is shown in figure 2. The plant consists of five sections: syngas conditioning, WGS, condensate recovery, CO_2 absorption and solvent regeneration, and CO_2 compression. Syngas is withdrawn from the Shell type coal gasifier downstream of the Sulfinol desulphurization unit at a rate of 1.2 t·h^{-1} (=0.8% of the syngas flow from the Buggenum gasifier, equivalent to 5 MW$_{th}$). The syngas is dry and contains between 5 and 20 ppm H_2S+COS. Water is added to the syngas and a hot feed splitter generates a wet gas quench to be added to the reactor 1 effluent. The remaining water + syngas leaving the bottom of this feed split vessel (2 phase flow) is then further heated to obtain the desired steam content for the syngas going to the WGS reactor 1. The shifted syngas coming from the 3rd WGS reactor is cooled and the condensate is recovered and recycled before the syngas enters the CO_2 absorber. In the absorber, the CO_2 is dissolved in the physical solvent (dimethyl-ether of poly-ethylene-glycol (DEPEG)), generating a H_2-rich syngas. The CO_2 from the rich solvent is released in a series of 3 flash vessels and the lean solvent is recycled to the absorber. Finally, the CO_2 product at a rate of 1.4 t$_{CO2}$·h^{-1} is compressed at an overall capture efficiency of 80-85%.
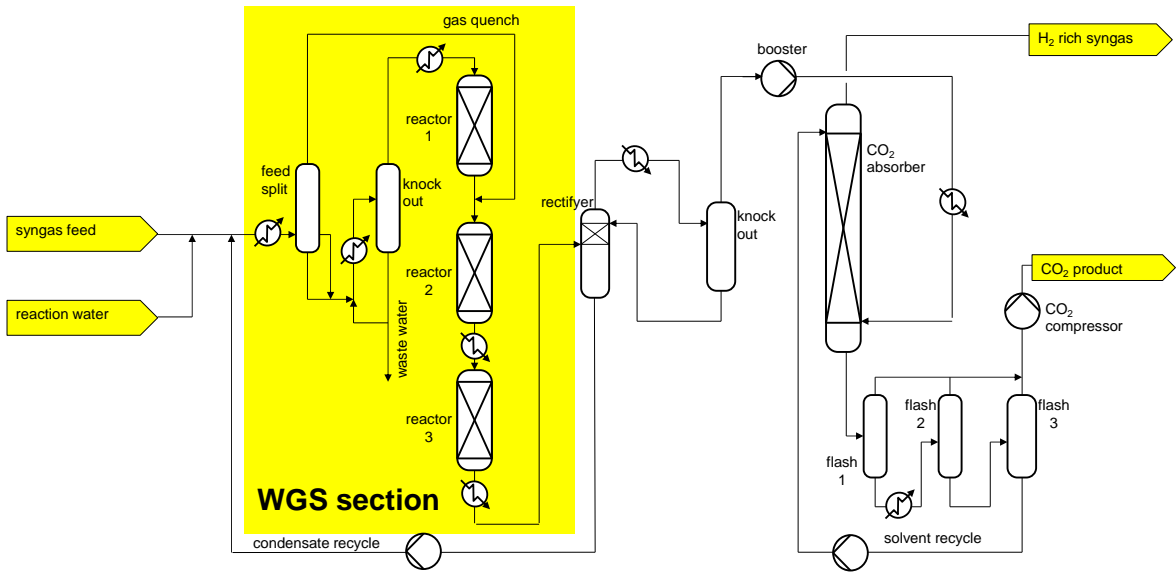
Fig. 1. Schematic layout of the Buggenum pilot plant, highlighting the split flow configuration of the WGS section.

Fig. 2. Photo of the pilot plant at the Buggenum power station.

The 3 WGS reactors are loaded with a FeCr-based shift catalyst (HT−23408) supplied by Haldor Topsøe. A split flow configuration is applied for the first 2 reactors to reduce the amount of steam required compared to an all-in-series configuration [4]. Typically, $1/3^{rd}$ of the syngas is directed to the 1st reactor, while the remaining is added as gas quench between the 1st and the 2nd reactor. The 3rd reactor is in series with the 2nd reactor. In this configuration, reactor 1 functions as a CO peak shaver to lower the CO content of the reactor 2 feed, resulting in a reduced steam requirement for the 2nd and 3rd reactor. For the Buggenum gasifier, a classic reactors-in-series configuration would require a steam/dry syngas ratio of 2.4 kg·kg^{-1} (steam/dry syngas=2.8 mol·mol^{-1}), while the split flow configuration

reduces this to 1.3 kg·kg^{-1} (steam/dry syngas=1.5 mol·mol^{-1}) to reach the targeted 90% CO conversion within the WGS section.

The aim of the pilot plant was to gain operational experience and to gather pilot plant data for model construction and validation of the major components of the pilot plant. These included, among others, the WGS reactors and the CO_2 adsorber-stripper section.

3. Pilot plant testing

The pilot plant catalytic reactors had a total operation time of 5840 hours. During this period an extended program of test-runs was executed to assess the performance of each component of the pilot plant as well as its integral operation. Two particular type of tests for the WGS section are discussed here. First, steady state operation experiments were performed at a wide range of inlet conditions regarding feed temperature, feed composition and throughput. These aimed at the validation of a reactor model for the WGS reactors. Second, operation at lowered steam contents of the syngas feed was performed to assess the catalyst resistance to carbiding.

3.1. WGS reactor model development

For the WGS section, after about 2000 hours time-on-stream a total of 20 runs were executed in which the reactor inlet temperature, throughput, and syngas composition were varied. The initial fast catalyst deactivation, which magnitude was in agreement with literature [5,6,7], was completed well before this 2000 hours operation. Accordingly, the total of 20 runs were performed on a catalyst having a low deactivation rate, thus represent a snapshot of the catalyst activity at about 2000 hours time-on-stream.

A reactor model was constructed and validated against this set of 20 operational points. The model is based on the intrinsic kinetics quantified in the lab at 350-450°C, 20 bar and a wide range of syngas compositions containing 5 to 20 ppm H_2S [8]. The intrinsic catalyst activity was found to be adequately described by a power-law rate model (equation 1), where the rate is shown to be independent from the investigated H_2S concentrations:

$$r_{WGS} = 4.4E6 \cdot \exp\left(-\frac{106000}{R \cdot T}\right) \cdot p_{CO}^{0.94} \cdot p_{H_2O}^{0.11} \cdot p_{CO_2}^{-0.32} \cdot p_{H_2}^{-0.08} \cdot \left(1 - \frac{p_{CO_2} \cdot p_{H_2}}{p_{CO} \cdot p_{H_2O} \cdot K_{eq}}\right) \qquad (1)$$

The equilibrium constant (equation 2) is written as [9]:

$$K_{eq} = \exp\left(\frac{4577.8}{T} - 4.33\right) \qquad (2)$$

In the one-dimensional heterogeneous reactor model, the catalyst relative activity factor and the length of the dead zone were tuned to the pilot data. The relative activity factor is a factor with which the intrinsic reaction rate has to be adjusted to comply with the catalyst activity state in the pilot plant. The length of the dead zone represents the fraction of the initial catalyst bed that is inactive due to setteling of the catalys pellets. The set of 20 runs for reactor 1 and reactor 2 are adequately described by a single set of values of these parameters for each reactor, see table 1. The estimated catalyst relative activity factors are within 1 order of magnitude to unity, meaning that the one-dimensional heterogeneous reactor model only requires moderate numerical correction to predict the pilot plant behaviour. This indicates that the kinetic rate equation measured in the lab combined with the physical mass and heat transport equations of the reactor model already closely predicts the measured catalyst activity in the pilot. Reactor 3 was not considered in this study, since the catalyst was slightly damaged during the comissioning, its performance thus not representative for normal operation.

Table 1. Estimated values for the relative activity factor and the length of the dead zone for reactors 1 and 2.

	Catalyst relative activity factor [-]	Dead zone [%]
Reactor 1	0.53 ± 0.03	2.3 ± 0.9
Reactor 2	1.09 ± 0.05	3.9 ± 0.5

In figure 3 below the adequate fits of the axial temperature profiles for a selection of different operating conditions are shown for reactor 1 and reactor 2. All trends are well described; the sharpening of the axial temperature profiles when decreasing the steam/CO feed ratio or increasing the feed temperature, as well as the change in final equilibrium temperature reached at 75% of the bed volume.
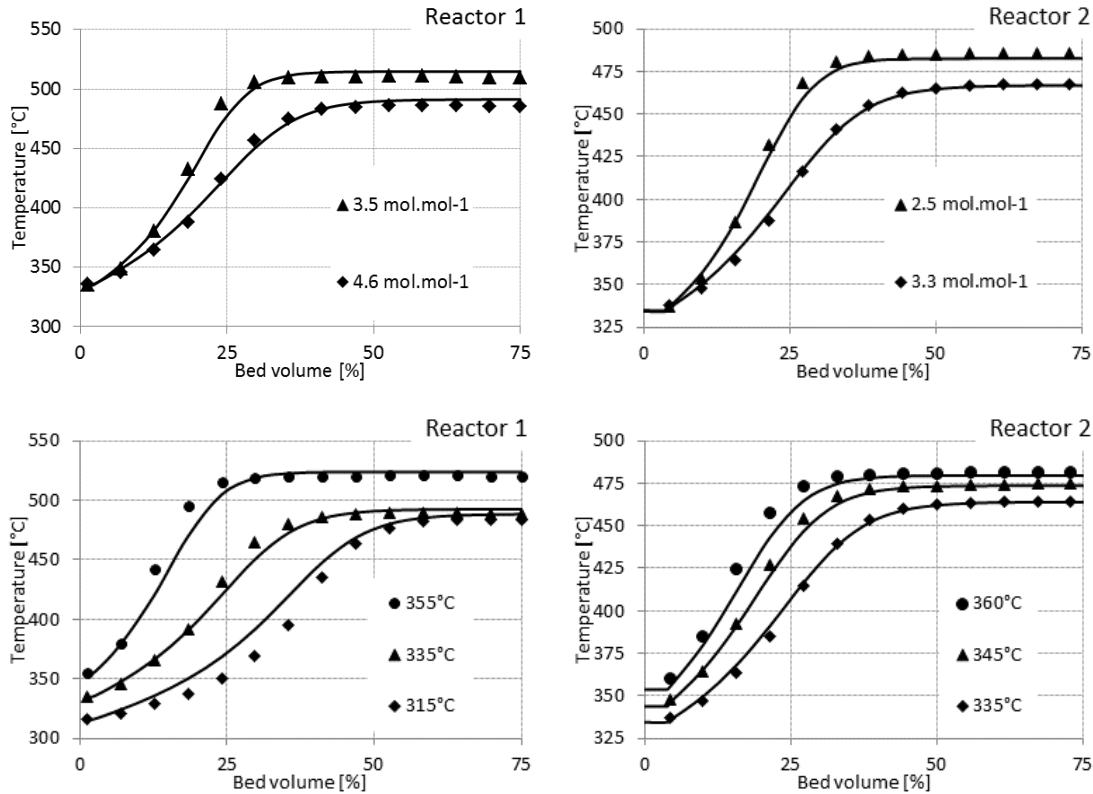

Fig. 3. Fits of a selection of pilot plant operations for reactor 1 and reactor 2. Top figures for varying steam/CO feed ratio, bottom figures for varying feed temperature. For detailed conditions, see [8].

3.2. Low steam testing

The steam required in the WGS section poses an important contribution to the capture penalty for pre-combustion systems. To this extent, the catalyst behavior towards low-steam operation was studied in the pilot plant. Too dry operation with a high CO content feed risks the reduction of the WGS active magnetite (Fe_3O_4) into iron carbide, being a catalyst for highly exothermal hydrocarbon formation. Besides the undesired high operating temperature, excessive carbiding can physically damage the catalyst pellets. The tests, therefore focused to identify the operating limits with respect to the reduced steam content. The split-flow configuration in the pilot plant allowed adjustment of the steam content of the reactor 2 feed, while the operation of reactor 1 was not affected. In individual 60-120 hours tests, the steam/CO content for reactor 2 was lowered from 3.1 mol·mol^{-1} to 1.5 mol·mol^{-1}. Between the tests, operation at a reference condition was performed.
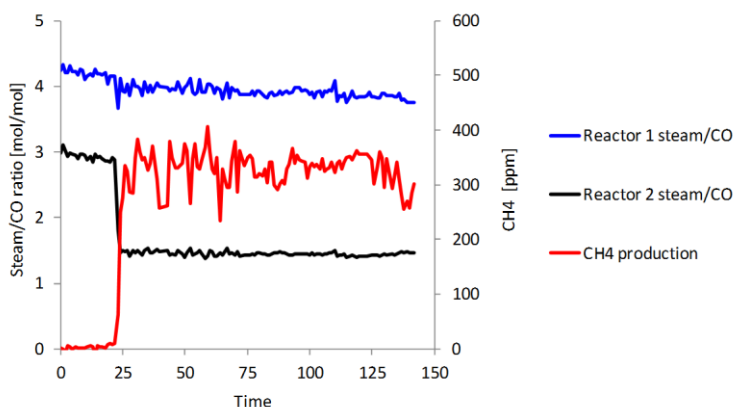
Fig. 4. Reactor 1 and 2 feed steam/CO ratios and the CH_4 production by the catalyst during the 120 h test at steam/CO=1.5 (Average molar feed composition prior to experiment: 17.1% CO, 8.58% CO_2, 19.5% H_2, 50.5% H_2O, 20 ppm H_2S. Average molar feed composition during lowered steam/CO operation: 24.8% CO, 9.36% CO_2, 23.9% H_2, 37.0% H_2O, 20 ppm H_2S).

Since single-stage entrained flow coal gasification produces a syngas with a low CH_4 content (typically < 100 ppm), the CH_4 production by a carbiding catalyst is readily monitored. A typical 120 h excursion to the lowest ratio tested of S/CO=1.5 is shown in figure 4. It is observed that the CH_4 content of the reactor effluent indeed increases at the moment the steam content of the feed is decreased. But more importantly, it remains constant once the lowered steam/CO ratio is set for the remaining duration of the test. This step-wise change in CH_4 content of the reactor effluent was observed for every excursion to lowered steam/CO feed ratio. Excessive catalyst carbiding would have led to a continuously increasing CH_4 content, which is clearly not observed. Moreover, when switching back to the high steam reference conditions after every test, the catalyst activity was restored to the value observed prior to the test. Another indication was that the catalyst pellet crush strength after pilot plant shutdown was according to expectations, thus not weakened due to excessive carbiding. Note that the experiment in figure 3 was performed on an aged catalyst that was already 5700 hours on stream.

These tests indicated that the catalyst is resistant towards excessive carbiding at the Buggenum syngas conditions and that the CH_4 content in the reactor effluent is a suitable variable to monitor excessive carbiding.

4. Pilot plant modelling

The WGS reactor model and the demonstrated excellent catalyst resistance to carbiding were combined with a model for the CO_2 scrubbing section in a system study to optimize the operation of the capture plant [10]. The plant CO_2 capture efficiency results from the extend of the CO conversion in the WGS section and the CO_2 removal rate by the scrubber system. To drive the CO converion in the WGS section, intermediate pressure (IP) steam is required, whereas in the scrubber system the solvent circulation rate is the most important parameter. It appears that when changing the desired CO_2 capture efficiency it is more efficient to adapt the CO conversion in the WGS section rather than the CO_2 removal rate in the scrubbing section because the IP steam savings have a larger impact than the decrease of the solvent recirculation rate. The CO_2 removal rate of the scrubbing system is, therefore, rather constant at 92-93% for a large variation in the overall capture efficiency from 76-90%, while the optimum CO conversion accordingly varies from 83% to 96%. A lower conversion in the WGS section can be realized by operating the reactors at a decreased steam/CO ratio.

Figure 5 illustrates what occurs when the overall CO_2 capture efficiency is decreased fom 90% to 78%. At a CO_2 capture efficiency of >87.5%, the CO conversion needs to be pushed beyond 93%, requiring additional IP steam and thus drastically increasing the total capture penalty expressed in $MJ_{electric} \cdot t_{CO2}^{-1}$. Below a capture ratio of 87.5%, the steam content cannot be lowered in case the conventional minimum of steam/CO=2.65 is applied. Then, a lowered capture ratio would imply that syngas has to bypass the capture unit, while the energy penalty does not decrease. If

lower steam/CO ratios are allowed, additional steam can be saved when lowering the CO_2 capture ratio, as illustrated by the lines for steam/CO=2.0 and steam/CO=1.5. For the latter case, a lowered CO_2 capture ratio of 78.5% results in the lowest total capture penalty of 1155 $MJ_{electric} \cdot t_{CO2}^{-1}$. This value is about 10% lower than the lowest value at the conventional steam/CO ratio of 2.65.

In conclusion, for a minimum steam/CO ratio of 1.5, the specific energy penalty for CO_2 capture reduces by 10% in comparison to the case for the conventional minimum steam/CO ratio of 2.65, which comes at the expense of a lowered optimal capture efficiency from 87.5% to 78.5%.
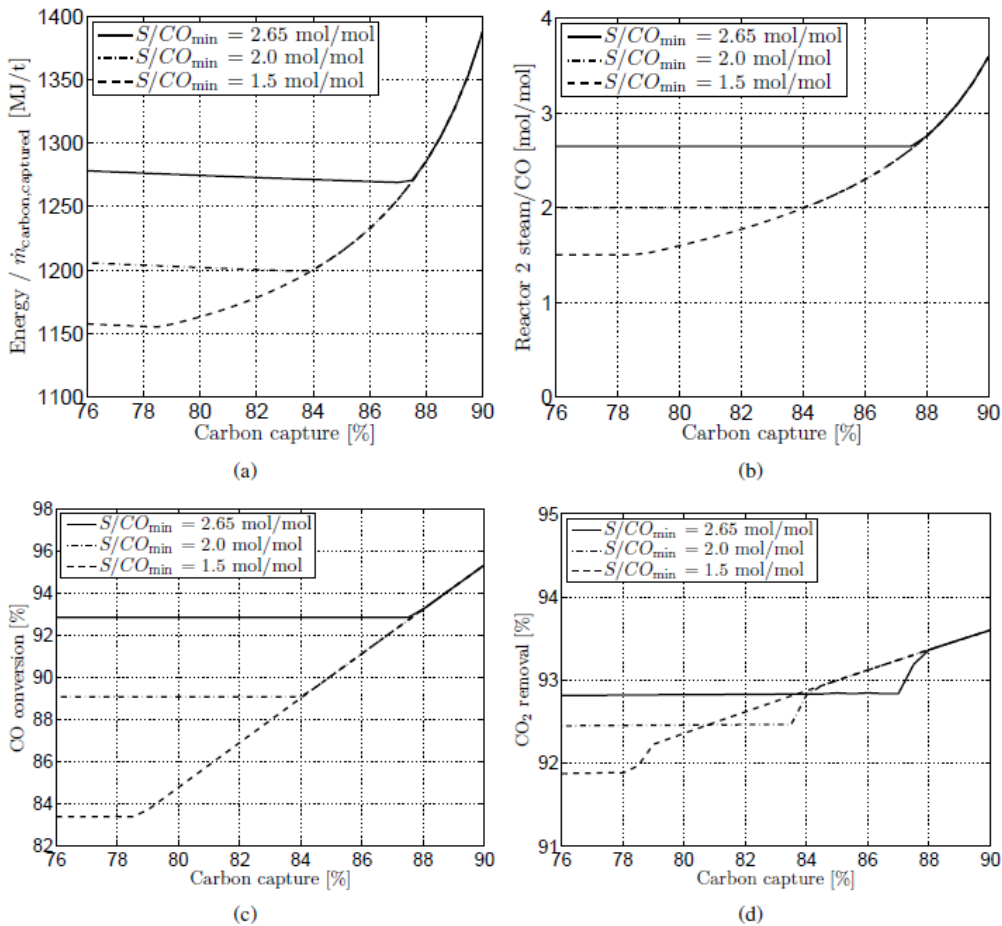

Fig. 5. Optimization results for different limits of the steam/CO ratio. a) specific energy consumption, b) reactor 2 steam/CO ratio, c) optimum CO conversion in the WGS section and d) optimum CO removal in the scrubbing section

5. Conclusions

The WGS section of the pre-combustion CO_2 capture pilot plant at the Buggenum IGCC power plant has been operated for 5840 hours, during which an extended program of test-runs was executed to assess the performance of each component of the pilot plant as well as its integral operation. A one-dimensional heterogeneous WGS reactor model was uscessfully validated against a set of 20 steady-state operational points originating from the pilot plant. The catalyst activity in the reactor model only required moderate tuning to adequately describe the WGS reactor performance. The catalyst proved very robust aginst low steam operation. In a 120 hr test with a feed steam/CO ratio of 1.5 $mol \cdot mol^{-1}$, catalyst carbiding was not observed.

Model-based optimization of the CO_2 capture section indicated that the steam addition to the WGS section required to drive the CO conversion reaction is above the conventional minimum steam/CO ratio of 2.65 mol·mol^{-1} for a capture efficiency of 90%. By lowering the capture efficiency, the steam requirement for the WGS section decreases and the specific energy penalty for CO_2 capture decreases. For the demonstrated minimum steam/CO ratio of 1.5 mol·mol^{-1}, the minimal specific energy penalty for CO_2 capture was estimated at 1155 MJ$_{electric}$·t$_{CO2}$$^{-1}$, which is about 10% lower than the lowest value at the conventional steam/CO ratio of 2.65. The optimum CO_2 capture efficiency, however, also decreases from 87.5% to 78.5%. This illustrates that from an energetical point of view the optimum CO_2 capture efficiency, i.e. minimal specific energy penalty for CO_2 capture, for this type of capture system can be significantly lower than the generally assumed 90%.

Acknowledgements

References

[1] Rostrup-Nielsen J.R., Sehested J. Hydrogen and synthesis gas by steam- and CO_2 reforming. Advances in Catalysis, 47, 2002, 65–139

[2] Higman C., van der Burgt M.J. Gasification. Gulf Professional Publishing, Burlington, 2003

[3] Damen K., Gnutek R., Kaptein J., Nannan N.R., Oyarzun B., Trapp C., Colonna P., van Dijk E., Gross J., Bardow A. Energy Procedia,4, 2011, 1214–1221

[4] Carbo M.C., Boon J., Jansen D., van Dijk H.A.J., Dijkstra J.W., van den Brink R.W. Verkooijen A.H.M., International Journal of Greenhouse Gas Control, 3 (6), 2009, 712–719

[5] Chinchen G.C., Logan R.H., Spencer M.S. Water-gas shift reaction over an iron oxide / chromium oxide catalyst. II: Stability of activity. Applied Catalysis, 12, 1984, 89-96

[6] Keiski R.L., Salmi T. Deactivation of the high-temperature water-gas shift catalyst in nonisothermal conditions. Applied Catalysis A: General, 87, 1992, 185-203

[7] Ratnasamay C., Wagner J.P. Water gas shift catalysis. Catalysis Reviews, 51, 2009, 325-440

[8] van Dijk H.A.J., Cohen D., Hakeem A.A., Makkee M., Damen K. Validation of a water-gas shift reactor model based on a commercial FeCr catalyst for pre-combustion CO_2 capture in an IGCC power plant, International Journal of Greenhouse Gas Control 29, 2014, 82-91

[9] Moe J.M. Design of water-gas shift reactors. Chemical Engineering Progress, 58, 1962, 33-36

[10] Trapp C. Advances in model-based design of flexible and prompt energy systems, the CO2 capture plant at the Buggenum IGCC power station as a test case, Ph.D. thesis TU Delft, Ipskamp Drukkers, The Netherlands, 2014