

Development of equipment design tools from experimental data using the example of autothermal reforming

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Autothermal reforming is a well known alternative for the production of synthesis gas from natural gas and has already been applied in GTL and CO plants where CO-rich syngases are required.

The reaction volume inside the autothermal reformer (ATR) consists of a first zone without catalyst and a second zone where the reactions are supported by catalyst. As the feed/steam mixture and the oxidant meet and pass through the reactor several reactions like partial and full oxidation, steam reforming and water-gas shift take place producing a so called synthesis gas. This product gas mainly consists of hydrogen, carbon monoxide and carbon dioxide as well as remnant methane and water.

ThyssenKrupp Uhde is maintaining an ATR development program and operates a pilot plant since June 2009. A considerable amount of operating data has been collected which covers the entire operating area relevant for an ATR in ammonia, methanol and GTL plants. From these data design tools for industrial scale reactors have been developed. Among these tools are a one-dimensional representation of the reaction kinetics to determine the volumes of the catalyst-free combustion zone and the catalyst bed for given operating conditions and a CFD calculation to optimize the geometry of the combustion zone.

The paper briefly covers the design of the pilot plant, the experimental program and the data acquisition and describes in some detail the development work for equipment design tools for industrial scale reactors.

A special feature of the ThyssenKrupp Uhde ATR reactor design is the arrangement of several oxidant nozzles around the circumference of the combustion zone whereas most

other designs use single central burners. The investigations so far show that the different reactor concept has a positive influence on flow and temperature distributions inside the reactor.

INTRODUCTION

Gas mixtures composed mainly of hydrogen and carbon monoxide are commonly addressed as synthesis gases. They are the base for important processes such as the syntheses of ammonia and methanol.

As required by the reactions which take place in the syntheses the syngases vary considerably in composition. Table 1 lists the most important processes and names the main requirements with respect to syngas composition.

process	synthesis gas composition requirements
ammonia	$(\text{H}_2 + \text{CO}) / \text{N}_2 \approx 3.0$
methanol	$(\text{H}_2 - \text{CO}_2) / (\text{CO} + \text{CO}_2) \approx 2.0$
hydrogen	max. H ₂ content
gas-to-liquids	$\text{H}_2 / \text{CO} \approx 2.0$

Given their main constituents hydrogen and carbon monoxide synthesis gases can be processed from practically any carbon containing feedstock such as natural gas, naphtha, coal or petrol coke plus water via cracking and (steam) reforming. Coke oven gas has also been an important source.

Due to the heats of formation of the species involved all these processes are highly endothermic. The transfer of heat to the process gases to force the desired reactions can be effected via heat transfer through surrounding walls or by internal (autothermal) heat generation through partial combustion of the process gas. An autothermal reformer (ATR) uses the combustion of natural gas within the reactor to generate this heat. Therefore an oxidant (e.g. pure oxygen) has to be added to the mixture of natural gas and steam.

Depending on the requirements of a downstream process the ATR can be run with specific operating parameters to produce the needed syngas composition. Different production scenarios are therefore simulated at the pilot plant which was built by ThyssenKrupp Uhde in Togliatti, Russia.

At this pilot plant a lot of different experiments have been carried out to cover the wide range of possible operating conditions. They generated very good information about the potential of the ATR. The huge amount of recorded data posed a challenge to organize and categorize these.

Using this database the goal is the development of design tools for industrial size ATRs with random operating conditions. This set of design tools consists of two computer models. The first model which includes the kinetics of the reactions is developed to obtain the required feed streams and the reactor size. The second tool is a CFD-model to find the best reactor geometry.

THYSSENKRUPP UHDE'S ATR TECHNOLOGY

Description of ThyssenKrupp Uhde's ATR test facility

The partial, i.e. substoichiometric combustion in autothermal reforming is in principal likely to generate soot. For any set of operating conditions defined by feed gas composition, pressure and steam-to-carbon ratio (S/C ratio) a minimum operating temperature exists below which soot is generated. Steam and hydrogen in principal reduce the soot forming potential, i.e. move the boundary for soot-free operation to

lower operating temperatures. The minimum temperature also depends on the burner design and the flow conditions in the combustion zone.

ThyssenKrupp Uhde has extensive experience in the design of secondary reformers for ammonia plants. These vessels operate under similar pressure and temperature, but in the following two important aspects enjoy considerably milder conditions compared to pure autothermal reformers:

- Secondary reformers process partly reformed gases which contain significant amounts of hydrogen and operate with quite high effective steam-to-carbon ratios. Hence, they do not provide a basis to determine the minimum possible operating temperatures with respect to soot formation. This temperature is directly related to the amount of oxygen supplied. Therefore, to minimize plant operating cost the ATR is to operate at the lowest possible operating temperature.
- The heat generation rates of secondary reformers are relatively small. With the considerably higher heat generation in autothermal reformers, increased wear and tear on the burner and thermal insulation must be expected. They have to be taken care of by modified design features. Also catalyst bed design and size can be expected to vary.

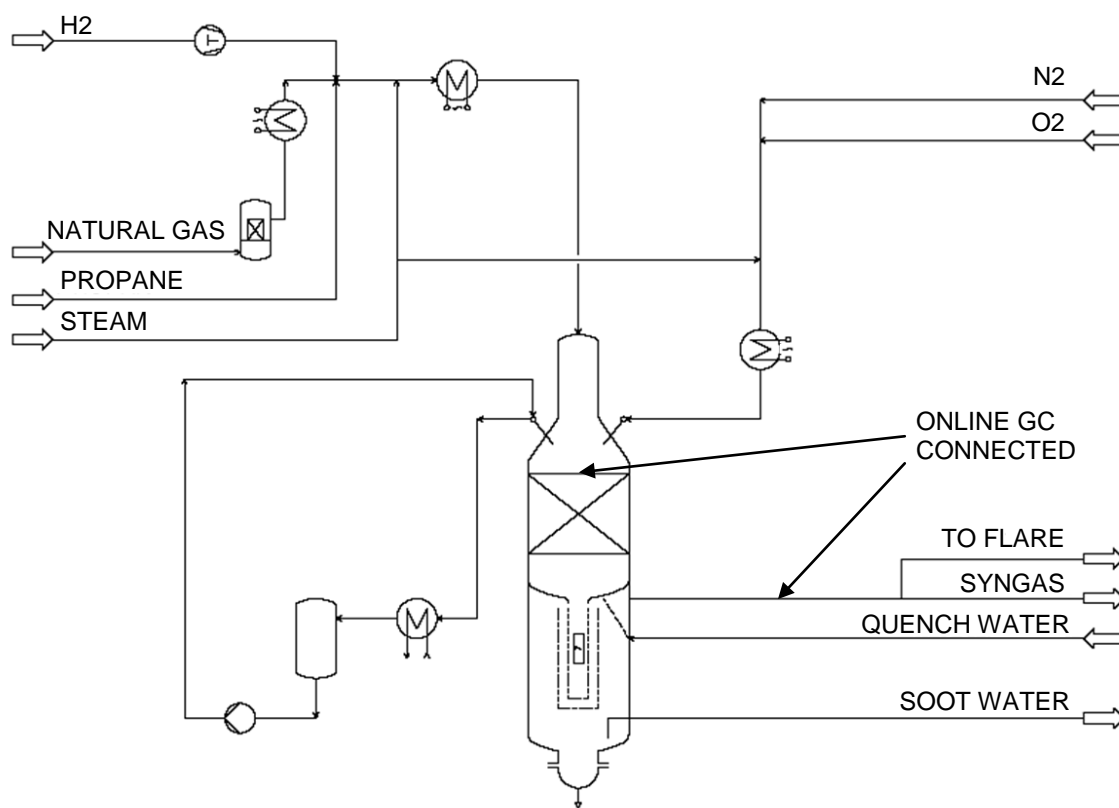


Fig. 1: Process flow diagram of the ATR test facility

To gain further insight into ATR operation and to produce the operational data required to adjust the design procedures, ThyssenKrupp Uhde set up a development program several years ago. Subsequently to being successful in finding a cooperation partner in the Russian company Kuibyshev Azot, a test facility was designed, built and commissioned at Kuibyshev Azot's production site.

Fig. 1 contains the process flow sheet of the test facility. The production site usually operates on fairly light natural gas with low contents of higher hydrocarbons and sulphur. Hence, to simulate heavier feedstock, the test facility was equipped with a device to add a stream of higher hydrocarbons, e.g. propane or butane, to the incoming natural gas.

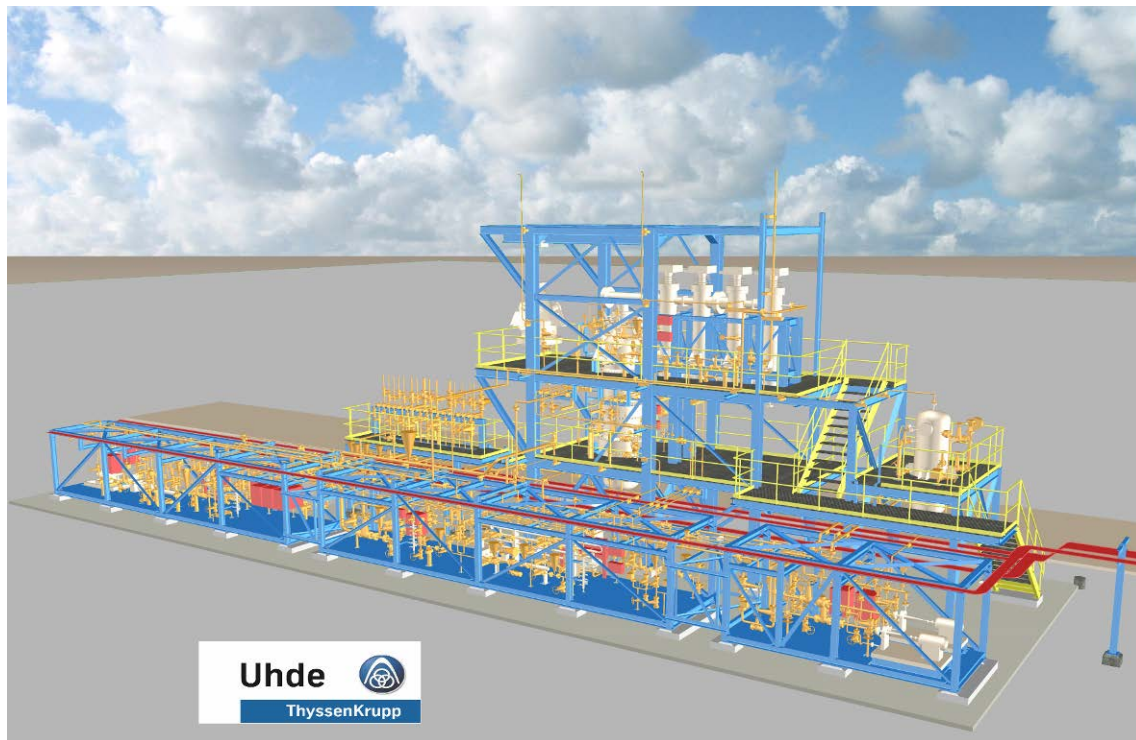


Fig. 2: CAD drawing of the ATR test rig

Provisions were also made for the addition of a hydrogen rich stream to the natural gas to simulate a pre-processed gas. With regard to the low sulphur content a further desulphurization of the incoming natural gas was considered unnecessary. It was also decided to take the required process steam from an external source. The heaters for natural gas, feed/steam mixture and oxidant are powered electrically.

The feed/steam mixture passes a swirler before entering the ATR. This device can be changed in size to analyze the influence of the swirl. The oxidant is added through three cooled nozzles, which are arranged at a certain angle to the surface of the ATR to improve mixing in the combustion zone.

At the ATR gas outlet a water quench is installed. Hence, only moderate gas temperatures are present outside the ATR pressure vessel. The ATR design capacity can be characterized best by a syngas flow rate at reactor outlet in the order of 1000 Nm³/h at 30 bar operating pressure. This is defined as 100% load.

The test rig is equipped with optical light extinction measurement devices to detect soot in the gas phase as well as in the process condensate.

Fig. 2 shows a CAD drawing of the test rig. The lower steel structures in the front contain the modules for burner cooling, hydrogen compression and feed preheating. The high steel structure at the back contains the ATR itself and the feed/ steam pre-heaters.



Fig. 3: View of the ATR test facility ready for start-up

The process plant occupies an area of approximately 30 m by 11 m. The height of the central steel structure is about 10 m.

The main part of the test rig has been assembled on-site from prefabricated parts. This was considered more cost efficient than complete preassembly and transport of the relatively huge structure to the production site. The three modules in front were preassembled and transported as complete units.

Fig. 3 presents a photograph, showing the test facility in its final state of construction ready for start-up. The picture contains a view on the facility from the opposite side compared to the CAD drawing in Fig. 2 with the main structure containing the ATR now in the front. On the right hand side of the picture the pipe rack for the utilities required by the test facility is visible.

EXPERIMENTAL SERIES

Several design and operating parameters are relevant for the ATR operation and have a big impact on the synthesis gas composition and the efficiency. Due to the associated costs and time spans not all of these influences can be analyzed with the same depth. The most important experimental investigations focus on:

- Soot formation boundaries
- Nitrogen content
- Amount of catalyst
- Process gas residence time / reactor load
- Steam-to-carbon ratio (S/C-ratio)
- Temperature level / oxygen-to-carbon ratio (O/C-ratio)
- Pressure

To be able to compare all these data the experiments are structured in series. During each set of experiments the operating factors nitrogen content, pressure, S/C-ratio and load as well as the amount of catalyst are kept constant. Only the outlet temperature is varied stepwise. For example one series represents an operation mode generating stoichiometric ammonia synthesis gas (called ammonia mode) at 100% load with an S/C-ratio of 1.8 at 28 bar over a fully loaded catalyst bed. Starting at an upper temperature level the O/C-ratio is then lowered step by step thus creating a sequence of operating points

which only vary in temperature. Subsequently, one of the main parameters (e.g. the S/C ratio) is varied to enter the next experimental sequence.

Before recording the process data of a new experimental point the ATR is always kept at steady-state operating conditions until temperature and gas composition at reactor outlet do not change anymore. On average this takes about four hours. For each of these stationary operating points all available data is collected, which consists of flow rates and temperatures of the feed streams, the temperatures and dry concentrations of all components in front and after the catalytic zone, the inlet pressure as well as the amount and temperature of the quench water. The species concentrations before and after the catalyst are determined by an online GC, which is calibrated automatically every two days.

OPERATIONAL RESULTS

Running the ATR for several years has provided us with a large amount of experimental data which cannot all be discussed here. Only the most important information resulting from the experiments are given below.

Soot formation boundaries

Specific investigations provide information on the soot formation boundaries. To detect soot formation the quench condensate is analyzed optically and visually. In order to avoid damage to the catalyst it is replaced by ceramic spheres during this set of experiments. Thus modified the reactor is operated in a sequence of experimental points under constant conditions with respect to nitrogen content in the oxidant, S/C ratio and load. The temperature is lowered stepwise until soot is discovered.

The experimental results are documented in special reporting charts. We use the approach to record data sets collected at the same pressure and load in one chart. So called soot points are highlighted, visualizing the influence of the design and operating parameters on the soot formation boundary. The charts indicate a strong influence of the oxidant composition. In the experiments the tendency to soot formation at higher temperatures with lower steam-carbon ratio is proved and respective temperature limits as well as associated O/C ratios for soot-free operation are determined. It is to point out that the soot formation boundaries also depend on the reactor load and pressure.

As the charts contain the capability of ThyssenKrupp Uhde's ATR technology with respect to soot-free operation and thus represent vital know-how they cannot be shown here.

Results of constant operating points

Experimental sequences at different operating conditions are carried out to understand the influence on the reactions inside the ATR. To achieve this, experiments with and without nitrogen in the oxidant stream are performed for four different pressures, four different loads and four different steam-to-carbon ratios. These data provide the basis for fitting the parameters of the developed kinetic reaction models.

The ATR is equipped with two nozzles upstream and downstream the catalyst bed, where process gas samples can be taken. The plant's online GC is permanently connected to these sampling points and determines the dry gas concentrations of methane, hydrogen, carbon monoxide, carbon dioxide and oxygen. Experimental data sets for a wide range of operating conditions are collected and interpreted. For experiments with and without nitrogen the S/C-ratio varies from 0.6 to 3 and the pressure between 20 bar abs and 31 bar abs. The temperature at the entrance to the catalytic zone is varied between 900°C and 1200°C and the load between 50% and 100%.

As an example, the results of a series with nitrogen are given in more detail in figure 4. The main operating conditions for these data points are summarized in table 2.

parameter	unit	value
feedstock higher hydrocarbon content	mol%	2
N ₂ content of oxidant	mol%	40-45
steam-to-carbon ratio	–	3
relative gas residence time in comb. zone	%	100
combustion zone temperature	°C	varying

In figure 4 the resulting methane conversion within the ATR is visualized by the drygas concentrations at the reactor inlet and upstream as well as downstream of the catalyst. The blue squares represent the dry molar concentration of methane at reactor inlet as calculated from the corresponding reactor inlet streams. The red triangles show the measured concentrations of methane at the first measuring point, just on top of the catalyst bed. The big difference in the methane content on the way from the inlet to the entrance of the catalyst bed is partly due to partial oxidation. On average, about 30% of the methane reacts directly with oxygen and therefore is not available for steam reforming. The non-catalytic reforming is very slow compared to the partial oxidation.

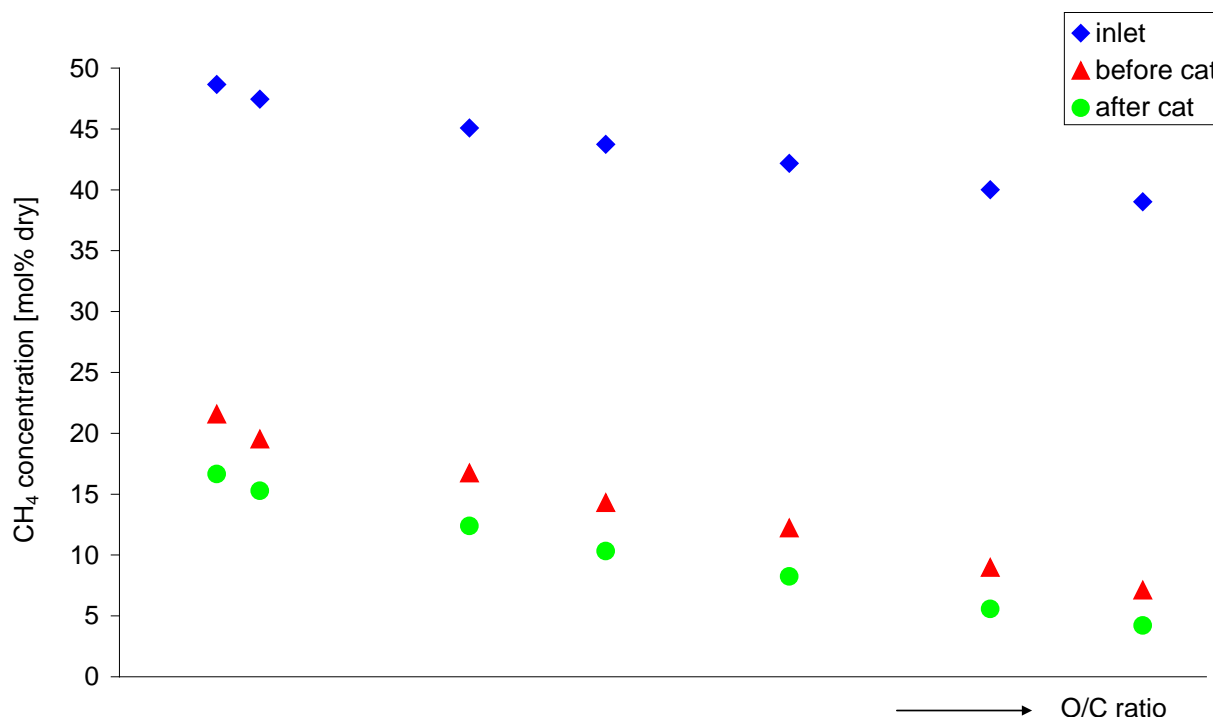


Fig. 4: Methane concentration for an ammonia operation mode series at constant pressure and S/C-ratio

The remaining methane reacts with steam in the catalyst bed and approaches the equilibrium state. The methane concentration after the catalytic zone is represented by green circles in figure 4. The methane concentration is reduced by 3-5 mol% over the catalyst, which is approximately 16% of the overall steam reforming in the reactor.

During the conversion of methane while passing through the ATR the product hydrogen is formed. This is visualized in figure 5. The red triangles show the hydrogen concentration after the catalyst free reaction zone. Again the dry molar concentration is given in percent. About 10-16% of the hydrogen is produced by catalytic reforming. This is presented by the green circles, which illustrate that the rising of concentration

over the catalyst bed is 5 mol% on average. With rising O/C-ratio, which is equivalent to higher temperature, the hydrogen content is consequentially increased due to the shift of equilibrium of the reforming reaction towards the products. The diagram also shows that the differences between the hydrogen concentrations before and after the catalyst bed are getting smaller by rising temperature respectively rising O/C-ratio. The main reason for this is the temperature influence on the reaction kinetic. With rising temperature the reaction rates are increasing. Therefore, at high temperature the reaction gets closer to the equilibrium state within the same residence time.

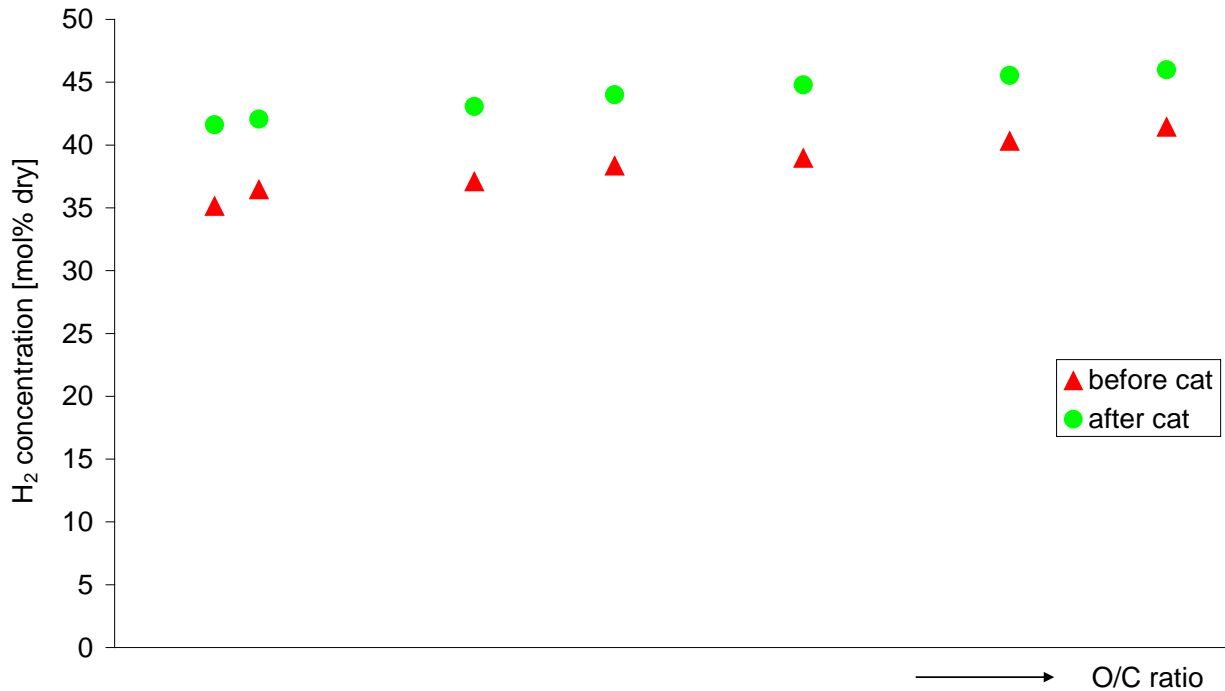


Fig. 5: Hydrogen concentration for an ammonia operation mode series at constant pressure and S/C-ratio

In the next diagram several experimental series are plotted together giving an overview of the experimental field. Figure 6 shows the experimentally determined concentrations of the main components plotted over decreasing O/C-ratio for an ammonia operation mode. In this graph only the pressure remains constant. The two experimental series on the left represent the results for 100% load. The column to the left shows the results for experiments with a higher S/C-ratio. The other three graphs on the right hand side show results of experiments with twice as long residence time corresponding to 50% load. Again the left curve shows the results for the highest S/C-ratio. The plotted concentrations were measured at the first analysis point, which is above the catalyst bed (see figure 1).

The diagram gives very good information about the influence of temperature and S/C-ratio. For all five cases the water (black crosses) and methane (blue bars) concentrations increase with decreasing temperature (from left to right). The reason for this is the strong influence of temperature on the equilibrium of the reforming reaction. Analog to this the concentrations of hydrogen (brown xs) and carbon monoxide (cyan triangles) decrease with decreasing temperature.

Comparing two curves with different S/C-ratios one can see that a decrease in water content leads to a higher concentration of hydrogen. But simultaneously the methane slip increases, too. This may have a negative effect on the downstream process; e.g. in an ammonia plant the purge rate in the ammonia synthesis would have to be increased.

Another effect is the influence of the residence time on the concentrations. Two experiments differing only in the load but having the same O/C-ratio and S/C-ratio can be compared for that. As expected the methane concentration and the water concentration are lower for the experiments with 50% load, due to

the longer residence time. At the same time the carbon monoxide and the hydrogen concentrations are higher.

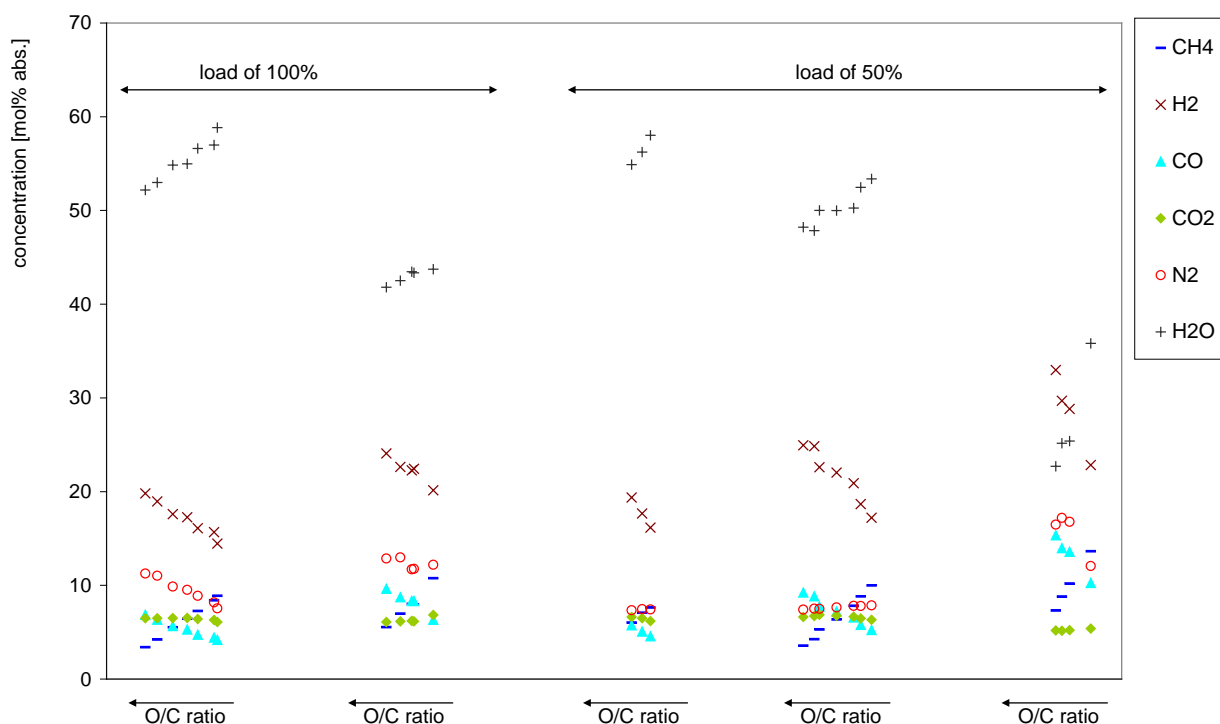


Fig. 6: Experimental data in ammonia operating mode at constant pressure for different S/C-ratios; concentrations plotted over decreasing O/C-ratio.

DEVELOPMENT OF ATR DESIGN TOOLS

The aim of the experimental work at the ATR pilot plant is to provide a basis for the development of ATR design tools for given operating conditions and capacities. These design tools enable ThyssenKrupp Ude to select the most suitable ATR dimensions for a given situation in a plant. The dimensions have a decisive influence on utilities consumption as well as capital costs and thus have to be chosen carefully in order to achieve the most economical setup. Therefore, it is important to understand the chemical kinetic and fluid mechanics in detail. The design tools should provide answers to the following two important questions:

Which are the most suitable sizes / volumes of the various reactor sections?

What is the best geometry of the partial oxidation section, especially the reactor diameter and the angle of the conical mixing zone?

Inside the ATR the feed gas passes through several stages:

- mixing with steam
- passing through a swirler
- entering the ATR
- mixing and reacting with oxygen
- non-catalytic reaction with steam before entering the catalyst bed
 - first analysis point
- catalytic reaction with steam in the catalyst bed
 - second analysis point

With respect to the ATR design ThyssenKrupp Uhde is using the following approach:

- Dimensioning the catalytic free zone and the catalyst bed via a one-dimensional process simulation based on AspenPlus.
- Optimizing the ATR geometry using a three-dimensional CFD-calculation based on Fluent.

Development of a one dimensional ATR sizing tool

The development of such a design tool can be split into two major steps.

- 1) Development of a set of kinetically controlled reaction equations, which covers the entire range of experimental data
- 2) Development of an algorithm, which determines the most suitable reactor size for a given set of operating parameters based on the kinetically controlled set of reactions. This algorithm must also take into account operational limitations such as maximum temperature, soot formation boundaries and maximum gas velocities.

AspenPlus was used to describe the set of reactions as well as the mixing and the heat losses. A model was set up to describe the kinetics of the reactions without catalyst participation. Figure 7 contains a schematic flow chart which represents the sequence of the reaction steps included in the one dimensional model.

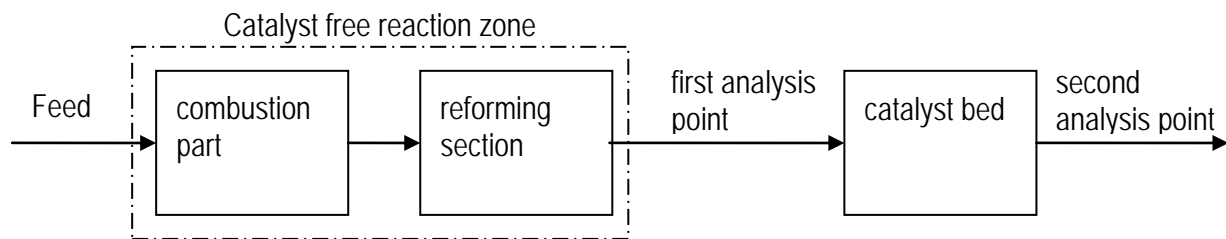
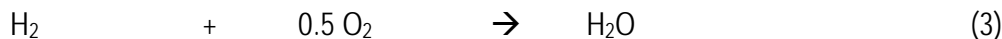
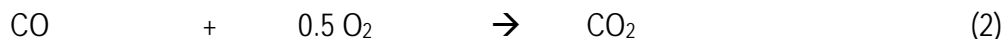
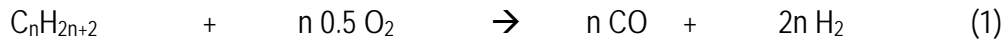


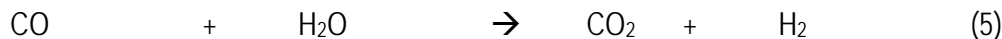
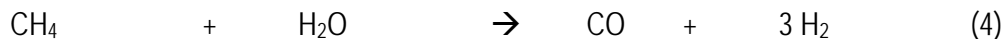
Fig. 7: Schematic flow chart of the one-dimensional process simulation.

In the combustion part of the catalyst free zone the following reactions take place:



The reaction according to equation 1 has to take place first in order to generate the reactants for the reactions according to equations 2 and 3. Since these reactions are very fast compared to the reforming reactions (4 and 5), no kinetics have been applied for the reactions 1 – 3 in the model. The individual reactions have been determined from the experimental data.

In the reforming section of the catalyst free zone the following reactions take place:



Both reactions show equilibria which depend considerably on temperature and the reforming reaction according to equation 4 on pressure as well. The progress of the reforming reaction according to residence time has been modeled by the following commonly used approach:

$$r(t) = A \cdot \exp\left(-\frac{E_A}{RT}\right) \cdot p_{CH_4}^\alpha \cdot p_{H_2O}^\beta \cdot p_{CO}^\gamma \cdot p_{H_2}^\delta \quad (6)$$

In equation 6 $r(t)$ is the actual reaction rate, A a constant, E_A the effective activation energy, R the universal gas constant, T the temperature and p_i the partial pressure of the species i .

Hence this approach contains six adjustable parameters A , E_A , α , β , γ and δ , which have to be determined from the experimental results in such a way that the entire range of operating conditions is represented adequately.

The reactions in the catalyst bed are basically the same as in the reforming section of the catalyst free zone (equations 4 and 5). However, a completely different set of model parameters has to be determined for these reaction equations, because of the acceleration of the reaction by the catalyst. Theoretically an adjustment of the activation energy and the pre-exponential constant should be sufficient to accommodate the influence of the catalyst. However, the experimental results show that the order of the reaction with respect to the individual species is also changing, demanding adjustment of the exponents $\alpha - \delta$.

It should be mentioned, that this kinetic approach is a considerable simplification of the actual species transformation taking place. Nevertheless, it is sufficiently accurate to represent the experimental results. The real reaction course comprises of much larger number of species and reactions. Such a rigorous approach would be very time consuming in the numerical calculations and very difficult to apply for the time being, at least in the 3D-CFD calculations.

The calculated results can be compared to the measured concentrations before and after the catalyst bed. The parameters of the model are fitted to the experimental data points for the entire range of operating points.

Figure 8 shows a comparison of the calculated values with the experimental data points in front of the catalyst bed for ammonia operation mode at constant pressure and two different reactor loads. Each series represents a set of operating point with similar S/C-ratios e.g. in the range of 2.9 to 3.1. Due to the operating conditions on site it is impossible to maintain exactly the same ratio from one experiment to the other. Owing to this fact and because the calculations are always based on the real input streams the simulated results - shown as solid lines in figure 8 - are no straight lines. The symbols in this figure depict the experimental data. Obviously the model can reproduce the measured values within the experimental error across the entire range of operating conditions.

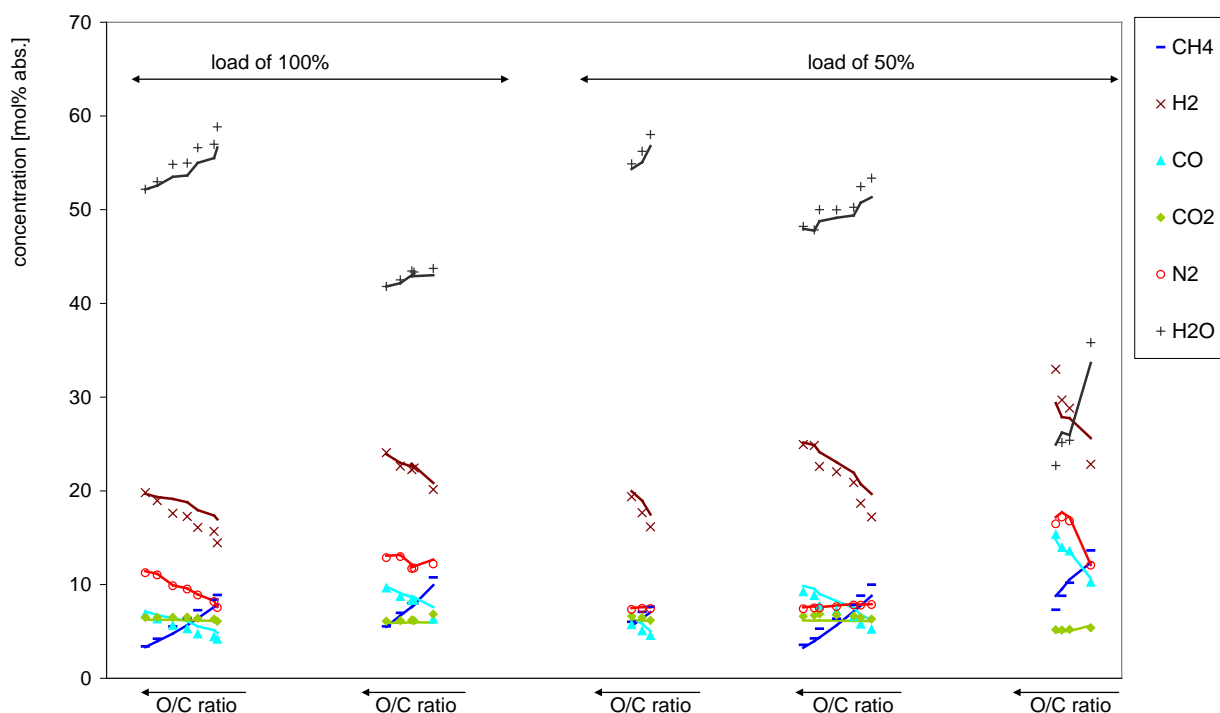


Fig. 8: Comparison of experimental data (symbols) with simulated results (solid line) for different S/C-ratios at constant pressure; concentration plotted over decreasing O/C-ratio.

Transfer of the AspenPlus® kinetics into Fluent®

Since the fluid flow through the catalyst bed is expected to be very smooth only the catalyst free reaction and combustion zone needs to be further examined overcoming the limitations of the aspen tool. In order to use the kinetic model gained in AspenPlus a simple Fluent geometry model was initially chosen for proving the proper implementation of all reaction features in the Fluent setup. The reaction calculations in

Aspen always assume ideal mixture of all components. The closest corresponding model in Fluent is a simple plug flow reactor. This tubular reactor is setup as a 2D-model divided into three fluid zones. The first zone is needed as an inlet zone for the combined feed of natural gas, steam and oxidant. In this part no reaction mechanism is activated in the Fluent setup. In the second zone all relevant reactions such as oxidation, water gas shift and reforming are implemented corresponding to the chemical kinetics derived with AspenPlus from the experimental data. The third outlet zone represents the pressure drop of the packed bed following downstream the reaction zone and is of no particular interest otherwise.

The performance of the reaction kinetics in Fluent was examined on three selected experimental points representing three very different ways of running the ATR. These points differ in S/C-ratio, O/C-ratio, pressure and nitrogen content. Figure 9 shows the temperature profile in the tubular reactor for the first operating point. In here the ATR was operated at 28 bara with pure oxygen as oxidant. Obviously the modeling of the reaction scheme is successful: At the beginning of the reaction zone the temperature rises rapidly due to the very quickly proceeding oxidation reactions. Over the length of the reaction zone the temperature decreases slowly due to the heat consumption of the reforming reaction as well as the heat loss which has been implemented in accordance to the measured heat loss on site.

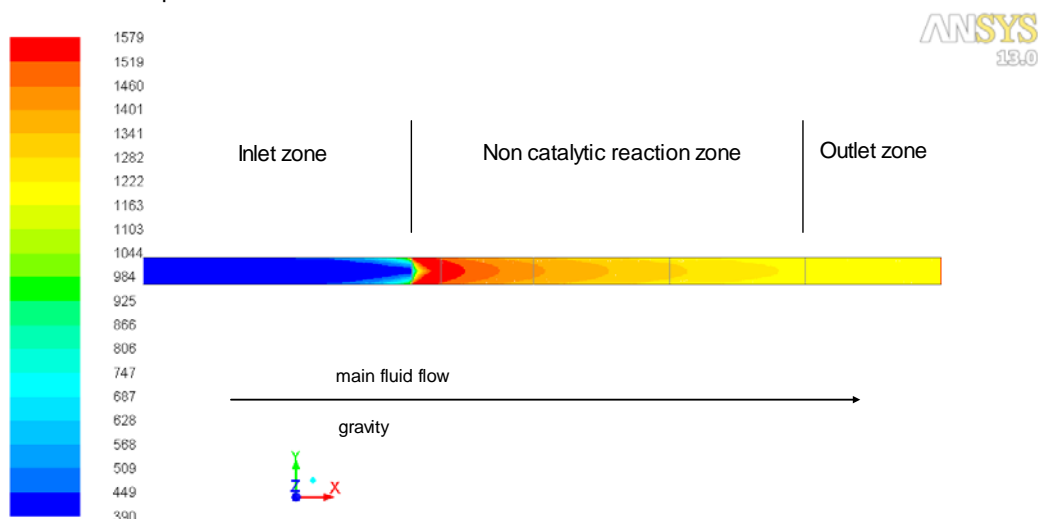


Fig. 9: Calculated temperature profile [°C] for tubular reactor with implemented kinetics for the non catalytic reaction zone for the first data point.

The Fluent simulation was further evaluated regarding the change in species concentrations over the length of the reaction zone or residence time respectively as depicted in figure 10. The solid lines mark the concentration changes calculated with AspenPlus; the dashed lines represent results of the Fluent simulation. The same color is used for the same species. The graphic shows a significantly higher production of hydrogen with simultaneously lower fractions of steam and methane in the AspenPlus calculation (marked with index A) compared to the Fluent simulation (marked index F). Obviously the progress of the reforming reaction is additionally influenced by fluid flow conditions and mixing processes. All these processes cannot be considered in AspenPlus. In order to compensate this the reforming kinetic in Fluent was accelerated. By readjusting only one parameter a good reproduction of the results is achieved as shown in figure 11.

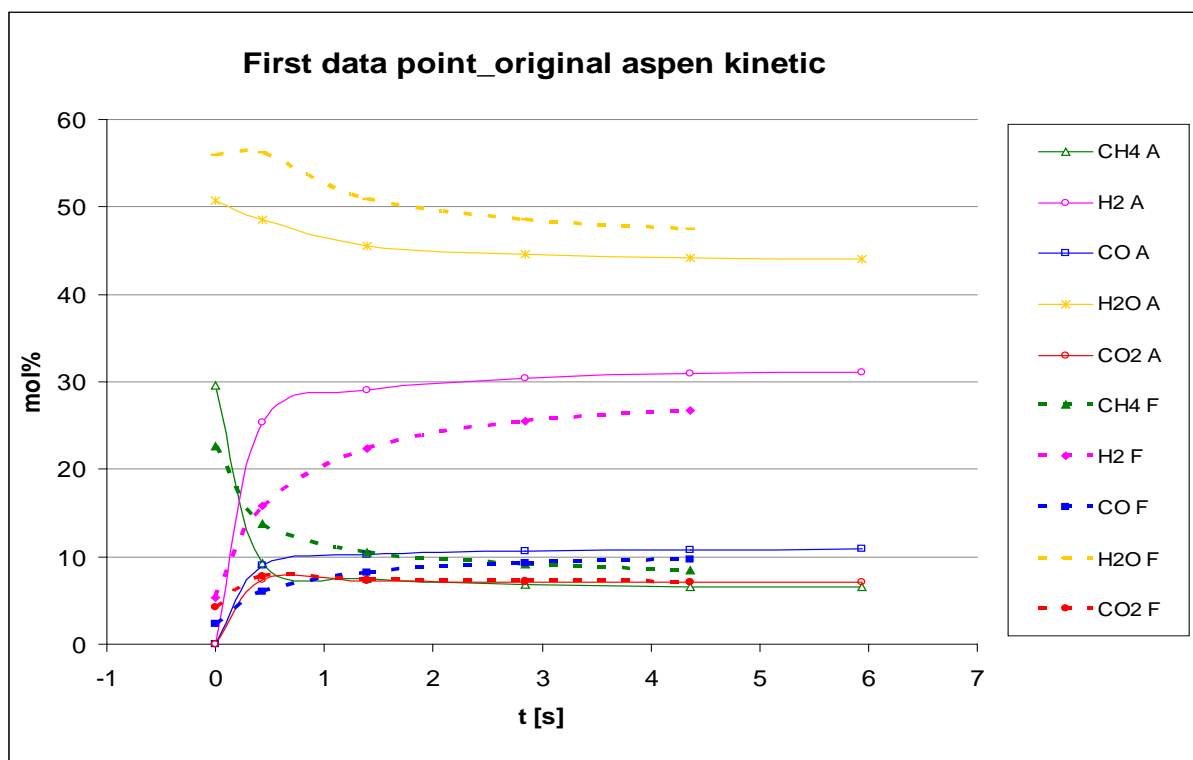


Fig. 10: Progress of component concentration over residence time with original AspenPlus kinetics

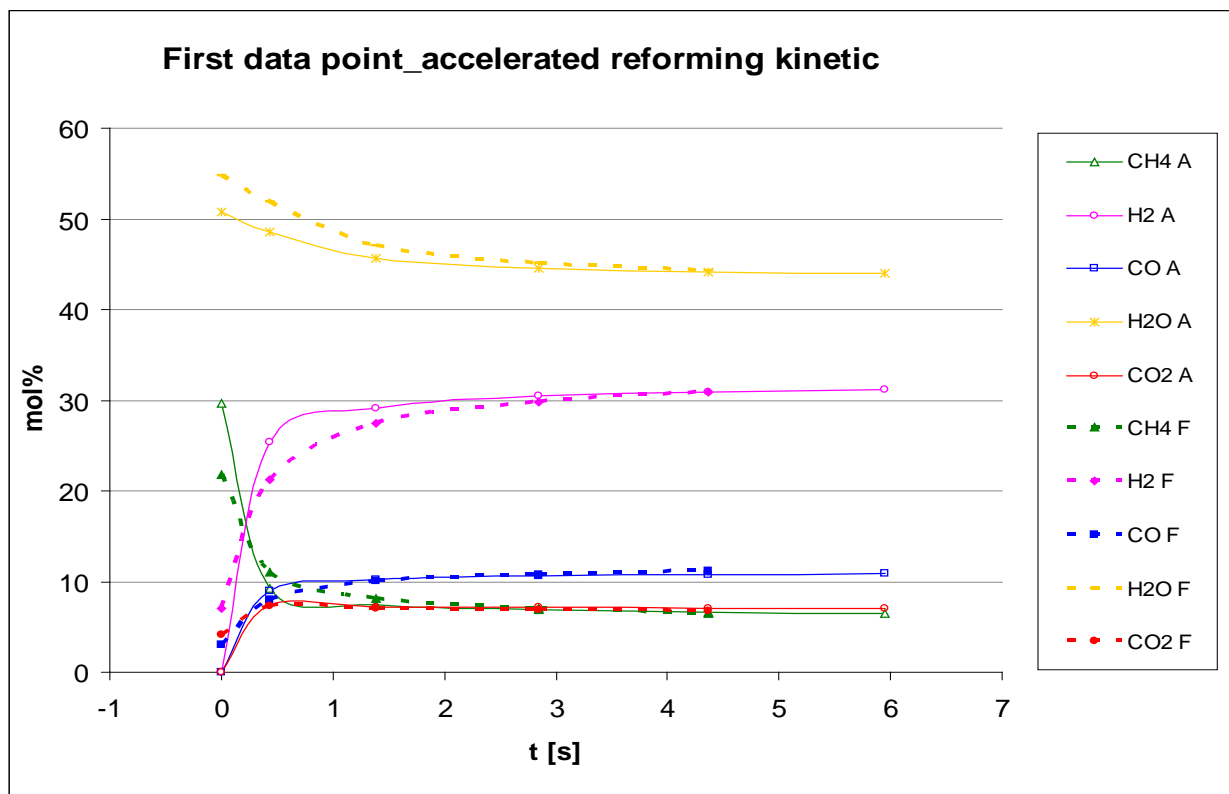


Fig. 11: Progress of component concentration over residence time with accelerated reforming kinetics

Accordingly the simulation results for two other data points with completely different operating conditions are compared in figure 12, calculated in Fluent with the original AspenPlus kinetics on the one hand and the accelerated reforming reaction on the other hand. The legend used here is the same as in figures 10 and 11.

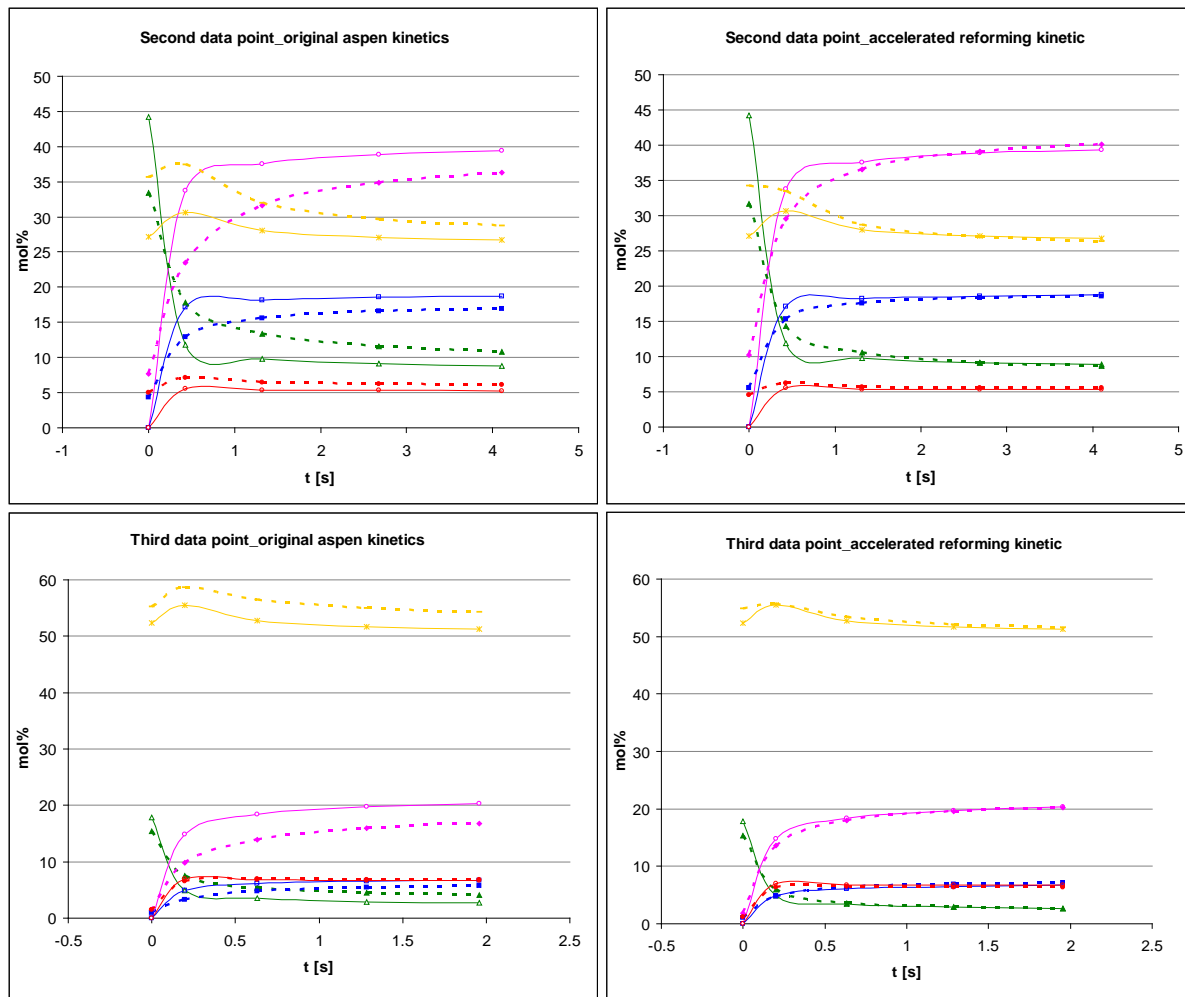


Fig. 12: Evaluation of original AspenPlus kinetics and acceleration of the reforming reaction on different ATR operating points

The two graphs in the upper part of the figure represent the results for the second operating point where the ATR was again run with pure oxygen at the same pressure and the same residence time but at a much lower steam-to-carbon ratio. The two graphs in the lower part of the figure represent the third operating point. In here nitrogen is added to the oxidant, the pressure was reduced, the residence time is shortened and the steam-to-carbon ratio changed, too. Since the operating conditions differ that much, the concentrations e.g. the methane concentration change quite significantly, too. Though the range of i.e. the methane concentration differs dramatically compared to the first operating point the essential statement remains the same. The CH_4 conversion in the Fluent simulation is again much lower using the original AspenPlus kinetics and can be improved similarly by the same acceleration factor. This means by readjusting only one parameter a wide range of operating conditions can be represented.

Verification of the Fluent® model with the real reactor geometry

After developing the Fluent kinetics for the simplified tubular reactor it has to be examined whether any adaptations are necessary for proper process calculations in the real geometry. The ATR design is modeled according to figure 13. The feed/steam mixture passes a swirler before entering the conical reactive zone. The oxidant is added through three cooled nozzles, which are oriented in a slight angle to the reactor wall. The packed bed of the catalyst homogenizes the fluid flow before the process gas leaves the reactor. The Fluent reaction kinetics as described above are implemented into the catalyst free reactive zone of the 3-D model. In order to minimize calculation times, the swirler and the porous zone are calculated without any reaction mechanism. As steep temperature gradients are to be expected in the vicinity of the oxidant nozzles the meshing needs to be narrowed down skillfully in the area of the burner flames.

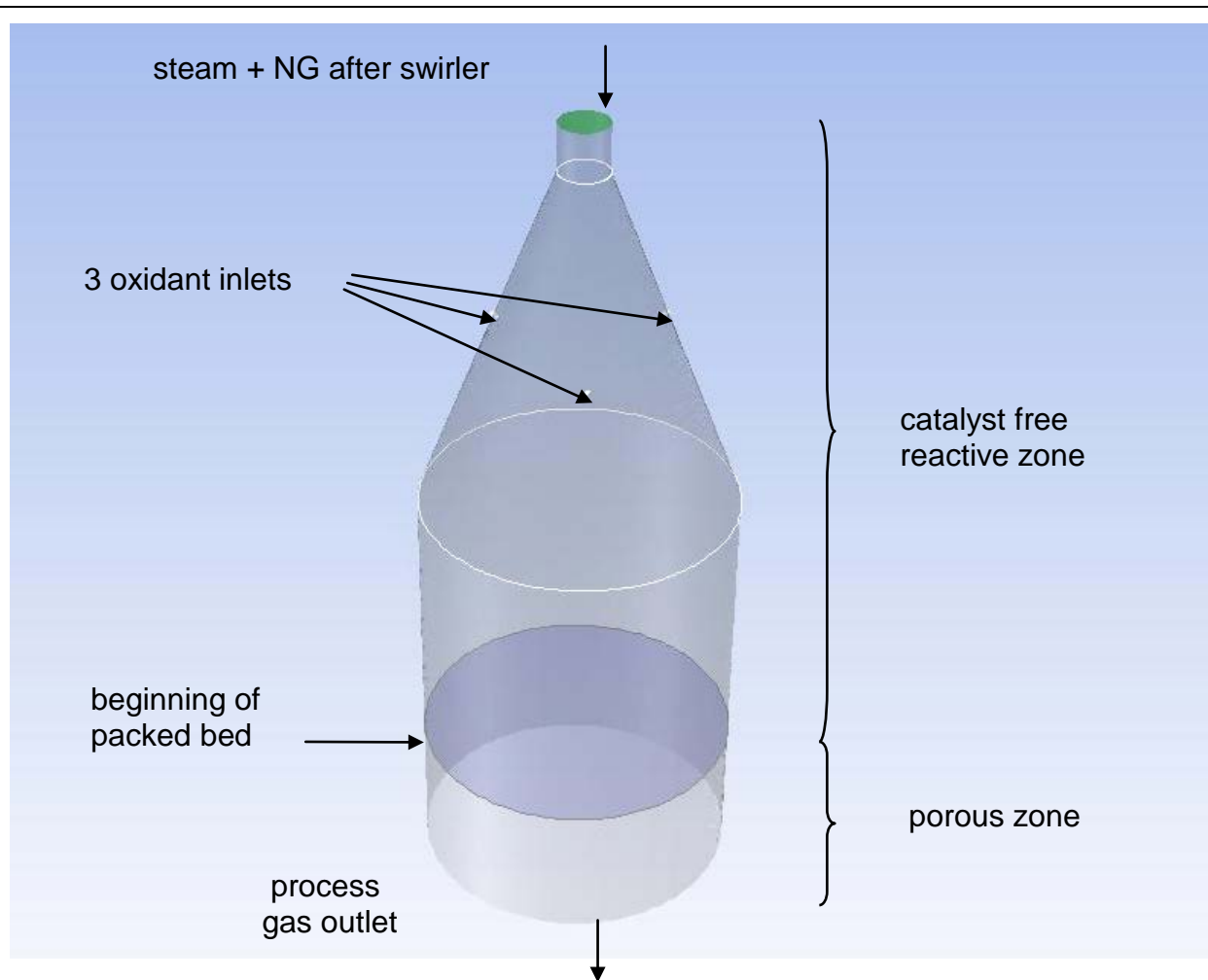


Fig. 13: Design model of the ATR for Fluent simulations of the catalyst free zone

First the accelerated kinetics derived in the cylindrical model is implemented in the simulation of the real plant. The Fluent simulation for the first design point is evaluated regarding the change in species concentrations with the results visualized in figure 14. The concentrations given for a specific residence time are calculated as the mass weighted average over the reactor cross-section at the corresponding reactor length. The solid lines mark the concentration change calculated with AspenPlus, the dashed lines represent the Fluent simulation results. The graph shows a significantly higher hydrogen production with simultaneously lower fractions of steam and methane in the AspenPlus calculation compared to the Fluent simulation.

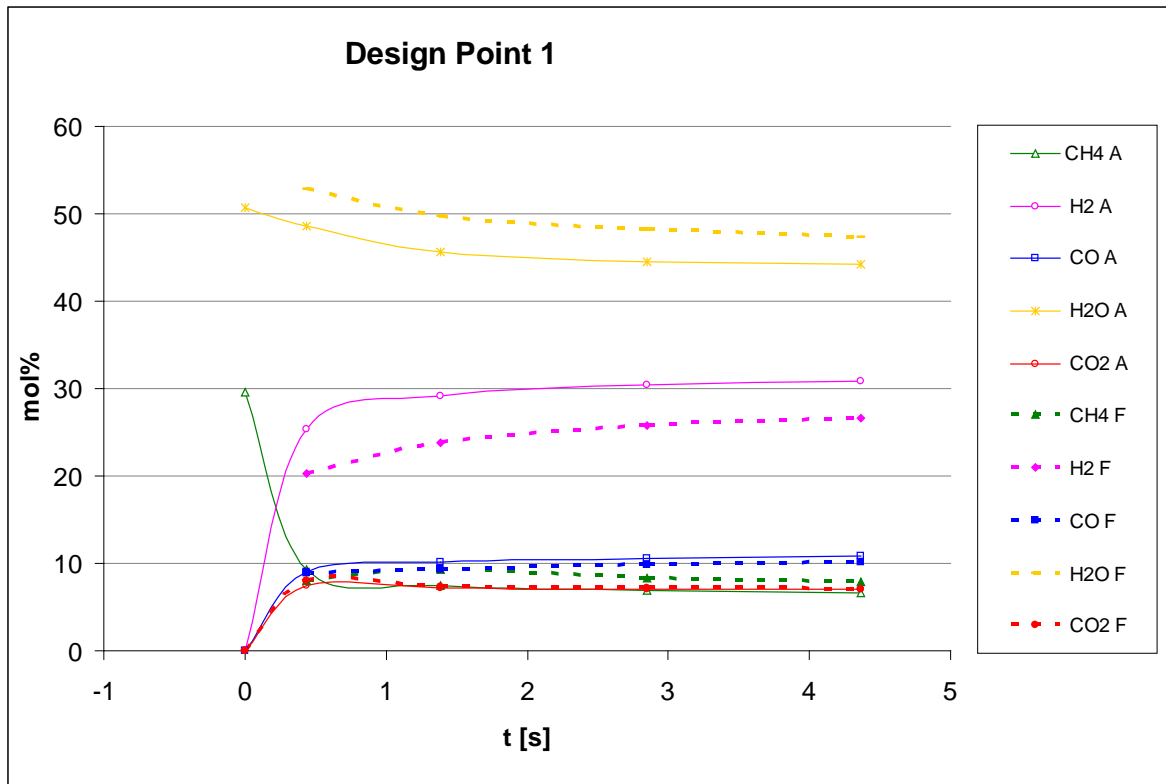


Fig. 14: Progress of component concentration over residence time in the Fluent simulation for the real ATR with the Fluent kinetics derived in the cylindrical model

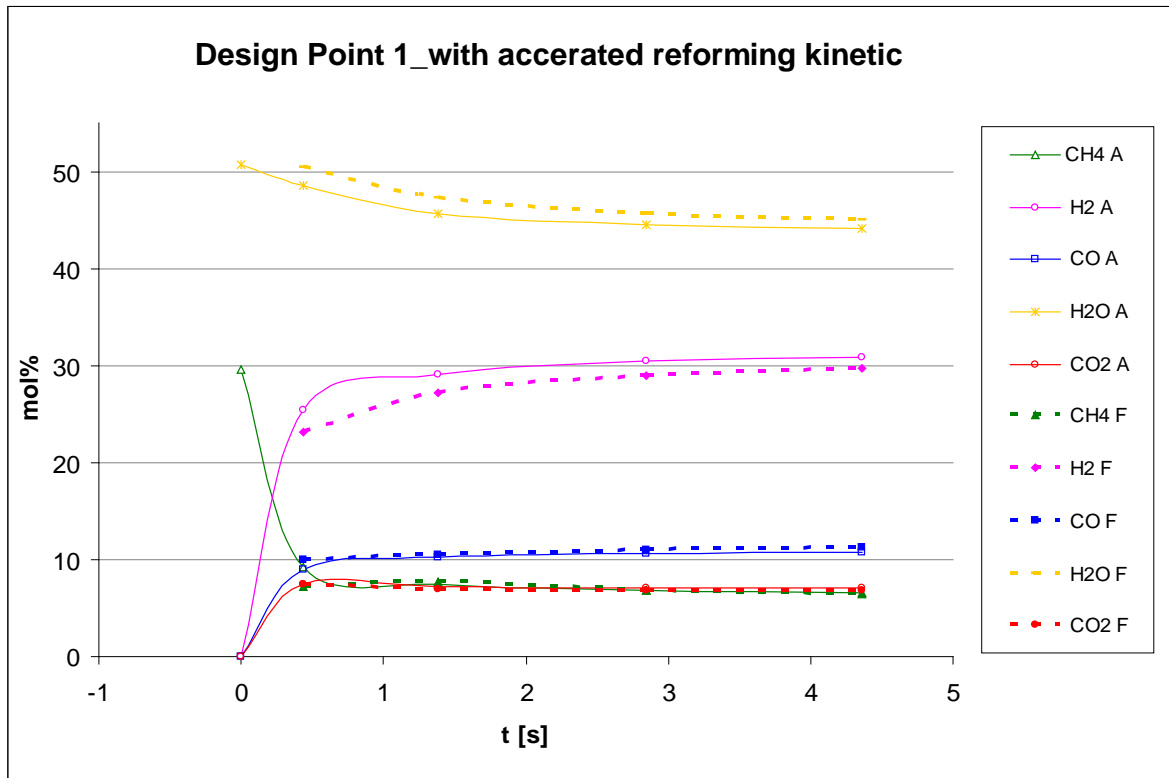


Fig. 15: Progress of component concentration over residence time in the Fluent simulation for the real ATR with accelerated reforming kinetics

Obviously the real fluid flow calculation reduces progress in the reforming reaction due to the development of recirculation areas as well as a delayed mixing of fuel and oxidant. In order to compensate these effects

the reforming kinetic in Fluent is again accelerated and a good reproduction of the AspenPlus results is achieved as shown in figure 15.

For further validation of the Fluent simulation model other design points need to be calculated which is time-consuming due to the required mesh refinement and the implementation of the numerous chemical reactions. Once the validity is proved for the operating range of interest comparisons can be made regarding local temperature distribution and its impact on the measured soot formation.

Method for scale-up

With these tools an ATR can be scaled and designed to any given operating conditions. However, the central goal is to identify the most economic way to operate the ATR. This includes low capital costs as well as low operating costs. The design program for this task is presently under development at ThyssenKrupp Uhde. One possible way to realize the required automated sequence is described below.

The required data for this optimization are the desired amount of syngas, the ratio of nitrogen in the syngas stream, the operating pressure and the allowed methane slip. First again AspenPlus® is used to obtain the residence time and the volume of the ATR respectively as well as the desired feed streams.

A simplified flow diagram for determining the optimal operation conditions is given in figure 16, which are the volume of the ATR and the feed streams natural gas, oxygen, air and steam.

The first feed stream to be calculated is the amount of nitrogen. By knowing the desired amount of syngas as well as the nitrogen ratio in the syngas, the amount of nitrogen is fixed. This corresponds to the needed feed stream of nitrogen. As the performance of the ATR mostly depends on the ratios O/C and S/C, these variables are used for variation in the program to come up with a more stable routine instead of the feed streams for oxygen and steam. With the third variable, the amount of natural gas (short NG), the feed streams of oxygen and steam can be determined, too. For these three variables (amount of natural gas, S/C-ratio and O/C-ratio) and the volume of the catalyst free zone of the ATR initial values have to be given.

With the known feed streams the reaction yields in the catalyst free zone can be determined. This calculation also provides the temperature in front of the catalyst. This temperature must be within the correct temperature range to avoid both soot formation and damage to the catalyst. To achieve this, the volume of the catalyst free zone can be adjusted.

Next the program calculates the reaction yields within the catalyst zone. This results in the produced syngas flow rate and the final composition. At this point the program checks whether the desired methane slip has been reached. If the methane slip is too high the steam to carbon ratio must be changed to higher values. If the methane slip is reached, there is only one given value to be checked. If the produced amount of syngas is too high, the amount of natural gas has to be lowered. If it is too low, more natural gas is needed respectively.

To determine the most efficient operating conditions a calculation of the respective utilities costs has to be done. If only the minimum of the operating costs are required, the specific costs of all input streams have to be given as input values. By summing up all costs for the feed streams the minimum of costs can be determined by varying the O/C-ratio. One important question is whether the capital costs should be included.

If capital costs shall be included too, the program will be more complex, especially the way of calculating the minimal price as there will be two. For determining the capital costs the following simplification needs to be done: The price of the ATR is divided into two parts: The cost of the pressure vessel and the catalyst. For both parts a price per volume needs to be estimated and included in the program. Very obviously a certain volume inside the catalyst zone is considerably more expensive than the same volume in the catalyst free section.

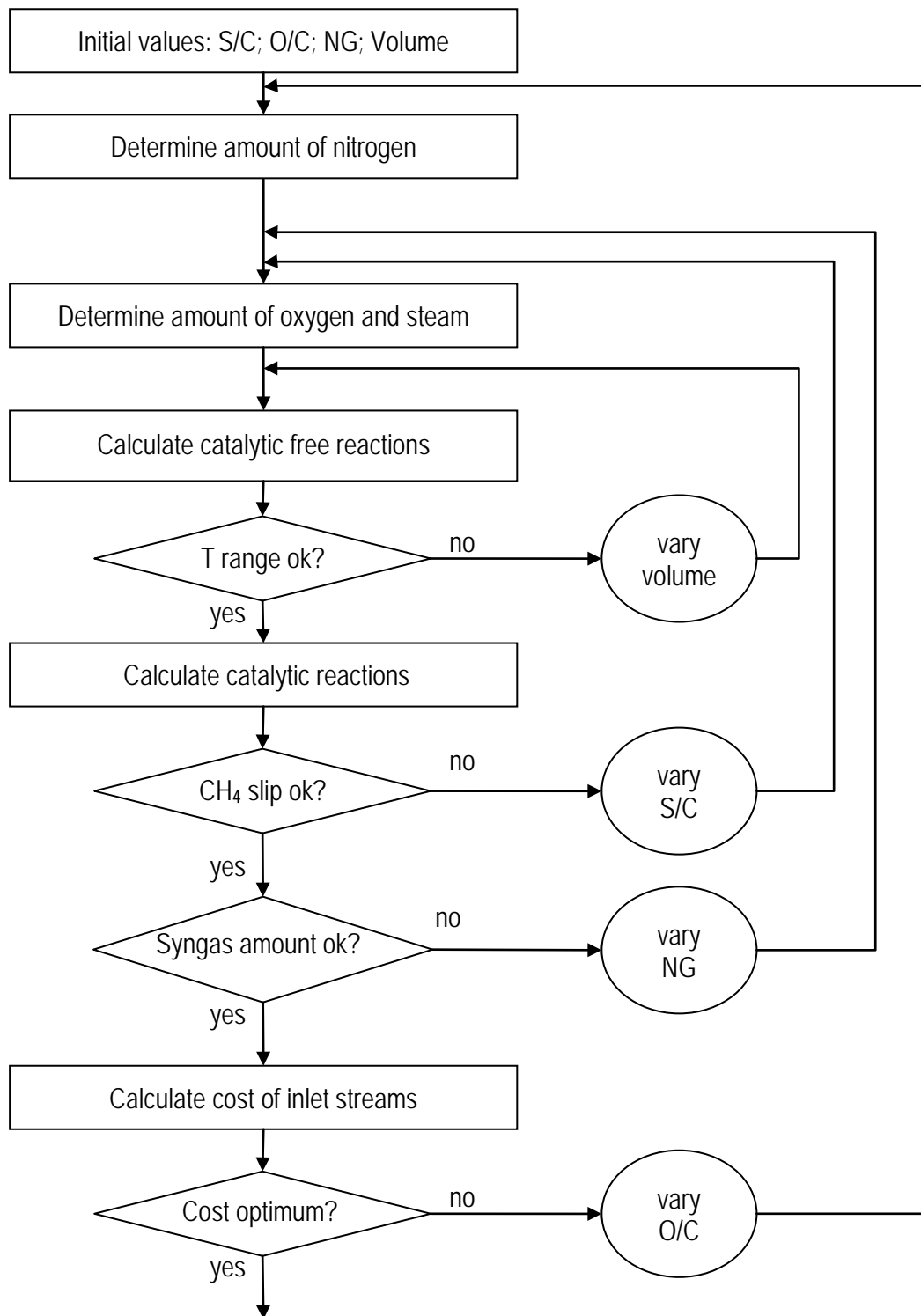


Fig. 16: Flow diagram of the design model to find the optimal operating condition

However, since the reaction ratios are considerably different and very dependent on local temperatures and species concentrations there is always a point in the overall conversion at which it is more cost efficient to provide catalyst.

This algorithm can be implemented in an AspenPlus program and will give the optimal feed streams as well as the ATR volumes as a result. However, AspenPlus cannot provide any information regarding the best geometrical design of the catalyst free reactive zone. For this purpose the Fluent simulation is used. A parametric geometry is setup in which the main dimensions like reactor height and diameter, conical angle, number and position of the oxidant nozzles can be easily set to the desired values and hence varied. The

meshing is adapted automatically. The reaction kinetics derived from the pilot plant is used to model species conversion. Thus it is possible to compare different reactor shapes for any desired production plant. The calculations using Fluent take a fairly long time. Hence, it is important to start with a suitable approximation to get good initial values for the reactor diameter and the number and position of oxidant nozzles.

CONCLUSION AND OUTLOOK

The autothermal reformer is an attractive syngas generator with considerable potential. To verify the viability of its ATR technology ThyssenKrupp Uhde built a pilot plant in Togliatti, Russia and carried out an extensive experimental program. The experiments covered the entire range of relevant operating conditions characterized by operating pressure, reactor temperature, S/C-ratio, oxidant composition and reactor load. The tests were conducted in such a way that the ATR produced synthesis gas suitable for various downstream processes namely ammonia and Fischer-Tropsch syntheses. On the basis of the experimental results many dependencies can now be understood much better, e.g. the soot formation boundaries. Also, several sensitivities to differing input conditions were analyzed in detail.

Based on the data recorded during these experiments ThyssenKrupp Uhde developed tools to facilitate and speed up the design step of an industrial size ATR for random capacities and operating conditions. This set of design tools combines the advantages of AspenPlus and Fluent applying one- as well as three-dimensional fluid calculations of the flow regime and the chemical reactions in the reactor.

A reduced set of reactions is used to model the conversion of species inside the reactor. The progress of the relatively slow reactions of methane reforming and water-gas shift conversion is calculated with kinetically controlled models. The AspenPlus design tool using this reaction models shows very good accuracy compared to the experimental results, thus justifying the choice of the reduced set of equations. The models can therefore predict the composition of the syngas produced from different feed streams. The final step will be the completion of an automated AspenPlus program to determine the optimal operating conditions. From given input data such as the required amount of syngas production, the operating pressure and the allowed methane slip this program determines the ATR feed streams (oxygen, natural gas and steam) which characterize the most economical operation. The design program also determines the volumes of catalyst-free section and the catalyst bed inside the reactor.

Once the overall volumes are specified the best reactor shape is elaborated, mainly by comparing the fluid flow in different reactor designs via CFD simulations. The corresponding Fluent simulations provide an improved understanding of the fluid flow within the catalyst free reaction zone. Thus it is possible to determine dependencies such as soot formation or reforming reaction progress on the reactor design.

For this purpose we continue working on the verification of the Fluent kinetics as well as on the setup of a parametric design model which will significantly facilitate setting up the CFD calculations.

As a result of this design strategy based on experimental data ThyssenKrupp Uhde is now in the position to quickly identify the most efficient ATR-based process for any given plant requirements and select the best reactor design.

References

Nölker, K. and Johanning, J. Autothermal reforming: a flexible syngas route with future potential, Nitrogen and Syngas (2010)

