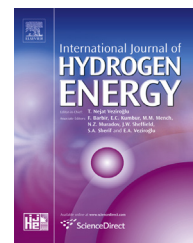


Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Review Article

BrOx cycle: A novel process for CO₂-free energy production from natural gas



Jesús González Rebordinos^{*}, Alexander H.J. Salten, David W. Agar

Technical University of Dortmund, Department of Biochemical and Chemical Engineering, Emil-Figge-Straße 66, 44227 Dortmund, Germany

ARTICLE INFO

Article history:

Received 30 April 2016

Received in revised form

1 September 2016

Accepted 13 September 2016

Available online 8 February 2017

Keywords:

Bromination

Oxidation

Methane

Energy

CO₂

BrOx cycle

ABSTRACT

Currently, the combustion of fossil fuels is the major anthropogenic source of CO₂ and the main reason for the significant increase in its atmospheric concentration over the past decades. Despite the increase in fossil fuel consumption in recent years, the available reserves have actually increased, indicating that the use of fossil fuels is limited less by their availability than by the emissions of CO₂ associated with their combustion.

Energy can be generated from methane without concomitant CO₂ emissions by means of a bromination-oxidation (BrOx) cycle. This process comprises two exothermic reaction steps, namely methane bromination and hydrogen bromide oxidation, with a bromine recycle from the latter to the former, that result in an overall exothermic reaction in which methane and oxygen yield water and solid carbon, thus avoiding CO₂ production.

Thermodynamic and kinetic simulations have been performed that show the feasibility of the BrOx cycle. The influence of temperature, residence time and feed composition on methane bromination reaction was studied and indicates that carbon formation starts at temperatures as low as 500 °C for excess methane, while temperatures over 750 °C are necessary in order to achieve noticeable carbon formation when working with excess bromine. The composition of the carbon produced has been determined and the mass fraction of bromine-containing by-products has been found to decrease with increasing reaction temperatures.

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Contents

Introduction	4711
Materials and methods	4712
Thermodynamic calculations	4712
Kinetic simulations	4712
Experimental study of methane bromination	4713
Results and discussion	4714
Thermodynamics of BrOx cycle	4714

^{*} Corresponding author.

E-mail address: agar@bci.tu-dortmund.de (D.W. Agar).

<http://dx.doi.org/10.1016/j.ijhydene.2016.09.071>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Kinetic simulation of methane bromination	4715
Experimental results on methane bromination	4716
Conclusion	4718
Acknowledgments	4719
References	4719

Introduction

Energy consumption and the standard of living are closely correlated and thus humanity needs abundant and uninterrupted energy supplies. Over the 20th century, global energy consumption has steadily increased, reaching more than 500 EJ in year 2014 [1]. This trend is expected to continue in the coming decades due to the predicted growth in both the worldwide population and economy.

In 2014, fossil fuels represented more than 80% of the total primary energy demand of the OECD (Organisation for Economic Co-operation and Development) members [1]. This energy is primarily obtained via the combustion of coal oil and natural gas, which implies the formation of CO₂, a by-product that is routinely released into the atmosphere. As a consequence, its atmospheric concentration has steadily increased over the past decades [2], which scientific consensus considers to be the main cause of climate change [2]. Recently, at the 2015 United Nations Climate Change Conference (COP21) held in Paris, an agreement was achieved, that intends to limit the increase in the global average temperature to less than 2 °C above pre-industrial levels [3]. In order to do so, a dramatic reduction of CO₂ emissions is inescapable. Since the largest anthropogenic source of CO₂ is that derived from energy generation, avoiding or minimising the associated emissions is the most direct strategy.

One approach for reducing energy-derived CO₂ emissions is to expand the use of renewable energy. A good example of this is the energy transition (*Energiewende*) that has been adopted in Germany, which aims to reduce greenhouse gases emissions by 40% by 2020 and by 80–95% by 2050 [4]. Although the share of renewable energy in Germany's gross power supply has reached 32.5% in 2015 [5], the impact on global energy production is negligible. Additionally, several studies predict that fossil fuels will remain the predominant energy source for the next decades, still supplying at least 75% of the world energy demand in 2040 [6].

Despite the increased fossil fuel consumption over the last century and contrary to popular belief, the proven reserves of fossil fuels have not decreased in the past few decades, but actually increased as exemplified by natural gas, whose proven reserves were 117.6 Tm³ in 1992 and 187.8 Tm³ at the end of 2011 [1]. In addition, if natural gas from unconventional sources, such as shale gas, coal-bed methane or methane hydrates, is taken into account, the estimates of the gas supply available can be measured in centuries [7]. Naturally, not all unconventional resources are technically or economically

exploitable at the present time, but this situation may soon change as new extraction technologies are developed. The shale gas boom provides a good example of such a development in the past. Although well-known, shale gas has remained non-exploitable for decades until a combination of new technologies, namely hydraulic fracturing (fracking) together with horizontal drilling and, most importantly, high gas prices made its economic exploitation feasible [8].

The aforementioned demonstrates that the use of fossil fuels is less restricted by their availability than by the CO₂ emissions resulting from their combustion. In view of this and from the fact that replacing the existing infrastructure for extraction, processing, transportation and storage would be extremely expensive, and in the short term, unfeasible, the decarbonisation of energy production from fossil fuels is a promising strategy to counter climate change.

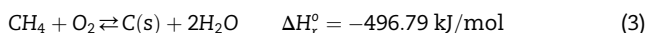
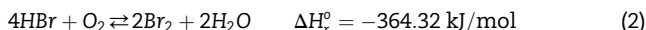
CCS (Carbon Capture and Storage) has been proposed to decarbonise fossil fuels by capturing the CO₂ before or after combustion and sequestering it either under the ocean or subcutaneously. It is a controversial technology that lacks the acceptance of a large section of the public and entails many uncertainties regarding costs, long-term reliability and storage capacity [9]. Moreover, up to 40% of the energy being generated may be sacrificed by this process.

Another approach that enables CO₂-free energy production from fossil fuels is methane pyrolysis. Despite the endothermic methane pyrolysis, the hydrogen produced can react exothermically with oxygen thus leading to a net reaction in which roughly half the total energy available is released, with solid carbon and water as the only by-products. This process has been widely studied, but it still is not technically feasible, mainly due to heat exchange issues and the fact that it is only kinetically feasible at temperatures above 1200 °C [10,11].

The BrOx cycle is a novel process that enables the use of natural gas for energy production without accompanying CO₂ emissions. It comprises two exothermic reactions, which result in the same net reaction as the combination of methane pyrolysis and hydrogen combustion. The BrOx cycle has thus the advantage of avoiding any heat transfer to an endothermic reaction at high temperatures.

In the BrOx cycle, methane and bromine are first fed to a reactor, where they react to yield solid carbon and hydrogen bromide (Eq. (1)). An excess of bromine is used to ensure that methane is completely consumed. Following subsequent separation of the solid carbon, that can be carried out with a combination of a cyclone and a filter to remove the fine particles, the remaining gaseous product stream is fed to a second reactor, in which hydrogen bromide reacts with an

oxygen feed stream to regenerate bromine and form water (Eq. (2)). Afterwards, bromine is separated from this water and recycled to the methane bromination reactor (see Fig. 1). This process results in an overall reaction, in which methane and oxygen yield energy with solid carbon and water as the only by-products, thus circumventing CO₂ production (Eq. (3)). All the process is carried out at atmospheric pressure in order to minimise the risk of leaks. By sacrificing, at least provisionally, the energy available in the carbon, one simplifies the sequestration problem dramatically.



The reason for selecting bromine from the halogens lies in its high compatibility with the process. Apart from being extremely difficult to handle, fluorine would react vigorously with methane forming hydrogen fluoride, a highly stable molecule which cannot be easily oxidised. Iodine's low reactivity renders it unsuitable stripping the hydrogen off methane iodination. Chlorine would react sufficiently with methane, but hydrogen chloride oxidation (Deacon reaction) has proved to be a challenging reaction and its commercial implementation since its development in 1866 for the production of chlorine has been plagued by problems [15]. Bromine has been selected for the cycle because it ensures a good reaction with methane and a later hydrogen bromide oxidation that is more favourable thermodynamically than Deacon reaction as its equilibrium conversion is higher than that of hydrogen chloride oxidation.

Materials and methods

Thermodynamic calculations

A preliminary thermodynamic analysis of the BrOx cycle was performed in order to assess its feasibility. Thermodynamic data calculated with NASA polynomials were used for the calculation of the reaction enthalpy and the change in Gibbs

free energy for methane bromination and hydrogen bromide oxidation [12].

$$\Delta H = \sum_i v_i H_i^\circ \quad (4)$$

$$\Delta G = \sum_i v_i G_i^\circ \quad (5)$$

First, the Gibbs energy minimisation method (Eq. (6)) with atomic balance constraints (Eq. (7)) was used only for the main reactions. The species considered were therefore CH₄, Br₂, C(s), HBr, O₂ and H₂O. Due to the high melting point of carbon it was considered as a solid phase for the thermodynamic calculations.

$$\min G = \min \sum_i n_i \mu_i \quad (6)$$

$$\sum_i n_i a_{ji} = b_j \quad (7)$$

It is known that reactions of methane with halogens may lead to the production of halogenated hydrocarbons. More detailed thermodynamic calculations were therefore carried out for methane bromination using the module RGibbs installed in the commercial software ASPEN Plus. The most likely by-products of methane bromination, described by SANDIA Laboratories were included [13,14].

Kinetic simulations

A reaction mechanism published in previous studies on methane bromination [13,14] was implemented with the freeware CHEMKED-I. This reaction mechanism takes 26 chemical species into account and includes 79 elementary reactions with the corresponding values for pre-exponential factor (k_{0n}), activation energy (E_n) and the exponential constant (β). With these parameters, the reaction rate constant can be calculated for any temperature with the modified Arrhenius expression (Eq. (8)).

$$k_n = k_{0n} T^{\beta n} e^{-\frac{E_{an}}{RT}} \quad (8)$$

In order to numerically solve the mass balances (Eq. (9)) for each component and the energy balance (Eq. (10)) initial

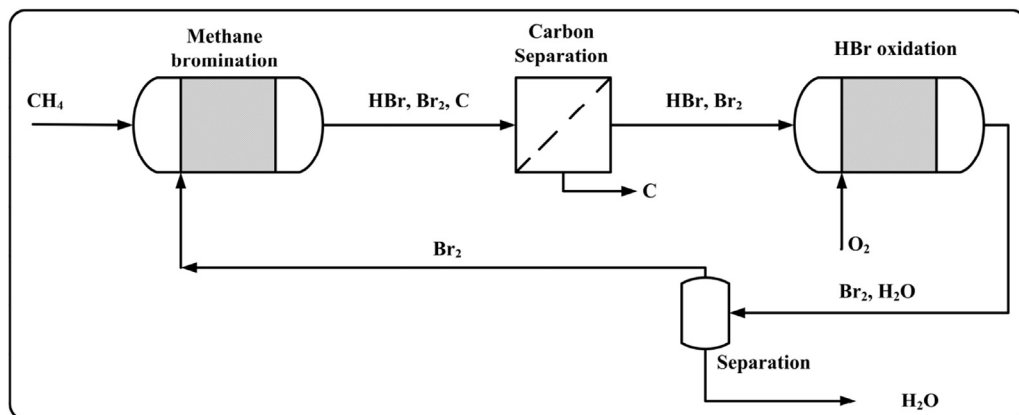


Fig. 1 – Schematic representation of the BrOx cycle.

conditions, T and C_{i0} , were supplied. CHEMKED-I can only simulate batch reactors, and therefore the results generated correspond to concentration and temperature development with time. Thermodynamic data for all chemical species was supplied to the program in the form of coefficients for NASA polynomials.

$$\frac{dC_i}{dt} = \sum_n v_{ni} k_n \left(\prod C_j^{v'_{nj}} - \frac{1}{K_n} \prod C_j^{v''_{nj}} \right) \quad (9)$$

$$\frac{dT}{dt} = \frac{\sum_n (-\Delta_r H^0) k_n \left(\prod C_j^{v'_{nj}} - \frac{1}{K_n} \prod C_j^{v''_{nj}} \right)}{\frac{P}{RT} \sum_i C_{pi} x_i} \quad (10)$$

Experimental study of methane bromination

An experimental set-up was constructed in order to investigate methane bromination (Fig. 2). The reactor (R-101) and the inlet lines are made of quartz glass and heated with electric heating bands. The flow of methane (B-101) and inert gases is controlled by means of rotameters (FC-101, FC-102, FC-103). Methane can be diluted with nitrogen (B-102) prior to pre-heating. A saturator (S-101) is used to introduce bromine into the system. The saturator is filled with liquid bromine and argon is bubbled through it as a carrier gas, so that it leaves the system saturated in bromine. In this way, the flow of bromine can be regulated by controlling the flow of argon (B-103) and

the temperature of the water bath in which the bromine saturator is located.

After the reactor, a PTFE filter (F-101) with a pore size of $2 \mu\text{m}$ insures retention of the carbon particles produced. A 3-way-valve (V-106) is used to direct the product stream to a bottle containing a solution of potassium iodide (T-102). Following the experiment, the solution can be titrated and thus the conversion of bromine determined. In order to avoid the release of bromine or hydrogen bromide to the atmosphere, two bottles (T-102, T-103) containing neutralising solution (NaOH and $\text{Na}_2\text{S}_2\text{O}_3$) are installed downstream. A wash bottle containing potassium iodide solution (T-104) is used as a bromine detector for the gas stream. The plant is automatically shut down when any change in the colour of this solution is detected by the monitoring spectrophotometer.

A maximum temperature of 760°C could be attained in the aforementioned laboratory/bench-scale reactor. The plant was subsequently modified so that temperatures as high as 1100°C could be achieved. The most important modification to the set-up was the substitution of an electric oven for electric heating bands and the use of a combined inlet line instead of the previous two separate ones (Fig. 3).

Since bromine is highly corrosive, glass, quartz glass and PTFE were used as materials of construction for all pipes and equipment that was expected to come into contact with bromine. The combination of high temperatures and the presence of bromine will make necessary the use of materials such as silicon carbide or titanium (if the gas stream contains

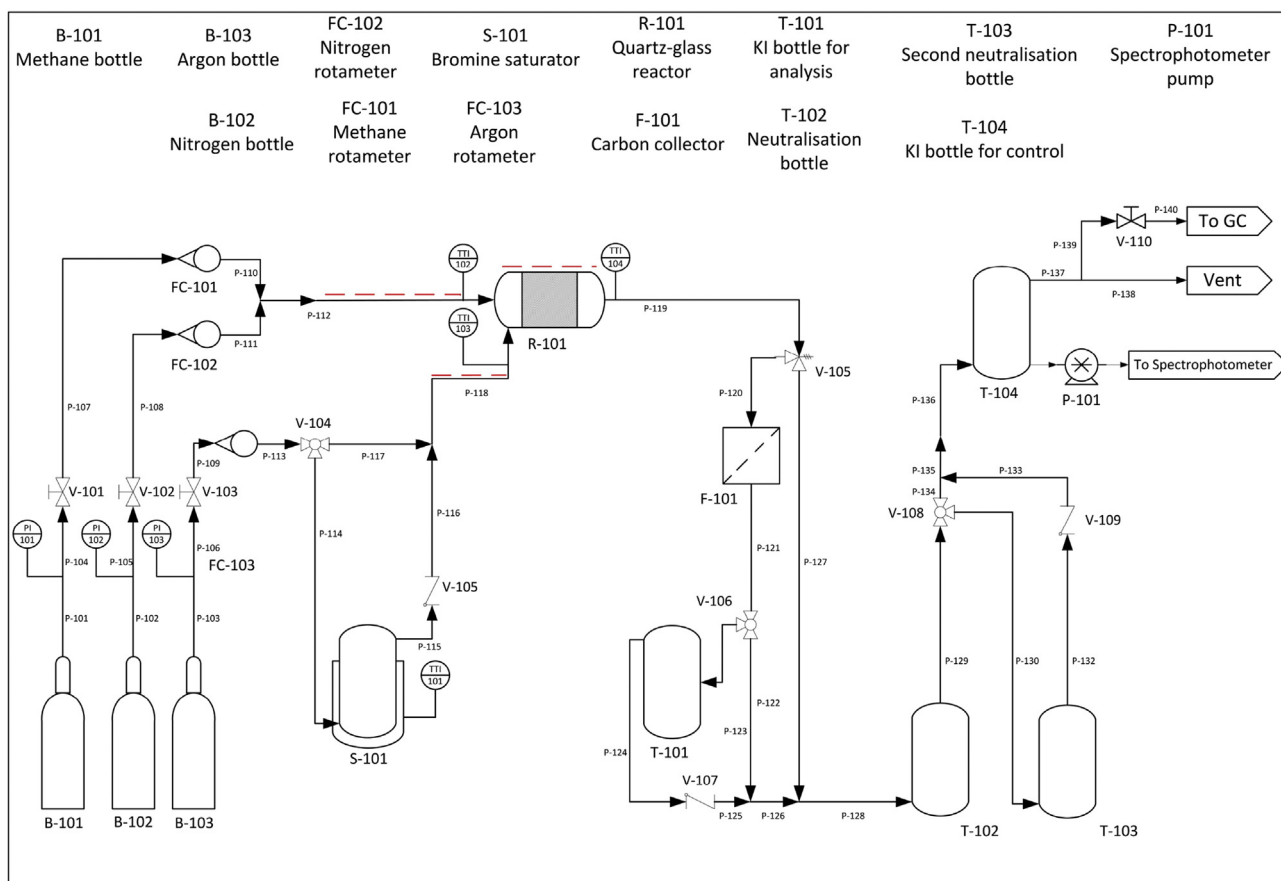


Fig. 2 – Flowsheet of the bench-scale plant for methane bromination.

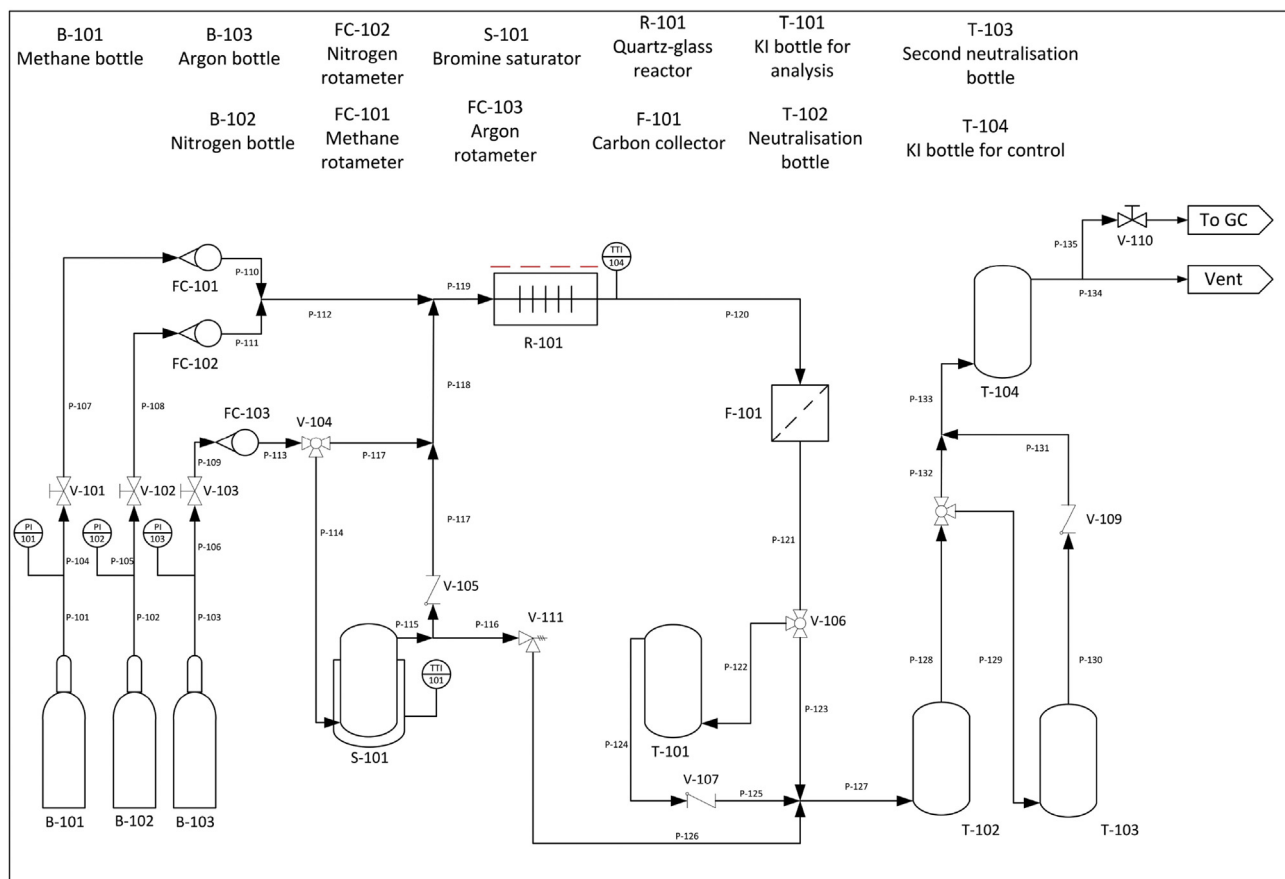


Fig. 3 – Flowsheet of the bench-scale plant for high temperature methane bromination.

water) for industrial scale, since glass will no longer be feasible as a construction material due to its fragility.

Samples of carbon produced during high temperature methane bromination experiments were analysed with SEM (Scanning Electron Microscope) and EDX (Energy Dispersive X-Ray Spectroscopy) with the main objective of determining the chemical composition of the carbon and to determine its bromine content. Due to the method used, the residual hydrogen content of the carbon samples could not be determined and therefore it will be studied in following research.

Results and discussion

Thermodynamics of BrOx cycle

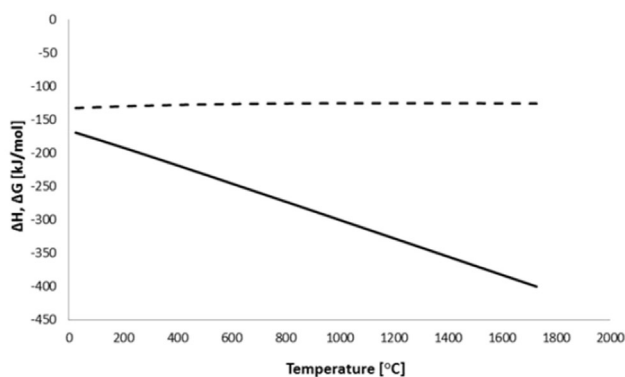
The results of the thermodynamic calculations (Fig. 4) show that both methane bromination and hydrogen oxidation are exothermic reaction and that their reaction enthalpy remains virtually unchanged with temperature. The Gibbs free energy change for methane bromination remains negative over a wide range of temperatures, indicating that the reaction is highly favoured thermodynamically and therefore that high conversion of methane can be expected. The Gibbs free energy change for hydrogen bromide oxidation is also negative at temperatures up to 1700 °C although its absolute value decreases with increasing temperature, showing that the

reaction is spontaneous, but that the equilibrium conversion will noticeably diminish with temperature.

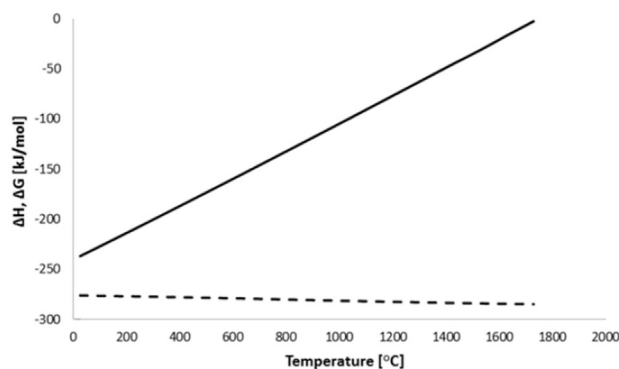
As mentioned earlier, incomplete methane bromination may lead to the generation of brominated organic compounds. In order to assess the feasibility of the BrOx cycle, it is essential to determine whether the presence of these by-products is negligible or not. The by-products considered are the organobromine compounds CBr_4 , $CHBr_3$, CH_2Br_2 , CH_3Br , C_2H_3Br , C_2H_5Br , and the by-products of methane pyrolysis C_2H_2 , C_2H_4 and C_2H_6 , as described in a previous study by SANDIA Laboratories [13,14].

The equilibrium composition for methane bromination over a wide range of temperatures is shown in Fig. 5a. All the species described above have been lumped together as by-products. The results of the thermodynamic calculations for stoichiometric conditions demonstrate that the main reaction products at equilibrium are solid carbon and hydrogen bromide. The amount of residual methane is close to zero, as would be expected from the analysis of the variation of the Gibbs free energy for methane bromination. The presence of by-products at equilibrium is confined to trace amounts for temperatures as high as 2000 °C and can thus be considered negligible.

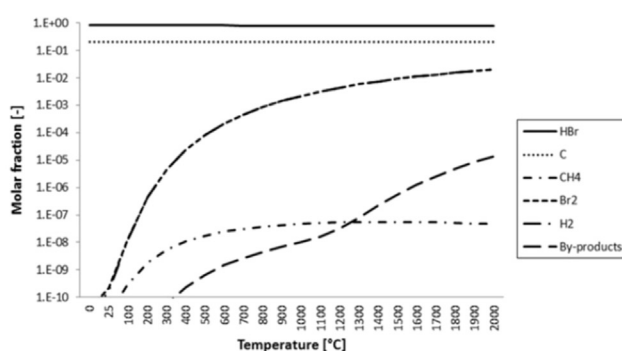
Although a low level of hydrogen is observed at equilibrium due to methane pyrolysis, it is likely that at operating temperatures in the window of 1000 °C to 1400 °C, the kinetics of methane bromination can be assumed to be much faster than



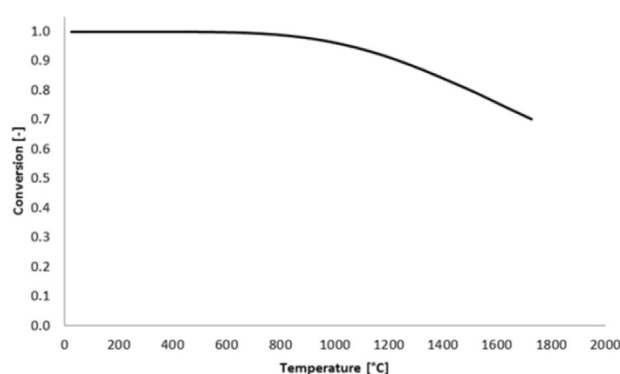
(a) Thermodynamics of methane bromination



(b) Thermodynamics of HBr oxidation

Fig. 4 – Thermodynamic calculations of the BrOx cycle (ΔH : dotted line; ΔG : solid line).

(a) Equilibrium composition of methane bromination



(b) Equilibrium composition of hydrogen bromide oxidation

Fig. 5 – Equilibrium state of BrOx cycle for stoichiometric feed conditions.

those of methane pyrolysis. Nevertheless, after separation of the carbon and during cooling of the reactor outlet stream the hydrogen will certainly combine with the unreacted bromine to yield hydrogen bromide.

The equilibrium conversion of hydrogen bromide oxidation under stoichiometric conditions falls with increasing temperature as expected. Up to 800 °C almost complete conversion can be expected, but it drops off steadily at higher temperatures. One strategy to obtain high conversion would be to carry out the reaction in two steps, an initial adiabatic thermal oxidation step for a rapid reaction followed by a catalytic oxidation step at lower temperatures to achieve complete conversion. Several catalysts have been suggested in many publications and patents for hydrogen bromide oxidation [16–18]. From these catalysts, $\text{CeO}_2/\text{ZrO}_2$, $\text{RuO}_2/\text{TiO}_2$ and TiO_2 offer a high activity at temperatures that range from 150 °C to 450 °C and therefore they will be studied in future works.

The results of the thermodynamic calculations demonstrate the underlying conceptual feasibility the BrOx process. It now remains to assess which temperatures and residence

times are necessary to approach these equilibria. For this purpose, kinetic simulations of methane bromination were performed.

Kinetic simulation of methane bromination

Due to the lack of reliable models describing carbon generation from the brominated intermediates, solid carbon formation was not implemented in the kinetic simulations. Thus no carbon appears in the results, and it is all effectively represented in the form of brominated compounds, even if the subsequent conversion of such compounds is almost certain.

The initial conditions for the methane bromination simulation were stoichiometric amounts of reactants, adiabatic conditions, atmospheric pressure and an initial temperature of 600 °C. The results (Fig. 6) illustrates that even at 600 °C methane and bromine react almost completely within the first 0.01 s causing a temperature rise of 300 °C. This means that the reaction of methane with bromine to the brominated precursors is very fast and hence it can be concluded that the limiting steps for complete methane bromination are those in

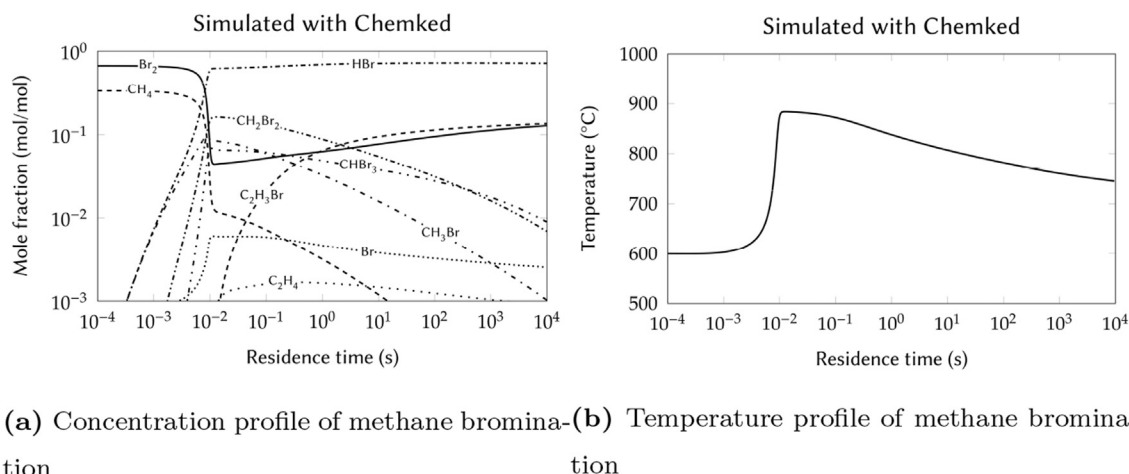


Fig. 6 – Kinetic simulations of SANDIA mechanism for methane bromination.

which these brominated intermediates react to yield solid carbon and hydrogen bromide.

The kinetic simulations for methane bromination suggest that the reaction could potentially take place within residence times as low as 0.01 s. Although these results are promising, the final objective is to produce solid carbon and hydrogen bromide, and thus the conditions required for the intermediate compounds to progress to equilibrium conversions are of crucial importance.

Experimental results on methane bromination

An experimental study on methane bromination was performed with the main objective of determining the conditions leading to solid carbon formation and to low by-product levels (especially of organobromine compounds). The key variables that may have an influence on whether solid carbon forms or not are the bromine/methane ratio, the temperature and the residence time.

The flow rates of methane in this experimental study lay in the range of 20 ml/min to 50 ml/min while those of bromine range from 50 ml/min to 120 ml/min (all measured under ambient conditions) and the bromine/methane ratio ranged from 0.9 to 2.7. Although it was initially attempted to operate the plant under adiabatic conditions, the amount of heat generated by such flow rates was so small that the insulation of the reactor necessary was unfeasible. The experiments were therefore carried out in a quasi-isothermal regime. The temperature inside the reactor was measured by means of a thermocouple (Ni–Cr/Ni–Al). In the first experiments, electric heating bands were used to heat up the reactor and to maintain a roughly constant temperature during the measurement.

Experiments numbers 1 and 2 were performed with excess methane, while in 3 and 4 excess bromine was employed. The results (Table 1) show that carbon was formed when working with excess methane at both 545 °C and 635 °C. Also, as expected from the kinetic simulation, methane and bromine conversion were complete.

When the experiment was repeated at 550 °C with excess bromine, no carbon formation occurred, although methane conversion was complete. This indicates that all the methane

and bromine had reacted in the reactor to give brominated compounds. Nonetheless, two black circles in the reactor were observed. These carbon spots appeared at the points where the heating band had two metallic rings. At these points, the conductivity is much higher than over the rest of the heating band and therefore so is the temperature, thus showing that higher temperatures are required in order to achieve carbon formation by decomposition of the brominated intermediates.

Experiment 4 was carried out at 755 °C, the maximum temperature achievable with the original set-up. Although some carbon was formed, it was much less than the amount generated in experiments 1 and 2 (Fig. 7). Also, it can be seen that a brownish residue appears at the outlet, which is probably some kind of organobromine compound.

For application in the BrOx cycle, it is of interest to operate the methane bromination with excess bromine because any gaseous brominated compounds, that will surely be produced if excess methane is used, will react with oxygen in the hydrogen bromide oxidation step thus yielding CO_2 . Therefore, determining if carbon formation can occur with a feed containing excess bromine is of critical importance, and, for this reason, a new plant was constructed in which higher temperatures could be attained.

A tubular oven from Heraeus with a maximum operating temperature of 1100 °C was substituted for the previously used heating bands. A new quartz glass tubular reactor that could fit into the oven was fabricated. Five experiments with an approximate duration of 1 h using excess bromine and temperatures ranging from 930 °C to 1070 °C were performed, all of which resulted in noticeable carbon formation (Fig. 8).

Table 1 – Experimental results for methane bromination.

No	Br_2/CH_4	T [°C]	X_{Br_2} [–]	X_{CH_4} [–]	Residence time at reaction temperature [s]	Carbon formation
1	1.7	545	1	–	24	YES
2	0.96	635	–	1	27	YES
3	2.62	550	–	1	17	NO
4	2.13	755	0.74	1	32	YES



(a) Quartz glass reactor after ca. 1 hour bromination experiment 1



(b) Quartz glass reactor after ca. 1 hour bromination experiment 4

Fig. 7 – Reactor following the bromination experiment.



Fig. 8 – Quartz glass reactor after 1 h methane of the bromination experiment.

Most of this carbon ended up coating the inner surface of the reactor, while only a small percentage was removed in the PTFE filter downstream.

In order to determine the bromine content of the carbon produced in the methane bromination experiments, samples were taken from several locations within the reactor: the inlet of the reactor, the middle, the outlet and from the filter located after the reactor. These samples were subsequently analysed using SEM (Scanning Electron Microscope) and EDX (Energy Dispersive X-Ray Spectroscopy). Table 2 shows the bromine content of the carbon samples from the centre of the reactor following experiments 1, 2 and 4. There is a clear decrease in the bromine content of the carbon with increasing operating temperature. This is due to the higher reaction rates achieved at higher temperatures which result in a faster decomposition of the brominated compounds to solid carbon.

The bromine content of the carbon is not homogeneously distributed within the reactor. In all experiments, the carbon samples obtained from the reactor zone between 15 cm and 60 cm from the reactor inlet exhibited the lowest bromine content, while the samples collected at the inlet, the outlet and in the filter, contained higher amounts of bromine. The temperature profile of the reactor was determined experimentally using a thermocouple (60 cm long, 0.5 cm of diameter) that was connected to the experimental set-up via a septum, so that it was possible to scan the reactor length. This process was repeated for several experiments at 1000 °C and 900 °C and always yielded a virtually identical profile.

The temperature profiles obtained can be subdivided into five different regions:

- Inlet zone (0 cm–15 cm): In this region, the temperature increases rapidly from ambient temperature to approximately 80% the maximum temperature.
- Inlet-middle zone (15 cm–30 cm): The slope of the temperature rise in this zone is less steep, and, at the end, reaches the maximum reactor temperature.
- Middle zone (30 cm–60 cm): The temperature remains constant at the maximum level in this section of the reactor.
- Outlet-middle zone (60 cm–75 cm): The temperature starts to decrease gradually down to 80% of the maximum value.
- Outlet zone (75 cm–90 cm): The temperature decreases steeply and almost reaches ambient temperature at the outlet.
- Filter: The filter operates at ambient temperature.

When the bromine percentage at the locations from which carbon samples were taken is compared with the temperature profile (Fig. 9) it becomes clear that a strong correlation exists between temperature and carbon purity.

The results also show that due to the low temperature in the inlet zone, the reaction rate is not sufficient for the organobromine compounds to be converted to solid carbon and hence the high content of bromine found at this location. In the inlet-middle and middle zone, the temperatures are higher and therefore the bromine content of the carbon is minimum. Following the same logic, the high content in the outlet-middle zone could be at first sight explained by an insufficient temperature and a too slow reaction rate. However, low reaction rate due to low temperatures cannot explain the high bromine content of the carbon found in the filter, since at ambient temperatures it is inconceivable that methane bromination reaction proceeds at all, let alone with carbon formation, suggesting that at least the carbon found in the filter has not formed there at ambient temperature.

Apart from the different carbon purity, there is another major difference that helps explain the presence of carbon with similar bromine contents in the filter and at the outlet-middle region. The carbon from the middle of the reactor was in the form of black flakes with a distinctive lustrous metallic sheen, very similar to the appearance of graphite. The carbon observed at the inlet, outlet and in the filter was a fine black matte powder. These differences are even more apparent when the samples are inspected by scanning electron microscope (see Fig. 10).

The presence of carbon flakes firmly attached to the reactor inner surface, as well as the relatively high purity of the carbon, is explained by the high temperature causing fast

Table 2 – Experimental results for high temperature methane bromination.

No	Br ₂ /CH ₄	T [°C]	Residence time at reaction temperature [s]	Bromine content [% w/w]
1	2.62	930	14	9.02%
2	2.64	970	14	4.66%
3	2.47	970	25	–
4	2.23	1070	12	1.95%
5	2.16	1070	22	–

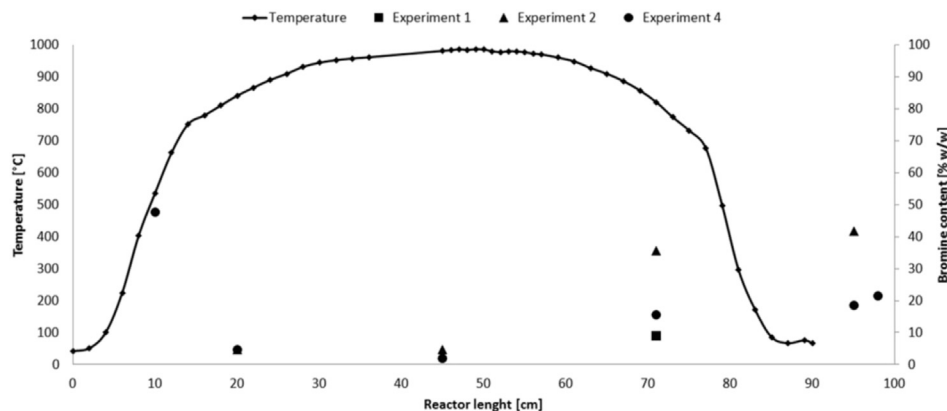


Fig. 9 – Relationship between bromine content in carbon samples and the temperature profile of the tubular reactor.

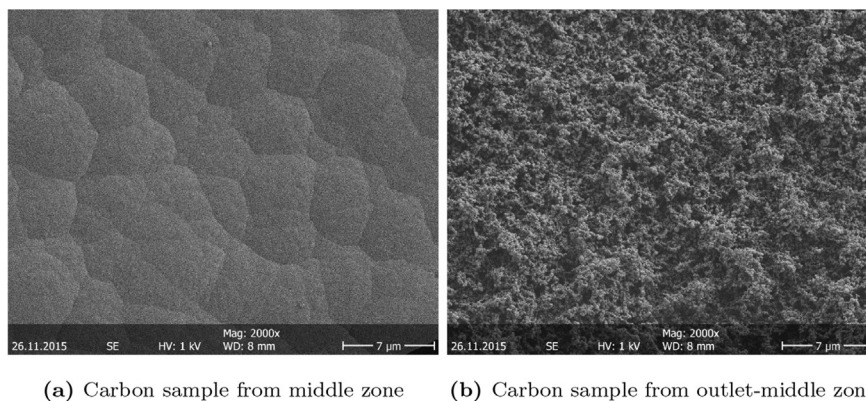


Fig. 10 – Carbon samples under Scanning Electron Microscope.

formation and growth of carbon deposits at the reactor wall. The carbon formed at the low temperature inlet of the reactor, however, contains a much higher amount of bromine, because of the low reaction rate. This also implies that the carbon does not form rapidly enough to result in a graphite-like film and instead generates very small particles that either stick on the inlet wall or are carried by the flow until they deposit loosely at a surface. Consequently, the smallest carbon particles formed can make their way through the reactor and reach the filter, which is consistent with the carbon powder observed there.

Conclusion

A novel process enabling CO₂-free energy generation from natural gas in a closed bromination-oxidation cycle has been presented in this paper. This process offers the advantage against conventional technologies, such as methane combustion or chemical looping combustion, of producing zero CO₂ emissions although roughly half the energy contained in the methane is liberated. Additionally, the same result obtained with methane pyrolysis combined with hydrogen combustion can be achieved with the BrOx cycle while at the same time the recuperative introduction of heat required in

the endothermic methane pyrolysis that leads to carbon deposition is avoided. The thermodynamics of this BrOx cycle and the kinetics of methane bromination have been examined, and an experimental study of methane bromination has been conducted with special focus on carbon formation and carbon purity.

From a thermodynamic point of view, the BrOx cycle has been found to be feasible means to access about 55% of the energy produced through methane combustion but without CO₂ emissions. Methane bromination is an exothermic reaction that occurs spontaneously for a wide range of temperatures up to 2000 °C. Possible by-products, such as brominated compounds, are only present in trace amounts at equilibrium, and therefore the reaction can optimally be carried out at conditions leading to concentrations close to the equilibrium values in reasonable residence times. Hydrogen bromide oxidation is also an exothermic reaction that takes place spontaneously for temperatures up to 1800 °C. The equilibrium conversion is effectively complete at temperatures lower than 800 °C, above which it starts to drop off. The use of a catalyst for hydrogen bromide oxidation may be necessary at lower reaction temperatures.

Through the implementation and simulation of the SAN-DIA reaction mechanism for methane bromination at different inlet conditions, it has been determined that

methane and bromine react with one another within the first 0.01 s. Short residence times would thus suffice to achieve conversions close to the equilibrium values. The absence of reliable models to describe the mechanism and kinetics by which brominated intermediates react to form solid carbon and hydrogen bromide means that carbon formation cannot yet be simulated and thus residence times required for minimising by-product generation cannot be ascertained theoretically.

A laboratory bench-scale plant was constructed in order to determine suitable conditions for temperature and residence time that lead to carbon formation and minimise brominated compounds. In the first experiments, it was observed that excess methane lead to carbon formation at temperatures as low as 550 °C, whilst, when working with excess bromine, moderate carbon formation commences at temperatures around 750 °C. At temperatures higher than 950 °C, carbon forms to a noticeable extent with excess bromine conditions, indicating that the rate of the reactions leading to solid carbon increases with the temperature.

The analysis of carbon samples exhibits a strong dependency of the bromine content on the reaction temperature. The comparison of the carbon composition at different locations in the reactor with its temperature profile also indicates that higher temperatures lead to lower bromine content. The low bromine content of the carbon entails bromine losses from the closed loop and therefore a make-up stream must be supplied. From the results of this study it is expected that higher temperatures will lead to carbon with much less than 1% and therefore it will have a small impact on the total amount of bromine being used. Nonetheless, the carbon could be treated subsequently and the bromine recovered if an economic analysis proves advantageous.

Due to the small flow rates of methane and bromine in the experimental set-up, the reactor was operated quasi-isothermally. The results obtained may be a consequence of this operating mode, since if the reaction had been carried out adiabatically, the final temperatures actually reached would have been higher than those achieved in the methane bromination experimental plant, which would therefore have led to a faster generation of solid carbon with a much lower bromine content. Future work will be devoted to increasing carbon formation rates and lowering by-product generation by using higher temperatures and employing a revamped plant with higher flow rates, so that methane bromination can be carried out in a quasi-adiabatic manner. Strategies for avoiding carbon fouling at the inner surface of the reactor and completely eliminating residual trace bromine from the carbon product formed in the reactor will also be developed.

Acknowledgments

Financial support from the Graduate School of Energy Efficient Production and Logistics (*Forschungsschule für Energieeffiziente Produktion und Logistik*) is gratefully acknowledged.

The authors would also like to express their appreciation for the assistance of the *Leibniz-Institut für Analytische*

Wissenschaften – ISAS – e.V and of Ms. Meuris from the *Lehrstuhl für Biomaterialien und Polymerwissenschaften* in the analysis of carbon samples.

REFERENCES

- [1] BP. BP statistical review of world energy 2015. London: BP; 2013.
- [2] IPCC. Climate Change 2014: mitigation of climate change. In: Edenhofer O, Pichs-Madruga R, Sokona Y, Farahni E, Kadner S, Seyboth K, et al., editors. Contributing Group III to the fifth assessment report of the intergovernmental panel on climate change. Cambridge and New York NY: Cambridge University Press; 2014.
- [3] IPCC. Climate change 2014: synthesis report. In: Pachauri RK, Meyer LA, editors. Contribution of working groups I, II and III to the fifth assessment report of the intergovernmental panel on climate change. Geneva: Core Writing Team; 2014.
- [4] Sustainable Energy System. 2050 expert committee of the ForschungsVerbund Erneubare Energien, "Energy concept 2050 for Germany with a European and global perspective. A vision for sustainable energy concept based on energy efficiency and 100% renewable energy. Contribution by the following institutes: Fraunhofer IBP, Fraunhofer ISE, Fraunhofer IWES, ISFH, IZES gGmbH, ZAE Bayern and ZSW, who have combined in the ForschungsVerbund Erneubare Energien (FVEE) [renewable energy research association] for the Federal Government energy concept". Berlin: FVEE; 2010.
- [5] Burger B. Power generation from renewable energy in Germany – assessment of first half of 2015. Freiburg: Fraunhofer Institute for Solar Energy Systems ISE; 2015, July 1.
- [6] U.S. Energy Information Administration. Annual energy outlook 2015 with projections to 2040. Washington DC: U.S. Energy Information Administration; 2015.
- [7] Rogner H-H, Aguilera RF, Archer C, Bertani R, Bhattacharya SC, Dusseault MB, et al. Chapter 7 – energy resources and potentials. Global energy assessment – toward a sustainable future. Cambridge University Press, Cambridge and New York, International Institute for Applied Systems Analysis, Laxenburg; 2012. p. 423–512.
- [8] Soeder DJ. Shale gas development in the United States. In: Al-Megren Hamid, editor. Advances in natural gas technology. InTech; 2012, ISBN 9789535105077. p. 423–512. <http://dx.doi.org/10.5772/37430>.
- [9] Hanson A, Bryngelsson M. Expert opinions on carbon dioxide capture and storage – a framing of uncertainties and possibilities. Energy Policy 2009;37(6). ISSN: 03014215:2273–82. <http://dx.doi.org/10.1016/j.enpol.2009.02.018>. Elsevier, Amsterdam.
- [10] Muradov N. Hydrogen via methane decomposition: an application for decarbonization of fossil fuels. Int J Hydrogen Energy 2001;26(3). ISSN: 03603199:1165–75. [http://dx.doi.org/10.1016/S0360-3199\(01\)00073-8](http://dx.doi.org/10.1016/S0360-3199(01)00073-8). Elsevier, Amsterdam.
- [11] Schultz I, Agar DW. Decarbonisation of fossil energy via methane pyrolysis using two reactor concepts: fluid wall flow reactor and molten metal capillary reactor. Int J Hydrogen Energy 2001;40(35). ISSN: 03603199:11422–7. <http://dx.doi.org/10.1016/j.ijhydene.2015.03.126>. Elsevier, Amsterdam.
- [12] McBride BJ, Zehe MJ, Gordon S. NASA Glenn coefficients for calculating thermodynamic properties of individual species. Cleveland: National Aeronautics and Space Administration, Glenn Research Center; 2002.
- [13] Bradshaw RW, Larson RS. Production of hydrogen bromide by bromine-methane reactions at elevated temperature. SANDIA Report. Livermore: Sandia National Laboratories; 2003.

-
- [14] Bradshaw RW, Larson RS. Production of hydrobromic acid from bromine and methane for hydrogen production. In: 2001 U.S. DOE hydrogen program review, Baltimore; 2001, April 17–19.
- [15] Schmittinger P, Florkiewicz T, Curlin LC, Lüke B, Scannell R, Navin T, et al. "Chlorine", Ullmann's Encyclopedia of industrial chemistry. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA; 2000, ISBN 3527306730. <http://dx.doi.org/10.1002/14356007.a06399.pub3>.
- [16] Waycuilis JJ, Moore PK, Lisewsky GA. US2011/0015458 A1: conversion of hydrogen bromide to elemental bromine. United States Patent Application Publication; 2011.
- [17] Moser M, Rodriguez Garca L, Prez Ramirez J. Catalyst distribution strategies in fixed-bed reactors for bromine production. *Ind Eng Chem Res* 2014;53(22). ISSN: 0888-5885-1520-5045:9067–75. <http://dx.doi.org/10.1021/ie4036675>. American Chemical Society, Washington D.C.
- [18] Moser M, Czekaj I, Lopez N, Prez Ramirez J. The virtue of defects: stable bromine production by catalytic oxidation of hydrogen bromide on titanium oxide. *Angew Chem Int Ed* 2014;53(33):8628–33. <http://dx.doi.org/10.1002/anie.201404022>. Wiley online Library, Weinheim; issn 1433-7851 0570-0833 1521-3773.