

# **Modeling of Sorption Enhanced Steam Methane Reforming. Part II: Simulation within a novel Ca/Cu chemical loop process for hydrogen production**

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## **ABSTRACT**

The initial stage of a novel Ca/Cu looping process for hydrogen production that involves the sorption enhanced reforming of methane (SER) at high pressure and at a moderate temperature is simulated using a mathematical model developed in Part I of this work. The SER reaction step has been analyzed under dynamic conditions within the framework of the following reactor parameters and operation conditions: catalyst/sorbent ratio, space time, operating temperature, operating pressure and steam/carbon ratio. The effect of these parameters on dynamic profiles, duration of the operation up to breakthrough, methane conversion, hydrogen yield, and CO<sub>2</sub> capture efficiency has been calculated. The model is shown to be a useful tool for quantifying trade-offs between the key design and operating variables. It has been found to be favored by operating under conditions of moderate temperature (650°C to 750°C), low pressure (5 bar to 15 bar) and high steam/carbon molar ratio (3 to 6).

**Keywords:** CO<sub>2</sub> capture; carbonation; packed bed; dynamic simulation; catalysis; chemical reactors

## 1. Introduction

As discussed in Part I of this series, hydrogen is an important raw material for the chemical and refining industries and it is expected to play a key role in the energy sector in the future. The sorption enhanced reforming (SER) is an innovative concept of precombustion technology for converting fuel (natural gas) into a higher-heating-value and high-purity fuel (H<sub>2</sub>) with in situ CO<sub>2</sub> capture (see review by Harrison (2008) on early developments of this technology). In this process, the thermodynamic equilibrium imposed on steam reforming reactions shifts to H<sub>2</sub> production by means of the selective removal of the CO<sub>2</sub> formed (Balasubramanian et al., 1999; Lopez Ortiz and Harrison, 2001; Lee et al., 2004). These reactions must be carried out using a suitable and effective sorbent (Rusten et al., 2007; Harrison, 2008; Solieman et al., 2009; Martavaltzi and Lemonidou, 2010). Several benefits can be achieved from the SER operation such as (1) lower operational temperatures (400–650 °C) compared to those in conventional steam reforming, (2) a higher methane conversion (> 95%) even at relatively lower temperatures, (3) the production of high purity H<sub>2</sub> (> 95%) over a wide range of pressure and temperature, (4) the reduction of CO in the gas effluent to ppm levels, (5) the elimination of the WGS reaction steps, (6) the elimination of downstream H<sub>2</sub> purification steps, (7) the minimization of unfavorable side reactions, (8) lower capital costs, (9) a lower energy requirement and (10) CO<sub>2</sub> ready for transport and storage (Yi et al., 2005; Cobden et al., 2007; Yoon et al., 2007; Harrison, 2008).

However, sorbent regeneration is required in order to carry out a multicycle SER operation. If a CaO-based sorbent is employed, the regeneration must be performed by

calcining the  $\text{CaCO}_3$ . This reaction is highly endothermic ( $\Delta H_{298\text{K}}=178.8$  kJ/mol), so additional energy is required to reach the high calcination temperatures that equilibrium demands (above  $900^\circ\text{C}$  in pure  $\text{CO}_2$  and at atmospheric pressure). Most publications on SER with  $\text{CaO}$  as a regenerable sorbent do not mention how to solve this serious problem in practice. However, several options have been reported in the literature and are briefly summarized below.

Chevron explored the possibility of using high temperature streams of combustion gases to provide the heat required for the calcination of the  $\text{CaCO}_3$  formed during the SER operation (Stevens et al., 2007). In these conditions,  $\text{CO}_2$  is not captured because it leaves the reactor highly diluted in the outlet flue gases. If  $\text{CO}_2$  capture is also an objective of the process, high temperature steam can be used instead of high temperature combustion gases. However, with this approach, the overall thermal efficiency of the reforming process tends to be very low because of the huge energy consumption needed to produce steam. Also, the cost of the equipment increases due to the need for additional pre-combustors and boilers (Stevens et al., 2007).

Boshu et al. (2008) and Meyer et al. (2011) described a novel system (the ZEG process) in which a solid fuel cell (SOFC) is coupled to the SER process so that the waste heat from the fuel cell is used to calcine the sorbent. This technology has the drawback that it requires specific materials for the SOFC (Ni-based and (La, Sr) $\text{MnO}_3$ -based electrodes).

General Electric (Lyon, 1996; Kumar et al., 2000) investigated an alternative reforming process using packed beds with  $\text{CaO}$  in which a redox chemical loop supplies the energy required to regenerate the sorbent. In this system, the exothermic oxidation of a metal (Fe, Ni) with air supplies the necessary heat for the endothermic calcination

of  $\text{CaCO}_3$  in the same bed. This may lead to a highly efficient hydrogen production process. However, the  $\text{CO}_2$  absorbed by  $\text{CaO}$  during the SER is released again during the calcination of  $\text{CaCO}_3$ , leaving the reactor in a highly diluted stream of oxygen-depleted air. Therefore, the problem of  $\text{CO}_2$  capture is not solved in this process.

On the basis of this concept, we proposed in previous works (Abanades and Murillo, 2009; Abanades et al., 2010; Fernández et al., 2012) a general process that employs the exothermic reduction of  $\text{CuO}$  to  $\text{Cu}$  as the key reaction to calcine  $\text{CaCO}_3$ . The use of this reduction reaction during the regeneration, produces a gas stream which is very rich in  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and can easily be separated for subsequent  $\text{CO}_2$  storage.

The Ca/Cu looping concept can be applied in a range of precombustion and postcombustion systems (Abanades and Murillo, 2009) using fixed bed or fluidized bed reactors. Some recent publications by other groups (Romano et al., 2011; Manovic et al., 2011a,b; Kierzkowska and Müller, 2011) appear to confirm the theoretical viability of the process and the availability of suitable materials.

In the present work we have only considered process schemes for sorption enhanced reforming as indicated in Fig. 1. This process requires adiabatic fixed bed reactors, in which the conditions of pressure and temperature must be modified to carry out the reactions outlined above (Fernández et al., 2012). The first stage (step A in Fig. 1) involves the production of a  $\text{H}_2$ -rich stream by means of the reforming of  $\text{CH}_4$  and the simultaneous carbonation of  $\text{CaO}$  with the  $\text{CO}_2$  formed. Next, a new stage begins (step B) whereby diluted air is fed in order to oxidize the present  $\text{Cu}$  to give  $\text{CuO}$  under conditions of minimum calcination. In stage C the regeneration of the  $\text{CaCO}_3$  is accomplished by means of reducing the  $\text{CuO}$  obtained in stage B with  $\text{CH}_4$ ,  $\text{CO}$  or  $\text{H}_2$ . If a suitable Cu/CaO molar ratio is employed, the heat obtained by the exothermic

reduction of CuO is sufficient for the endothermic calcination of CaCO<sub>3</sub>, so that no supplementary energy is required (Abanades et al., 2010).

The purpose of this work is to simulate in detail the performance of the SER stage within the boundary conditions of the Ca/Cu looping process. The effect of the key design variables and operating conditions on the sorption enhanced reforming performance is used to demonstrate the theoretical viability of this process.

## **2. Simulation of a sorption enhance reforming reactor in a Ca/Cu chemical loop**

A pseudo-homogeneous model was developed in Part I of this work to describe the sorption enhanced reforming at large scale in a reference case (10 kg/s of CH<sub>4</sub> fed into the reformer reactor). The SER operation was described by means of a dynamic model due to the time-dependent nature of the CO<sub>2</sub> capture process performed in a fixed bed reactor, where the CaO-based sorbent is progressively converted during the operation. An adiabatic and multi-component system with pressure drop and overall mass and energy balances were considered in the simulation.

Once a set of physical parameters, reactor characteristics and operating conditions was defined (Table 1), a simulation of the SER reactor's performance is carried out below to investigate the effect of the catalyst/sorbent ratio, space velocity, operating temperature, operating pressure and S/C molar ratio on the evolution of the product's composition and on the temperature profiles during an adiabatic SER performance.

### **2.1. Effect of catalyst/sorbent ratio**

The catalyst to sorbent ratio is a critical parameter in both conventional sorption enhanced reforming processes and in Ca/Cu based reforming processes. In both cases, the proportion of the reforming catalyst and the CO<sub>2</sub>-sorbent in the reactor will determine the degree of methane conversion and the hydrogen yield during the SER

performance. In the Ca/Cu looping process, the Cu-based material may not provide enough activity to carry out the steam reforming at temperatures up to 700°C, so that a certain amount of reforming catalyst may be required in order to achieve the maximum hydrogen yield allowed during the SER operation. The presence of the catalyst as a third solid makes it necessary to minimize the proportion of reforming catalyst and inert supports of Cu and Ca sorbents in order to reduce the thermal ballast of the solid bed and therefore the heat requirements of the overall process (Abanades et al., 2010; Fernández et al., 2012). Low catalyst fraction will also make it possible to increase the proportion of the CaO-based sorbent per unit of reactor volume so that the SER operation can be carried out at a higher space velocity.

A Ni-based material was considered as the reforming catalyst to carry out the simulation of the SER operation. The effect of the catalyst-to-sorbent ratio on hydrogen production and methane conversion has been studied at 650°C, 35 bar and a S/C molar ratio of 5 (see Table 1). Under these operating conditions, the superficial velocity reached by the gas in the reforming reactor is 0.5 m/s, which is close to the normal range of operation in industrial steam methane reformers (Rostrup-Nielsen et al., 2002).

In Fig. 2 the composition of the product gas (H<sub>2</sub> and CH<sub>4</sub> on a dry basis) during the SER operation before sorbent saturation (prebreakthrough period) is represented for different catalyst/sorbent ratios. The results of the simulation show that Ni-catalyst to sorbent ratios of around 0.3 are sufficient to yield a H<sub>2</sub> purity in the product gas of about 92%, which is close to the maximum permitted by the SER equilibrium under the operating conditions listed in Table 1 (94% on a dry basis).

Catalyst/sorbent ratios much higher than 0.3 are not acceptable in the Ca/Cu looping process because the catalyst acts as thermal ballast during the critical CaCO<sub>3</sub> regeneration step (Fig. 1). The amount of reforming catalyst can be significantly

reduced by using more reactive reforming catalysts containing noble transition metals (Jones et al., 2008). For example, if a Pt-based catalyst, 1.8 times more reactive than a Ni-based catalyst (Rostrup-Nielsen et al., 2002), is considered for the simulation, the minimum catalyst/sorbent ratio required can be reduced to 0.15, as shown in Fig. 2.

Fig. 3 confirms the need to use a minimum amount of reforming catalyst in order to achieve the maximum possible hydrogen production. A deficient reforming activity in the solid bed results in a lower methane conversion and therefore longer prebreakthrough periods which would lead to a poor hydrogen production and unacceptably high carbon losses. As the catalyst/sorbent ratio decreases from 0.3 to 0.1, the H<sub>2</sub> purity drops from 92% to 85% and likewise the methane conversion from 85% to 60%. The resulting operational time increases from 15 min to 25 min but at the expense of a lower hydrogen yield and elevated carbon losses due to the release of large amounts of unconverted methane.

## 2.2. Effect of space velocity

The space velocity is a significant operating parameter in the SER process because it affects the hydrogen yield and the CO<sub>2</sub> capture efficiency. Industrial tubular reformers usually operate at elevated superficial velocities of gas in order to maximize the production of hydrogen per unit of cross-sectional area with an acceptable pressure drop in the reformer. The high activity of the commercial reforming catalysts and the rapid kinetics of reforming and WGS reactions allow reaching the equilibrium concentrations at the exit of the reactors operating at around 1.5-2 m/s (Rostrup-Nielsen et al., 2002). However, the temperature and gas concentration profiles in a SER operation (see Part I of this work) show that carbonation reaction is significantly slower than the reforming reaction. Several authors have demonstrated that hydrogen yield and methane

conversion are strongly dependent on the gas velocity in the sorption-enhanced reforming (Rusten et al., 2007; Halabi et al., 2011). Therefore, until more reactive CO<sub>2</sub> sorbents are developed, lower space velocities (i. e. higher gas residence times) for the SER are required.

Fig. 4 shows the composition profiles on a dry basis of the product gas at different space velocities (14, 7 and 3.5 kg/m<sup>2</sup>s), at 650°C, 35 bar and at a S/C molar ratio of 5 (see Table 1). Under these operating conditions, the superficial velocity reached by the gas in the reforming reactor is 2, 1 and 0.5 m/s, respectively.

The results of the simulation show that lower space velocities lead to higher H<sub>2</sub> yield and CH<sub>4</sub> conversion, as well as a longer reactor operation time prior to breakthrough. The stationary SER period can be prolonged from 1.5 min to 15 min by reducing the space velocity from 14 kg/m<sup>2</sup>s to 3.5 kg/m<sup>2</sup>s. This is also reflected in an increase in H<sub>2</sub> purity from 81% to 92% on a dry basis (close to equilibrium) and an increase in CH<sub>4</sub> conversion from 65% to 85%. These results confirm the need to carry out the sorption enhanced reforming at lower space velocities than those usually employed in the conventional SMR in order to reach the maximum possible hydrogen yield allowed by the SER equilibrium.

### 2.3. Effect of the steam/carbon ratio

The dynamic behavior during the SER operation has been studied assuming different proportions of steam and methane in the feed. Fig. 5 shows the composition profiles of the product gas on a dry basis at different S/C molar ratios, between 3 and 6. These values come within in the normal range of the SER performance as reported in the literature (Rusten et al., 2007; Reijers et al., 2009; Halabi et al., 2011; Rout et al., 2011). The results of the simulation confirm that the steam/carbon ratio fed into the reformer



determines the degree of methane conversion and accordingly the hydrogen yield during the SER operation (prebreakthrough period) and once the sorbent has been depleted (postbreakthrough period).

As can be seen, increasing the S/C molar ratio from 3 to 6 enhances the hydrogen purity during the prebreakthrough period from 83% to 94% on a dry basis (close to equilibrium), while the methane concentration decays from 16% to 6% (corresponding to methane conversions between 65% and 90%, respectively). These results show that the excess of steam enhances hydrogen selectivity and therefore less CO<sub>2</sub> is formed in spite of the higher degree of CH<sub>4</sub> conversion. A lower CO<sub>2</sub> formation delays the carbonation of the sorbent present in the reformer and consequently the stationary SER period is extended from 7 min to 16 min, as can be seen in Fig. 5.

During the postbreakthrough period (conventional SMR operation), the excess of steam also improves hydrogen selectivity. The H<sub>2</sub> purity in the flue gas increases from 45% to 60% on a dry basis (which corresponds to methane conversions from 21% to 34%), while the CO<sub>2</sub> concentration hardly rises from 11% to 14% .

As indicated in Fig. 6, during the SER period, the concentrations of CO and CO<sub>2</sub> in the gas product remain below 0.1% on a dry basis, for all S/C molar ratios tested in the present work. A steam/carbon ratio higher than 3 reduces the CO produced by the water-gas shift reaction, increases methane conversion and reduces carbon formation via the Boudouard reaction (Tavares et al., 1996). Carbon deposition on the reforming catalyst is hence avoided, ensuring that the catalytic activity carries on for longer period of time.

The results indicate that the increase in the steam/methane molar ratio enhances the SER performance. However, the amount of steam employed is necessarily a trade-off between the need to obtain a high degree of H<sub>2</sub> purity in the gas product and overall

process efficiency, because the latent heat of water cannot be totally recovered from the steam (Stevens et al., 2005).

Because of the slight exothermicity of the overall reforming and carbonation reaction, the product gas gradually increases its temperature during the prebreakthrough period. However, the temperature profile barely changes at the different S/C molar ratios employed, as shown in Fig. 7. The maximum temperature reached is approximately 680°C for every S/C molar ratio introduced, which means a rise of 30°C above the feed gas temperature ( $T_{\text{gin}}=650^{\circ}\text{C}$ ). During the breakthrough, the CO<sub>2</sub> capture efficiency decays because the sorbent is approaching its maximum degree of conversion. Therefore, the reforming reaction prevails over the carbonation reaction and the overall process becomes endothermic. The minimum temperature is reached in the postbreakthrough period, when the CO<sub>2</sub>-sorbent is totally saturated and the reactor performs as a conventional steam reformer. The temperature of the depleted bed is approximately the same at every S/C molar ratio employed (around 595°C), as can be seen in Fig. 7.

#### 2.4. Effect of pressure

It is well known (Harrison, 2008) that the sorption enhanced reforming is favored at low pressure because of the rise in the number of gas moles associated with the overall reaction that involves the steam reforming and the carbonation of the sorbent. However, the high-pressure performance in the range of 20-40 bar is particularly interesting because the H<sub>2</sub> produced in the process can be used to feed a gas turbine for power generation. This situation is common in some pre-combustion CO<sub>2</sub> capture technologies from natural gas, because the high energy cost of H<sub>2</sub> compression would make it highly inefficient to generate H<sub>2</sub> at atmospheric pressure (Metz et al., 2005). This operation at high pressure is also important in the Ca/Cu looping process. As pointed out by

Abanades et al. (2010), the following stage after the reforming (Cu oxidation as shown in Fig. 1) must be carried out at the highest allowable temperature in order to maximize the energy efficiency of the process. High pressure operation during this oxidation step allows higher temperatures with a minimum calcination of the  $\text{CaCO}_3$  present in the reactor (formed during the previous SER reaction stage) and therefore higher  $\text{CO}_2$  capture efficiencies.

The dynamic behavior during the SER operation has been investigated at different operating pressures. Fig. 8 shows the composition of the product gas on a dry basis at different pressures (5, 15, 25 and 35 bar), at  $650^\circ\text{C}$ , a S/C molar ratio of 5 and at  $3.5 \text{ kg/m}^2\text{s}$ . The results show that both hydrogen purity and methane conversion are favored at lower pressure.

The product gas composition during the prebreakthrough period reached a maximum hydrogen purity of about 95% on a dry basis at 5 bar, as against 92%  $\text{H}_2$  purity at 35 bar. On the other hand, the methane concentration increased from 2%, obtained at 5 bar, to 8.2% at 35 bar, corresponding to methane conversions of 95% and 82%, respectively. The huge excess of steam in the feed (S/C=5) in all cases leads to a high hydrogen selectivity and high methane conversion, as pointed out above. Although  $\text{CO}_2$  sorption is favored at high operating pressure, as can be seen in Fig. 8, the total carbon loss is not favoured in the same way because of the drop in the methane conversion at higher pressure. The  $\text{CO}_2$  capture efficiency is 95% at 5 bar, whereas it is 86% at 35 bar, taking into account the unconverted methane released in the flue gas. Moreover, Fig. 8 shows that the stationary SER period before bed saturation can hardly be extended by performing at higher pressure (around 15 min at all pressures tested).

The postbreakthrough period corresponding to conventional steam methane reforming (SMR) is significantly affected by altering the pressure when compared to the

SER operation. Hydrogen purity and methane conversion are also favored at lower pressure, but both change significantly even at elevated S/C molar ratios. If the operating pressure is increased from 5 to 35 bar, the hydrogen purity decreases from 70% to 55% on a dry basis (see Fig. 8), whereas the methane concentration increases from 10% to 30% (corresponding to a drop in methane conversion from 63% to 32%, respectively). Because of the drop in methane conversion and the subsequent decrease in CO<sub>2</sub> formation by steam reforming at higher pressures, total sorbent saturation takes longer and the beginning of the postbreakthrough period is postponed from 26 min to 31 min, corresponding to 5 bar and 35 bar, respectively.

Fig. 9 represents the influence of the operating pressure on the temperature of the flue gas. The temperature profile during the prebreakthrough period is similar for all the conditions tested. The maximum temperature reached barely changes (around 680°C) for each pressure, with a rise of approximately 30°C above the feed gas temperature ( $T_{\text{gin}}=650^{\circ}\text{C}$ ). However, the minimum temperature reached in the postbreakthrough period differs significantly depending on the operating pressure. The stationary temperature for the depleted bed is 595 °C at 35 bar, whereas this value falls to 560 °C at 5 bar. The depleted bed must remain at the highest allowable temperature in order to ensure optimal performance in the subsequent stage (Cu oxidation) of the Ca/Cu looping process. This is another reason why the SER operation should be carried out at high pressure.

## 2.5. Effect of temperature

Temperature is an important operating parameter in the SER process because it has a decisive effect on the hydrogen yield, methane conversion and CO<sub>2</sub> capture efficiency. Fig. 10 shows the composition of the product gas on a dry basis at different operating

temperatures (from 600°C to 750°C), at 35 bar, a S/C molar ratio of 5 and 3.5 kg/m<sup>2</sup>s. The same temperature was used for the feed gas ( $T_{gin}$ ) and for the initial solids bed ( $T_{s0}$ ) in this study.

Hydrogen production is favored at operating temperatures above 700°C, a maximum H<sub>2</sub> purity of about 96.5% on a dry basis being recorded at this temperature. Although higher temperatures in the reformer lead to higher conversions of methane, the CO<sub>2</sub> capture efficiency decreases while the H<sub>2</sub> purity remains stable, as can be seen in Fig. 10. When the operating temperature is increased from 600°C to 750°C the concentration of methane drops from 14% to 3.5% (corresponding to methane conversions of 80% and 88%, respectively). The CO and CO<sub>2</sub> contents in this range of temperatures are almost negligible (lower than 1% on a dry basis). At temperatures higher than 750°C, CO<sub>2</sub> sorption is less effective and the CO<sub>2</sub> content in the flue gas increases rapidly. Balasubramaniam et al. (1999) showed that CO<sub>2</sub> separation above 850°C is not effective and the equilibrium composition of the product is the same as that of a stream under conventional steam methane reforming.

As pointed out above, higher operating temperatures lead to higher methane conversions and therefore more CO<sub>2</sub> is produced by steam reforming. Total saturation of the CO<sub>2</sub> sorbent (postbreakthrough) is therefore extended from 25 min to 35 min, performing at 750°C and 600°C, respectively.

During the prebreakthrough period, the exit gas increases its temperature gradually because of the slight exothermicity of the overall SER process. The temperature profiles are significantly different at all of the operating temperatures tested. During the first minutes of the SER performance, the gas temperature is different because it depends directly on the starting operating temperature. Moreover, the maximum temperature increase ( $\Delta T_{max}$ ) rises if the SER is performed at growing temperatures, as shown in

Fig. 11. The temperature of the product gas obtained at 600°C barely changes during the prebreakthrough period, reaching a maximum temperature of 618°C. However, if the SER is performed at 750°C, the flue gas achieves a maximum temperature of about 782°C, with a rise of 32°C above the starting operating temperature of solids and gas.

The minimum temperature reached during the postbreakthrough period also differs significantly depending on the operating temperature. Higher operating temperatures promote the steam reforming reaction ( $\Delta H_{298K} > 0$ ), which may lead to important temperature drops under adiabatic conditions. The final stationary temperature during SMR operation is 670 °C when  $T_{gin}=T_{s0}=750^\circ\text{C}$ , whereas this value falls to 555 °C when  $T_{gin}=T_{s0}=600^\circ\text{C}$ .

Different temperatures have been considered for the feed gas ( $T_{gin}$ ) and for the initial solids bed ( $T_{s0}$ ) in order to study separately the effects of these parameters on the performance of the SER reactor. Fig. 12 shows the effect of the feed gas temperature on the composition of the product gas. The results of the simulation show that only by feeding in the incoming gas at a temperature equal to or higher than 650°C, it is possible to obtain a hydrogen purity of at least 92% for a significant period of time (around 15 minutes). Although the use of higher temperatures for the incoming gas leads to higher methane conversions, CO<sub>2</sub> capture efficiency decreases at 750°C (Fig. 12, right) while hydrogen production remains stable and close to the maximum allowed by equilibrium. The fact that the hydrogen yield is not dependent on temperature is a result of the thermal neutrality of the overall SER reaction (Harrison, 2008). Gas temperatures lower than 650°C lead to shorter stationary SER operation in which the maximum yield hardly reaches 90% on a dry basis. When  $T_{gin}$  is about 600°C, maximum hydrogen purity is only achieved during the first 1.5 minutes after which it falls rapidly until total sorbent saturation is reached (37 minutes after the beginning of the operation).

The temperature profiles also significantly differ for every feed gas temperature employed, as shown in Fig. 13. During the first 4 minutes of the SER reaction, all the temperature profiles match each other and are equal to the initial solid temperature (650°C). For longer operation times, the temperature profiles are largely affected by  $T_{gin}$ . The maximum temperature increase with respect to  $T_{s0}$  ( $\Delta T_{max}$ ) occurs with the rise in the temperature of the incoming gas. The maximum temperature achieved is 678°C, when the incoming gas is at 650°C, whereas  $\Delta T_{max}$  is close to 785°C when the gas is fed in at 750°C. Gas temperatures lower than 650°C signify that SER operation is being conducted far from optimal conditions and therefore the amount of hydrogen produced is much lower. Furthermore, the minimum temperature reached during the postbreakthrough period is also very different depending on  $T_{gin}$ . The stationary temperature during the postbreakthrough period reaches 670 °C when the incoming gas is at 750°C, whereas this value drops to 555 °C when the gas is fed in at 600°C.

Fig. 14 represents the composition of the product gas on a dry basis at different initial solid bed temperatures (from 600°C to 750°C) when feeding in 3.5 kg/m<sup>2</sup>s at 650°C ( $T_{gin}$ ) with a S/C molar ratio of 5. During approximately the first 7 minutes, the flue gas composition depends on  $T_{s0}$ . The hydrogen purity achieves a maximum of about 95% if the SER is performed at initial temperatures higher than 650°C, whereas less than 92% of H<sub>2</sub> is obtained if the solids are originally at 600°C. The gas composition profiles match each other during the rest of the SER performance until total sorbent carbonation is reached. These results demonstrate that that initial solid bed temperature hardly affects on the flue gas composition in the interval of temperatures considered.

The temperature profiles differ markedly during the first 7 minutes of the SER operation depending on the initial temperature of the solids contained in the reformer

( $T_{s0}$ ), as shown in Fig. 15. When the initial temperature exceeds 650°C, the resulting flue gas is released at a gradually higher temperature because of the solid-gas heat transfer along the reformer and because of the slight exothermicity of the overall SER reaction. A maximum temperature of about 770°C can be achieved when the initial solid bed is 750°C. For a lower  $T_{s0}$ , the amount of heat transferred by the solids is logically lower and the resulting increase in temperature depends almost entirely on the heat of the SER reaction. For a longer operation time ( $t > 7$  min), the solids reach the temperature of the incoming gas (650°C) and the temperature profiles are therefore identical for all the  $T_{s0}$  investigated.

### 3. Conclusions

Adiabatic sorption enhanced reforming (SER) can be simulated using the pseudo-homogeneous model described in Part I of this work. The transient behaviour of a sorption-enhanced fixed-bed reformer up to total bed saturation via the carbonation of the CaO-based sorbent present in the reactor can be simulated at conditions suitable for a novel H<sub>2</sub> production process that uses SER principles in a double Ca-Cu chemical loop. Operating parameters, such as, the catalyst/sorbent ratio, space velocity, feed temperature, initial solids temperature, pressure and steam/carbon molar ratio are found to have a substantial effect on the SER performance in terms of hydrogen purity, methane conversion, temperature variation and effective operational time. A catalyst/sorbent ratio of about 0.3 is sufficient to achieve maximum hydrogen production using a common Ni-based catalyst reforming. The Ca/Cu looping process requires reforming activity of the Cu-based material at normal operating conditions, or a drastic reduction in this proportion by using a more active catalyst than the commercial Ni-based catalyst. Space velocities lower than to those used in the conventional steam reforming (SMR), are required due to the limiting effect of the modest carbonation



reaction rates in the SER process. The excess of steam enhances hydrogen purity and increases the methane conversion. It is possible to achieve a maximum H<sub>2</sub> purity of about 95% on a dry basis and a methane conversion higher than 90% by performing at 35 bar with a S/C molar ratio of 6. Low operating pressures lead to higher H<sub>2</sub> yields and higher methane conversions, although high-pressure reforming is especially attractive for power generation and for the optimal performance of the overall Ca/Cu looping process. Hydrogen production is favored at operating temperatures above 700°C, allowing a maximum H<sub>2</sub> purity of about 96% to be achieved on a dry basis. The CO and CO<sub>2</sub> contents at this range of temperatures are almost negligible. The feed gas temperature has a greater impact on the SER performance than the initial temperature of the solids. Reasonable operating windows for the SER stage in a novel Ca/Cu hydrogen production process have been identified and these confirm the theoretical viability of the process.

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### **Nomenclature**

$k_{\text{carb}}$	rate constant of CaO carbonation, h <sup>-1</sup>
L	reactor length, m
P	total pressure, bar
T	temperature, °C
$T_{\text{gin}}$	gas feed temperature, °C
$T_{\text{s0}}$	initial solid temperature, °C
$X_{\text{max}}$	maximum fractional carbonation conversion of CaO, dimensionless

Greek letters

$\varepsilon$	bed void fraction, dimensionless
$\Delta H_{298K}$	heat of reaction at STP, kJ/mol
$\Delta T_{\max}$	maximum adiabatic temperature increase, °C
$\rho_{\text{CaO}}$	apparent density of CaO-based material, kg/m <sup>3</sup>
$\rho_{\text{cat}}$	apparent density of reforming catalyst, kg/m <sup>3</sup>
$\rho_s$	apparent density of the solids bed, kg/m <sup>3</sup>

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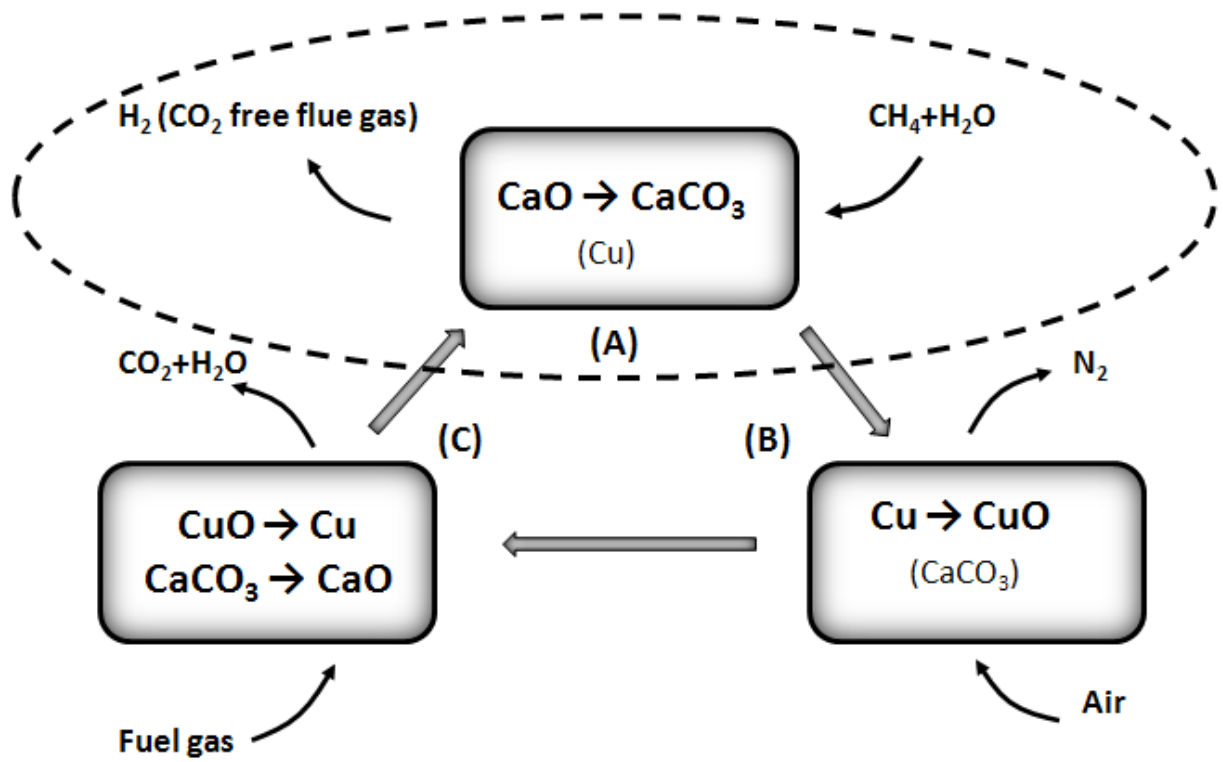
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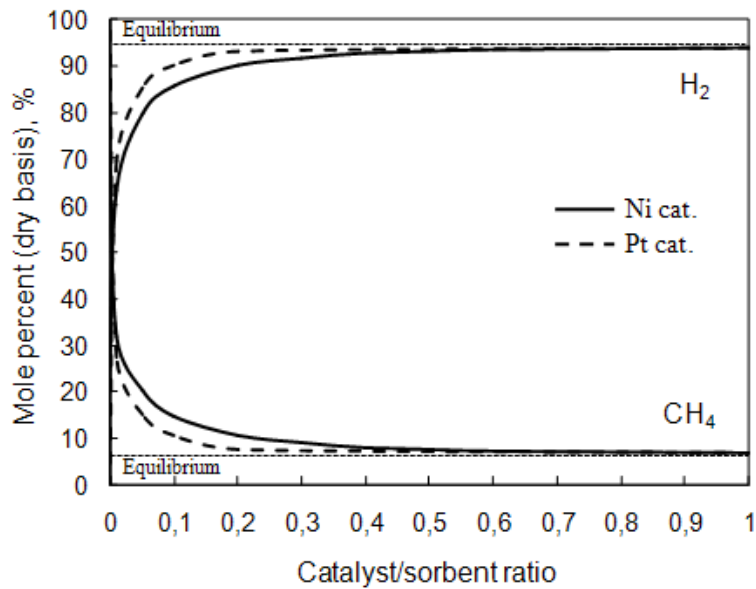
**Figure captions.**

**Fig. 1.** General scheme of the Ca/Cu three-step chemical loop for hydrogen production.

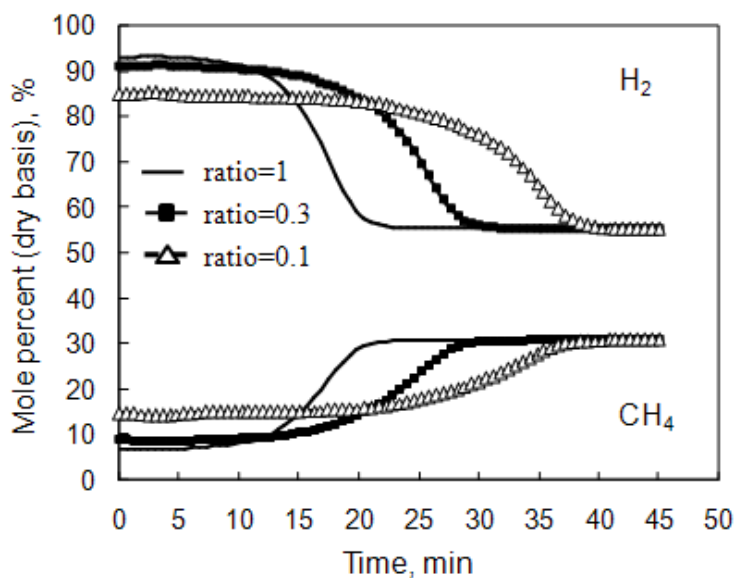




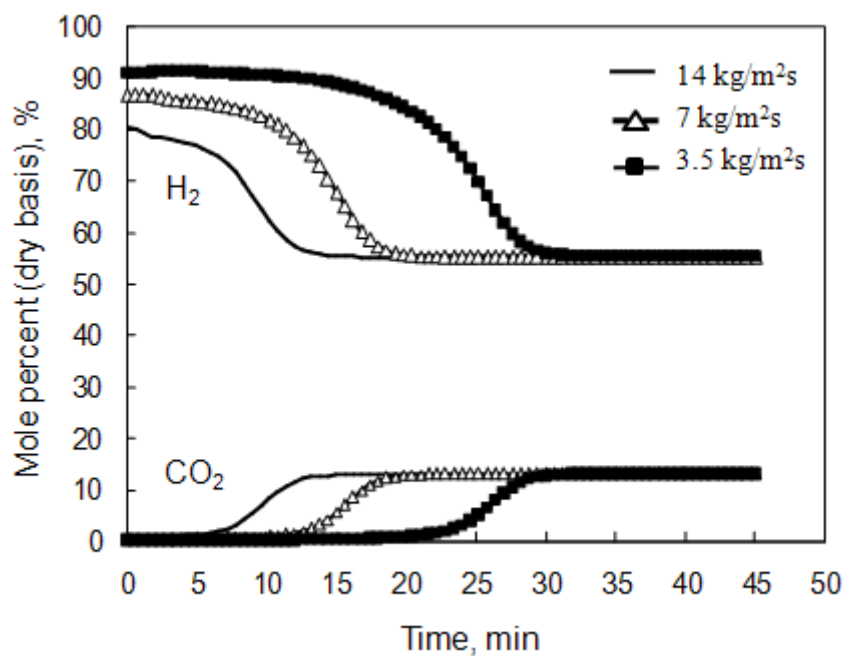
**Fig. 2.** Effect of catalyst/sorbent ratio on H<sub>2</sub> production and CH<sub>4</sub> conversion during the prebreakthrough of a SER operation (at the conditions shown in Table 1: 650°C, 35 bar, S/C molar ratio of 5, 3.5 kg/m<sup>2</sup>s). A Ni(9%)/Al<sub>2</sub>O<sub>3</sub> and a Pt(0.5%)/Al<sub>2</sub>O<sub>3</sub> were employed for comparison.



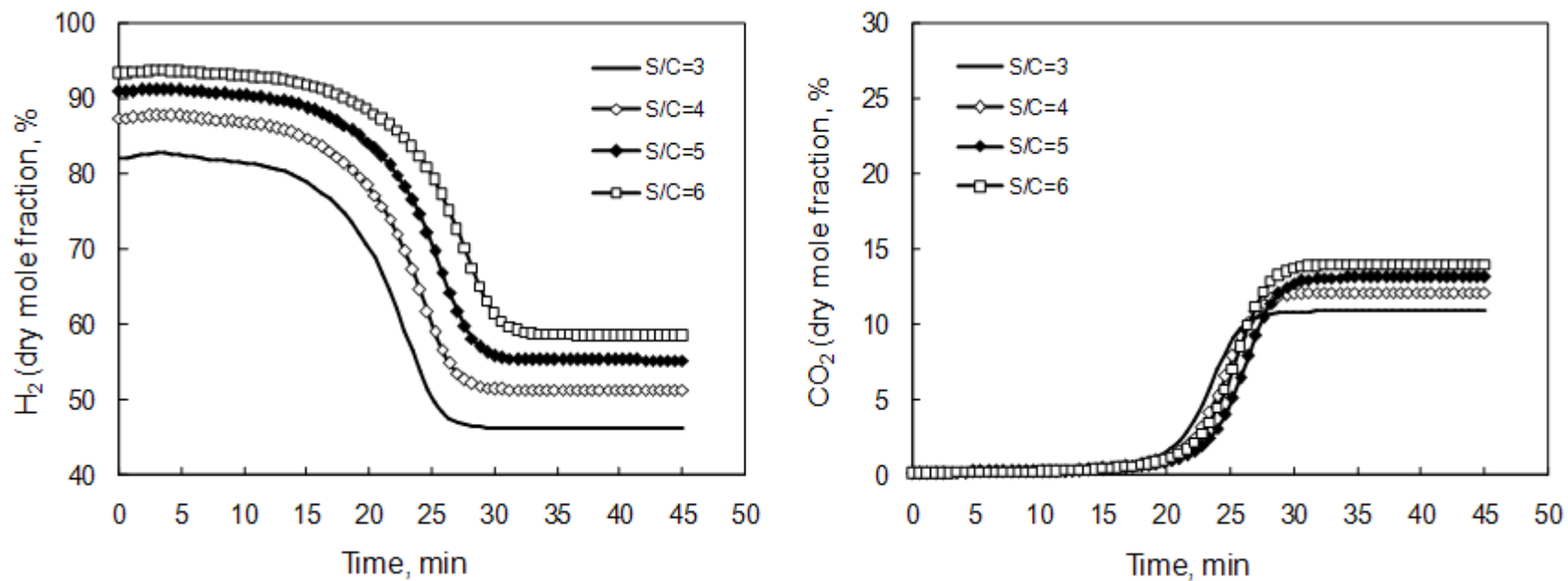
**Fig. 3.** Dynamic H<sub>2</sub> and CH<sub>4</sub> profiles on a dry basis at the reactor exit at different catalyst/sorbent ratios (at the conditions shown in Table 1: 650°C, 35 bar, S/C molar ratio of 5, 3.5 kg/m<sup>2</sup>s).



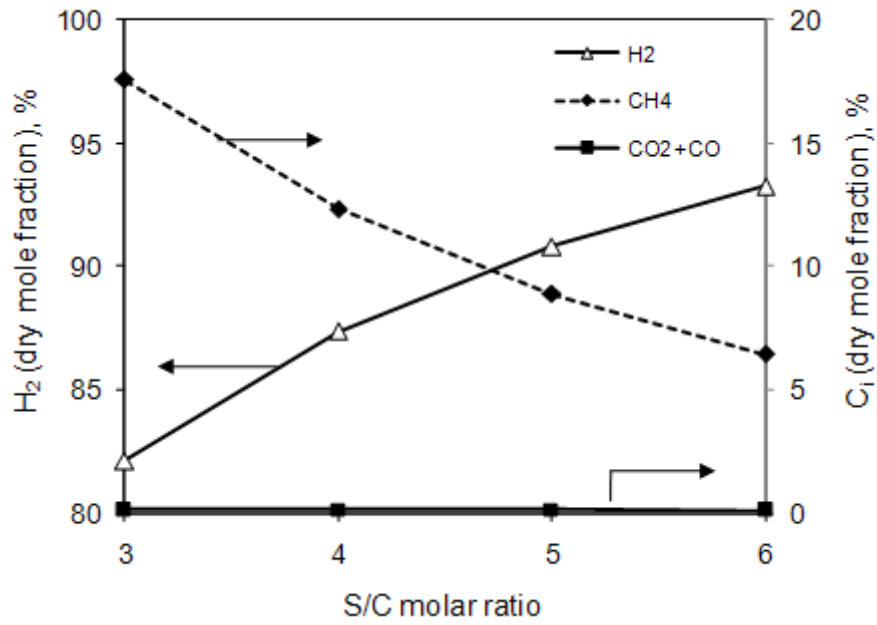
**Fig. 4.** Dynamic profiles of the product gas composition (dry basis) at the reactor exit at different space velocities (at the conditions shown in Table 1: 650°C, 35 bar, a S/C molar ratio of 5).



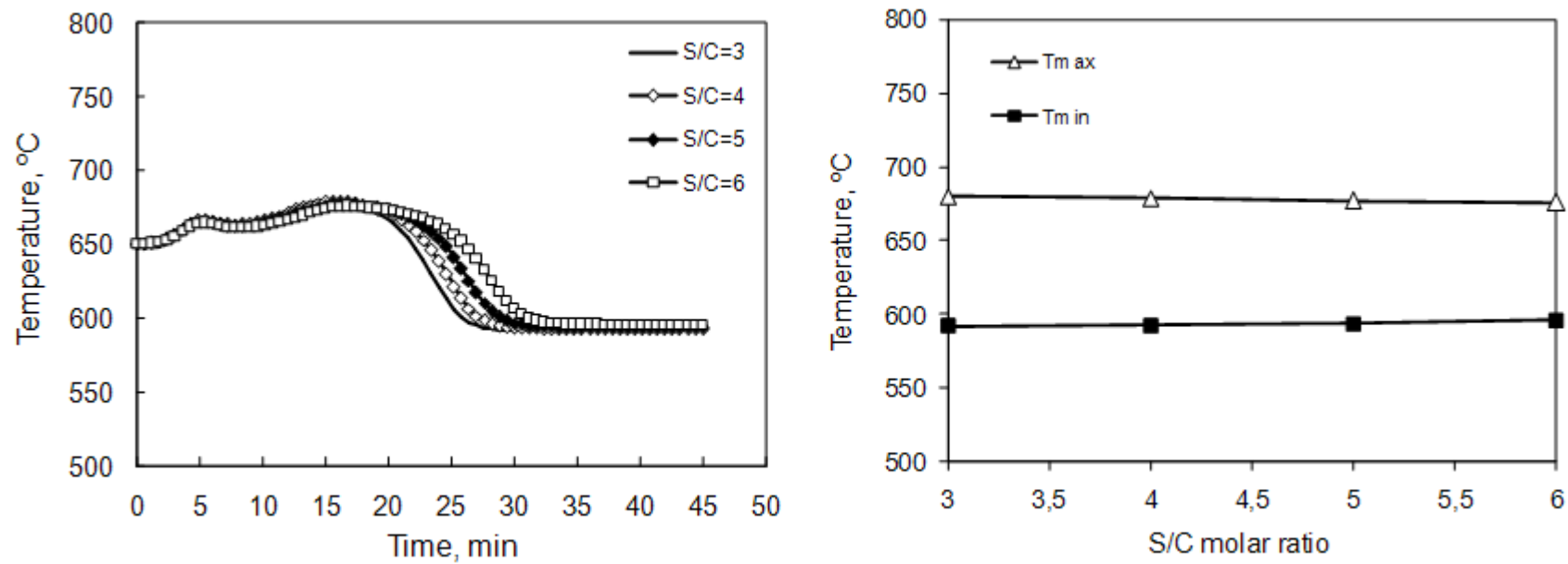
**Fig. 5.** Dynamic profiles of the product gas composition on a dry basis at the reactor exit at different S/C molar ratios (at the conditions shown in Table 1: 650°C, 35 bar, 3.5 kg/m<sup>2</sup>s).



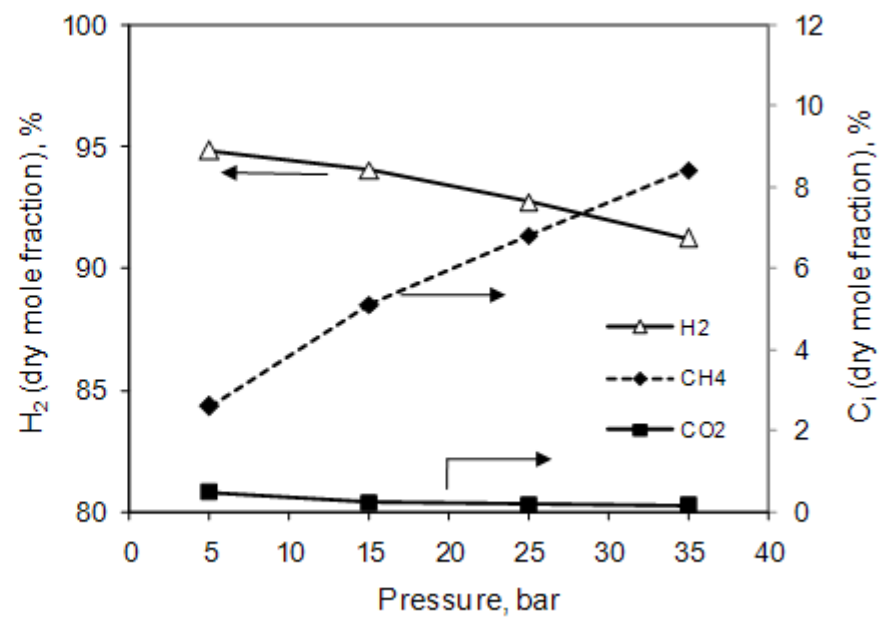
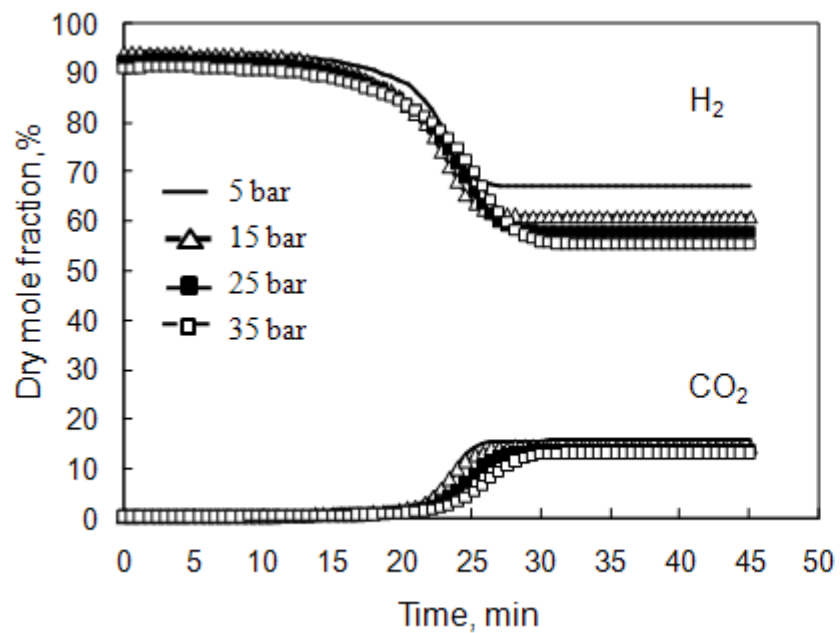
**Fig. 6.** Effect of S/C molar ratio on the composition of the product gas during the prebreakthrough period (at the conditions shown in Table 1: 650°C, 35 bar, 3.5 kg/m<sup>2</sup>s).



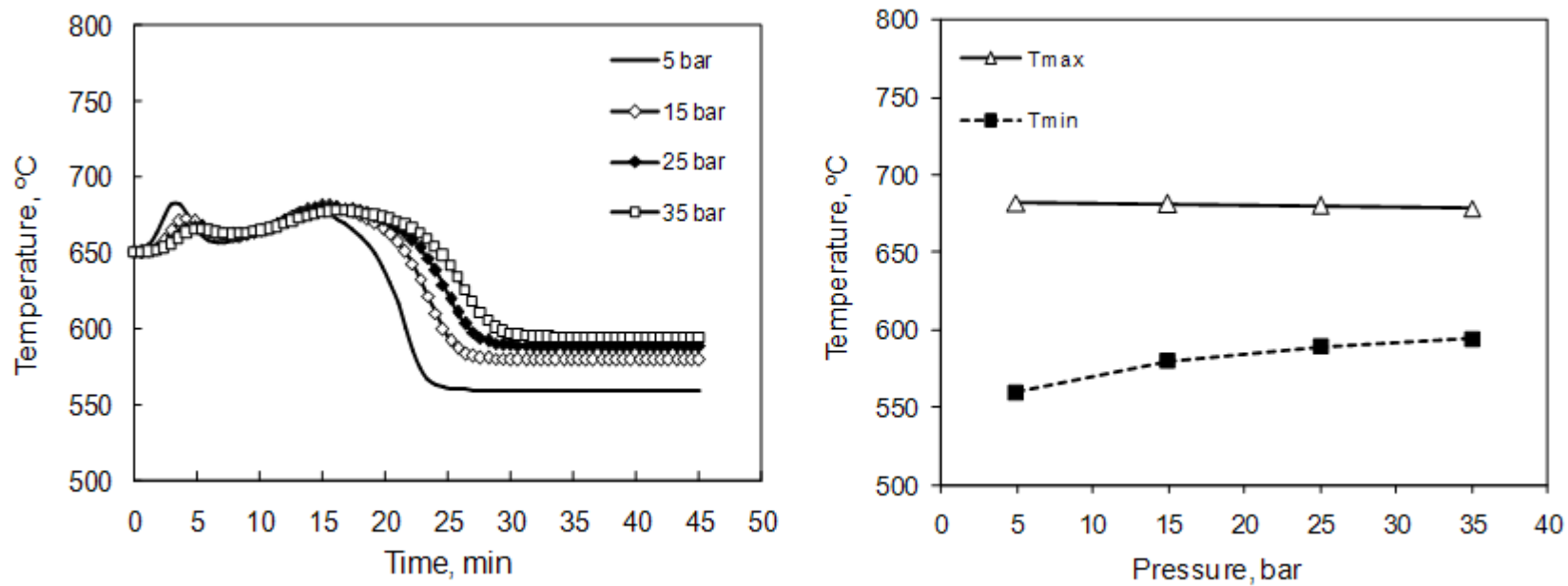
**Fig. 7.** Effect of S/C molar ratio on the temperature of the gas leaving the reactor (at the conditions shown in Table 1: 650°C, 35 bar, 3.5 kg/m<sup>2</sup>s).



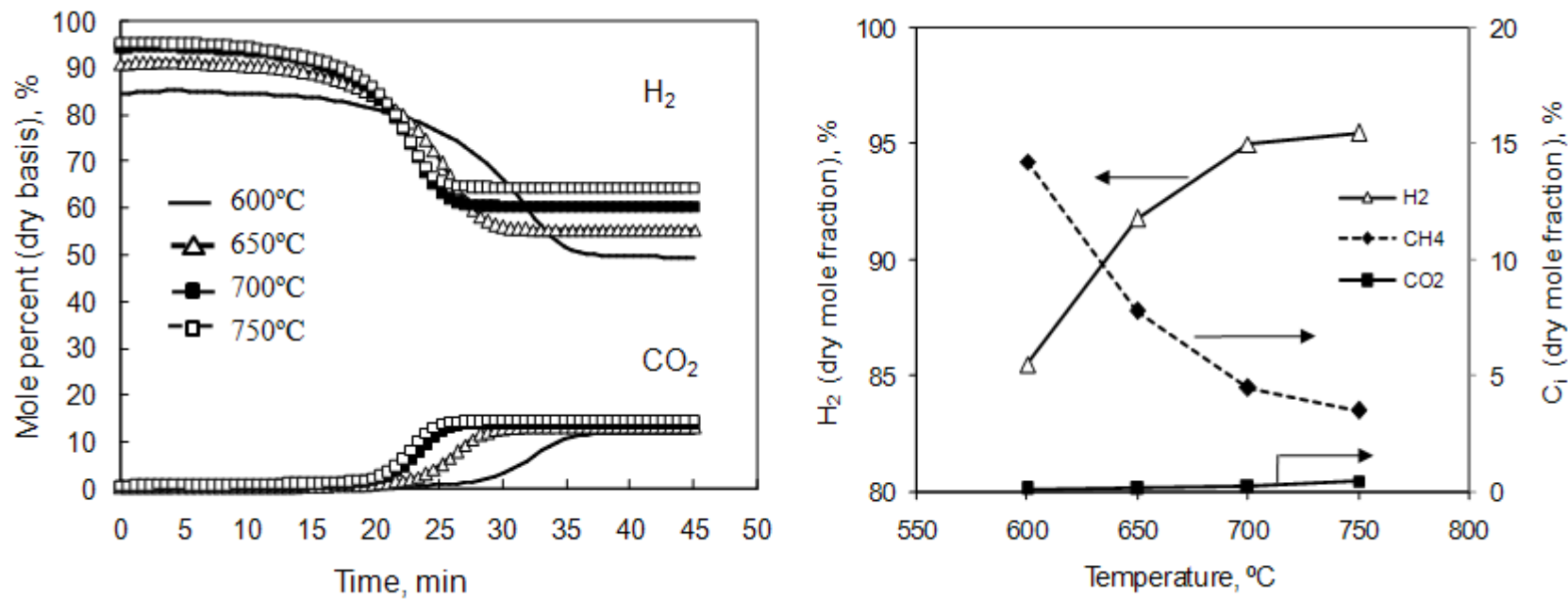
**Fig. 8.** Effect of pressure on the product gas composition (at the conditions shown in Table 1: 650°C, S/C=5, 3.5 kg/m<sup>2</sup>s).



**Fig. 9.** Effect of pressure on the product gas temperature (at the conditions shown in Table 1: 650°C, S/C=5, 3.5 kg/m<sup>2</sup>s).

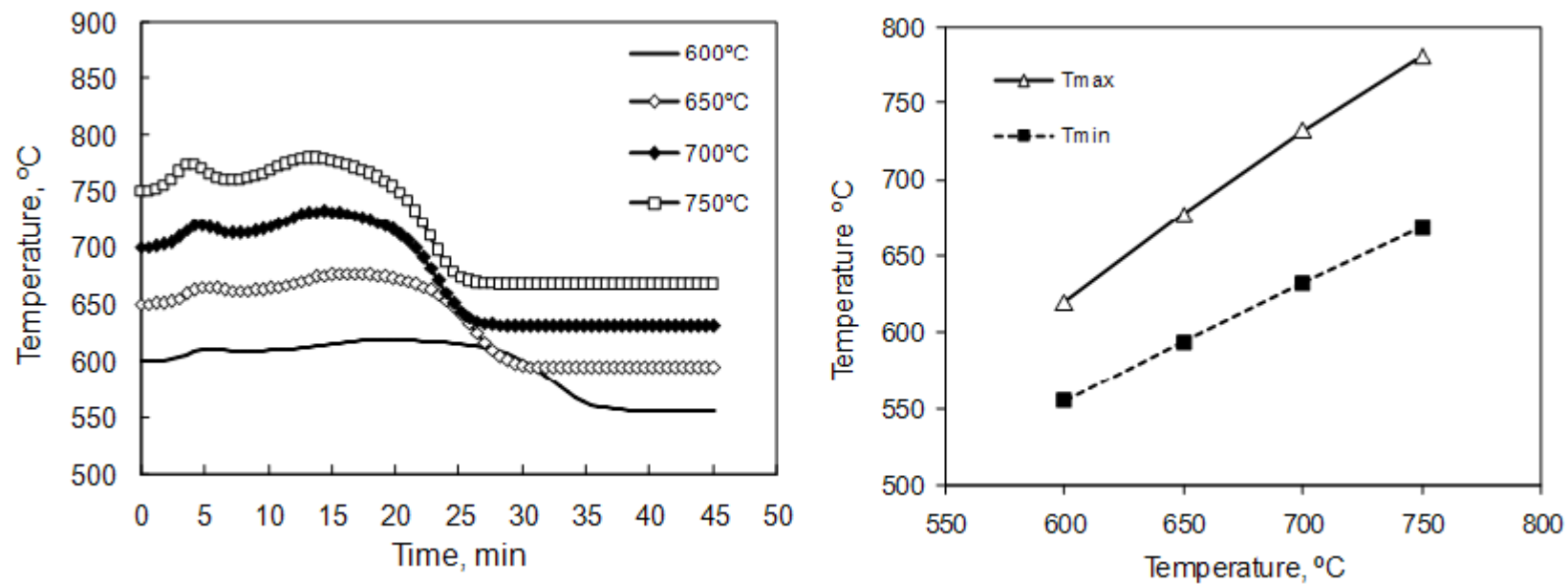


**Fig. 10.** Effect of initial reactor temperature and gas temperature ( $T_{\text{gin}}=T_{\text{s0}}$ ) on the composition of the product gas at the exit of the reactor (at the conditions shown in Table 1: 35 bar, S/C=5, 3.5 kg/m<sup>2</sup>s).

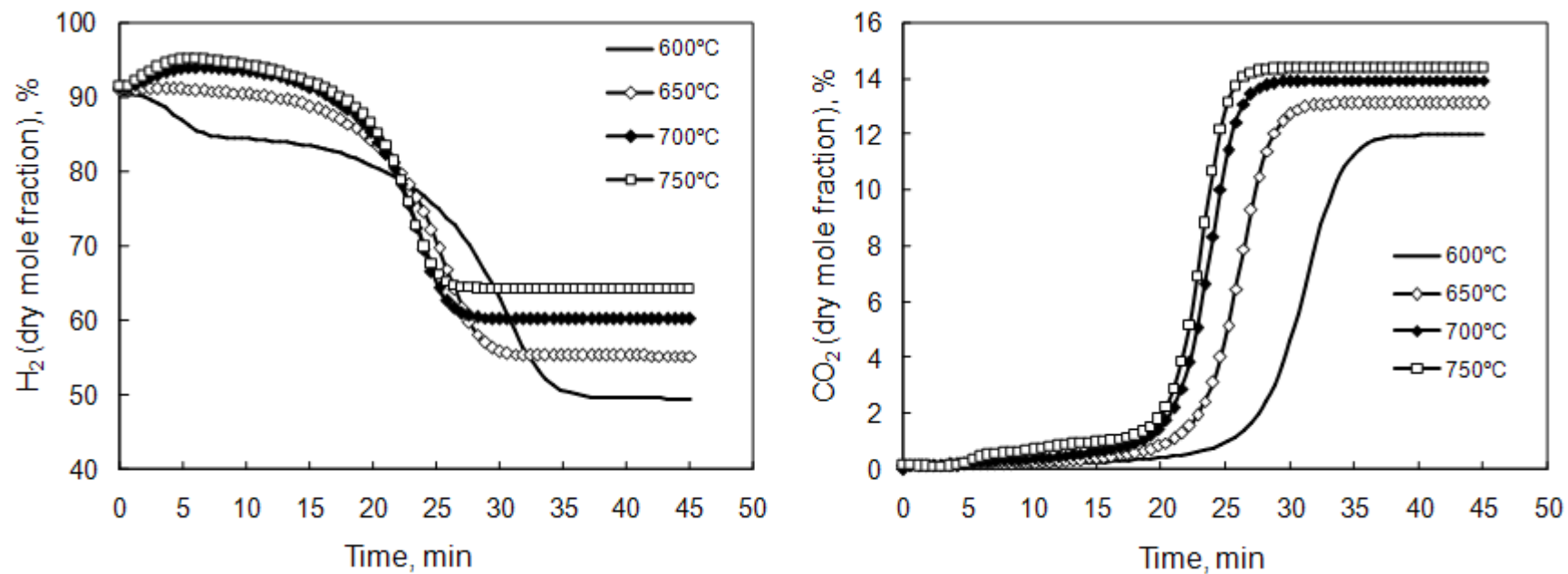




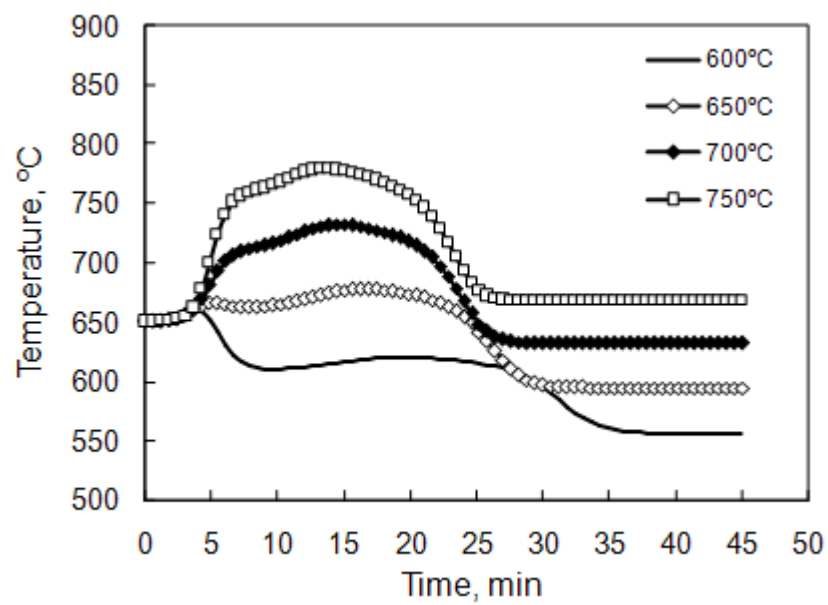
**Fig. 11.** Effect of operating temperature on the product gas temperature (at the conditions shown in Table 1: 35 bar, S/C=5, 3.5 kg/m<sup>2</sup>s).



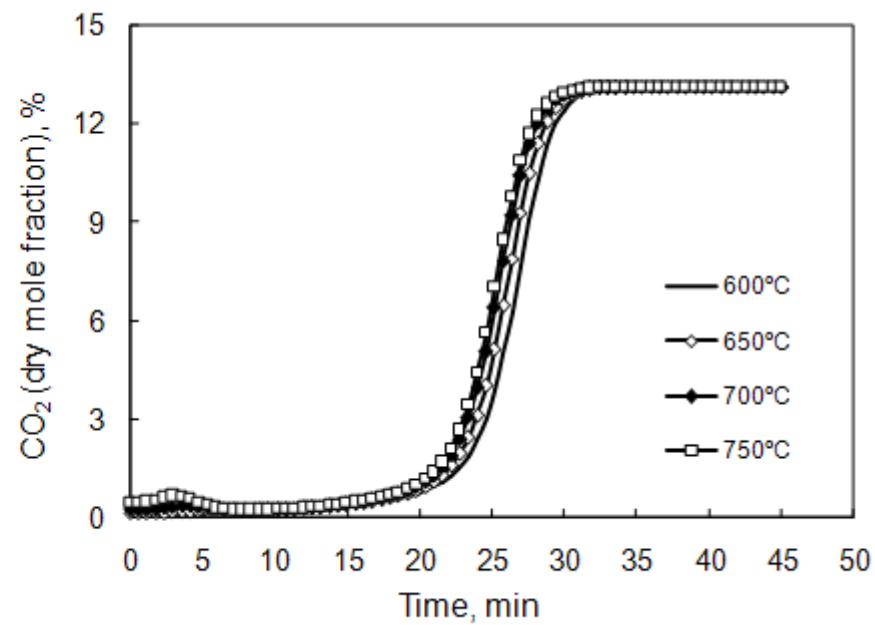
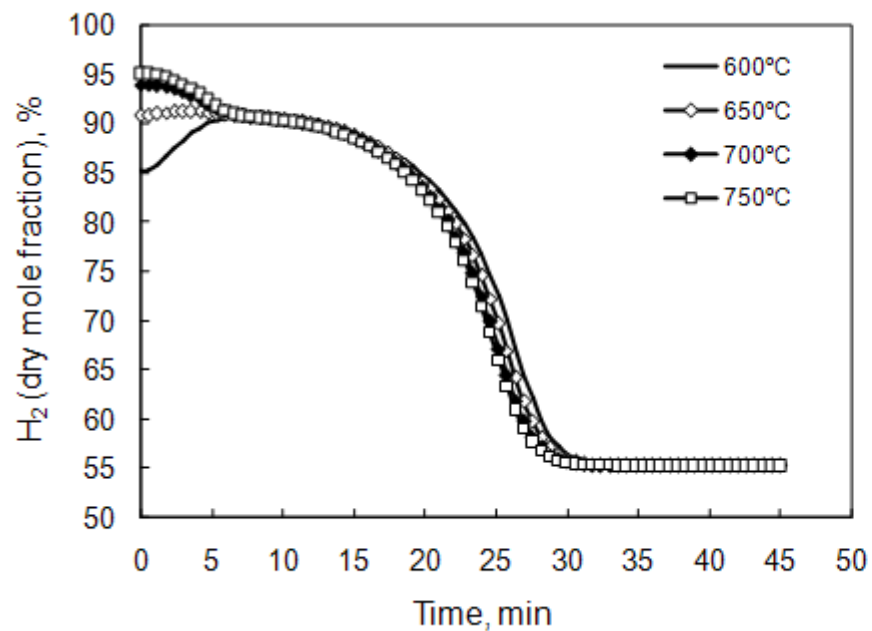
**Fig. 12.** Dynamic profiles of the product gas composition on a dry basis at the reactor exit at different gas feed temperatures (at the conditions shown in Table 1:  $T_{s0}=650^{\circ}\text{C}$ , 35 bar, S/C=5,  $3.5\text{ kg/m}^2\text{s}$ ).



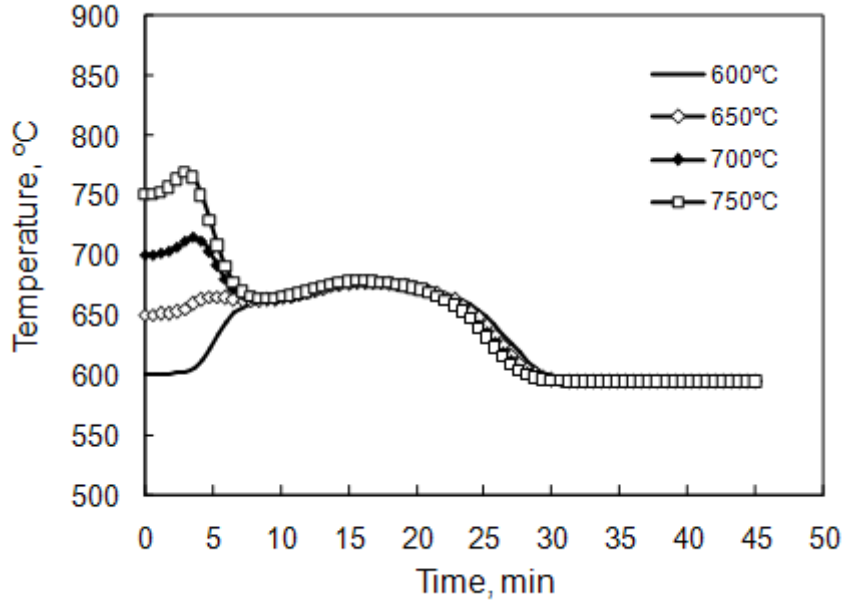
**Fig. 13.** Effect of gas feed temperature on the product gas temperature at the exit of the SER reactor (at the conditions shown in Table 1:  $T_{s0}=650^{\circ}\text{C}$ , 35 bar,  $S/C=5$ ,  $3.5 \text{ kg/m}^2\text{s}$ ).



**Fig. 14.** Dynamic profiles of the product gas composition on a dry basis at the exit of the SER reactor at different initial solids temperatures (at the conditions shown in Table 1:  $T_{\text{gin}}=650^{\circ}\text{C}$ , 35 bar, S/C=5,  $3.5 \text{ kg/m}^2\text{s}$ ).



**Fig. 15.** Effect of initial solid temperature on the product gas temperature (at the conditions shown in Table 1:  $T_{gin}=650^{\circ}\text{C}$ , 35 bar, S/C=5,  $3.5\text{ kg/m}^2\text{s}$ ).



**Table 1.** Central operating conditions and reactor and  $\text{CO}_2$  sorbent characteristics.

Parameters	Values
Feed gas temperature, $T_{gin}$	$650^{\circ}\text{C}$
Initial solids temperature, $T_{s0}$	$650^{\circ}\text{C}$
Pressure	35 bar
S/C molar ratio	5
Inlet gas mass flow velocity	$3.5\text{ kg/m}^2\text{s}$
$X_{max}$	0.4
$k_{carb}$	$1260\text{ h}^{-1}$
$\rho_{cat}$	$330\text{ kg/m}^3$
$\rho_{CaO}$	$1100\text{ kg/m}^3$
$\rho_s$	$2600\text{ kg/m}^3$ <sup>a</sup>
$d_p$	0.01 m
L	7 m
$\varepsilon$	0.5

<sup>a</sup>The presence of a Cu-based material is assumed for the apparent density of the solids bed.