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Thermodynamics of hydrogen production from urea by steam reforming with and without *in situ* carbon dioxide sorption.

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Abstract

The thermodynamic effects of molar steam to carbon ratio (S:C), of pressure, and of having CaO present on the H_2 yield and enthalpy balance of urea steam reforming were investigated. At a S:C of 3 the presence of CaO increased the H_2 yield from 2.6 mol H_2/mol urea feed at 940 K to 2.9 at 890 K, and decreased the enthalpy of bringing the system to equilibrium. A minimum enthalpy of 180.4 kJ was required to produce 1 mole of H_2 at 880 K. This decreased to 94.0 kJ at 660 K with CaO-based CO_2 sorption and, when including a regeneration step of the $CaCO_3$ at 1170 K, to 173 kJ at 720 K. The presence of CaO allowed widening the range of viable operation at lower temperature and significantly inhibited carbon formation. The feasibility of producing H_2 from renewable urea in a low carbon future is discussed.

1. Introduction

Urea ($CO(NH_2)_2$) has recently been the focus of research because of its potential for environmentally friendly H_2 storage compared to many other chemical hydrogen carriers and storage media. With its 6.71 wt% hydrogen content (increasing to a yield of 10.09 wt% of urea when steam reformed), urea is non-toxic, non-flammable and odourless. Provided it is maintained in dry conditions, it remains in solid crystal form in ambient conditions. These properties make it extremely attractive for easy, economic and safe hydrogen storage and transport, a winning combination not yet matched by the most advanced materials or hydrogen carriers. In a future world where biomass will increasingly be converted to transport biofuels, most likely necessitating a hydrodeoxygenation (HDO) stage to increase their H/C ratio closer to that of petrol or biodiesel, varied sources of renewable hydrogen will be required at biorefineries. Different methods of recovering H_2 from urea have been explored, divided between electrolysis [1-8], and thermochemical means.

The thermochemical conversion of urea has been mostly investigated in the context of reduction of the air pollutants collectively known as 'NOx' ($NO + NO_2$) which are generated by combustion of hydrocarbon fuels in air. Selective catalytic and non-catalytic reduction of NOx ('SCR'-'SNCR') are used mainly in the cases where the combustion fuel also contains significant chemically bonded nitrogen (fuel-N) such as coal, fuel oil, or biomass, and when other NOx mitigating techniques cannot be used, such as in diesel engines exhausts. During SCR and SNCR, the first steps consist of urea thermolysis -an endothermic reaction which produces isocyanic acid (HCNO) and ammonia (NH_3) at 150-300 °C- readily followed by the exothermic hydrolysis of the HCNO into CO_2 and NH_3 (below 200 °C). The production of NH_3 from urea as the final reducing agent of NO ('urea thermohydrolysis' [9]) is the aim of SCR and SNCR, but increasing the water concentration leads to complete HCNO hydrolysis, and further raising the temperature above 450 °C results in ammonia cracking, which generates H_2, and N_2. Thus overall, the complete reaction of one mole urea with one mole of water above 450 °C, which can be considered 'steam reforming of urea', produces 3 moles of H_2, one mole of N_2 and one mole of CO_2. Rahimpour et al [10] demonstrated 4588 ton/yr of H_2 production using wastewater containing 2-9 wt% NH_3 and 0.3-1.5 wt% urea from a 1500 tonnes of urea per day production plant. They carried out the H_2 separation in a Pd/Ag countercurrent catalytic membrane reactor where ammonia cracking was the last stage in a multi-step process of urea hydrolysis. Zamfirescu and Dincer evaluated the theoretical energy savings from using urea as a source of H_2 additive in combustion engines [11].

In industry, urea production relies on reacting ammonia with carbon dioxide via the intermediate ammonium carbamate in an exothermic reaction. This urea is utilised as synthetic agricultural fertiliser. Statistics on current growth of urea production can be found in [12]. Urea production is associated with ammonia plants, which currently use natural gas as the original H_2 feedstock for steam methane reforming. Thus mass production of urea is at present fossil fuel based. Other than water, urea is the main component of urine, where it is found in average of 2 wt%, depending on protein diet. Urine can be separated from human waste using urine diversion ('UD') toilets or 'waterless' urinals, and has great potential as a natural fertiliser [13, 14]. The presence of urine in wastewater requires expensive retrofitting wastewater treatment plants with a de-nitrification stage to prevent the pollution of nearby waterways and coastline. Converting the N-content of urine's urea into N_2 gas through the production of H_2 from a bio-feedstock/urine system by making use of 'steam reforming' would avoid denitrification retrofitting costs. In another publication we have outlined the renewable sources of urea [15]. This group has also demonstrated the experimental conditions leading to good chemical conversion from urea-water solutions using a commercial catalyst [16, 17]. In the present work, we identify the conditions leading to the most energy efficient way of producing hydrogen from the urea-water system by means of thermodynamic equilibrium calculations. The potential for additional energy savings are considered by introducing a solid CO_2 sorbent in the system (CaO) which produces the 'sorption enhancement' effect, a process whose feasibility has previously been demonstrated by the authors using variable feedstocks [18-22].

2. Methodology of the thermodynamic equilibrium calculations

The code EQUIL from the CHEMKIN II package [23] was used to perform the thermodynamic equilibrium calculations of the urea-water system with and without $CaO_{(S)}$. The program relies on a procedure of minimisation of Gibbs function to compute the mole fractions of the equilibrium mixture, based on one mole of initial (feed) mixture. The EQUIL calculations were performed for isothermal and isobaric conditions, allowing for molar and volume changes of the system. Included in the program's outputs were the specific enthalpy, internal energy, and entropy of one gram of the initial and equilibrium mixtures, as well as their molar mass. The authors applied their own post-processing subroutines allowing the

calculations of reactants conversions, molar yields of products (mol / mol urea feed), dry gas mol fractions. They also incorporated as a post process the enthalpy balance, including the enthalpy terms associated with bringing to the reaction temperature the reactants from an initial temperature of 298 K and in their natural phases (crystalline urea, liquid water, $CaO_{(S)}$). An additional enthalpy term associated with decomposition of calcium carbonate ($CaCO_{3(S)}$) was also included in the calculations featuring regeneration of the sorbent, when the sorbent was present.

The species considered in the procedure of minimisation of the Gibbs function in the urea-water system were: $CO(NH_2)_{2\ (g)}$, CH_4, CO_2, H_2, $H_2O_{(g)}$, CO, N_2, $C_{(S)}$, $CaO_{(S)}$, $CaCO_{3(S)}$, $Ca(OH)_{2(S)}$, NH, NCO, HCNO, NH_3, NH_2, HCN, CN, Ar.

In all the calculations a symbolic, negligible, mole fraction of 0.01 argon gas was used in the initial reactant mix to facilitate the calculation of the equilibrium total moles produced per mole of initial mixture via an argon balance. Knowledge of the total moles produced at equilibrium was required for the calculation of all the products yields, as well as the enthalpy terms of the energy balance for each condition tested. The temperature and absolute pressure ranges covered in the calculations were 291-1280 K and 1-20 atm respectively.

The thermodynamic properties for CH_4, CO_2, H_2, $H_2O_{(g)}$, CO, N_2, NH, NCO, HCNO, NH_3, NH_2, HCN, CN, Ar, were from [24], $CO(NH_2)_{2\ (g)}$ from [25], $CaCO_{3(S)}$ (calcite) from [26], $CaO_{(S)}$ (lime) and $Ca(OH)_{2(S)}$ (calcium dihydroxide) from [27]. Two references were used for the three types of $C_{(S)}$ modelled: [28] for amorphous carbon, and [29] for graphitic and filamentous carbons.

Conditions at equilibrium were provided on the basis of the molar steam to carbon ratio ('S:C'), the molar calcium to carbon ratio ('Ca:C'), the reaction temperature 'T', and reaction absolute pressure, and whether any form of solid carbon was considered as a potential product.

Three S:C equilibrium conditions (1, 3 and 6.92) were calculated in the present study. Their choice is justified as follows. S:C=1 is the stoichiometric S:C for complete conversion of urea and water to CO_2, H_2 and N_2, thus it represents the minimum S:C of practical operation for H_2 production. S:C=3 is a typical condition of 'excess steam' used in industrial steam reforming aimed at H_2 rather than syngas production, the excess of steam prevents carbon deposition on the catalyst and also improves the yield of H_2 through Le Chatelier's principle. S:C=6.92 corresponds to the commercial eutectic mixture of 32.5 wt% urea-water solution, also known as AUS32 and AdBlue®. The latter is commonly used as the reducing agent in the selective catalytic reduction of nitrogen oxides to nitrogen gas in diesel powered vehicles

[30]. It has also been proposed recently as a novel fluid for the storage of latent heat [31]. The Ca:C was kept at 1, representing the stoichiometry of the CaO and Ca(OH)$_2$ carbonation reactions.

Presentation and discussion of the results was based on the following outputs:

(i)   Product yield for species 'i': $i\ \text{yield} = \dfrac{n_{eq} \times y_{i,eq}}{1 \times y_{urea,feed}}$ with $n_{eq} = \dfrac{y_{Ar,feed}}{y_{Ar,eq}}$

Where n_{eq} is the total number of moles of product at equilibrium per mole of feed (initial) mixture, $y_{i,eq}$ is the equilibrium mole fraction of species i, while $y_{urea,feed}$ and $y_{Ar,feed}$ are the input mole fractions of gaseous urea and argon.

(ii)   Dry gas mol fraction of species 'i': $y_{i,dry,eq} = \dfrac{y_{i,gas,eq}}{\displaystyle\sum_{l=1}^{k} y_{l,gas,eq,except\,H_2O}}$

In the special case where i was H$_2$, the dry gas mol fraction was also called 'H$_2$ purity'.

(iii)   Individual enthalpy balance terms 'ΔH' and overall enthalpy balance ΔH_{total}:

-'urea ΔH'= Enthalpy 'H' of feed urea gas at T, minus H of feed solid (crystalline) urea at 298 K (kJ/mol urea feed).

-'H$_2$O ΔH'= (H of feed H$_2$O vapour at T, minus H of liquid feed H$_2$O at 298 K) in kJ/mol urea feed.

With H of feed H$_2$O = Enthalpy at given temperature, converted from kJ/mol H$_2$O to kJ/mol urea feed as follows:

$H_{H_2O=}\dfrac{y_{H_2O,feed}}{y_{urea,feed}} \times h_{H_2O} = Y_{feed,H_2O} \times h_{H_2O}$ where h_{H2O} is the enthalpy of feed water in kJ/mol of water and Y_{feed,H_2O} is the feed molar ratio of H$_2$O to urea.

-'Reaction ΔH'= $\sum H_i$ of products at T, minus $\sum H_j$ of reactants at T.

Where $H_{i\ product}= i\ \text{yield} \times h_i$ with h_i the enthalpy of product i in kJ/mol of i, and 'i yield' as defined above in (i).

$H_{j\ reactant}= Y_{feed,j} \times h_j$ where $Y_{feed,j}$ is the molar feed of reactant j per mole of urea feed, and h_j is the enthalpy of reactant j in kJ/mol of j.

-'decarbonation ΔH'= CaCO$_3$ yield $\times(h_{CaO,1170K} + h_{CO_2,1170K} - h_{CaCO_3,T})$ in kJ/mol of urea feed.

The regeneration temperature of 1170 K was chosen to reflect temperatures used in practice for decarbonation of calcium carbonate in mixtures that may contain significant CO_2 [32]. -'ΔH_{total}' is sum of the 'urea', 'H_2O', 'reaction' and 'decarbonation' terms.

$$(iv) \qquad \Delta H \text{ ratio} = \frac{\Delta H_{total}}{H_2 \text{yield}} \times \frac{1}{\Delta H_{WSP}}$$

Where ΔH_{WSP} is the enthalpy change of the complete reaction $H_2O \rightarrow H_2 + 0.5O_2$ ('water splitting') in kJ per mol of H_2 produced.

In ΔH_{WSP}, the reactant water is liquid at 298 K and the gas products H_2 and O_2 are at the same reaction temperature T as that used for the calculation of ΔH_{total}.

ΔH ratio is a measure of the enthalpy cost of producing 1 mol of H_2 through the urea-water system compared to that of producing 1 mol H_2 through water splitting, starting from reactants in their natural phases (crystalline urea, liquid water) at 298 K. It could also be interpreted as a measure of the energy cost of producing H_2 through the urea-water system compared to the energy gain by heat release from burning/oxidising the H_2 produced with oxygen, representing its final use in a fuel cell or a combustion engine.

ΔH ratio <1 represents an efficient process and viable from an energy viewpoint. The furthest ΔH ratio is from 1, the more efficient it can be considered. Conversely, ΔH ratio >1 represents a non-viable process from energy viewpoint because it would need more energy to produce the hydrogen than the energy subsequently generated by its combustion or oxidation in a fuel cell or combustion engine.

3. Results and discussion

In the following discussion the effects of four input parameters are discussed on the equilibrium conditions: temperature, steam to carbon ratio, carbon formation, pressure and the presence of CaO. A comparison of steam reforming of urea vs. methane is also performed to help assessing the feasibility of the process, given that steam methane reforming is at present the industry standard of hydrogen production.

3.1 Effect of temperature

Table 1 lists the main global reactions relevant to the urea-water system with and without CaO as well as their reaction enthalpy change at 298 K. The list of main reactions reflects an amalgam of many other reactions identified over the years during investigations of urea's kinetics of thermolysis and hydrolysis. These studies mainly focussed on the utilisation of urea as reducing agent in the selective catalytic reduction of NO_x to N_2. An exhaustive list of intermediate thermolysis and hydrolysis reactions of urea involving the by-products biuret, triuret, and melamine, in addition to ammonia and isocyanic acid can be found in [33].

Table 1

The major products from the urea-water system for S:C of 3 at 1 atm included CH_4, CO_2, CO, and H_2, as shown by the yields and dry mole fractions profiles in Fig. 1ab. Knowledge of equilibrium dry gas compositions is useful to the experimentalist as they can be directly compared to measurements from on-line and off-line analyses of the process gas products.

Figure 1

Sublimation of urea (solid to gas phase change), with a ΔH of 97.6 kJ/mol, is reported to occur at around 354 K [34], but to streamline the calculation of equilibrium condition, the urea feed was input in gaseous phase in the EQUIL code, and the enthalpy change of sublimation was subsequently accounted for in the 'urea ΔH' term of the total enthalpy balance 'ΔH_{total}'. Similarly, the water feed was input in the gaseous phase. This means that the yield profiles shown in Fig. 1b ought to be disregarded below 373 K as they do not account for the two phase changes of urea sublimation and water evaporation.

At low temperatures the carbon products were dominated by methane, but as temperature increased the yield of methane dropped, replaced by CO_2. Above 700 K, CO_2 was gradually replaced by CO. H_2 appeared in the equilibrium products above 500 K, and sharply increased with temperature to become the main product at 900 K. H_2 then underwent a slow decrease above 900 K. These trends began at the lowest temperatures (< 500 K) with urea decomposition (R1), where all the H_2 produced then underwent methanation of CO (R2), leaving the excess CO (i.e. 25%) to undergo water gas shift (R3). This resulted in the net molar yields of 0.75 CH_4, 0.25 CO_2, 0.5 H_2O and 1 N_2 per mol of urea. At increasing temperature (T<900 K), CO methanation weakened to let the urea decomposition and water gas shift (R1+R3) gradually take over, which can generate a maximum of 3 mol of H_2 per mol of urea feed. The conditions S:C=3, 1 atm indicated a maximum equilibrium H_2 yield of 2.6 mol/mol urea feed, i.e. 87% efficiency compared to theoretical maximum. At the higher

temperatures, the H_2 production became increasingly mitigated by the reverse water gas shift reaction at the highest temperatures (R1+(1-x)R3). Ammonia production through (R4) remained small, with a peak yield of just 1.5×10^{-3} mol /mol urea feed at 680 K. Similarly, equilibrium yields of isocyanic acid, a known intermediate in the urea thermohydrolysis process (R5), were negligible in all the conditions tested. Therefore the only significant H-containing co-product -apart from H_2- was CH_4 in the temperature range investigated (300-1280 K).

3.2 Effect of S:C ratio

Figure 2

The effect of S:C ratio on the H_2 yield and on the energy balance of the 'basic' urea-water system (without CaO in the feed and without $C_{(S)}$ in the products) can be seen in Fig. 2. The dependence of the H_2 yield on S:C was governed by Le Chatelier's principle, whereby an increase in H_2O concentration in the system shifted the equilibrium towards more consumption of H_2O, resulting in higher H_2 yield. The shift of the peak H_2 yield towards lower temperatures with increasing S:C was the result of the mismatch between the ΔH of R1+R3 (dominant between 500 and 900 K and both H_2O dependent) and that of $-x$R3, which begins above 900 K and is H_2 dependent). This trend is exhibited by all hydrocarbons undergoing steam reforming and indicates that from a chemistry viewpoint only, operating at higher S:C is always beneficial to the H_2 yield.

At a given S:C, the ΔH ratio was shaped by featuring the H_2 yield at its denominator, lending it a mirror image from that of the H_2 yield with increasing temperature. The profiles in Fig. 2 indicate that the ΔH ratio penetrated the <1 viability area at similar temperatures (~720 K) for the three S:C investigated (1, 3 and 6.92).

Figure 2 confirms the growing energy costs of operating at increasing S:C, as exemplified by a minimum ΔH ratio of 0.58 at S:C =3, which became 0.80 at S:C = 6.92. This was equivalent to a 39% rise in enthalpy demand between the two S:C at their most energy efficient. Furthermore the temperature range of ΔH ratio <1 narrowed for increasing S:C. Thus, while beneficial for the H_2 yield, raising the S:C incurs a heavy energy penalty and restricts the temperature range of process viability.

The ΔH ratio's behaviour was further analysed with the help of Fig. 3, which shows the change with temperature of the individual ΔH terms in the urea-water equilibrium system at 1 atm for both S:C=3 and 6.92.

Figure 3

The results of Fig. 3 underline that the total enthalpy of the process, and consequently, the ΔH ratio, were dominated by the heating requirements of converting the reactants urea and water (initially in condensed phase at 298 K) to gaseous phase at reaction temperature, i.e. the 'urea' and 'H_2O' ΔH terms. The isothermal reaction term was comparatively smaller than both the 'urea' and 'H_2O' enthalpy terms. Moreover, the 'H_2O' ΔH more than doubled for S:C between 3 and 6.92, increasing ΔH_{total} by 90% at 300 K and by 54% at 1280 K compared to the S:C =3 values. Thus the 'H_2O' ΔH had the largest effect on the ΔH ratio's variations with S:C. This stresses the need for a compromise between operating at the expensive high values of S:C that produce more and purer H_2 per mol of urea, and the cheaper low values of S:C associated with lower yield and lower purity H_2. In practice, using pinch analysis, all steam reforming plants feature multiple heat integration stages that make the most of recuperating the energy contents of both excess steam and the syngas leaving the reformer. This means that the energy of the excess steam of operating at larger S:C could become advantageous downstream of the reformer with the introduction of a steam turbine as well as heat exchanger networks, allowing export of heat and power. Yet this involves significant capital investment and carries efficiency losses at each heat transfer/energy conversion stage. Therefore such economic considerations may lead to choosing to operate at the lower energy costs of moderate S:C such as 3 when heat and power exports afforded by large steam excesses are not possible.

3.3 Comparison with steam methane reforming

To gauge the energy cost of producing H_2 from the urea-water reaction compared to the industry standard (steam methane reforming), the total enthalpy change of the urea-water system was compared to that of methane-water at S:C of 4 and 1 atm. Both the methane and urea molecules have the same number of carbon (1) and hydrogen (4), which helps the comparison. Also, for fairness, both feedstocks were considered initially in the gas phase. In this case the $\Delta H_{total,}$ was significantly lower for urea than methane per mole of carbon in the feed, (e.g. by an average of 53.6 kJ above 900 K). In spite of this, the lower H_2 yield for urea than for methane, by an average of 0.84 mol H_2/ mol of C above 900 K, resulted in similar ΔH ratios in the 600-900 K range, and also to comparable minima of ΔH ratios (urea: 0.51 at 860 K, methane: 0.46 at 920 K). Above 900 K, the ΔH ratio for methane remained slightly lower than urea, ending with a difference of just 0.13 at 1250 K. Thus comparing like with

like, the two systems incurred very similar enthalpy changes on the basis of one mole H_2 produced.

The thermodynamic 'ease' of steam reforming of the two gaseous feedstocks (urea/methane) could also be predicted and compared on the basis of the respective Gibbs function changes of the two complete reactions with steam, generating CO_2 and H_2 (Fig. 4).

Figure 4.

As expected, at low temperatures the steam methane reforming reaction began with positive ΔG, reflecting conditions favouring the reactants, but as temperature reached 860 K, ΔG of steam methane reforming became negative, indicating the H_2 and CO_2 products were favoured. In contrast, steam reforming of urea gas thermodynamically favoured the products H_2 and CO_2 from as low as 400 K, with a ΔG that was increasingly negative as temperature increased. Comparing the ΔG of the two reactions, that of urea steam reforming was roughly 140 kJ/mol of C in the feed below that of methane, which indicated steam reforming is more thermodynamically favourable when using urea gas than methane.

3.4 Effect of Carbon formation

Another reason for aiming to operate with excess of steam in industrial steam reforming is the inhibition of the formation of carbon. Solid carbon in the products not only diminishes the H_2 yield because it represents carbon that did not react with steam to generate H_2, but also covers active sites of the reforming catalyst, causing its deactivation. The formation of carbon is self-catalysing and thus its inhibition is crucial. In practice, the carbon produced is more or less amenable to removal by the oxidative effects of steam according to its different forms, e.g. amorphous, filamentous, graphitic. Figure 5 shows the effect of introducing these three forms of carbon as potential products in the urea-water equilibrium system at S:C=3 and 1 atm, compared to the $C_{(S)}$-free system.

Figure 5

All three forms of carbon saw their yield merge above 900 K and become negligible (<0.05 mol/mol urea feed) above 1070 K. In practice $C_{(S)}$ yields would not become as prominent in the carbon products as suggested by Fig. 5, because the mechanisms of solid carbon formation and removal on reactor bed materials are strongly kinetically driven. The K_c of the Boudouard equilibrium data used to derive the thermodynamic properties of graphitic and filamentous $C_{(S)}$ were originally intended to indicate threshold conditions for formation of

$C_{(S)}$ [29]. Accordingly, the $C_{(S)}$ yields shown in Fig. 5 should be considered as indicative of significant $C_{(S)}$, and point to the desirability of avoiding temperatures below 1070 K. Product yield distributions of the urea-water system calculated with the three forms of $C_{(S)}$ in the products (not shown) indicated that at the lowest temperatures, there was a combination of urea decomposition reaction (R1, Table 1), CO disproportionation (Boudouard reaction, R6) and methanation of CO_2 (R7), resulting in a global reaction of $C_{(S)}$ formation from urea gas (R1+R6+R7: $CO(NH_2)_2 \rightarrow 0.5C_{(S)}+0.5CH_4+H_2O+N_2$). At higher temperature, both methanation and CO disproportionation waned, allowing H_2 yield to increase while still remaining lower than in the $C_{(S)}$-free system, as per Fig. 5.

Only a small influence of the presence of $C_{(S)}$ in the products was recorded on the ΔH ratio in the region of peak H_2 yield above 800 K. The ΔH ratio profiles for the three forms of carbon were clustered together, but were also close to that of the $C_{(S)}$-free system. This is because, while the H_2 yield was lower with $C_{(S)}$ compared to $C_{(S)}$-free system, the 'reaction' term contribution to ΔH_{total} itself decreased in the region of peak $C_{(S)}$ production (800-1000 K) due to the exothermicity of $C_{(S)}$ formation through R6 (Table 1). The ease of $C_{(S)}$ formation from urea gas can be evaluated against that of its steam reforming, based on the ΔG of the relevant reactions (Fig. 4). Comparing the ΔG of steam reforming of urea gas with that of filamentous $C_{(S)}$ formation from urea gas through (R1+R6+R7) shows that at lower temperatures, the $C_{(S)}$ forming reaction had the lowest negative value (e.g. -113.2 kJ/mol of urea at 400 K) and this indicated $C_{(S)}$ formation would have been more thermodynamically favourable than urea steam reforming (R1+R3). At 870 K, the ΔG curve of (R1+R6+R7) and that of (R1+R3) crossed each other, with the ΔG of the latter becoming more negative. This suggested that above 870 K, $C_{(S)}$ and CH_4 would have been thermodynamically suppressed, while the products CO_2 and H_2 became thermodynamically favoured. This effect was not sensitive to the form of carbon considered, with negligible differences obtained in the ΔG values when amorphous and graphitic $C_{(S)}$ data were substituted in the calculation. Similarly, comparing $C_{(S)}$ formation from urea gas vs. that from methane via thermal decomposition ($CH_4 \rightarrow C_{(S)}+2H_2$), the more negative values of the former denoted that $C_{(S)}$ formation from urea would be easier to achieve than through thermal decomposition of CH_4.

3.5 Effect of pressure on H_2 yield and enthalpy balance

In practice, implementing the process of H_2 production from urea-water at larger scales is likely to require working at pressures higher than atmospheric, as this would allow smaller

size plants by processing denser flows, similarly to steam methane reforming plants. The following section explores the effect of pressures above 1 atm on the product yields and the ΔH ratio, based on the profiles shown in Fig. 6ab obtained for S:C of 3 without $C_{(S)}$ or $CaO_{(S)}$ in the system.

Figure 6

As found previously for 1 atm in the $C_{(S)}$-free system, at the lowest temperatures, the reactions were dominated by urea steam reforming combined with methanation of CO and water gas shift, with an overall balance corresponding to R1+0.75R2+0.25R3. This would have generated a gaseous molar balance of 1.5, i.e. one mole of urea gas generated 1.5 moles of gas product mixture. With higher temperatures (<900 K), the exothermic R2 was no longer favoured, and R1+R3, with a gaseous molar balance of 3, dominated. At even higher temperatures (>900 K), with water gas shift becoming limited, the overall R1+(1-x)R3 would still have a molar balance of 3, because R3 is an equimolar reaction. According to Le Chatelier's principle, increasing the pressures to above atmospheric would have had a greater negative effect on the reactions with the largest gaseous molar balance (i.e. R2+R3), shifting their equilibrium to the left to a larger extent. This translated into lower H_2 yield and higher CH_4 yield with increasing pressure. Hence the ΔH ratio moved closer to 1 at higher pressures, restricting the temperature range for which the urea-water process is viable.

3.6 Effect of $CaO_{(S)}$ on H_2 yield, $C_{(S)}$ formation and enthalpy balance

The CO_2 solid sorbent $CaO_{(S)}$ (lime) lowered considerably two of the hurdles to energy savings in the process of H_2 production from urea with water: the ΔH ratio's closeness to 1, and $C_{(S)}$ formation at temperatures below 1070 K.

Figure 7

With Ca:C of 1, where the Ca:C represents the stoichiometry of the carbonation reactions of $CaO_{(S)}$ and of $Ca(OH)_2$ (R8 and R10 in Table 1), the carbon containing products were redistributed towards a large yield of calcium carbonate ($CaCO_{3(S)}$). Calcium carbonate exhibited a large peak of 0.87 mol/mol urea feed at 730 K (Fig. 7), from a theoretical maximum of 1. The yield of the by-product $Ca(OH)_{2(S)}$ reached a generous peak of 0.633 mol/mol urea feed at 360 K (not shown for clarity), and decreased with temperature to negligible values above 750 K. The formation of $Ca(OH)_2$ through the hydration reaction R9 lowered the steam available for H_2 production. At temperatures above 730 K, $CaCO_{3(S)}$ steadily decomposed back to $CaO_{(S)}$ through the decarbonation reaction (-R8).

Up to six positive effects were identified in the temperature zone of highest $CaCO_{3(S)}$ yield (500-1000 K) on the urea-water system at equilibrium. The first was an increase in the peak H_2 yield, bringing it closer to the theoretical maximum of 3 mol/mol urea feed. This increase was larger for the $C_{(S)}$-free system. The second was the extension by roughly 200 K of the conditions resulting in high H_2 yield, shifted towards lower and therefore more materials-friendly temperatures. The third (not shown) was the resulting higher maximum purity of H_2 in the syngas produced: the peak H_2 dry mole fraction was 0.564 at 940 K without $CaO_{(S)}$, compared to 0.716 at 810 K with $CaO_{(S)}$, out of a theoretical maximum of 0.75. The latter was accompanied by significant reductions in CO and CO_2, with dry mole fractions below 0.01. The fourth was energy savings, as shown by a ΔH ratio notably below that of the Ca-free system, even when accounting for regeneration of the $CaCO_{3(S)}$ back to $CaO_{(S)}$ through decarbonation (-R8) at 1170 K. Calculations of the influence of the decarbonation temperature were performed in the range 970-1170 K (not shown), but the ΔH ratio exhibited no sensitivity to it. The potential energy savings stopped above 900 K for the ΔH ratio that included regeneration of the $CaCO_{3(S)}$, but persisted all the way to 1100 K without regeneration. Above 1100 K, the ΔH ratios of the systems with and without Ca merged to similar values due to decarbonation being thermodynamically favoured. The case with $CaO_{(S)}$ without decarbonation as a final procedure would represent a process with disposal of the carbonate rather than its recycling by regeneration. However, since the cheapest source of $CaO_{(S)}$ is by calcination of naturally occurring carbonate (e.g. limestone, dolomite), it makes sense to use the material over several cycles and to perform multiple regenerations before disposing of the used carbonate, so as to achieve genuine energy and CO_2 emissions reductions. Research efforts are taking place worldwide to understand the reasons for the loss of CO_2 capacity with repeated cycling and increase the durability of Ca-based CO_2 sorbent with this very aim [35-43].

Table 2 allows comparison of the minima of enthalpy changes of the urea-water system at 1 atm (and the temperatures at which they occur) with those of the urea-water-CaO system (with Ca:C=1), in kJ/mol of H_2 produced, alongside the ΔH ratio, maxima of H_2 yield and of H_2 purity, also listed with their corresponding temperatures.
These reveal the magnitude of potential energy savings brought about by in situ CO_2 sorption by CaO and the range of optimum conditions available to the process operator. To illustrate this point for the most likely case of S:C = 3, the minimum energy required to bring the

system at equilibrium starting from feed materials of solid urea and liquid water at 298 K, was 180.4 kJ/mol H_2, produced at 880 K without CaO. This decreased to 94.0 kJ/mol H_2 at the much lower 660 K with CaO in the system, but not including regeneration of the $CaCO_3$. When including the enthalpy change of the $CaCO_3$ regeneration back to CaO at 1170 K, it got back to 173 kJ/mol H_2 at 720 K, however this was still lower than the Ca-free system.

Table 2

As fifth positive effect, $CaO_{(S)}$ extended the temperature zone of process energy viability 200-300 K lower than the Ca-free process. Finally, as the sixth beneficial outcome, $C_{(S)}$ formation was largely inhibited by $CaO_{(S)}$. This can be seen in Fig.7 by the peak of filamentous $C_{(S)}$ yield of just 0.122 mol /mol urea feed at 860 K for the urea-water system with $CaO_{(S)}$, compared to 0.622 mol /mol urea feed at 690 K without $CaO_{(S)}$. Clearly the presence of $CaO_{(S)}$ and of CO_2 in the products allowed $CaCO_{3(S)}$ to form in the conditions that would otherwise have favoured $C_{(S)}$, CO, and CH_4 as precursors to CO_2 in the urea-water system.

4. Conclusion and final remarks

The conditions for practical hydrogen production from the urea-water system will, like steam methane reforming, represent a compromise between the higher hydrogen yields and lower risks of catalyst coking achieved by high steam to carbon ratios, balanced against the enthalpy costs of raising excess steam. For a total pressure of 1 atm, the steam to carbon ratio of 3 represented such a compromise, as it offered a wide window of temperature with reasonably large H_2 yield (> 2.2 mol/mol urea feed at 830-1000 K) for which the energy requirements were significantly lower than those of producing hydrogen by water splitting alone (ΔH ratio <0.6), and very close to those of producing hydrogen from steam methane reforming. Comparison of urea with methane steam reforming on the basis of the change in Gibbs function indicated the former ought to be easier to perform, as it favoured the H_2 and CO_2 products for as low as 400 K, in contrast to methane which required at least 900 K. Conditions without in-situ CO_2 capture will require, like a steam methane reforming plant, the post processing stages of CO-shift and H_2 separation from the CO_2/N_2 rich mixture. CaO in the reformer could allow energy efficient and catalyst-friendly operation at lower scale because of the eliminated need for downstream CO-shift and thus reduced purification requirement. Indeed the product gas would be 71.6% H_2, 25.8 % N_2 with roughly equal ~1%

impurities of CO, CO_2 and CH_4 in the conditions of highest H_2 purity (S:C=3, 810 K, 1atm). The opportunity for operating at lower scale could in turn reduce the need for high pressure, bringing the conditions more favourable to high H_2 yield at lower enthalpy cost. Currently, operating with a urea feedstock from urine alone would not be viable. Urea's content in urine is maximum 3 wt%, representing a protein rich diet and corresponding to a steam to carbon ratio of 108. The cost of obtaining H_2 from urine alone would be overwhelmed by raising the excess steam. However, balancing the steam to carbon ratio by addition of another sustainable source of carbon, also readily available in households such as waste cooking oil, could enable the utilisation of this abundant and valuable natural resource. Challenges to realise this potential will include developing efficient and economical means of neutralising impurities from the bio-feedstocks that can potentially poison the catalysts, such as metals, sulphur, chlorine, phosphorus, and of converting them to valuable by-products.

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Table 1 Main reactions identified in the urea-water equilibrium system from composition of the equilibrium mixture and their (forward) reaction enthalpy at 298 K for the provided molar stoichiometry.

	Reaction	Stoichiometry (mol)	$\Delta H_{R,298K}$ (kJ)$\rightarrow$
R1	Gaseous urea decomposition to CO$\rightarrow$	$CO(NH_2)_{2,g} \rightleftarrows CO+2H_2+N_2$	125.0
R2	Methanation of CO$\rightarrow$/$\leftarrow$Steam methane reforming (SMR)	$CO+3H_2 \rightleftarrows CH_4+H_2O_g$	-206.2
R3	Water gas shift$\rightarrow$/$\leftarrow$Reverse WGS	$CO+H_2O_g \rightleftarrows CO_2+H_2$	-41.2
R4	Ammonia synthesis$\rightarrow$/$\leftarrow$ammonia cracking	$N_2+3H_2 \rightleftarrows 2NH_3$	-91.9
R5	Gaseous urea decomposition to isocyanic acid$\rightarrow$	$CO(NH_2)_{2,g} \rightleftarrows HCNO+NH_3$	87.9
R6	Boudouard reaction (disproportionation of CO)$\rightarrow$	$2CO \rightleftarrows C_{(S)}+CO_2$	
		graphitic $C_{(S)}$	-185.2
		filamentous $C_{(S)}$	-166.7
		amorphous $C_{(S)}$	-138.7
R7	Methanation of $CO_2\rightarrow$/complete SMR	$CO_2+4H_2 \rightleftarrows CH_4+2H_2O_g$	-165.0
R8	Carbonation of $CaO_{(S)}\rightarrow$/$\leftarrow$Decarbonation	$CaO_{(S)}+CO_2 \rightleftarrows CaCO_{3(S)}$	-177.3
R9	Hydration of $CaO_{(S)}\rightarrow$/$\leftarrow$Dehydration	$CaO_{(S)}+H_2O(g) \rightleftarrows Ca(OH)_{2(S)}$	108.2
R10	Carbonation of $Ca(OH)_2\rightarrow$/$\leftarrow$Decarbonation	$Ca(OH)_{2(S)}+CO_2 \rightleftarrows CaCO_{3(S)}+H_2O_g$	-69.1

Additional enthalpy data on phase change:
Sublimation of urea: $\Delta H_{354 K}$ of $CO(NH_2)_{2,(S)}\rightarrow CO(NH_2)_{2,g}$ = 97.6 kJ/mol
Vaporisation of water: $\Delta H_{298 K}$ of $H_2O_{liq}\rightarrow H_2O_g$ = 44.0 kJ/mol

Table 2 Best equilibrium outputs (minimum ΔH_{total} and ΔH ratio, maximum H_2 yield and maximum H_2 purity in the dry gas) at their respective temperatures, for S:C of 1, 3 and 6.92 at 1 atm and without $C_{(S)}$ in the products. 'no calcin./with calcin.' mean calculations not including/including $CaCO_3$ regeneration to CaO at 1170 K respectively.

S:C ratio	Conditions	min ΔH_{total} (kJ/mol H_2)	@T (K)	min ΔH ratio	@T (K)	max H_2 yield (mol H_2 / mol urea feed)	@T (K)	max H_2 purity (%)	@T (K)
1	without CaO	158.0	940	0.50	950	2.26	1030	53.1	1030
1	with CaO, no calcin.	111.8*	940	0.35*	940	2.45	970	63.6	860
1	with CaO, with calcin.	147.6	690	0.49	710	2.45	970	63.6	860
3	without CaO	180.4	880	0.58	890	2.59	940	56.4	940
3	with CaO, no calcin.	94.0	660	0.31	660	2.86	890	71.6	810
3	with CaO, with calcin.	173.0	720	0.56	850	2.86	890	71.6	810
6.92	without CaO	248.1	840	0.80	850	2.82	880	58.5	880
6.92	with CaO, no calcin.	168.1	650	0.56	670	2.97	840	73.5	760
6.92	with CaO, with calcin.	244.4	700	0.80	770	2.97	840	73.5	760

*this condition had ΔH_{total} monotonically increasing with temperature (no minimum), the value entered in the table corresponds to the ΔH_{total} with CaO not including regeneration, at the temperature of the minimum ΔH_{total} without CaO.
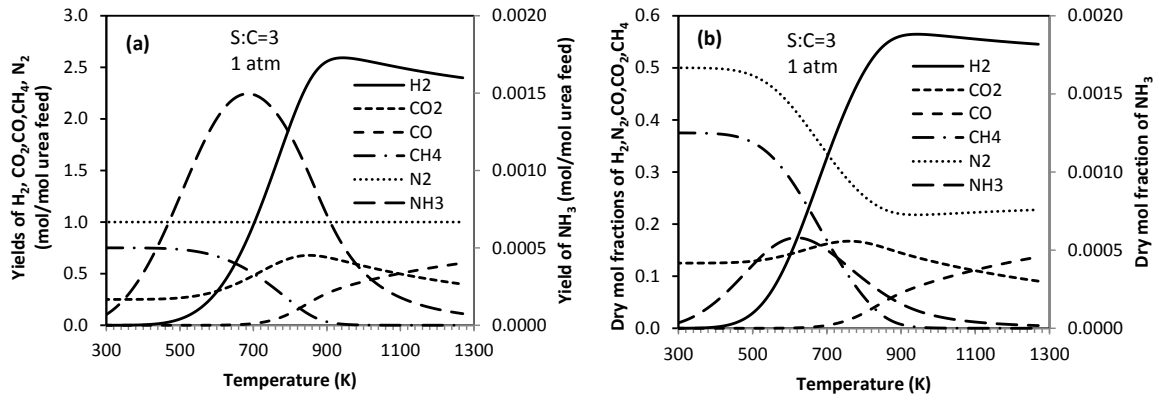
Figure 1 (a) Products yield distribution and (b) Dry gas mol fractions for S:C =3, 1 atm, calculation performed without CaO in the reactants and no $C_{(S)}$ in the products. (Note there is a smaller scale on the right y axis for NH_3).
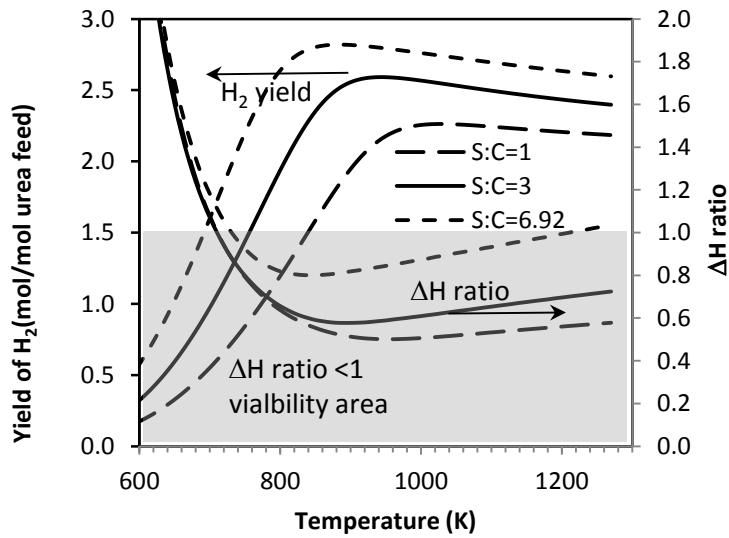

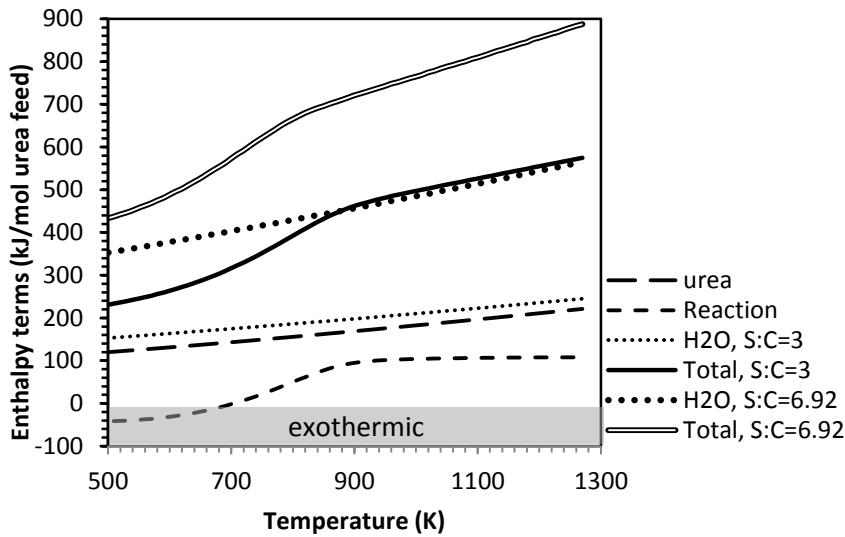Figure 2 Effect of S:C ratio on H_2 yield and ΔH ratio with reaction temperature

Figure 3 Enthalpy terms vs. temperature for S:C=3 and 6.98 at 1 atm, in kJ/mol of urea feed. Calculation performed without $CaO_{(S)}$ in the feed and without $C_{(S)}$ in the products.
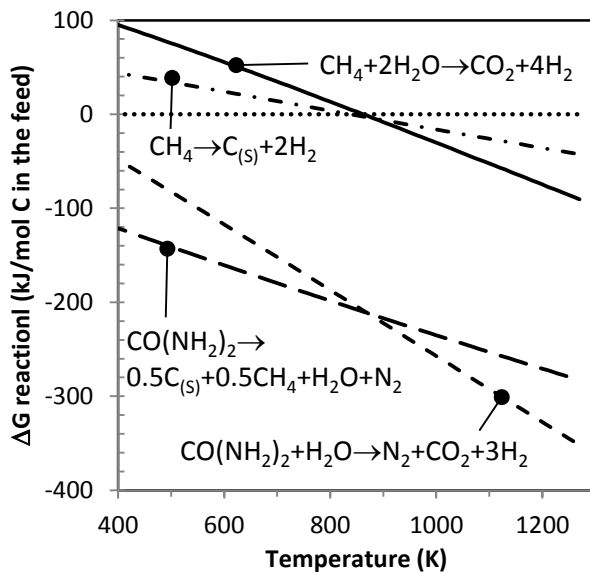
Figure 4. Comparison urea gas and methane feedstocks: Gibbs function change for the two reactions of complete steam reforming and the two reactions of filamentous $C_{(S)}$ formation.
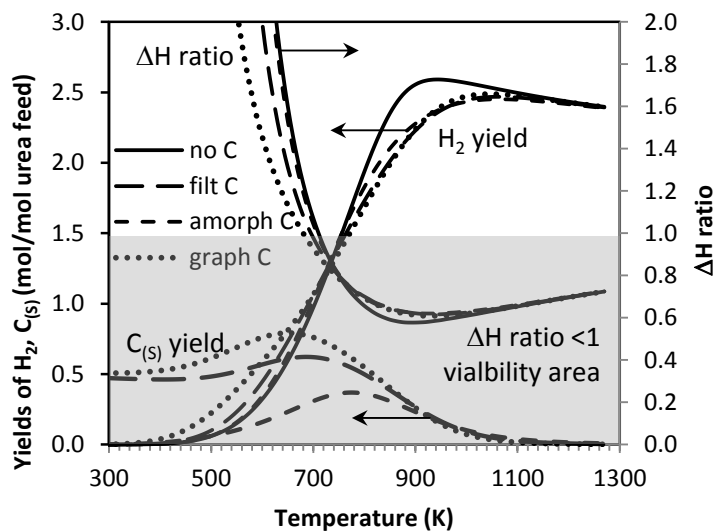
Figure 5 Effect of accounting for $C_{(S)}$ in the products on yields of H_2 and $C_{(S)}$, and on ΔH ratio at S:C=3, 1 atm. 'amorph C': amorphous $C_{(S)}$ on Ni catalyst,'filt C': filamentous $C_{(S)}$ on Ni catalyst, 'graph C': graphitic $C_{(S)}$, independent on catalyst, 'no C': no $C_{(S)}$ allowed in the products.
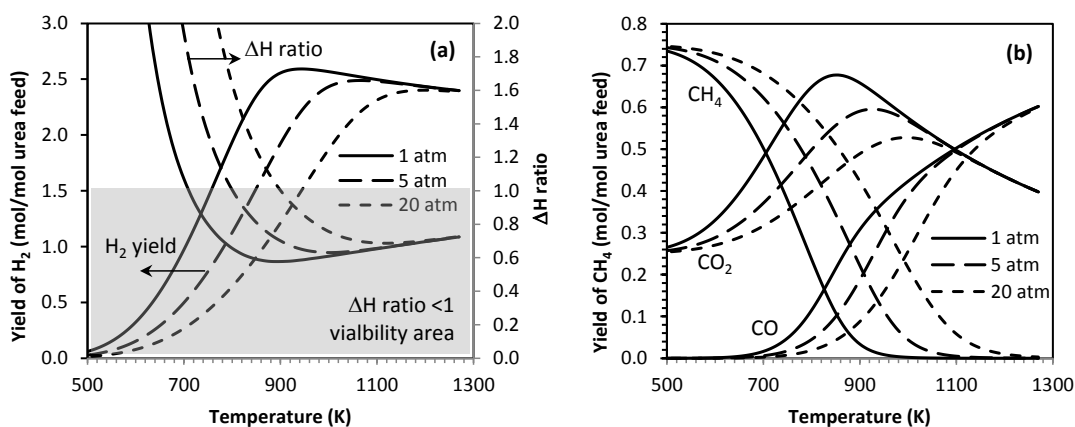

Figure 6 Effect of pressure on (a) H_2 yield and ΔH ratio (b) Carbon products yield for S:C=3. Calculations performed without $CaO_{(S)}$ in the reactants, and without $C_{(S)}$ in the products.
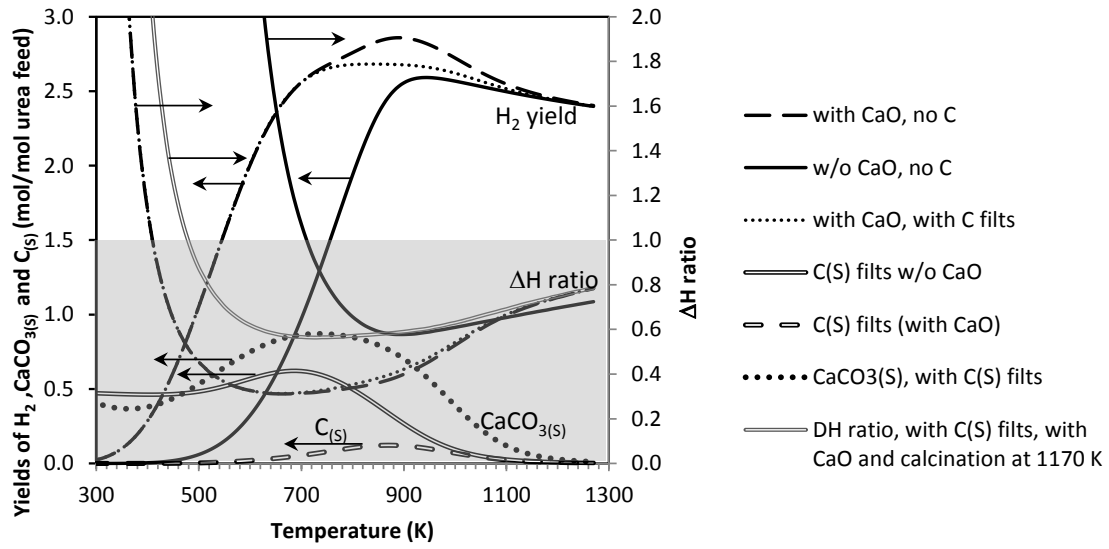
Figure 7 Effect of $CaO_{(S)}$ in the reactants (Ca:C =1) on H_2 yield and ΔH ratio at S:C =3, 1 atm. Calculations with and without filamentous $C_{(S)}$ in products.