Decentralized production of hydrogen from hydrocarbons with reduced CO\textsubscript{2} emission

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ABSTRACT:
Currently, most of the industrial hydrogen production is based on steam methane reforming process that releases significant amount of CO\textsubscript{2} into the atmosphere. CO\textsubscript{2} sequestration is one approach to solving the CO\textsubscript{2} emission problem for large centralized hydrogen plants, but it would be impractical for decentralized H\textsubscript{2} production units. The objective of this paper is to explore new routes to hydrogen production from natural gas without (or drastically reduced) CO\textsubscript{2} emissions. One approach analyzed in this paper is based on thermocatalytic decomposition (TCD) of hydrocarbons (e.g., methane) to hydrogen gas and elemental carbon. The paper discusses some technological aspects of the TCD process development: (1) thermodynamic analysis of TCD using AspenPlus\textsuperscript{TM} chemical process simulator, (2) heat input options to the endothermic process, (3) catalyst activity issues, etc. Production of hydrogen and carbon via TCD of methane was experimentally verified using carbon-based catalysts.

KEYWORDS: hydrogen, carbon, CO\textsubscript{2} emission, methane, catalyst

1. Introduction

Fossil fuels (predominantly, natural gas, NG) are likely to play a major role in hydrogen production in the near- to medium-term future. On the other hand, fossil fuels are the main source of air pollution, producing CO\textsubscript{2}, NO\textsubscript{x}, SO\textsubscript{x} and other pollutants that cause considerable damage to the environment of our planet. Currently, most of the industrial hydrogen production is based on steam methane reforming (SMR) process that releases significant amount of CO\textsubscript{2} into the atmosphere. It was estimated that the global warming potential (GWP, which is defined as a combination of CO\textsubscript{2}, CH\textsubscript{4} and N\textsubscript{2}O emissions expressed as a CO\textsubscript{2} equivalence for a 100 year time frame) of hydrogen production via SMR process is 13.7 kg CO\textsubscript{2} (equiv.) per kg of net hydrogen produced [1]. CO\textsubscript{2} accounts for 77.6% of the system’s GWP. Almost half of the overall CO\textsubscript{2} emissions from SMR process is released in the form of diluted CO\textsubscript{2} streams (stack gases) with CO\textsubscript{2} concentrations of about 5 vol.%, which are very difficult and costly to treat. Geologic or ocean sequestration of CO\textsubscript{2} generated in large-scale hydrogen plants is actively debated in the literature as a potential solution to this environmental predicament. Three major challenges, however, are associated with this approach: (1) uncertain long-term ecological consequences of CO\textsubscript{2} sequestration on a large scale, (2) high cost and (3) impracticality of this approach to decentralized (distributed, or on-site) hydrogen production units. It would be technically challenging and economically prohibitive to collect CO\textsubscript{2} generated at a myriad of scattered small sources and transport them to a sequestration site.

The objective of this paper is to explore new routes to hydrogen production from natural gas (NG) and other hydrocarbon feedstocks without (or drastically reduced) CO\textsubscript{2} emissions. One approach analyzed in this paper is based on thermocatalytic dissociation (TCD) (or pyrolysis, cracking) of hydrocarbons to hydrogen gas and elemental carbon [2,3]:

$$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \quad \Delta H^\circ = 75.6 \text{ kJ/mole} \quad (1)$$

The amount of CO\textsubscript{2} emissions from the process could potentially be as low as 0.05 mole CO\textsubscript{2}/mole H\textsubscript{2} (if methane is used as a process fuel), compared to 0.43 mole CO\textsubscript{2}/mole H\textsubscript{2} for SMR [3]. CO\textsubscript{2} emissions could potentially be eliminated, if a part of hydrogen product is combusted to produce process heat.
Due to very strong C-H bonds in methane molecule (440 kJ/mole) its thermal (non-catalytic) decomposition occurs at very high temperatures (>1200°C). Different transition metal catalysts (e.g., Ni, Fe, Co) have been used to reduce the maximum temperature of methane thermal decomposition [4,5]. The major problems associated with the use of metal catalysts relate to their rapid deactivation (due to blocking of surface active sites by carbon deposits) and difficulties with metal-carbon separation. The use of carbon-based catalysts offers certain advantages over metal catalysts due to their availability, durability and low cost. In contrast to metal-based catalysts, carbon catalysts are sulfur and temperature resistant and do not require the separation of a carbon-product from a carbon-catalyst. The technical feasibility of using carbon materials as catalysts for methane decomposition reaction is discussed in several publications (e.g., [6,7]). The data on catalytic activity of a variety of carbon materials of different origin and structure, including a wide range of activated carbons (AC) and carbon blacks (CB), toward methane decomposition reaction is reported in [6-9].

In this paper we discuss several process development issues related to carbon-catalyzed methane decomposition: (1) factors affecting carbon catalyst activity, (2) kinetics and mechanism of methane decomposition over carbon catalysts, (3) heat input options for the methane decomposition process, (4) thermo-neutral (or autothermal) catalytic decomposition of methane

2. Factors determining carbon catalyst activity and nature of active sites

Many of the chemical properties of carbon materials, including their catalytic activity has been shown to be related to the presence of impurities and various surface groups [10]. The amount and type of impurities present depend on the carbon origin and the method of preparation. Earlier we reported that transition metals (Fe, Ni, V, etc.) present in CB and AC have a minor effect on the catalytic activity for methane decomposition [11]. The effect of surface oxygenated groups is more complex and is not completely clear. In our previous work we reported that although carbon-oxygen surface groups may play a role in methane dissociation, particularly, at the initial stage of the process, the catalytic activity of carbons, in general, could not be solely attributed to the presence of such surface functional groups [11].

It is well known that the majority of catalytic reactions in a gas-solid interface involve surface defects, dislocations, vacancies, low-coordination sites, etc. Therefore, the possibility of this type of catalytic action in the carbon-catalyzed methane decomposition reaction needs to be closely examined. Various modifications of carbon could be distinguished in terms of crystallinity or the degree of order, i.e. from highly ordered carbons, such as graphite and diamond, to less ordered (turbostratic and pyrolytic carbons) and, finally, to disordered (or amorphous, microcrystalline) carbons, such as carbon black, charcoal, activated carbon. On the surface of amorphous carbons, the regular array of carbon bonds is disrupted, forming "free" valences, discontinuities (i.e., the edges and corners of crystallites) and other energetic abnormalities that could be generalized as high-energy sites (HES). Evidently, the surface concentration of HES increases with the decrease in carbon crystallite size, and, vice versa, decreases as carbon becomes more ordered (e.g., during graphitization). Amorphous carbons (e.g., AC, CB) are particularly active in methane decomposition reaction, compared to well-ordered carbons such as graphite, diamond, and carbon nanotubes. This may point to the direct correlation between the surface concentration of HES and catalytic activity in methane decomposition reaction. The driving force for the catalytic action of carbon is that carbon atoms in HES tend to react with approaching methane molecules in order to satisfy their valency requirements and energetically stabilize.

It would be worthwhile to give some more consideration to how carbon structure affects its catalytic activity. The carbon-carbon distance within the hexagon layers in amorphous carbons is the same as in graphite (1.420 Å), however, interlayer spacing is considerably larger (about 3.6 Å vs 3.354 Å in graphite) [12]. XRD studies conducted in this work demonstrated that in the original carbon black sample (BP2000) the plates are not stacked in a columnar arrangement, but, instead, are randomly oriented with respect to each other. However, after exposure to hydrocarbons the ordering in the "columnar" (or stacking) direction has evolved. The distance between layers (d-spacing) was found to be d =3.4948 Å, which lies between the d-spacing for amorphous carbon and pure graphite. Thus, carbons produced by decomposition of methane and propane feature more ordered structure compared to amorphous carbons, but they are less structurally ordered than graphite (which is characteristic of turbostratic carbon). This clearly correlates with the order of catalytic activity of carbons toward methane decomposition (amorphous> turbostratic> graphite). Thus, the difference in catalytic activity between different carbons can be explained by the difference in their crystallinity and surface morphology.

The apparent reaction order of carbon-catalyzed methane decomposition reaction was determined to be 0.5 for both AC- and CB-based catalysts [9,13]. Thus, the rate equation for carbon-catalyzed decomposition of methane can be written as follows:
The apparent activation energies for carbon-catalyzed methane decomposition varied in a wide range not only within different types of carbon (e.g., AC vs CB), but also within the family of carbons. For example, amongst the AC-based catalysts tested, the apparent activation energies ($E_a$) varied in a range of 160-201 kJ/mole (at 600-900°C). These data are in fairly good agreement with the reported activation energies for a number of coal-derived AC (186-198 kJ/mol [9]). For CB-based catalysts, the measured $E_a$ were somewhat higher (205-236 kJ/mole, at the same conditions). It is interesting to note that the values of activation energies for carbon-catalyzed methane decomposition lie between the $E_a$ for non-catalytic and metal-catalyzed reactions. For the reference, the activation energies for non-catalytic methane decomposition were reported in the range of 370-433 kJ/mol (e.g., [14]), whereas, $E_a$ for metal-catalyzed reactions were reported 60 kJ/mol and below (e.g., [15]).

No definite conclusion has yet been made on the mechanism for carbon-catalyzed methane decomposition. Most likely, the reaction proceeds through the series of stepwise dissociation reactions leading to elemental carbon and H$_2$:

\[
\begin{align*}
(CH_4)_a &\rightarrow (CH_3)_a + (H)_a \\
(CH_3)_a &\rightarrow (CH_2)_a + (H)_a \\
(CH_2)_a &\rightarrow (CH)_a + (H)_a \\
(CH)_a &\rightarrow (C)_a + (H)_a \\
n(C)_a &\rightarrow 1/n(C_n)_c \\
2(H)_a &\rightarrow (H_2)_g
\end{align*}
\]

where: superscripts (a), (c) and (g) denote adsorbed, crystalline and gaseous species, respectively. Equation 7 relates to carbon crystallite growth.

3. Heat input options for methane catalytic decomposition

Methane decomposition is a moderately endothermic reaction: the thermal energy requirement per mole of hydrogen produced is only 37.8 kJ/mole H$_2$ compared to 63 kJ/mole H$_2$ for SMR. Less than 10% of the methane heating value is needed to drive the endothermic process. There are several possible technological options for the heat supply to the endothermic TCD process. According to the first option the process heat is introduced to the reactor by externally heated catalyst particles similar to fluid catalytic cracking or fluid coking processes widely used in refineries (see Figure 1). This approach was discussed in details in our previous work [16].

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**Figure 1.** Simplified block-diagram of TCD of NG with externally heated catalyst particles. NG- natural gas, SG- stack gases, C$_c$- "cold" carbon particles, C$_h$- hot carbon particles. 1- methane decomposition reactor, 2- catalyst particles heater.
According to the second approach the heat source is located inside the reaction zone (see Figure 2). It could be a heat pipe, a heat exchanger or a tubular catalytic burner that uses NG, or off-gas, or a portion of hydrogen product as a fuel. As an example, the use of sodium-based heat pipes as a mode of efficient heat transfer in methane steam reformers has been demonstrated in [17]. This approach could potentially provide a process for zero-emission hydrogen production if a portion of hydrogen product (theoretically, 16%) is used as a fuel for the process. The major challenge associated with this approach relates to a catalyst deactivation-regeneration problem. Furthermore, if metal-based catalysts are used in the process, the separation of carbon product from the catalyst may become a complicating issue.

In the third approach, a relatively small amount of oxygen is fed to the reactor along with the methane feedstock to generate necessary heat to carry out the endothermic methane decomposition reaction. One can notice that the concept looks similar to the well-known partial oxidation (POx) process. There is, however, a fundamental disparity between two processes. In particular, POx process proceeds to complete conversion of methane into synthesis gas and, therefore, it requires relatively large amount of oxygen (\(O_2:CH_4 = 0.5\) mole/mole). In contrast, the objective of oxygen-assisted methane decomposition is to maximize the yields of both hydrogen and carbon products by introducing oxygen in the quantity just enough to sustain the endothermic methane decomposition reaction. Thus, the process involves the combination of an endothermic (methane decomposition) and exothermic (methane combustion) processes in one apparatus (i.e., the process operates in a thermo-neutral, or autothermal regime). Hereafter we designate the process as autothermal pyrolysis (ATP) process. It is evident that the ATP process would use much less oxygen and, consequently, produce less \(CO_2\) emissions than POx or SMR or autothermal methane reforming due to relatively low endothermicity of methane decomposition (it is almost three times less endothermic than SMR, per mole of \(H_2\)) and the fact that it does not proceed to synthesis-gas as a final product. Advantageously, in the ATP process most of the feedstock carbon ends up in the form of elemental carbon rather than \(CO_2\).

Figure 2. Schematic diagram of TCD of NG with internal heat supply. 1- fluidized bed reactor, 2- cyclone, 3- heat exchanger, 4- gas separation unit, 5- carbon/catalyst separation unit, 6- catalyst regeneration unit.

Figure 3 depicts a simplified block-diagram of the ATP process with NG as a feedstock. The presence of oxygen in the feedstock results in the production of \(CO\) byproduct that would require the addition of water-gas shift (WGS) reactors to the technological chain of the process. However, due to relatively low concentration of \(CO\) in the gaseous product (~17 vol.%) the WGS unit in ATP process would be much
smaller than that in conventional SMR and POx processes. In the final stage of the process, high-purity hydrogen (>99.99 vol.%) could be recovered from $\text{H}_2$-$\text{CO}_2$ gaseous mixture (or $\text{H}_2$-$\text{CH}_4$-$\text{CO}_2$ mixture if some portion of methane remains unconverted) using off-the-shelf gas separation units (e.g., a pressure-swing adsorption, or a $\text{H}_2$-permeable membrane, or a cryogenic separation). Unconverted methane is separated from the gaseous mixture and recycled to the reactor.

Due to relatively low endothermicity of the methane decomposition reaction and the elimination (or reduction in size) of energy-intensive steam production and gas conditioning stages, the $\text{CO}_2$ emission from the ATP process could potentially be much less than that from conventional processes. It is estimated that $\text{CO}_2$ emissions from ATP process could be as low as 0.17 $\text{m}^3/\text{m}^3\text{H}_2$, which is almost three times less (per $\text{m}^3\text{H}_2$) than that from the SMR process (or about five times less than from steam-oxygen gasification of coal). On the down side, ATP process utilizes an expensive oxygen production unit, which may add to the cost of hydrogen production. The usage of air instead of oxygen may result in a larger and more expensive gas separation unit. Therefore, alternative means of introducing oxygen into the fluidized bed reactor have to be considered. One promising approach relates to the use of ceramic oxygen-permeable membranes.

It is well known that dense ceramic membranes made of the mixture of ionic and electron conductors are permeable to oxygen at elevated temperatures. For example, perovskite-type oxides (e.g., La-Sr-Fe-Co, Sr-Fe-Co and Ba-Sr-Co-Fe based mixed oxide systems) are good oxygen-permeable ceramics. Oxygen permeation rates (or oxygen flux density) could reach 10 mL/min.cm$^2$ and higher. Extensive research has been carried out on the application of ceramic $\text{O}_2$-permeable membranes to POx and other processes requiring pure oxygen. For example, a membrane reactor containing $\text{O}_2$-permeable ceramic membrane made of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ was applied to partial oxidation of methane at 900°C [18].

Figure 4 depicts a conceptual drawing of the ATP fluidized bed reactor equipped with a tubular oxygen-permeable dense ceramic membrane (for simplicity, only two tubular membrane units are shown on the drawing). A detail of the ceramic membrane wall explaining the mechanism of oxygen permeation through the membrane is shown on the left side of the Figure 4. The gradient of oxygen pressure (or its chemical potential, $\mu$) is the driving force for oxygen transportation across the ceramic membrane. Advantageously, the $\text{O}_2$-permeable ceramic membranes efficiently operate at the same temperature range as ATP process (i.e., 800-900°C). Stoichiometrically, ATP process requires 2.5 times less oxygen per mole of methane than POx ($\text{O}_2/\text{CH}_4$ ratios for these processes are 0.2 and 0.5, respectively). Consequently, oxygen flux
requirements for a membrane in the case of ATP process would be much less demanding compared to POx process (which may potentially have important practical implications).

The advantages of using $O_2$-permeable membrane are two fold: (i) it would potentially reduce the hydrogen production cost (by eliminating an air separation plant), and (ii) $CO_2$ byproduct could be produced in a concentrated form ($\sim 100$ vol.%), which would simplify its capture and further handling.

![Figure 4. Schematics of ATP fluidized bed reactor equipped with a tubular oxygen-permeable ceramic membrane. The section on the left shows the detail of the ceramic membrane wall (explaining the mechanism of $O_2$ permeation across the membrane).](image)

4. Thermodynamic analysis of thermoneutral decomposition of methane

AspenPlus™ chemical process simulator (CPS) was used to conduct thermodynamic analysis of $CH_4+\chi O_2$ system. The reactions involved were modeled using a Gibbs reactor to minimize the free energy in order to calculate thermodynamic parameters of the process at the given operating conditions. Input parameters are: inlet pressure and temperature, reactor temperature and pressure, and $\chi = O_2/CH_4$ (mol/mol). Peng-Robinson property package was used for the reaction equilibrium calculations. Methane conversion, products yields, pyrolysis gas composition, process enthalpy, entropy and Gibbs energy flows as a function of temperature, pressure and $\chi$ have been determined. The temperature range of $T=300-1200^\circ C$, pressures of $P=0.1-2.5$ MPa and $O_2/CH_4$ ratio of $\chi = 0-1.5$ (mole/mole) were chosen for the thermodynamic analysis of the process.

Figure 5 illustrates the temperature dependence of hydrogen and carbon yields with $\chi$ as a variable at $P=200$ kPa. The Figure 5 indicates that the hydrogen yield is not appreciably affected by the change in $O_2/CH_4$ ratio.
within the range of 0<χ<0.5. However, at χ>0.5 hydrogen yield drops markedly, which is accompanied with the increase in water production yield. In contrast, carbon yield is quite sensitive to even slight increase in χ value in a whole range of O₂/CH₄ ratios. At χ>0.6 carbon is not present among the reaction products at temperatures above 800°C.

![Figure 5](image.png)

The total enthalpy flow within the reactor as a function of temperature and χ was determined. The total enthalpy flow rate was calculated as a sum of outlet enthalpies of all products minus sum of inlet enthalpies of CH₄-χO₂ mixtures. A negative enthalpy flow indicates that at the given conditions (χ, T and P) the reactive system produces heat, which would require the removal of the excess heat from the reactor. In contrary, positive enthalpy flow indicates that at given conditions a certain amount of thermal energy has to be supplied to the reactor in order to accomplish methane decomposition. It was found that for the practical range of temperatures (600-900°C) and pressures of P=0.1-2.5 MPa the enthalpy flow is close to zero (which corresponds to autothermal or thermo-neutral regime) at O₂/CH₄ ratio of χ≈0.2.

Figure 6 demonstrates molar fraction of methane conversion products as a function of temperature at atmospheric pressure and χ=0.2. It can be seen that over the range of temperatures 500-850°C hydrogen and carbon are main products of the reaction with the CO yield steadily increasing at the same range and reaching a plateau. At T>850°C the molar fractions of the methane decomposition/oxidation products (H₂, C and CO) is nearly independent of temperature. At these conditions (i.e., T≥850°C, P=100 kPa and χ=0.2), the distribution of the products of methane ATP is consistent with the following stoichiometric equation:

\[
\text{CH}_4 + 0.2\text{O}_2 \rightarrow 2\text{H}_2 + 0.6\text{C} + 0.4 \text{CO} 
\]
Thus, the equilibrium composition of the gaseous products of ATP of methane at \( P=100 \text{ kPa}, \chi \approx 0.2 \) and \( T \geq 850^\circ \text{C} \) corresponds to the following mixture: \([\text{H}_2] \approx 83\%\), \([\text{CO}] \approx 17\%\). It is noteworthy that the concentration of hydrogen (83 vol.\%) is significantly higher than that in the reformate gases of SMR (\([\text{H}_2] \approx 52\%\) in a raw gas and 72 vol.\% in a dry gas) and POx (\([\text{H}_2] \approx 66\%\) with oxygen and 35 vol.\% with air) processes [19].

![Figure 6. Molar fraction of methane conversion products as a function of temperature at \( P=100 \text{ kPa} \) and \( \chi \approx 0.2 \).](image)

5. Experimental verification of TCD of methane

The experimental studies of thermocatalytic pyrolysis of methane were conducted using pure (99.99 v.\%) and industrial grade (i.e., pipeline NG) methane. The composition of natural gas used in the experiments is shown in Table 1.

<table>
<thead>
<tr>
<th>Composition of NG, vol.%</th>
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<tbody>
<tr>
<td>N(_2)</td>
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<tr>
<td>CH(_4)</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
</tr>
<tr>
<td>C(_3)H(_8)</td>
</tr>
<tr>
<td>C(_4)</td>
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<tr>
<td>CO(_2)</td>
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<tr>
<td>CH(_3)SH</td>
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In our previous work [7,11] we reported the results of catalytic pyrolysis of methane using carbon-based catalysts, e.g., activated carbons (AC), carbon blacks (CB), etc. In this study we tested Fe-doped carbon catalysts. It was found that doping carbon with Fe improves the activity of the catalyst. Figure 7 (A and B) depicts the results of methane decomposition at 900\(^\circ\)C in the presence of Fe-doped carbon catalyst at the residence time of 2.2 and 1 s, respectively. It is evident from the Figure 7 that at higher residence time (2.2 s) initial hydrogen concentration in the effluent gas reaches up to 83 v.\%. This however followed by a decrease in hydrogen yield to a quasi-steady level (hydrogen concentration about 60 v.\%). During first hour there was a small amount CO present in the effluent gas, which could be attributed to some residual oxygen in the catalyst. At lower residence time (1 s) (or higher space velocity) the initial concentration of hydrogen in
the effluent gas was somewhat lower and the process was not sustainable (i.e., H\textsubscript{2} concentration gradually dropped). This implies that the catalyst needs further improvement in its activity and stability.

We also conducted a series of experiments on oxygen-assisted catalytic decomposition of methane using AC (lignite) as a catalyst. We observed that at O\textsubscript{2}:CH\textsubscript{4}=0.2 (molar) ratio and the temperature range of 850-1000°C the yields of two major reaction products: hydrogen and carbon steadily increased, while the CO\textsubscript{x} yields remained almost independent of temperature. The yields of water and C\textsubscript{2} hydrocarbons dropped at the same range of temperatures. The molar fraction of hydrogen in the products mix (including carbon and water) reached 60 mol.% at 1000°C, which is in fairly good agreement with the thermodynamic equilibrium data (within less than 10% margin of error). Among gaseous and non-condensable products of the reaction the hydrogen yield reached 80 vol.% Figure 8 presents data on TCD of methane with and without oxygen present. It is evident that doping AC (lignite) with iron (10 wt.%) improved activity and stability of carbon-based catalysts. The initial induction period of about 0.5 hr could be attributed to reduction of iron oxide to metallic iron (which is an active form of the catalyst).

6. Experimental

Methane (99.99 v.%) and oxygen (99.99 v.%) (both from Air Products and Chemicals, Inc.) were used without further purification. Samples of activated carbons (lignite, peat and coconut) were obtained from Alfa
Aesar and Barneby Sutcliffe and were used in the form of pellets (1-1.5 mm). Surface area of AC samples were (m$^2$/g): lignite- 650, peat- 900, coconut- 1150. Oxygen-assisted methane decomposition experiments were conducted using a quartz micro-reactor (inner diameter 8 mm) with a bed of a catalyst material (0.1 g). Carbon-supported iron (10 w.% based on metallic iron) catalysts were prepared by the conventional soaking-drying technique using iron (III) nitrate followed by calcination of the catalyst at 650°C for 2 hrs. All catalyst samples were dried (400°C, 2 hrs) before the experiments in a stream of Ar to remove adsorbed water and pore-entrained air. The catalysts were weighed before and after experiment to determine the amount of carbon produced. The amount of water produced in the reaction was determined by measuring the weight gain of a bed of adsorbent pellets (Drierite) placed downstream the reactor during the experiment (the margin of error: 5%). The reactor was maintained at a constant temperature via a type K thermocouple connected to a Love Controls temperature controller. All experiments were conducted at atmospheric pressure. The residence time in the catalyst layer varied in the range of 0.1-1.0 s. On-line analysis of the effluent gas (H$_2$, O$_2$, CO, CO$_2$, CH$_4$, C$_2$H$_6$, C$_2$H$_4$) was performed gas chromatographically (the combination of two SRI- 8610A chromatographs with TCD, Ar-carrier gas, silica gel column and FID, He-carrier gas, HysepD$_8$ column). Analysis of carbon products was conducted by X-ray diffraction (XRD, Rigaku) and scanning electron microscopic (SEM, Jeol 6400F) methods.

7. Conclusion

In the near- to medium-term future, hydrogen production will likely continue to rely on fossil fuels, primarily, natural gas. However, present-day hydrogen production technologies produce enormous amounts of CO$_2$ emissions. Thermocatalytic decomposition of methane is an environmentally attractive option for producing both hydrogen and carbon without (or with drastically reduced) CO$_2$ emissions. The value-added carbon byproducts could be marketed, thus reducing the net cost of hydrogen production. Methane decomposition is a moderately endothermic reaction. Several technological approaches to the process heat supply including internal, external and autothermal (or thermo-neutral) options are discussed in this paper. Thermodynamic analysis (AspenPlus™) of methane decomposition reaction in the presence of oxygen indicated that at the practical range of temperatures (600-900°C) and pressures (0.1-2.5 MPa) autothermal pyrolysis of methane could be accomplished at O$_2$/CH$_4$ molar ratio of about 0.2. ATP of methane was
experimentally verified using activated carbon and iron-doped carbon catalysts. CO₂ emissions (per m³ of H₂ produced) from the process could potentially be a factor of 3-5 less than conventional hydrogen production processes. The latter option offers certain advantages over other approaches due to its simplicity and versatility. Due to its simplicity and versatility and drastically reduced CO₂ emissions (compared to SMR, POx) the TCD technology could potentially be suitable for environmentally friendly decentralized production of hydrogen.

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