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# Catalytic Solar Thermochemical Processing for Enhance Heat Transfer and Emission-free Production of Hydrogen

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Solar thermochemical processing offers production of many commodities via reduced or completely eliminated emission footprint. Although solar reactor design and flow configuration play key role in process efficiency, use of right catalyst further enhances the overall efficiency. Our research efforts to explain the physical phenomenon behind the increase of the overall efficiency via catalyst addition showed that there is a direct effect on the heat transfer which in turn effects methane decomposition rate. In this paper, a compilation of our research results on the testing of carbon based catalyst and its impact on the heat transfer is summarized along with kinetics analysis of methane decomposition.

## 1. Introduction

Currently, the world depends on fossil fuels as its main source of energy for steam, power, and commodity production (Costandy et al., 2012). Fossil fuel consumption, however, continues to raise many concerns due to its continuous release of carbon dioxide and other greenhouse gases into the atmosphere. In order to oppose the rising levels of carbon dioxide emissions, decarbonisation of fossil fuels is essential and the ultimate step is hydrogen production (Rodat et al., 2011a). Hydrogen production is favored because hydrogen is viewed as the future’s ultimate clean power source (Kim et al., 2004). Furthermore, the market demand for hydrogen as a commodity is substantial. For instance, there is a great demand for it in the chemical industry where it is used as a feedstock for the production of various chemicals such as methanol (Soltanieh et al., 2012) and ammonia (Sutton et al., 2008). There is also a great demand for it in refineries as it is the key feedstock in the hydrotreating and hydroprocessing of hydrocarbons during crude oil processing (Assabumrungrat et al., 2012; Castaneda et al., 2011). Alternatively, it can also be used in fuel cells and internal combustion engines as a clean alternative fuel for transportation and power generation. Natural gas is composed primarily of methane and is the preferred source of hydrogen because of its high ratio of hydrogen to carbon. Current conventional hydrogen production methods utilize natural gas in a variety of reforming processes including steam methane reforming (SMR), partial-oxidation reforming (POR), and auto-thermal reforming (ATR), of which SMR is most commonly used (Dahl et al., 2004a). The SMR process, although economically attractive, produces approximately 11.9 kg of carbon dioxide eq. per kg of hydrogen produced, thereby resulting in a substantial release of carbon dioxide into the atmosphere (Rodat et al., 2011b). Furthermore, these industrial processes are endothermic and the heat is usually supplied by burning a significant amount of the feedstock methane. For instance, in methane reforming, about 40 % of the feedstock methane needs to be burned for supplying the necessary process heat (Hirsch et al., 2001). As a result, significant research is currently underway to develop novel methods for producing hydrogen in a more environmentally-friendly manner (Dunker and

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Jerome, 2005; Herzog, 2001). The thermal decomposition of methane into hydrogen and carbon black (CB) offers an attractive route for the decarbonisation of fossil fuels (Trommer et al., 2004) with zero emissions (Costandy et al., 2012). In addition to hydrogen, the process produces another commodity that is highly desired in industry. Carbon black is an important additive for rubbers, inks, batteries and several polymers (Rodat et. al, 2011b) and it is also used in power generation, soil amendment and environmental remediation (Muradov and Veziroglu, 2005). Moreover, it is easier to filter, store and transport carbon black as comparison to carbon dioxide (Trommer et al., 2004). Therefore, carbon black as a byproduct is more desirable than having carbon dioxide as a byproduct. However, in industry, carbon black is currently produced via the furnace process (Lockwood and Van Niekerk, 1995) which produces more hazardous gases than that of conventional methods of hydrogen production. Approximately 5.7 kg of carbon dioxide eq. are released per kg of carbon black produced (Rodat et al., 2011a). These facts make direct thermal decomposition of methane an attractive method for co-production of carbon black and hydrogen. The thermal decomposition process of methane, also known as the thermal cracking of methane, is represented by the following reaction:

$$CH_4 \rightarrow C\ (\text{solid}) + 2H_2,\ \Delta H_{298} = 75\ \text{kJ/mol} \qquad (1)$$

Like the other hydrogen production methods, the thermal cracking of methane also requires energy. Concentrated solar energy can be used to sustain the endothermic decomposition process in a process known as solar thermochemical processing (Costandy et al., 2012). First, it avoids the consumption of feedstock methane to produce steam. Second, it offers the following added advantages (Trommer et al., 2004; Hirsch et al., 2001): no pollutants are discharged as part of the process, the gaseous products are not contaminated, and the fuel is upgraded in calorific content. Using solar energy as the source of high-temperature process heat in thermal cracking of methane is known as the solar thermal cracking of methane. The process is carried out at high temperatures (1500 – 2000 K) to obtain a reasonable yield of hydrogen (Rodat et al., 2011a). It is a desired process that results in 92% pollution reduction relative to conventional production of hydrogen and carbon (Rodat et al., 2011a).

This solar process is housed in a solar reactor that is placed at the focal point of a highly concentrated solar system. During the last years, significant research has been conducted in the development of different solar reactor designs. These various designs employ different heating concepts and flow patterns (Rodat et al., 2011a; Trommer et al., 2004; Dahl et al., 2004a; Kogan and Kogan, 2004; Hirsch and Steinfeld, 2004; Dahl et al., 2004b; Wyss et al., 2007). In this paper, an overview of our research efforts on solar thermal cracking of methane are summarized from the heat transfer point of view by showing the impact of catalyst use on the temperature distribution within the reactor and eventually methane decomposition. The paper also provides a kinetic analysis of the process based on the mechanisms involving production of intermediate species and byproducts for catalytic and non-catalytic cases. Finally, the paper includes a comparison of determined theoretical values with experimental and numerical results from various research groups working on solar thermal cracking of methane.

## 2. Methodology

As stated previously, solar thermal cracking of methane can be catalytic or non-catalytic, where microporous carbon was favored due to its low cost, which eliminates the need for regeneration (Amin et al., 2011). In this section, first, we provide a kinetic analysis associated with both catalytic and non-catalytic solar cracking of methane. Then we provide impact of carbon catalyst on the enhancement of heat transfer and methane decomposition inside a solar reactor.

### 2.1 Kinetics of non-catalyzed and carbon-catalyzed solar thermal methane cracking

Several prior studies propose various mechanisms dealing with the decomposition of methane in the presence of heat. The mechanisms present complex reaction schemes that are used to explain the appearance of by-products and intermediates during the decomposition reaction, such as: $C_2H_6$, $C_2H_4$, $C_2H_2$, $C_6H_6$ and polycyclic aromatic hydrocarbons. For methane cracking in the absence of carbon catalyst, a simplified stepwise dehydrogenation of methane was presented as follows: $2CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2 \rightarrow C+2H_2$ (Back and Back, 1983). However, more complex schemes that account for thermal methane coupling using free radical mechanisms were proposed by Olsvik et al. (1995) and Olsvik and Billaud (1993). In this paper, the 36 step mechanism presented by Olsvik and

Billaud (1993) was adopted in order to develop the kinetics of methane thermal decomposition in the absence of carbon catalyst. The rate parameters were adopted from literature findings (Olsvik and Billaud, 1993; and literature cited therein).The proposed mechanism consists of 35 reversible free radical reactions and one irreversible free radical reaction. An additional irreversible reaction of $C_2H^{\cdot} \leftrightarrow 2C_B + H^{\cdot}$ was added to the presented model in order to account for the formation of carbon from $C_2H$ free radical, based on a suggestion by Chen et al. (1976). For methane cracking in the presence of carbon catalyst, the kinetic model developed by Dunker et al. (2006) was adopted to represent the surface chemistry occurring on the carbon catalyst. The model is a modification of a mechanism used for modeling soot formation in combustion. It was used as a supplement to the gas-phase reactions we explained above. The surface chemistry is represented by six reactions occurring on two surface types: carbon atoms with one hydrogen attached ($C_s$-H) and carbon atoms with no hydrogen attached ($C_s$). Carbon formation path involves addition of $C_2H_2$ to $C_s$ resulting in deposited carbon ($C_B$) and $C_s$-H. The rate parameters were adopted from literature findings (Dunker et al., 2006; and literature cited therein). Arrhenius constants were determined from collision efficiency (γ) based on the methodology presented in Dunker et al. (2006). In the present work, the CHEMKIN code package was used to simulate the process (Kee et al., 1980). The decomposition of methane was simulated in a PFR model based on Olsvik and Billaud (1993).

### 2.2 Heat transfer analysis of non-catalyzed and carbon-catalyzed solar methane cracking

In order to achieve detailed understanding of methane decomposition in a solar reactor, velocity and temperature distributions are needed. For that, three dimensional CFD simulations of the flow behavior and the heat transfer analysis have been done for two solar reactor geometries using commercial software Fluent. The convective heat transfer and the absorption / emission of radiation at the particle surface is given by

$$m_p C_p \frac{dT_p}{dt} = hA_p\left(T_\alpha - T_p\right) + \varepsilon_p A_p \sigma\left(\theta_R^{\,4} - T_p^{\,4}\right) \tag{2}$$

The DO (Discrete ordinate) model is employed to calculate the radiation field inside the reactor. The radiation transfer equation for the spectral intensity $I_\lambda(\vec{r},\vec{s})$ is given as

$$\frac{dI_\lambda\left(\vec{r},\vec{s}\,\right)}{d\,S} + (a_\lambda + \sigma_S) I_\lambda\left(\vec{r},\vec{s}\,\right) = a_\lambda n^2 I_{b\lambda} + \frac{\sigma_S}{4\pi}\int_0^{4\pi} I_\lambda\left(\vec{r}',\vec{s}'\right)\Phi\left(\vec{r},\vec{s}\,\right)d\Omega' \tag{3}$$

In this model, the radiative transfer equation is solved for a finite number of discrete solid angles in direction $\vec{s}$ which is fixed in the Cartesian system (x, y, z). The energy and radiation equations are solved one by one by assuming prevailing values for other variables.

## 3. Results

The change of equilibrium composition as a function of temperature and pressure was determined by Hirsch et al. (2001) using an in-house software. It was assumed that the decomposition can be represented as follows: $CH_4$ + heat → equilibrium products ($C_2H_2$, $C_2H_4$, $H_2$, and C). As determined by their plot, $CH_4$ begins to decompose at about 500 K, and by 1500 K, the only species at equilibrium are $H_2$ and C. The presence of equilibrium by-products was determined to be negligible at all temperatures ($<10^{-5}$ mole fraction). Chemical conversion was also observed to decrease as pressure increases, in accordance with Le Chatelier's principle.

### 3.1 Kinetic simulation of non-catalyzed methane cracking

The influence of residence time on methane cracking in the absence of carbon catalyst was simulated using CHEMKIN and compared to the findings reported by Rodat et al. (2011a) at 1823 K for a feed comprised of 10 % CH4 and 90 % Ar. Experimental and simulated results are shown in Figure 1(a).

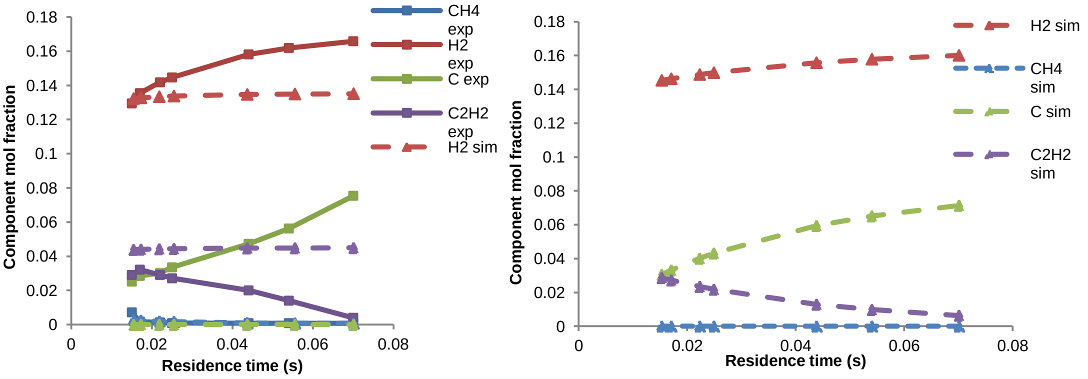


*Figure 1: (a) simulated and experimental component mole fractions versus residence time (10% $CH_4$ in Ar) at 1823 K for non-catalyzed methane cracking, (b) simulated component mole fractions versus residence time (10 % $CH_4$ in Ar) at 2300 K for non-catalyzed methane cracking*

For both sets of results, $CH_4$ conversion was determined to be 100 % for residence times greater than 0.04 s. Mole fraction of $H_2$ is predicted to be lower in the simulation than determined experimentally. It is also notable that the simulation indicates near 0 % formation of carbon solid. Although decomposition of $C_2H_2$ is observed experimentally, simulated mole fraction of $C_2H_2$ remains relatively constant for different residence times. Therefore, theoretical kinetic mechanisms are not sufficient to explain the formation of carbon black from methane cracking. This coincides with previous literature conclusions, in which non-kinetic factors, such as flow dynamics and heat transfer, were determined to play a major role in the conversion and yield of the decomposition reaction (Ozalp and Devanuri, 2010).

### 3.2 Kinetic simulation of carbon-catalyzed methane cracking

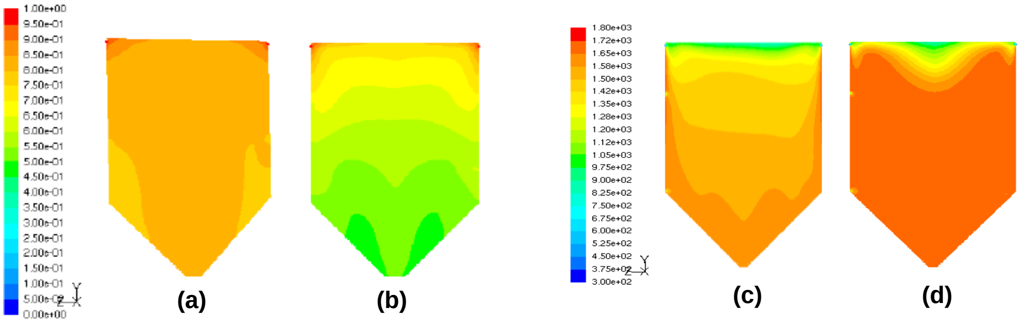
The influence of residence time on methane cracking in the presence of carbon catalyst was simulated using CHEMKIN at a temperature of 1823 K for a feed of 15 % $CH_4$ in Ar. In comparison to non-catalytic findings at 1823 K, the most notable difference was the formation of carbon. This suggests that surface reactions occurring on the carbon catalyst play a major role in the deposition of carbon from by-products such as $C_2H_2$. Methane conversion was determined to be 100 % for a residence time greater than 0.10 s, and the yield of by-products was determined to be negligible for the residence times simulated. In terms of rate, no particular difference was noted for the decomposition rate of methane in the presence of catalyst and in the absence of catalyst. The simulation results at 1500 K observed similar conversion (90 %) as reported by Trommer et al. (2004) at a residence time of 0.3 s.

### 3.3 Heat transfer analysis of carbon-catalyzed methane cracking

Carbon particles absorb radiation from the reactor tube wall and convectively transfer that energy to the gas phase, which enhances the heat transfer and increases the methane conversion rate (Dahl et al., 2004b). Crystallographic structure, surface area, presence of surface groups and energetic abnormalities are among major factors governing catalytic activity of carbons (Muradov et al., 2006).

*Figure 2: (a) contours of static temperature of reactor walls for $m_p$ = 0.2 g/min, (b) contours of static temperature of reactor walls for $m_p$ = 0.6 g/min*

Our CFD simulations shows that formation of thicker particle cloud with the increase in particle loading absorbs more radiation leading to the reduction of wall temperature, which supports and explains the experimental observation done by Dahl 2004b. Figure 2 gives the results of our CFD simulations for two different catalyst loading rate. In addition to this finding, our CFD results also showed that with the increase in carbon particle diameter, the average outlet temperature increases. As it is seen in Figure 3, carbon particle seeding considerably increases the temperature inside the reactor and the temperature distribution becomes more uniform towards reactor core.



(a) without particle seeding
(b) with particle seeding

(c) without particle seeding
(d) with particle seeding

*Figure 3: temperature distribution on a vertical mid-plane of the reactor geometry on the left, and mass fraction contours of methane inside the reactor on the right*

## 4. Conclusions

In this paper, the overall impact of carbon on the conversion of methane to hydrogen and carbon was studied from a multi-parametric point of view. The findings on catalytic and non-catalytic solar thermal cracking of methane based on kinetic mechanisms were reported. Kinetic parameters affecting the decomposition of methane were related to other parameters such as heat transfer and flow dynamics. Residence time and conversion efficiencies were also looked at closely in the kinetic analysis. Additionally, the effect of carbon based catalysts on methane to hydrogen conversion from heat transfer aspect was presented where carbon particles act as radiant absorbers and reaction site providers for the decomposition of methane. In summary, results show that increase in carbon particle flow rate reduces the wall temperature of the solar reactor. It is also observed that the formation of thicker particle cloud with the increase in particle loading absorbs more radiation leading to the reduction of wall temperature. As for the impact of carbon particle diameter, it was seen that with the increase in particle diameter, the average outlet temperature increases. Finally, increase in the solar reactor internal temperature and the enhancement of homogeneity in temperature distribution due to carbon particle addition yield with higher methane to hydrogen conversion.

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