

## **THERMOCATALYTIC CO<sub>2</sub>-FREE PRODUCTION OF HYDROGEN FROM HYDROCARBON FUELS**

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### **Abstract**

Conventional processes of hydrogen production are among major producers of CO<sub>2</sub> emissions. It has been proposed recently that CO<sub>2</sub> produced in steam reforming (or partial oxidation) processes could be captured and sequestered under the ocean or underground. However CO<sub>2</sub> sequestration is an energy intensive and costly process associated with ecological uncertainties. CO<sub>2</sub>-free production of hydrogen via thermocatalytic decomposition of hydrocarbon fuels as a viable alternative to the conventional processes is discussed in this paper. The technical approach is based on a single-step decomposition (pyrolysis) of hydrocarbons over carbon catalysts in air/water free environment. This approach eliminates the need for water-gas shift reactor, CO<sub>2</sub> removal, and the catalyst regeneration, which significantly simplifies the process. Clean carbon is also produced as a valuable byproduct of the process. Over 30 different samples of carbon were screened for the catalytic activity in methane decomposition reaction and several of them were selected for the further evaluation. The factors affecting carbon catalyst activity and long term stability in hydrocarbon decomposition reactions were studied. It was found that the crystallographic structure and the surface area of carbon species mostly determine the catalytic activity of carbon catalysts. Carbon species produced in the process were characterized by XRD and SEM methods. A kinetic model of methane decomposition over carbon catalysts was developed, and major kinetic parameters of methane decomposition reaction (rate constants, activation energies, etc.) over selected catalysts were determined. Various conceptual designs for the hydrocarbon decomposition reactor, including packed bed, tubular, free volume, fluid wall and fluidized bed reactors, were evaluated. A bench-scale thermocatalytic fluidized bed reactor was designed, fabricated and tested. The reactor was tested using methane, propane, methane-

propane mixture, and gasoline, and CO/CO<sub>2</sub>-free production of hydrogen-rich gas and carbon was demonstrated. Preliminary techno-economic assessment of the process indicated that the hydrogen could be produced at a cost of \$5.0/MMBTU (if carbon sold at \$100/t), which is less than that for steam reforming process coupled with CO<sub>2</sub> sequestration. Comparative assessment of CO<sub>2</sub> emissions from different hydrogen production processes clearly demonstrated the significant ecological advantages of the thermocatalytic decomposition of natural gas.

## Background

Given the advantages inherent in fossil fuels, such as their availability, cost-competitiveness, convenience of storage and transportation, they are likely to play a major role in global energy supply for the 21<sup>st</sup> century. On the other hand, fossil fuels are major source of anthropogenic CO<sub>2</sub> emissions into the atmosphere. There are several possible ways to mitigate CO<sub>2</sub> emission problem. Among them are traditional (e.g. more efficient use of fossil fuel energy resources, increase the use of non-fossil fuels, etc.) as well as novel approaches which include:

- hydrogen production by conventional processes (steam reforming, partial oxidation, etc.) coupled with CO<sub>2</sub> sequestration
- hydrogen production via decomposition (pyrolysis) of hydrocarbons with co-production of carbon

Steam reforming (SR) of natural gas (NG) is the most efficient and widely used process for the production of hydrogen. The theoretical energy requirement per mole of hydrogen produced for the overall process is equal to 40.75 kJ/mole H<sub>2</sub>. There is no by-product credit for the process and, in the final analysis, it does not look environmentally benign due to large CO<sub>2</sub> emissions. The total CO<sub>2</sub> emissions (including stack gases) from SR process reach up to 0.3-0.4 m<sup>3</sup> CO<sub>2</sub> per each m<sup>3</sup> of hydrogen produced. In partial oxidation (PO) and autothermal reforming (AR) processes a fuel, oxygen and steam are combined in proportions such that a fuel is converted into a mixture of H<sub>2</sub> and CO. PO process can be carried out catalytically or non-catalytically. The maximum theoretical concentration of hydrogen in the effluent gas using pure oxygen is 66.7 v.%, however, the concentration drops to 40.9 v.% if air is used as an oxidizer. Amount of CO<sub>2</sub> produced by PO process depends on the composition of the feedstock used and could reach up to 0.5 m<sup>3</sup> CO<sub>2</sub> per each m<sup>3</sup> of hydrogen produced.

## CO<sub>2</sub> Sequestration

The perspectives of CO<sub>2</sub> capture and sequestration is actively discussed in the literature (Nakicenovic 1993, Block et al. 1997, Audus et al. 1996). The commercially available processes for CO<sub>2</sub> capture include: physical and chemical absorption, physical and chemical adsorption, low temperature distillation and gas-separation membranes. It should be noted that the capture, transportation and sequestration of CO<sub>2</sub> are energy intensive processes. The total electric energy consumption to capture CO<sub>2</sub> from both concentrated and diluted (stack) gases, pressurize, transport 100-500 km and inject it to the underground disposal site was estimated at approximately 5000 kJ/kg CO<sub>2</sub> (Muradov 2000). World average for CO<sub>2</sub> emission associated with the electricity production is 0.153 kg of CO<sub>2</sub> per each kWh produced (Block et al. 1997). In

consequence, the total CO<sub>2</sub> emissions from CO<sub>2</sub> sequestration could potentially reach 0.25 kg CO<sub>2</sub> per kg of sequestered CO<sub>2</sub>.

There have been some estimates reported in the literature on the economics of CO<sub>2</sub> sequestration associated with hydrogen production from fossil fuels. Thus, according to Audus et al. (1996), the capture and disposal of CO<sub>2</sub> (80-85% of CO<sub>2</sub> captured from the concentrated streams of SR process) add about 25-30% to the cost of hydrogen produced by the SR of NG. The capture and disposal of CO<sub>2</sub> from diluted stack gases is even more costly. For example, it was estimated that the cost of eliminating CO<sub>2</sub> emissions from stack gases of advanced power generation plants range from \$35 to 264 per ton of CO<sub>2</sub> (IEA 1998). Thus, CO<sub>2</sub> sequestration is an energy intensive and expensive process and, in the final analysis, does not completely eliminate CO<sub>2</sub> emission. In addition to this problem, some uncertainties remain regarding the duration and extent of CO<sub>2</sub> retention (underground or under the ocean) and its possible environmental effect.

### **Methane Decomposition**

One alternative to the conventional hydrogen production processes is decomposition of hydrocarbon fuels (e.g. NG) into hydrogen and carbon, e.g.



Methane decomposition reaction is moderately endothermic process. The energy requirement per mole of hydrogen produced (8.9 kcal/mole H<sub>2</sub>) is somewhat less than that for the SR process. Due to a relatively low endothermicity of the process, less than 10% of the heat of methane combustion is needed to drive the process. In addition to hydrogen as a major product, the process produces a very important byproduct: clean carbon. Unlike SR and PO processes, NG decomposition process does not include water-gas shift (WGS) reaction and energy intensive gas separation stages.

There has been attempts to use catalysts in order to reduce the maximum temperature of methane thermal decomposition (Calahan 1974, Muradov 1993). It was found that the majority of transition metals (d-metals) to some extent exhibited catalytic activity toward methane decomposition. Some of them, for example Ni, Fe, Co and others, demonstrated a remarkable activity in methane dissociation reaction. However, there is a catalyst deactivation problem associated with the carbon build up on the catalyst surface. Carbon is produced as a byproduct of the process and over period of time it accumulates on the catalyst surface affecting its activity and in some cases causing the reactor clogging. Thus, in the vast majority of related publications and patents (e.g. Pourier 1997) carbon produced was burned off the catalyst surface in order to remove it from the reactor and regenerate the original catalytic activity. Since all the carbon produced from hydrocarbon is burned, the amount of CO<sub>2</sub> produced is comparable to that of the conventional processes (SR and PO), and no byproduct carbon is produced in this process. All these factors impose serious limitations to overcome before the process becomes commercial.

## Technical Approach

Our technical approach is based on thermocatalytic decomposition of hydrocarbons over carbon-based catalysts in air/water-free environment. The use of carbon-based catalysts offers the following advantages over metal catalysts:

- no need for the separation of carbon from the catalyst
- no need for the regeneration of the catalyst by burning carbon off the catalyst surface
- no CO/CO<sub>2</sub> production due to the combustion of carbon
- no contamination of hydrogen with carbon oxides and, consequently, no need for the additional gas purification (e.g. via methanation)
- the process could be arranged in a continuous mode similar to the industrial processes of fluid coking or fluid catalytic cracking.

## Current Year Objectives:

- To demonstrate the technical feasibility of CO<sub>2</sub>-free production of hydrogen and carbon via catalytic decomposition of hydrocarbons
- To determine efficient carbon catalysts and conditions for sustainable production of hydrogen-rich gases from different hydrocarbons (methane, propane, gasoline)
- To determine factors affecting catalyst activity and long-term stability
- To evaluate different conceptual designs for the thermocatalytic reactor suitable for simultaneous production of hydrogen and carbon
- To preliminarily estimate economic benefits of producing hydrogen and carbon in comparison with steam reforming coupled with CO<sub>2</sub> sequestration

## Results and Discussion

### Methane Decomposition over Carbon Catalysts

We determined the catalytic activity of the variety of carbon-based materials of different structure and origin toward methane decomposition. Table 1 summarizes the experimental results of methane decomposition reaction in the presence of different modifications of elemental carbon including wide range of activated carbons (AC), carbon blacks (CB), carbon fiber, glassy carbon, and crystalline graphites, and others, at 850°C and residence time of approximately 1 s. Each carbon sample was characterized by two important parameters: initial activity presented as an initial methane conversion rate, in mmole/min-g ( $K_m^0$ ) and sustainability displayed in the Table 1 as the ratio of methane conversion rate after one hour to the initial methane conversion rate ( $K_m^1/K_m^0$ ). The available data on the surface area (SA) of carbon samples tested are also presented in the Table 1.

It is understood that higher are both  $K_m^0$  and  $K_m^1/K_m^0$  parameters, better is the carbon catalyst. The experiments indicated that, in general, activated carbons exhibited highest initial activity (per unit of catalyst weight), but relatively low sustainability ( $K_m^1/K_m^0$ ). It is noteworthy that AC

samples of different origin and surface area displayed relatively close initial activity ( $K_m^0$ ) in the range of 1.6-2.0 mmole/min-g.

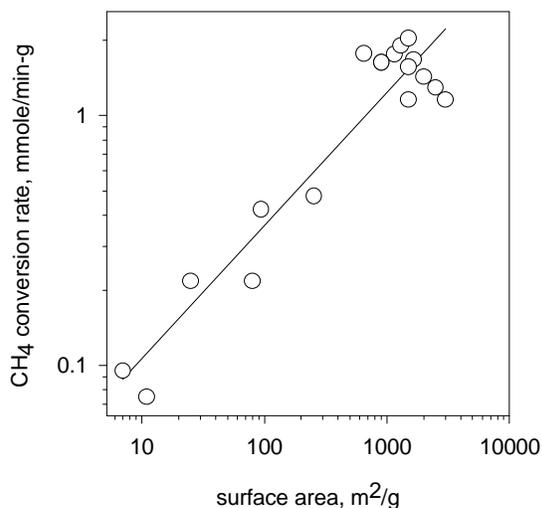
**Table 1. Comparative Assessment of Different Carbon Catalysts in Methane Decomposition Reaction**

Carbon Catalyst	SA, m <sup>2</sup> /g	$K_m^0$ , mmole/min-g	$K_m^1/K_m^0$	Carbon Catalyst	SA, m <sup>2</sup> /g	$K_m^0$ , mmole/min-g	$K_m^1/K_m^0$
AC, Coconut KE	1150	1.76	0.05	Acetylene Black	80	0.22	0.98
AC, Coconut CL	1650	1.67	0.18	CB, Black Pearls	25	0.22	0.48
AC, Coconut GI	1300	1.90	0.07	CB, Regal 330	94	0.42	0.40
AC, Hardwood	1500	2.04	0.32	CB, Vulcan XC72	254	0.48	0.41
AC, G-60	900	1.63	0.28	CB, Black Pearls	1500	1.15	0.60
AC, Lignite	650	1.77	0.31	Glassy Carbon	-	0.95	0.06
AC, Peat RO	900	1.63	0.19	Diamond Powder	-	0.16	0.48
AC, petrol. coke	-	1.29	0.47	Carbon FibersPAN	-	0.05	0.50
Graphite, natural	4-6	0.02	2.87	Carbon Nanotubes	-	0.08	0.92
Graphite, crystal.	3-10	0.10	0.63	Soot (Fullerene)	-	1.90	0.63
Graphite, crystal.	10-12	0.07	0.82	Fullerenes C <sub>60/70</sub>	-	1.34	0.11

Carbon black catalysts (including acetylene black) exhibited somewhat lower initial activity than AC, but better sustainability. Carbons with the ordered structure (graphite, diamond, carbon fiber) demonstrated the lowest initial activity toward methane decomposition reaction. Fullerenes C<sub>60/70</sub> and fullerene soot displayed relatively high initial activity, whereas, multi-walled carbon nanotubes showed very low catalytic activity in methane decomposition.

It was found that besides the nature of carbon material, its relative catalytic activity in methane decomposition reaction was proportional to the surface area of carbon. Figure 1 depicts the methane conversion rate (in mmole/min-g) as a linear function of the surface area of carbon catalysts in semi-log coordinates. The plot includes data for all the modifications of carbon tested, including AC, CB, graphites and others. It should be noted that only limited number of carbon catalysts could be compared based on the unit of surface area. For example, activated carbon (KBB) produced from hardwood (with SA=1500 m<sup>2</sup>/g) demonstrated the initial methane conversion rate of 1.36 μmole/min-m<sup>2</sup>, comparing to 0.77 μmole/min-m<sup>2</sup> for carbon black (BP-2000) with the same surface area.

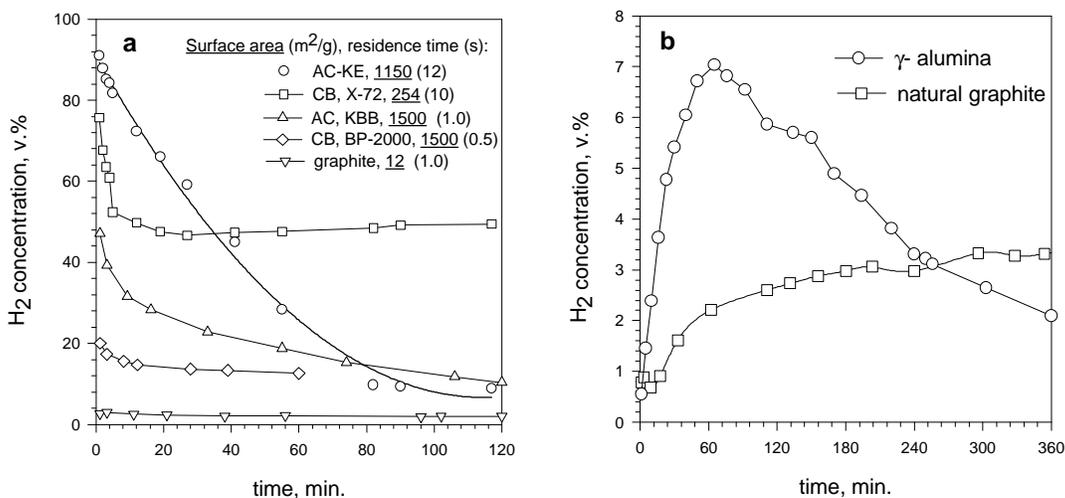
Figure 2 (a) demonstrates the kinetic curves of methane decomposition over different types of AC, CB and graphite at 850°C and different residence times. It can be seen that at comparable



**Figure 1 - Methane Conversion Rate as a Function of Catalyst Surface Area**

conditions AC catalysts have higher initial activity than CB catalysts, although, CB-catalyzed decomposition of methane is more sustainable than AC-catalyzed. At relatively high residence times AC catalysts produced H<sub>2</sub>/CH<sub>4</sub> mixtures with the initial hydrogen concentrations reaching up to 90 v.% and higher, which is an indication of the high catalytic activity. This, however, was followed by the rapid drop in the catalytic activity and the decrease in methane decomposition rate. CB-catalyzed methane decomposition reached quasi-steady state rate over 20-30 min and remained practically stable for several hours, followed by the gradual decline in the reaction rate.

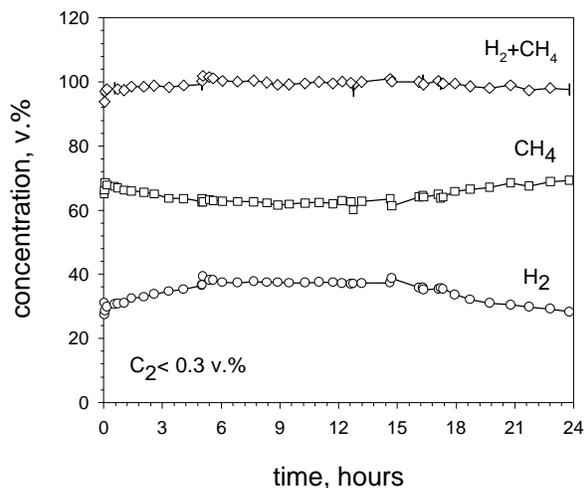
The initial rate of methane decomposition over amorphous carbons (e.g. acetylene black and others) was relatively low, but the process demonstrated good sustainability over long period of time. Figure 3 demonstrates the kinetic curves of methane decomposition over acetylene black which was conducted at 850°C and residence time of 12 s for almost 24 hours.



**Figure 2 - Methane Decomposition over Different Carbon Catalysts at 850°C**

Over period of 6 hours the process reached quasi-state regime which lasted for 9 hours, after which the methane decomposition rate slowly declined. No methane decomposition products other than hydrogen and carbon and small amounts of C<sub>2</sub> hydrocarbons ( $\Sigma(C_2H_4+C_2H_6) < 0.3$  v.%) were detected in the effluent gas during the entire process. The amount of carbon produced

corresponded to the volume of H<sub>2</sub> within the experimental margin of error (5%).



**Figure 3 - Methane Decomposition over Acetylene Black at 850°C**

It was found that the initial methane conversion rates in the presence of synthetic and natural graphites (with SA from 3 to 12 m<sup>2</sup>/g) and three different modifications of Al<sub>2</sub>O<sub>3</sub> (including  $\alpha$ - and  $\gamma$ -forms) with the surface area from 6 to 275 m<sup>2</sup>/g were in the same range of 0.2-1.0 mmol/min-g (at the same temperature and residence time). This experiment indicates that methane decomposition over graphites is most likely due to the thermal rather than catalytic processes. Inertness of graphite toward methane decomposition was earlier reported by Diefendorf (1960), who demonstrated that at 800°C no methane conversion was observed over graphite surface for 2 weeks.

It is noteworthy that the sustainability factor ( $K_m^1/K_m^0$ ) for natural graphite is more than unity, which indicates that the catalytic activity of carbon produced from methane is higher than that of the graphite. The same kinetic behavior was observed with both  $\alpha$ - and  $\gamma$ - modifications of alumina. Figure 2 (b) depicts the kinetic curves of hydrogen production over natural graphite (SA=4-6 m<sup>2</sup>/g) and  $\gamma$ -alumina (SA= 275 m<sup>2</sup>/g) at 850°C and residence time of approximately 1 s. These experiments clearly point toward certain catalytic properties of carbon produced from methane. However the catalytic activity of this form of carbon is quite low and, obviously, much less than that of AC and CB-type catalysts.

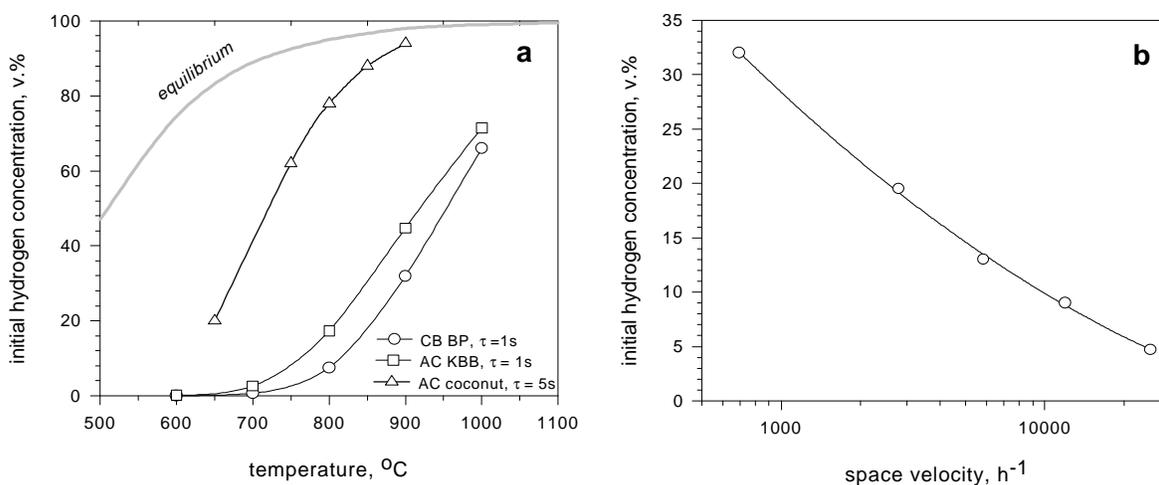
These experimental results can be explained as follows. It is known that the initial rate of hydrocarbon decomposition depends on the nature of a support (substrate). As the substrate surface is covered with carbon species, the rate of methane decomposition may increase or decrease, depending on the relative catalytic activity of the substrate and the carbon produced. The total rate of the methane decomposition process is the sum of the rates of carbon nuclei formation and carbon crystallites growth. It was determined that the activation energy of the carbon nuclei formation during methane decomposition (75.6 kcal/mole) is much higher than the

According to the Table 1 and Figure 2 graphites have the lowest initial catalytic activity (per unit of weight) in methane decomposition reaction. Among other factors, this could be attributed to the low surface area of graphites. However, the following experimental observation proves that graphites are indeed catalytically inert toward methane decomposition. In this experiment the catalytic activity of carbon materials with different chemical composition and surface area toward methane decomposition was compared.

activation energy of the carbon crystallites growth (54.2 kcal/mole) (Tesner 1987). Thus, in general, the rate of carbon crystallites growth tends to be higher than the rate of carbon nuclei production. The carbon particles produced during methane decomposition over AC catalysts, most likely, tend to have an ordered graphite-like structure and the rate of carbon crystallite growth exceeds that of nuclei formation. The catalyst surface is rapidly covered with relatively large graphite-like crystallites, which occupy active sites and result in inhibition of the catalytic activity toward methane decomposition. In the case of CB-type catalysts, the rates of crystallites growth and nuclei formation become comparable, resulting in the quasi-steady state methane decomposition. Low initial hydrogen production rate over alumina and natural graphite surface is due to high activation energy of nuclei formation over these materials. The increase in hydrogen production rate after the short induction period can be explained by the increase in the concentration of carbon nuclei on the surface and the methane decomposition rate over relatively small carbon crystallites. This is followed by the growth of the existing carbon crystallites and, as a result, the reduction of the active surface area and gradual decrease in methane decomposition rate. In case of graphite, methane decomposition rate slowly reached the steady state conversion rate controlled by the catalytic activity of carbon produced from methane. The nature of active sites responsible for the efficient decomposition of methane over the fresh surface of AC and CB catalysts is yet to be understood.

### Effect of Temperature and Space Velocity on Methane Decomposition Yield

We studied the effect of temperature and methane space velocity on the yield of methane decomposition using different carbon catalysts. Figure 4 (a) depicts the temperature dependence of the initial  $H_2$  concentration in the effluent gas in the presence of carbon black and activated carbon catalysts at different residence times ( $\tau$ ). It is clear that the initial activity of AC catalysts is higher than that of CB catalysts over the entire range of temperatures 600-1000°C.



**Figure 4 - Effect of Temperature (a) and Methane Space Velocity (b) on Methane Decomposition Yield.**

At sufficiently high temperatures (e.g. 900°C and higher) and residence times (e.g. 5 s and higher) the initial concentration of hydrogen in the effluent gas approaches the thermodynamic equilibrium concentration, which is an indication of high catalytic activity at these conditions. At 650°C and below the methane conversion rate was negligible.

Figure 4 (b) demonstrates the effect of methane space velocity on the initial concentration of hydrogen in the effluent gas produced by methane decomposition over carbon black (BP-2000) at 850°C, presented in semi-log coordinates. Ten fold increase in space velocity of methane results in 3-4 fold decrease in methane decomposition yield. It should be noted that in this paper, for the sake of comparability, both the residence time and the space velocity relate to the volume of the carbon catalyst within the reactor.

### Kinetic Model and Major Kinetic Parameters of CH<sub>4</sub> Decomposition

We developed a kinetic model of the methane decomposition reaction over carbon catalysts. It was assumed that CH<sub>4</sub> decomposition over the surface of carbon catalyst is controlled by two simultaneous processes:

1. decrease in methane decomposition rate due to the blocking of catalytic active sites by the carbon species produced via methane decomposition:

$$-\frac{d[CH_4]}{dt} = k_1 S_1 (1 - q) [CH_4]$$

where,  $k_1$ - rate constant,  $S_1$ - catalyst surface area,  $q$ - the fraction of catalyst surface covered by carbon produced from methane;  $q$  is a function of time

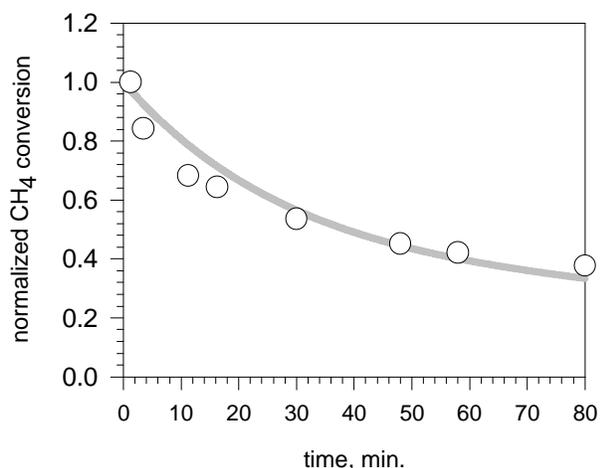
2. increase in methane decomposition rate due to the formation of catalytically active carbon species produced from methane

The sum of two components results in the following kinetic equation for the methane conversion:

$$c_{CH_4} = e^{-k_1 S_1 (1 - q)t} + \frac{[CH_4]_e}{[CH_4]_o} (1 - e^{-k_2 S_2 t})$$

where,  $c_{CH_4}$  is methane conversion,  $[CH_4]_o$  and  $[CH_4]_e$  are the initial and quasi-steady state methane concentrations in the effluent gas, respectively,  $S_2$  and  $k_2$ , are catalyst surface area and rate constant, respectively, for methane decomposition over carbon particles produced from methane;  $S_2$  is a function of time

The first component of the equation describes the decrease in methane conversion by the exponential decay law, whereas, the second component represents exponential rise to maximum, i.e. to the quasi-steady state value of methane conversion.



The kinetic equation obtained satisfactorily describes the experimental data during the initial stage of the methane decomposition process (1-1.5 hour). For example, Figure 5 compares the experimental results for methane decomposition over carbon black (BP-2000) catalyst at 850°C (circles) with the curve produced by fitting the data to the above kinetic model (gray line). The model can explain the peculiarities of the kinetic curves for methane decomposition over different types of carbon catalysts.

**Figure 5 - Experimental Data (circles) and Curve Fit Using Kinetic Model (gray line)**

The initial catalytic activity of AC is much higher than that of carbon produced from methane, therefore, the second component of the kinetic equation could be neglected, which results in a typical exponential drop shape of the kinetic curve. In contrast to AC, graphite catalysts (particularly, natural graphite) have very low initial catalytic activity toward methane decomposition reaction, therefore the first component of the kinetic equation is negligible, and the resulting kinetic curve is either flat, or is described by the exponential rise to maximum law (see also Figure 2, b). The same is true for the methane decomposition over alumina surface.

We determined the kinetic parameters of methane decomposition reaction over different carbon catalysts. Table 2 summarizes the major kinetic parameters (apparent reaction rate constants, frequency factors and activation energies) for CB and AC catalysts at the range of temperatures 700-900°C.

**Table 2. Apparent Reaction Rate Constants and Activation Energies for CH<sub>4</sub> Decomposition over CB and AC Catalysts**

Catalyst	T°C	k, s <sup>-1</sup>	E <sub>a</sub> , kCal/mol	α, s <sup>-1</sup>
Carbon black, BP-2000 SA= 1500 m <sup>2</sup> /g	750	0.035	56.3	4.3×10 <sup>9</sup>
	850	0.480		
	950	2.125		
Activated carbon, KBB SA= 1500 m <sup>2</sup> /g	600	0.0015	47.9	4.9×10 <sup>8</sup>
	700	0.026		
	800	0.178		
	900	0.602		

Thus, the apparent rate constants for methane decomposition in the presence of carbon black BP-2000 ( $k_{CB}$ ) and activated carbon KBB ( $k_{AC}$ ) catalysts could be expressed as follows:

$$k_{CB} = 4.3 \times 10^9 \exp(-56.3/RT) \quad 750-950^\circ\text{C}$$

$$k_{AC} = 4.9 \times 10^8 \exp(-47.9/RT) \quad 600-900^\circ\text{C}$$

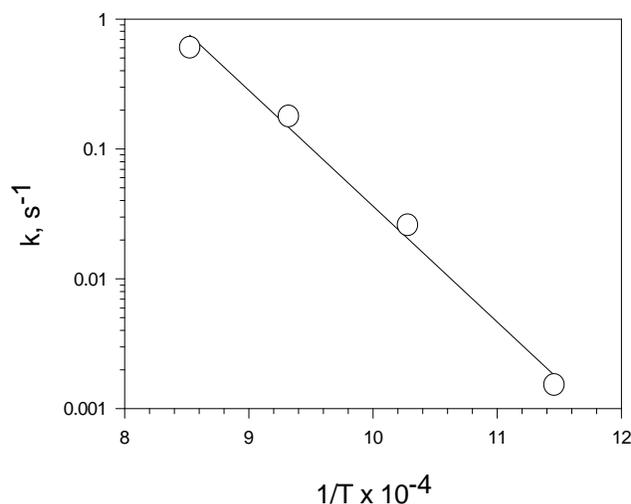


Figure 6 depicts the Arrhenius plot for methane decomposition over AC (KBB) catalyst. The activation energies of methane decomposition reactions over carbon catalysts are characteristic of surface reaction rate controlled processes.

**Figure 6 - Arrhenius Plot for CH<sub>4</sub> Decomposition**

### Propane Pyrolysis over Carbon Catalysts

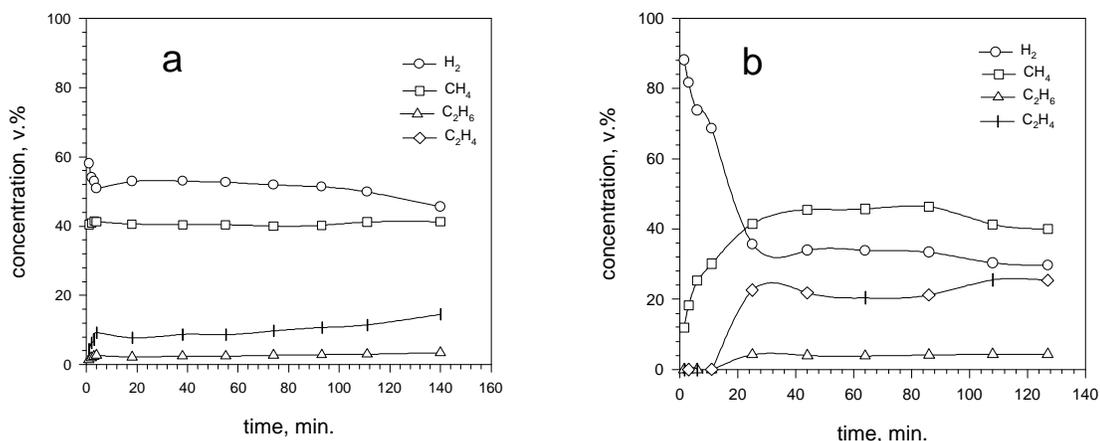
Due to a relatively weak C – H bond in propane molecule (96 kcal/mol) it is somewhat easier to split propane than methane molecule (methane C – H bond energy is 105 kcal/mol). 6.2 kcal is required to produce one mole H<sub>2</sub> from propane, comparing that to 8.9 kcal for methane:



However thermal cracking of propane at high temperatures proceeds via a thermodynamically more favorable formation of methane and ethylene:



Therefore, during pyrolysis of propane, in most cases, we observed the production of gaseous mixture containing hydrogen, methane, ethylene and small amounts of ethane and propylene. Figure 7 depicts the experimental results of propane catalytic pyrolysis over CB (a) and AC (b) type catalysts at 800°C in a packed bed reactor. Similar to methane decomposition, activated carbon demonstrated high initial activity followed by the rapid drop in catalytic activity. At the onset of the process hydrogen and methane were the only products of propane pyrolysis. Practically no C<sub>2</sub><sup>+</sup> byproducts were found in the effluent gas during first 10 min.



**Figure 7 - Propane Pyrolysis over CB (XC-72) (a) and AC (KE) (b) at 800°C**

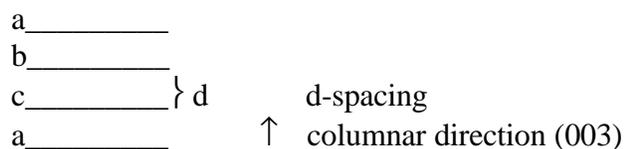
Quasi-steady state pyrolysis of propane was established after 30-40 min with methane being the major product of pyrolysis and significant concentration of ethylene in the effluent gas. The composition of the effluent gas of propane pyrolysis over AC catalyst approximately corresponded to the following chemical equation:



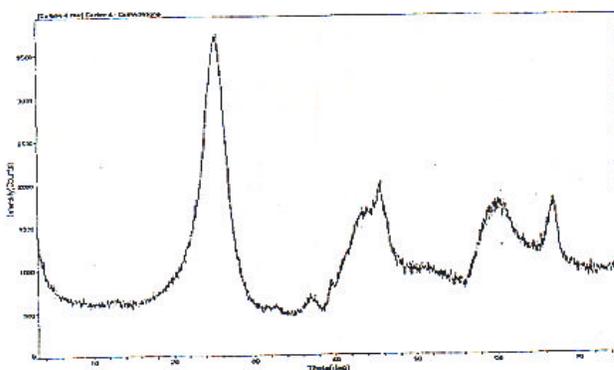
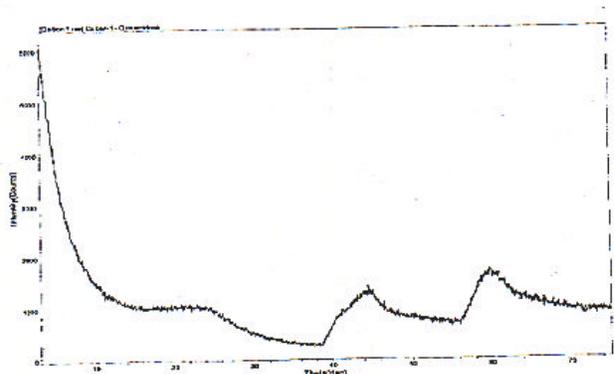
Propane pyrolysis over carbon black was characterized by lower initial rate, but was more sustainable comparing to AC catalyst, as shown on Figure 7 (a). Quasi-steady state rate of propane pyrolysis was reached in approximately 5 min and the process remained stable for approximately 2 hours. Hydrogen was a major component of the effluent gas during CB-catalyzed pyrolysis of propane.

### XRD Studies of Carbon Catalysts

We conducted X-ray diffraction (XRD) studies of the original carbon catalysts and carbon samples produced during hydrocarbon (methane or propane) decomposition. Carbon black BP-2000 with the surface area of 1500 m<sup>2</sup>/g and activated carbon Darco KBB (produced from hardwood) with the same surface area were used in these studies. Figure 8 depicts XRD spectra of the original carbon black (BP-2000) sample (top) and the carbon produced by propane pyrolysis at 850°C (bottom). It was found that the original sample had one- or, possibly, some two-dimensional ordering, whereas, sample produced from propane had ordering in the “columnar” or stacking (003) direction. The following diagram illustrates this concept:



where, a, b, and c are alternating arrangements of carbon ring plates. The d-spacing (lattice spacing) or spacing between plates is practically uniform, so that the (003) columnar reflection is clearly present. Thus, carbon produced during propane pyrolysis clearly has a typical graphite a-b-c-a type stacking of the carbon ring plates.



The actual d-spacing ( $d = 3.4948 \text{ \AA}$ ) of this (003) peak is larger than that of the standard graphite structure ( $d = 3.3480 \text{ \AA}$ ), which indicates that the plates are slightly further apart in the columnar stacking direction. This reflection is almost absent in the original carbon black sample which indicates that the plates are not stacked in a columnar arrangement, but, instead, are randomly oriented with respect to each other. The other two crystalline diffraction peaks in carbon sample produced by propane decomposition ( $43.5$  and  $46.2^\circ 2\theta$ ) also result from the three dimensional ordering, and result from the regular arrangement of spacings in various directions with respect to the columnar direction. The peaks  $62.2$  and  $67.2^\circ 2\theta$  are due to scattering rather than to crystalline diffraction.

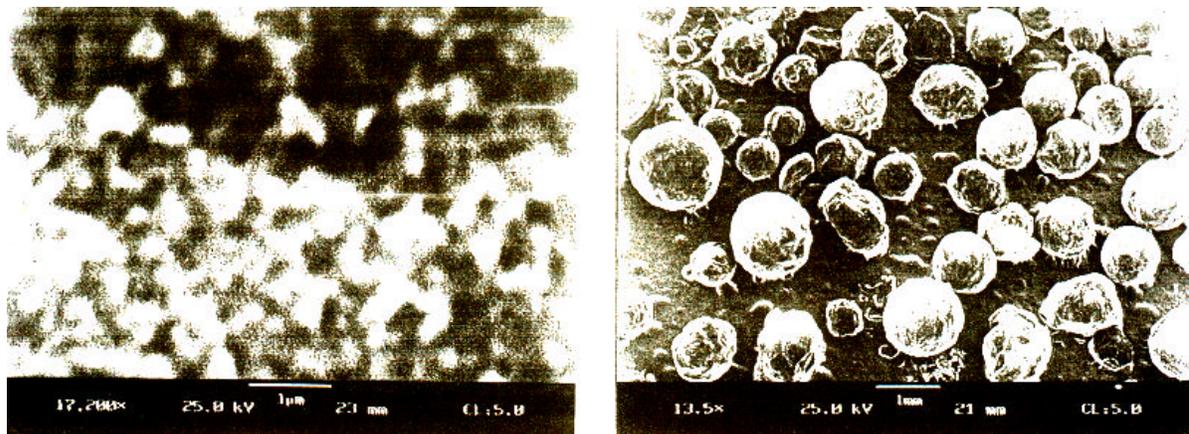
**Figure 8 - XRD Spectra of Carbon Samples**

The peak at  $62.2$  is due to C – C atomic distance for atoms which are out-of-plane, and the peak at  $67.2$  results from the C – C atomic distance for the in-plane carbon atoms. The size of graphite crystallite produced by propane decomposition was estimated at 23 Angstrom. XRD spectrum of the sample of activated carbon (Darco KBB) also indicated the lack of clear three dimensional ordering.

Thus, XRD studies confirmed that carbon species produced by decomposition of alkanes (methane and propane) at  $850^\circ\text{C}$  predominantly have an ordered (graphite-like) structure. This fact explains the gradual drop in the activity of AC and other carbon catalysts during methane and propane pyrolysis.

## SEM Studies of Carbon Catalysts

We conducted Scanning Electron Microscope (SEM) studies of the surface of carbon catalysts. Average particle size of powdered activated carbons was 40-100  $\mu\text{m}$ . Carbon black particles were significantly smaller in size and varied in the range of 0.1 – 1  $\mu\text{m}$ . Figure 9 depicts SEM micrographs of CB (BP-2000) catalyst before (left) and after exposure to propane at 850°C for 3.5 h (right).



**Figure 9 - SEM Micrographs of Carbon Black (BP-2000) Sample Before (left, 1  $\mu\text{m}$  scale) and After Exposure to Propane at 850°C for 3.5 h (right, 1 mm scale)**

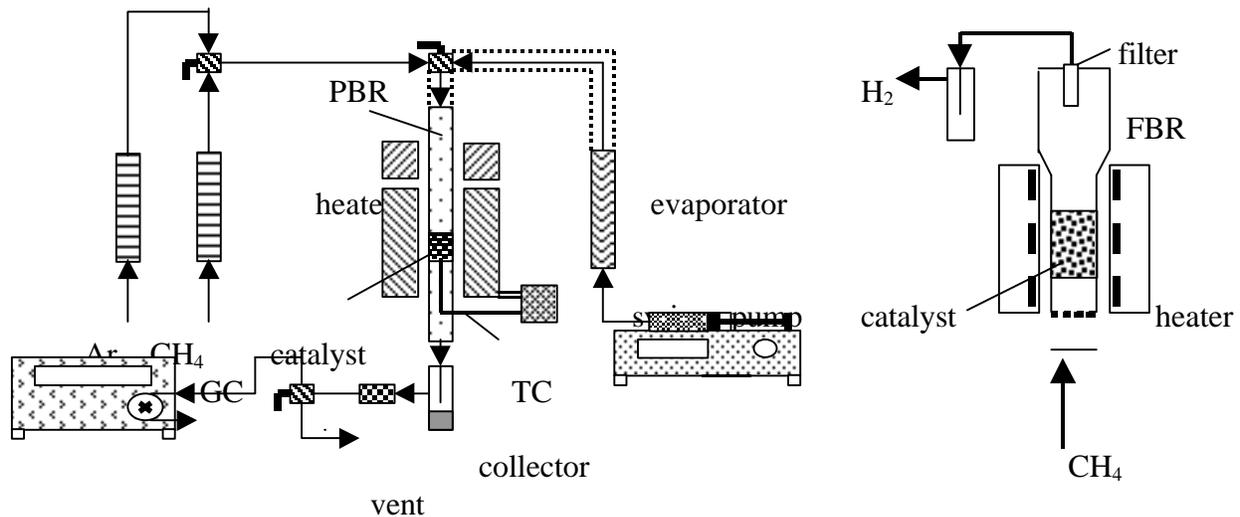
It can be seen that the average diameter of carbon particles increased from 0.1-0.3  $\mu\text{m}$  (for the original carbon sample) to approximately 0.1-1 mm due to carbon deposition during propane pyrolysis, which corresponded to more than thousand fold increase in particles mean diameter. On the other hand, the amount (weight) of carbon in the reactor increased only 6 times as a result of propane pyrolysis. This implies that a great deal of the agglomeration of carbon particles occurred during the process. Surface area calculations indicate that propane pyrolysis over CB catalyst would result in the reduction of the total geometrical surface of carbon particles by two orders of magnitude. This would have led to a drastic decrease in propane pyrolysis rate due to a significant reduction in the catalytic surface, which did not happen. The reason for that is that the actual surface area of each particle was much higher than its geometrical surface due to the presence of clusters of carbon particles about 3-10  $\mu\text{m}$  in diameter on the surface of the larger carbon particles (not shown on the micrograph).

## Thermocatalytic Reactors for Hydrocarbon Decomposition

The objective was to conduct studies on various conceptual designs for the thermocatalytic reactor for hydrocarbon decomposition. The reactors were designed, fabricated and tested for the simultaneous production of hydrogen and carbon using methane, propane and gasoline as feedstocks.

5 different types of reactors for hydrocarbon decomposition were considered:

- packed bed reactor (PBR)
- tubular reactor (TR)
- free volume reactor (FVR)
- fluid wall reactor (FWR)
- fluidized bed reactor (FBR)



GC- gas chromatograph, TC- thermocouple

**Figure 10 - Schematic Diagram of the Experimental Set-up with PBR (left) and FBR (right) Reactors**

Figure 10 demonstrates the experimental set-up with a packed bed reactor (left) used for the decomposition of methane, propane and gasoline. It should be noted that the same experimental set-up was also used for testing of the fluidized bed (right) and other reactors.

### ***Packed Bed Reactor***

PBR was mainly used for carbon catalysts screening, and studies on the effect of operational parameters (temperature, space velocity) on hydrogen yield, and kinetic measurements. Several examples of PBR test runs are presented in the Table 3. In some cases, it was difficult to conduct long run experiments with PBR due to carbon build up within the reactor and potential reactor clogging. It is apparent that the continuous removal of carbon from PBR would be a daunting technical problem, therefore, this type of the reactor is unlikely to be used in large scale hydrogen production units.

### ***Tubular Reactor***

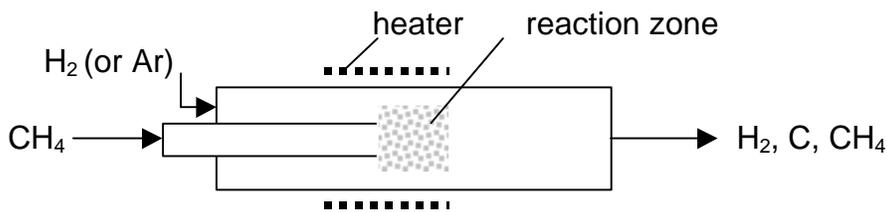
We conducted a series of experiments on methane decomposition using tubular reactors. The objective was to thermally decompose methane into hydrogen and carbon in a continuous process. Tubular reactors with the internal diameters of 3-6 mm and a small reaction zone enabling to achieve the residence times in the range of 1-20 milliseconds, were used in these experiments. Preheated (400°C) methane stream entered the reaction zone where it was subjected to decomposition (pyrolysis) at the temperatures of 1000-1300°C. At these conditions the conversion of methane was a function of the residence time. For example, at the residence time of 1.0, 2.0 and 6.2 ms, methane conversions were (mol.%): 0.1, 2.0 and 16.1, respectively. Hydrogen, carbon and unconverted methane accounted for more than 80-90 m.% of the products. Unsaturated (mostly, C<sub>2</sub>H<sub>4</sub>) and aromatic (including polynuclear) hydrocarbons were also produced in significant quantities as byproducts of methane decomposition. For example, at the residence time of 6.2 ms the yields of gaseous and liquid products were as follows (mol.%): C<sub>2</sub>H<sub>6</sub>- 0.9, C<sub>2</sub>H<sub>4</sub>- 3.3, C<sub>2</sub>H<sub>2</sub>- 5.8, C<sub>3</sub>-C<sub>6</sub>- 1.5, polynuclear aromatics (mostly, naphthalene)- 2.0. Unidentified liquid products of pyrolysis accounted for approximately 5 w.% of methane pyrolysis products. Carbon (coke) was mostly deposited on the reactor wall down-stream of the reaction zone, which indicated that methane decomposition reaction occurred predominantly homogeneously in gas phase. At higher residence times (tens of seconds), the yields of C<sub>2</sub><sup>+</sup> and polyaromatic hydrocarbons dramatically dropped. These experiments demonstrated that TR could potentially be scaled up for the use in full scale methane decomposition process, although, it would require the elevated temperatures (above 1000°C) and special surface-treated tubes to prevent carbon deposition in the reaction zone.

### ***Free Volume Reactor***

Free volume reactor is designed to carry out high temperature reactions by contacting a reagent gas with a stream of preheated carrier gas. FVR could be advantageous for the conducting of different dissociation reactions with formation of solid phase products, including methane decomposition reaction. For example, Shpilrain et al. (1999) reported on testing of a regenerative type FVR in a cyclic methane decomposition process. In our work we designed and tested FVR for a continuous production of hydrogen and carbon via methane decomposition. Methane decomposition occurred homogeneously by contacting a hot carrier gas such that carbon was produced in a free volume of the reactor and carried away by the gaseous stream, thus preventing carbon from deposition on the reactor wall. Two options for introducing thermal energy into the reaction zone were considered: by the stream of inert gas (Ar) or hydrogen. Figure 11 shows the schematic diagram of FVR used for decomposition of methane and propane.

Methane was introduced into the reactor through the inner ceramic tube, and the heat carrier gas entered the space between the inner and outer (quartz) tubes of FVR. We used Ar or hydrogen as heat carrier gases in a ratio 4:1 (by volume) to methane. The heat carrier gas was heated by the electric heater to 1200-1300°C and entered the reaction zone where it contacted the preheated

stream of methane. The results of the FWR testing using hydrogen as a carrier gas are presented in the Table 3.

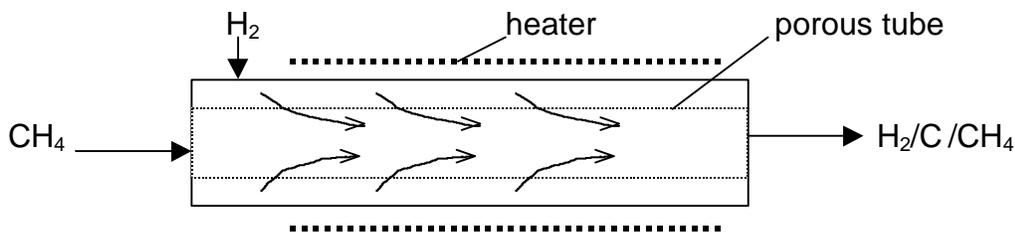


**Figure 11 - Schematic Diagram of Free Volume Reactor**

There were some carbon deposits around and, especially, downstream of the reaction zone, which indicated that some portion of methane contacted the hot surface of the outer wall due to a mixing of gases in the reaction zone. This could be prevented if the temperature of a heat carrier gas was higher than that of the wall in the reaction zone. The use of an inert gas as a heat carrier requires a subsequent gas separation stage, which would add to the cost of hydrogen. On the other hand, the use of hydrogen would somewhat reduce the net hydrogen yield.

### ***Fluid Wall Reactor***

The objective of FWR is to carry out the high temperature hydrocarbon decomposition reactions in the layer of a carrier gas heated to the required temperature, thus preventing carbon from deposition on the reactor wall. This can be done by passing a preheated inert gas (or hydrogen) through the porous tubing (which acts as an internal reactor wall) such that it thermally decomposes methane in the reaction zone and carries away produced carbon. Simplified schematic diagram of the FWR is shown on Figure 12.



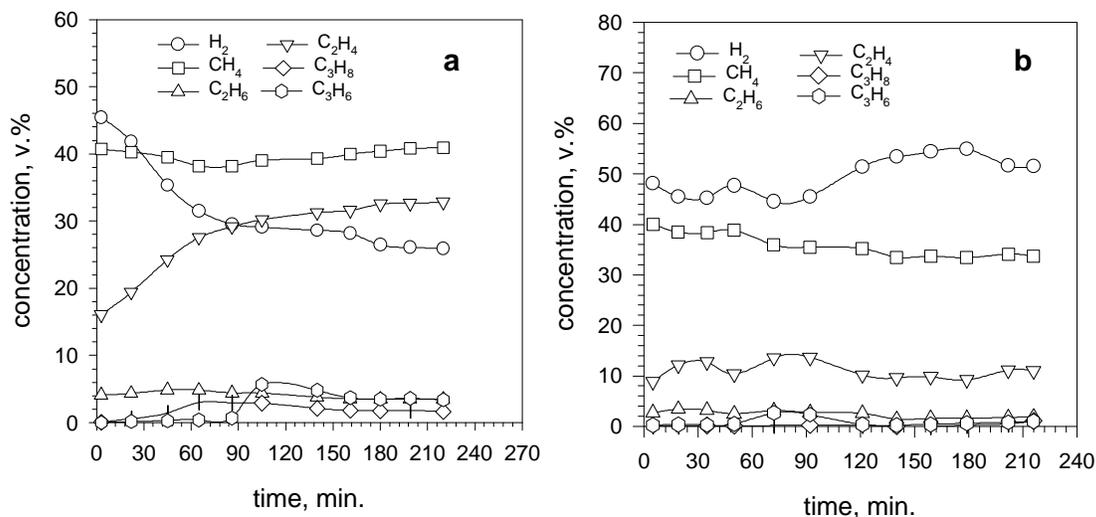
**Figure 12 - Schematic Diagram of Fluid Wall Reactor**

We conducted methane decomposition test runs using small size FWR. A flow of hydrogen at positive pressure was introduced into annulus between outer tube (quartz) and the internal porous ceramic tube, and a flow of methane at the atmospheric pressure was introduced into the inner ceramic tube at  $H_2/CH_4$  ratio of 1:3. The outer wall of the reactor was heated by the electric heater to 1100-1300°C. A stream of heated hydrogen permeated through the porous ceramic tube and entered the reaction zone where it contacted a preheated stream of methane. A mixture of hydrogen and unconverted methane after the reactor was metered and analyzed by GC method.

Methane conversion was about 10-15%. Carbon was collected in the down stream trap. More experiments will be conducted to optimize the yield of products. These proof-of-concept experiments demonstrated that FWR could potentially be suitable for medium and large scale units for the simultaneous production of hydrogen and carbon from NG and other hydrocarbons.

### Fluidized Bed Reactor

Fluidized bed reactors are widely used in chemical, metallurgical and petroleum industries. FBR could be particularly suitable for hydrocarbon decomposition process since it allows to continuously remove carbon from the reactor, similar to fluid catalytic cracking processes. A schematic diagram of FBR used in our experiments is shown on Figure 3 (right). It was found that an adequate fluidization of carbon (particularly, CB) particles could be achieved at space velocities of 300-600 h<sup>-1</sup>. Preheated to 400-500°C a hydrocarbon stream entered the FBR from the bottom, and contacted with the fluidized bed of carbon particles heated to 850-950°C in the reaction zone, where decomposition (pyrolysis) of hydrocarbons occurred. A hydrogen-rich gas exited from the top of the reactor through a ceramic wool filter. FBR reactor was tested using methane, propane, methane-propane mixtures, gasoline vapor and gasoline-methane mixture as feedstocks. Because of relatively short residence times (1-3 s) in the reaction zone methane decomposition yields were relatively low, whereas, propane and gasoline were almost quantitatively converted into hydrogen-rich gas using FBR. Figure 13 depicts the experimental results of propane and gasoline vapor pyrolysis over CB (BP-2000) catalyst at 850°C using FBR.



It is noteworthy that pyrolysis of propane and gasoline in FBR produce more C<sub>2</sub><sup>+</sup> byproducts comparing to PBR. Thermocatalytic pyrolysis of gasoline over CB catalyst lasted more than 3.5

hours during which the gaseous mixture with the average hydrogen concentration of 50 v.% was produced.

### **Comparative Assessment of Different Reactors for Hydrocarbon Decomposition**

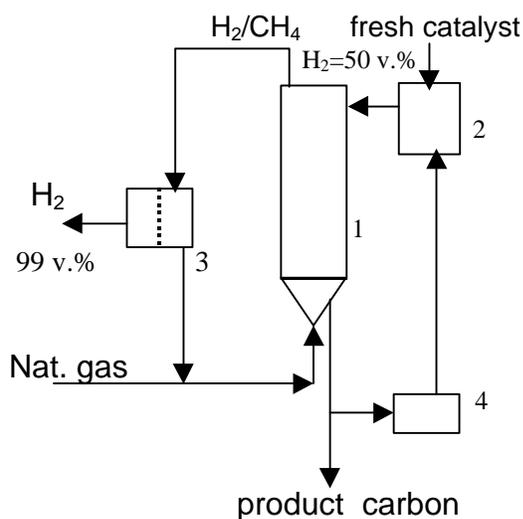
The results of testing of different thermocatalytic reactors for decomposition/pyrolysis of methane, propane and gasoline using carbon catalysts are presented in Table 3. Note that the data on the hydrocarbon conversion and the effluent gas composition relate to the average quasi-steady state values.

**Table 3. Thermocatalytic Reactor Test Results**

Hydrocarbon	Catalyst	Reac-tor	T°C	Conver-sion, %	Gaseous Products, v.%					
					H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub> (C <sub>2</sub> H <sub>2</sub> )	ΣC <sub>3</sub>	C <sub>4</sub> <sup>+</sup>
Methane	CB, BP-2000	PBR	950	30.9	47.2	52.7	0	0.1	0	0
Methane	Acetylene Black	PBR	850	23.3	37.8	61.9	0.1	0.2	0	0
Methane	CB, XC-72	PBR	850	28.0	43.7	56.2	0	0.1	0	0
Methane	CB, BP-2000	FBR	850	9.1	16.7	83.1	0	0.2	0	0
Methane	-	TR	1200	53.8	63.8	27.4	0.1	1.2 (7.5)	0	0
CH <sub>4</sub> /H <sub>2</sub> (4:1)	-	FVR	1200		89.3	10.7	0	0	0	0
CH <sub>4</sub> /C <sub>3</sub> H <sub>8</sub> (3:1)	CB, BP-2000	FBR	850	38.2	50.1	2.1	9.0	0.6	0	
CH <sub>4</sub> /C <sub>2</sub> H <sub>4</sub> (3:1)	CB, BP-2000	FBR	850		36.2	53.9	2.0	7.9	0	0
Propane	AC, KE	PBR	800	100.0	88.3	11.7	0	0	0	0
Propane	Acetylene Black	PBR	850	100.0	62.1	37.9	0	0	0	0
Propane	CB, BP-2000	FBR	850	98.0	27.0	39.5	1.5	29.4	2.6	0
Gasoline	AC, KE	PBR	800	100.0	49.4	37.6	2.1	9.8	0.6	0.5
Gasoline	CB, BP-2000	FBR	850	100.0	52.0	33.2	2.1	11.1	0.7	0.9
CH <sub>4</sub> /gasoline	CB, BP-2000	FBR	850		40.0	55.5	0.3	3.0	0.5	0.7

## Economic Analysis

We conducted a preliminary economic analysis of the thermocatalytic decomposition (TCD) process for production of hydrogen and carbon from natural gas. Figure 14 depicts the simplified flow diagram of the thermocatalytic process employing a fluidized bed reactor (FBR).



**Figure 14 - Simplified Flow Diagram of TCD Process for Production of Hydrogen and Carbon. 1- FBR, 2- heater, 3- membrane, 4- grinder**

According to this flow diagram hydrogen concentration in the reactor effluent gas is 50 v.%, with balance being methane and small amounts of  $C_2^+$  hydrocarbons. Thus, the employment of the membrane gas separation unit is required to produce 99 v.% hydrogen.

Non-permeate is recycled back to the reactor. Product carbon is removed from FBR and some portion of it is ground and recycled to maintain the average particle size in the range suitable for fluidization (100 – 500  $\mu\text{m}$ ). The catalyst is heated in the heater to the required temperature 800-900°C. Thus, the technological scheme of the process is very close to that of fluid coking (FC) process, except, in case of FC process the temperature is lower (510-550°C), and the hydrocarbon feedstock is heavier.

Therefore, for the preliminary estimate, the capital cost of the FC plant (including grinder) and its annual operational costs were taken as a basis for the hydrogen cost estimate for TCD process (it was assumed that FC and TCD have the same capacity on a feedstock BTU basis) (Garrett 1989).

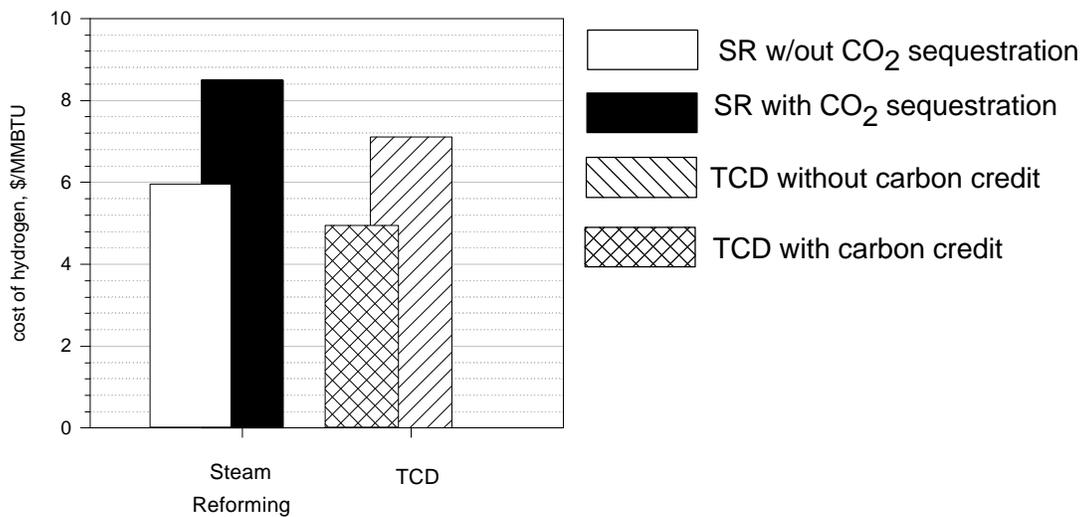
It was estimated that the usage of 17% of the non-permeate gas as a process fuel would cover thermal requirements of the TCD process. Carbon is a valuable byproduct of the process, with prices from several hundreds to several thousands of dollars per ton depending on its quality. Thus, the credit for byproduct carbon could significantly reduce the cost of hydrogen. For the purpose of our estimate we used a conservative sale price of carbon at \$100/ton, which is the average cost of carbon (in the form of petroleum coke) used in metallurgical industry (Kirk-Othmer 1978). The following Table demonstrates the results of the economic evaluation of TCD plant with the capacity of  $10^6 \text{ m}^3/\text{day}$  (which is close to that of a typical steam reforming plant).

Cost of hydrogen production from natural gas by thermocatalytic decomposition process was compared to that of steam reforming process. Figure 15 depicts the comparative assessment of TCD of NG (with and without carbon credit) and SR of NG (with and without CO<sub>2</sub> sequestration) processes.

**Table 4. Cost of Hydrogen Production by TCD Process**

Capacity: 10<sup>6</sup> m<sup>3</sup> H<sub>2</sub>/day  
 H<sub>2</sub> purity: 99.0 v.%  
 Natural gas: \$2.5/MMBTU

	\$10 <sup>6</sup>	\$10 <sup>6</sup> /Year	\$/MMBTU
<u>Capital Cost:</u>			
Reactor/ Heater/ Grinder (from FC plant)	18.0		
Membrane Hydrogen Separator	2.0		
Total Capital Cost	20.0		
<u>Annual Operating Cost:</u>			
Feedstock (Natural Gas)		33.9	
Catalyst/reagents/desulfurization		1.0	
Power		0.3	
Labor		0.1	
Depreciation (10%)		2.0	
			7.1
Total Hydrogen Production Cost		10.7	
Carbon Credit (\$100/t)			5.0
Net Hydrogen Production Cost			



**Figure 15 - Comparative Assessment of Hydrogen Production Cost by SR and TCD Processes**

For the purpose of the comparative economic evaluation we used the cost of hydrogen produced by modern methane steam reforming plant (Ogden 1997). As mentioned in the Background section, capture of CO<sub>2</sub> from concentrated streams of SR plant and its disposal adds 25-30% to the cost of hydrogen production by SR process. One should also add to it the cost of eliminating CO<sub>2</sub> emissions from the diluted (stack) gases of SR process.

The results of the comparative economic assessment of different options for hydrogen production from NG are as follows. TCD with carbon credit is the most cost effective process followed by SR without CO<sub>2</sub> sequestration. Note that the cost of hydrogen produced by the TCD without carbon credit (that is, carbon is not sold, but stored for the future use) is still lower than that of SR coupled with CO<sub>2</sub> sequestration (assuming that the cost of carbon storage is negligible compared to that of CO<sub>2</sub> sequestration). This is a preliminary economic assessment of TCD process, and more detailed cost analysis will be conducted upon testing pilot scale unit.

### Current and Future Markets for Carbon

Currently, the total world production of carbon black is close to 6 mln tons per year, with prices varying in the range of hundreds to thousands dollars per ton, depending on the carbon quality (Fulcheri 1995). For example, prices for the good quality carbon black could reach \$1000-4000 per ton. The carbon black has a great market potential both in traditional (rubber industry, plastics, inks, etc.) and new areas. For example, Gaudernack et al. (1996) identified the metallurgical industry as a very promising market for carbon black. Carbon black is particularly valuable as a reducing reagent for the production of SiC and other carbides, and as a carbon additive (carburizer) in steel industry. The carbon black market for these applications in Europe currently approaches 0.5 mln ton/year with the prices for the high quality materials reaching \$615 per ton. Carbon-based composite and construction materials potentially can absorb a tremendous amount of produced carbon. Besides the traditional markets for carbon, some novel applications for the carbon produced via methane decomposition are discussed in the literature. For example,

Kvaerner has initiated R&D program to investigate the potential of novel grades of carbon black as a storage medium for hydrogen, and as a feedstock for the production of solar grade silicone (Linum 1998).

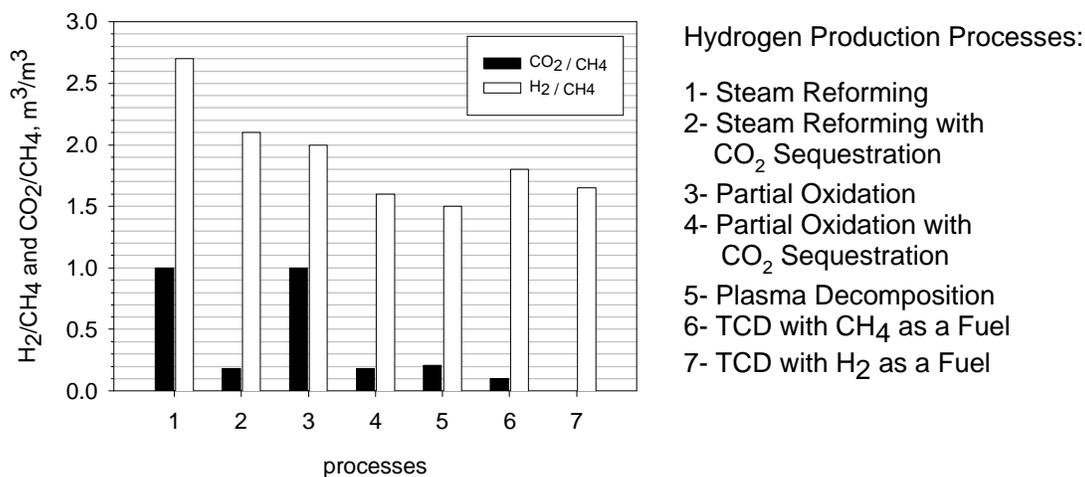
A market for carbon-based materials is continuously growing, however, it is unlikely that all the carbon produced via NG decomposition for mitigating the global warming will be absorbed by the traditional and perspective application areas. In this case, carbon can be stored for the future use, as discussed by Muradov 1993, and Steinberg 1999). No significant energy consumption would be expected with regard to the storage of solid carbon (comparing to CO<sub>2</sub> sequestration).

### Comparison of CO<sub>2</sub> Emissions from Different Hydrogen Production Processes

A comparative assessment of CO<sub>2</sub> emissions produced by different hydrogen production processes is shown on Figure 16. The following NG-based processes were compared:

- SR (without and with CO<sub>2</sub> sequestration),
- partial oxidation (without and with CO<sub>2</sub> sequestration),
- plasma-assisted decomposition (PAD), and
- TCD (with CH<sub>4</sub> and H<sub>2</sub> as a process fuel options).

PAD of methane is a well developed technology for the production of hydrogen and carbon black via high temperature decomposition of natural gas (Linum 1998). However, it consumes up to 1.9 kWh of electric energy to produce one normal cubic meter of hydrogen. Due to relatively low endothermicity of the methane decomposition process, the thermal energy requirements of the TCD process could be covered either by 10% of methane feedstock, or 14% of hydrogen produced in the process.



**Figure 16 – Comparison of CO<sub>2</sub> Emissions from Different Hydrogen Production Processes**

The comparison is based on two parameters, which reflect the energetic and ecological features of

the processes. The  $E_1$ -parameter is equal to the volume of  $H_2$  produced from the unit volume of NG consumed as a feedstock and a process fuel ( $E_1 = H_2/NG$ ,  $m^3/m^3$ ). The  $E_2$ -parameter is equal to the total volume of  $CO_2$  (from the process and stack gases) produced from a unit volume of NG ( $E_2 = CO_2/H_2$ ,  $m^3/m^3$ ). Evidently, the higher is  $E_1$  and lower is  $E_2$  parameter, the better is the hydrogen production process.

For the sake of simplicity and comparability, it was assumed that NG was the primary fuel for the supply of both thermal and electric energy for all the processes, including PAD of NG, and for  $CO_2$  sequestration. Almost 80% of the total world energy supply is based on fossil fuels, and NG average share is 19% (Nakicenovic 1993). Since NG produces 1.9 and 1.7 times less  $CO_2$  (per kWh produced) than oil and coal, respectively, this assumption would result in somewhat more conservative values for  $CO_2$  emissions.

The following conclusions can be extracted from Figure 16.

- Plasma decomposition of NG has lowest hydrogen yield and highest  $CO_2$  emissions because of large consumption of electric energy (note that this estimate is based on the world average energy production scenario, therefore, in countries with a large non-fossil fuel energy sector, e.g. hydroelectric, nuclear energy, both  $E_1$  and  $E_2$  parameters could be higher and lower, respectively).
- PO produces less hydrogen than SR process per unit of NG, although, both processes have comparable  $CO_2$  emission levels.
- TCD of NG (with NG as a fuel option) produces almost half of the  $CO_2$  emissions produced by SR with  $CO_2$  sequestration.
- TCD of NG (with  $H_2$  as a fuel option) produces hydrogen in quantities comparable with that of PO and SR (with  $CO_2$  sequestration), however, it does not produce any  $CO_2$ . Thus, it is the only fossil fuel based process which shows a real potential to be a completely  $CO_2$ -free hydrogen production process.

## Experimental

*Reagents.* Methane (99.99%v.) (Air Products and Chemicals, Inc.) was used without further purification. Samples of activated carbons, graphites, glassy carbon, synthetic diamond powder, fullerenes, carbon nanotubes and acetylene black were obtained from Alfa Aesar and used without further purification. Barneby Sutcliffe Corp. and Cabot Corp. supplied different CB and AC (coconut) samples, respectively. All carbon samples were used in the form of fine powder (<100 $\mu$ m). Activated alumina samples (Fisher Scientific and Alfa Aesar) were used without further purification.

*Apparatus.* The experimental set-up depicted on Figure 3- was used for the screening of carbon catalysts, kinetic measurements and testing of different thermocatalytic reactors. The set-up consisted of 3 main subsystems: (1) a thermocatalytic reactor (with temperature-controlled electric heater and pre-heater), (2) a feedstock metering and delivery sub-system for gaseous and liquid hydrocarbons, and (3) analytical sub-system. The catalytic reactors were made out of a fused quartz or ceramic (alumina) in order to reduce the effect of the reactor material on the rate

of hydrocarbon decomposition. The reactor temperature was maintained at a constant temperature via a type K thermocouple and Love Controls microprocessor. Amount of carbon catalyst used in the experiments varied in the range of 0.03-5.0 g. Gaseous hydrocarbons flow rates varied from 5 ml/min to 2 l/min.

Gaseous hydrocarbons (methane, propane) were metered by flow meters, and liquid hydrocarbons were metered and delivered to the reactor by a syringe pump via a temperature-controlled evaporator. Gaseous products of hydrocarbon decomposition passed through a condenser (for separation of liquid byproducts), a filter (for separation of airborne carbon particles and aerosols) and were analyzed gas-chromatographically).

*Analysis.* The analysis of the products of methane decomposition was performed gas chromatographically: SRI- 8610A (a thermal conductivity detector, Ar carrier gas, a silicagel column, temperature programming from 27 to 180°C) and Varian-3400, FID, He-carrier gas, Hysep D<sub>b</sub>. SEM studies were performed using Amray 1810 scanning electron microscope. XRD studies were conducted using Rigaku diffractometer with D/MAX 2200T/PC ULTIMA accessory. Polynuclear aromatic byproducts were analyzed spectrophotometrically (Shimadzu UV-2401PC).

## Summary

- The technical feasibility of CO<sub>2</sub>-free production of hydrogen via one-step thermocatalytic decomposition of hydrocarbons was demonstrated. Methane, propane and gasoline were efficiently converted into hydrogen and carbon using carbon catalysts.
- The catalytic activity and stability of more than 30 different forms and modifications of carbon were examined, and several of them were selected for further evaluation.
- The effect of operational parameters on the H<sub>2</sub> yield was determined. H<sub>2</sub> concentration in the effluent gas varied in the range of 30-90 v.%, the balance being CH<sub>4</sub> and small amount of C<sub>2</sub><sup>+</sup> hydrocarbons. CO or CO<sub>2</sub> were not detected among the products. Intermediate and byproducts of methane and propane decomposition reactions were identified and quantified.
- The factors affecting carbon catalyst activity and long term stability in hydrocarbon decomposition reactions were studied. It was found that the surface area and crystallographic structure of carbon species mostly determine the catalytic activity of carbon catalysts. This was confirmed by XRD and SEM studies of carbon catalysts.
- A kinetic model for methane decomposition over carbon catalysts was developed. Major kinetic parameters of methane decomposition reaction (rate constants, activation energies, etc.) over selected catalysts were determined.
- Various conceptual designs for the thermocatalytic reactors suitable for simultaneous production of hydrogen and carbon were evaluated. The following reactors were built and tested: packed bed, tubular, fluidized bed, free volume and fluid wall reactors.
- A bench-scale thermocatalytic fluidized bed reactor was designed and fabricated. The reactor was successfully tested using methane, propane, methane-propane mixture, and gasoline as feedstocks. Simultaneous production of hydrogen-rich gas (free of carbon oxides) and carbon was demonstrated.

- Preliminary techno-economic assessment of the TCD process indicated that the thermocatalytic unit with the capacity of an average steam reforming plant would yield hydrogen at a cost of \$5.0/MMBTU (if carbon sold at \$100/t), which is less than that from steam reforming process coupled with CO<sub>2</sub> sequestration.
- Comparative assessment of CO<sub>2</sub> emissions from different hydrogen production processes was conducted. It was shown that the TCD is the only fossil fuel based process which shows a real potential to be completely free of CO<sub>2</sub> emissions.
- If cost effective processes of hydrogen production via decomposition of NG will be developed and implemented, there would be practically no environmental constraints on using fossil fuels on a large scale.

### **Current Year Publications:**

1. "Hydrogen from Fossil Fuels without CO<sub>2</sub> Emissions", N. Muradov, in *Advances in Hydrogen Energy*, Kluwer Academic/Plenum Publishers, 2000, p.1-16
2. "On Perspectives of CO<sub>2</sub>-free Production of Hydrogen from Hydrocarbon Fuels for Small Scale Applications", N. Muradov, *Symposium on Hydrogen Production, Storage and Utilization, 1999 ACS Meeting*, New Orleans
3. "Hydrocarbon-based Systems for CO<sub>2</sub>-free Production of Hydrogen", N. Muradov, *13th World Hydrogen Energy Conference, Beijing, China, 2000*
4. "Compact Fuel Reformer for Mobile/Stationary Applications", N. Muradov, *Summit on Miniaturization of Energy, Chemical and Biomedical Systems*, Orlando, 1999
5. "Thermocatalytic Process for CO<sub>2</sub>-free Production of Hydrogen and Carbon from Hydrocarbon Fuels", N. Muradov, U.S. Patent Application No. 60/194828, filed 04/05/2000, assignee: University of Central Florida

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## List of Figures

Figure 1 - Methane Conversion Rate as a Function of Catalyst Surface Area

Figure 2 - Methane Decomposition over Different Carbon Catalysts at 850°C

Figure 3 - Methane Decomposition over Acetylene Black at 850°C

Figure 4 - Effect of Temperature (a) and Methane Space Velocity (b) on Methane Decomposition Yield.

Figure 5 - Experimental Data (circles) and Curve Fit Using the Kinetic Model (gray line)

Figure 6 - Arrhenius Plot for CH<sub>4</sub> Decomposition

Figure 7 - Propane Pyrolysis over CB (XC-72) (a) and AC (KE) (b) at 800°C

Figure 8 - XRD Spectra of Carbon Samples

Figure 9 - SEM Micrographs of Carbon Black (BP-2000) Sample Before (left, 1 μm scale) and After Exposure to Propane at 850°C for 3.5 h (right, 1 mm scale)

Figure 10 - Schematic Diagram of the Experimental Set-up

with PBR (left) and FBR (right)

Figure 11 - Schematic Diagram of Free Volume Reactor

Figure 12 - Schematic Diagram of Fluid Wall Reactor

Figure 13 - Thermocatalytic Pyrolysis of Propane (a) and Gasoline (b)  
over CB (BP-2000) at 850°C Using FBR

Figure 14 - Simplified Flow Diagram of TCD Process for Production of Hydrogen and Carbon  
1- FBR, 2- heater, 3- membrane, 4- grinder

Figure 15 - Comparative Assessment of Hydrogen Production Cost by SR and TCD Processes

Figure 16 – Comparison of CO<sub>2</sub> Emissions from Different Hydrogen Production Processes