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Methane cracking over commercial carbons for hydrogen production

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Abstract

A bench scale unit has been designed and developed indigenously for producing hydrogen from methane in the presence of a catalyst. Five number carbon samples (two carbon blacks and three activated carbons) of different origin procured from Indian market have been investigated in the bench scale unit with stainless steel continuous fixed bed reactor at a constant temperature of 850 ^{0}C and space velocity (VHSV) of 1.62 Lit/hr.g. Among all the five samples, activated carbon produced from coconut shells with BET surface area of 1185 m^2/g showed promising activity with a sustainability factor (R_1/R_0) of 0.33 and initial activity (R_0) of 0.623 mmol/min.g of catalyst. Accumulated carbon yield (over a period of four hours) of the above catalyst is 564 mg/g of catalyst.

Keywords: Hydrogen, Carbon catalysts, Methane cracking, Thermo catalytic decomposition.

1. Introduction

The demand for hydrogen is increasing day by day due to its usage in hydro treating processes in petroleum industries and also in automobile sector. Hydrogen is a non polluting fuel as it produces only water on its usage in fuel cells or IC engines. Major part of the world's hydrogen production (about 45 million tons/annum) is accomplished by Steam Reforming (SR) of natural gas followed by water gas shift reaction [1] as shown below:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^0_{298} = +206 \text{ kJ/mol} \qquad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^0_{298} = -41 \text{ kJ/mol} \qquad (2)$$

Steam reforming reactions are largely endothermic. Heat required for this process is obtained by burning fossil fuels which produce huge amount of CO_2. Venting of CO_2 generated during steam reforming process to atmosphere causes global warming. Alternatively hydrogen can be produced by methane cracking [2-4] which takes place at atmospheric pressure.

$$CH_4 \leftrightarrow C + 2H_2 \qquad \Delta H^0_{298} = +75 \text{ kJ/mol} \qquad (3)$$

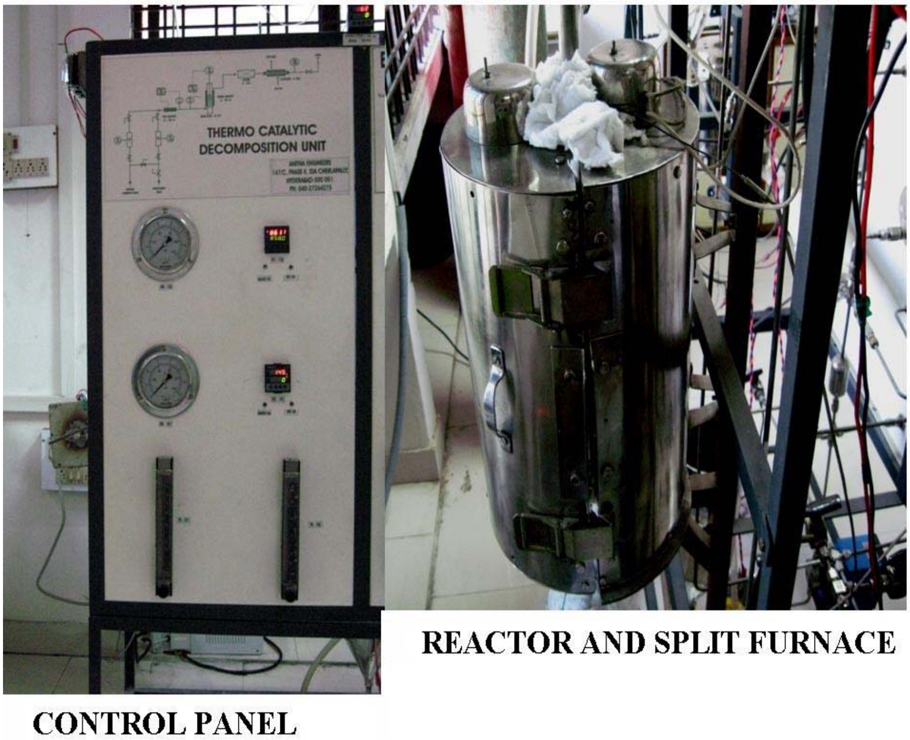
The amount of CO_2 emissions from this process is as low as 0.05 mole of CO_2/mole of hydrogen produced (if methane is used) compared to 0.43 mole of CO_2/mole of hydrogen for steam reforming process [3,5]. Methane cracking reaction is moderately endothermic. The energy requirement for methane cracking process (37.8 kJ/mole of H_2) is less than that for steam reforming process (63.3 kJ/mole of H_2). Due to this relatively low endothermic nature of methane cracking process, less than 10% of methane combustion heat is needed to drive this process [4]. Alternatively the heat required for the methane cracking can be supplied by burning 10 – 15 wt% of hydrogen produced [5].

Also methane cracking process doesn't require water gas shift reaction and CO_2 removal stages which significantly simplifies the process. As a by product it also produces clean carbon which can be utilized in metallurgical industries. The methane cracking reaction is carried out in the presence of either a carbon catalysts at 850^{0}C [6, 7, 8] or nickel based catalysts at 550^{0}C [9, 11].

The present work discusses about the design/developmental aspects of the bench scale unit used in methane cracking reaction and the performance studies carried out on five commercial carbon samples procured from Indian market.

2. Experimental details

A bench scale methane cracking unit has been designed and fabricated indigenously. The bench scale unit and its flow scheme are given in Figures 1 and 2 respectively. It comprises of various components like pre-heater, split furnace, reactor, filter and cooler.



REACTOR AND SPLIT FURNACE

CONTROL PANEL

Figure 1. Methane cracking bench scale unit

Methane from gas cylinder enters the reactor at required pressure (slightly above atmospheric pressure) through a two stage CONCOA gas regulator. It gets heated up to 450 ^{0}C in a pre-heater. The pre-heater is a properly insulated electrical heater which heats a 1/2" Schedule 40 pipe of length 300mm filled with ceramic beads (for better heat transfer). A K–type thermocouple and a Honeywell microprocessor based controller controls its temperature within ± 1^{0}C. The preheated gas enters the reactor where it is heated up to the test temperature (850 ^{0}C) by a cylindrical box type split furnace in two steps (say 600 ^{0}C in the first step and 850^{0}C in the second step). The cylindrical box type split furnace is made up of Kanthal wire and is insulated with mineral wool properly. It can be operated up to 900 ^{0}C. Methane cracking reaction takes place in a fixed bed tubular stainless steel reactor (Grade SS316) of internal diameter 16 mm and heating zone length of 250 mm. The product gases from the reactor pass through a filter filled with glass wool to remove particulate substance (if any). The filter is made up of 1" Schedule 40 stainless steel pipe of length 100mm. The hot gases from the filter pass through a cooler where they are cooled to ambient temperatures by a water circulation system. The cooler is a double pipe counter current flow type heat exchanger made up of 1” and 1/4" Schedule 40 pipes respectively. Calibrated rotameters with needle valves procured from IEPL, India have been connected in line to the pre-heater to measure the flow rates of methane and second gas (say nitrogen). The methane gas flow rate can be varied up to 75 sccm and nitrogen flow rate can be varied up to 150 sccm. Pressure gauges (Make: Waree, India) are provided at necessary points to measure the pressure up to 7 kg/cm^2. Adequate numbers of ball valves are provided for proper isolation of gases both in the up stream and down stream of rotameters. The flow rate of product gases can be measured with the help of a wet gas flow meter (Make: INSREF, India). A check valve provided before the pre-heater prevent the back flow of reactant gases. The system has been designed in such a way that it can be operated up to a design pressure of 7 kg/cm^2 and a temperature of 900 ^{0}C. Entire piping used for all gases is of 1/4”, Schedule 40 stainless steel (Grade SS 316). The instruments have been calibrated before the study.

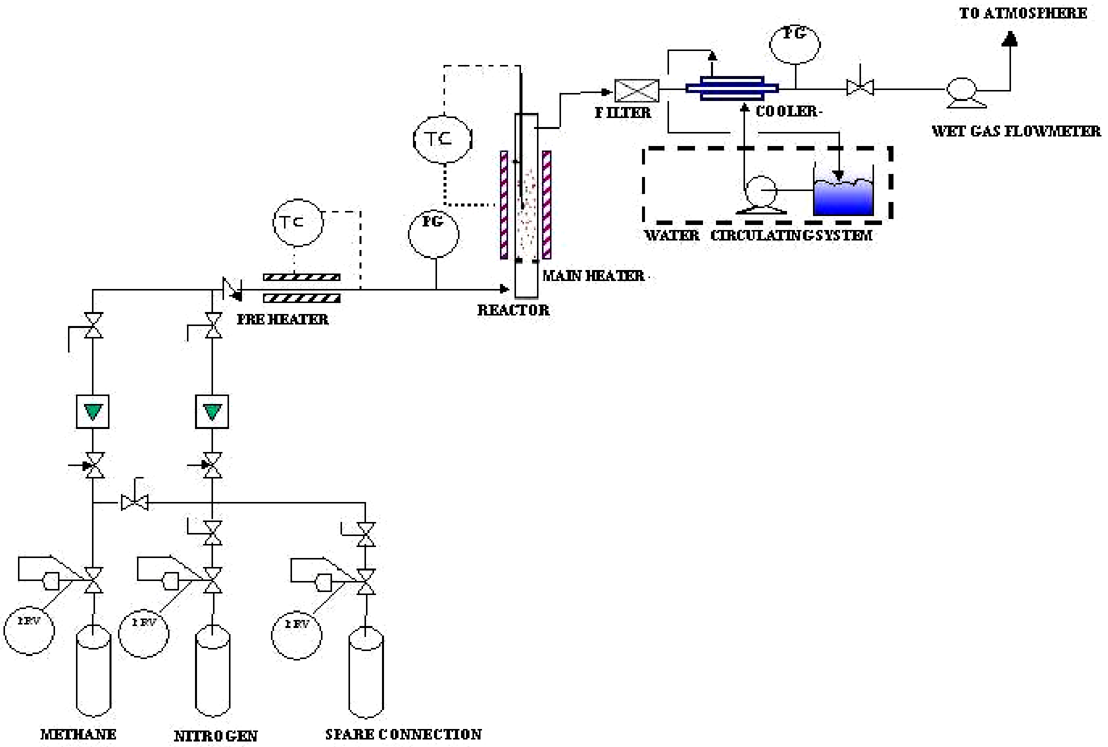


Figure 2. Process flow scheme of methane cracking bench scale unit

3. Experimental procedure

3.1 Blank run

As methane gas is a carburizing agent and may carburize stainless steel, in the present experiments the stainless steel reactor is subjected to a blank run without carbon catalyst. The metallic reactor is filled with cylindrical ceramic beads of size 5 mm x 5 mm and is heated up to the reaction temperature (850 ^{0}C) under nitrogen (Purity: 99 vol% , Make: BOC India Ltd) flow. On the attainment of reaction temperature, the nitrogen is slowly replaced with high purity methane (99.995 vol % of BOC gases, India). The methane gas flow rate is set at 54 cm^3 (STP)/min.

The experiment is conducted for four hours and the gas samples have been collected in Teddlar^{TM} bags on hourly basis. The methane conversion has been estimated by analyzing the gas samples. The methane conversion in mole% is plotted against time in hours (Figure 3). It may be observed from Figure 3 that the effect of metal on methane conversion is negligible at 850 ^{0}C in four hour duration (<5 mole %) similar to that reported in the literature [14]. Hence stainless steel reactor has been used in the activity studies of all the five carbons.

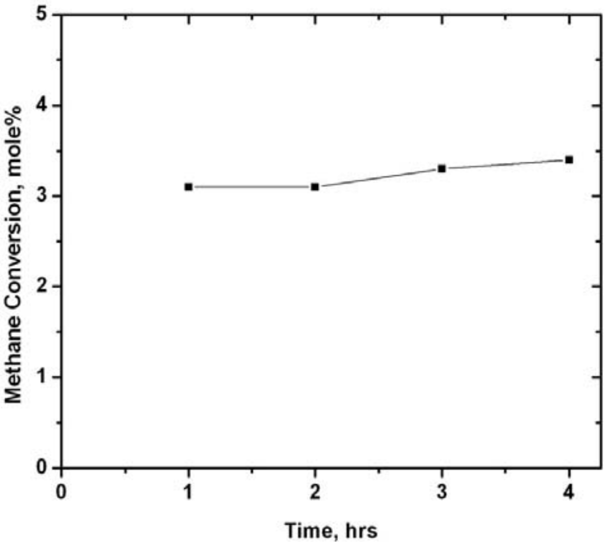


Figure 3. Methane cracking reaction - a blank run (T: 850^{0}C; Methane Flow: 54 cm^3 (STP)/min)

3.2 Activity studies

The stainless steel reactor has been used in the methane cracking activity studies of all the five carbon catalysts. All the carbon samples have been used as obtained. Activated carbons steam activated at producer end have been used. Table 1 gives the details of source and supplier of different carbon catalysts tested. The reactor is filled up with cylindrical ceramic beads of size 5 mm (Φ) x 5mm (length) up to the center. All the carbon samples have been ground to less than 100 micron size.

A thin bed of quartz wool has been placed above the ceramic beads over which 2gms of carbon sample is placed. As carbon samples have a tendency to decompose above 350^{0}C [13], the reactor is heated gradually up to the reaction temperature 850 ^{0}C under nitrogen atmosphere. On the attainment of the reaction temperature, nitrogen is slowly replaced with methane of purity 99.995 vol%. All experiments have been carried out under atmospheric pressure and selected temperature (850 ^{0}C) at a constant methane flow rate of 54 sccm (Which corresponds to a VHSV of 1.62 Lit/hr.g). Prior to the start of each experiment, the Teddlar^{TM} bags have been flushed three times with nitrogen to avoid any contamination. The gas samples collected in Teddlar^{TM} bags at an interval of one hour for 4 hours have been analyzed for methane cracking products using Nucon 5700 gas chromatograph equipped with a Thermal conductivity detector (Oven Temperature: 120^{0}C; Detector temperature: 110 ^{0}C; Injector temperature: 120 ^{0}C) and Porapak Q column. Nitrogen has been used as carrier gas. AIMIL's Gas Chromatograph data station (DASTA-710) has been used in the analysis of GC data. The concentrations of hydrogen and methane have been determined using the standard gases: hydrogen (99.99 vol%, BOC India Ltd) and methane (99.995 vol%, BOC India Ltd). In all the experiments no methane cracking products other than hydrogen and unconverted methane have been detected in the effluent gas. This is in confirmation with thermodynamic analysis reported in the literature which states that the methane cracking produces only hydrogen and unconverted methane below 1127^{0}C and the reaction proceeds heterogeneously up to 900 ^{0}C [12]. The amount of carbon produced has been calculated by weighing method.

Table 1. Carbon sample source and supplier details

S.No	Sample Code	Sample	Sample source	Supplier
1.	CB	Carbon Black	Fossil Fuels	S. D. Chemicals, India
2.	SAF	Special Abrasion Furnace	Hydrocarbon Fuels	M.I.D.C, India
3.	AC1	Activated carbon1	Hard Wood based	Apex Chemicals Ltd, India
4.	AC2	Activated carbon2	Vegetable based	Merck, India
5.	AC3	Activated carbon3	Coconut based	Active carbon India Pvt Ltd., India

3.3 Catalyst characterization

The N_2 BET surface area measurement has been carried out before and after catalytic tests using surface area analyzer SMART SORB 93 by pre treating the samples at 200 ^{0}C for 2 hours under nitrogen purging. Nitrogen adsorption/desorption isotherms obtained at -196 ^{0}C have been used to calculate the BET surface area. Total Pore volumes (PV) has been estimated according to the Barret–Joyner–Halenda (BJH) method from the adsorption data [10]. Average particle size is calculated using the following method:

$$\text{Average particle size (dp)} = 6/(\rho_p \times \text{BET SA}) \tag{4}$$

where, ρ_p is particle density and BET SA is the BET surface area.

Table 2 presents the BET surface area, average particle size and total pore volume of carbon samples before and after experiments. Particle density before and after experiments has been determined experimentally by displacement method. Bulking density of solid material before experiment has been determined by "Tapping method". Table 3 presents the particle density before/after experiments and bulk density before experiments. The Proximate analysis has been carried out with the help of thermo gravimetric analyzer (Model No: TG/DTA 6200). During proximate analysis, the sample has been heated from 20 ^{0}C to 600 ^{0}C at the rate of 10 ^{0}C per minute in air. The amount of ash in the carbon samples has been determined by completely burning the carbons in air at 600 ^{0}C for sufficient time. Table 4 presents the proximate analysis of carbon samples. All the carbon samples contain 0 – 2.5 wt % of ash. The ash content in coconut charcoal (AC3) is 1.0 wt % while that of the activated charcoals from hard wood (AC1) and vegetable sources (AC2) are 1.2 wt% and 2.5 wt% respectively. The Ultimate analysis has been carried out using CHNS Elemental Analyzer (VARIO MICRO TUBE, ELEMENTAR).Table 5 presents the ultimate analysis of the carbon samples. The ash obtained by completely burning the carbon samples at 600 ^{0}C have been dissolved in aqua regia and then analyzed using ICP-OES (Model: GBC XP of GBC Scientific). Table 6 presents the inorganic composition of ashes. It may be observed from Table 6 that the major elements in the carbon samples are K, Na, Si, Mg Al and Ca respectively. These elements have been known to be inactive for methane cracking reaction. Although Fe and Ni have been found to be active they are present in small percentages in all the carbon samples and hence have negligible effect on methane cracking reaction.

Table 2. Details of BET surface area and total pore volume

Sample Code	**dp, before test, (nm)**	**dp, after test, (nm)**	**BET SA before test, (m^2/g)**	**BET SA after test (m^2/g)**	**PV_{total} before test (cm^3/g)**	**PV_{total} after Test (cm^3/g)**
CB	42	61.4	120	65.17	0.024	0.013
SAF	59	83	101.67	45.07	0.02	0.009
AC1	3.7	16	1292.33	250.56	0.258	0.050
AC2	4.3	19.4	1174.88	200.17	0.235	0.04
AC3	3.8	6.3	1185.05	577.63	0.237	0.116

Table 3. Comparison of particle/bulk densities

Sample Code	**Particle density, Before test, gm/cc**	**Particle density, After test, gm/cc**	**Bulk density, gm/cc****
CB	1.22	1.5	0.44
SAF	1.00	1.61	0.41
AC1	1.25	1.5	0.45
AC2	1.20	1.55	0.40
AC3	1.35	1.65	0.48

**Before Experiments

Table 4. Proximity analysis of Carbon samples

Sample Code	**Water Loss (wt %)**	**Other volatiles (wt %)**	**Ash content (wt %)**
CB	1.3	2.9	0.0
SAF	1.3	2.5	0.0
AC1	17.2	3.7	1.2
AC2	16.8	2.1	2.5
AC3	24.1	2.3	1.0

Table 5. Ultimate analysis of Carbon samples

Sample code	**Nitrogen (wt %)**	**Carbon (wt %)**	**Hydrogen (wt %)**	**Sulfur (wt %)**	**Oxygen (wt %) ***
CB	3.46	79.66	0.7	1.34	14.84
SAF	5.15	93.0	0.38	1.27	0.20
AC1	4.26	71.15	2.23	0.11	22.25
AC2	4.56	70.03	1.76	0.47	23.18
AC3	4.76	72.67	2.36	0.20	20.01

*By difference

Table 6. Elemental analysis of ashes (wt %)

Sample	**Na**	**K**	**Al**	**Si**	**Fe**	**Mg**	**Ca**	**Ni**	**Others ***
AC1	10	41	0	41	0.3	1.2	2	0.5	4
AC2	13	35.7	2.2	37	0.8	3.0	5	0.3	3
AC3	12.6	38	0.4	38	0.6	5	2	0.4	3

4. Results and discussion

The catalytic activity has been reported in terms of methane conversion and methane cracking rate and sustainability factor, K (Muradov 2000). They are defined as follows:

Methane conversion, Y (mole %) =H_2 vol% x 100/ (200 – H_2 vol %) (5)

Methane cracking rate = Methane inlet flow rate (mole/min) x Y/
(mmole/ min.g) (Weight of catalyst) (6)

Sustainability factor (K) = Methane cracking rate after 1 hr (R_1)/
Initial methane cracking rate (R_0) (7)

It may be noticed from Figures 4 and 5 that the initial methane conversions (14.5% for CB; 5% for SAF) and initial methane cracking rates (0.17mmol/min.g for CB; 0.055mmol/min.g for SAF) are much lower than that of activated carbon catalysts produced from different origins. Carbon black with initial methane cracking rate of 0.17mmol/min.g and sustainability factor (K) of 0.9 (Table 7) seems to be more stable catalyst among all the five carbons tested.

The initial methane conversion (50% for AC1, 45% for AC2 and 51% for AC3) and initial methane cracking rates (0.6mmol/min.g for AC1, 0.55mmol/min.g for AC2 and 0.623mmol/min.g for AC3) of activated carbons have been observed to be much higher than that of CB and SAF catalysts. However the methane conversion of all the three activated carbons falls quickly to 9% (AC1), 11% (AC2) and 15% (AC3) in four hour duration (Figures 4,5). Also it may be observed from Table 7 that the initial methane cracking rate of coconut charcoal (AC3) is 0.623mmol/min.g and its sustainability factor is 0.33. The accumulated carbon over four hour duration is the lowest (185 mg.C/g.Catalyst) in case of special abrasion furnace (SAF) carbon and the highest (545 mg.C/g.Catalyst) in case of activated carbon (AC3). Compared to SAF, CB with high external surface area (120m^2/g) and total pore volume (0.024cm^3/g) result in steady state methane decomposition rate. The surface area and pore volume of CB after four hours duration reduces to 65.17m^2/g and 0.013cm^3/g (i.e., a loss of 46% in SA and PV) implying that the CB catalyst still has active sites and the process can go on for several hours until most of the surface is covered by carbon crystallites produced from methane. Hence carbon blacks in general have longer sustainability compared to other carbon samples. Activated carbons with higher surface area (1100-1300m^2/g) and higher pore volume (0.235 – 0.258 cm^3/g) posses higher initial activities. However it may be noticed from Figures 4 and 5 that their activity decreases with time. Among all the activated carbon samples, the one that produced from hard wood (AC1) has highest surface area (1292 m^2 /g) and has the highest initial catalytic activity. But the activity falls rapidly in four hours duration. The activity of activated carbon samples produced from vegetable source (AC2) with a surface area 1175 m^2/g also decreases over a period of four hours in line with that produced with hard wood samples. However the activity of activated carbons produced from coconut shells (AC3) with surface area 1185 m^2/g (which is in between activated carbons produced from hard wood and vegetable sources) has decreased moderately compared to other two. The initial methane conversion of AC3 catalyst is 51% and reduces to 15% by the end of fourth hour which is higher than that of AC1 and AC2. In the case of AC3 the surface area as well as pore volume reduces moderately (Surface area: from 1185m^2/g to 577.63m^2/g; Pore volume: from 0.237 cm^3/g to 0.116 cm^3/g - 51% loss in SA & PV) leaving a scope for further reaction. Whereas for AC1 the surface area reduces from 1292.33m^2/g to 250.56m^2/g (81% loss in SA & PV) and for AC2 it reduces from 1174.88m^2/g to 200.17m^2/g (83% loss in SA & PV). It may be observed from the above data that the loss in surface in case of AC3 is 51% which is much lesser than that of AC1 (81% loss) and AC2 (83% loss). This indicates that the source of carbon plays an important role in methane cracking reaction which is in line with the studies carried out earlier [4, 5]. The difference in catalytic activity of carbons can be explained by their difference in crystallinity, surface morphology and apparent energies (160-201kJ/mol for ACs and 205-236kJ/mol for CB). The rate of methane cracking reaction is the sum of rates of carbon nuclei formation and carbon crystallites growth. The rate of carbon nuclei formation is proportional to the surface area. As the reaction proceeds, blocking of pores takes place by growing carbon crystallites which hinder the internal diffusion of methane. The decrease in surface area/total pore volume, increase in particle size (Table 2) and increase in particle density (Table 3) confirm the above phenomenon.

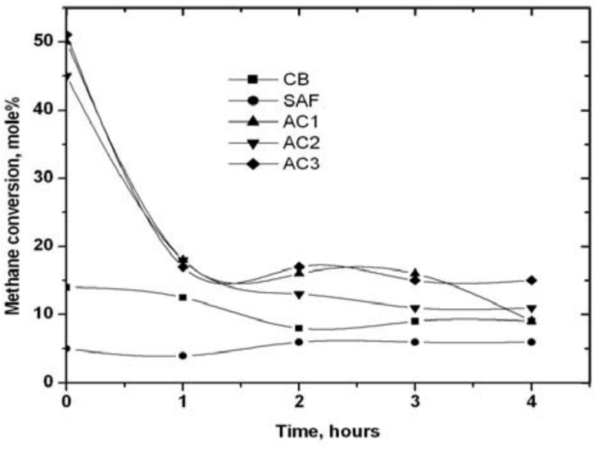


Figure 4. Methane conversion (mole %) for different Carbons (T: 850^{0}C; VHSV 1.62 Lit/hr.g)

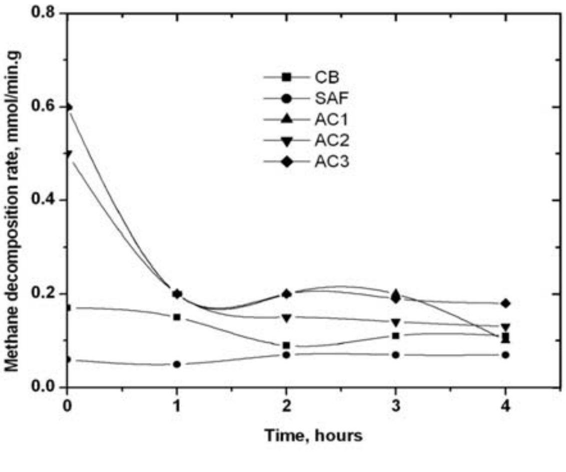


Figure 5. Methane decomposition rate (mmol/min.g) for different carbons (T: 850^{0}C; VHSV: 1.62 Lit/hr.g)

As the performance of activated charcoal (AC3) happens to be the best among all the five carbons tested, it has been decided to investigate the crystalline and morphological studies for AC3 catalyst before/after experimentation. The morphology and the crystalline data of the AC3 sample before and after the catalytic activity have been analyzed using SEM (Hitachi S-3700) and XRD (Phillips PW 1830) respectively. The SEM image (Figures 6, 7) shows the morphology of the sample (AC3) before and after the catalytic reaction within the reactor. From the Figure 6, it may be noted that the pre-reacted sample is predominantly made up of irregular shaped, highly granulated carbonaceous structures in the crevices of the conducting tape and the particles measure approximately in the range of 10-20 µm in size. The Figure 7 shows the image of a post catalyzed sample which consists of carbonaceous soot with granule sizes measuring approximately in the range of 30 – 90 µm. In this figure a long microfiber can also be seen.

Table 7. Test conditions and sustainability factors for carbon samples

Sample Code	**Temperature (^{0}C)**	**VHSV (Lit/hr.g Catalyst)**	**Space Time (sec)**	**R_0 (mmol/min.g)**	**$K=R_1/R_0$**	**Accumulated carbon (mg-C/g-catalyst)***
CB	850	1.62	5.1	0.170	0.9	320
SAF	850	1.62	5.4	0.055	0.95	185
AC1	850	1.62	5.0	0.600	0.36	505
AC2	850	1.62	5.6	0.542	0.39	450
AC3	850	1.62	4.6	0.623	0.33	545

where * 4 hour run; Space Time (ST) = 3600/ (VHSV (Lit/hr.g) x Bulk density (gm/cc) X 1000)

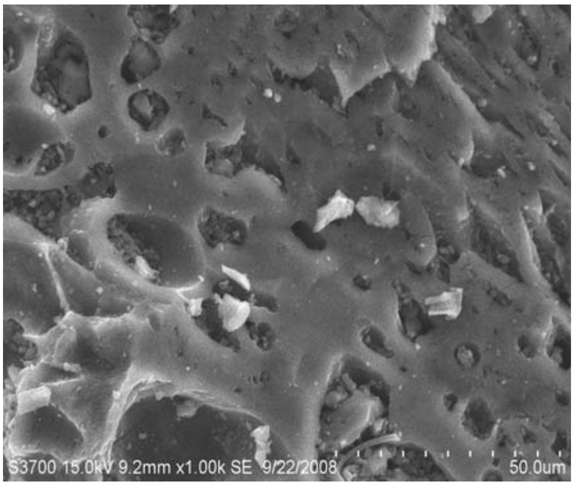


Figure 6. SEM of activated charcoal

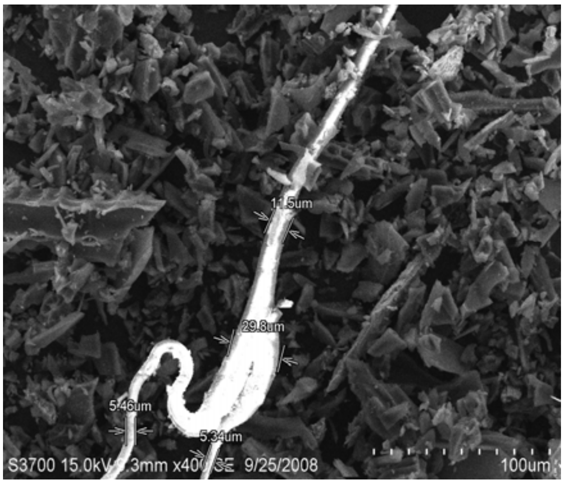


Figure 7. SEM of activated charcoal (AC3) – used (T: 850^{0}C; VHSV: 1.62Lit/hr.g)

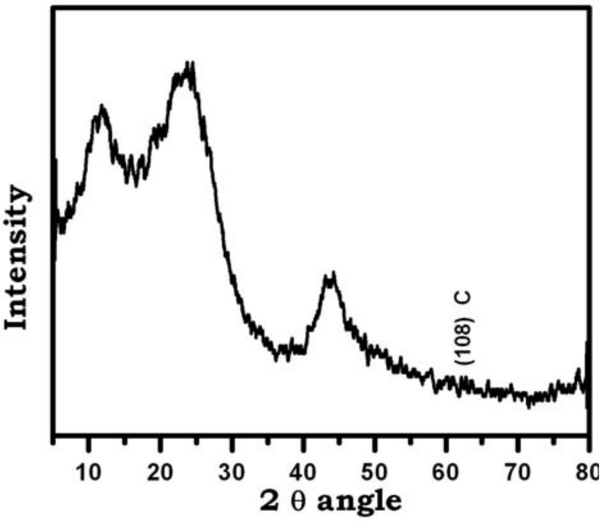


Figure 8. XRD plot of AC3 before test

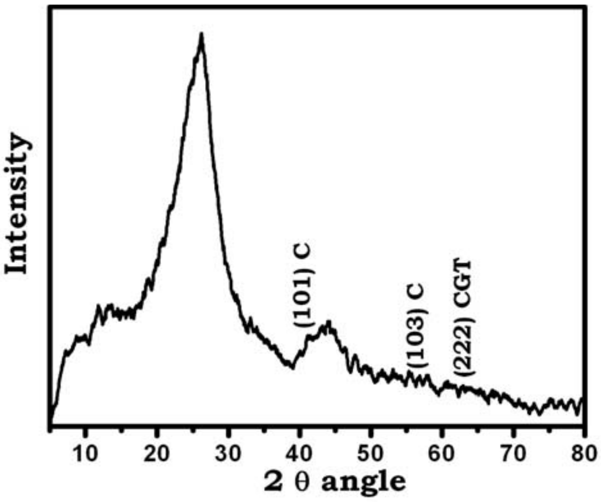


Figure 9. XRD plot of AC3 after test: (T8500C; VHSV: 1.62 Lit/hr.g)

The presence of highly broad and irregular patterns of X-Ray diffractograms (Figure 8) of AC3 may be accounted for amorphous state of the sample. The diffractograms shows a single peak at 2θ angle of 62.22^0. Using the Pdf -2 release ICDD database 2003, it has been found that the sample has a (108) type of orientation of atoms along its plane. Whereas the XRD (Figure 9) of post catalyzed sample (AC3-used), shows few modifications in the diffractograms. The raw scan detected three peaks at a 2θ angle of 42.717^0, 57.244^0 and 62.936^0 with (101), (103) and (222) orientation of atoms along its plane. Based on the Pdf-2 release ICDD database 2003, the first two peaks corresponds to carbon, where as the last peak shows the presence of theoretical graphite (CGT) possibly showing the presence of low quality graphene structures in the form of micro fibers as seen in the SEM image (Figure 6).

5. Conclusions

A bench scale unit for producing hydrogen by methane cracking has been designed and developed indigenously. Five number carbon samples namely carbon black, special abrasion furnace and activated carbons from three different sources namely: hard wood, vegetable and coconut shells have been investigated for hydrogen production.

- The similarity in the behavior of special abrasion furnace and carbon black may be due to their amorphous nature resulting in steady state methane conversion which can go on for several hours.
- Activated carbons have higher initial activities but as time progresses their activities fall. This may be due to loss in surface area and total pore volume.
- Among all the carbon catalysts, activated carbons produced from coconut shells (AC3) showed promising results with average conversion levels of 16 mole%, initial methane cracking rate of 0.623 mmol/min.gm of catalyst and sustainability factor of 0.33. The sample AC3 also produces 564 mg of carbon /gm of catalyst in 4 hours duration.

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