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# Catalyst behavior of plasma state in methane decomposition to hydrogen and solid carbon

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***Abstract*** **–** A novel continues plasma reactor with rotating electrodes was designed and constructed to investigate methane decomposition to hydrogen and solid carbon. This new reactor structure causes stable operation. Hydrogen is main part of gaseous products which contain little amounts of $C_2$ hydrocarbons while, carbon is deposited in solid phase. It was shown that plasma has catalyst property because, it causes reaction to happen at much lower temperatures due to generation of enough reactive species for reaction initiation and provides additional adjustable parameters toward selective production of hydrogen. By rotation of high voltage electrode, plasma state approaches non-equilibrium state and therefore its catalytic role becomes apparent which is beneficial in terms of energy efficiency as a major challenge facing methane decomposition. Methane conversion and energy efficiency reached around 60% and 40% respectively.

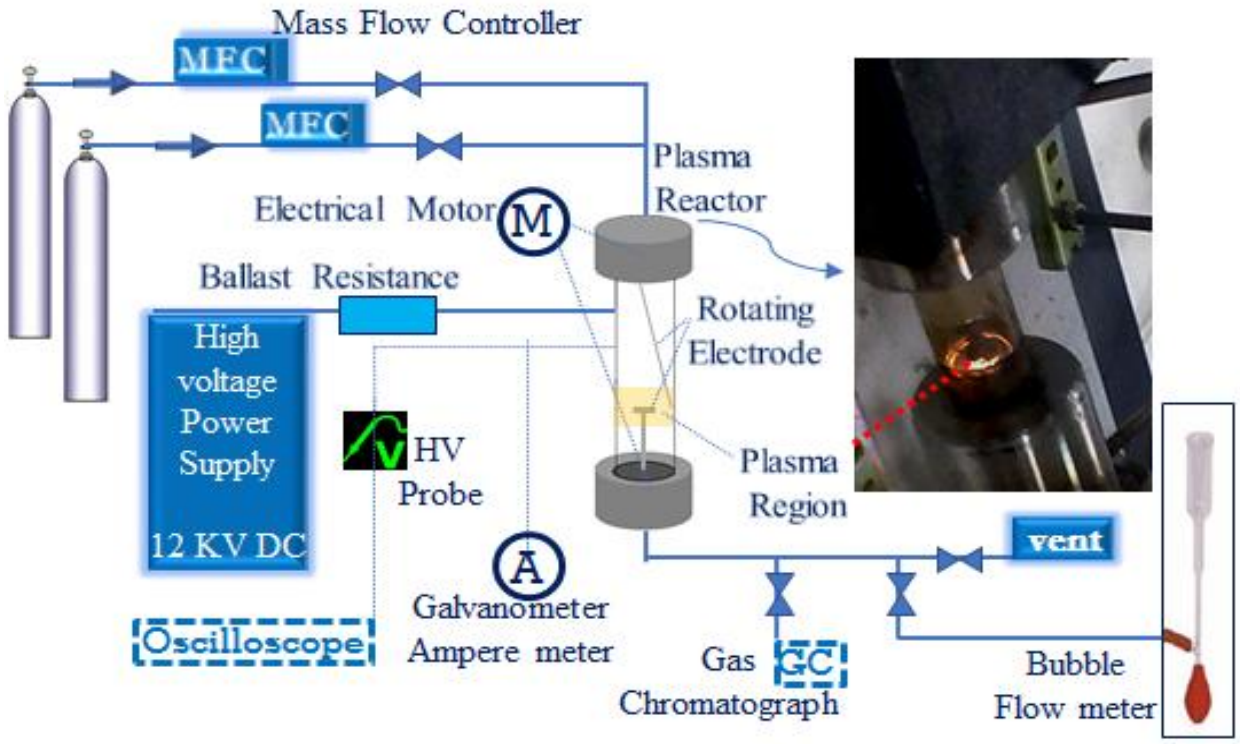
*Keywords – Methane, Decomposition, Hydrogen, Plasma*

## I. INTRODUCTION

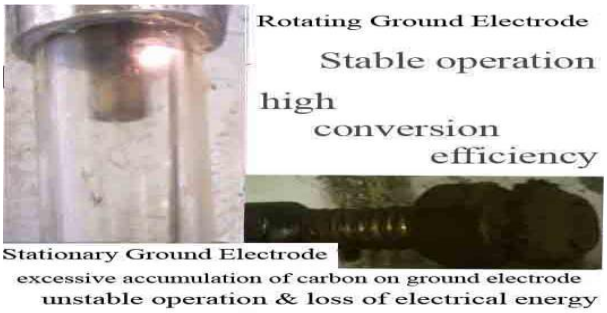
Economy and environment are two main concerns in energy sector regarding sustainability issue. Hydrogen is an important source of green energy and methane, the major constituent of natural gas, is a good source of hydrogen due to its high hydrogen to carbon atom ratio and its availability. Direct decomposition of methane into hydrogen and solid carbon has no potential of global warming since this process is free from COx emission. Many experts believe that hydrogen is main candidate for sustainable and clean energy in near future. Also regarding energy storage issues hydrogen is among alternatives as an energy carrier [1]. Hydrogen is conventionally produced through steam reforming of hydrocarbons. However, high CO2 emission is a major environmental problem facing steam reforming these days. In comparison, catalytic methane decomposition seems to be a suitable alternative. Generally catalytic methane decomposition requires high heat for the process which by itself emits large amounts of CO2. Also, catalyst in addition to its own concerns such as deactivation, charging, discharging and etc. forces the process design to take into account pretreatment unit for gas purification due to catalyst poisoning problems. Catalysts such as iron [2], ceria, zirconia and lanthana supported nickel [3], nickel-copper based [4], silica porous solids [5], carbon active [6] and etc. have been comprehensively investigated for this purpose. On the other hand, many studies have been carried out for reforming of hydrocarbons by using plasma reactors [7-11] which could be as alternative. Some used hybrid system of plasma and catalyst, e.g., [12-14], while others used only plasma [15-17]. In present study, a new type of plasma reactor with rotating electrodes is developed which will increase the degree of non-equilibrium state to some extent which is a forward step in this technology. In this reactor, the plasma zone due to external rotary force linked to the high voltage and ground electrodes is itself in rotation which makes it possible to investigate effect of operating parameters such as feed flow rate, plasma power, and velocity of arc rotation in a more independent manner. It is worth mentioning that the present design has conceptual differences with those reported by other authors, e.g., [18, 19]. The arc in all those studies is rotated by the force of fluid flow and therefore there exist high order of dependency and interaction between operating parameters. In previous version of the current reactor only the ground electrode was rotating and arc discharge was fixed as reported by the authors [20-23].

In this study, certain improvements are done to produce a homogeneous discharge due to arc rotation which leads to more stable operation as well as increase in energy efficiency.

## II. EXPERIMENTAL SET UP




Describe Experimental setup consists of three main parts namely feed supply system, power supply system and reactor. Gas tanks, mass flow controller, steel tubes, on/off valves and connections are parts of feed supply system. Variable auto-trans controls high voltage of transformer which is manually coupled by diode and capacitor in our laboratory in order to have direct current (DC). Due to high electrical conductivity of plasma zone, reactor and ballast resistance (1MΩ) were connected in series in order to prevent sudden current rise and damage to transformer. Fig. 1 shows schematic of electrical diagram and experimental set-up. Methane and Argon were both 99.999 % pure and were supplied from separate gas tanks by mass flow controllers andionized gas exists. In all experiment feed enter the reactor at room temperature (28 oc -30 oc) and atmospheric pressure. Argon dilutes gaseous stream for gas chromatography. Input and output flow rates of reactor were measured by bubble flow meter. Plasma power measuring system consisted of high voltage probe (PINTEK HVP-39pro), oscilloscope (GW Instek, GOS-620), and galvanometer ammeter. Produced gas was directed to the inline calibrated Gas Chromatograph (GC, Agilent, 6890N) for composition analysis. Generally, plasma reactors are known to have rapid startup time. GC had a flame ionization detector (FID) and also a thermal conductivity detector (TCD). Reactor structure is shown in Fig. 1.




## III. RESULTS AND DISCUSSION

In methane decomposition process, collisions between energetic electrons and CH4 molecules lead to formation of either active species that continue further reactions or to formation of products. Hydrogen is major constituent of gaseous product with little amount of C2 hydrocarbons while, carbon is deposited in solid phase. Due to electron collisions in addition to standard thermodynamic reactions plasma chemistry has a complex nature. Electrons impact create active species while reactions between radicals belong to standard thermodynamic reactions. To interpret experimental results, reaction zone is thought to include plasma zone where electron collision reactions are dominant as well as recombination of active species with each other or initiation of new elementary reactions. Also, we propose that carbon atoms and hydrogen radicals that exist in the plasma zone, subsequently undergo

Fig. 1 Experimental set-up.

carbon deposition and initiation of thermodynamic reactions respectively.

Excitation, ionization and dissociation are main reactions in plasma zone. Electron collisions provide ions and cascade of electrons which create electrical conductive gas zone called plasma. Excitation rate for methane and ethane decomposition in atmospheric pressure plasma jet is insignificant. Also, to reduce complexity ionization rate is ignored in this study and only dissociation reactions are considered.

### *A. Reaction path way*

Excitation, ionization and dissociation are main reactions in plasma zone. Electron collisions provide ions and cascade of electrons which create electrical conductive gas zone called plasma. Excitation rate for methane and ethane decomposition in atmospheric pressure plasma jet is insignificant [17]. Also, to reduce complexity ionization rate is ignored in this study and only dissociation reactions are considered. From theoretical point of view solid carbon could be formed by electron impacts or radicals' reaction in plasma zone. Accepted mechanisms for carbon formation by radicals' reactions are on the basis of PAH or C2H2 formation [24, 25]. However, in plasma zone of the reactor both temperature and residence time are quite low and even if PAH & C2H2 were produced they would be stable with no chance to undergo carbon nucleation to form solid carbon for deposition. Therefore, electron impacts are responsible for carbon deposition, i.e., breaking of molecular bonds of methane by electron collisions. On the basis of aforementioned analysis, reactions path way for methane decomposition in the plasma zone of reactor is proposed (Fig. 2). With reference to this path way, dissociation reactions are responsible for solid carbon deposition while, production of C2 hydrocarbons are attributed to standard thermodynamic reactions.

The target product "hydrogen", is produced by radicals' reactions while it may again dissociate to atomic hydrogen by electrons collision. The chemical reactions presented in Fig. 2 are based on kinetic suggested by Sinaki et al. [26]. It is important to note in cold plasma reactor the required energy to break methane bonds is not supplied by a high temperature heat source, but it is the electrons high energy that upon collisions with methane molecules create active species in the plasma region which have ability to initiate thermodynamic reactions at even near ambient temperatures. Therefore, it could be said plasma possesses catalyst role as well in such process. Generally, time scale for plasma reaction is extremely short (Nano seconds) [27]. Hence hydrogen which is the target product is formed as soon as electrical discharge occurs. Consequently, local H2 concentration at discharge zone increases causing probability of undesirable reaction of hydrogen dissociation to increase instead of desirable electron collisions with reactant (CH4) molecules. Also, the zone away from electrical discharge does not effectively participate in the reactions. On the contrary, rotation of the high voltage electrode causes occurrence of arc rotation as well which would lead to better distribution of species resulting in higher conversions.

### *B. Methane conversion*

*Methane conversion at different stable operation conditions of feed flow rate, plasma power and electrode velocity are illustrated in Fig. 3. Increasing power and reducing flow rate causes increase in methane conversion. Also effect of power on conversion rise is pronounced as flow rate decreases, i.e., residence time increases. It has become possible to study effect of the degree of non-equilibrium state by using the reactor of this study which has rotating electrodes. High voltage electrode rotation will cause only ions to accompany plasma zone due to the force of electrical field and neutral*

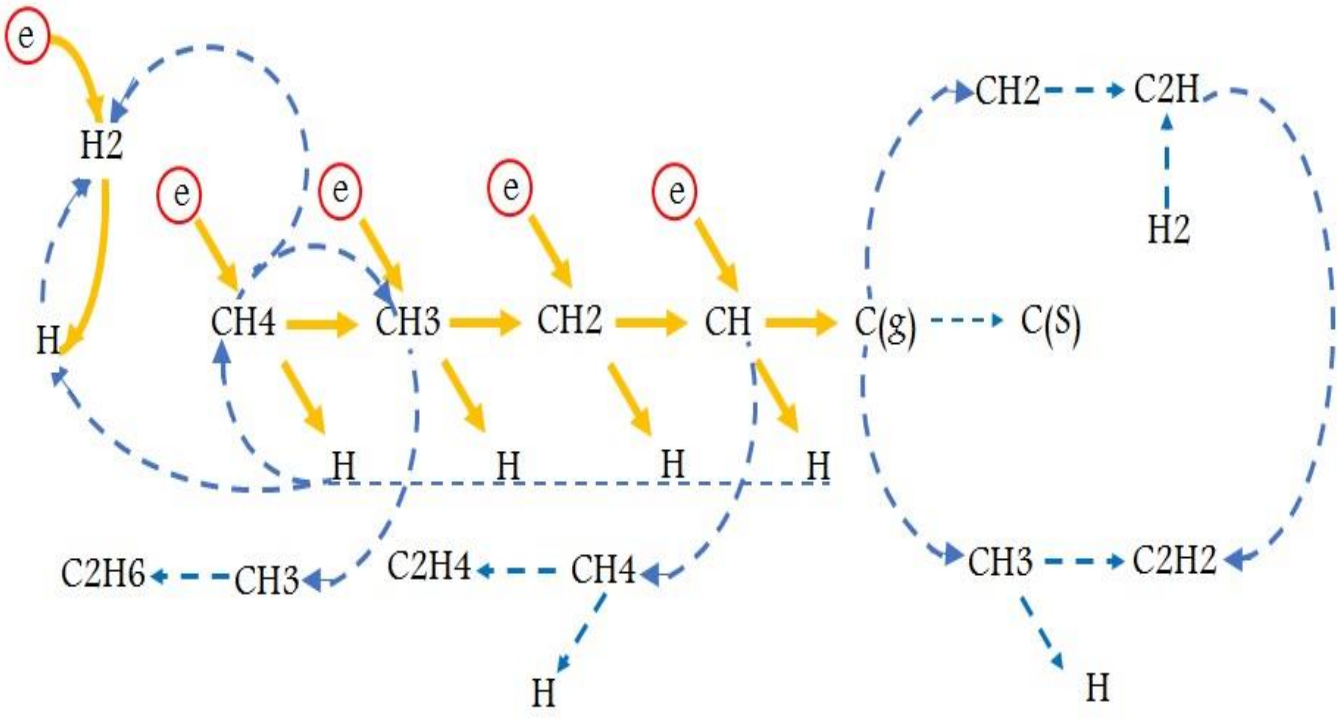



*Fig. 2 Reaction path way*

*species such as hydrogen molecules leave discharge zone and*

*Therefore undesirable reactions of electron collision with them would be prevented to some extent.*

### *C. Energy efficiency*

Energy efficiency is defined as the energy value of produced hydrogen divided by input energy required. Zero electrical power leads to maximum value of **η** around 64%. However, electron collisions are not really fully efficient due to various energy losses especially joule heating, i.e., performance of electrons discharge as a heat source. Approaching non-equilibrium state from quasi equilibrium state of plasma results in more and more efficient performance. Therefore, efforts are needed to try various practical designs in order to provide high order of non-equilibrium state. The idea of rotating electrodes was on this basis. Table 1 presents energy efficiency for rotating high voltage plasma reactor as function of power and flow rate which shows better results (energy efficiency around 40%) compared to stationary high voltage electrode (energy efficiency of around 34%). This is due to achieving higher methane conversion at constant hydrogen selectivity for rotating electrode reactor.

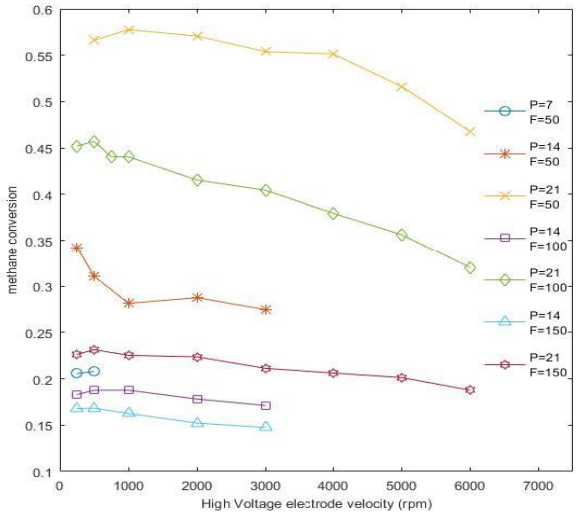



Fig. 3 Conversion of methane versus electrode velocity at various feed flow rate and power

## IV. CONCLUSION

Methane decomposition to hydrogen and solid carbon in a novel continuous plasma reactor with rotating electrodes was presented. This new structure causes stable operation. A reactions path way is proposed which attributes formation of atomic hydrogen and carbon to electron dissociation reactions while hydrogen molecules to standard thermodynamic reactions.

It was shown that plasma possesses catalyst property because, it causes reactions to happen at much lower temperatures due to generation of sufficient reactive species for reaction initiation and provides additional adjustable parameters toward selective production.

Also, it is concluded that by rotation of high voltage electrode, plasma state approaches non-equilibrium and therefore its catalytic role becomes pronounced which is beneficial in terms of energy efficiency as a major challenge facing methane decomposition. Methane conversion and energy efficiency are improved compared to fixed high voltage electrode and reached around 60% and 40% respectively.

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