Plasma Catalytic Conversion of Methane in Ultra Rich Flame using Transient Gliding Arc Combustion Support

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Abstract:

A new approach for hydrogen rich gas or synthesis gas production from hydrocarbon fuels is presented in the present paper. Steam reforming or partial oxidation reaction of hydrocarbon gives syn-gas. But such reactions require high-energy input and catalyst for efficient operation. Plasma was used as a catalyst for the process to achieve maximum efficiency at minimum power input. Transitional non-thermal plasma reactor was fabricated and experiments were carried out. The reactor was based on Gliding Arc in Tornado (GAT) design. Such a plasma catalytic reactor can sustain an ultra rich flame of methane at desired power level and was very effective in achieving this conversion. In this plasma chemical reactor we have high power density and high selectivity of chemical process using transient gliding arc (GA) in a reverse vortex or tornado reactor configuration. Also the discharge is a strongly non-equilibrium, low current, high voltage arc column, which moves over the electrodes with relatively high power density and high electron density for selective partial oxidation of methane. At the same time, this reverse vortex design enhances recirculation of active species and thermal insulation of the reactor zone.

This experimental setup was tested for long hours at different conditions and process parameters were analyzed. The results showed plasma energy cost for this conversion could be as small as 0.06 KW-hr/m^3 of syngas, which is much lower compared to other plasma chemical systems reported in the literature. The experimental results were encouraging and in good agreement with numerical simulation done in ChemKin using GRI 2.11 mechanism for methane conversion.

I. Introduction

Conversion of light hydrocarbons (HC) into synthesis gas (syn-gas) is an important chemical conversion process. Syn-gas, a mixture of hydrogen and carbon monoxide, is used as a major intermediary for the production of hydrogen or other chemical compounds like ammonia, liquid fuels, solvents etc. Commercially syn-gas production can be carried out in a number of ways: steam reforming, thermo-catalytic reforming, partial oxidation, etc. [1]. Syn-gas production from hydrocarbons has specific energy and temperature requirements. Syn-gas formed via endothermic reactions (steam and CO2 reforming) requires high-energy input. The simplest and most efficient way for the large scale production would be partial oxidation [1]. This process involves conversion of hydrocarbon fuel in ultra rich (oxygen deficient) flame. The partial oxidation of hydrocarbons in air is usually described by idealized equation as:

$$C_nH_mO_p + x\,(O_2 + 3.76N_2) \rightarrow n\,CO + m/2H_2 + 3.76(n/2\text{-}p)\,N_2 \quad [\text{when, } x = (n/2\text{-}p)] \qquad (1)$$

The oxygen to fuel ratio (x) determines the heat of the reaction and amount of syn-gas generated. Increase in x, increases heat of reaction but at the same time produces carbon dioxide and water vapor thus reducing the amount of syn-gas generated. For methane the above reaction becomes:

$$CH_4 + 1/2\,(O_2 + 3.76\,N_2) \rightarrow CO + 2\,H_2 + 36\ \text{kJ/mol-}CH_4 \qquad (2)$$

To maximize syn-gas yield the oxygen fuel ratio (x) for methane partial oxidation should be as close to 0.5 as possible. Due to a low standard enthalpy of the above reaction (2), to achieve flame in these regimes, we need efficient combustion support. To achieve this use of highly active electrical discharges (plasmas) has been experimented with during the last decade. Use of plasma sources can provide many advantages such as economically attractive operation, no problems related to catalyst poisoning, continuous flow reactors etc. Cold plasma sources of non-thermal nature (glow discharge, corona etc.) provide chemical selectivity and high energy efficiency but are limited by power level and low pressure

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operation. On the other hand thermal plasma sources including arcs or radio frequency inductively coupled plasma (RF ICP) discharge are associated with Joule heating and thermal ionization. They enable to deliver a high power at high operating pressures. However low excitation selectivity, a very high gas temperature and serious quenching requirements limit their use for this application [2].

There are also discharges with plasma parameters between those of the thermal and cold non-thermal discharges called the transitional non-thermal discharges, where the gas temperature increases considerably but the discharges still are not in the thermal regime. Gas temperature in the case of transitional discharges is in the order of 2,000-4,000K, which is much less than the electron temperature (>10,000 K) [3]. The ionization of gasses in transitional discharges is defined by direct electron impact or step-wise electron ionization [4]. Such transitional discharges can be achieved in Gliding Arc (GA) reactor. GA reactors in flat geometry for this purpose have been experimented with before. But in this kind of reactor a lot of gas flows around the arc so it has many disadvantages like not enough residence time in plasma, loss of active species very fast, initial high temperature regime, etc. that make the process less efficient. A new GA approach by the authors called the Gliding Arc in Tornado (GAT) to achieve transitional plasma is used [4].

II. Gliding Arc in Tornado (GAT)

GAT reactor (Fig. 1) design, based on cylindrical geometry, generates transitional plasma in a volumetric continuous flow reactor providing uniform flow treatment. Reverse Vortex Flow (RVF), which is very similar to the natural tornado, is set up inside the reactor. It has a circular disc shaped electrode and a spiral electrode both are arranged such that they are locally parallel to the streamlines thus causing minimum disturbance to the gliding arc. These two electrodes in RVF are in effect diverging electrodes in the "plane" of the flow. As high voltage is applied the arc is ignited at the smallest gap between the spiral and flat circular disc electrode. The arc is then forced by the strong vortex flow to move down along the spiral electrode and elongate as shown in Fig. 1 b, these pictures were taken at different times with very short exposition. In Fig 1c arcs (1) and (2) would correspond to times T1 and T2 in Fig 1b. Elongating arc demands more power to sustain itself. Thus the voltage on the arc increases and the current drops. As the arc elongates, the electric field and electron temperature increases but the gas temperature decreases. Thus the plasma becomes more non-equilibrium [4]. This, non-equilibrium regime is stabilized in the reactor by placing a ring, smaller in diameter than the spiral, at the end of the spiral. In this regime the arc is rotating fast on the two electrodes. Both these electrodes are now circular rings in RVF. So in effect they are parallel in the plane of the flow. But the flow velocity near these electrodes is different. This difference in flow velocity causes the arc to elongate further.

Reverse vortex flow provides perfect thermal insulation of the discharge zone form the reactor walls at the same time intense convective cooling of the arc. Also there is a recirculation zone near the exit. Here the active species from the plasma zone are retained inside the reactor [5]. This recirculation is very important for plasma-catalytic reactions. The velocities in the plane of the electrodes inside the reactor are large (> 10 m/s) which is important for moving the arc on electrodes, at the same time volume flow rate is small to give large residence time (> 0.15 sec) in the discharge zone for the current application. All gas flow passes through the discharge zone; this was not achievable in case of flat geometry, in fact in that case most of the gas flow was around the arc.

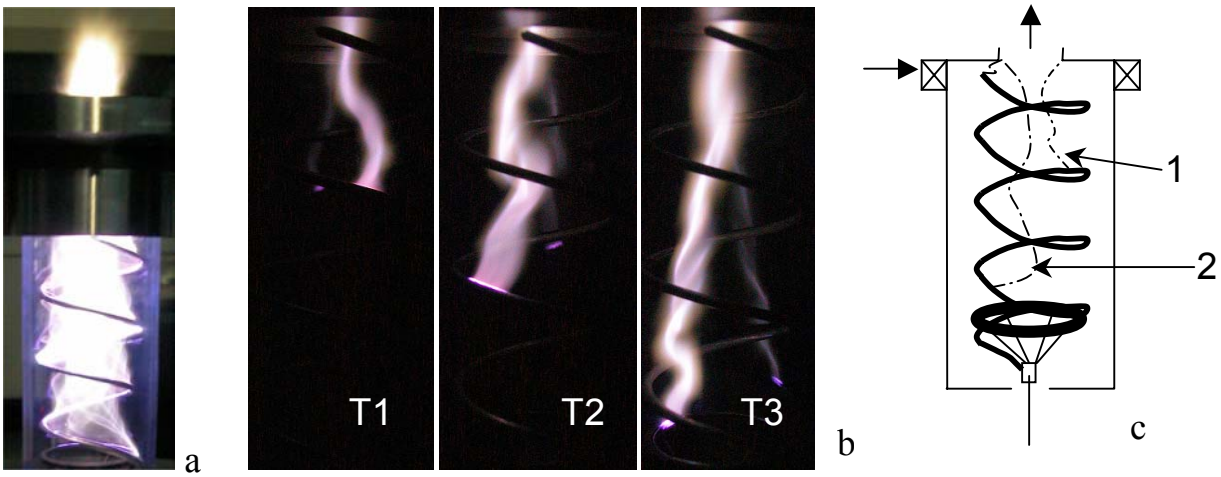

Fig. 1. Gliding arc in Tornado

III. Experimental Setup:

A large-scale laboratory experimental unit for GAT assisted syn-gas generation was developed at Drexel Plasma Institute. This unit had 3 important components: (1) GAT reactor, (2) Power supply and (3) Instrumentation.

GAT Reactor: Gliding arc in tornado reactor consists of a reverse vortex flow chamber with high voltage electrodes arranged inside to get low current high voltage transitional plasma inside this volume. The geometry of electrodes, gas flow rate and characteristics of power supply determine the nature of discharge. In addition a heat exchanger is used for internal heat recuperation.

A schematic of this reactor is shown in Fig. 2. Reacting components for the plasma-chemical process are injected through inlet tubes (1) and (2). These are connected to a counter flow heat exchanger (3) made of inconel. The inconel alloy has been selected for its superior heat and oxidation resistance. The inlet tube (1) exits the heat exchanger and enters directly into a swirl generator (4). The swirl generator (4) has tangential inlet holes into a quartz tube (5) (with length = 150mm and diameter = 44mm) enclosing a cylindrical volume (6). Through this swirl inlet hydrocarbon feed (methane) enters the plasma reactor. This swirling flow is responsible for the gliding of the arc on the electrodes. The outlet (7) from this volume (6) is on the same side as the swirl generator, thus setting up a strong reverse vortex flow. The inlet tube (2) enters this reaction chamber through axial inlet (8) so that it does not cause any disturbance to the reverse vortex that has been setup. This inlet gives flexibility to work as a non-premixed gas reactor system. The circular edge (9) of the outlet hole (7) in the inconel disc acts as the ground electrode for discharge. An inconel spiral (10) is arranged co-axially inside the reactor very close to the walls. The angle of this spiral is made such that it is parallel to the streamlines of the flow avoiding any disturbance to the flow setup. At the end, near the axial inlet (8), this spiral shapes to form a ring (11) smaller in diameter than the spiral (10). The discharge starts at the point (12) when the electric field across the electrodes is high enough. This initial discharge elongates as the swirling flow drives the arc on the spiral electrode. The elongating arc finally reaches the ring (11); since the diameter of the ring is smaller the arc now stabilizes in this low-pressure column and forms a cylindrical column. The arc moves very fast on the electrodes the contact time is very short so we don't see

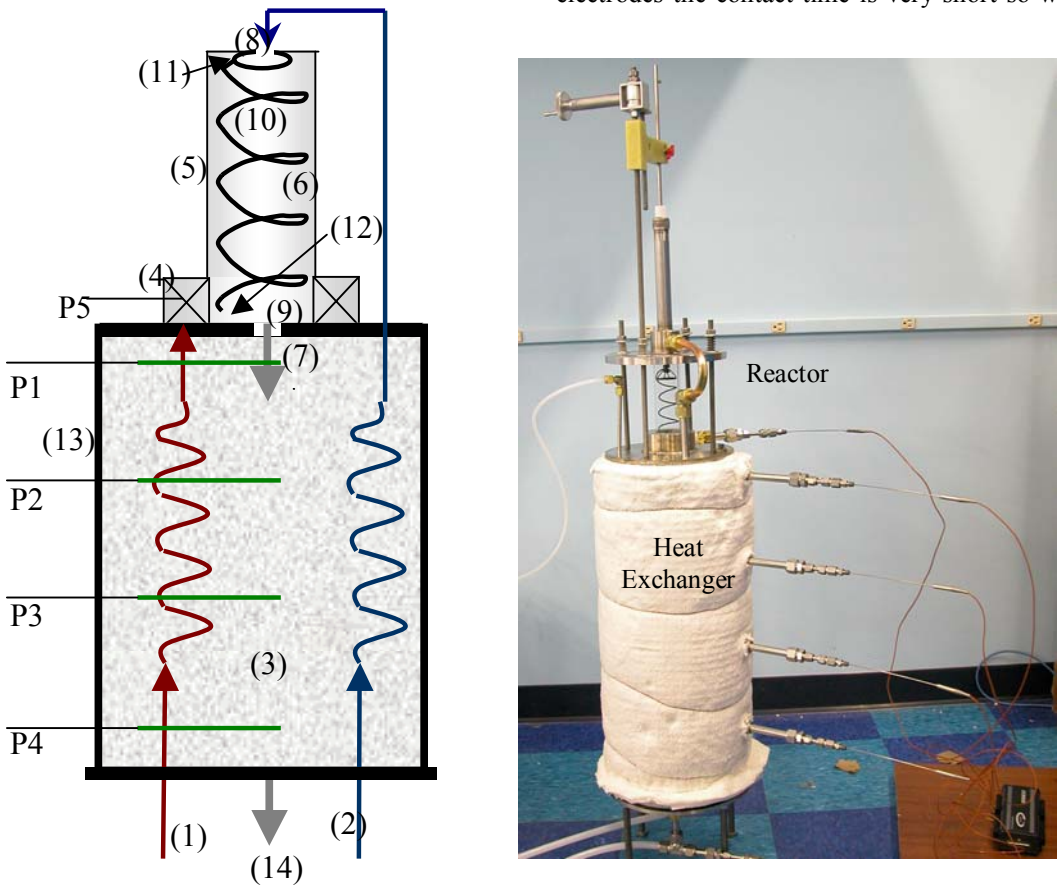

Fig. 2. GAT Reactor System (a) Schematic, (b) Picture of the fabricated system

any deterioration or erosion from the electrode surface. Once the arc is stabilized in the central region its length does not vary much and we have stable low current regime. Even though, the arc is still elongating. This elongation is essentially due to difference in velocity of the gas near the electrodes. The tornado flow obtained in the RVF ensures high gas velocities necessary for the gliding arc and very effective heat and mass exchange at the central zone of the plasma inside the cylindrical volume because of the fast radial migration of the turbulent micro-volumes and deceleration near the tube walls [6]. The reactor is secured by tight end plates and can withstand normal operating pressures of up to 5 atm. Hot gas mixture of partially converted methane enters heat exchanger (3), this also acts as the secondary reactor. The total volume of plasma reactor as well as the heat exchanger is well insulated by Kaowool insulation (13). The design of this reactor was based on two factors: (a) effective heat transfer and (b) enough residence time for reaction completion. These two parameters came from numerical modeling of the process done in ChemKin and discussed later. Probe points (P1-5) are present at different locations in the system to measure temperature and pressure at these points. Through the exit (14) from the heat exchanger (3), the gas mixture is collected for analysis and then finally directed to the incinerator before it is let out to the atmosphere.

Power Supply: The spiral and the ring electrodes [see 10, 11 in Fig. 2] were connected to the high voltage power supply (Universal Voltronics), and the flat circular disc electrode (9) was used as the ground. It was possible to change the resistance applied in series to the plasma channel from 12 KΩ to 200 KΩ in order to have the flexibility to vary the power characteristics of the gliding arc. The initial breakdown for 10 KV occurred (in air) at about 3 mm gap between anode and cathode. Subsequently the arc was elongated according to the reactor geometry.

Instrumentation: Measurements of temperature, pressure and gas composition were carried out using various analytical instruments. Omega data acquisition board and thermocouples are employed to get temperature readings at different points on the heat exchanger, outlet gas temperature, inlet temperature (at the plasma reactor) and exit temperature. Dwyer rotameters gave inlet flow composition. At the out flow Siemens Ultramat 22 gives composition as regards to CO and CO2 percentage in the mixture. TSI hot wire probe gave thermal conductivity of out flow and thus hydrogen concentration in the gas mixture. HP 5970 GC/MS (gas chromatogram / Mass spec.) gives concentration of CO, CO2 and hydrocarbons from C1 to C6. California instruments NOx analyzer helped in determining NOx concentrations in outflow process.

IV. Numerical Modeling:

The authors earlier reported numerical simulation (pure Chemistry) for a similar system [7]. The time evolution of the chemical composition of the flowing methane-containing mixture has been modeled using the specially developed numerical code. The entire process includes three main stages:

1.) Electric discharge stage.

2.) Mixing of air and post discharge hydrocarbon.

3.) Post discharge regime.

Only the swirling methane flow drives the gliding arc so for modeling of the above process it is considered that discharge exists only in methane. The electric discharge operates in two regimes: thermal (heating effect) and non-thermal (dissociation). In the post discharge region the gas mixture is allowed to react within a certain residence time, no other energy input is present here. The neutral species chemistry was described by the GRI-MECH 2.11 kinetic scheme including 65 species and 200 reactions [7]. All the input conditions for this modeling were optimized for minimal electric power and maximum conversion.

The syn-gas production is characterized by two stages: the first, the short combustion zone, and, the second, the longer zone, which can be called as a reforming zone. At the first stage the concentrations of O and OH radicals are relatively large, and it is characterized by very fast chemistry, close to the combustion chemistry. This stage is over, when no more oxygen is available. Fast methane combustion reactions are exothermic here, and the gas temperature increases at this stage. At the second stage, much slower chemistry takes place. Water, CO2 and CH4 are consumed, yielding hydrogen and CO, the corresponding reaction are endothermic ones, causing the observable temperature decrease. The chemical transformations, favorable to the hydrogen production, are stopped, when the temperature becomes somewhat smaller. First, we studied the dependence of conversion degree and energy cost of syn-gas production on the equivalence ratio between methane and oxygen. The complete partial oxidation conversion corresponds to the equivalence ratio 4:

$$CH_4 + 1/2\ (O_2 + 3.76\ N_2) \rightarrow CO + 2\ H_2 + 36\ \text{kJ/mol-}CH_4$$

The conversion degree, methane energy cost, electric energy cost (plasma power), total energy cost and efficiency of the system as a function of equivalence ratio, are determined for this system with plasma acting to enhance the reaction extent. Experiments were carried out for these and corresponding numerical simulation calculated. The conversion degree α was calculated taking

into account an amount of methane transformed into hydrogen and CO:

$$\alpha = ([H2] + [CO]) / 3[CH4] \text{ in.}$$

Some amount of methane is transformed obviously into water and CO2. Here [X] refers to the volume or mass flow rate of X after the reactor and [X]in refers to the inlet flow rate of X.

The electric energy cost is calculated taking into account the total electric power W_{el} and the amount of syn-gas produced:

$$\text{Electric Energy Cost} = W_{el} / ([H2] + [CO])$$

Methane energy cost is calculated using total methane input and converted to commercial unit KW-hr. per unit of syn gas generated:

$$\text{Methane cost} = [CH4] \text{ in}/([H2] + [CO]).$$

Total energy cost is the amount of energy spent to get one meter cube of syngas, so it takes into consideration both electric energy cost and methane energy cost.

Total energy cost = Electric Energy cost + Methane Energy cost (J per meter cube).

All of the above energies are defined and calculated in KW-hr, which is industrial unit and most widely used.

Efficiency of the system is best defined in terms of energy efficiency of the process. We take fuel as input, which as some energy value and we produce syngas, used as fuel. So the ratio of these energies is the efficiency of the system:

Efficiency = KW-hr of syngas produced / Total energy input in KW-hr.

V. Results:

Numerous tests were conducted on the pilot unit with atmospheric air and methane. The system was kept running for several hours at different conditions. The experimental results: the conversion degree (methane conversion to syn-gas) and energy cost analysis were plotted vs. the equivalence ratio.

Conversion Degree is a good measure of the system performance and evaluation as shown in Fig. 3. Numerical results (curve in fig 3) show that the conversion is best for equivalence ratio 3.0 to 3.6, and not 4.0. This is because of the fact that as we go to lower equivalence ratio we have higher heat in the system.

This heat helps achieve better conversion and reaction rates. Experimental points as shown in fig. 3 are in good agreement with the numerical results.

Electrical Energy is added to the system in the form of plasma power. Plasma acts as a catalyst and thus this power should be optimized. We should not spend too much power on one hand and lesser power should not restrict the extent of reaction on the other. See Fig. 4. At high equivalence ratio the heat of the system is low so more plasma power is required. But as we decrease the equivalence ratio we need lesser power and we achieve a minimum power level, which again rises as production rates start decreasing rapidly. Comparison with Experimental results reveal similar trend. Experimental values of power required are just lower this signifies the importance of reverse vortex geometry and positive impact of recirculation.

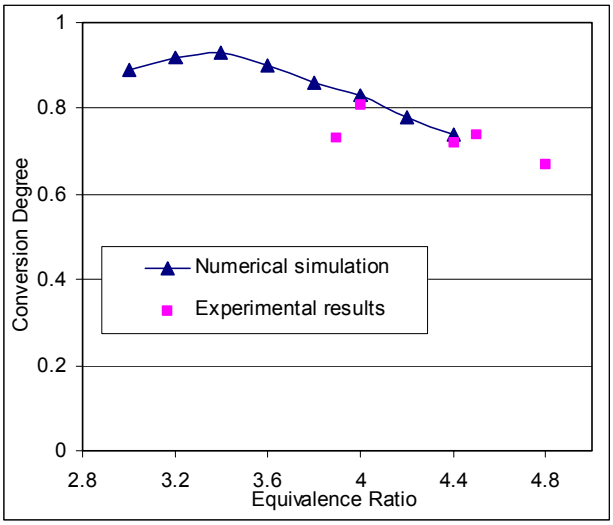

Fig. 3. Conversion Degree vs. Equivalence ratio

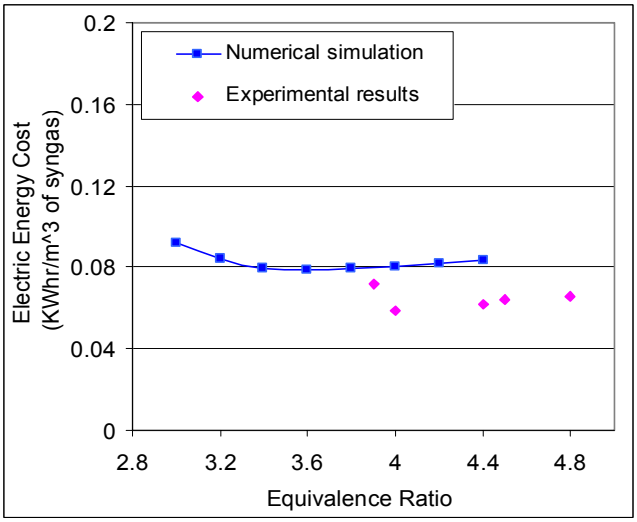

Fig. 5 Efficiency of the system vs. Equivalence ratio

In addition to electric energy for plasma we spend methane as input to the system. Methane is raw material for syn-gas generation but it's also a fuel which has some energy associated with it. So in all we input some energy to the system (methane +electricity) and we get syn-gas, which is potentially again a source of energy.

In such a system one of the best parameters for analysis would be efficiency based on energy ratios as defined above. The maximum thermodynamic efficiency of a methane to syn-gas system can be 0.84 shown by the dotted line in Fig. 5. This is achieved considering that we convert each molecule of methane to 3 molecules of syngas and there are no losses form the system. Efficiency achieved for the pilot plant, in long experiments was about 68% (maximum) and is in full agreement with the numerical simulation.

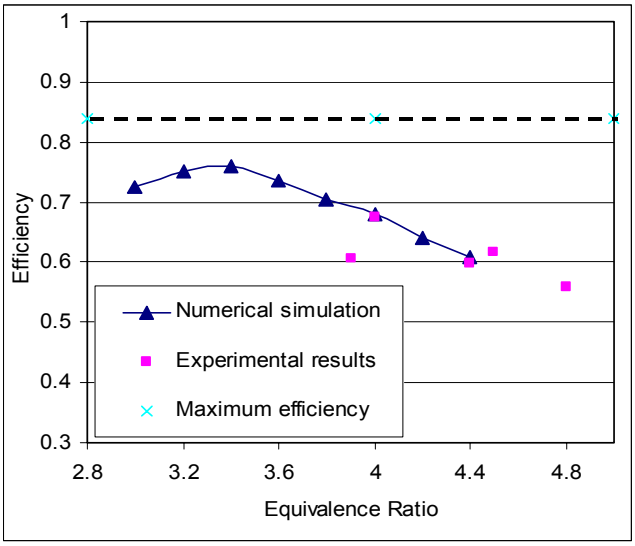

Fig. 4. Electrical energy vs. Equivalence ratio

Discussion:

Experimental system built for syn-gas production from hydrocarbon fuel was tested and evaluated based on various production parameters. Syn-gas was generated in this continuous volumetric flow reactor pilot plant at output of about 1.1 L/S. Electric energy spent in the process was as low as 0.06 KW-hr/m^3 of syn-gas. High chemical process selectivity is obtained using GAT. GC/MS analysis of the reactants shows no production of C2 to C5 hydrocarbon species.

The experimental system worked predominantly at higher equivalence ratio. This was due to the fact that since methane flow was driving the arc there was a lower limit to this flow rate. Lower equivalence ratio can be achieved by designing fine nozzle for gas injection. The system can run continuously without the need of any maintenance, as there are no consumables, electrode erosion or cooling requirements. In fact the reverse vortex burner stabilizes flame at very high equivalence ratio without any combustion support. In that case we have very low conversion to syn-gas and high soot formation. This result signifies the importance of selectivity of chemical processes that can be achieved by non-thermal transitional gliding arc discharge.

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