PLAMSAS FOR GREENHOUSE GAS UTILIZATION

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Introduction

Natural gas is considered the energy source of the future, because it is environmentally friendly with clean and low carbon emissions. However, it is not an easy-to-transport fuel. Unfortunately, many of the large proven reserves are located far away from the major markets, and it is not economical to transport the gas to the markets.

Methane, the major component of natural gas, is currently used primarily for its heating value. However, methane has a tremendous potential to be used as a building block to form other more valuable fuels and chemical feedstock. In indirect methane conversion processes, methane is first converted to synthesis gas, a mixture of CO and hydrogen, either via partial oxidation or steam reforming of methane. From synthesis gas, chemicals can be produced via many routes, or hydrogen can be extracted and used as a clean fuel used to power fuel cells. These indirect methane conversion processes are energy-intensive and less feasible at small capacity due to the high operating cost of the syngas generation unit.

Different advanced gas conversion technologies are desired to utilize and monetize the natural gas resources, whether it is stranded gas or not. From methane, different chemicals such as oxygenates, unsaturated C_2 hydrocarbons, and heavier hydrocarbons could be directly produced via different routes. The gas conversion technology using the non-equilibrium plasma generated by the AC corona discharge is such a technology, which can be used to convert methane to hydrogen and C_2 hydrocarbons under atmospheric pressure and room temperature.

The applications of indirect gas conversion technologies can be dated back before the 1950s. These technologies were based on the Fischer-Tropsch reaction (FT), discovered in the 1920s by the German scientists Franz Fischer and Hans Tropsch. They heated coal to produce synthesis gas, which when passed over a metal catalyst produced liquid hydrocarbons. Since synthesis gas can also be produced from natural gas, several processes have been designed and built to make liquid hydrocarbons from natural gas (GTL process). SASOL, the South Africa's state-owned oil company, is the most experienced in GTL processes. They have built GTL plants since the 1950s. Exxon-Mobil also has a 10 thousand barrel per day plant in Bintulu, Malaysia, in which synthesis gas was produced using pure oxygen. Other major energy companies such as Cocono-Phillips are developing similar GTL processes, which would be built on large scale.

Non-equilibrium Plasmas

Non-equilibrium plasma technology has been used to convert methane to various products. It can be non-catalytic or catalytic.[3-25] Methane is converted to other products, such as C_2s and synthesis gas, under the temperature and pressure conditions that traditional chemistry cannot.

The non-equilibrium plasma is a type of plasma, in which the electron has much higher energy or temperature than the neutral gas species.[2, 3] In the non-equilibrium plasma, total number density of the charged particles is much less than the total number density of the neutral particles. When a potential difference is imposed across a gaseous mixture, the electric field acts upon the charged particles such as the electron but not the neutral species. The interaction transfers energy from the field to those charged particles in terms of kinetic energy. The electron, due to its light weight, is accelerated to higher velocity in the time between collisions. The electron has higher kinetic energy than the energy of gas molecules in random motion, if the applied field is high enough. Then, the non-equilibrium plasma is generated.

There are five common types of non-equilibrium discharges: glow discharge, silent (dielectric barrier) discharge, radio frequency discharge, microwave discharge, and corona discharge. The corona discharge is not homogenous, while the silent discharge is considered homogeneous and both can occur at atmospheric pressure conditions. This is the plasma type used in most recent work when a high voltage AC or pulsed waveform on the order of several KVs is applied across two metal electrodes. In the case of the silent discharge, a dielectric barrier such as glass electrically isolates one or both electrodes. The average electron energy in these discharges is in the range of 1-10 eV and both cause only a small degree of ionization.[2]

The only commonly known industrial application using plasmas to produce chemicals is ozone production using the silent (DBD) discharge. However, plasmas have been used in large screen plasma televisions. The electron in the traditional CRT TV, emitted by an electron gun and accelerated via a strong electric field, is replaced by the electron initiated inside the plasma. The plasma TV can be as thin as 4 inches and as large as 72 inches.

Equilibrium Plasmas

The non-equilibrium plasma is different from the thermal plasma, or equilibrium plasma, in which all particles have approximately the same high temperature or kinetic energy. Thermal plasmas will not be discussed here as they may be generally regarded in many respects as conventional high temperature homogenous processes, with some exceptions. Also, these plasmas typically have prohibitively large energy input that is unsuitable to cost effective methane and CO_2 utilization. An intermediate category might be considered for plasmas that are nearly thermal, but of more moderate temperature. An example would be what might be called an igniting plasma in which the primary purpose of the plasma is to provide a rapid preheating of the gas where once the plasma has initiated the reactions they become thermally self sustaining.

Partial Oxidation of Methane

Many efforts have been concentrated on the partial oxidation of methane using the AC plasmas. Liu[4] introduced helium into the methane-oxygen feed as a diluting species. The frequency was in the range of 10 Hz to 60 Hz. With methane to oxygen ratio varying from 2 to 10, it was reported that as the oxygen mole fraction increased, the methane conversion and the carbon monoxide selectivity increased, however, the ethane selectivity decreased. The ethylene selectivity did not change much. Theoretically, it is expected that hydrogen and acetylene be present in the product. However, these two species were not reported in this work.

The partial oxidation of methane using helium as a diluting species was also conducted in a higher frequency range from 150 Hz to 300 Hz.[8] It was reported that increasing the oxygen mole fraction up to 20% increased the methane conversion and decreased the C_2 selectivities. Hydrogen and acetylene were not reported, as in Liu's case. This could be due to the limitation of the GC analysis. Even though the C_2 yield was said to reach a maximum at 0.6 atm helium

partial pressure, the major C_2 product was ethane, which is not a very useful product. The CO_x selectivity did not change noticeably. This implies that helium does not help the partial oxidation of methane.

The partial oxidation of methane using the AC plasma was also studied by Caldwell.[9] The operating frequency was between 100 Hz and 800 Hz, covering the higher frequency range that previous works left. Increasing the oxygen mole fractions from 5% to 33% was reported to increase the methane conversion and energy efficiency. The CO_2 selectivity varied from 1% to 6%, suggesting that over-oxidation of methane was not excessive. The methane throughput compared to Liu and Hill's could be eight times higher, while the obtained methane conversions were in similar range, confirming that it was more energy efficient not to use any diluting species such as helium in the feed. The hydrogen selectivity was as high as 55%. All C_2 hydrocarbons and CO_x were reported in the products as expected. At 33% oxygen mole fraction in the feed, the carbon monoxide selectivity reached 55%. The lowest energy consumption was 6 eV per methane molecule converted. In addition to pure oxygen, air was used as the oxygen source. The energy consumption when using air was higher than the energy consumption when using pure oxygen. The lowest energy consumption reported in the air-methane system was ~15 eV/molecule of methane converted, higher than that in the methane-oxygen system, suggesting that nitrogen dilutes the feed and decreases the reaction rates. This result is consistent with the results from the methane-oxygen-helium system.

In Liu's work, it was reported that under a constant applied voltage, the methane conversion reached a maximum at 30 Hz. The maximum C_2 yield, obtained at 60% conversion of methane, was around 20%. It was explained that as the frequency was reduced to 30 Hz, the discharge changed from the corona discharge to the spark discharge. According to Eliason,[2] this change occurs when the applied voltage has exceeded a threshold. This implies that as the frequency was reduced the actual applied voltage to the electrodes increased. Therefore, at 10 Hz and 20 Hz frequencies, the discharge should also be the spark discharge. The authors did not give an explanation why the methane conversion at 10 Hz (~ 5%) was much lower than that at 30 Hz (~ 58%). The change in the input power with varying the frequency was not reported. Thus, there was no reported conclusion if the frequency influenced the energy efficiency of the system.

Hill[8] also studied the effect of frequency with the same approach as Liu. It was reported that the methane conversion decreased when the frequency was increased from 150 Hz to 300 Hz, and the applied voltage was kept constant. The input power decreased from 15 W to 10 W, and the methane conversion decreased from 32% to 17%. Therefore, the energy efficiency did not change much within this frequency range.

Similarly, Caldwell[9] studied the effect of the frequency with a different approach. Instead of keeping the applied voltage constant, the input power was kept constant. It was reported that the methane conversions were similar at the frequencies between 100 Hz to 800 Hz. The experimental data, such as flow rate, power, and oxygen ratio, were not reported.

Supat[7] and Caldwell[9] reported that increasing the input power by changing the frequency or increasing the applied voltage resulted in increasing the methane conversion. However, as the input power reached a certain threshold, excessive coke formation started. It could be because the heating of the bulk gas led to thermal dehydrogenation of methane to form coke.[9] A higher input power would allow more energy to form more CH and CH_2, which are less stable than CH_3. Therefore, there were more CO, unsaturated C_2s as well as coke produced, when the input power increased.

Hill[8] reported that at a constant feed flow rate and applied voltage, increasing the gas gap between the two electrodes increased the methane conversion. It could be explained that increasing the gas gap increased the residence time, therefore, increased the methane conversion.

The Steam Reforming and the Combined Steam Reforming with Partial Oxidation of Methane

The conventional steam reforming normally involves high temperature and catalysts. However, plasma technology allows it to be carried out at much lower temperatures. Hammer[10] used the silent discharge in a Dielectric Barrier Discharge (DBD) reactor to study the steam reforming of methane. The steam mole fraction was varied from 50% to 75% at temperatures in the range of 200°C to 600°C. The products included CO_x, C_2s, C_3s, and butane. Based on the author's data, the energy consumption per methane molecule converted was in the range of 50 eV to 100 eV, an order of magnitude higher than the energy consumption in the partial oxidation of methane. High energy consumption has been the main disadvantage of the DBD system.

Supat[7] studied the combined steam reforming and partial oxidation at the steam mole fractions less than 50%. The methane to oxygen ratio (MTOR) was in the range of 2:1 to 5:1. The CO selectivity was as high as 62%. The estimated H_2 selectivity (not reported by the author) was 80%, about 20% higher than that in the partial oxidation of methane. The lowest energy consumption per molecule of methane converted was 9 eV, much higher than that in the partial oxidation of methane.

Also using the combined steam reforming and partial oxidation with air as the oxygen source, Bromberg[11] reported a high efficiency plasmatron producing hydrogen from natural gas using the catalytic DC plasma. The feed conversions were as high as 100%. Most of the methane was converted to carbon monoxide. There was only a small amount of ethylene reported. Even though the input power was high (270 W), the high feed conversions as well as high methane throughput led to a low energy consumption: ~ 0.24 eV/molecule of methane converted. This is the lowest energy consumption ever reported and may reflect more of an ignition phenomena than an initiation phenomena. Since the partial oxidation and steam reforming of methane is thermodynamically favored at high temperatures, the use of catalysts at high operating temperatures helps increase the feed conversions. The plasma source could be considered as an ignition stage providing heat to preheat the gas and the catalysts. As a result, the plasmas could be replaced by a conventional heater without impacting the results.

Dry reforming of methane has been studied using the AC Dielectric Barrier Discharge[22], the AC arc discharge[24], and the pulsed discharge.[21] The CO selectivity above 82% was obtained in the AC DBD[22] and the AC arc discharge.[24] The ethylene selectivity was not reported[22] or was very low (2.3%).[24] On the other hand, the ethylene selectivity, as high as 64%, was obtained in the pulse discharge.[21] The lowest energy consumption per molecule of carbon (including CH_4 and CO_2) converted was 15 eV.[24] This seemed to be more efficient than the steam reforming of methane. However, the energy consumption was still much higher than that that in the partial oxidation of methane.

Conclusions and Prospects

Methane as a greenhouse gas is misleading in the context of GHG utilization in that methane that is consumed is produced for its utilization (or might be recovered for that purpose in relatively small quantities). Thus it seems that the primary impact of plasma

based processes on GHG utilization when converting methane would be to reduce CO_2 emitted as a result of its consumption, e.g. to be more energy efficient than conventional processes. As a crude comparison, methane has an energy content of about 8 eV/molecule and conventional steam reforming is about 70 percent efficient, using direct fired combustion for the input heat, thus approximately 5.6 eV/molecule is retained in the products (hydrogen and CO). For a plasma, the allowable energy "cost" is then about 2.4 eV/molecule. However if this is supplied by electricity, generated with an efficiency of about 35 % (single cycle fossil energy), then the maximum electrical energy that can be supplied competitively is about 0.8 eV/molecule of methane converted. No plasma system has yet achieved this. The silent discharge systems appear to be sufficiently inefficient that this will be difficult to conceive, however some corona discharge results are certainly within an order of magnitude and perhaps substantially closer to this. So there seems to be some promise that improvements may make this achievable and may also apply to steam combined with CO_2 reforming to some extent. This could be particularly valuable where CO_2 is a significant contaminant of the natural gas resource. (Note that CO_2 reforming as a net sink for CO_2, say recovered from power production, is not a net sink for CO_2!).

In the case of partial oxidation, no net energy input is required for convention conversion due to its exothermicity, and therefore even for an ignition type plasma system, the net greenhouse gas "consumption" for a plasma will always be less. Fortunately, oxygen is the most efficient initiator for methane conversion in low temperature plasmas and energy consumption can be quite low under the best conditions, approximately 1eV/molecule. So even here, other factors, such as the ability to operate on a much smaller scale, with less need and cost, for heat recovery, may allow application of low temperature corona type plasma methane conversion even with some loss in net energy efficiency (and therefore greenhouse gas consumption) compared to conventional processes.

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