

THIRD-BODY ENHANCED METHANE CONVERSION IN A DIELECTRIC-BARRIER DISCHARGE REACTOR

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ABSTRACT

A great deal of recent research in fuel chemistry has been focused on the utilization of the vast global natural gas reserves. A dielectric barrier discharge has proven to be an effective method of activating methane, the primary component of natural gas, which leads to the formation of higher hydrocarbons with hydrogen as a byproduct. Carbon chain building begins with the combination of activated C_1 species to form C_2 . C_2 can react with C_1 to form C_3 or react with another C_2 to form C_4 . C_3 may also react with C_1 to form C_4 species. Hydrogen is produced when a carbon-carbon bond forms. The reverse "chain scission" reactions also occur. Olefin production becomes more likely when H_2 concentrations are reduced. Other species, such as helium, hydrogen, and light paraffins have been added to the methane feed stream to determine if they have any synergistic effects on methane conversion or if they alter product selectivity.

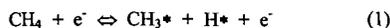
INTRODUCTION

Recent projections indicate that the majority of global oil reserves will be depleted within the next century. Therefore, it has become necessary to study new methods of obtaining the required fuels for the world's vehicles and energy suppliers and to find alternate sources of feedstocks for the petrochemical industry. One plentiful resource that has shown a great deal of promise in relieving the world's dependence upon rapidly diminishing oil reserves is natural gas. Natural gas, which is composed primarily of methane, exists in large quantities trapped within the Earth's crust. Large natural gas reservoirs are found in many different parts of the world, many of which are in very remote locations.

Presently, natural gas is used primarily as an environmentally friendly combustion fuel in industrial processes. Since methane is composed of carbon and hydrogen only, its potential as a building block to form synthetic, impurity-free fuels and chemical feedstocks is significant. Most of the proven technologies for methane conversion are processes that include the initial reaction of methane with high pressure steam to form a mixture of carbon monoxide (CO) and hydrogen (H_2) known as synthesis gas. The synthesis gas can then be converted to methanol using a nickel catalyst or to higher hydrocarbons using an iron or cobalt catalyst via Fischer-Tropsch synthesis. Unfortunately, the methods that require the initial formation of synthesis gas from methane are multi-step processes that have high capital costs that limit their application.

In recent years, extensive research has been conducted on the conversion of methane using single step processes. Some of these methods include the direct partial oxidation of methane to methanol and the oxidative coupling of methane to C_2 hydrocarbons. Each of these processes uses oxygen to activate the methane molecule at elevated temperatures and/or pressures to form the desired products. Unfortunately, these conditions not only result in higher utility and capital costs, the high temperatures tend to favor the oxidation of the desired intermediate species to undesired species such as carbon monoxide, carbon dioxide, and water.

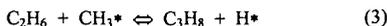
The dielectric-barrier discharge, commonly referred to as a *silent electric discharge*, has proven to be an effective method of activating methane. The silent electric discharge occurs in the gas gap between a pair of electrodes that have the same geometry, that is, between two flat-plate electrodes or in the annulus between two concentric cylindrical electrodes. A dielectric barrier that is often made of glass covers at least one of the electrode surfaces. The dielectric controls the charge transfer within the reactor and promotes a uniform charge distribution. A high voltage alternating current is used to provide the electrical potential across the electrodes. When the potential across the gas gap exceeds the minimum breakdown voltage of the system, a large number of micro-discharges are formed. These discharges are spread uniformly over the electrode surface and in the reaction volume. The discharges produce high energy electrons that interact with the methane molecules and transform the methane into a reactive species.



The resulting reactions lead to the formation of higher hydrocarbons, primarily alkanes, with hydrogen as a byproduct. The carbon chain building begins with the coupling of activated C_1 species to form a C_2 species.



The C₂ species can then react with C₁ species to form C₃ or react with another C₂ species to form C₄. C₃ may also react with C₁ to form a C₄ species. Hydrogen (H₂) is produced when a carbon-carbon bond forms.



The high energy electrons within the reaction zone also cause the reverse "chain scission" reactions to occur. The listed equations are meant to illustrate possible chain building reactions and do not represent a complete and accurate mechanism.

The silent electric discharge reactor (SEDR) is capable of converting over 50% of the methane feed to higher hydrocarbons. Presently, this high conversion requires significant power and lengthy residence times. Since methane is a relatively stable molecule compared to the other species within the reaction environment, the rate limiting step for the chain building process appears to be the activation of the methane molecule. The activation of methane must become more efficient before a process based upon the SEDR can be cost effective.

In an attempt to enhance the activation of the methane molecule, other species have been added to the methane feed stream. Mallinson et al. (1987) and Bhatnager et al. (1995) conducted extensive research using oxygen in the methane feed stream. Oxygen is more easily activated in the electric discharge environment than methane. Therefore, a larger fraction of activated oxygen species would be present than activated methane species under the same discharge conditions. It was hoped that the activated oxygen would interact with methane causing it to activate and react more readily. Their work showed that the presence of oxygen did indeed increase the rate of methane conversion in a SEDR. However, the presence of oxygen also promoted the continued oxidation of the desired intermediate species, primarily methanol, to less valuable products like carbon monoxide, carbon dioxide, and water.

Other species, such as helium, hydrogen, and light paraffins have been added the methane feed stream to determine their effect on methane conversion and product selectivity. These other species were selected because they are either chemically inert or are already present in the product stream when pure methane is run as the feed.

EXPERIMENTAL

A schematic of the silent electric discharge reactor is shown in Figure 1. The reactor system consisted of two metal electrodes made from flat aluminum plates. A dielectric barrier made of glass covered one electrode surface. The dielectric had a thickness of 0.090 in. A Teflon spacer 0.070 in. thick was situated between the dielectric and the opposite electrode. The spacer provided a channel for the inlet gases to flow axially through the reaction zone. The spacer also provided an airtight seal. The total volume of the reaction zone was about 150 cm³.

The back side of one electrode was in contact with cooling water that was maintained at a temperature between 10 and 20 °C. Thermocouples were placed at the inlet and outlet of the cooling water jacket to measure the heat given off by the reaction. No significant temperature change was ever measured in the cooling water. This means that the reactor generated little heat during operation.

Two different power supply systems were used for these experiments. The first system was powered by wall current with a voltage of 220 V and a frequency of 50 Hz that was connected to a step-down variable transformer. The transformer allowed the voltage to be varied from 0 to 110 V while the frequency remained at 50 Hz. The output line of the variable transformer was connected to a secondary high voltage AC (HVAC) transformer. The HVAC stepped up the voltage by a factor of 125. This allowed voltages as high as 15 kV to be generated. The output lines of the HVAC were then connected to the aluminum plate electrodes to generate the high potential required for electric breakdown.

The second power supply used a wall current with a voltage of 120 V and a frequency of 60 Hz. The wall current was used to supply power to an Elgar Model 501SL AC power supply that was able to generate potentials up to 250 V. Connected to the power supply was a BK Precision 5 MHz Function Generator. This instrument generated a sinusoidal waveform and allowed the frequency to be varied over the range used, from 50 to over 300 Hz. Also connected to the output line of the power supply was a Microvip MK 1.2 Energy Analyzer that was used to measure the voltage, current, power, power factor, and frequency generated by the power supply. The output of the power supply was connected to a Franceformer Gaseous Tube Transformer that has a voltage multiplying factor of 125. The high voltage cables from the transformer were then connected to the electrodes of the reactor system.

The volumetric flow rates of the feed and product gases were measured by using soap bubble flowmeters. The analysis of the gas stream was done using a Perkin-Elmer "Autosystem" Gas Chromatograph or a Carle 400 Series AGC. The latter also had the capability of measuring hydrogen. The resulting chromatogram peak areas were converted to mole fractions by correlating the individual gas concentrations to their component peak responses. The correlations were derived from calibrations using known gas compositions.

The pressure within the reactor system was assumed to be approximately atmospheric ($1 \text{ atm} \pm 0.05 \text{ atm}$). Each experiment was conducted at ambient temperature ($25^\circ\text{C} \pm 5^\circ\text{C}$). Any increase in the reactor temperature due to the electric discharge and any exothermic reactions was assumed to be negligible.

RESULTS

Previous experiments with the SEDR were conducted using a feed of pure methane at a flow rate of 20 ml/min. A typical plot of the methane conversion and product selectivity versus applied voltage is shown in Figure 2. The frequency of the alternating current for these initial experiments was 50 Hz. The methane conversion increases significantly as the applied voltage increases. However, the selectivities of the products remain essentially the same.

For the remaining experiments, the applied voltage was set at 4.5 kV and the frequency was adjusted to 100 Hz. The methane conversion was maximized at 100 Hz for this reactor configuration. The molar flow rates for the major chemical species produced from the conversion of pure methane are shown in Figure 3. Since the concentrations of the product species are much lower than that of the feed species, the product flow rates are displayed on an inset graph with a different scale for clarity. The major products for this reaction are ethane and hydrogen. For each carbon-carbon bond formed, a hydrogen molecule is produced. The propane concentration is about a third less than that of ethane while the butane production is about half that of propane. Only a trace of C_2 or higher olefins are produced using pure methane.

Figure 4 shows the molar flow rates of the species produced from the reaction of pure ethane in a SEDR. The overall conversion of ethane is greater than the conversion of pure methane. Ethylene formation is significantly higher than that seen for the pure methane reaction. Also, the concentrations of the higher paraffins, propane and butane, are greater as well. Chain scission to form methane is also significant.

The next test involved adding an ethane fraction to the methane feed stream. The methane to ethane feed ratio was maintained at 4:1. The resulting molar flow rates are displayed in Figure 5. The total conversion of methane was larger than was the case for pure methane. The production of C_2 olefins is much greater than that for pure methane as well. Also, the production rate of propane and butane nearly tripled.

Figure 6 shows the molar flow rates associated with the reaction of ethane and hydrogen at a 1:1 feed ratio. The overall hydrogen to carbon ratio is the same as that for the pure methane case. Like the pure methane experiment, olefin production was very low. However, the chain scission reaction did not completely dominate as one might expect. A significant fraction of methane was formed, but a greater fraction of higher paraffins was formed as well, particularly butane.

DISCUSSION

The product selectivities shown in Figure 2 for the pure methane experiments suggest the following predominant reaction pathway for this feed condition: an activated C_1 species reacts with another C_1 species to form ethane and hydrogen. The ethane may crack to reform methane, or it can react with a C_1 species to form propane or with another C_2 species to form butane. Since olefin production is very low, it is apparent that dehydrogenation reactions are not favored. Also, the reaction of activated species to form unsaturated products is not significant. The high methane to ethane ratios in the exit gas stream suggests that the activation and reaction of methane is the rate limiting step or that the cracking reactions of the C_2+ species dominate.

The data in Figure 4 for the pure ethane experiment shows that although the chain scission reactions are significant, they do not overwhelm the chain building steps. A significant fraction of C_3+ species were formed along with methane. Also, the lower hydrogen to carbon ratio in the feed stream resulted in the formation of a large fraction of unsaturated hydrocarbons through dehydrogenation.

Ethane was added to the pure methane feed to determine its effect on the activation of the methane molecule. The resulting methane conversion was significantly higher than that for the pure methane case. It appears that the active species derived from ethane assist in the activation of methane resulting in enhanced methane conversion to higher hydrocarbons. Again, the lower hydrogen to carbon ratio in the feed stream results in a larger fraction of unsaturated species.

To test the effect of the hydrogen to carbon feed ratio on product selectivity, a feed consisting of an equimolar mixture of ethane and hydrogen was reacted. The ethane conversion

in this experiment was significantly higher than for the pure ethane experiment. Also, dehydrogenation was suppressed by the high hydrogen concentration. Judging from the relatively high ethane conversions for each of these experiments, it appears that ethane is activated and reacts much more readily than methane. These tests indicate that the low activation rate of the methane molecules limits the production of more valuable species for the pure methane feeds.

Several researchers have attempted to enhance the conversion of methane to higher hydrocarbons by adding a chemically inert species to the feed stream. The hope was to find a third-body that would lower the activation energy of the methane molecule without disrupting the conversion pathway to more valuable products. Thanyachotpaiboon et al. (1998) studied the synergistic effect of helium on methane conversion in a SEDR. A helium to methane feed ratio of 1:1 resulted in a significant increase in the methane conversion. If helium did not interact with the methane in the discharge environment, one might expect the helium to serve only as a diluent and cause a decrease in the overall methane conversion due to the decreased partial pressure of methane. These results suggest that some of the helium is "activated" within the discharge environment and aids the activation of methane molecules through a third-body energy transfer. Unfortunately, on an industrial scale, adding helium to the methane feed stream, removing it from the product gases, and recycling it back to the feed may prove to be costly. Therefore, experiments on methane conversion enhancement were conducted using chemical species that are already present in the pure methane reaction process.

Some preliminary experiments have been conducted using propane and butane in the methane feed stream. In these cases, it appears that chain scission begins to dominate the reaction. The product concentrations are similar to those produced from ethane enhanced methane conversion.

CONCLUSIONS

The silent electric discharge reaction has proven to be a relatively effective means of activating methane molecules allowing them to react to form more valuable products. However, the activation rate is presently too low to make this process economically feasible on a large scale. Therefore, attempts have been made to enhance the conversion of methane by adding other species to the methane feed stream. Oxygen, helium, hydrogen, and light paraffins have all aided the conversion of methane with varying degrees of success. With the exception of helium, these species also change the selectivities of the reaction products. These changes may prove beneficial depending on the nature of the application. For example, the formation of liquid oxygenates by using oxygen may be favored in areas where the transportation of liquids through pipelines is possible. Olefin formation by limiting the amount of hydrogen in the feed may be encouraged in industrialized areas where poly α -olefin production takes place.

ACKNOWLEDGEMENTS

The authors would like to express their appreciation to the National Research Council of Thailand, the National Science Foundation for sponsoring a Graduate Research Traineeship in Environmentally Friendly Natural Gas Technologies, and the United States Department of Energy (Contract DE-FG21-94MC31170).

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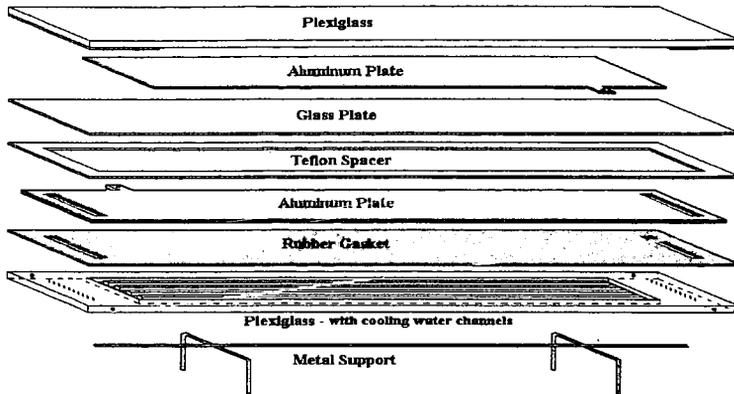


FIGURE 1: A DIAGRAM OF THE SILENT ELECTRIC DISCHARGE REACTOR.

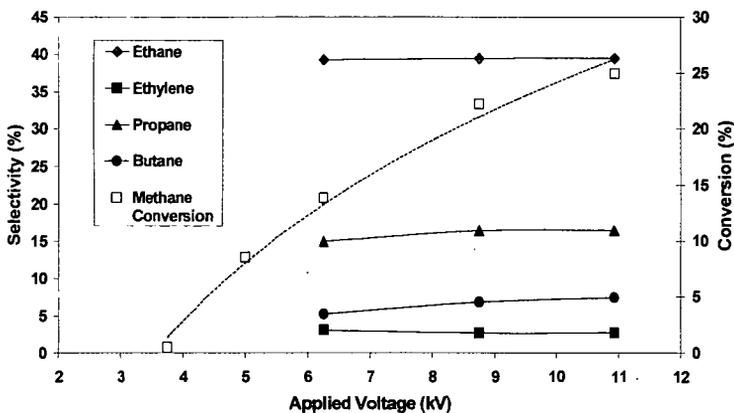


FIGURE 2: DISTRIBUTION OF PRODUCT SELECTIVITIES AS A FUNCTION OF THE APPLIED VOLTAGE. FREQUENCY = 50 HZ

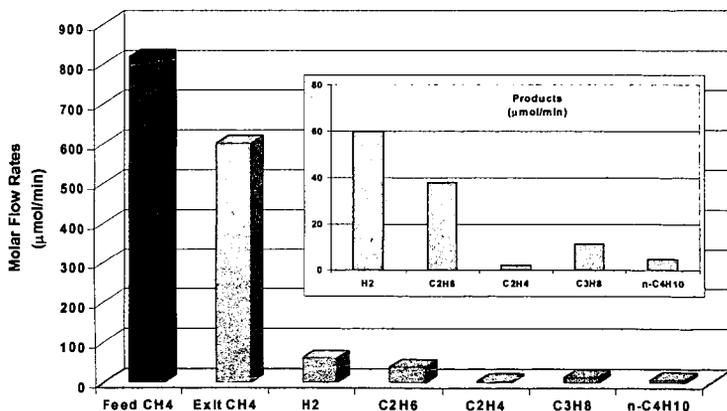


FIGURE 3: MOLAR FLOW RATES OF THE CHEMICAL SPECIES PRODUCED DURING THE REACTION OF PURE METHANE IN A SEDR. 4.5 KV 100 HZ

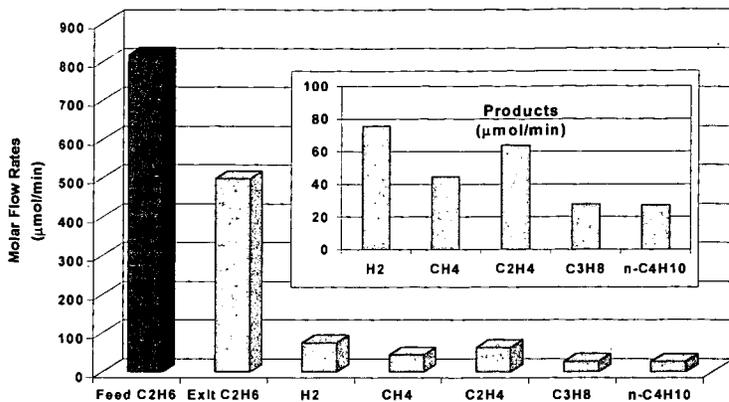


FIGURE 4: MOLAR FLOWRATES OF THE CHEMICAL SPECIES PRODUCED DURING THE REACTION OF PURE ETHANE IN A SEDR. 4.5 KV 100 HZ

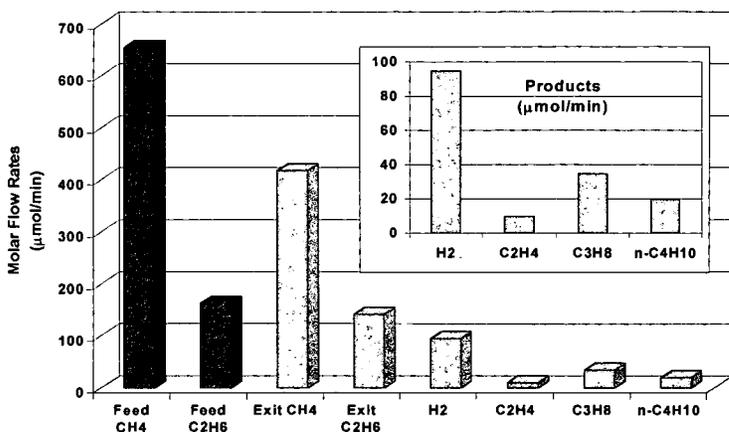


FIGURE 5: MOLAR FLOWRATES OF THE CHEMICAL SPECIES PRODUCED DURING THE REACTION OF A 4:1 MOLAR RATIO OF METHANE TO ETHANE IN A SEDR. 4.5 KV 100 HZ

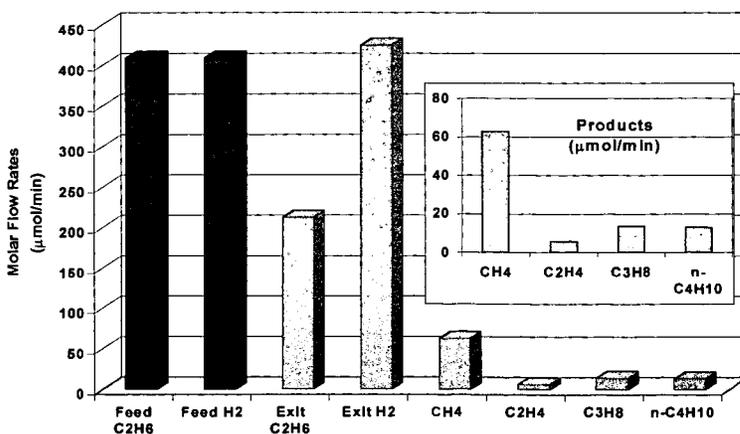


FIGURE 6: MOLAR FLOWRATES OF THE CHEMICAL SPECIES PRODUCED DURING THE REACTION OF AN EQUIMOLAR MIXTURE OF ETHANE AND HYDROGEN IN A SEDR. 4.5 KV 100 HZ