Methane Decomposition and C₂ Hydrocarbon Formation under the Condition of DC Discharge Plasma

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Abstract: The infrared emission spectra of methane, H, CH and C₂ hydrocarbons in natural gas were measured. The processes of methane decomposition and formation of C₂ hydrocarbons were studied. The experiment shows that methane decomposition can be divided into three periods as the reaction proceeds. In the first period, a large number of free radicals were formed. While in the last period, the formation of C₂ hydrocarbons and the decrease of free radicals were observed. The time and conditions of methane decomposition and formation of C₂ hydrocarbons are different.

Key words: plasma, natural gas, methane, spectrum analysis, C₂ hydrocarbons

1. Introduction

The oil crisis has urged people to accelerate the study on the effective utilization of natural gas. The synthesis of C₂ hydrocarbons through methane coupling has become a hot subject since the 80’s in the 20-century [1]. But because of the high stability of methane molecule, it is difficult to get a breakthrough in the conventional catalytic method. So the exploration of other means becomes a new trend recently. Using plasma is not a conventional way of carrying out the reaction. Plasma is regarded as the fourth state of matter. It is a partly or wholly ionized gas. In addition to ground state and excited-state molecule, all kinds of charged particles, such as positive ions, negative ions, electrons, radicals and so on are involved. At present, the study on methane conversion by low temperature plasma has become quite exciting [2].

The method of detection and measurement in this experiment is not the conventional chemical analysis but the spectrum method. It is known that the luminescent spectrum of substances in plasma can be observed when the substance transits from the excited state to a low energy state [3,4]. Colliding with electrons in the plasma, the substance in the ground state can also radiate. The formation or dissociation products can be identified by the method of plasma optical spectroscopy.

The intensity of the spectrum is related to the electric current density and gas pressure. By measuring the intensity of the discharge spectrum under DC discharge conditions, the relation between input quantity giving rise to the optimum yield of C₂ hydrocarbons and electric current density can be established. The time characteristic of methane decomposition and C₂ hydrocarbons formation has been investigated.

2. Experimental

2.1. Experiment system

The equipment for reaction and detection is schematically shown in Figure 1. Natural gas
introduced into an evacuated quartz tube reactor. Plasma was formed by the DC discharge excitation set. Methane was converted under the DC discharge conditions. The strong characteristic spectrum of methane is at 2.3 μm or so, while that of C₂ hydrocarbons appears at about 3.3 μm [5]. By selection of suitable monochromator, windows and receiver, one can definitely and quickly detect the intensity of methane and C₂ hydrocarbons. The detector was made of PbS or InSb. The former was used to detect methane (2.3 μm), while the latter was used to examine C₂ hydrocarbons formation (3.3 μm). However, the effect of thermal radiation must be deducted, which is one of the key factors that affect detection and measurement. In the experiment, the curve of background noise in heat radiation was first measured, and then the effect of heat radiation was subtracted from the experimental data.

2.2. Discharge reaction tube

The plasma generator is of hollow cathode structure, as shown in Figure 2. The inner diameter of the reaction cavity is 6 mm, and the length is 160 mm. The windows, made of quartz or CaF₂, are separately fixed on both sides of the quartz reactor. Because the plasma and electrode area are separated from each other, and the ionization degree is high, spectrum can be measured conveniently.

3. Results and discussion

3.1. The rules of methane decomposition

The curve of methane decomposition can be drawn by experimental data. Regardless of the experimental conditions, the curve can be divided into three zones as the time progresses, as shown in Figure 3 [6].

![Figure 3. The process of methane decomposition][1]

I: the period of violent methane decomposition, II: the period of transition, III: the period of quasi-equilibrium

The period of violent methane decomposition lies between the time of starting the discharge and the point where the spectrum intensity value drops to \( I_p(1 - \frac{1}{3}) \). \( I_p \) means the peak value of spectrum intensity. The rate of reaching its peak value speeds up with the decrease of methane input quantity or the increase of electric current density. But the former plays a more important role in this respect than the latter. The formation of many free radicals can be observed.

For the period of transition, methane decomposition keeps on while formation of C₂ hydrocarbons begins. The rate of methane decomposition is obviously slow, complying with quasi-linear rule.

For the period of quasi-equilibrium, the rate of methane decomposition becomes even slower obeying an exponential rule. The methane decomposition and formation of C₂ hydrocarbons reach a dynamic balance.

3.2. Middle products of methane decomposition

Plasma has a very strong ability to activate reactants, such that methane is excited to become radi-
cals: CH₂, CH₃, CH, H, C. In succession all of these radicals interact and react, and thus C₂ hydrocarbons can subsequently be formed. In this experiment, we measured and detected the spectrum intensity of H (656.3 nm) and CH (431.25 nm), as shown respectively in Figure 4 and Figure 5.

When the input quantity is low, the spectrum intensity of H rises gradually to its peak, and then drops to its equilibrium value, as shown by curve 1 in Figure 4. The process coincides with the violent decomposition period in Figure 3. On the other hand, if the input quantity is high, as shown by curve 2, it is worth noting that the spectrum intensity is weak, mainly because of hydrogen self-absorption. High content of hydrogen in natural gas results in a decrease in spectrum intensity.

Compared with H radicals, the changing process of CH is similar, apart from the self-absorption phenomenon, as shown in Figure 5.

### 3.3. The rules of C₂ hydrocarbons formation

With a given input quantity, the quantity of C₂ hydrocarbons formed increases with the increase of electric current density. However too high an electric current density would lead to the decomposition of C₂ hydrocarbons, thus reducing their yield [7], as shown in Figure 6.

At certain electric current density level, the curves 1,2,3 in Figure 7 indicate that with the increase of methane input quantity, the yield of C₂ hydrocarbons increases, and then reaches a peak value (as shown by...
curve 2). But if the input quantity is too high (as shown by curve 3), the C$_2$ hydrocarbons formed will drop. It can be concluded there must exist an optimum input quantity under the discharge conditions.

On the other hand, if input quantity is high, the time needed for C$_2$ hydrocarbons to reach its peak value is short.

The experiment shows that in such discharge space, methane decomposition is rapid within the first few seconds, then reaching an equilibrium. The decomposition process finishes in 1 minute. Thereafter the formation of C$_2$ hydrocarbons is detected at about 1 minute, and after 2 minutes, the C$_2$ hydrocarbons reach the maximum value. While methane decomposes very effectively in the plasma, the formation of C$_2$ hydrocarbons needs an appropriate time to allow the decomposed free radicals and atoms have enough collision time to form the targeted products. In future reactor design, it should be possible to separate the decomposition of methane and the formation of C$_2$ hydrocarbons in time and space so that each of them reacts under their own optimum conditions.

References


