Methane Polymerization Using a Hollow Cathode

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Introduction

The polymerization of methane, or other low-molecular weight hydrocarbons, in the presence of electrical discharges or in low temperature plasmas, has been the subject of a large number of reports in the literature (1-3). Common features are the operation under vacuum and the production of radicals diffusing towards the reactor wall with subsequent polymerization to a solid product. The gas phase is generally composed of hydrocarbons up to C_5. The polymerization of hydrocarbons can be initiated through the positive-ion molecule type reaction and the radical molecule type reaction (4). The hollow cathode is a medium of high interest for generating a large concentration of highly energetic electrons, leading to the possible formation of CH_4^+ ions.

Preliminary results obtained in this lab (5-6) have shown that methane conversion can be effected using a hollow cathode as the source of polymer initiators. The present work investigates the effects on the process of the cathode metal used (Tungsten, Tantalum and a Tungsten-Platinum solid solution) as well as the influence on the yield of the gas used as a diluent (argon and helium).

Theory

Within the hollow cathode, an atom or molecule is ionized following energy transfers resulting from atom - electron collisions or charge transfer (7). With mixtures of Ar-CH_4 and He- CH_4, the ionization step of methane takes place according to the reactions:

$$Ar + e \rightarrow Ar^+ + 2e \qquad (1)$$
$$Ar^+ + CH_4 \rightarrow Ar + CH_4^+ \qquad (2)$$

Also, argon metastables $^3P_2$ (11.54 eV) and $^3P_0$ (11.72 eV) can be generated:

$$Ar + e \rightarrow Ar^* + e \qquad (3)$$
$$Ar^* + CH_4 \rightarrow Ar + CH_4^+ + e \qquad (4)$$

Similar reactions may occur with He* which presents a metastable level at 19.8 eV, this particle being then much more energetic than the argon metastables. The polymerization then proceeds following the equation:

$$CH_4^+ + CH_4 \rightarrow C_2H_n^+ + n/2\ H_2 \qquad (5)$$

the chain reaction yielding $C_mH^+_n$. Termination of the process occurs when low velocity electrons are available:

$$C_mH^+_n + e \rightarrow C_mH_n \qquad (6)$$

The steps described are not unique and low velocity electrons can also lead to the formation of radicals, this likely occurring at the outlet of the cathode:

$$CH_4 + e \rightarrow CH_3^* + H^* + e$$

$$CH_3^* + CH_4 + H^* \rightarrow C_2H_6 + H_2 \qquad (7)$$

and the process continues through hydrogen abstraction.

Experimental

The reactor is shown in Figure 1. It consisted mainly of an arc discharge with a cylindrical hollow cathode 4 cm long and 0.2 cm thick. The cathode materials used were tungsten, a solid solution of tungsten and platinum and finally tantalum. The anode was made of stainless steel with a water-cooled tungsten discharge tip. The electrodes were located in a cooling chamber where the polymer obtained was collected on the water-cooled walls. A Varian 1015SL quadrupole mass spectrograph was used for the effluent gas analysis. High purity argon and chemical pure (99.9% purity) methane were used in mixtures up to 25% methane by volume. Depending on the experiment, the electrode gap was adjusted between 1.5 and 4.0 mm. The cathode furnace was adjusted to 2400°K while the arc discharge was started and the required methane flow added to the main argon stream. Further adjustments were then made in order to operate at the pre-determined conditions. The duration of an experiment was typically 10 minutes and the initial adjustments lasted about 30 seconds. At the end of the run, the polymer deposited on the cooled wall of the reactor was collected, together with the carbon appearing on the electrodes. They were weighed to the nearest ±0.1 mg.

Results and Discussion

The main product resulting from the conversion of methane using the hollow cathode is a solid polymer. Figure 2 illustrates the relationship between polymer yield, defined as weight of polymer/weight of methane fed, and E/P (E = electric field between electrodes, $V\text{-}cm^{-1}$; P= pressure, Torr). This yield is a function of the average electron energy. The maximum polymer yield is about 50% higher in helium than in argon, the corresponding E/P value for helium being about twice the one required for argon. The higher polymer yields obtained with helium are possibly related to a higher rate of formation of CH_4^+. For instance:

$$He^* + CH_4 \rightarrow CH_4^{++} + 2e \qquad (8)$$
$$CH_4^{++} + CH_4 \rightarrow 2\ CH_4^+ \qquad (9)$$

taking into account the presence of the highly energetic He^+ (ionization voltage 24.6V) and He* (19.8V).

When Helium is used as diluent higher CH_4 concentrations do not seem to significantly affect the maximum polymer yield (Figure 3). In argon, increases in methane concentration lead to decreasing polymer yields as shown in Figure 4 curve 2 B. Higher polymer yields can be obtained at high concentration by increasing the cathode voltage. At high methane concentration only methane, acetylene and ethylene were found in the gas phase which is probably the result of propagation reaction steps having been interrupted by termination reactions with slow electrons or radicals recombination.

Another interesting feature observed in the case of CH_4/He mixtures is the complete absence of carbon deposits. The hydrocarbon species present are characterized by higher diffusivities in He than in Ar (8). This may be responsible for higher deposition rates of the hydrocarbon species present in the gas phase on the reactor wall. It could also, at least partly, explain the decreasing effect of competitive reactions leading to the formation of carbon when argon is used as a diluent gas.

Besides tungsten (work function Q_W = 4.6 eV), tantalum (Q_{Ta}= 4.1 eV) and a tungsten-platinum solid solution were used to study the influence of cathode material on polymer yield. The work function of the W-Pt cathode was evaluated to be 6.5 eV. This result compares rather closely with the 6.3 eV obtained for the Pt cathode.

These cathodes were tested with Ar+CH_4 mixtures. Figure 4 illustrates the comparative behaviour of W-Pt and W cathodes. For 10% CH_4 mixtures a high yield is obtained for the W-Pt cathode, the yield decreasing with increasing electrons energy (curve 1A). For the 25% CH_4 mixture the yield increases with increasing electron energy for both the W-Pt and the W cathodes (Curve 1B and 2B). Tungsten cathodes operating at the same conditions show significantly lower conversions, although the behaviour of yield vs E/P is the same (curves 2A and 2B).

The current density for the W-Pt cathode is estimated to be 10% that obtained with the W cathode. The drift velocity being similar in both cases, one would expect a lower electron concentration (of the same energy) for W-Pt cathodes. As a consequence, lower rates of formation of polymerization promotors and lower polymer yields should be obtained with the W-Pt cathode compared to the W cathode. To explain the higher yields observed the assumption is then made that the W-Pt cathode surface does play a catalytic role whose contribution increases as electron energy decreases (6). Figure 5 shows the relative behaviour of tantalum and tungsten cathodes. Although the thermoemissive characters of Ta and W are rather similar, tantalum does show only an increase in yield with a corresponding increase of electron energy (curve 1C, Figure 6).It is possible that catalytic effects are absent in this case, in opposition to the tungsten behaviour (curve 2A).

Conclusion

Using helium instead of argon in the polymerization of methane, by means of a hollow cathode, increases the rate of polymerization and suppresses carbon formation. These conclusions only apply to low methane concentrations (10%). Tungsten (1), tantalum (2) and a solid solution tungsten-platinum (3) have been used for making hollow cathodes. Besides being the site of highly energetic collisional processes, cathodes 1 and 3 seem to play a catalytic role in the formation of polymerization promoters. In this respect, cathode 3 shows high yields of polymer formation.

Acknowledgement

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Figure 1 Outside view of reactor

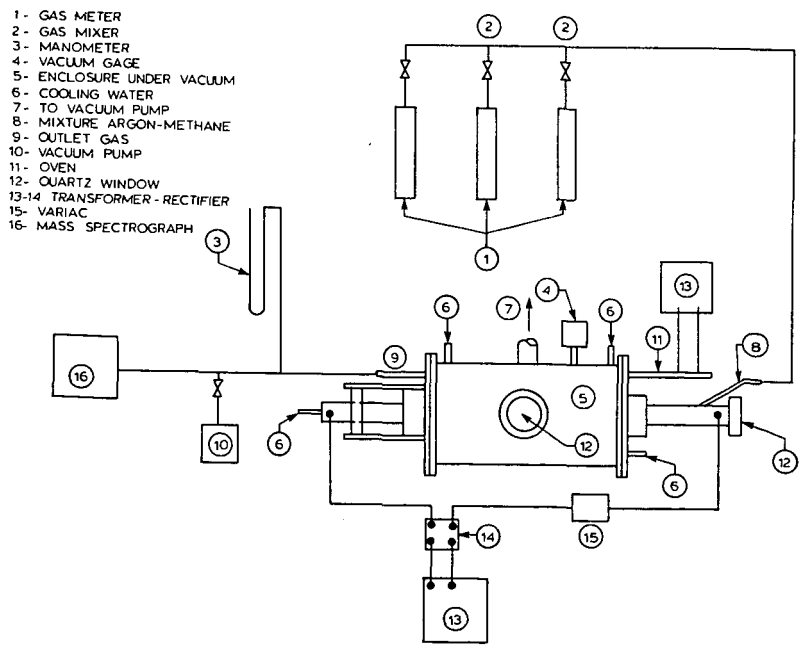

Figure 2. EFFECT OF GAS DILUENT

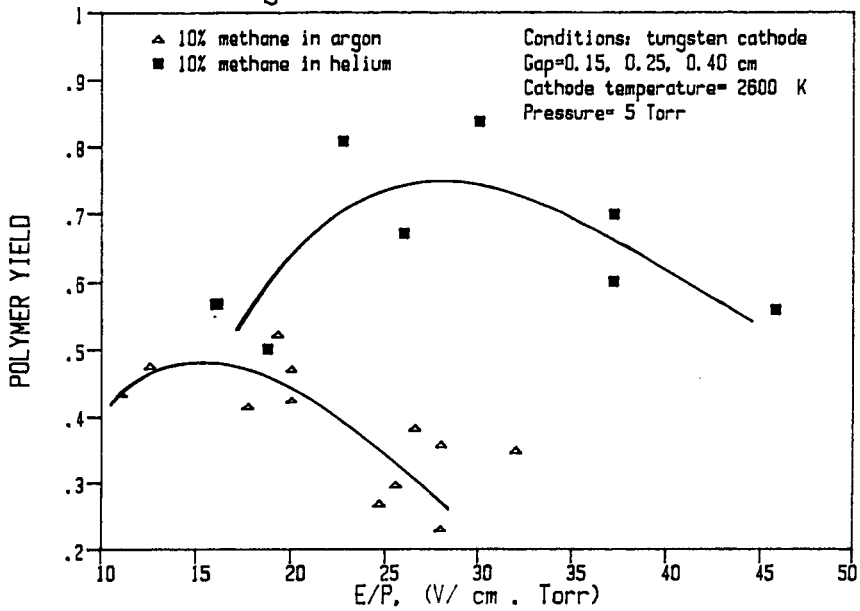

Figure 3. EFFECT OF METHANE CONCENTRATION

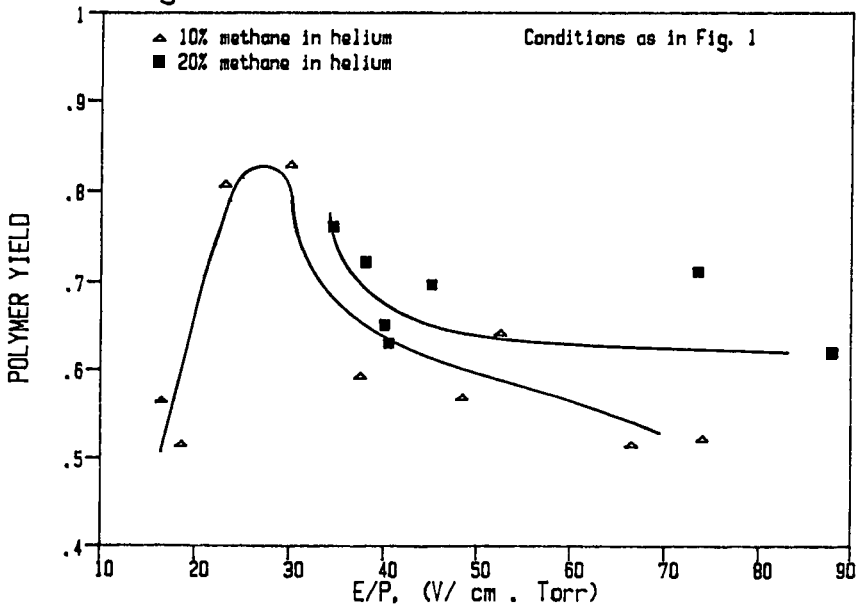

Figure 4. EFFECT OF CATHODE MATERIAL

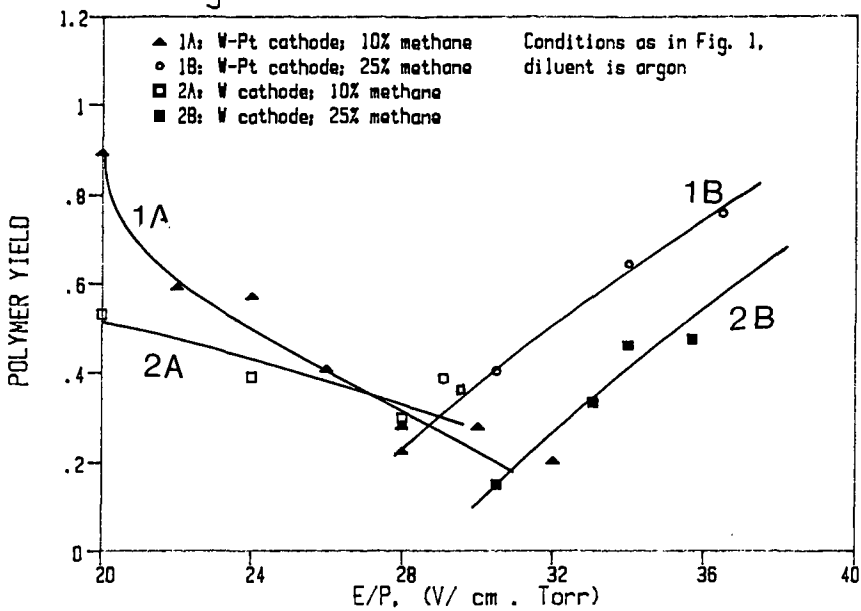
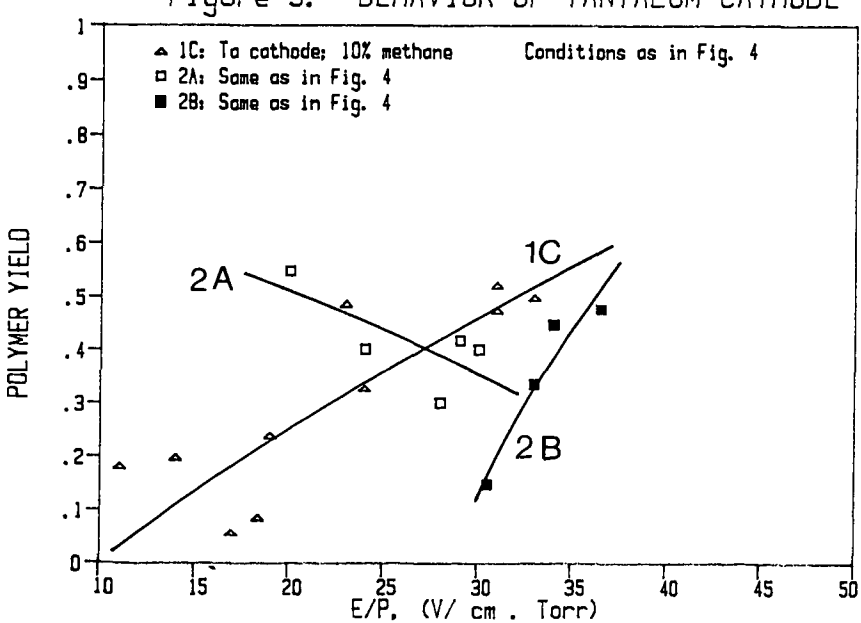
Figure 5. BEHAVIOR OF TANTALUM CATHODE