PYROLYSIS OF PROPYLENE IN FLOWING MICROWAVE PLASMA

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Keywords: Microwave, Electric Probes. Quadrupole.

Compounds: Pyrocarbon from Propylene.

ABSTRACT.

The flowing microwave (2.45 G Hz) plasmas of propylene and propylene-argon mixtures were analyzed by electrical double floating probe system (DFPS) and quadrupole mass spectrometry along the flow stream. The measured electric variables of the microwave plasma were: current density, electric field strength, electron temperature, positive ion and electron concentration. They indicate an irreversible process, of the polymerization of C_3H_6 and C_3H_6 + Ar mixtures, taking place in the plasma. The polymerization process reaches its maximum "down stream", after the position of the microwave cavity. The polymerization was correlated to the concentration of hydrocarbon ions and electrons in the plasma.

1. INTRODUCTION.

The urania (UO_2) Kernels, used as nuclear fuel in the high temperature reactor (HTR), helium cooled, are coated with pyrocarbon[1]. The pyrocarbon is obtained from the pyrolysis of gaseous hydrocarbons (CH_4, C_2H_2 or C_3H_6) in a high temperature (CVD technique) fluidized bed system. The heated C_3H_6-Ar mixture (up to 2000°C) fluidize the UO_2 kernels bed, pyrolyze and polymerize the hydrocarbons to the pyrocarbon deposit as the end product [1,2].

The purpose of using microwave excitation on gaseous hydrocarbons is to investigate the pyrolysis-polymerization processes leading to the formation of the solid pyrocarbon[3].

The diagnostics of the propylene and propylene-argon mixtures flowing microwave plasmas were performed by the electrical double floating probe system (DFPS) and by sampling the plasma by a quadrupole mass spectrometer (QPMS). The DFPS allows the measurement of electric variables

of the plasma such as : current density, electron temperature, electric field strength and concentration of positive ions and electrons in the plasma[3].

The QPMS measures the relative concentration of hydrocarbon ions formed from the C_3H_6 pyrolysis in the microwave discharge.

The hydrocarbon ions, measured by the QPMS, and their concentration allow the kinetic evaluation of ion-molecule reactions in the microwave plasma leading to the polymerization of propylene. The reactions responsible for the polymerization process and their kinetics were reported for a stationary microwave plasma in a previous report[4]. In the polymerization by ion-molecule reactions, the C_3H_6 is for any reaction considered the reactant molecule. The propylene molecules having the highest concentration in the flowing microwave plasma, act as a reservoir for interactions with excited radicals like CH_3, CH_2, CH_5, C_2H_5, etc. and ions such as CH_3^+, CH_4^+, CH_5^+, $C_2H_2^+$, $C_2H_3^+$, C_2H_5, among other hydrocarbon ions with a higher number of carbons[3].

Based upon this consideration the reaction of the hydrocarbon ions with CH_4 molecules are treated as being reactions of the second order type (pseudo first order).

The aims in the present investigation are :

1. Diagnosis of the C_3H_6 and C_3H_6 + Ar microwave plasmas along the stream with respect to the position i.e., before, in the center and after the microwave cavity: The variables of the plasma are expressed as function of flow, pressure, microwave power and position arround the microwave cavity.
2. Evaluation of the influence of Ar on the C_3H_6 microwave plasma and on the polymerization processes taking place in the plasma : Ion density and gradients alog the flow stream with and without argon are correlated to the increase of ionization products of propylene pyrolysis due the addition of Ar to the plasma.

2. EXPERIMENTAL.

The DFPS measuring devices are shown in Fig. 1a together with the flowing system of gases and microwave excitation. The QPMS system for sampling the plasma is shown in Fig.1 b.

Fig.2 shows the sampling positions H, G and F which are identical for both DFPS and QPMS. With regard to the direction of the flowing stream of C_3H_6 and C_3H_6+Ar mixtures, position H samples the plasma before the center of the microwave cavity ($\lambda/4$ Evenson cavity), position G is in the center of the cavity, while position F samples the plasma after the microwave cavity.

The microwave equipments as well the equipment used for the DFPS were described elsewhere[3,4]. The QPMS system is formed from "Balzers 311" quadruple, "Leybold" vacuum equipment with a differential pumping. The orifice (1.0 mm diam) vacumed by the differential pumping (10^{-5} mmHg)

samples the plasma. The position H,G and F were obtained by moving the microwave cavity with respect to the orifice. The mass spectra data is collected and treated by a PDP 11/10 computer (Digital). The output of the data is given by two tables and a m/e plot. The first table consist of the real data of m/e, integral intensity, maximum height of the peak and its width; the second table consist of elaborated data, background substraction and the relative concentration of each mass peak with regard to the summation over the intensity of all mass peaks.

The fragmentation of the hydrocarbon excited molecules and ions in the ionization chamber of the QPMS was avoided by using low electron energy of 22 ev.

3. RESULTS.

Only few results are presented in this preprint. The QPMS results show the pyrolysis of propylene (C_3H_6) to lower hydrocarbon ions (C<3) and its polymerization to higher hydrocarbon ions (C ⩾3) measured in the gaseous state. Among the lower, C<3, species, such as $C_2H_5^+$, $C_2H_4^+$, $C_3H_3^+$, C_3H_3, CH_4^+ and CH_3^+ show relative concentration above 1% while for C>3 hydrocarbons ions in the group C_4, C_5 and C_6 up to C_6H_6 were detected and measured with relative concentrations between 1-5%. In the C_4, C_5 and C_6 groups mainlyunsaturated hydrocarbons were detected resulting with measured relative high concentration ($\sim$ 10%) of H_2^+.

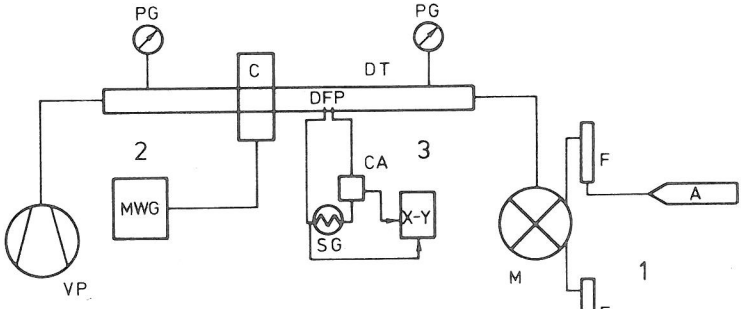
Fig.3 shows the behaviour of the relative concentration, $I/\Sigma I$ of several hydrocarbon ions with microwave power input in position G.and Fig.4 show the behaviour of $I/\Sigma I$ with the total gas pressure in the microwave plasma in position G. Fig.5 shows the behaviour of $I/\Sigma I$ in the different positions H, G and F. The polymerization process leading to the formation of pyrocarbon will be discussed with respect to the reactivity of various hydrocarbon ions with the propylene molecule.

Some of DFPS results are shown in Figs.6, 7. The total positive ion concentration (n_i) and electron density (n_e) in the plasma are given as a function of total pressure in positions H, G and F. The effect of adding argon to the C_3H_6 plasma is shown in Fig.7, in H,G, and F positions. Argon increases the values of n_i.

Based upon ion-molecule reactions model[3,4] the high reactivity in position F for the polymerization processes towards solid pyrocarbon formation, will be discussed.

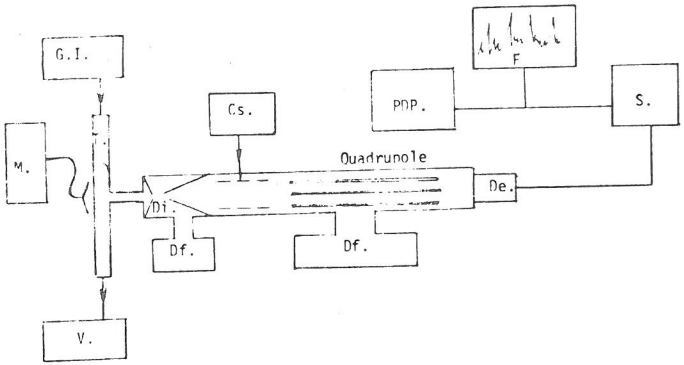
REFERENCES.

(1) E. Gyarmaty, K. Koizlik, P. Krautwasser, H. Luhleich, H. Nickel and H.A. Schulze, KFA, Jül. Rep. 1052 Rw (1974).
(2) E. Pollmann, H. Schuster and H. Nickel, KFA, Jül Rep.1309 Rw(1976).
(3) U. Carmi, A.A. Inspektor, R. Avni and H. Nickel, KFA Jül Rep. 1499 Rw (1978).
(4) R. Avni, J.D. Winefordner and H. Nickel, KFA Jül.Rep. 1188 Rw. Part I-III (1975).



A-Argon Cylinder; B - CH_4 Cylinder; F - Flowmeter; M - Gas Mixer; PG - Pressure Guage; DT - Discharge Tube; DFP - Double Floating Probes; C - $\lambda/4$ Evenson Cavity; MWG - Microwave Generator; VP - Vacuum Pump; SG - Sweep Function Generator; CA - Current Amplifier; X - Y Recoreder

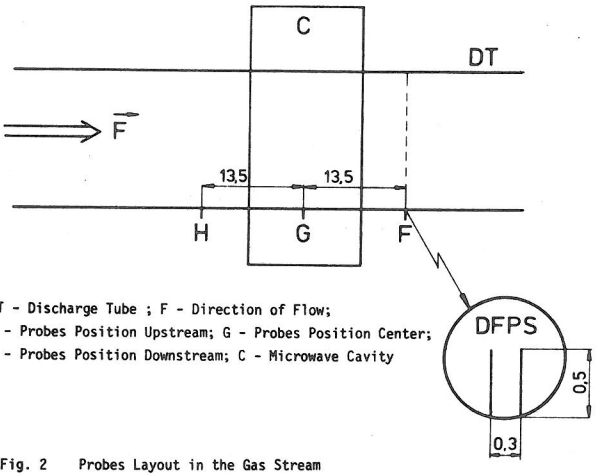
Fig. 1a - DFPS



G.I. - Gas Inlet.
M. - MW. Generator.
T. - Reaction Tube.
V. - Rotary Vacuum Pump.
Di. - Differential Pumping Unit.
Df. - Diffusion Pump.

PDP. - PDP 11/10 Data Processing Computer.
S. - Quadrupole electonic control.
F. - Fast Chart Recorder or Scope.
Cs. - Chamber Controls.
De. - Detector.

Fig. 1b - QPMS



DT - Discharge Tube ; F - Direction of Flow;
H - Probes Position Upstream; G - Probes Position Center;
F - Probes Position Downstream; C - Microwave Cavity

Fig. 2 Probes Layout in the Gas Stream

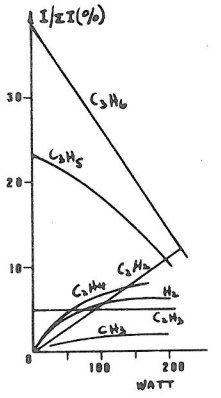


Fig.3.Relative conc. vs. microwave power.

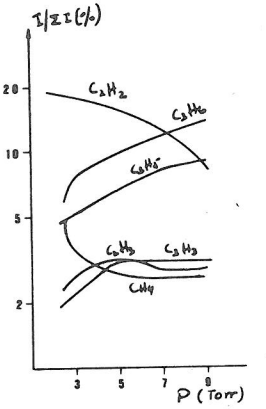


Fig.4 Relative conc. vs. total pressure.

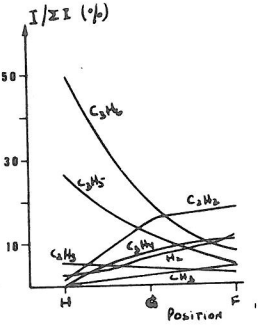


Fig.5 Relative conc. at sampling positions.(H,G,F).

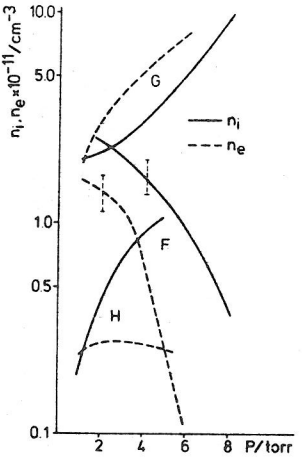


Fig. 6 ; n_i and n_e vs total pressure.

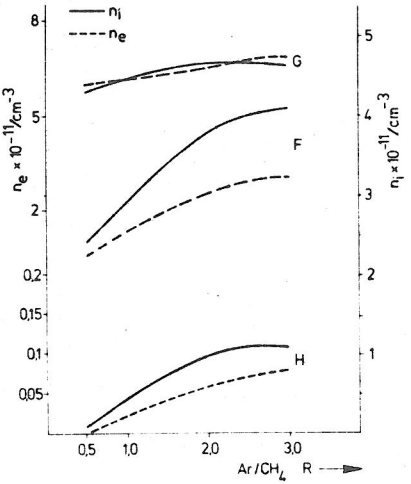


Fig. 7 : n_i and n_e vs Argon-Hydrocarbon ratio.