PYROLYSIS OF LIQUID HYDROCARBONS IN A CHEMICAL PLASMA REACTOR[1])

PŁOTCZYK, W. W.;[2]) Warsaw

A system was studied in which either hexane or decane was introduced into a hydrogen plasma jet or a heat exchanger. The influence of the specific energy of hydrocarbons on the yield of pyrolysis was discussed.

I. INTRODUCTION

Pyrolysis of hydrocarbons in a low temperature plasma jet is an effective source of acetylene and ethylene [1—4]. Acetylene is the main product of plasma pyrolysis of methane. In case of liquid hydrocarbons, apart from C_2H_2 substantial amounts of C_2H_4 are obtained [1—6]. The reactivity of liquid hydrocarbons greatly exceeds that of gaseous hydrocarbons. Liquid hydrocarbons are pyrolyzed not only to C_2H_2 but also to C_2H_4 and other simple gaseous hydrocarbons, and also to soot, particularly at high temperatures of high specific energies of substrates. This presents great difficulties in the realization of a process aimed at the production of C_2H_2 and C_2H_4, and causes considerable limitations in experimental practice. Thus, it is necessary to experimentally determine the variation ranges of the working parameters of pyrolysis. On the other hand, the high reactivity of liquid hydrocarbons can be utilized for the evaluation of the effectiveness of a freezing process in a diaphragm heat exchanger of the "double-pipe" type. In this case the hydrocarbons are introduced into the inlet parts of the freezing chamber. Both these problems were considered in the studies presented.

II. EXPERIMENTAL

Plasma pyrolysis of hydrocarbons was carried out in an appropriately modified reactor like that used previously in the studies of the production of acetylene from liquid hydrocarbons [5, 6].

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[2]) Dept. of Chemistry, Warsaw University, Pasteura 1, 02-093 WARSAW, Poland.

The substrates and the liquid post-reaction mixture (only when decane was used) were examined by an IR and an UV spectrophotometer and by PMR. The spectra were recorded at the Laboratory of Molecular Spectroscopy of the Warsaw Univ. using a Carl Zeiss Jena UR-20 spectrophometer, a Specord UV ViS spectrophometer and TESLA 567A (H¹, 100 MHz) units, respectively.

The experiment were performed at a constant hydrogen flux (4.4 m³/h), hexane flux (3.78 kg/h) and decane flux (3.64 kg/h). The specific energy of the substrate (defined as the ratio of plasma jet power to the hydrocarbon flux) varied by changing the arc discharge power from 18 to 37 kW.

In the studies n-hexane(p) and n-decane(p) (prod. of USSR) were used.

The earlier used experimental methods [5, 6] were modified. On the basis of the volume substrate and of the nature of the gaseous products, the following degrees of conversion (U_i) of hexane and decane into CH_4, C_2H_2, C_2H_4, C_2H_6 were computed by the formula

$$U_i = \frac{V c_i d_i 10^{-2}}{G} \qquad (1)$$

where V is the volume flux of the post-reaction mixture, c_i is the content of the i-products (in %), d_i is the density of the i-product, G the mass flux of the substrate.

The overal degree of conversion of the substrates into $C_1—C_2$ was calculated by the formula:

$$U_{C_1-C_2} = U_{CH_4} + U_{C_2H_2} + U_{C_2H_4} + U_{C_2H_6} \qquad (2)$$

III. RESULTS AND DISCUSSION

The experimental results (concerning the place of introduction of substrates into the reaction chamber) are presented in Fig. 1.

According to Fig. 1, C_2H_2 and C_2H_4 were the main gaseous reaction products. As it results from Fig. 1 an increase in the specific energy of substrates causes a linear rise of effective energy consumption EC_{pl} (for C_2H_2 synthesis) and EC' (for the sum C_2H_2 and C_2H_4) — calculated relative to the plasma jet power. Moreover, with an increase in the specific energy of the substrate, the concentrations of C_2H_2 and C_2H_4 rise. In case of the hexane the concentration of C_2H_2 increases from 7 to 17 vol. % and C_2H_4 from 5 to 8 vol. %. In case of decane, the respective values are 8—16 and 5—7 vol. %. When the specific energy of substrates exceeds 15 MJ/kg, an intensive deposition of soot in the reaction chamber and the inlet part of the freezing chamber takes place.

In another experiment, hexane was introduced into the inlet part of the freezing chamber. The specific energy of the substrate was 9 MJ/kg. Under these

conditions, the decane conversion degree amounted for C_2H_2, C_2H_4, and C_{12} to 9.9, 2.8 and 17.8 vol % respectively. These conversion degrees indicated that pyrolysis of decane proceeds to a slight degree in the freezing chamber as compared with that in the reaction chamber. This suggest the need of modifying the system of the reaction products freezing, e.g. a reduction of the "space" between the external cooler and the front of the internal cooler, as well as the introduction of an additional cold gas flux.
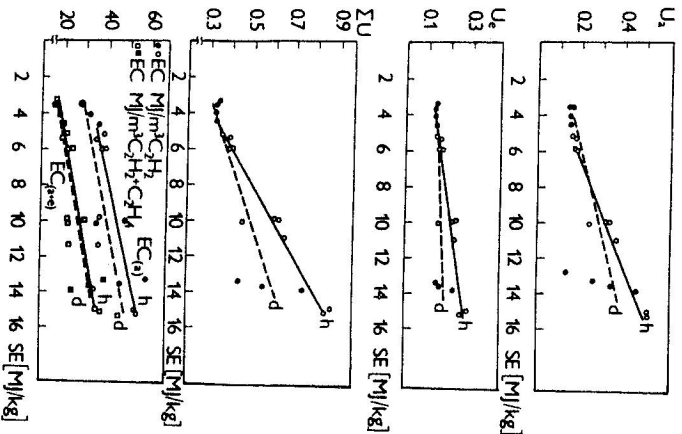

Fig. 1. Effect of specific energy of hydrocarbons on: the substrate — to — acetylene conversion degree U_a, the substrate — to — ethylene conversion degree U_e, the overall substrate conversion degree U and effectiveness of energy consumption EC_{pj} and EC'_{pj}.

In the analised case the energy consumption EC_{pj} and EC'_{pj} was 185 MJ/m³ C_2H_2 and 128 MJ/m³ $C_2H_2 + C_2H_4$, respectively.

The subsequent part dealt with some selected physico-chemical properties of the post-reaction mixture obtained in the experiment with decane at the specific energy of the substrate of 9 MJ/kg. It was found that 99 wt. % were removed by distillation at 345—347 K. It could be assumed that this liquid consists of notreacting decane. The remaining, intensely brown liquid failed to be removed by distillation at temperatures below 573 K. The post-distillation liquid was examined by molecular spectroscopy methods described in [7, 8]. The IR, UV and PMR spectra are examplified in Fig. 2.

An analysis of the UV spectrum indicated that the postdistillation material contained a coupled chromophoric system. According to the PMR and IR spectra, this material is probably a hydrocarbon with a long chain containing a conjugated system including an unknown number of double bonds and aromatic rings.
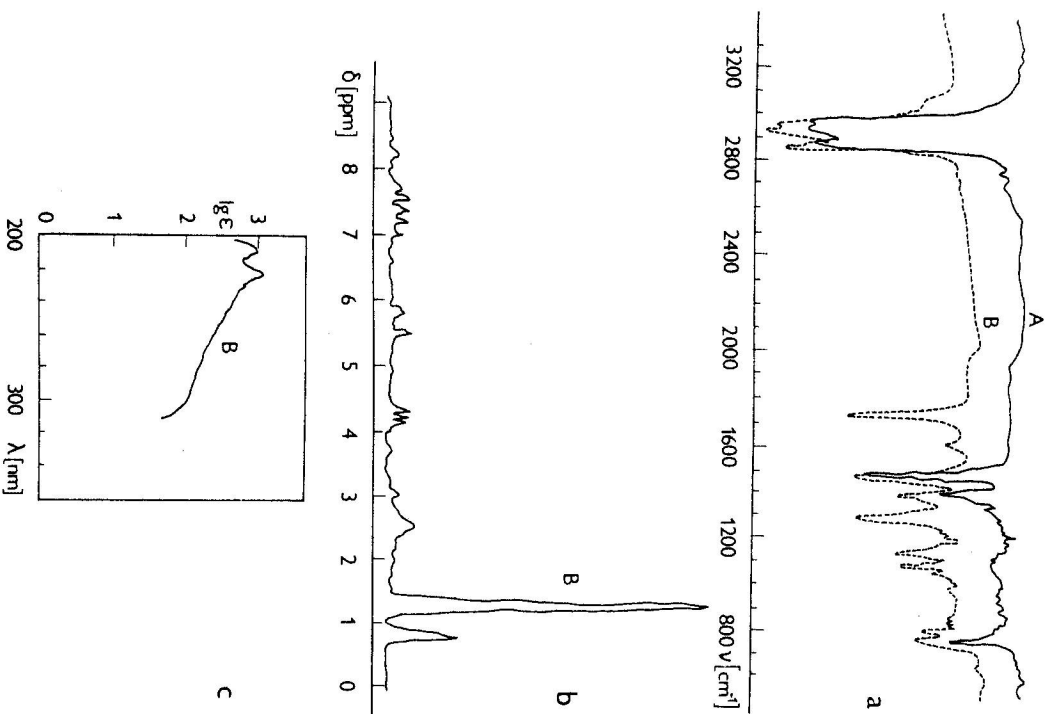

Fig. 2. The IR (a). NMR (b) and UV (c) spectra of the pre-reaction (A) and post-reaction substances (B).

It can be assumed that the action of the plasma jet causes the carbon chain to break into short fragments which are immediately transformed into relatively thermostable products, i.e. C_2H_2 and C_2H_4 and — to a smaller extent — CH_4.

After the formation of the above mentioned short chain fragments a small part of the substrate (2—3 wt. %) undergoes condensation (with dehydrogenation) to a hydrocarbon containing a couplet system of double bounds and aromatic rings.

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ПИРОЛИЗ ЖИДКИХ УГЛЕВОДОРОДОВ В ХИМИЧЕСКОМ ПЛАЗМЕННОМ РЕАКТОРЕ

В работе проведено исследование разложения гексана и декана, вводимых в струю водородной плазмы или теплообменник. Обсуждается влияние удельной энергии углеводородов на эффективность процесса пиролиза.