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PREDICTION OF HYDROCARBON THERMOLYSIS BY THERMODYNAMIC ANALYSIS

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ABSTRACT

STANJAN computer program based on the "Element Potential" method was used to predict the species involved in thermolysis of hydrocarbons or mixtures of oxygen and hydrocarbons.

INTRODUCTION

Thermolysis of hydrocarbons or mixtures of oxygen and hydrocarbons is a conventional process in the petrochemical industry. The determination of working conditions for optimal conversion of compounds in thermolysis processes requires extensive experimental work. Tedious experimental work is usually involved in determining optimal conditions of temperature and volume ratio in thermolysis processes. Consequently it is of great practical importance to be able to predict theoretically the identities of the species involved in thermolysis and try to identify the conditions for optimal conversion [1]. A powerful "menu-driven" personal computer implementation [2] of code STANJAN V3.6 for solving chemical equilibrium problems was employed in this research. The standard P.C. version of STANJAN permits the inclusion of up to 20 compounds in the equilibrium computation. By judicious selection many more than 20 species can be predicted under the same specification of temperature and pressure by repeatedly solving the equilibrium problem with new "minor" species. As an input to the program one has to enter the atomic population of the thermolysis mixture. As the output of the program we get the mole fraction of the 20 compounds. An example of thermolysis of pyridine is presented here.

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MATHEMATICAL MODEL OF THE BASIC THEORY OF ELEMENT POTENTIAL

The Gibbs function of a system is

$$1) \qquad G = \sum_{j=1}^{s} \bar{g}_j N_j$$

where $\bar{g}_j$ is the partial molal Gibbs function and N_j is the number of moles of species in the system.
The partial molal Gibbs function is given by:

$$2) \qquad \bar{g}_j = g_j(T,P) + RT \ln x_j$$

where $g_j(T,P)$ is the Gibbs function of pure j evolved from the system. The atomic population constraints are:

$$3) \qquad \sum_{j=1}^{s} n_{ij} N_j = p_i \ , \qquad i = 1, \dots, a$$

where n_{ij} is the number of i atoms in a j molecule, Pi is the population (moles) of i atoms in the system and "a" is the number of different elements (atoms types) present in the system.
For convenience, we denote $\tilde{g}_j = g_j(T,P)/RT$, and seek the minimum of G/RT. Using (2) we find that for arbitrary variations in the mole number

$$4) \qquad d\left(\frac{G}{RT}\right) = \sum_{j=1}^{s} \left(\tilde{g}_j + \ln x_j\right) dN_j + \sum_{j=1}^{s} N_j \frac{1}{x_j} dx_j$$

We denote the number of moles in phase m by $\bar{N}_m$ then, $x_j = N_j/\bar{N}_{(j)}$
Where $\bar{N}_{(j)}$ is the number of moles in the phase containing species j

The second sum in (4) can therefore be replaced by $\displaystyle\sum_{m=1}^{p} \bar{N}_m \sum_{\substack{j=1 \\ \text{in } m}}^{s} dx_j$

Where p is the total number of phases which may be present. This vanishes because the mole fraction in each phase always totals 1.

Now the dNj are not all independent because of the atomic constraints. Relationships among the dNj obtained by differentiating (3) are

$$5)\quad \sum_{j=1}^{s} n_{ij} dN_j = 0 \ , \qquad i = 1, \ldots, a$$

We must solve for the "a" restricted dNj in terms of the "s-a" free dNj and then substitute these relations into (4) in order to express the G variation in terms of freely variable Nj. this process is equivalent to subtracting multiples of (5) from (4).

$$6)\quad d\left(\frac{G}{RT}\right) = \sum_{j=1}^{s} \left(\tilde{g}_j + \ln x_j\right) dN_j - \sum_{i=1}^{a} \lambda_i \sum_{j=1}^{s} n_{ij} dN_j$$

The λ_i are the "Lagrange Multiplier" that are required to drop out the set of restricted dNj from this equation. Thus setting the coefficients of these dNj to zero one has:

$$7)\quad \tilde{g}_j + \ln x_j - \sum_{i=1}^{a} \lambda_i n_{ij} = 0 \qquad \text{for the restricted } j.$$

For every species we get:

$$8)\quad x_j = \exp\left(-\tilde{g}_j + \sum_{i=1}^{a} \lambda_i n_{ij}\right)$$

Equation (8) is the main result of the element potential for mixtures of ideal gases or for ideal solutions. The multiplier λ_i is called the "Element Potential" for i atoms. Using (8) we see that:

$$9)\quad \bar{g}_j/RT = \sum_{i=1}^{a} \lambda_i n_{ij}$$

and hence λ_i represnts the Gibbs function/RT per mole of i atoms. What is even more amazing is that each atom of an element contributes the same amount to the Gibbs function of the system irrespective of which molecule or phase it is in. The λ_i are properties of the system, however, and cannot be tabulated as a function of atom or molecule. The values of the element potential are determined by the atomic constraints (3) which we rewrite as:

$$10)\quad \sum_{j=1}^{s} n_{ij}\bar{N}_{(j)}x_j = p_i \quad , \quad i = 1, \ldots, a$$

where $\bar{N}_{(j)}$ is the number of moles in phase containing species j. This becomes a set of equations for the unknown i and the p unknown phases. To this we add the p equations:

$$11)\quad \sum_{\substack{j=1 \\ \text{in } m}}^{s} x_j = 1 \quad , \quad m = 1, \ldots, p$$

Equations 10, 11 must be solved simultaneously to determine the element potentials and phase moles.

COMPUTER PROGRAM

The block diagram of the computer program is shown in Fig 1.

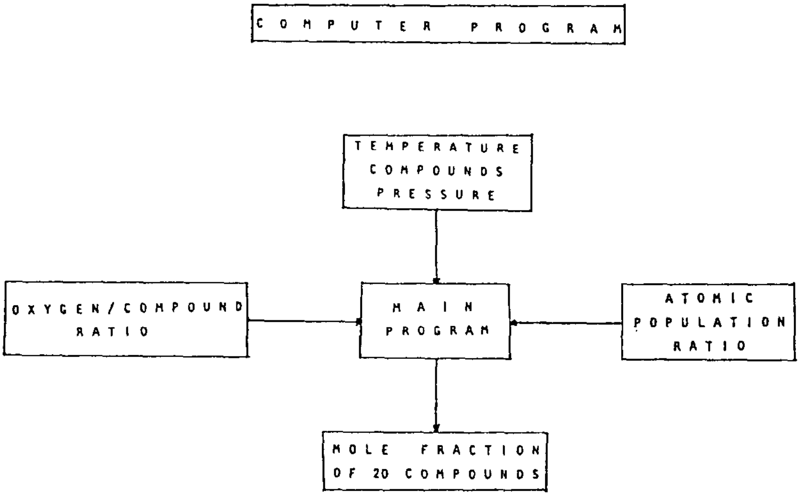


Fig 1. Block diagram of the computer program

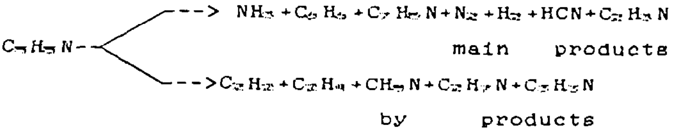
The computer program is very user friendly and easy to use. The user has to enter the following data:

- the pressure of the system.
- the temperature range, in which the reaction happened.
- the atomic population ratio of the hydrocarbon.
- the mole ratio of the oxygen and the hydrocarbon.

The output of the computer program is the mole fraction of the predicted compounds.

RESULTS

As an example of prediction of hydrocarbon thermolysis we studied pyridine thermolysis. The thermolysis reaction of pyridine is shown in Fig 2.



C_5H_5N --> $NH_3 + C_6H_6 + C_7H_5N + N_2 + H_2 + HCN + C_3H_3N$

main products

--> $C_2H_2 + C_2H_4 + CH_5N + C_2H_7N + C_2H_3N$

by products

Fig 2. Thermolysis of pyridine.

The mole fractions of the pyridine thermolysis calculated values are shown in figures 3, 4a, 4b.

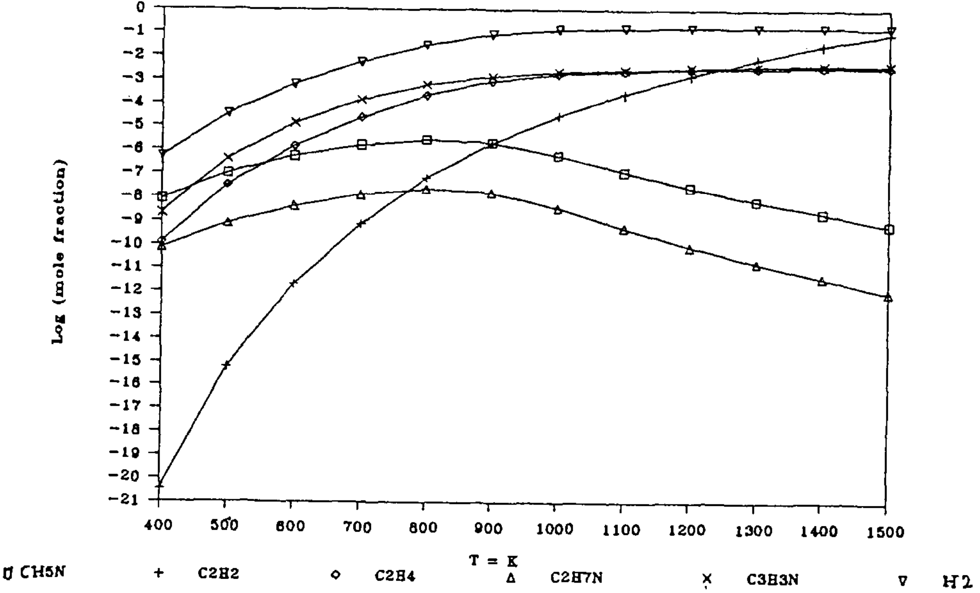


Fig 3. Thermolysis of pyridine P = 1 atm.

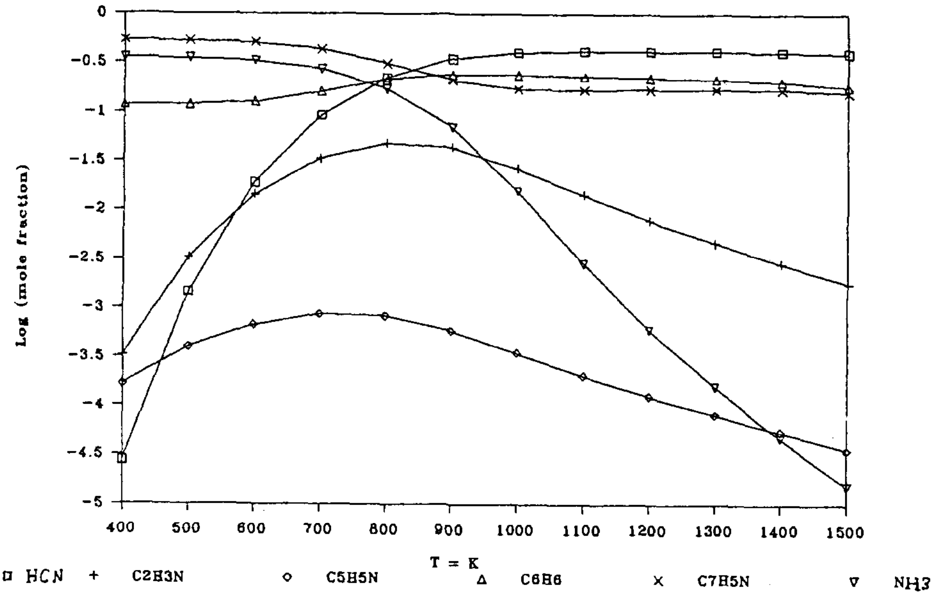


Fig 4a. Thermolysis of pyridine P = 1 atm.

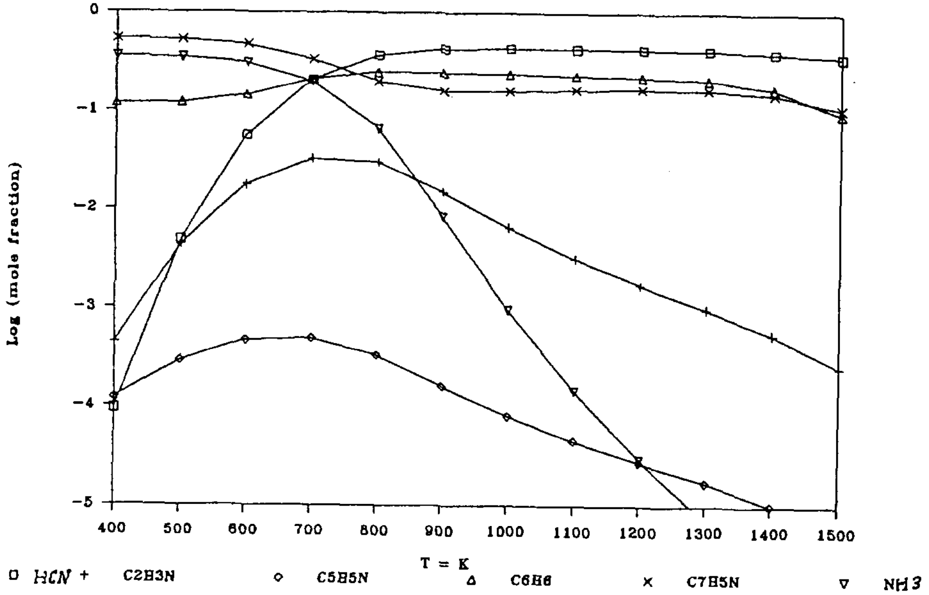


Fig 4b. Thermolysis of pyridine P = 0.1 atm.

CONCLUSIONS

The prediction of pyridines thermolysis by the "Element Potential" method shows that:

- the main compounds that are produced at pressure of 1 atm and temperature between 500°-750°K as shown in Fig 4a are C_6H_6, NH_3 and C_7H_9N.

- when the temperature reaches 750°K the mole fraction of NH_3 decreases and the mole fraction of HCN increases.

- the mole fraction of H_2 that was produced (Fig3) is very small at low temperature and increases rapidly when the temperature increases. The presence of H_2, which was identified experimentally by mass spectra, is predicted by the theoretical calculations.

- At a low pressure of 0.1 atm (Fig 4b) the mole fraction of NH_3 decrease and the mole fraction of HCN increases rapidly with temperature increase.

REFERENCES

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