COMPUTER-ASSISTED LABORATORY TRAINING COURSES IN PETROCHEMICAL TECHNOLOGY

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Future chemical engineers need a new attitude to develop more then the strictly meant professional knowledge. It is very important for the students to get accustomed to using computers in solving their tasks; computers should be their everyday aids. This is why the Department of Chemical Technology of the Technical University Budapest introduced such exercises within the subject matter of the petrochemical laboratory for presenting the uses of and the benefits from computers in calculations of the hydrocarbon industry and in analysis of different technological processes.

A typical application is presented in this paper.

1. Study of the decomposition of methane with water vapour in a model reactor

Small-scale model reactors lend themselves for studying continuous technologies used in the hydrocarbon industry. Such technologies are *e.g.* the decomposition of natural gas with water vapour and air, different pyrolysis technologies, hydrogenation processes etc. The students make measurements during the laboratory practice of conventional education as well, on peculiar model reactors or pilot plant equipment. They examine the relationship between input and output parameters in stationary state for a given, predetermined operation.

For studying the decomposition of methane with water vapour a measuring set-up has been elaborated some years ago at the Department [8]. The diagram of the layout is shown in Fig. 1.

The catalytic conversion of the methane–water vapour mixture is accomplished in a tubular reactor.

Our choice fell on this process because the decomposition of methane with water vapour is a standard technology in the chemical industry, and on the other hand this process can be modelled in a relative simple and expressive way. The pressure and temperature values applied in decomposition are easy to achieve even under laboratory conditions. In conventional practice there are two parameters to be calculated at first:

a) the flow rate of natural gas to be adjusted [l/h];

b) the necessary temperature of water vapour saturator.

These are calculated from the given input parameters: reactor temperature, flow rate and input composition. During the measurement the changing parameters must be read off every 5 minutes.

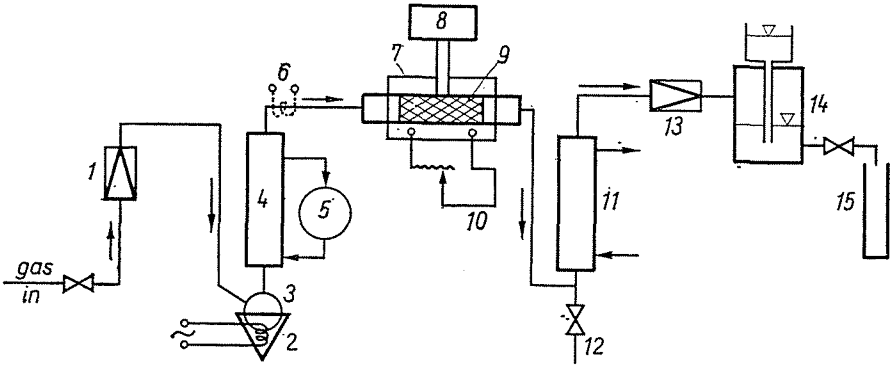

Fig. 1. Converting equipment — 1. Gas-flow meter. 2. Electric heater. 3. Flask with water. 4. Water vapour set. 5. Ultrathermostat. 6. Overheater. 7. Tubular reactor. 8. Thermocouple instr. 9. Catalyst bed. 10. Heater adjuster. 11. Water cooler. 12. Steam trap valve. 13. Gas flow meter. 14. Gasometer. 15. Measuring cylinder

The gas decomposed in the reactor has to be analysed, its quantity calculated and the quantity of the condensed water left out of the ion reaction has to be measured.

The measurement is evaluated by calculating the equilibrium composition of the decomposed gas and then comparing it with the measured composition, resulting a "material balance".

There are three possibilities to exercise computer technique:

a) for the exact calculation of the equilibrium composition by the "free energy minimization" method;

b) for the evaluation of the regression model of the reactor applying planned experiments under about the working conditions of the process to be examined,

c) and — with the model at hand there is a possibility for a small optimization task answering some simple questions, such as finding the flow rate for the maximum conversion or for the highest capacity of the reactor unit at a given temperature and methane–water vapour proportion.

2. Methods to determine the equilibrium composition

During the conventional exercise the students determine the equilibrium composition of the product gas only in one point of the "parameter space". Our aim in modernizing the exercise was to give the students an impressive picture not only in one point but in a given part of the parameter space in the vicinity of the equilibrium conditions, to impart them a preliminary idea about the influence of the input parameters on the results. To calculate the equilibrium composition in the conventional way is a time consuming job. Now the students may choose one of the two methods to calculate the isotherm–isobar equilibrium composition:

a) a method based on the knowledge of equilibrium constants or

b) a method which operates on minimizing the free energy.

As under laboratory conditions there is no possibility to determine quantitatively the carbon produced, the experimental conditions are determined in such a way that the equilibrium gas mixture leaving the reactor contains only CO_2, CO, H_2O, H_2 and CH_4.

a) *Calculation of the isobar–isotherm equilibrium composition based on the equilibrium constants.*

The reaction mixture can be characterized by the "atom matrices" of the components, containing the stoichiometric indices [3].

$$A \hat{=} \begin{array}{c|ccccc} & \mathrm{CH_4} & \mathrm{H_2} & \mathrm{CO} & \mathrm{CO_2} & \mathrm{H_2O} \\ \hline \mathrm{C} & 1 & 0 & 1 & 1 & 0 \\ \mathrm{H} & 4 & 2 & 0 & 0 & 2 \\ \mathrm{O} & 0 & 0 & 1 & 2 & 1 \end{array}$$

As in our case the atom matrix is of the third order and there are five components in the system, the number of the independent reactions is two. Let us consider the following two reactions:

$$CH_4 + H_2O = CO + 3\,H_2 \qquad (1)$$

$$CO + H_2O = CO_2 + H_2 \qquad (2)$$

The reaction equations can be summarized concisely in the so-called reaction matrix. The reaction matrix of the above two reactions is the following:

$$R \triangleq \begin{array}{c|ccccc} & CH_4 & H_2 & CO & CO_2 & H_2O \\ \hline (1) & 1 & -3 & -1 & 0 & 1 \\ (2) & 0 & -1 & 1 & -1 & 1 \end{array}$$

The two reactions are independent, since the order of the reaction matrix is two.

In fact,

$$\varrho(A) + \varrho(R) = k \tag{3}$$

where k means the number of components,

$\varrho(A)$ means the order of matrix A,

$\varrho(R)$ means that of matrix R.

The choice of the independent reactions is of course not clearcut. Taking Eq. (2) and substituting

$$CH_4 + CO_2 = 2CO + 2\,H_2 \tag{4}$$

for Eq. (1) again results in a reaction matrix order two; also these two reactions are independent.

$$R' \triangleq \begin{array}{c|ccccc} & CH_4 & H_2 & CO & CO_2 & H_2O \\ \hline (4) & 1 & -2 & -2 & 1 & 0 \\ (2) & 0 & -1 & 1 & -1 & 1 \end{array}$$

In this form the law of conservation of mass is expressed by:

$$A \cdot R^T = 0 \tag{5}$$

Let us express the equilibrium mole numbers from reactions (1) and (2), supposing that for one mole of methane "a" moles of water vapour and "b" moles of CO_2 are fed into the reactor. The reaction is carried out at atmospheric pressure. Denoting the equilibrium conversion of methane by x, that of carbon monoxide by y, the mole numbers are the following:

$$\begin{aligned} n_{CH_4} &= 1-x & n_{H_2O} &= a-x-y \\ n_{CO} &= x-y & n_{CO_2} &= b+y \\ n_{H_2} &= 3x+y & \sum_i n_i &= 1+a+b+2x \end{aligned} \tag{6}$$

Expressing the equilibrium constants of reactions (2) and (4) by these mole numbers:

$$K_2 = \frac{(b+y)\cdot(3x+x)}{(x-y)\cdot(a-x-y)} \tag{7a}$$

$$K_4 = \frac{(x-y)^2\cdot(2x+y)^2}{(b+y)\cdot(1-x)} \cdot \left(\frac{1}{1+a+b\,2x}\right)^2 \tag{7b}$$

In knowledge of the values of equilibrium constants K_2 and K_4 at the given temperature and pressure, Eq. (7a) and (7b) are suitable to calculate x and y. A relatively small desk calculator (*e.g.* a Hewlett—Packard 9100 B) is enough to solve the equation system (7).

The program computes x and y. Knowing these values the mole numbers at equilibrium and the equilibrium composition of the gaseous reaction mixture are easy to calculate.

b) *Computing the isobar–isotherm equilibrium composition by the method of "free energy minimization".*

In 1958, White *et. al.* [9] suggested the method of free energy minimization for computing multicomponent vapour–solid phase reactions. This is based on fundamental thermodynamic properties, and there is no need of considering mechanism, independent equations for chemical reactions or simplifying assumptions. Naturally, it is necessary to predetermine all compounds which will be present at equilibrium. Oliver *et. al.* [6] worked out a method where the quadratic approximation of the free energy expression is minimized subject to the mass balance constraints using the technique of Lagrange multipliers. Dluzniewsky and Adler [2] were the first authors who considered non-idealities in the vapour phase and could handle systems with one or more liquid phases and non-reacting systems. In case of this simple reaction system for education purposes, the method of Oliver was clear enough, so we have chosen this one, and worked out a program in Algol based on this version.

The fundamental steps of the procedure are:

I) calculation of the free energy of the feed system;

II) estimation of the free energy of the equilibrium mixture (of unknown composition) by using the quadratic form of the Taylor series;

III) minimization of the free energy of the estimated equilibrium system — subject to the mass balance constraints — using the technique of Lagrange multipliers;

IV) solving the resulting system of linear simultaneous equations to obtain improved equilibrium approximations;

V) repetition of the first four steps until the equilibrium approximation is adequate.

Since the description of the mathematical method is well known, it will not be discussed here.

This program facilitates investigation of the equilibrium composition of the gaseous mixtures formed in water vapour conversion of methane and the quantity of accidentally precipitating solid carbon for different H_2O/CH_4 ratios and at different temperatures.

The program was run on a computer type ODRA 1204. To compute the equilibrium composition at 77 points of the experimental space and to convert the data into dry state took 24 minutes.

The results are made more illustrative by plotting the equilibrium concentration of the components concerned in the dry gaseous mixture against the H_2O/CH_4 ratio and the temperature in a three dimensional system of Cartesian co-ordinates (Figs 2 to 5).

Figure 2 shows the trend of methane concentration in the dry equilibrium mixture. In the investigated factor space the surface is monotone throughout and above 750 °C no methane is practically seen at equilibrium in the product gas. Either with increasing temperature, or with increasing H_2O/CH_4 ratio the conversion rate of methane is higher and the concentration of methane is lower. Diagrams 3, 4 and 5 can be interpreted by the same way. The calculation of equilibrium composition by minimizing the free energy was — in this case —

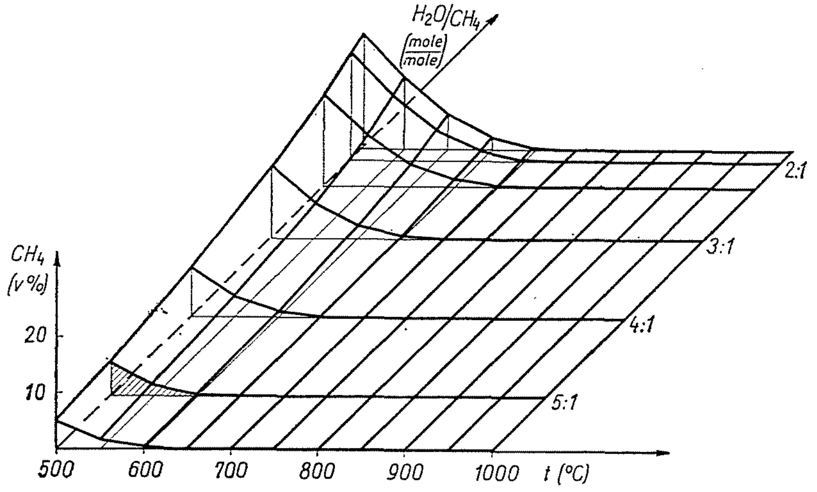

Fig. 2. Concentration of methane in the dry equilibrium mixture

very fast and demonstrative. The investigation of equilibrium surfaces gives the students more new experiences and knowledges than the calculation of equilibrium composition at one point of the factor space. In addition, the method of free energy minimization has another great advantage: solid carbon formation at equilibrium would not cause difficulties, because the program calculates the quantity of carbon precipitated from the gaseous mixture. Calculating the equilibrium composition in the customary way (through the equilibrium constants of reactions) this would only appear after a subsequent control.

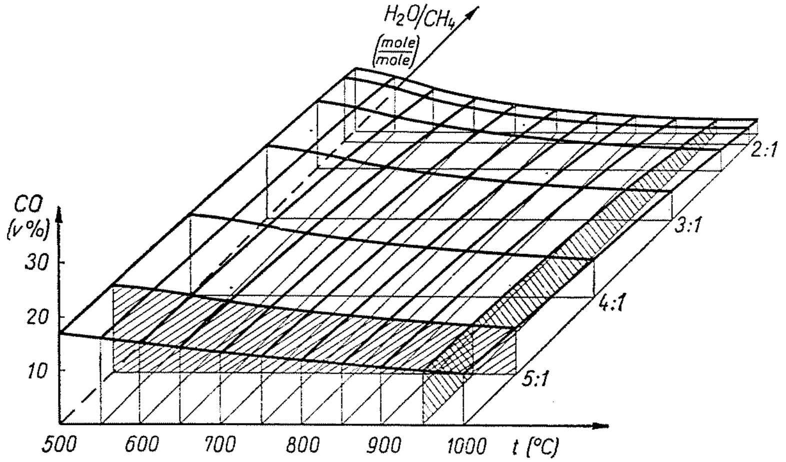

Fig. 3. Concentration of CO_2 in the dry equilibrium mixture

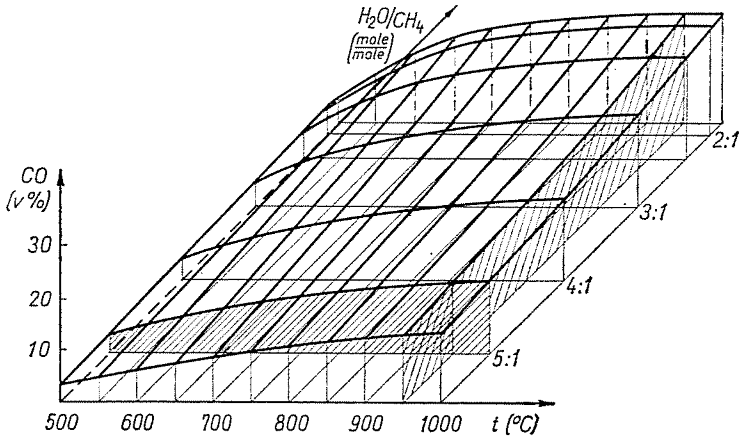

Fig. 4. Concentration of CO in the dry equilibrium mixture

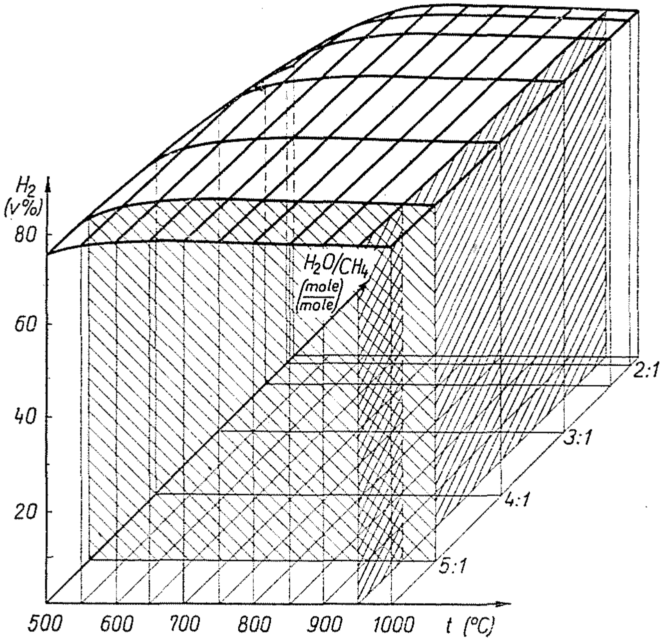

Fig. 5. Concentration of H_2 in the dry equilibrium mixture

3. Application of regression analysis and planning of experiments

To keep in hand and to control the chemical technological processes the effect of input variables on the output (response) variables have to be known. The measurable input variables of each process can be divided into two groups: into the so-called controllable "factors" and the uncontrolled variables. The response variable also depends on uncontrollable and measurable effects interpreted as accidental effects.

Factors of the conversion of methane in a model reactor, are the following:

reactor temperature (t_r, °C)
H_2O/CH_4 ratio
flow rate (W, $Nl \cdot l_{cat}^{-1} \cdot h^{-1}$)

Measurable, but uncontrollable parameters are the composition of the methane-containing input natural gas, the properties of the catalyst etc. The values of these variables can be regarded as constant because of the relative short time of the experiment.

In planning the experiments, the effect of changes in the composition of the natural gas is irrelevant and so it can be left out of consideration. The responses are random variables because of the existence of *uncontrollable and unmeasurable variables.* This fact confirms the authority of application of the method of regression analysis and the planning of experiments in the study of the problem. This provides a new aspect of experimental strategy for the students: they meet the stochastic rather than deterministic approach to experimentation.

As a response, any variable characteristic of the composition of the output gaseous mixture, or of the quantity of a component formed during unit time can be chosen.

Let us choose the difference of the H contents of the output mixture and of the dry input natural gas (practically methane) as a response! The model of our problem is defined as:

$$(\mathrm{H}\% \text{ out} - \mathrm{H}\% \text{ in}) = f(t_r, \mathrm{H_2O/CH_4} \text{ ratio}, W). \tag{8}$$

The three-dimensional sub-space of the four-dimensional factor space is the vector space stretched by the independent variables. Supposing that at the given narrow parameter range each factor affects the value of the response only linearly, it is enough to make a two-level factorial design to characterize the effect of the factors, and to calculate the constants of the linear model (design type 2^k). The properties of such designs, the benefits and disadvantages are well known [1, 5].

Putting our linear model in the form

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3, \tag{9}$$

the coefficients of the model can be calculated by the formula

$$b_j = \frac{1}{N}\sum_{i=1}^{N} X_{ji}Y_i \tag{10}$$

where N is the number of measurements (eight in our case),

b_j is the coefficient in Eq. (9).

The design type 2^k have the advantages that the constants of the model are simple to calculate and the model can be completed by terms of b_{ij} and b_{123}, characteristic of the double and triple interrelations without any further measurement.

Assuming that in repeating the measurements the deviation of reproduction is the same at any point it is enough to make repeated measurements only at one point (practically in the centre of the design), and then the deviation of reproduction can be calculated in a simple manner as well.

The confidence of the coefficient b_j can be evaluated by Student's t test knowing the deviation of reproduction [4]. Taking the value of t_{crit} from a statistical table (at the proper confidence level and degree of freedom) in case of $t_{crit} < t_j$ the value of the coefficient can be regarded as reliable. The orthogonality of 2^k-type designs eliminates unreliable coefficients omitting the repetitive calculation of the other coefficients.

Fitting of the regression hyperplane can be checked by Fischer's F test [7]. In case of proper fast gas analyses (*e.g.* by gas chromatography) and controlled stable input parameters the eight measurements can be carried out during the two laboratory exercises lasting six hours each. As the time required to get a new stationary state is the longest one when the temperature is changed, the students make measurements at one six hours'lab session at a given temperature with two flow rates and two CH_4/H_2O proportions, according to the flow diagram of the lab exercise (Fig. 6).

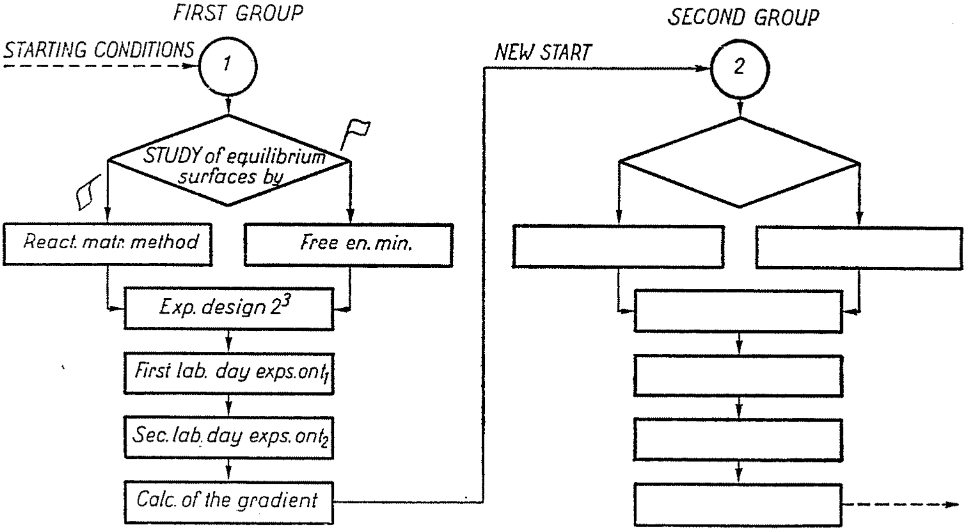

Fig. 6. The flow chart of the laboratory exercise

4. Optimization of the chosen output parameter

Assuming the function to be an equation of a three-dimensional hyperplane in a four-dimensional space, the direction of gradient on the hyperplane is meant by

$$\operatorname{grad} Y = \left(\frac{\partial Y}{\partial X_1} i + \frac{\partial Y}{\partial X_2} j + \frac{\partial Y}{\partial X_3} k\right) \tag{11}$$

where i, j, k are the three unit vectors.

The gradient of function (9) can be calculated by the following known formula

$$\frac{\partial Y}{\partial X_1} = b_1 \qquad \frac{\partial Y}{\partial X_2} = b_2 \qquad \frac{\partial Y}{\partial X_3} = b_3 . \tag{12}$$

Shifting the centre of the design by one unit in the gradient direction and carrying out series of experiments around the new centre, increasing values of the output parameter are obtained, namely a "higher" point is reached on the response surface. The method mentioned is referred to in the literature as "Box—Wilson method" or "optimization by the method of the steepest ascent". If each group of students carries out one 2^3-type design in the two lab sessions lasting six hours each, but shifting the centres of design of the consecutive groups by one unit in the direction of the gradient helps the students to acquire one optimization method in practice by evaluation of the results of other groups.

Standard programs in nearly all programming languages are available for calculating the coefficients of regression equation (9) and for carrying out the t and F test on a computer of medium capacity. Programming of the method is not too complicated because of the simplicity of the method and of the orthogonality of vectors containing the values of single factors.

Summary

The application of computer technique for education in petrochemical technology is discussed. Methods operating by two alternative ways in calculating the equilibrium composition (the so-called "Reaction Matrix Method" and the "Free Energy Minimization"), using the regression analysis in planned experiments and an optimisation technique with the "steepest ascent" formula are described. The method is illustrated on the example of a typical continuous hydrocarbon technology: the process of methane decomposition with water vapour. The model reactor and the measuring set-up has been elaborated at the Department.

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