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DESCRIPTION OF THE THERMAL DECOMPOSITION OF NAPHTHAS

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In a laboratory tubular reactor at atmospheric pressure and in a temperature range of 580-830°C the pyrolysis of a straight-run Romashkino naphtha cut with a boiling range of 40-160°C was investigated.

New characteristics were introduced to characterize the degree of the decomposition of the naphthas. Substituting the conversion in kinetic equations developed for flow reactors by the decomposition grade, appropriate correlations were derived for describing the overall decomposition rate of the naphthas.

It was demonstrated that in the temperature and residence time ranges of industrial pyrolysis processes, the expansion and the yield distribution of the main reaction products depend only on the decomposition grade.

For predicting the product distribution in naphtha pyrolysis a simplified kinetic model was elaborated.

INTRODUCTION

Roughly half the annual world production of ethylene of nearly 20 million tons is produced by the pyrolysis of gaseous hydrocarbons, the other half is produced by the pyrolysis of liquid petroleum fractions, mainly of naphthas [1].

Despite the large and rapidly increasing production capacities for the pyrolysis of hydrocarbons, relatively few and often contradictory data were published in literature regarding the description of the pyrolysis process, reaction kinetics and product distribution. Most publications deal with the investigation of gaseous hydrocarbons. Very limited detailed and reliable data are available concerning the description of the pyrolysis of liquid hydrocarbon mixtures and naphthas.

To characterize the degree of decomposition in the pyrolysis of naphthas the "severity function" introduced by LINDEN et al. was generally used in the past [2, 3]. Recently, ZDONIK and his associates introduced the "kinetic severity function" based on the conversion on n-pentane under the given pyrolysis conditions and the $\int kdt$ values calculated by a first-order kinetic equation are used to define the degree of decomposition for naphthas.

On the basis of the previous investigations, the sum of the conversions of the feed components weighed by their mole fractions on the one hand, and the relative expansion on the other hand were introduced for characterizing the decomposition grade for hydrocarbon mixtures, and methods were elaborated for the calculation of the overall decomposition rate and the description of product yield curves, respectively [5, 7].

In this publication the application of the above mentioned methods will be described for the evaluation of the pyrolysis of a straight-run Romashkino naphtha cut carried out in a laboratory tubular reactor at atmospheric pressure and in a temperature range of 580-830°C. The specification of the naphtha investigated was as follows:

Density (g/cm^3)	0.7077
Boiling range (°C)	40-160
Molecular weight (average)	111
n-Paraffins (wt.%)	38.7
iso-Paraffins (wt.%)	37.9
Cycloparaffins (wt.%)	17.3
Aromatics (wt.%)	6.0

DECOMPOSITION GRADE FOR NAPHTHA

Between expansion and decomposition grade the correlation can be given by Equation (1) [5-7]:

$$E = 1 + (E_v - 1)X \tag{1}$$

where E expansion,

$E_v = \sum_j^k \sum_i^{k'} y_j \, v_{ji}$ limiting value of expansion,

v_{ji} = overall stoichiometric coefficients of the reaction products,

$X = \sum_j^k y_j x_j$ decomposition grade.

As regards its form and physical meaning Equation (1) is the same as the correlation between expansion and conversion for the pyrolysis of individual hydrocarbons [8, 9]. The only difference is that in the case of the pyrolysis of hydrocarbon mixtures, instead of the conversion and the stoichiometric coefficients, the sum of the conversions of the feed components weighed by their mole fractions will be introduced.

In the case where the conversions cannot be determined with sufficient precision because of the large number of components or analytical difficulties (mainly for petroleum fractions), in possession of the expansion (E) and limiting expansion (E_v) values and rearranging Equation (1) the decomposition grade can be estimated by the "relative expansion", given in Equation (2) [5, 6].

$$X = \frac{E - 1}{E_v - 1} \tag{2}$$

The detailed gas chromatographic analysis of the products made it possible to determine the conversions of the components and the decomposition grade of the naphtha investigated was defined by the sum of the conversions of the feed components weighed by their mole fractions.

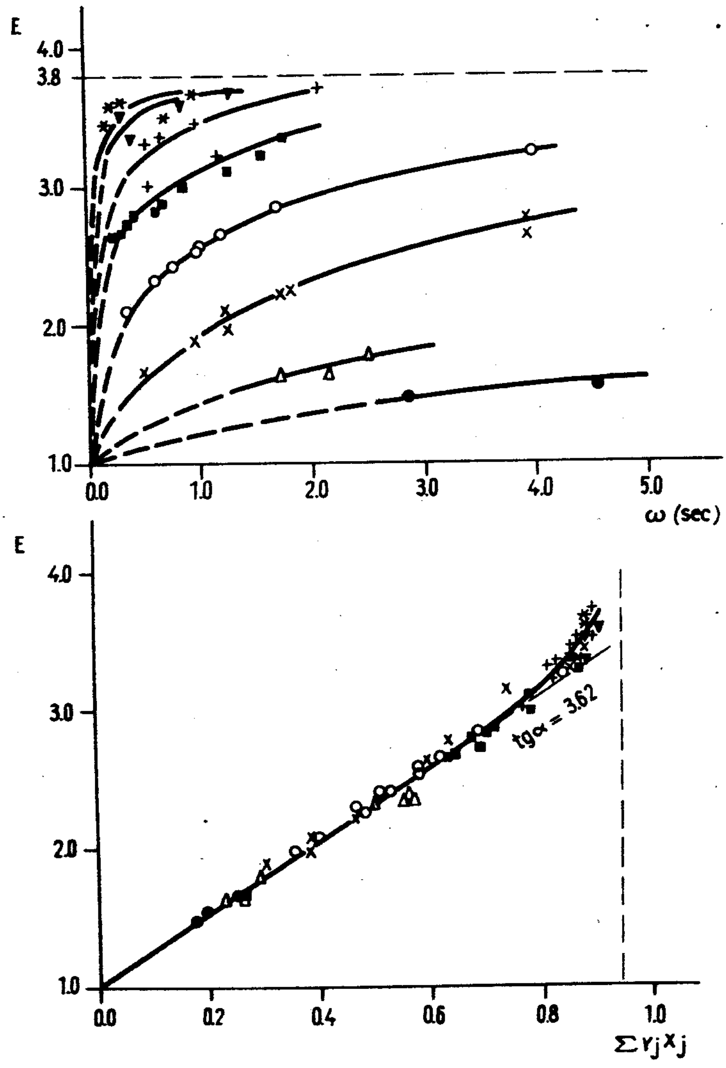

Fig.1. Expansion as a function of the fictive reaction time and the decomposition grade. • 581°C; Δ 624°C; x 660°C; o 699°C; 737°C; + 773°C; ✱ 834°C.

In Fig. 1 the expansion is plotted as a function of the fictive reaction time and the decomposition grade, respectively. The naphtha feed contained 6 wt.% aromatics that practically do not decompose under the given conditions. For this reason the decomposition grade varies only up to the 0.94 value, which is marked by a dotted line in Fig. 1 and in the forthcoming figures. From the top figure in Fig. 1 the limiting expansion value was estimated to be 3.62. As can be seen from the bottom figure, the variation of expansion as a function of the decomposition grade can be approximated by a single curve independently of the temperature.

DESCRIPTION OF THE OVERALL DECOMPOSITION RATE

A description of the overall decomposition rate for the individual components of the feed naphtha, as well as for the naphtha cut investigated, was carried out by using the kinetic equations for the individual hydrocarbons. Substituting the conversion in these equations by the conversions of the hydrocarbons composing the naphtha (x_j) and by the decomposition grade (X) characteristic for the given naphtha, respectively, the overall decomposition rate for the individual feed components and the naphtha cut, respectively, can be calculated. This method was previously applied for the description of the pyrolysis of binary, ternary and six-component hydrocarbon mixtures [5-7].

As examples in Fig. 2 the conversion of 2,4-dimethylpentane, and in Figs. 3 and 4 the decomposition grades of the naphtha cut are shown as a function of the true and fictive reaction time. The conversion curves for the individual hydrocarbon are similar in shape to the curves for the naphtha cut i.e. by increasing the temperature the rises of the curves - which are proportional to the decomposition rate - steeply increase.

To describe the overall decomposition rate i.e. the conversion curves shown in the figures, an integral as well as a differential method were applied [8, 9].

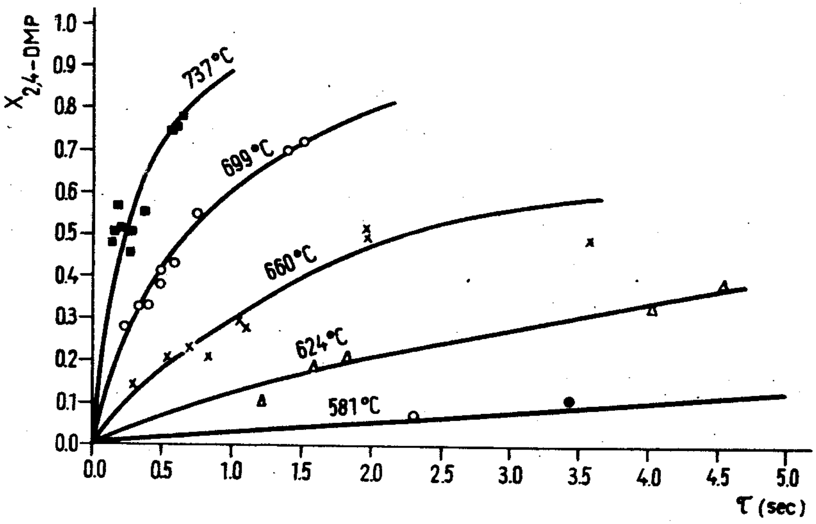

Fig. 2. Conversion of 2,4-dimethylpentane as a function of the true reaction time in naphtha pyrolysis. — Calculated by Eq.(5)

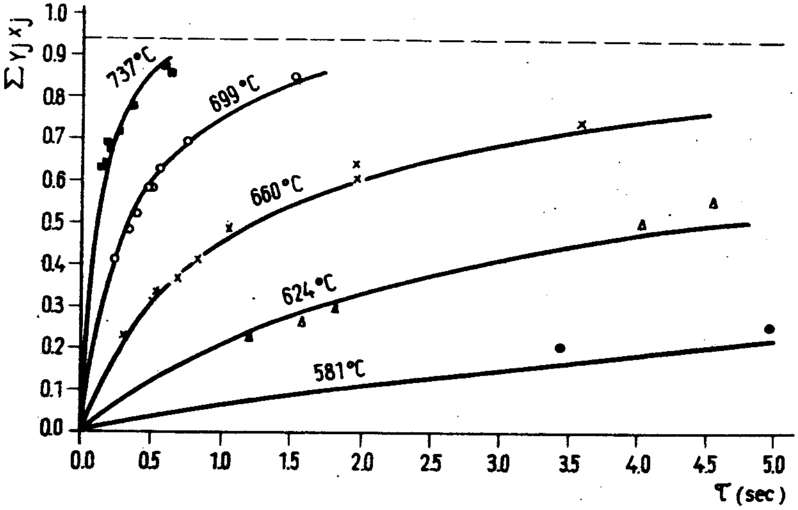

Fig. 3. Decomposition grade vs. true reaction time. — Calculated by Eq. (5).

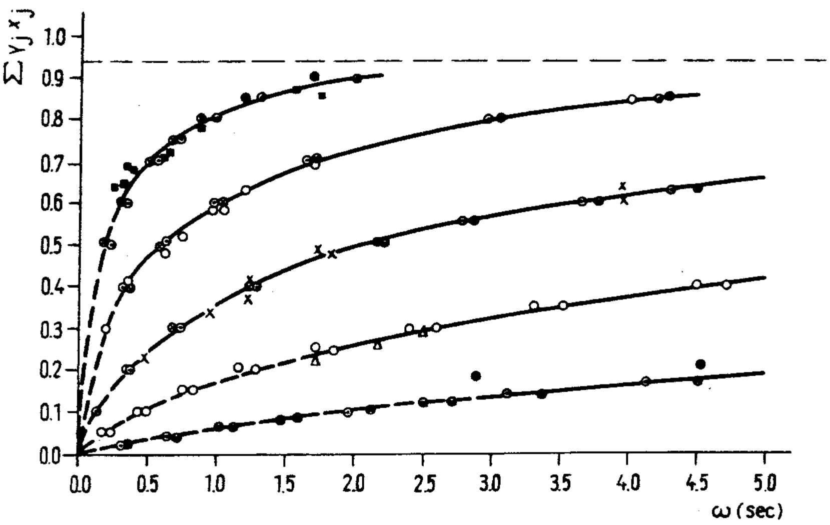

Fig.4. Decomposition grade vs. fictive reaction time.
⊠ Calculated by Eq. (4). ⊙ Calculated by Eq. (7).

Integral Method

In the first step of the evaluation, the decomposition rate constants were calculated for the measured data by using the first-order reaction kinetic equations valid for flow reactors. The calculated k values were plotted against conversion for 2,4-dimethylpentane and against the decomposition grade for the naphtha cut in Figs. 5 and 6, respectively. The figures show that in accordance with the results obtained from the data of the pyrolysis of individual hydrocarbons and model mixtures, the decomposition rate constants calculated by the first-order kinetic equation decrease with increasing conversion and the degree of this decrease depends on the temperature. The values given in Figs. 5 and 6 measured at a given temperature can be approximated by the

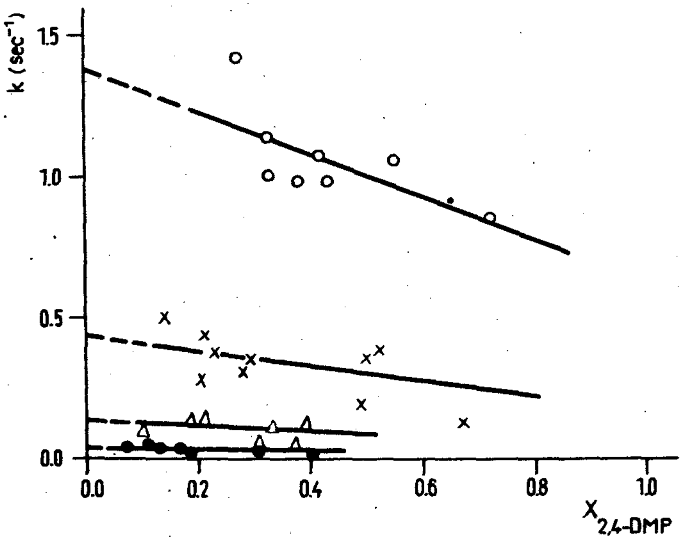

Fig. 5. Decomposition rate "constants" for 2,4-dimethylpentane vs. conversion. • 581°C; Δ 624°C; x 660°C; o 699°C.

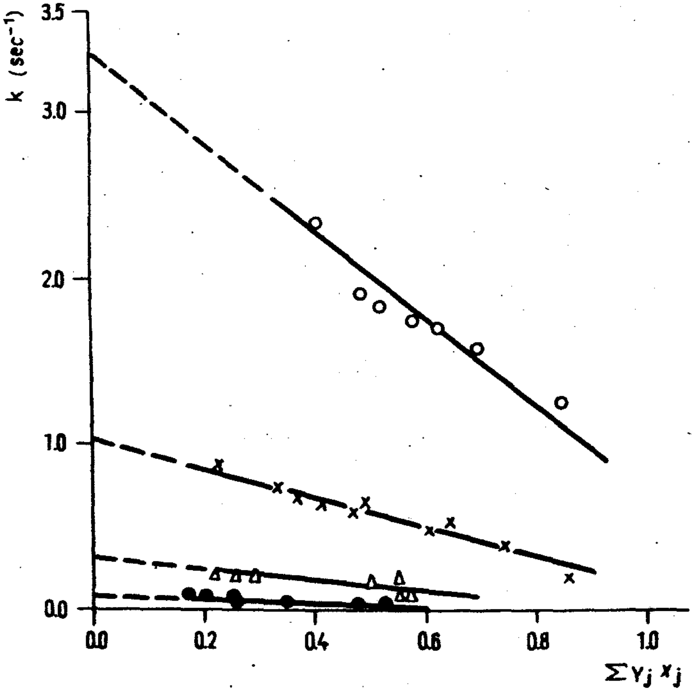

Fig. 6. Decomposition rate "constants" for naphtha vs. decomposition grade. • 581°C; Δ 624°C; x 660°C; o 699°C.

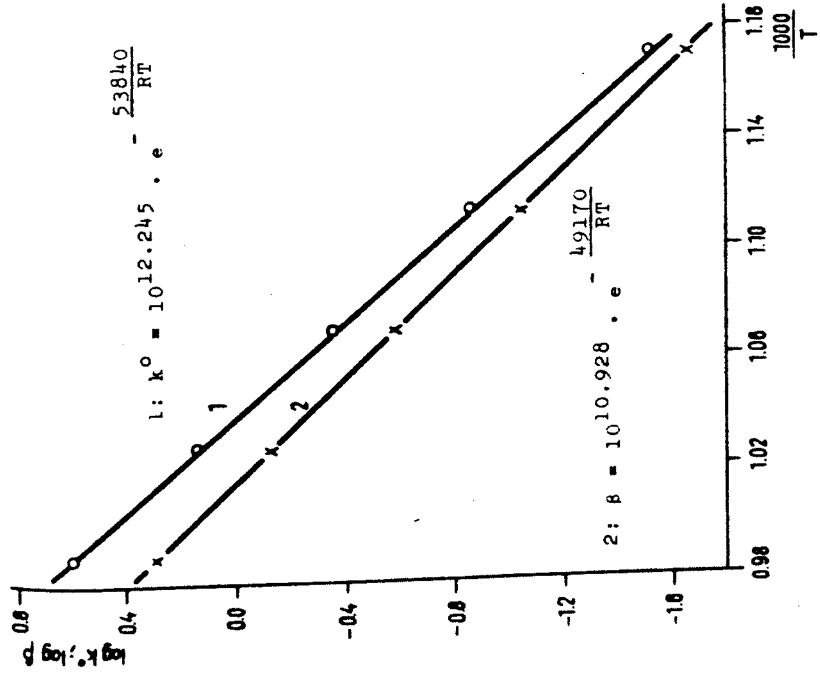

Fig. 7. Arrhenius-plot of the decomposition rate constant (k^o) and the restraining coefficient (β) for 2,4-dimethylpentane.

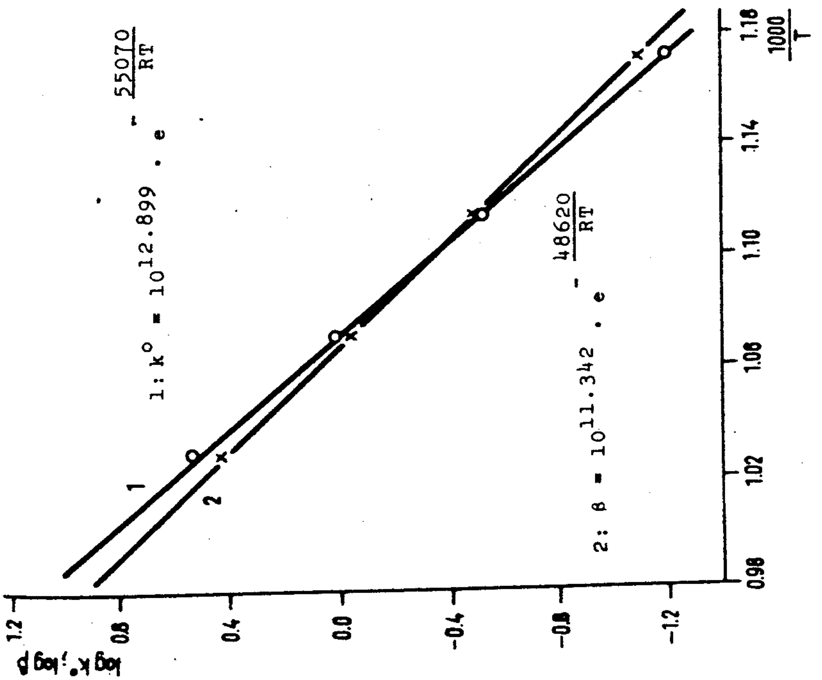

Fig. 8. Arrhenius-plot of the decomposition rate constant (k^o) and the restraining coefficient (β) for naphtha.

following linear relationship:

$$k = k^{o} - \beta X \qquad (3)$$

where k^{o} decomposition rate constant at zero conversion,
β restraining coefficient.

The (k^{o}) and (β) constants can be determined from Figs. 5 and 6.

Figs. 7 and 8 show the decomposition rate constants and restraining coefficients plotted against the temperature for 2,4-dimethylpentane and naphtha. It can be seen that the temperature dependence of both constants can be described by Arrhenius-type equations.

Substituting Equation (3) into the integrated rate equations for first-order reactions the following correlations were obtained between the overall decomposition rate and the fictive and true reaction time [5-9]:

$$\omega = \frac{1}{k^{o} - \beta X} \left[E_v \, 2.303 \log \frac{1}{1-X} - (E_v - 1)\, X \right] \qquad (4)$$

$$\tau = \frac{2.303}{k^{o} - \beta X} \log \frac{1}{1 - X} \qquad (5)$$

To check Equations (4) and (5), conversions for 2,4-dimethylpentane as well as decomposition grades for the naphtha were calculated as a function of the fictive and the true reaction times for the measured temperatures. For this calculation, first the k^{o} and β values were calculated for the given temperatures using the Arrhenius-plots in Figs. 7 and 8. Putting these values into Equations (4) and (5), the fictive and true reaction times were calculated for different conversions and decomposition grades, respectively. The full lines in Figs. 2, 3 and 4 represent the calculated curves. The satisfactory agreement between the calculated and measured values confirms that the elaborated method is suitable for the description of the overall decomposition rate of naphthas.

Differential Method

In this method the kinetic equation was used in the linearized form given below [8, 9]:

$$\log (dX/d\omega) = \log (k/C_o) + n \log C \qquad (6)$$

where C_o and C are concentration of the feed components (moles/litre) at the reactor inlet and outlet.

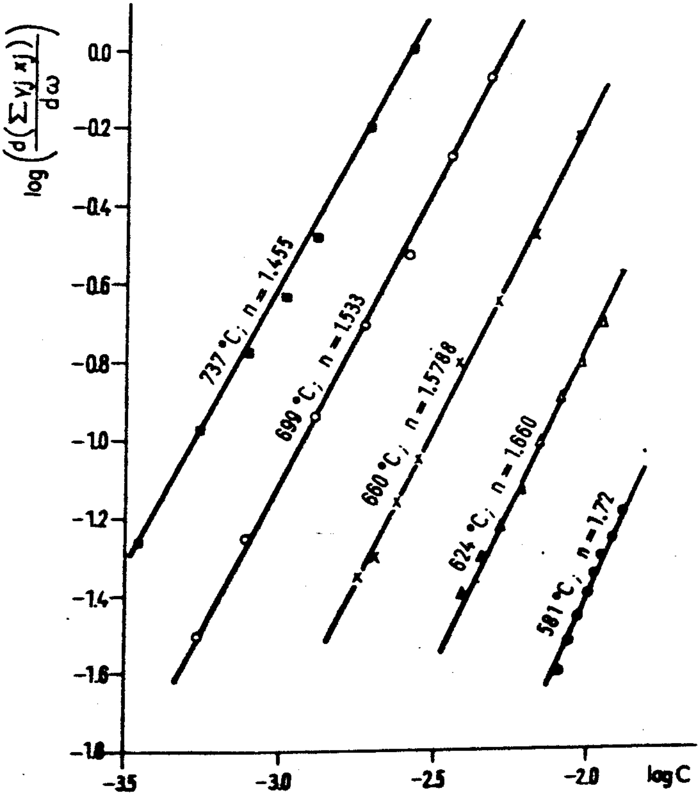

Fig. 9. $\log (\frac{dX}{d\omega}) = \log (\frac{k}{C_o}) + n \log C$ correlation for naphta.

For determining the constants of Equation (6) the curves of the decomposition grade vs. the fictive reaction time (Fig.4) were graphically differentiated and the momentary rates were plotted in logarithmic scale against the actual concentration. This relationship is shown in Fig. 9 for the naphtha investigated.

On the basis of the above figure the k and n values were determined and substituting these values into Equation (7) the decomposition grade values were calculated at different reaction times and temperatures:

$$\omega = \frac{C_o}{k} \int_o^X \left(\frac{1}{C}\right)^n dX \qquad (7)$$

The integration in Equation (7) was performed graphically. The calculated values were plotted in Fig. 4. These data square well with the curves plotted through the measured values which proves the suitability of the method for the description of the overall decomposition rate of naphthas.

DISCUSSION AND INTERPRETATION OF PRODUCT DISTRIBUTION

In Figs. 10-18 the yields of the main reaction products in wt.% are plotted against the decomposition grade of the naphtha cut. It is apparent from the figures that by increasing decomposition there is a considerable change in product distribution. The yields of some products will also be influenced to some extent by the temperature.

The yields of hydrogen and methane continuously increase with the increase of the decomposition grade (Figs.10 and 11). The yield curves run above the tangents constructed to the initial part of the curves, which indicates that the amounts of these products related to the naphtha consumed (the stoichiometric coefficients) increase in the entire decomposition range. These products are stable under pyrolysis conditions. By increasing the temperature at

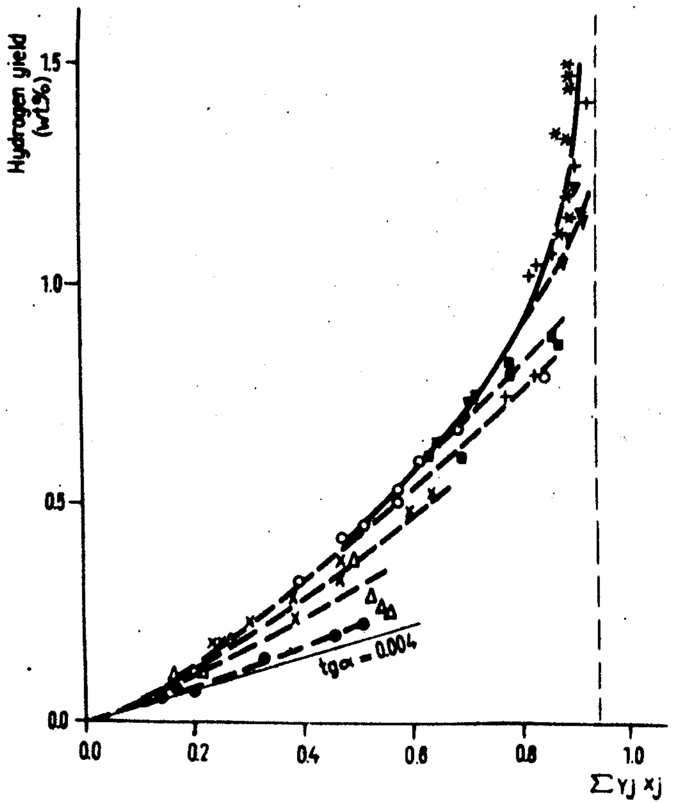

Fig.10. Hydrogen yield vs. decomposition grade
• 581°C; Δ 624°C; x 660°C; o 699°C;
■ 737°C; + 773°C; ▼ 806°C; ✱ 834°C.

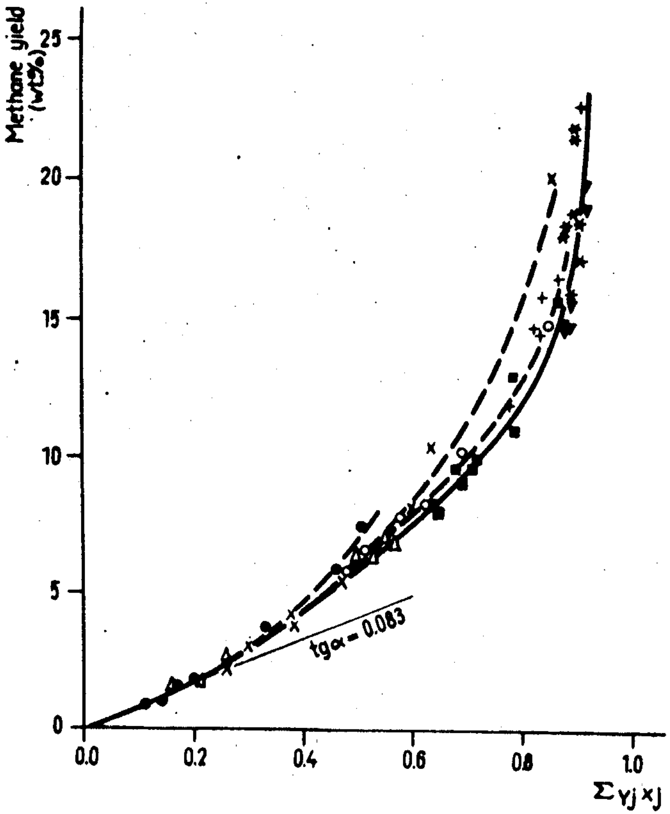

Fig.11. Methane yield vs. decomposition grade
• 581°C; Δ 624°C; x 660°C; o 699°C;
■ 737°C; + 773°C; ▼ 806°C; ✱ 834°C.

a given decomposition, the hydrogen yield increases, and the methane yield slightly decreases.

In Fig. 12 the ethylene yields are plotted against the decomposition grade.

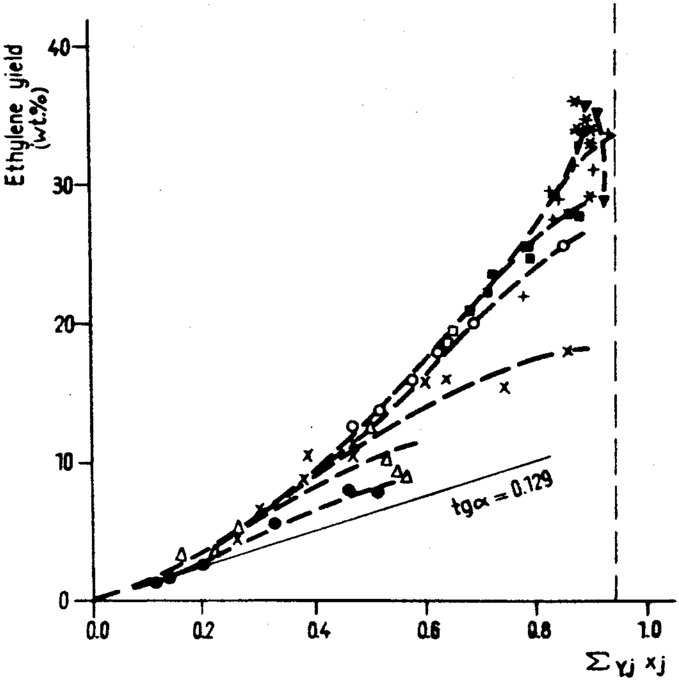

Fig. 12. Ethylene yield vs. decomposition grade. • 581°C; Δ 624°C; × 660°C; o 699°C; ■ 737°C; + 773°C; ▼ 806°C; ⁎ 834°C.

The curves run above the initial tangent i.e. the relative amount of the ethylene considerably increases with increasing decomposition.

Performing the pyrolysis at a higher temperature up to a given decomposition grade, the ethylene yield will increase. It can be observed that the yield curves tend to level out, which indicates that they probably pass through a maximum, at very severe conditions.

The yield curve constructed through the points measured at 806°C shows a definite maximum at about 1 second residence time. Performing the pyrolysis above 800°C with very short (0.1-0.4 second) residence time about 33-34 wt.% ethylene yield related to the naphtha feed can be obtained.

The propylene yield increases with an increased decomposition grade up to a value of about 0.7 (Fig. 13). The yield curve runs above the initial tangent, has a maximum at about the 0.7-0.75 decomposition grade and over this the propylene yield sharply decreases. The maximum propylene yield is about 16 wt.%. Under the conditions investigated, the propylene yield curve is independent of the temperature.

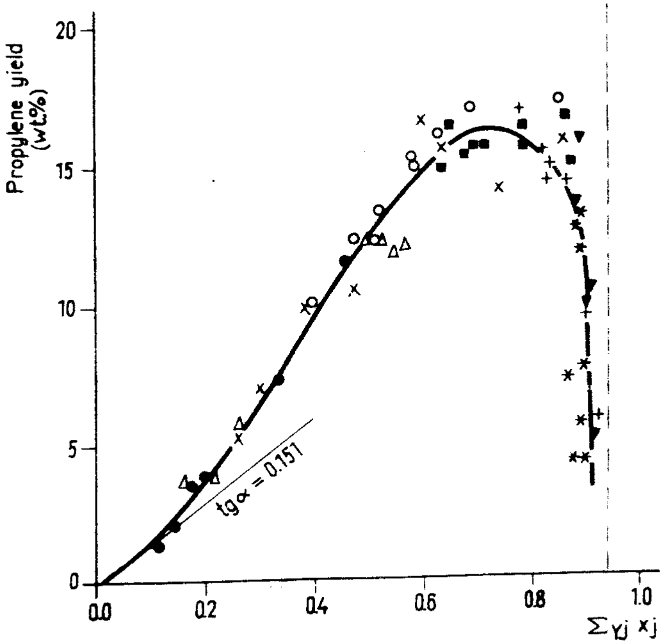

Fig. 13. Propylene yield vs. decomposition grade. • 581°C; Δ 624°C; × 660°C; o 699°C; ■ 737°C; + 773°C; ▼ 806°C; ⁎ 834°C.

Depending on the reaction conditions about 2-10 wt.% ethane is also produced in the pyrolysis process. It can be seen in Fig.14 that the ethane yield increases up to about the 0.85 decomposition

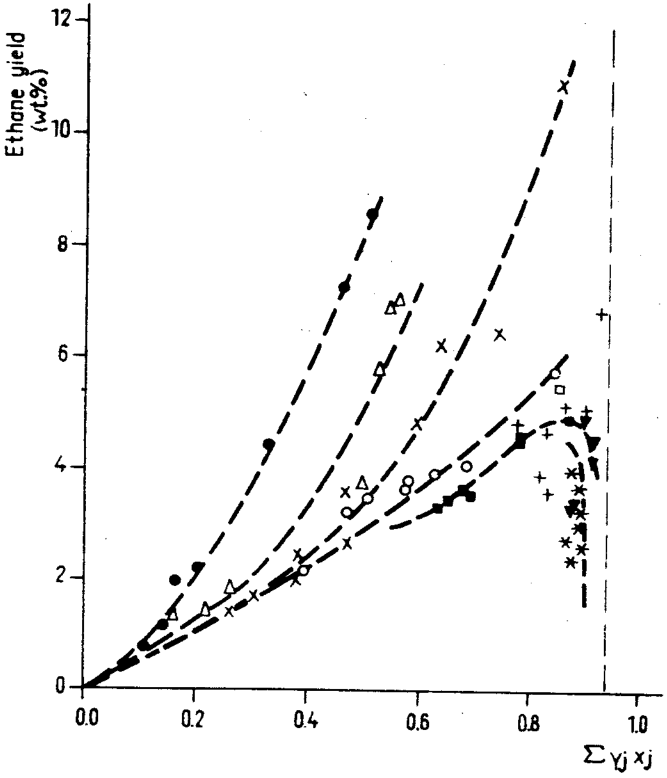

Fig. 14. Ethane yield vs. decomposition grade. ● 581°C; Δ 624°C; x 660°C; ○ 699°C; ■ 737°C; + 773°C; ▼806°C; ✱ 834°C.

grade. At a higher decomposition grade, the yield curves measured above 800°C show a maximum. By increasing the temperature, the ethane yield at a given decomposition grade decreases. The propane yield curves are similar in shape to the ethane curves. The propane yield is one order of magnitude smaller than the ethane yield.

Fig. 15 shows the butylene yields against the decomposition grade. Through the measured values a single curve can be constructed, which means that under the conditions investigated the butylene yield is independent of the temperature. The yield curve shows a maximum at about 0.6 decomposition grade. The maximum butylene yield is about 7 wt.%. The yield curve runs below the tangent constructed to the initial part of the curve, that is the relative amount of the butylene produced decreases with the increasing decomposition grade. The butadiene yield is considerably influenced by the pyrolysis temperature (Fig. 16). At a given decomposition grade, a much higher butadiene yield can be obtained at higher temperatures. The yield curves show a definite maximum at about the 0.6-0.8 decomposition grade. By increasing the temperature, the maximum shifts in the direction of the higher decomposition

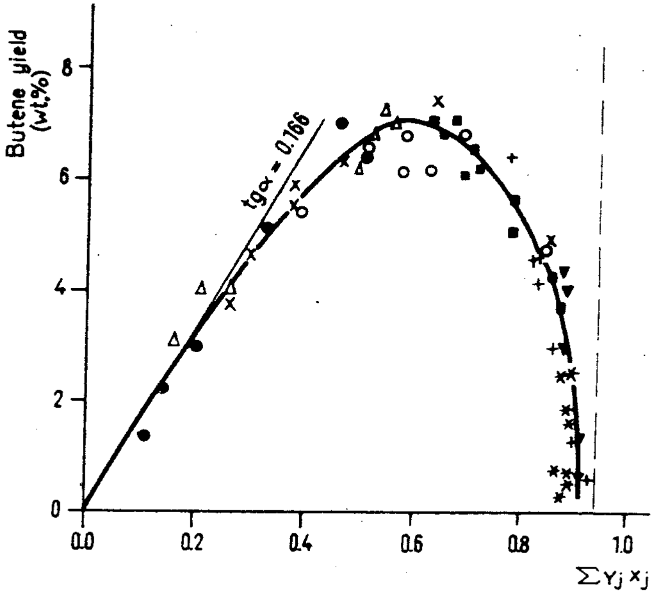

Fig. 15. Butene yield vs. decomposition grade. • 581°C; Δ 624°C; x 660°C; ○ 699°C; ■ 737°C; + 773°C; ▼ 806°C; ✱ 834°C.

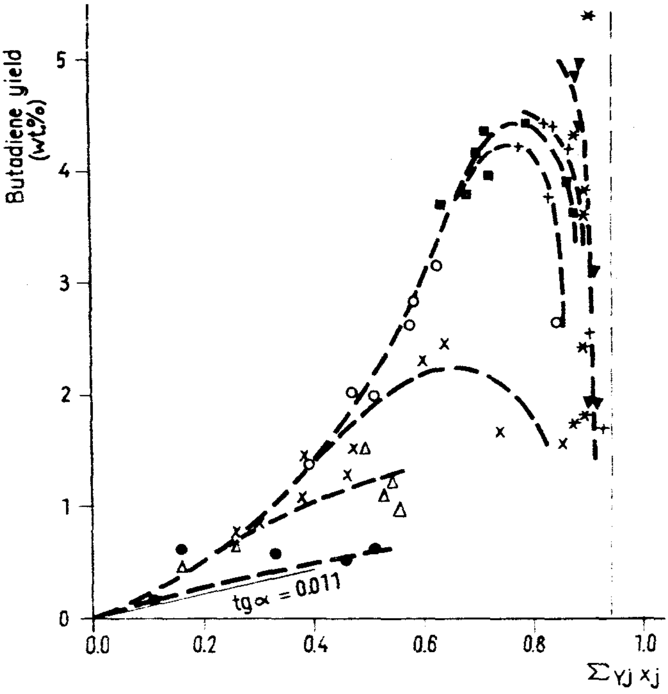

Fig. 16. Butadiene yields vs. decomposition grade. ● 581°C; Δ 624°C; x 660°C; ○ 699°C; ■ 737°C; + 773°C; ▼ 806°C; ✱ 834°C.

grades. The maximum butadiene yield is about 4.5-5.0 wt.%. The shape of the yield curves (the low value of the initial tangent) indicates that the butadiene is mainly formed in secondary reactions.

In naphtha pyrolysis small amounts of pentenes (Fig. 17) and pentadienes are also formed. The yield curve for pentenes shows a maximum at about the 0.6 decomposition grade. The maximum pentenes yield is about 1.6-1.7 wt.%. The yield curves of pentenes as well as of pentadienes are independent of the temperature.

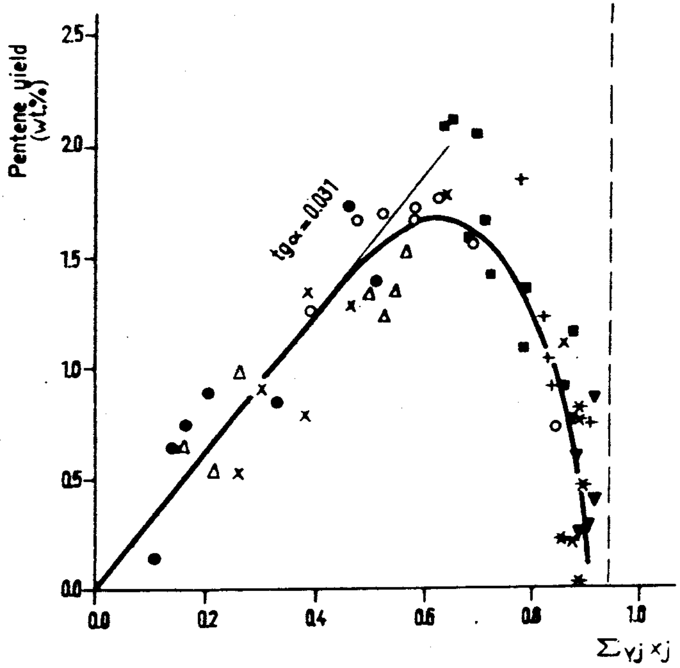

Fig. 17. Yield of pentenes vs. decomposition grade. • 581°C; Δ 624°C; x 660°C; o 699°C; ■ 737°C; + 773°C; ▼ 806°C; ж 834°C.

In Fig. 18 the yields of benzene, toluene and styrene are plotted against the decomposition grade. The benzene yield shows a very small increase up to about the 0.5 decomposition grade i.e. practically equal with the benzene content of the naphtha feed. Over the about 0.6 decomposition grade the yield curves rise considerably and over the 0.8 decomposition grade they rise abruptly.

The toluene yield, compared to the toluene content of the naphtha feed, slightly decreases up to about the 0.5 decomposition grade then continuously increases above this value. At a given decomposition grade, the yields of both products decrease by increasing temperature.

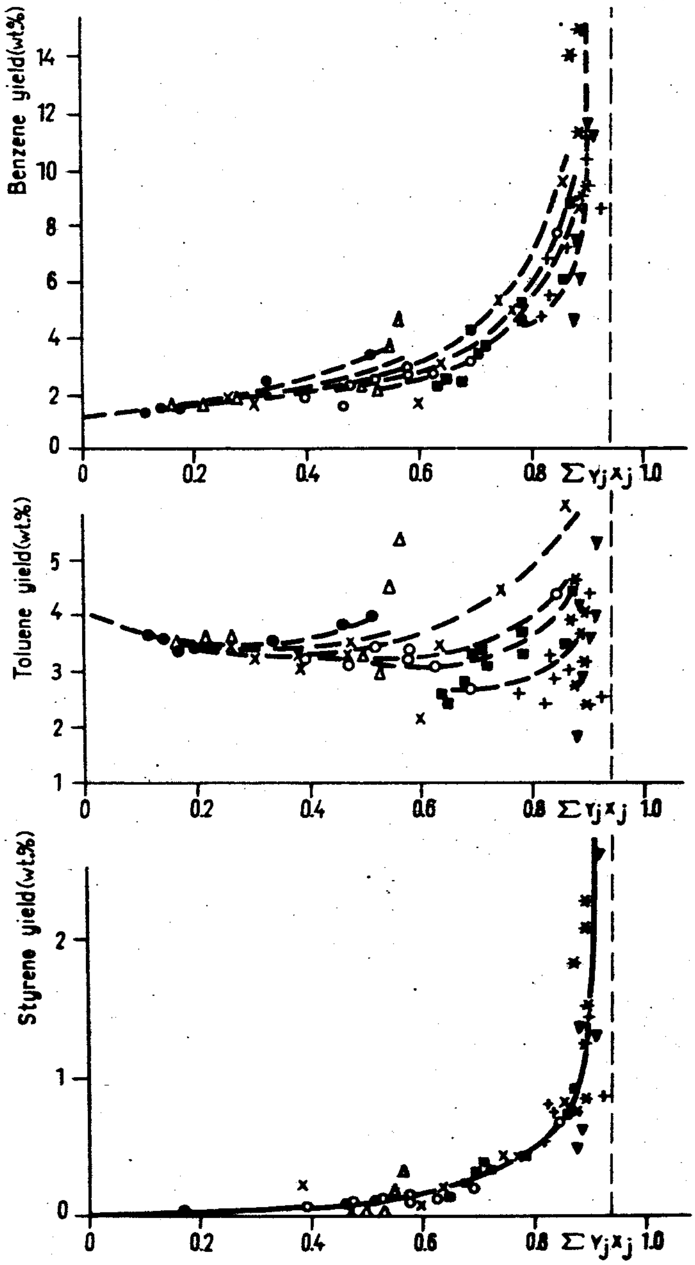

Fig. 18. Yields of benzene, toluene and styrene vs. decomposition grade. • 581°C; Δ 624°C; x 660°C; ■ 737°C; + 773°C; ▼ 806°C; ✱ 834°C.

The yield curve of styrene is independent of the temperature. The styrene curve is similar in shape to the benzene curve, above the about 0.8 decomposition grade it steeply rises. The amount of styrene formed is about one order of magnitude smaller than the amount of benzene.

The above mentioned changes in product distribution are caused by the simultaneous effects of several factors. These changes can to some extent be explained on the basis of the free-radical chain mechanisms.

At a given decomposition grade, the increase in the hydrogen and ethylene yields and the simultaneous decrease in the ethane yield by increasing the temperature are caused by the change of the relative velocities in the hydrogen abstraction and decomposition reactions of the ethyl radicals. By increasing the temperature the velocity of the ethyl radical decomposition will considerably increase compared to the velocity of the hydrogen abstraction, because of the much higher temperature coefficient of the decomposition reaction, which results in an increase of the hydrogen and ethylene yields and an equivalent decrease of the ethane yield.

The decrease in the propane yield by increasing temperature can be explained in a similar way by the different temperature coefficients of the hydrogen abstraction and decomposition reactions of the propyl radicals.

The considerable changes in product distribution by increasing the decomposition grade in naphtha pyrolysis are caused by the secondary reactions among the product olefins and the chain-propagating radicals. From among these reactions the most important are the combination reactions of higher olefins and chain-propagating radicals and the radical decomposition following these reactions.

$$(\text{Olefin})_1 + R_1 \rightleftharpoons \text{Alkyl radical} \rightarrow (\text{Olefin})_2 + R_1' \qquad (8)$$

As a result of the above mentioned decomposition of higher primary olefins (pentenes, butenes) lower olefins (ethylene, propylene) and methane are formed. The rise in the methane as well as in the ethylene and propylene yields and the decrease of the amounts of higher olefins can be explained mainly on the basis of the above reactions.

In the case of higher decomposition grades the hydrogen abstraction reactions among the olefins and chain-propagating radicals also have a considerable effect on product distribution. In these reactions small molecules (H_2, CH_4) as well as vinyl-, allyl- and higher molecular weight unsaturated radicals are formed. The reactions of these radicals among themselves and with the olefins lead to the formation of higher molecular weight dienes and aromatics. As it is apparent in Fig. 18 the amounts of aromatics steeply increase with the decomposition grade above the about 0.6 value.

SIMPLIFIED KINETIC MODEL FOR THE CALCULATION OF PRODUCT YIELDS

In the preceding sections the method for the description of the overall decomposition rate for naphthas was outlined and the constants of the kinetic equations for the naphtha investigated were determined. In these kinetic correlations the decomposition grade introduced instead of the conversion is the dependent variable.

On the basis of the pyrolysis of individual hydrocarbons [8, 9] it was earlier demonstrated that the expansion and yield curves plotted against the conversion were independent of the temperature for most of the hydrocarbons investigated in the temperature and residence time ranges of industrial processes. This means that the expansion and yield curves can be described by mathematical functions containing the conversion as the independent variable.(In most cases this description can be made satisfactory by a polynomial.) In such cases when the temperature independence is not fulfilled, the above curves can be described by functions containing the temperature as a parameter.

It was shown that among the principal reaction products the yield curves of propylene, butenes, pentenes, pentadienes and styrene are independent of the temperature. In the Figures all the measured values were presented. A considerable part of these values were obtained above 1 second residence time. Taking into account only the values measured in the residence time range $0 < \tau < 1$ second of industrial interest, the independence from temperature is also valid approximately for the yield curves of the other products.

To illustrate the above statement, the yield curves of ethylene are shown in Fig. 19 measured in the $0 < \tau < 1$ residence

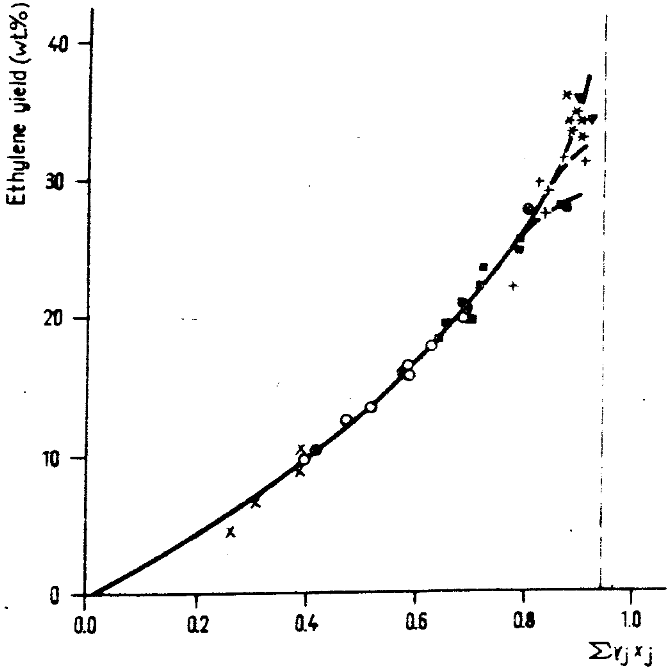

Fig. 19. Ethylene yield vs. decomposition grade in reaction time range of $0 < \tau < 1$ sec. x 660°C; ○ 699°C; ■ 737°C; + 773°C; ▼ 806°C; ✱ 834°C. ⊛ Calculated values.

time range. The small discrepancies at higher decomposition grades do not cause difficulties in describing the yield curves.

The simplified kinetic model developed for the calculation of the product distribution consists of the kinetic equations suitable for the description of the overall decomposition rate i.e. the changes of the decomposition grade, and of the mathematical equations describing the yield curves as a function of the decomposition grade.

$$\begin{aligned} X &= f\,(T,\ \omega,\ \text{or}\ \tau) \\ H_i &= \psi(X) \end{aligned} \tag{9}$$

Fig. 19 also presents some values calculated on the basis of the above model. In this calculations first the decomposition grades were determined for the temperatures investigated using the kinetic constants presented in Fig. 8 and the kinetic Equation (5). The decomposition grade values so obtained were put into the polynomials describing the yield curves and the product yields were determined for the given reaction conditions.

The yields calculated by the above method fit in well with the full line constructed through the measured values which indicates the suitability of the given method for the description of the thermal decomposition of naphthas.

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USED SYMBOLS

C_o, C	total concentration of the naphtha components (undergoing decomposition) at the reactor inlet and outlet, resp. (moles/litre)
E	expansion, defined by the ratio of mole numbers of the mixture leaving and entering the reactor (dimensionless)
E_v	limiting expansion value (expansion value for the complete decomposition of 1 mole feed mixture)(dimensionless)
H_i	yield of the i^{th} reaction product (mole product/mole feed or kg product/kg feed)
k	decomposition rate constant (sec^{-1})
k^o	decomposition rate constant at zero conversion (sec^{-1})
$\int kdt$	severity function (dimensionless)
n	reaction order
R_1, R_1'	chain-propagating radicals
ν_{ji}	overall stoichiometric coefficient of the i^{th} reaction product in the case of the complete decomposition of the j^{th} component of the feed mixture as individual hydrocarbon (moles product/mole decomposed)
x_j	conversion of the j^{th} component in the feed mixture (dimensionless)
X	decomposition grade (dimensionless)
y_j	mole fraction of component j in the feed mixture (dimensionless)
β	restraining coefficient giving the inhibiting effect of the reaction products (sec^{-1})
τ	true reaction time (sec)
ω	fictive reaction time (sec)

REFERENCES

1. de BLIECK, J.L., CIJFER, H.J., JUNGERHANS, R.J., Erdöl u. Kohle Erdgas Petrochemie 24, 452 (1971)
2. LINDEN, H.R., et al., Ind. Eng. Chem. 47, 2467 (1955)
3. LINDEN, H.R., REID, J.M., Chem. Eng. Progr. 55, 71 (1959)
4. ZDONIK, S.B., GREEN, E.J., HALLE, L.P., The Oil and Gas J. July 10, 192 (1967)
5. ILLÉS, V., Acta Chim. Acad. Sci. Hung. 72, 117 and 133 (1972)
6. ILLÉS, V., Magyar Kémiai Folyóirat 76, 663 (1970)
7. ILLÉS, V., WELTHER, K., SZEPESY, L., The 2nd Conference of Hung. Chem. Soc., Some Applications of Phys. Chem., Veszprém (Hungary), August. 2-5 (1971); Vol. 2, p. 257-265.
8. ILLÉS, V., Acta Chim. Acad. Sci. Hung. 59, 35 (1969); ibid 59, 229 (1969); ibid 67, 41 (1971); ibid 67, 339 (1971)
9. ILLÉS, V., Erdöl u. Kohle Erdgas Petrochemie 25, 464 and 542 (1972)

РЕЗЮМЕ

Бензиновая франция с пределами точки кипения 40-160°С ромашкинской нефти была подвергнута пиролизу в лабораторном трубчатом реакторе, при давлении 1 атм и в диапазоне температур 580-830°С.

Для характеризовки степени разложения бензиновой франции введены авторами новые показатели. В кинетических уравнениях разработанных для проточных реакторов была замещена степень разложения, определенная авторами, в место конверсии, и таким образом были получены соотношения подходящие к описанию общей скорости разложения бензиновой франции.

Авторами показано,что экспансия и выход по основным продуктам реакции — в диапазонах температуры и времени пребывания, принятых при производственном внедрении пиролиза — являются однозначными функциями степени разложения.

На основе найденных соотношений, авторами была разработана упрощенная кинетическая модель для расчета состава смеси реакции пиролиза.