

Thermal cracking of ethylene, propylene and
light hydrocarbon mixtures

Froment G.F., Van De Steene B.O.

Laboratorium voor Petrochemische Techniek, Rijksuniversiteit,
Gent, Belgium.

Goossens A.G.

Kinetics Technology International, B.V., The Hague, The Netherlands.

1. Introduction

There are quite a few publications dealing with the thermal cracking of ethylene, of propylene and of their mixtures with alkanes (1,2,3,4,5), but most of them are confined to rather narrow ranges of the process variables. Further, there is little agreement as to the product distribution and the kinetics of the overall reaction, although it would seem that a gradual transition between polymerization and decomposition processes could explain some of the contradictions.

The thermal cracking of ethane, propane, n and i-butane has been investigated rather intensively, but the thermal cracking of binary and ternary mixtures has received far less attention. Although industrial practice generally deals with mixtures, there are no guiding lines to day for the prediction of reaction rates and product distributions of mixtures cracking from data on the cracking of individual components. The question whether or not the reaction partners significantly interact to alter the product distributions from those calculated from pure additivity has not been settled yet.

The work reported in the present paper aimed at determining kinetics and product distributions of the thermal cracking of ethylene, propylene, of mixtures of ethane-propylene and of binary and ternary mixtures of ethane, propane, n- and i-butane from an experimental program covering wide ranges of process variables and carried out in a pilot plant. Further, it aimed at reconciling some of the above mentioned contradictions in olefins cracking and at deriving some general rules for mixtures cracking.

2. Experimental program

The pilot plant has been described in detail by Van Damme et al (6) and Froment et al (7).

A. Ethylene

The ethylene was high purity grade (Air Liquide CH25) and contained less than 0.2 wt % C_2H_6 .

The process variables were varied over the following ranges :

Variable	Range
ethylene flow rate (kg/hr)	0.5 - 3
dilution (kg steam/kg hydrocarbon)	0.4 - 4
Reynolds number	4,500-8,000
exit temperature (°C)	625-850
exit pressure (atm.abs.)	1.2-2.3
pressure drop (atm.)	0.1-0.5

The majority of the 150 experiments were grouped into 5 classes depending upon the partial and the total pressure.

class	exit pressure (atm.abs.)	dilution (kg/kg)	inlet partial pressure (atm)
1	1.5	0.4	0.92
2	1.5	1	0.59
3	2.0	0.4	1.36
4	2.0	1	0.77
5	1.5	4	0.235

B. Propylene

The propylene was also high purity grade, containing less than 0.2 wt % C_5^+ . The operating conditions were similar to those described above, except for the inlet partial pressure, which was varied between 0.164 and 1.16 atm.abs. and for the temperature range, which extended from 625 to 870°C.

C. Binary and ternary hydrocarbon mixtures

Ethane-propylene mixtures containing from 25 to 75 wt % of propylene were investigated under class 1 conditions in a temperature range from 675 to 850°C and with hydrocarbon flow rates ranging from 2 to 3.6 kg/hr. Similar conditions were chosen for the investigation of ethane-propane, n.butane-propane, n.butane-i.butane and ethane-n.butane mixtures.

Finally, the following ternary mixtures were investigated under these conditions :

ethane	propane	n.butane (wt %)
20.81	67	11.65
41.39	37.53	20.78
30.63	11	58.32
42.23	18.40	39.35
70.61	18.45	10.93

3. Product Distributions.

A. Thermal cracking of ethylene.

The main products of ethylene cracking are H_2 , CH_4 , C_2H_2 , C_2H_6 , C_3H_6 , $1,3C_4H_6$ and a C_5^+ -fraction.

Figures 1 to 5 show the yields of some of these products. The results are plotted versus the ethylene conversion with the partial pressure of the hydrocarbon and the total pressure as parameters. Plotted in this way, there is practically no influence of temperature. From these figures it is clear that the range of investigated partial pressures has to be split in an area with $p_{C_2H_4} < 0.6$ atm, i.e. the class 5 experiments, and an area with $p_{C_2H_4} > 0.6$ atm, i.e. the experiments of the classes 1 to 4. This will be explained in the last section, in which the location of the border line between polymerization and decomposition zone is discussed. Table 1 summarizes the influences of partial and total pressure on the product yields. The C_5^+ yield is favored by an increase in partial and total pressure, but there was also a strong influence of the temperature : high temperatures lead to high C_5^+ yields. At temperatures below 800°C most of the C_5^+ formed were heavier than toluene, but at the higher temperatures the product spectrum shifts towards lighter C_5^+ products.

TABLE 1

Influence of the partial pressure of ethylene and the total pressure on the yields.

component	increase of partial pressure		increase of total pressure
	p < 0.6 atm	p > 0.6 atm	
H ₂	↓	↓	↓
CH ₄	↑	↓	none
C ₂ H ₂	↓	↓	↓
C ₂ H ₆	↑	no	none
C ₃ H ₆	↑	no	none
1,3C ₄ H ₆	↑	little or none	slight decrease

B. Thermal cracking of propylene

Figures 6 to 11 show the yields of the different products in propylene cracking.

The primary products of propylene cracking are H₂, CH₄, C₂H₄, 1,3C₄H₆ and C₅⁺. Considering only classes 1 to 4, the initial selectivities of these products are independent of partial and total pressure. The following values were found: H₂=.05; CH₄=.15; C₂H₄=.15; 1,3C₄H₆=.05; C₅⁺=.6.

In the class 5 experiments the initial C₅⁺ and 1,3C₄H₆ selectivities are lower and the initial H₂ selectivity is higher, however. Table 2 summarizes the influence of partial - and total pressure on the product spectrum.

TABLE 2

Influence of partial pressure of the hydrocarbon and of the total pressure on product yields for propylene cracking.

component	increase of partial pressure	increase of total pressure
H ₂	none	none
CH ₄	none	none
C ₂ H ₄	none	none
C ₂ H ₆	↑	↑
C ₂ H ₂	↓	↓
C ₃ H ₈	↑	↑
1C ₄ H ₈	none	none
1,3C ₄ H ₆	↑	↑
C ₅ ⁺	↑	↑

C. Thermal cracking of binary and ternary hydrocarbon mixtures

Figure 12 shows the experimental selectivities for the different products in ethane-propylene mixtures, versus the feed composition.

The selectivity of a component I in the cracking of a mixture A-B is defined as :

$$y_I = \frac{\text{mols of I from A} + \text{mols of I from B}}{\text{mols of A cracked} + \text{mols of B cracked}} \quad 1)$$

When there is no interaction, Froment et al (7) showed that equation 1 is identical with :

$$\hat{y}_I = \frac{y_{I,A} x_{A,M} \psi'_A + y_{I,B} x_{B,M} \psi'_B}{x_{A,M} \psi'_A + x_{B,M} \psi'_B} \quad 2)$$

This predicted value of the selectivity will be called the non-interaction selectivity.

The pure additivity selectivity : $y_I = y_{I,A} \psi'_A + y_{I,B} \psi'_B$ 3), used in the literature so far, is obviously a very special case of 2) valid only for $x_{A,M} = x_{B,M}$.

It is clear from Figure 12 that 2) allows a far better prediction of the experimental results than 3). Analogous figures were plotted for different conversions and for all binary mixtures mentioned in the experimental program. From all these curves, the following rule can be deduced : "The experimental selectivities deviate from the pure additivity lines in the same direction as the non-interaction selectivities". This means that the effect of interaction can be predicted when the selectivities from the individual components and the relative rates of cracking are known.

The selectivities for cracking of ternary mixtures may be represented in diagrams of the type shown in figure 13. In this figure the ethylene selectivity at conversions $x_{E,M}=40\%$, $x_{P,M}=73\%$;

$x_{N,M}=88\%$ is plotted with respect to the ternary feed composition. With ternary mixtures the pure additivity, non interaction and experimental lines of Fig. 12 become surfaces. Here too the experimental selectivities deviate from the pure additivity surface in the same sense as the non-interaction surface.

4. Kinetics

The kinetics of the cracking of a component E, are derived from the experiments by means of its continuity equation. For ethane in a binary mixture ethane-propylene e.g., cracked in a tubular reactor with plug flow conditions, the continuity equation may be written :

$$F_{E,0} dx_{E,P} = A \exp\left(-\frac{E}{RT(z)}\right) \cdot (C_{E,P})^n dV \quad 4)$$

with :

$$C_{E,P} = \frac{1-x_{E,P}}{(1-x_{E,P}) + \gamma(1-x_{P,E}) + \xi(x_{E,P} + \gamma x_{P,E}) + \delta(1+\gamma)} \cdot \left(\frac{p_t(z)}{RT(z)}\right)$$

$$\xi = \text{expansion} = \frac{(\text{total molar flow rate})_{\text{exit}} - (\text{mols } C_2H_6 + \text{mols } C_3H_6)_{\text{exit}}}{\text{mols } C_2H_6 \text{ cracked} + \text{mols } C_3H_6 \text{ cracked}}$$

γ = molar ratio propylene/ethylene

λ = dilution factor : mols H₂O/mol hydrocarbon

In 4) the experimental temperature and total pressure profile are also accounted for.

The kinetics can now be derived from 4) as such or by making use of the equivalent reactor volume concept.

A. The equivalent reactor volume concept

In this approach, the non-isothermal, non-isobaric data are first reduced to isothermality and constant pressure. This leads to an equivalent reactor volume V_E rather than the physical volume V in 4), while $T(z)$ is replaced by a reference temperature and $p_t(z)$ by a reference pressure (6,7,8). The kinetic parameters of the thermal cracking of individual alkanes were determined by means of this concept. Figure 14 shows the Arrhenius plot of the first order rate constants for ethane, propane, n.butane and i.butane. The concept was also used to calculate the kinetic coefficients of the cracking of the individual components in the mixture, assuming first order. The integration of 4) then requires a relation $x_{p,E} = f(x_{p,p})$. From the experimental data, this relation was found in all cases to be parabolic, so that equation 4 could be integrated analytically. Figure 15 shows the value of $k_{p,p}$ versus the feed composition. The inhibiting effect of propylene on the ethane rate coefficient is very pronounced. The same procedure was followed to calculate the individual rate coefficients for all the components of the different feed mixtures.

Table 3 summarizes the relative influences, caused by cocracking.

TABLE 3

Effect of the addition of various components on the rate coefficient for the cracking of ethane, propane, n.butane, i.butane and propylene.

Addition of	Effect on rate coefficient				
	$k_{C_2H_6}$	$k_{C_3H_8}$	$k_{nC_4H_{10}}$	$k_{iC_4H_{10}}$	$k_{C_3H_6}$
C_2H_6	-	↑	↑	no data	↑
C_3H_8	↓	-	↓	no data	↑
nC_4H_{10}	↓	↓	-	↓	no data
iC_4H_{10}	no data	no data	↑	-	no data
C_3H_6	↓	↓	no data	no data	-

The individual rate coefficients in the ternary mixture ethane-propane-n.butane were calculated in an analogous way. Figure 16 shows the effect on the rate coefficient for ethane cracking of the addition of one or two components in various ratios. Analogous diagrams could be shown for $k_{p,M}$ and $k_{N,M}$. All three of them clearly illustrate the effect on the rate coefficients of interaction between reaction partners.

B. Determination of the kinetics from the non-isothermal, non-isobaric data as such.

The equivalent reactor volume concept requires an initial guess of the activation energy, valid over the whole range of investigated temperatures. This is no problem with alkanes but, as will be discussed in the next section, the ethylene and propylene cracking experiments cover a transition zone in which polymerization processes with activation energies of ± 35 kcal/mol and decomposition processes with activation energies of ± 70 kcal/mol simultaneously occur. In such cases it is preferable to resort

to the non-isothermal non-isobaric approach used by Van Damme et al (6). Equation 4, with the experimental temperature and pressure profile included, was integrated numerically and the residual sum of squares, $\sum(x_{\text{exp}} - x_{\text{calculated}})^2$ was minimized with A, E and n as parameters, using Marquardt's search routine (22). The results are shown in Table 4,5,6 and 7 respectively, from which it follows that there is a strong influence of temperature, partial and total pressure on the kinetic parameters in both ethylene and propylene cracking.

TABLE 4
Influence of the temperature on the kinetic parameters of the overall ethylene disappearance.

T(°C)	A	E(kcal/mol)	n
725	1.707 10^8	39.600 ± .984	1.61 ± 0.025
750	6.56 10^{13}	65.420 ± 7.090	1.46 ± 0.122
775	3.71 10^{17}	84.330 ± 1.690	1.43 ± 0.042
800	1.39 10^{13}	60.150 ± 2.520	1.19 ± 0.034
825	4.05 10^{15}	77.295 ± 5.890	1.22 ± 0.042

TABLE 5
Influence of the temperature on the kinetic parameters of propylene cracking

T	A	E(kcal/mol)	n
725	5.69 10^7	36.310 ± 1.200	1.33 ± 0.16
750	9.42 10^7	36.400 ± 5.500	1.46 ± 0.035
775	4.43 10^{12}	60.030 ± 11.000	1.24 ± 0.18
800	1.62 10^{11}	54.990 ± .280	1.10 ± 0.075
825	2.99 10^{11}	57.530 ± 3.800	0.95 ± 0.048

TABLE 6
Influence of inlet partial pressure and total pressure on the kinetic parameters of ethylene cracking.

	A	E(kcal/mol)	n
Class 1	2.48 10^{11}	54.220 ± 1.260	1.29 ± 0.046
Class 2	1.11 10^{17}	81.910 ± 1.340	1.54 ± 0.01
Class 3	1.65 10^{11}	54.430 ± 2.170	1.27 ± 0.023
Class 4	5.47 10^{13}	66.400 ± .211	1.35 ± 0.023
Class 5	1.50 10^{15}	72.840 ± .191	1.36 ± 0.018
All classes	2.51 10^{13}	60.400 ± .975	1.30 ± 0.027

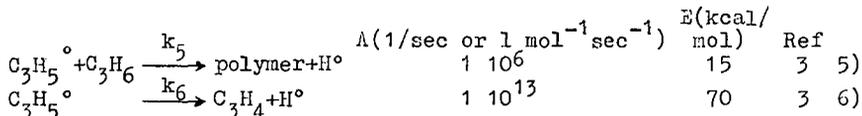
TABLE 7
Influence of inlet partial pressure and total pressure on the kinetic parameters of propylene cracking.

	A	E(kcal/mol)	n
Class 1	2.80 10^{10}	51.320 ± 2.600	1.02 ± 0.035
Class 2	1.86 10^{13}	66.020 ± 28.000	1.02 ± 0.37
Class 3	2.44 10^{11}	56.690 ± 2.900	1.05 ± 0.028
Class 4	1.89 10^{13}	63.960 ± 1.080	1.18 ± 0.040
Class 5	5.18 10^9	47.710 ± 2.150	1.15 ± 0.063
All classes	2.43 10^{10}	50.650 ± 1.600	1.08 ± 0.033

5. Decomposition and polymerization zones in olefines cracking

A. Propylene cracking

In the thermal cracking of propylene, polymerization and decomposition processes are in competition (1,2,3,12,13,14). Low temperatures and high partial pressures favor polymerization, high temperatures and low partial pressures favor decomposition. Allene and/or methylacetylene are obtained when decomposition is predominant, whereas they are not formed when only polymerization occurs. To account for both polymerization and for decomposition, all authors consider the following two reactions :



This means that the allyl radical acts as a β radical in the polymerization and as a μ radical in the decomposition processes. Combined with the termination : $C_3H_5^\circ + H^\circ \rightarrow C_3H_6$ and with the first order initiation : $C_3H_6 \rightarrow C_3H_5^\circ + H^\circ$, 5) leads to an overall order of 3/2 for polymerization and 6) to an overall order of 1 for decomposition.

From 5) and 6) and by setting $k_5(C_3H_6) = k_6$, Amano (3) calculated a border line between both zones in a temperature versus inlet partial pressure diagram. This is the dashed line in Figure 17. To permit a direct comparison with the literature, the propylene partial pressure is expressed in mm Hg. From Amano's border line, it follows that the present results would be completely located in the polymerization zone and indeed no allene is found. However, the order of the global disappearance reaction is not 3/2 but varies from 3/2 to 1 as the temperature is increased, while the activation energie varies from 36 to 66 kcal/mol. This suggests that the present data would be located in the transition area and this in turn requires the border line to be shifted towards the left of the figure. Such a shift could result from a decomposition of allyl into acetylene instead of allene :

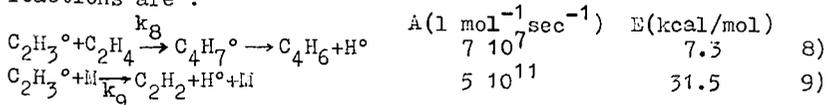


An isothermal, unsteady state radical simulation of the propylene experiments (10) led to a frequency factor of $1 \cdot 10^8$ and an activation energy of 32.4 kcal/mol for 7). These values are plausible, when compared with Allara's data (9) for the decomposition of C_5 radicals into C_2H_2 . When reaction 7 instead of reaction 6 accounts for the μ -behavior of the allyl radical, the border line between the two areas is calculated from : $k_5(C_3H_6) = k_7$. This is the full line on Figure 17. Both Kunugi's (2) and our experiments are now located in the transition zone. The experiments of Laidler (1) and Ingold (12) lie in the polymerization area and these of Szwarc (13) and Sakakibara (14) in the decomposition zone. This is in agreement with the fact that neither Laidler nor Ingold found acetylene, while Kunugi and Sakakibara did. The results of Szwarc are doubtful because of his rudimentary analytical technique. At 1200°C and higher, the decomposition of allyl into allene becomes more and more important, because of the high activation energy, so that Sakakibara, whose work is mainly situated in the temperature range 1200°C-1400°C, found more allene and methyl-

acetylene then acetylene.

B. Ethylene cracking

In complete analogy with propylene cracking, the two major initial reactions are :



The vinylradical acts as a β radical in 8) and as a γ radical in 9). The kinetic parameters of these reactions were derived from an extensive literature survey (11,15,16,17).

The border line between the two areas is now given by :

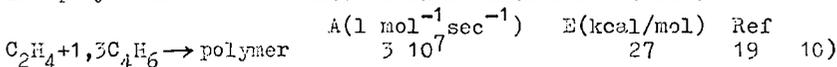
$$k_8(C_2H_3^\circ)(C_2H_4) = k_9(C_2H_3^\circ)(M)$$

This line is the full line in Figure 18. With a second order initiation like $2C_2H_4 \rightarrow C_2H_3^\circ + C_2H_5^\circ$ and a termination involving two vinylradicals ($2C_2H_3^\circ \rightarrow 1,3C_4H_6$), an order of 2 is predicted for conditions in the polymerization zone and an order of 1 for conditions in the decomposition zone.

Simon and Back (15) and Silcocks (18) observed second order kinetics, while Kolera and Stubbs (16) found second order kinetics in the region 3 of Figure 18 and first order kinetics in region 3', in agreement with the proposed border line. Kunugi's data (11) which are located in the transition area lead to an order of 3/2 for the global disappearance reaction.

The pilot plant experiments cover the transition zone. The order was shown in Tables 4 and 6 to evolve from 1.6 to 1.2 as the temperature is increased and the activation energy from 40 to about 75 kcal/mol.

The polymerization can also be of a molecular nature :



The ratio of the radical reaction and molecular condensation rates was calculated from an isothermal non steady state radical simulation of the ethylene experiments by Sundaram & Froment (10), to be 31 at 800°C and 1% conversion, 15 at 800°C and 3% conversion and 10 at 825°C and 8% conversion.

It follows that molecular condensation cannot be neglected at 800°C and higher. This explains why the experimental C_5^+ fraction was so strongly correlated with the temperature. In propylene cracking the ratios of the rates of the radical polymerisation and the molecular condensation at 800°C would be of the order of 1000 because the allyl radical is high and butadiene is low.

It is clear also from Figure 18 for ethylene and from Figure 17 for propylene that the influence of the partial and total pressure on the order and activation energy will be more or less pronounced depending upon the distance from the border line. The higher activation energies given in Tables 6 and 7 for the conditions of the classes 2, 4 and 5 may be related to this effect.

Finally, it should be added that even with an ethane content of less than 0.2 wt % in the ethylene feed, the initiation reaction $C_2H_6 \rightarrow 2CH_3^\circ$ cannot be neglected, as concluded already by

Kunugi (11) and by Towell and Martin (20).

From the mechanistic point of view the initiation then becomes of first order and the order of the global disappearance should vary between 3/2 and 1/2. On the other hand, the molecular reactions will increase the overall order. All these trends substantiate the variation of the order from 1.6 to 1.2 observed in the present work.

Notation

A	frequency factor	sec^{-1} or $l \text{ mol}^{-1} \text{ sec}^{-1}$
E	activation energy	kcal/mol
C	concentration	mol/l
C_T	concentration, total hydrocarbons	mol/l
F_0	molar flow rate of the cracked component at the inlet	mol/sec
k	rate coefficient	sec^{-1} or $l \text{ mol}^{-1} \text{ sec}^{-1}$
n	order of reaction	
P_t	total pressure	atm. abs.
R	gas constant	kcal/kmol $^{\circ}\text{C}$
r	rate of reaction	mol/l sec
T	temperature	$^{\circ}\text{K}$ or $^{\circ}\text{C}$
V_E	equivalent reactor volume	l
x	conversion	
y	selectivity	mol/mol
z	tube length	m
γ	mol ratio	mol/mol
δ	dilution ratio	mol steam/mol hydrocarbon
ϵ	expansion factor	mol products/mol hydrocarbon cracked
ψ	mol fraction	mol/mol

Subscripts

E	ethane
P	propylene
M	mixture
O	initial value
t	total
m	mean

Table captions

- Table 1 : Ethylene cracking. Influence of the total pressure and the partial pressure of ethylene on the yields of the different products.
- Table 2 : Propylene cracking. Influence of the total pressure and the partial pressure of propylene on the yields of the different products.
- Table 3 : Effect of the addition of various components on the rate coefficient for the cracking of ethane, propane, n-butane, i-butane and propylene.

- Table 4 : Influence of temperature on the kinetic parameters of the overall ethylene disappearance.
- Table 5 : Influence of temperature on the kinetic parameters of the overall propylene disappearance.
- Table 6 : Influence of inlet partial pressure and total pressure on the kinetic parameters of ethylene cracking.
- Table 7 : Influence of inlet partial pressure and total pressure on the kinetic parameters of propylene cracking.

Figure captions

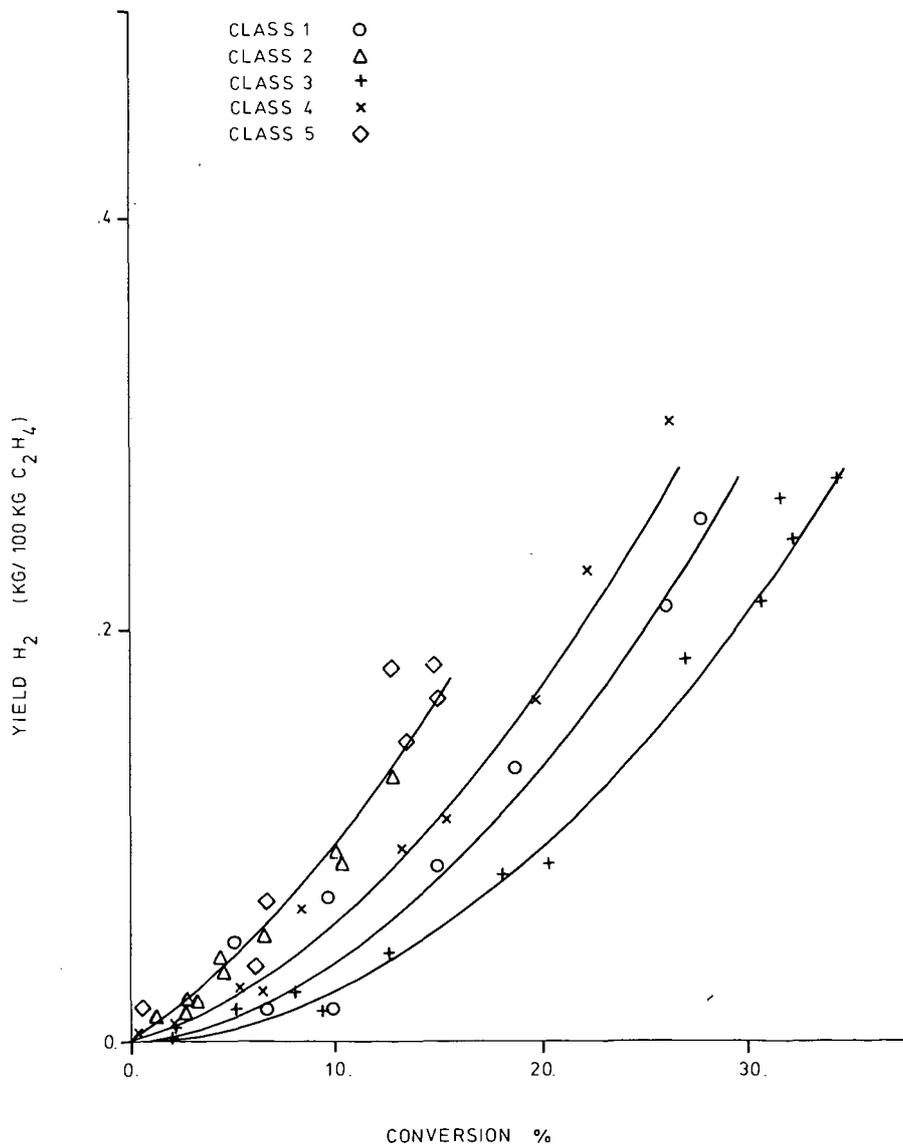
- Figure 1 : Ethylene cracking : hydrogen yield
 Figure 2 : Ethylene cracking : methane yield
 Figure 3 : Ethylene cracking : acetylene yield
 Figure 4 : Ethylene cracking : propylene yield
 Figure 5 : Ethylene cracking : butadiene yield
 Figure 6 : Propylene cracking : hydrogen yield
 Figure 7 : Propylene cracking : methane yield
 Figure 8 : Propylene cracking : acetylene yield
 Figure 9 : Propylene cracking : ethylene yield
 Figure 10 : Propylene cracking : butadiene yield
 Figure 11 : Propylene cracking : C_5^+ yield
 Figure 12 : Selectivity of H_2 , CH_4 and C_2H_4 versus mol fraction propylene in the mixture
 Figure 13 : Selectivity of C_2H_4 versus feed composition in the ternary mixture ethane-propane-n.butane
 - - lines on non-interaction surface ; + non interaction points ; . experimental
 Figure 14 : Arrhenius plot of rate coefficients for the cracking of light hydrocarbons
 Figure 15 : Rate coefficient for the cracking of ethane in an ethane-propylene mixture versus feed composition
 Figure 16 : Rate coefficient for the cracking of ethane in ternary mixtures of ethane-propane and n-butane
 Figure 17 : Polymerization and decomposition zones in propylene cracking
 Figure 18 : Polymerization and decomposition zones in ethylene cracking.

References

- 1) Laidler K.J., Wojciechowski B.W., Proc.Roy.Soc. (London), A259, 257 (1960)
- 2) Kunugi T., Sakai T., Soma K. and Sasaki Y., Ind.Eng.Chem. Fundam., vol.9, N°3 (1970).
- 3) Amano A., Uchujama M., J.Phys.Chem., 68, 1133 (1964).
- 4) Sakai T., Soma K., Sasaki Y., Tominaga H. and Kunugi T., Refining Petroleum for Chemicals, 68 (1970).
- 5) Kallend A.S., Purnell J.H., Shurlock B.C., Proc.Roy.Soc. (London), A300, 120 (1967).
- 6) Van Damme P.S., Narayanan S. and Froment G.F., A.I.Ch.E. Journal, vol.21, N°6, 1065 (1975).

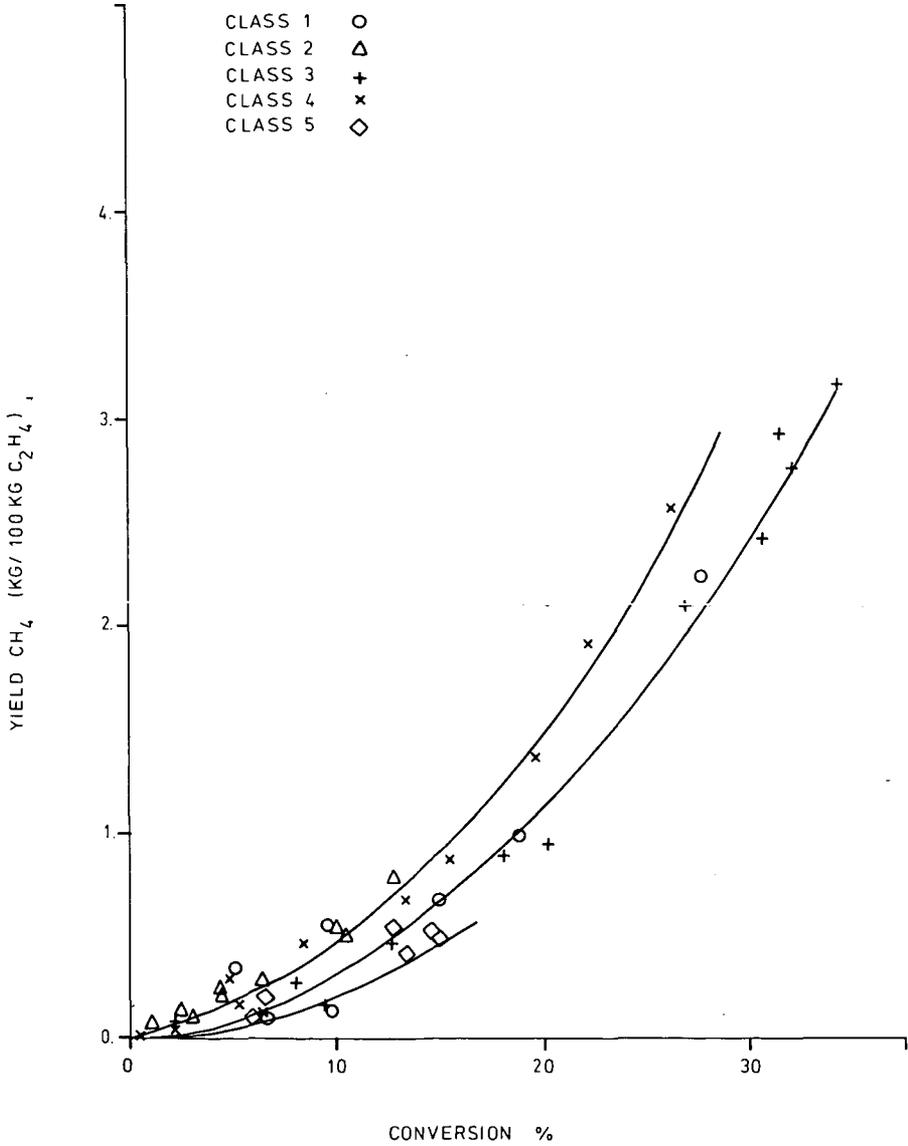
- 7) Froment G.F., Van de Steene B.O., Van Damme P., Narayanan S. and Goossens A.G., Ind.Eng.Chem.Process Des.& Develop. (to be published)
- 8) Froment G.F., Pycke H., Goethals G., Chem.Eng.Sci.,13, 173, 180 (1961)
- 9) Allara D.L., A compilation of kinetic parameters for the thermal degradation of n-alkane molecules
- 10) Sundaram M., Froment G.F., (to be published)
- 11) Kunugi T., Sakai T., Soma K., Sasaki Y., Ind.Eng.Chem.Fundam. Vol.8, 374 (1969)
- 12) Ingold K.U., Stubbs F.J., J.Chem.Soc., 1749 (1951)
- 13) Szwarc M., J.Chem.Phys., 17, 284 (1949)
- 14) Sakakibara Y., Bull.Chem.Soc. Japan, 37, 1262 (1964).
- 15) Simon M., Back M.H., Can.J.Chem., 47, 251 (1969)
- 16) Molera M.J., Stubbs F.J., J.Chem.Soc., 381 (1952)
- 17) Benson S.W., Hougen G.R., J.Phys.Chem., 71, 1735 (1967)
- 18) Silcocks C.G., Proc.Roy.Soc., A233, 465 (1955)
- 19) Bowley D., Steiner H., diss.Trans.Faraday Soc., 10,198(1951)
- 20) Powell G.D., Martin J.J., A.I.Ch.E. Journal, vol.7,N°4,693(1961)
- 21) Froment G.F., Van De Steene B.O. and Goossens A.G. (to be published)
- 22) Marquardt D.W., Soc.Ind.Appl.Math.J., 11, 431 (1963).

Figure 1.



THERMAL CRACKING OF ETHYLENE

Figure 2.



THERMAL CRACKING OF ETHYLENE

Figure 3.

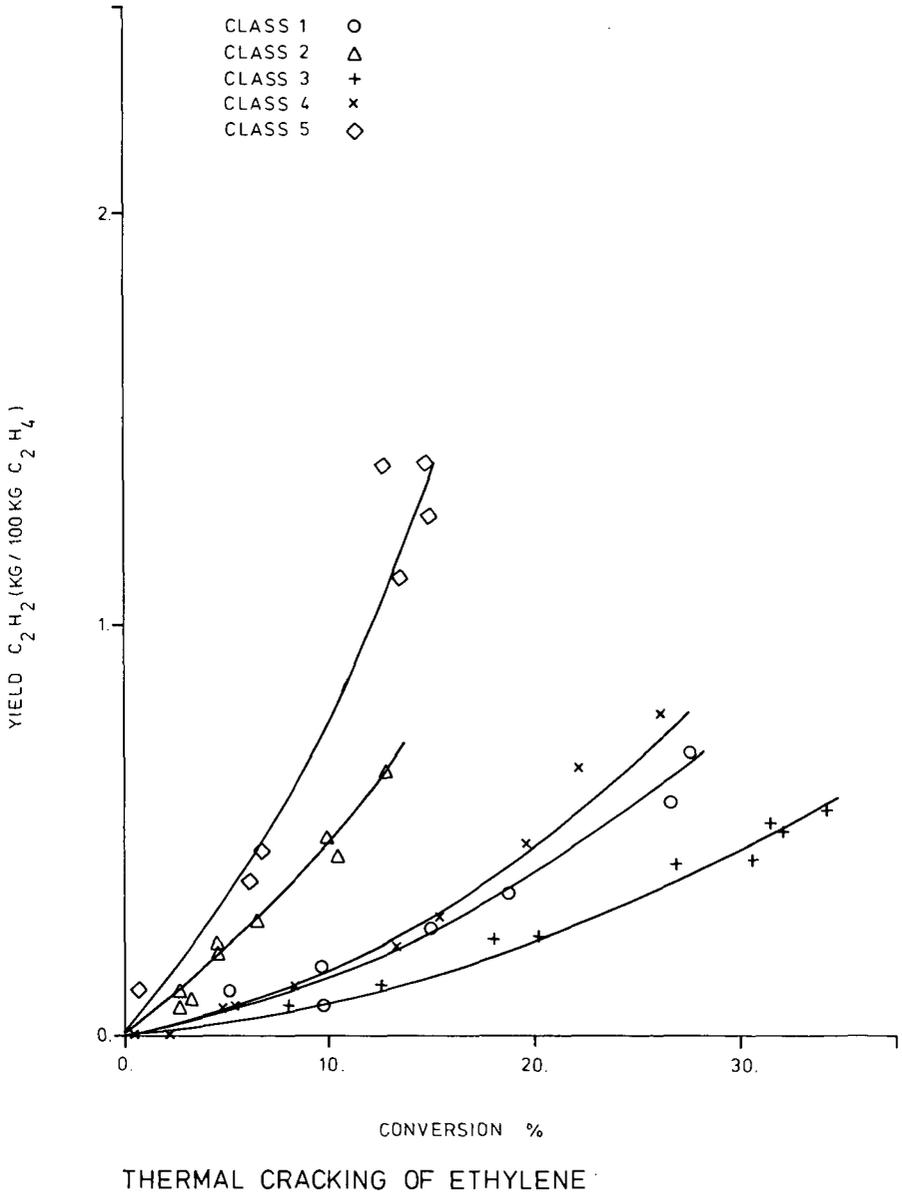
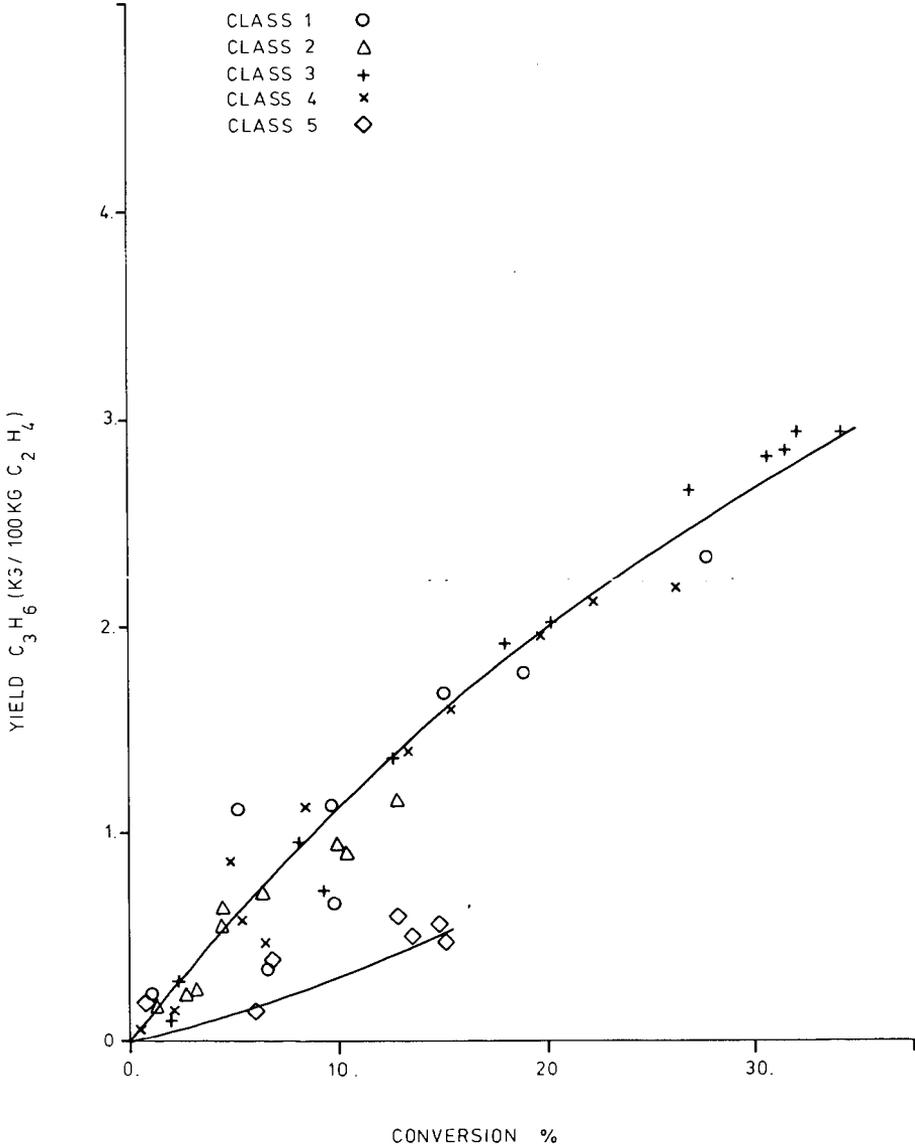
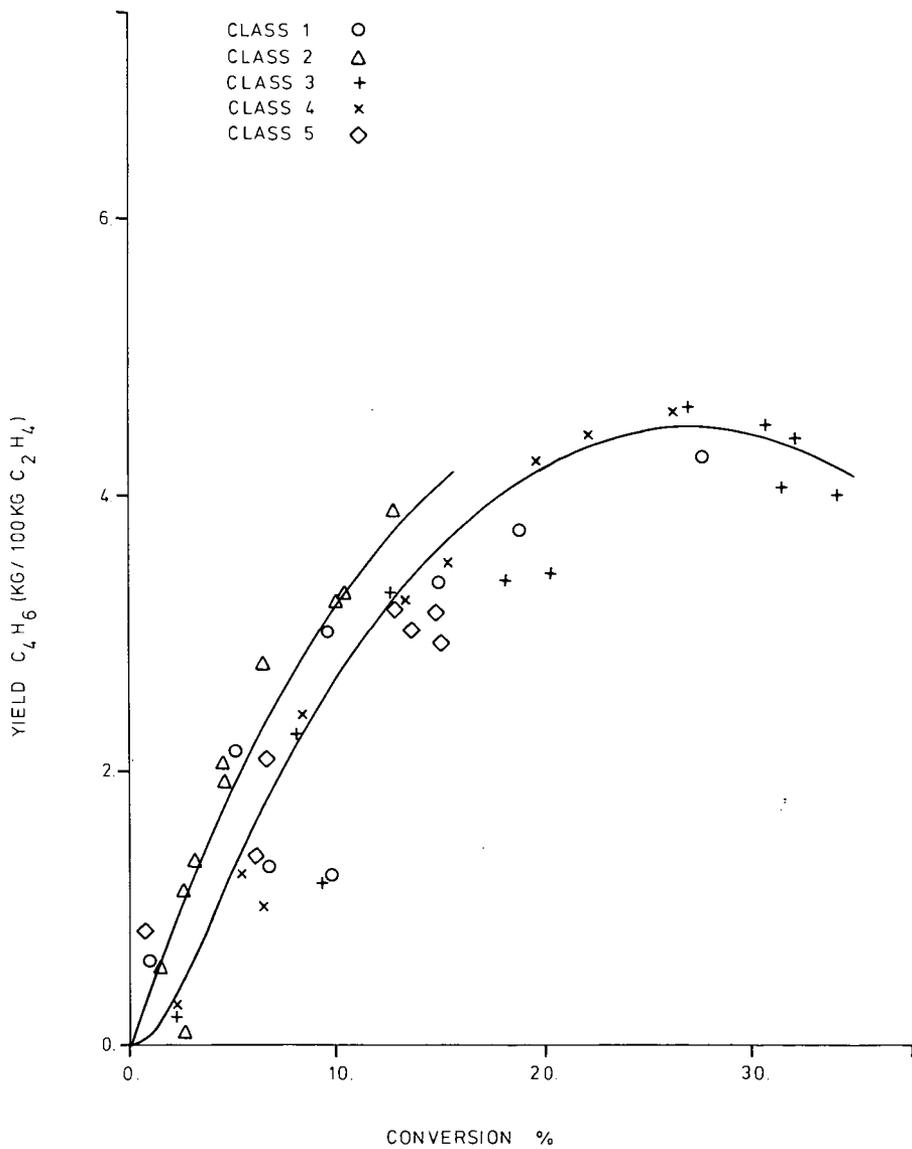


Figure 4.



THERMAL CRACKING OF ETHYLENE

Figure 5.



THERMAL CRACKING OF ETHYLENE

Figure 6.

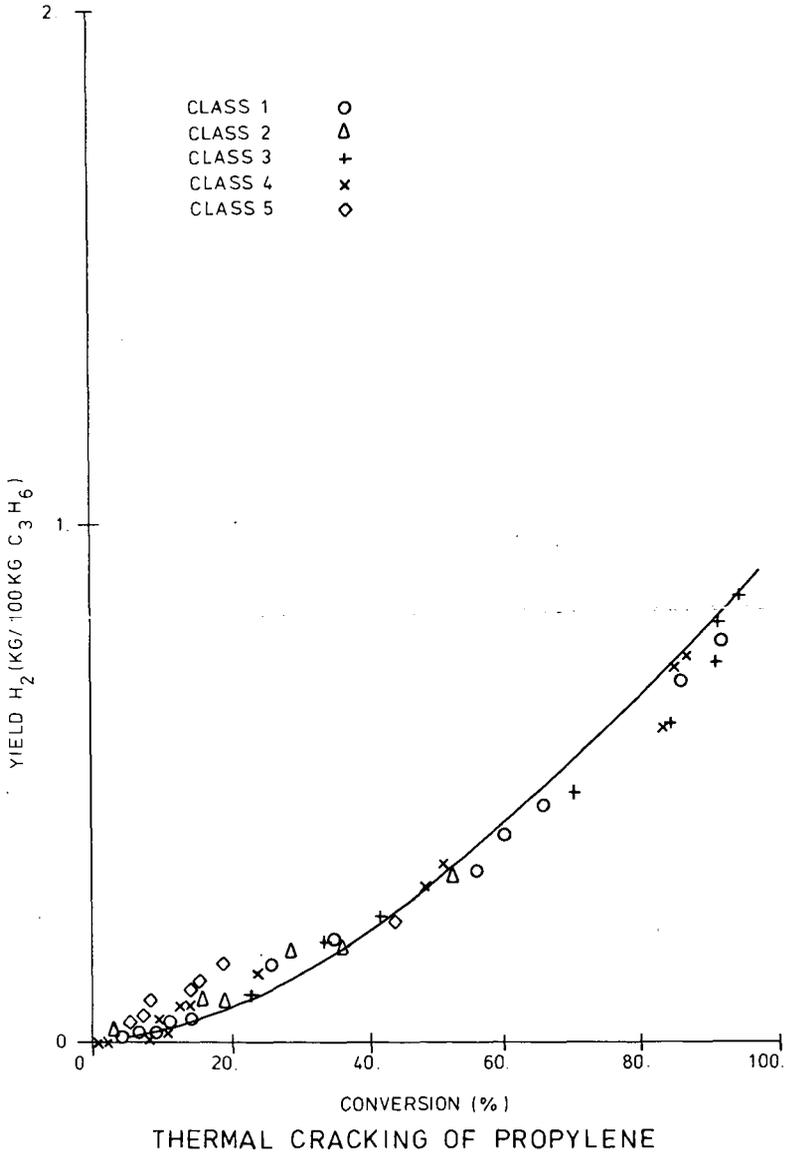


Figure 7.

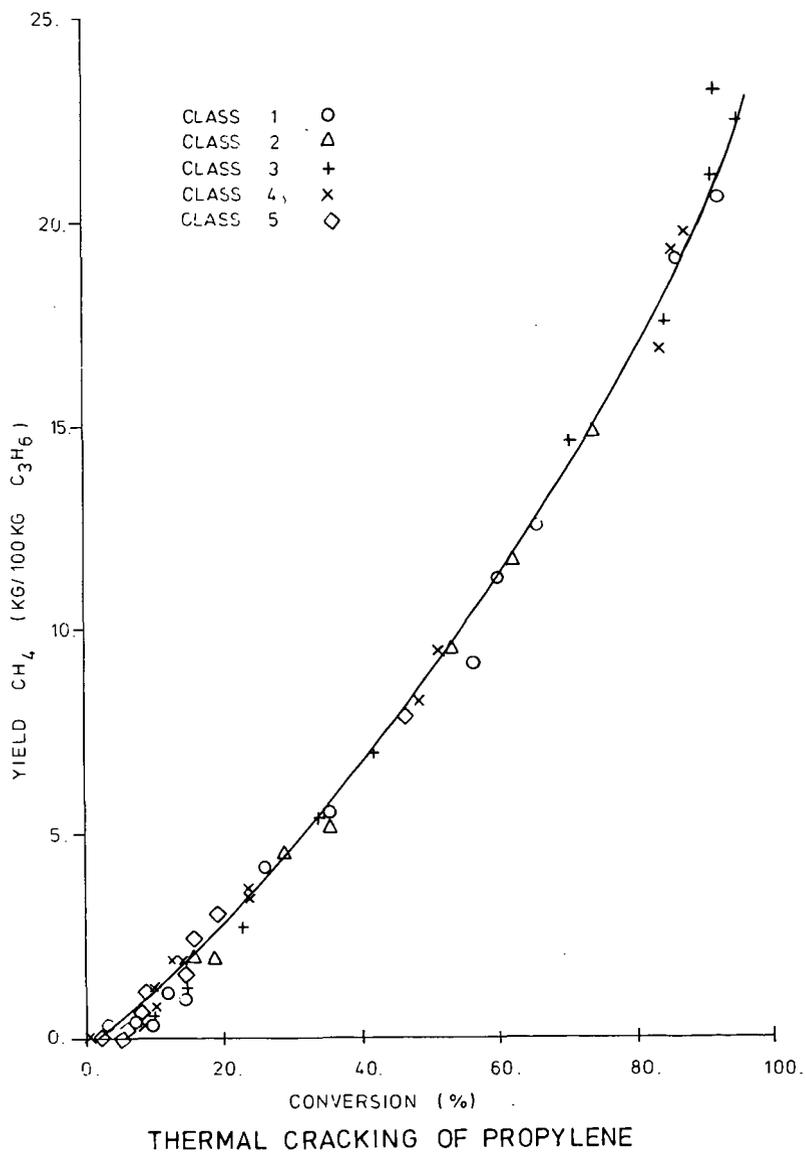


Figure 8.

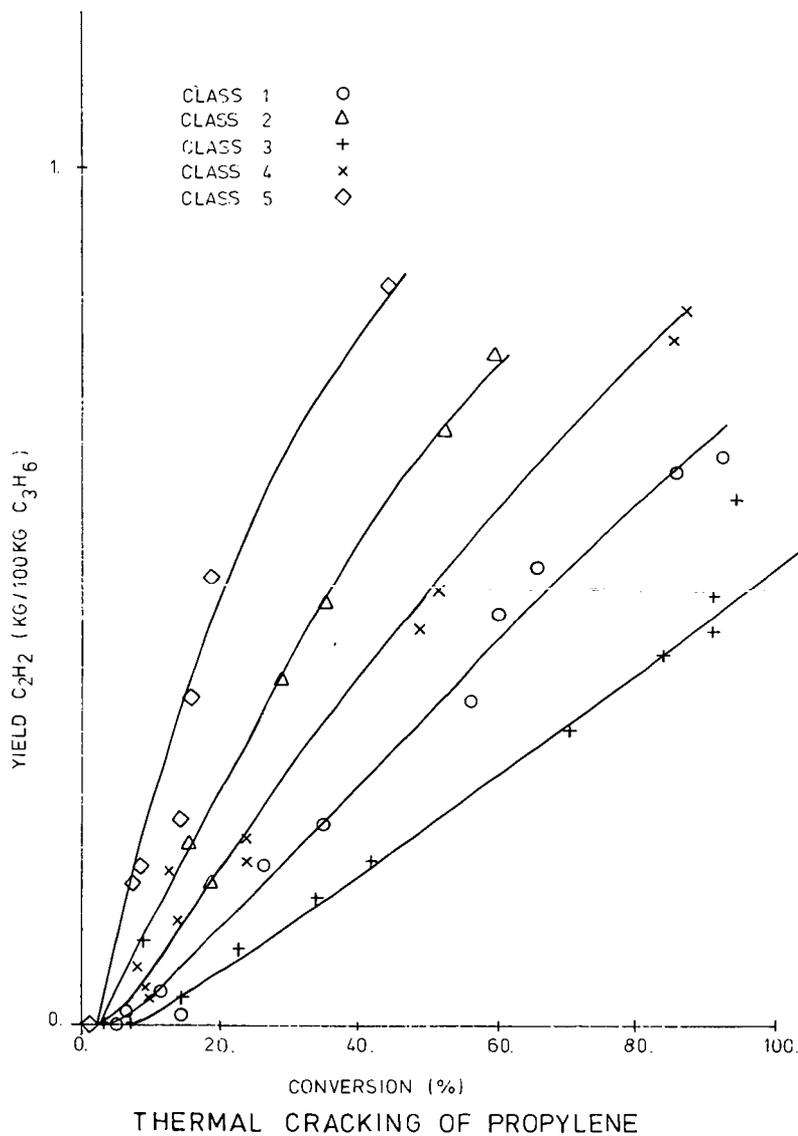


Figure 9.

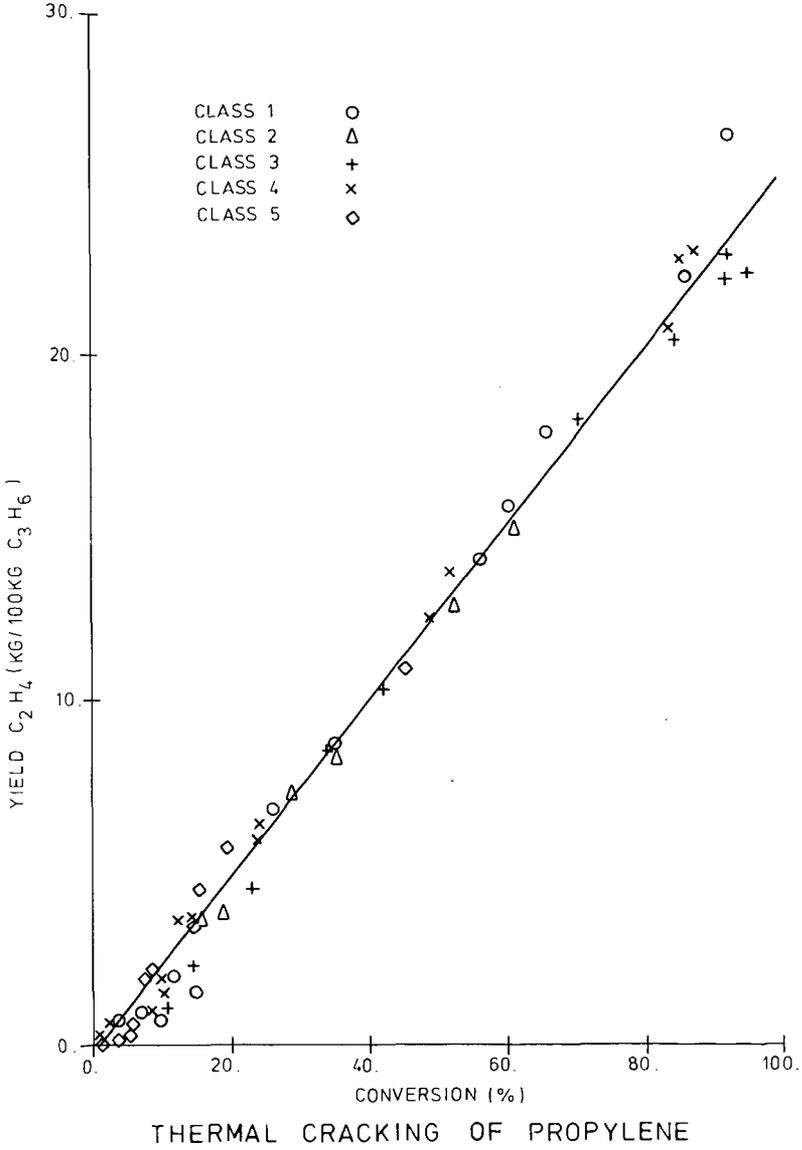


Figure 10.

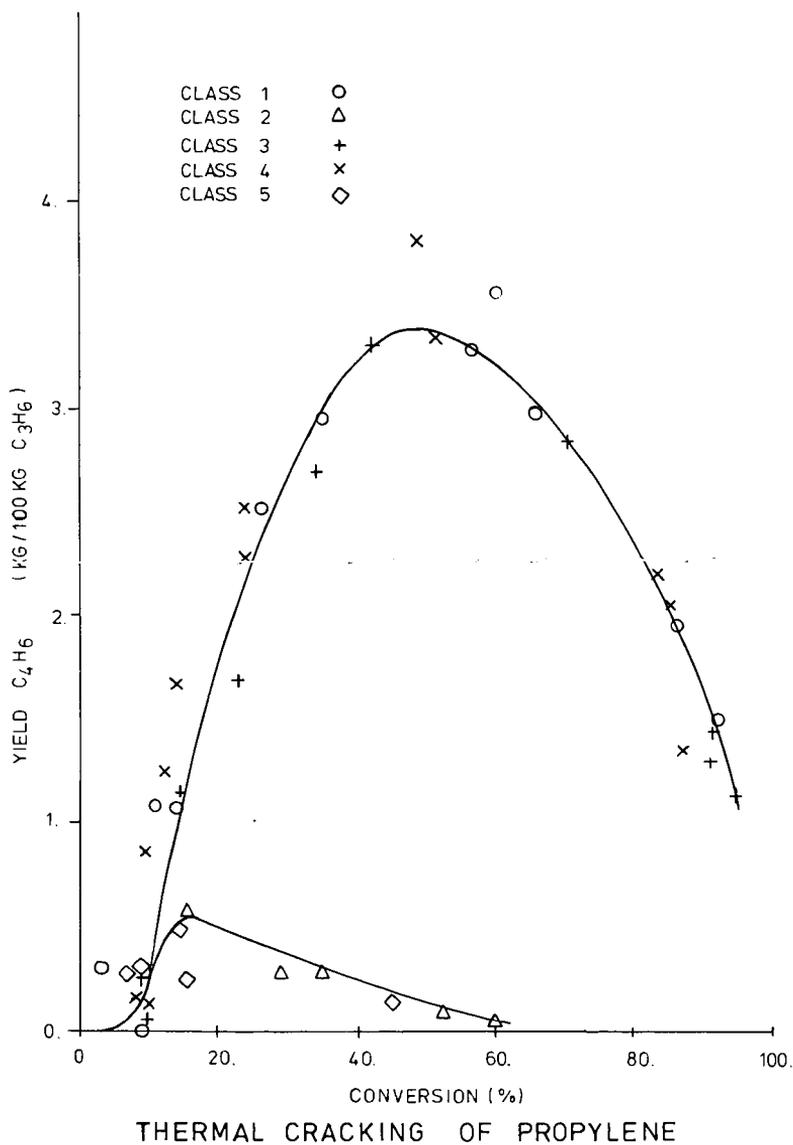


Figure 11.

CLASS 1 ○
CLASS 2 △
CLASS 3 +
CLASS 4 ×
CLASS 5 ◇

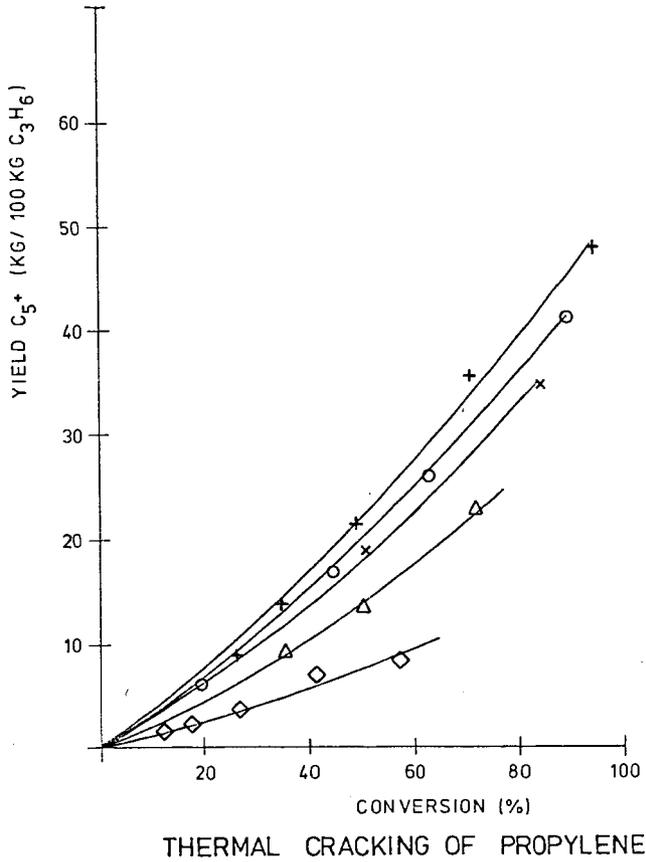


Figure 12.

ETHANE-PROPYLENE MIXTURES

CLASS 1

$X_E = 49\%$

$X_P = 70\%$

SELECTIVITY

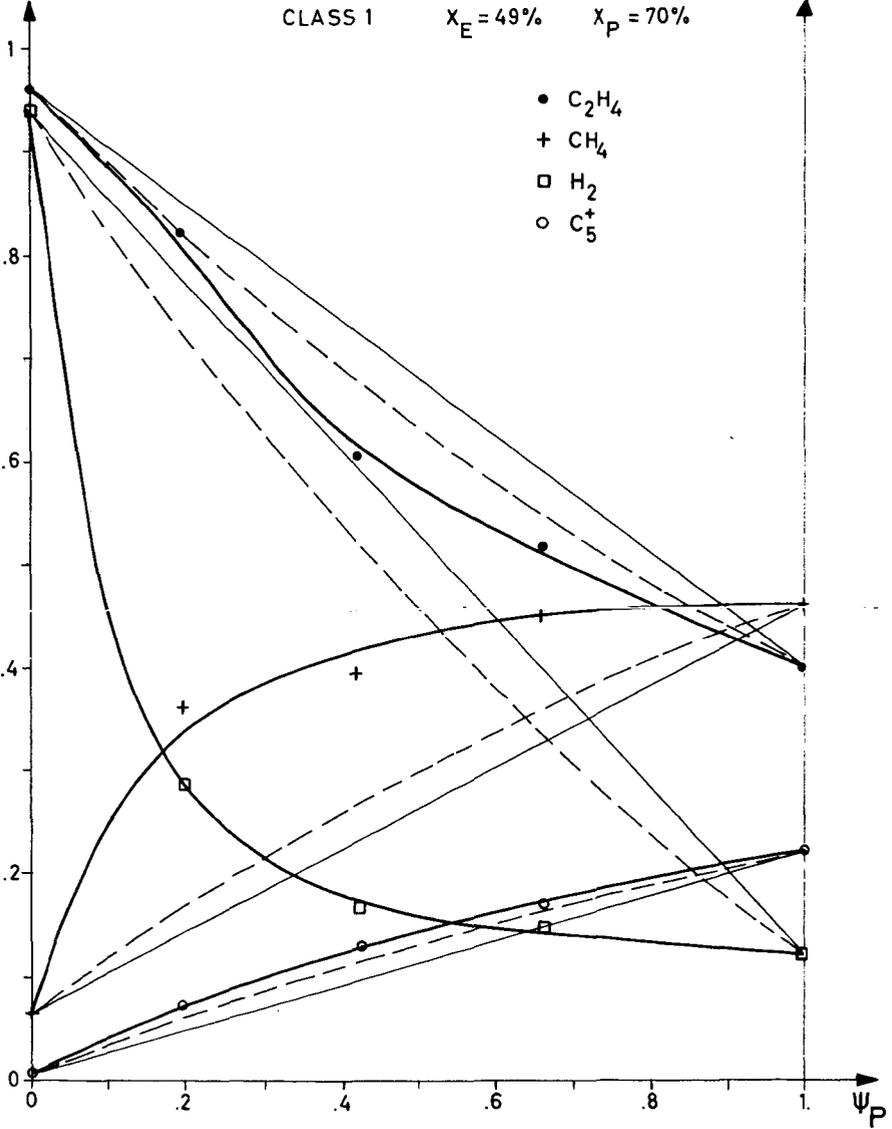
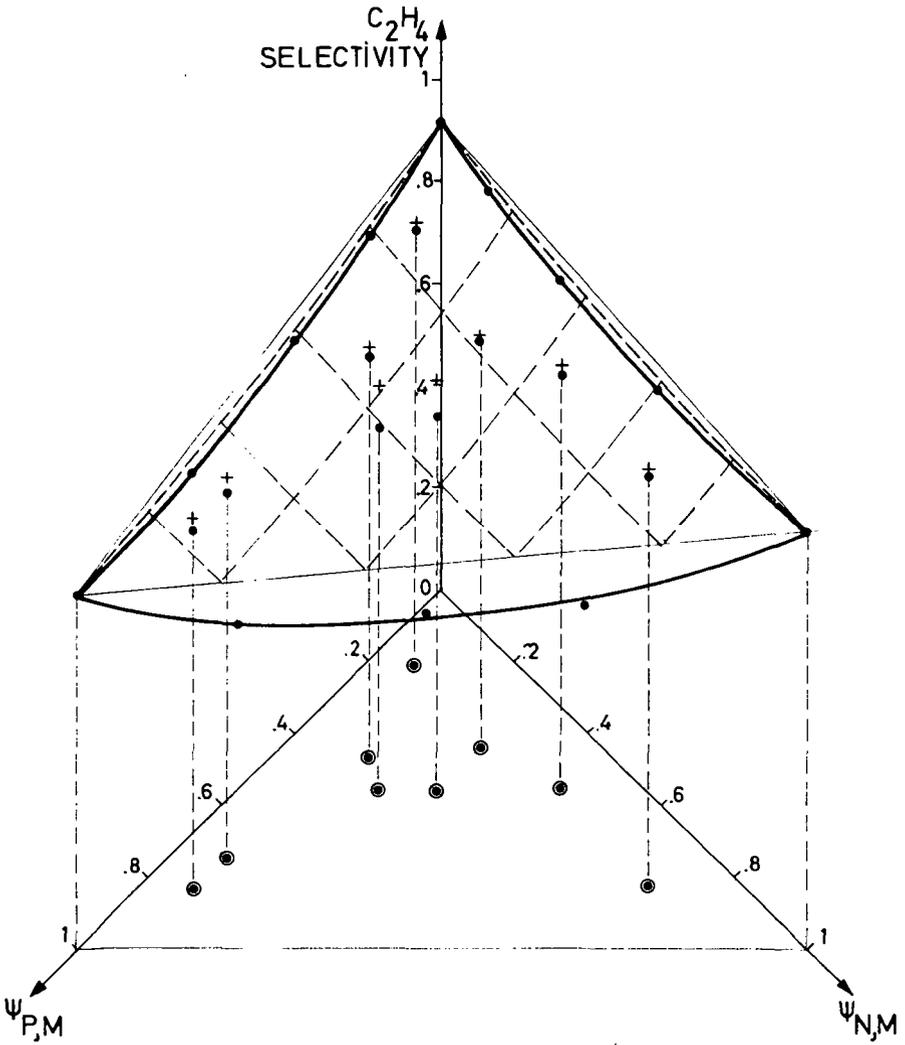


Figure 13.

TERNARY MIXTURES
ETHANE - PROPANE - N. BUTANE

CLASS 1 $X_{E,M} = 40\%$ $X_{P,M} = 73\%$ $X_{N,M} = 88\%$



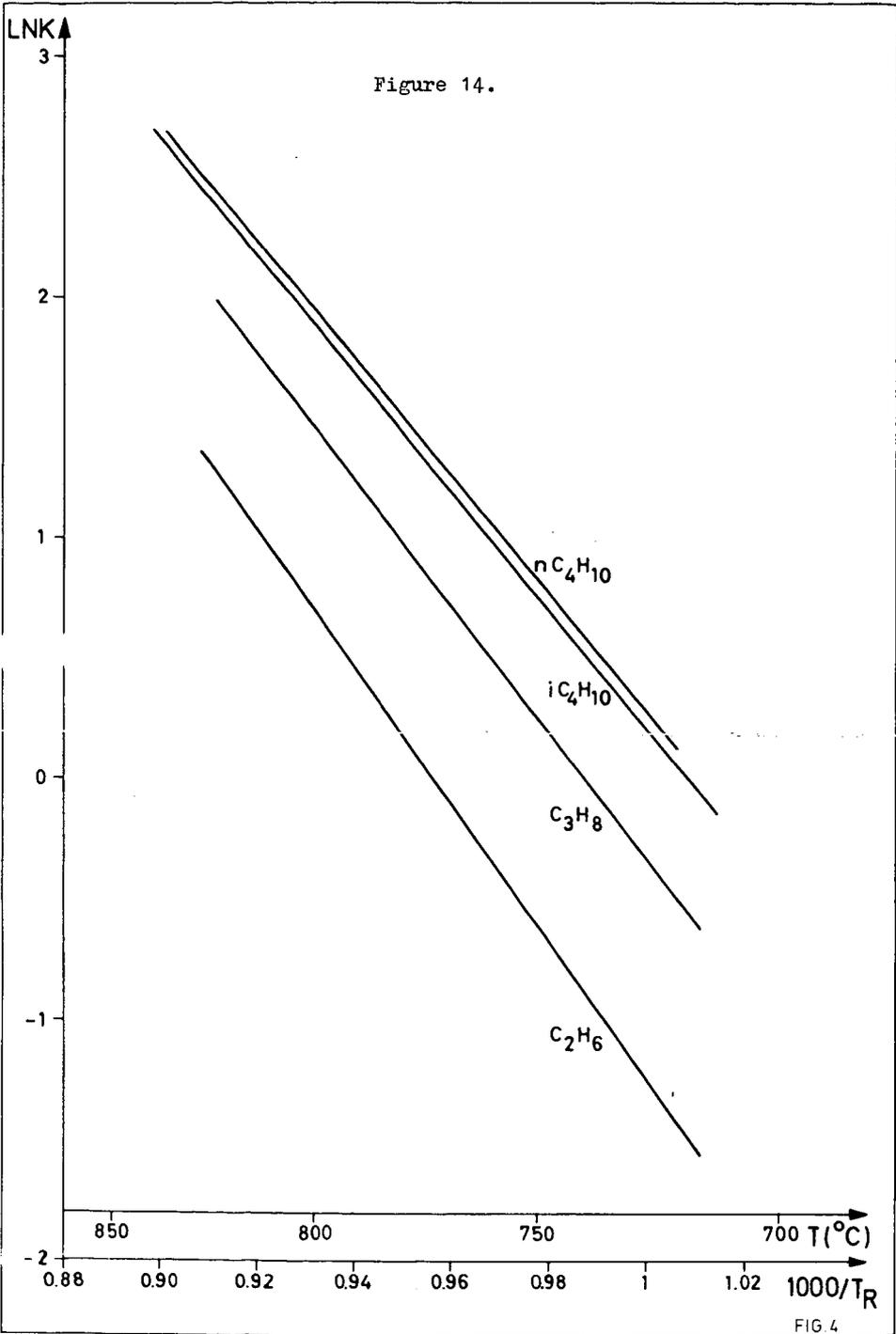


FIG. 4

Figure 15.

ETHANE - PROPYLENE MIXTURES
CLASS 1

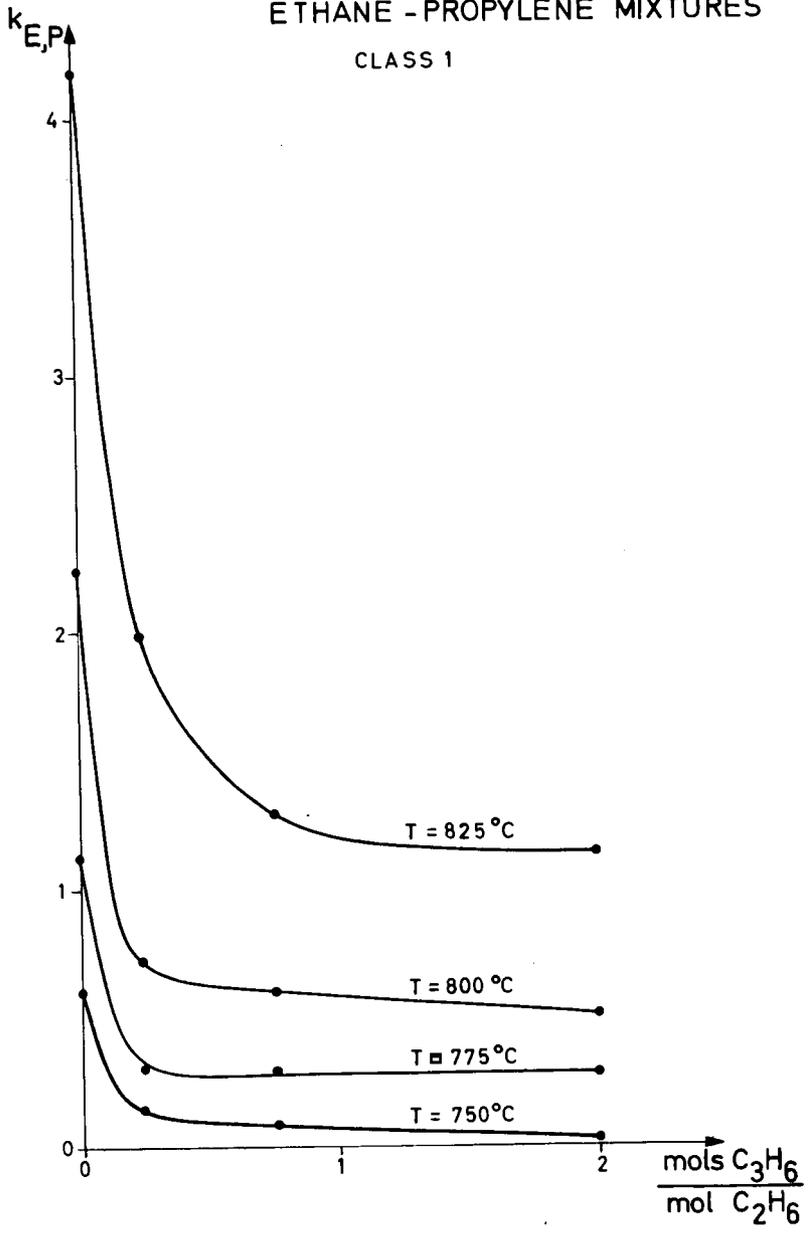
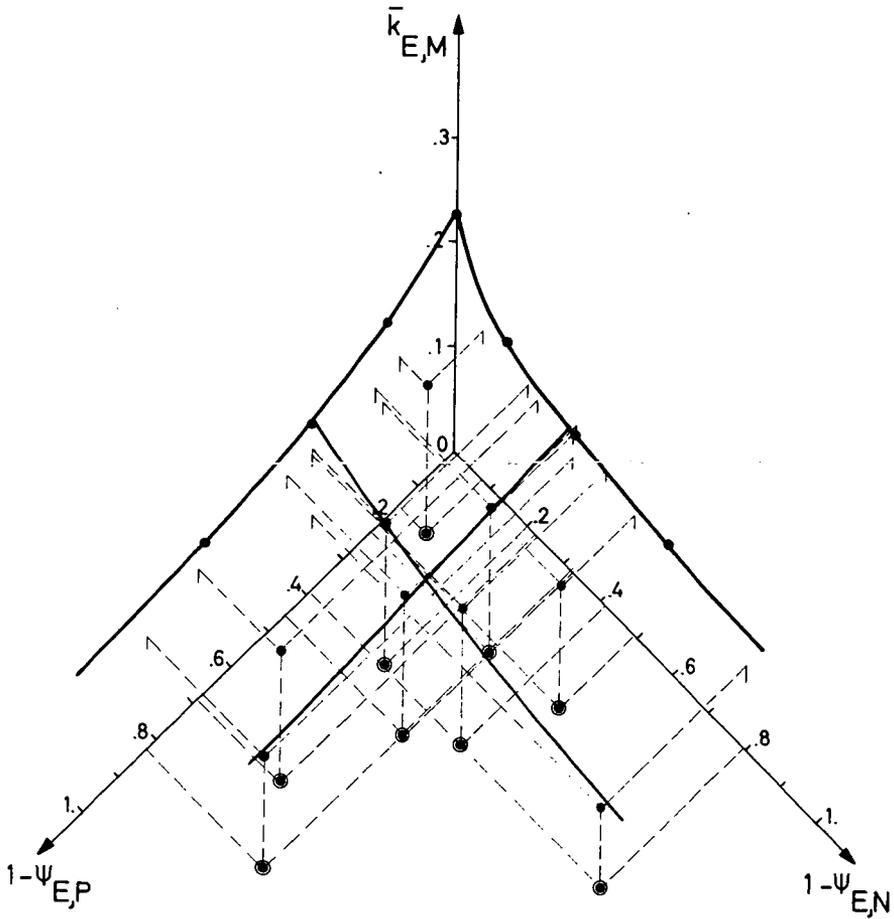


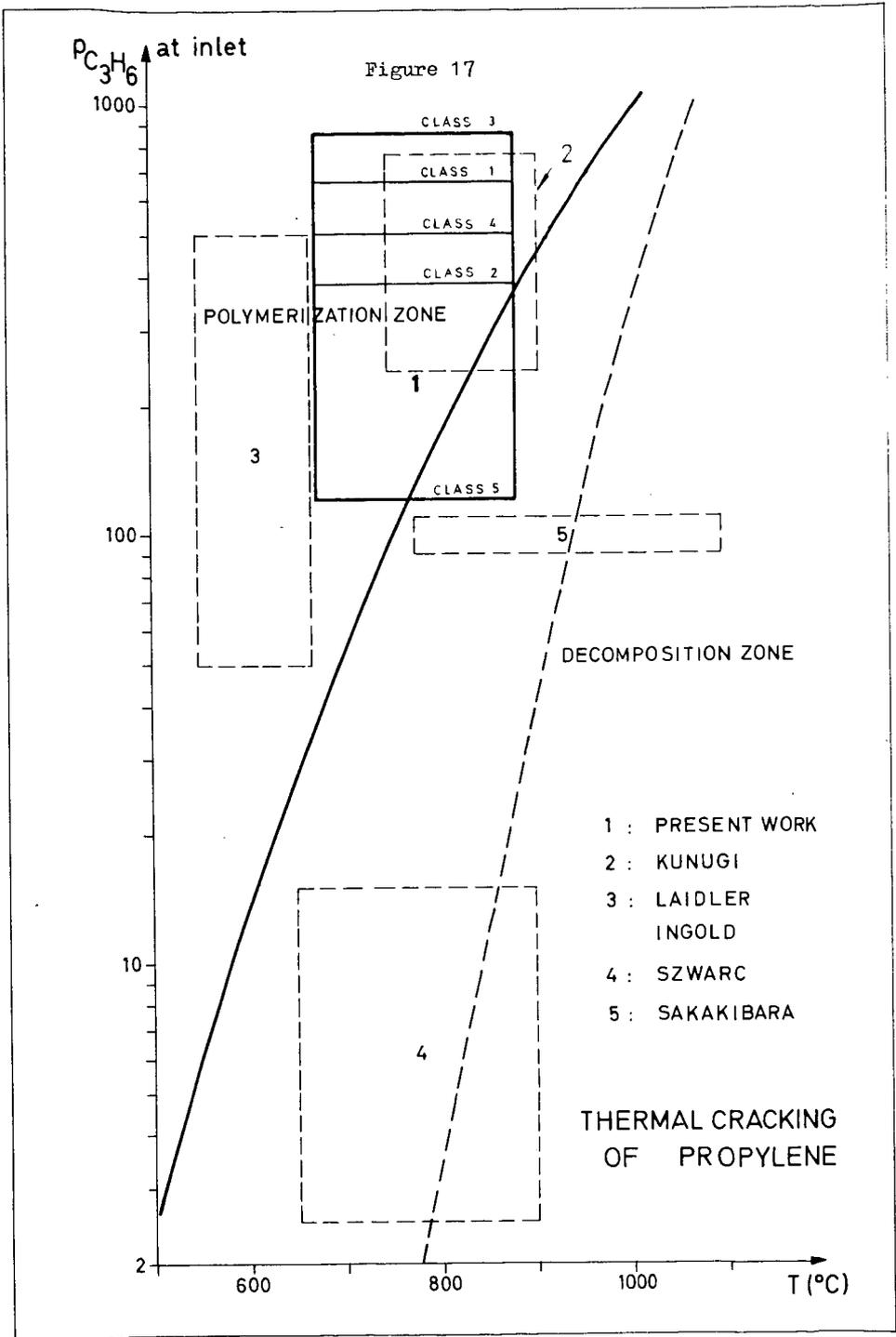
Figure 16.

TERNARY MIXTURES
N.BUTANE - PROPANE - ETHANE

CLASS 1

T = 800°C





PC_2H_4 at inlet

Figure 18.

