Thermal Decomposition of Ethylene–Comonomer Mixtures under High Pressure

Jens Albert and Gerhard Luft
Institut für Chemische Technologie, Darmstadt University of Technology, 64287 Darmstadt, Germany

Ethylene is unstable above certain limits of pressure and temperature decomposing into carbon, hydrogen, and methane. The influence of comonomers on this limit were studied. Vinyl acetate, acrylic acid, methyl methacrylate, 1-butene, and 1-hexene were added in various concentrations to ethylene and by filling the mixture into a preheated autoclave under high pressure (up to 450°C and 150 MPa). As a function of starting pressure and temperature, two reaction pathways can be distinguished: (1) stable (co-)polymerization and (2) (co-)polymerization with decomposition. Lowering the boundary between these two pathways seemed to be caused mainly by the thermal stability of the comonomer, for mixtures with vinyl acetate and methyl methacrylate, while an inhibition effect and increase in the limits occur in the comonomer acrylic acid, 1-butene, and 1-hexene. The maximum values of pressure, pressure increase, and temperature during decomposition were also influenced by comonomers. The maximum explosion pressure as a function of mixture density has a maximum for pure ethylene. As a function of ethylene concentration, the maximum explosion pressure has minimum values for pure ethylene. At a constant wall temperature and small initial pressures, the maximum rate of pressure increases reached a maximum, while, at high pressures, it decreased again. The position of this maximum depends on wall temperature and comonomer. Adding comonomers to ethylene decreases the maximum temperatures during decomposition reaction.

Introduction

Ethylene is one of the most important basic products of the chemical industry. It is used on a large scale for the production of polyethylenes (Hatzmann et al., 1996). Figure 1 shows the importance of polyethylenes in Western Europe. Most important, polyethylene is still low-density polyethylene (LDPE). It is produced in tubular or in autoclave reactors under pressures up to 300 MPa and temperatures up to 350°C. Because of these high pressures and temperatures, the producers of LDPE have frequently encountered thermal runaway problems.

Above certain limits of pressure and temperature ethylene decomposes into carbon, hydrogen, and methane:

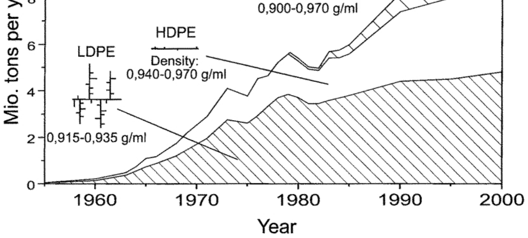

Figure 1. Polyethylene consumption in Western Europe.

Correspondence concerning this article should be addressed to G. Luft.

Table 1. Characteristics and Uses of Ethylene Copolymers

Copolymer	Characteristics	Uses
Ethylene–vinyl acetate	Flexibility	Heat shrinkable tubes, sealings, paper coatings, adhesives
Ethylene–1-alkene	Flexibility, transparence, high tensile strength, good properties at low temperatures	Films, coatings, cable sheatings
Ethylene–methyl methacrylate	Flexibility, good thermal stability	Textile auxiliaries, weatherproof paintings and coatings
Ethylene–acrylic acid	Good adhesion to metals, glass, and polyethylene	Packing films, laminates with aluminium films

$$C_2H_4 \longrightarrow (1+z)C+(1-z)CH_4+2zH_2 \quad \text{with } 0 \le z \le 1.$$

There are several possible reasons for the decomposition reaction during LDPE production:

In a high-pressure compressor the compression heat or friction can trigger the decomposition. The reaction energy in the reactor and the negative Joule-Thomson coefficient in the high-pressure separator can cause the decomposition. Decomposition reactions of ethylene have been observed even in relatively mild conditions (4–10 MPa, 4–40°C) (Britton et al., 1986; Howard, 1975; Worell, 1979).

Two ignition mechanisms are possible: an induced ignition caused by "hot spots" like sparks or because of welding work; and a thermal runaway reaction caused by insufficient heat removal.

For an optimized production process it is important to know the decomposition boundaries. The decomposition reaction is a safety concern because of the accelerating pressure and temperature increase, and results in loss of production time. It is important to reduce the damage if decomposition occurs. In order to achieve this goal, it is necessary to know the explosion characteristics, for example, the maximum explosion pressure or the maximum rate of pressure increase.

Most investigations on ethylene decomposition refer to pure ethylene (Bönsel and Luft, 1995; Britton et al., 1986; Conrad and Kaulbars, 1975; Howard, 1975; Worell, 1979; Zimmermann and Luft, 1994), while the influence of additives like comonomers is rarely investigated. There are only few reports on the effect of vinyl acetate using small vessels up to 15 cc (Luft and Neumann, 1978) and on the influence of vinyl acetate and methyl methacrylate using a hot-spot technique (Zimmermann, 1994; Zimmermann and Luft, 1994). However, the influence of copolymers of ethylene is important: they are produced under high pressure and they are an important part of the plastics market. Special characteristics and uses of some copolymers are listed in Table 1.

Table 2. Analyzed Ethylene Mixtures and Abbreviation

Mixture	Abbreviation
Ethylene	Et
Ethylene, 10 wt. % vinyl acetate	VA10
Ethylene, 30 wt. % vinyl acetate	VA30
Ethylene, 10 wt. % methyl methacrylate	MMA10
Ethylene, 57 wt. % 1-butene	Bu57
Ethylene, 67 wt. % 1-hexene	He67
Ethylene, 6 wt. % acrylic acid	AA6
Ethylene, 15 wt. % acrylic acid	AA15

This article deals with the influence of vinyl acetate, acrylic acid, methyl methacrylate, 1-butene, and 1-hexene on the thermal decomposition of ethylene and on the explosion characteristics (see Table 2).

Experimental Studies

The experiments were carried out in a high-pressure laboratory with the apparatus shown in Figure 2. To prepare the mixtures, we constructed the mixing equipment that is shown in the left part of the figure. The ethylene is taken from gas cylinders. Traces of water and oxygen were removed by a molecular sieve and a BASF catalysator based on copper. A diaphragm compressor (1) was used to compress the ethylene into the mixing autoclave (3), which had a volume of 2500 cc. Once the mixing autoclave (3) was filled with ethylene, the screw press (2) was used to add the comonomer and the mixture was homogenized by means of a stirrer. It was possible to prepare mixtures up to 200 MPa.

The most important part of our high-pressure equipment was the reaction autoclave (4). The reactor was made from stainless steel in the form of a double cylinder and was sealed using two self-tightening screws. It had an inner diameter of 5 cm and a height of 10 cm, which was equivalent to 200 cc in volume. The reactor was heated by two heating filaments and was insulated to avoid heat dissipation. The reactor wall temperature was measured and controlled by a NiCr-Ni thermocouple.

The temperature and pressure inside the reactor (4) increased to 1400°C and 400 MPa, respectively, during decomposition reactions. To record the pressure and temperature

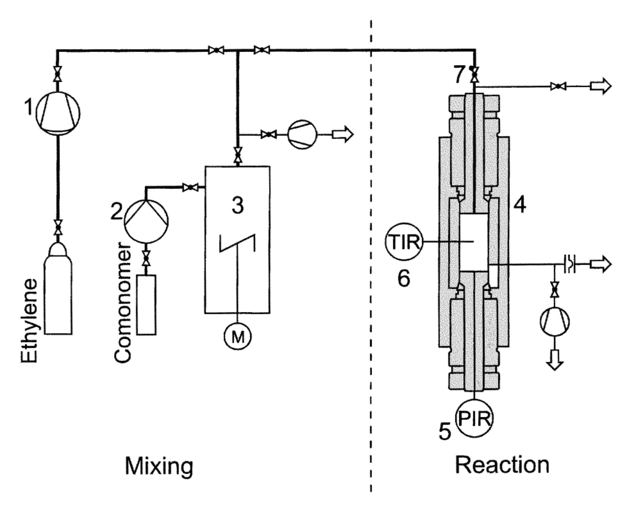

Figure 2. High-pressure equipment for determination of decomposition boundaries.

(1) Diaphragm compressor; (2) screw press; (3) mixing autoclave; (4) reactor; (5) pressure gauge; (6) thermocouple; (7) remote-controlled valve.

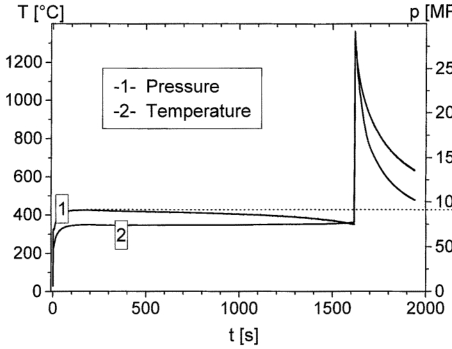

Figure 3. Course of pressure and of temperature for decomposition during polymerization.

Ethylene/6 wt. % acrylic acid; $p_0 = 91$ MPa; $T_w = 350°C$.

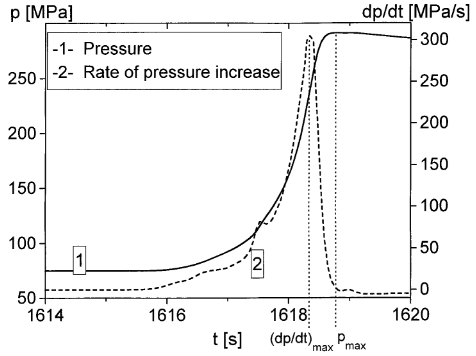

Figure 4. Pressure and rate of pressure increase during a decomposition.

Ethylene/6 wt. % acrylic acid; $p_0 = 91$ MPa; $T_w = 350°C$.

data inside the reactor during the reaction we used a pressure gauge (5) and a PtRh-Pt thermocouple (6). The pressure gauge was connected directly to the reactor by a quarter-inch high-pressure tube that was 15 cm long. The maximum measurement error was 0.25%. The thermocouple (6) was in the reactor center. It was a construction with open measuring point. Thus we had a very fast temperature response that made it possible to realize a sampling rate of 1.5 ms with 0.5% maximum error. We used a computer to record the data.

Before an experiment was carried out, the following actions had to be carried out: the ethylene/comonomer mixture had to be prepared (calculated on the basis of Amagat's rule; Amagat et al., 1959) and the reactor (4) had to be evacuated to less than 50 Pa and heated to a preset wall temperature. The ethylene/comonomer mixture was fed to the reactor (4) from the mixing autoclave (3) by opening a remote-controlled valve (7). As soon as the mixture was injected, pressure and temperature were recorded continuously for 30 minutes. The data would show whether the mixture had undergone thermal decomposition. After each experiment the reactor was cleaned and leak tested.

Decomposition boundaries

By varying the initial pressure and wall temperature, the boundary above which the mixture becomes unstable could be determined. Figure 3 shows the pressure and temperature profile of a thermal decomposition of an ethylene/6 wt. % acrylic acid mixture. The wall temperature was 350°C and the initial pressure 91 MPa. A few seconds after the mixture was fed to the autoclave it reached 350°C and initial pressure. The thermal polymerization started to occur soon afterward. This is evidenced by the pressure decrease and the slight temperature increase in the reactor. Two different reaction pathways were then possible:

1. Stable polymerization: the pressure decreases continuously with diminishing strength and the temperature inside the reactor passes a small maximum.

2. Decomposition: in this case, the profiles shown in Figure 3 are observable. The polymerization reaction starts after the mixture is injected. During the polymerization reaction an abrupt increase in pressure and temperature can be seen. The mixture decomposes and the reactor (4, Figure 2) is completely filled with soot.

The time between the injection of the mixture and the beginning of the decomposition is called the induction period. During the induction period and polymerization, no signs of decomposition are detectable. As you can see in Figure 4, pressure starts to increase in less than 2 s. The induction period decreases with increasing wall temperature. Above a certain wall temperature, the induction period disappears and the mixture decomposes immediately after the injection. This reaction called spontaneous decomposition.

In our work we determined the boundary between stable polymerization and decomposition during polymerization. This boundary is the important boundary for safety concerns. Figure 5 shows the experimental data points for the ethylene/10 wt. % methyl methacrylate mixture. The triangles represent the data points where decomposition occurs, and the circles represent the data points where polymerization is stable. These experiments result in the boundary between these two reaction profiles (dashed line). For simplicity we present only the boundaries for the examined mixtures (Figures 6 and 7).

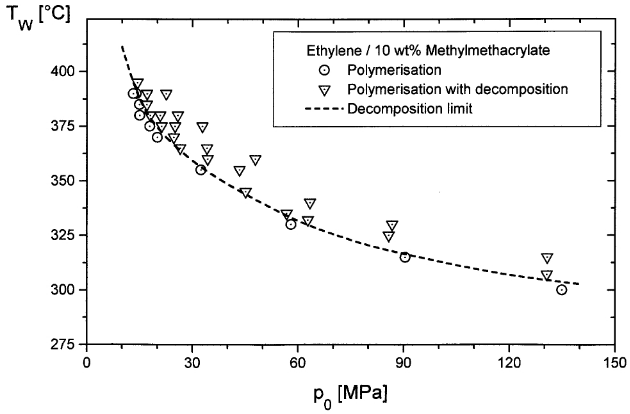

Figure 5. Polymerization and polymerization with decomposition of ethylene/10 wt. % methyl methacrylate mixtures.

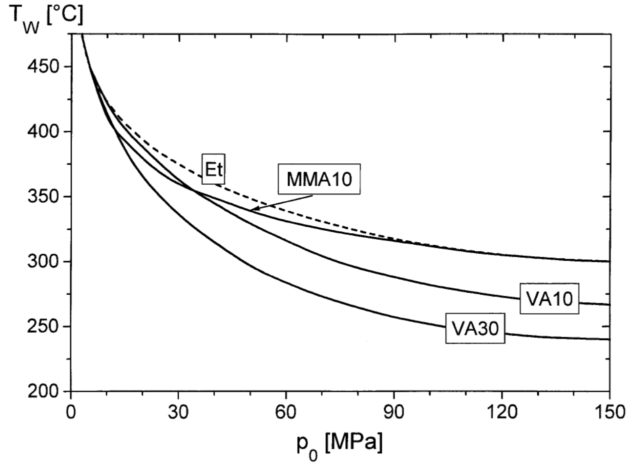

Figure 6. Decomposition boundaries for ethylene (Bönsel, 1994; Bönsel and Luft, 1995) and mixtures with vinyl acetate and methyl methacrylate.

Explosion effects

While the decomposition boundaries are important for copolymer production, the maximum explosion pressure, maximum rate of pressure increase, and the maximum temperatures during decomposition are required for the technical design of plants and safety devices.

As shown in Figure 4 the maximum explosion pressure and the maximum rate of pressure increase can be determined from the pressure profile (1), respectively from the rate-of-pressure-increase profile (2). The maximum explosion temperature during an explosion can be determined from the temperature profile.

Results and Discussion

Decomposition boundaries

Figures 6 and 7 show the decomposition boundaries of the examined ethylene/comonomer mixtures compared with ethylene (Bönsel and Luft, 1995).

Figure 6 shows the boundaries for mixtures with 10 and 30 wt. % vinyl acetate (VA10 and VA30) and 10 wt. % methyl methacrylate (MMA10). The decomposition boundaries are shifted to lower temperatures compared to pure ethylene. But there are certain differences between the two comonomers. The influence of vinyl acetate increases with increasing pressure and vinyl acetate concentration. It appears that, above 125 MPa, the influence of pressure levels off. The maximum shift of the decomposition boundary is 30 K for 10 wt. % vinyl acetate and 60 K for 30 wt. % vinyl acetate.

The influence of methyl methacrylate on the decomposition boundary of ethylene is very strong at low pressures, and becomes less strong as the pressure increases. Maximum shift is about 19 K at approximately 25 MPa. Above 25 MPa, the boundary of the mixture with methyl methacrylate approaches the boundary of ethylene, and above 110 MPa there is no detectable difference.

In contrast to vinyl acetate and methyl methacrylate, the addition of acrylic acid (AA6 and AA15), 1-butene (Bu57), and 1-hexene (He67) to ethylene causes the ethylene decomposition boundary to shift to higher temperatures. This is demonstrated in Figure 7. The influence of the comonomers becomes stronger with increasing pressure. It appears that the influence of pressure levels off above 125 MPa. The comonomer mixture boundaries are parallel to the ethylene boundary.

The concentrations of 1-butene (57 wt. %) and 1-hexene (67 wt. %) are equivalent to 40 mol %. The two paths of mixture decomposition boundaries are similar. Maximum shift is about 28 K.

The influence of comonomer concentration on the shift of the boundary is demonstrated using acrylic acid (AA6 and AA15). An increase in concentration shifts the decomposition boundary to higher temperatures. Maximum shift is about 25 K for 6 wt. % acrylic acid and about 36 K for 15 wt. %.

What are the reasons for the different influences of these comonomers? Three aspects have to be considered:

1. The physical properties of the comonomers and their effect on heat transfer and dissipation.
2. Polymerization enthalpy and the reactivities of the comonomers as well as the effect on heat production.
3. Thermal stability of the comonomers.

1. The physical properties affect the heat-transfer and dissipation characteristics ($\dot{Q}_{\mathrm{Trans}}$). An increase in heat capacity, heat conductivity, or density improves the heat transfer. An increase in viscosity causes a reduction in heat transfer (Fitzer et al., 1995).

The physical properties of ethylene and vinyl acetate are compared in Table 3. The addition of vinyl acetate to ethylene improves the heat transfer. The decomposition boundary to higher temperatures can be expected to shift. Instead of the expected result, there is a shift to lower temperatures.

Furthermore, the physical properties of other comonomers (for example, density; see Table 4) lead to a better heat transfer. A shift in the decomposition boundary to higher temperatures can be expected (Table 7). It is obvious that physical properties are one reason for the boundary shift to

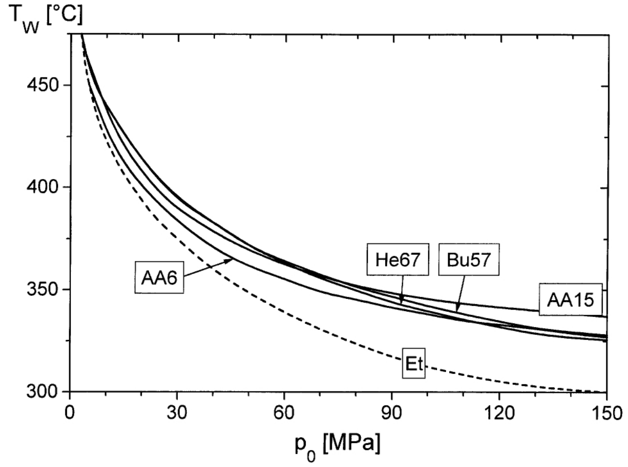

Figure 7. Decomposition boundaries for ethylene (Bönsel, 1994; Bönsel and Luft, 1995) and mixtures with acrylic acid, 1-butene, and 1-hexene.

Table 3. Physical Properties of Ethylene and Vinyl Acetate

	ρ [kg/m^3]	C_p [J/kg/K]	λ [W/m/K]	η [kg/m/s]
Ethylene	398 (Angus et al., 1972)	2,687 (Benzler and Koch, 1955)	0.1176 (Owens and Thodos, 1960)	5.54×10^{-5} (Stanislawski and Luft, 1987)
Vinyl acetate	904 (Sülzner, 1996)	2,675 (Sülzner, 1996)	0.2271 (Gallant, 1968a,b; VDI, 1984)	3.11×10^{-4} (Sülzner, 1996)

Table 4. Density of the Investigated Monomers

	Ethylene	VA	1-Butene	1-Hexene	MMA	AS
ρ [kg/m^3]	398 (Angus et al., 1972)	904 (Sülzer, 1996)	576 (Olds et al., 1946)	668 (Kerimov and Apaev, 1972)	870 (Gallant, 1968a,b; Perry and Chilton, 1973)	1,030 (Gallant, 1968a,b; Perry and Chilton, 1973)

higher temperatures (1-butene, 1-hexene, acrylic acid), but they cannot explain the shift to lower temperatures (vinyl acetate, methyl methacrylate).

2. The heat production rate ($\dot{Q}_{\mathrm{Reac}}$) during polymerization is influenced by polymerization enthalpy and comonomer reactivities. Table 5 shows the polymerization enthalpies of the monomers used. All comonomers have polymerization enthalpies that are similar to or smaller than ethylene.

The polymerization rate is the second aspect that influences the heat-production rate. It can be described by the reactivity ratios of the monomers. Table 6 shows the reactivity ratios of the comonomers in the copolymerization with ethylene. In general, alkenes (1-butene, 1-hexene) are less reactive than ethylene. This aspect can be derived from the r_1 values that are between 1 and 10. Vinyl ester (vinyl acetate) have similar reactivity ratios as ethylene ($r_1 \approx 1$), and the small r_1 values of acrylic monomers (methyl methacrylate, acrylic acid) are an indicator for a much higher reactivity toward ethylene (Scholsky, 1993). In the case of $r_2 > 1$, the overall polymerization rate decreases due to the resonance-stabilized comonomer radicals (Whiteley, 1992).

Table 5. Polymerization Heat of the Investigated Monomers

Comonomer	$-\Delta_R H_{\mathrm{Po}}$ [kJ/mol]
Ethylene	88 (Thies, 1967)
Vinyl acetate	89 (Hammer and Ray, 1986)
1-Butene	86 (Elias, 1990)
1-Hexene	85 (Elias, 1990)
Methyl methacrylate	57 (Harmon and King, 1976)
Acrylic acid	77 (Harmon and King, 1976)

If the heat-production rate during copolymerization is similar to the ethylene homopolymerization (vinyl acetate) or smaller (acrylic acid, 1-butene, 1-hexene, methyl methacrylate), a shift of the boundary to higher temperatures is expected (Table 7). Thus, polymerization enthalpies and reactivity ratios are the second reason that helps to explain the decomposition boundary shift to higher temperatures (1-butene, 1-hexene, acrylic acid). However, they cannot explain the shift to lower temperatures (vinyl acetate, methyl methacrylate).

3. The thermal stability of comonomers is another possible reason for shifting the decomposition boundaries, because any organic compound can decompose above certain temperature limits. Investigations of the thermal stability of the used comonomers under high pressure and high temperature are rare. We found only one publication that refers to this subject. In his dissertation, Neumann (1975) described the ther-

Table 6. Copolymerization Ratios of Ethylene (r_1) and the Investigated Comonomers (r_2)

	r_1	r_2	Polymerization Conditions	Reference
Vinyl acetate	1.1	1.2	160–240°C, 120–240 MPa	Raetzsch et al. (1971)
	1.07	1.08	90°C, 105 MPa	Raetzsch et al. (1971)
	0.82	0.99	120°C, 102–204 MPa	Scholsky (1993)
1-Butene	3.4	0.8	130–220°C, 102–170 MPa	Scholsky (1993)
	3.2	< 0.64	130–220°C, 102–170 MPa	Mortimer (1965)
	2.0	—	140°C, 196 MPa	Whiteley (1992)
1-Hexene	1.4	—	140°C, 196 MPa	Whiteley (1992)
Methyl methacrylate	0.02	—	160–200°C, 204 MPa	Scholsky (1993)
	0.03	18	—	Ehrlich and Mortimer (1970)
	0.2	17	150°C, 82 MPa	Ehrlich and Mortimer (1970)
Acrylic acid	0.1	—	213–238°C, 110–145 MPa	Scholsky (1993)
	0.02	4	—	Ehrlich and Mortimer (1970)
	0.09	—	140°C, 116–204 MPa	Ehrlich and Mortimer (1970)

Table 7. Expected and Experimental Influences on the Limiting Decomposition Temperature

	$\dot{Q}_{\text{Trans}}$	$\dot{Q}_{\text{Reac}}$	T_{Bo} Pred.	T_{Bo} Exp.	Thermal Stability*
Vinyl acetate	↑	↔	↑	↓	↓**,†
1-Butene	↑	↓	↑	↑	(↑)†
1-Hexene	↑	↓	↑	↑	(↑)†
Methyl methacrylate	↑	↓	↑	↓	(↓)†
Acrylic acid	↑	↓	↑	↑	(↑)†

*In comparison to ethylene.
**Neumann (1975).
†Conclusion from experiment.

mal stability of ethylene and vinyl acetate. He used a heating method for his experiments: he put the mixture in a cold reactor and heated it to a preset wall temperature and observed if there is a thermal runaway. The volume of his reactor was only 15 cc. Because of the higher surface-to-volume ratio and the better heat removal, he measured a decomposition boundary for pure ethylene that is about 50 K higher than ours. Neumann carried out the same experiments with pure vinyl acetate and with mixtures. He found a 50 K lower decomposition boundary for pure vinyl acetate than for pure ethylene. The decomposition boundaries for the mixtures were between those of the two pure components. These results prove that the lower thermal stability of comonomers compared to ethylene is responsible for shifting the decomposition boundary to lower temperatures.

Table 7 summarizes the results of the discussion. An up arrow means an increase or improvement, a down arrow a decrease or deterioration, and ↔ no changes in the value or a characteristic in comparison to ethylene. The heat removal rate, Q_{Trans}, describes the heat transfer from the mixture to the environment, and Q_{Reac} is the polymerization heat-production rate. Column three shows the expected influence on the decomposition boundary derived from columns one and two. Column four shows the influence determined by experiment. The thermal stability of the comonomer compared to ethylene is shown in column 5. The thermal stability of the comonomer is the most important aspect that has to be considered when predicting the influence of comonomers on the decomposition boundary of ethylene.

Maximum explosion pressure

We need to know the maximum explosion pressure in order to construct a pressure-proof apparatus. Figure 8 shows the maximum explosion pressure of various mixtures as a function of mixture density. The highest values can be seen for the pure-ethylene case. The addition of comonomers decreases the explosion pressure.

One reason for this behavior is the smaller maximum explosion temperatures of ethylene–comonomer mixtures. Two other effects are also responsible. At constant density the total number of molecules decreases if a comonomer with a higher molecular mass than ethylene is added. On the other hand, we can expect more gaseous decomposition products from the comonomers than from ethylene (Albert, 1998; Bamford and Tipper, 1972; Allan et al., 1955; Forman et al., 1968). The experimental results show that the first effect should be more important.

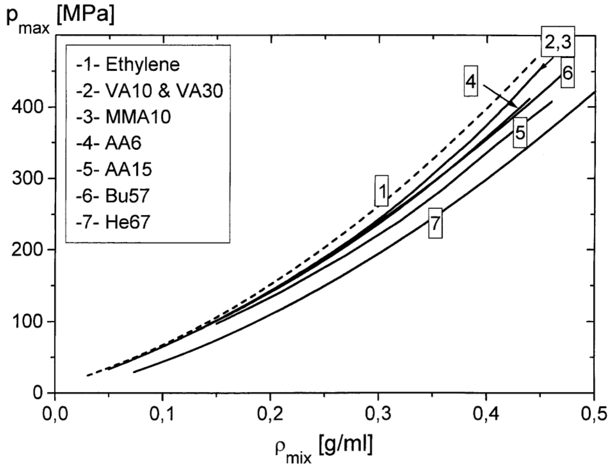

Figure 8. Maximum explosion pressure as a function of mixture density for ethylene (Bönsel, 1994; Bönsel and Luft, 1995) and ethylene comonomer mixtures.

The maximum explosion pressure as a function of the ethylene concentration is shown in Figure 9. The values of ethylene are the lowest ones. The increase of explosion pressure in mixtures is an effect of the additional comonomers volume. Both the thermal expansion of undecomposed comonomer and the decomposition products of comonomers cause an increase in the maximum explosion pressure. Due to the thermal decomposition of the comonomers (Albert, 1998; Bamford and Tipper, 1972; Allan et al., 1955; Forman et al., 1968), the second effect is regarded as more important.

Maximum rate of pressure increase

These values are required for the construction of pressure-release devices, such as rupture discs. In older publications the maximum rate of pressure increase was dis-

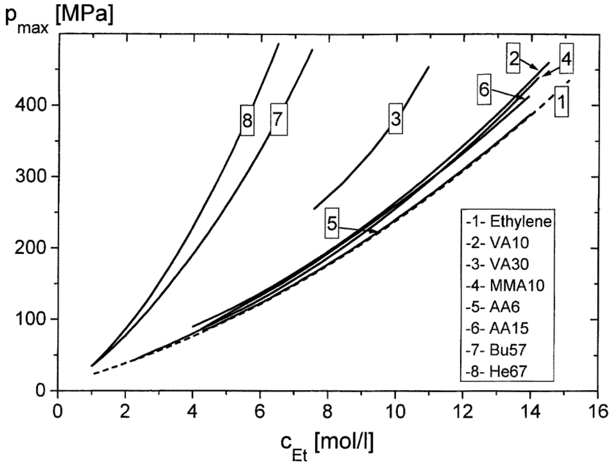

Figure 9. Maximum explosion pressure as a function of ethylene concentration for ethylene (Bönsel, 1994; Bönsel and Luft, 1995) and ethylene comonomer mixtures.

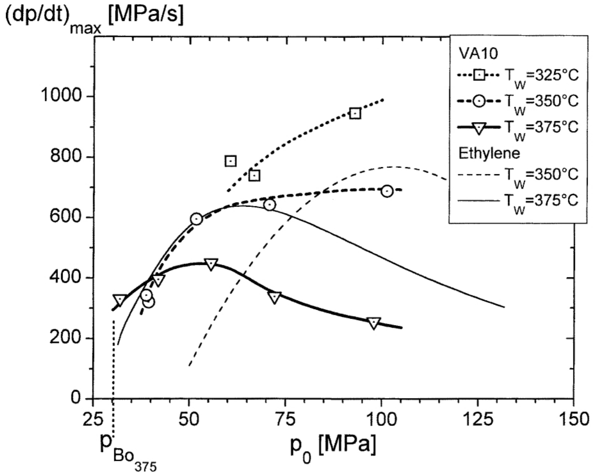

Figure 10. Maximum rate of pressure increase as a function of initial pressure at several wall temperatures for ethylene and ethylene/10 wt. % vinyl acetate.

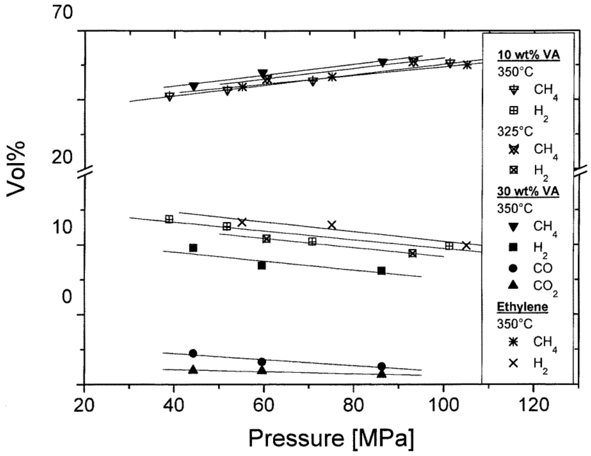

Figure 11. Gaseous decomposition products after polymerization with decomposition of ethylene and ethylene/vinyl acetate mixtures.

cussed as a linear function of initial pressure (Bönsel and Luft, 1995; Albert and Luft, 1998). Newer investigations lead to the conclusion that there is no linear dependence. Figure 10 shows the maximum rate of pressure increase as s function of initial pressure p_0 and wall temperature T_w for ethylene and a mixture with 10 wt. % vinyl acetate. The graphs have a maximum that depends on the initial pressure and wall temperature. Extrapolation of the curves to the x-axis leads to the limiting pressure of the boundary. This is shown for ethylene at a wall temperature of 375°C. The extrapolation leads to $p_{\mathrm{Bo}_{375}} = 30$ MPa. This is equal to the experimental value.

An explanation of the dependence of the maximum rate of pressure increase can be given by the free-radical chain mechanism of ethylene decomposition suggested by Watanabe and Takehisa (Watanabe and Takehisa, 1982; Roscoe et al., 1996; Roth and Just, 1973). The main steps of this mechanism are chain initiation, chain propagation, and chain termination (see Table 8).

After passing the decomposition boundary, the maximum rate of pressure increase rises with growing initial pressure. This is an effect of the higher density and monomer concentration. Thus, the reaction rates of initiation and propagation increase. Because of the low radical concentration, the termination is not greatly influenced. The higher the concentration and the higher the initiation rate, the more radicals are formed, and the probability of a reaction of the two radicals and chain termination increases. Thus, the decomposition reaction slows down and the maximum rate of pressure increase diminishes.

Table 8. Mechanism of Ethylene Decomposition Under High Pressure

Chain Initiation	$2\,C_2H_4 \longrightarrow C_2H_3\cdot + C_2H_5\cdot$
Chain Propagation	$C_2H_5\cdot \rightleftharpoons C_2H_4 + H\cdot$ $C_2H_5\cdot + C_2H_4 \longrightarrow C_2H_6 + C_2H_3\cdot$ $H\cdot + C_2H_4 \longrightarrow H_2 + C_2H_3\cdot$ $C_2H_3\cdot + M \longrightarrow C + CH_3\cdot + M$ $CH_3\cdot + C_2H_4 \longrightarrow CH_4 + C_2H_3\cdot$
Chain Termination	$2\,CH_3\cdot \longrightarrow C_2H_6$ $C_2H_3\cdot + CH_3\cdot \longrightarrow C_2H_2 + CH_4$ or C_3H_6 $2\,C_2H_3\cdot \longrightarrow C_2H_2 + C_2H_4$ or C_4H_6

Source: Watanabe and Takehisa (1982).

The decomposition mechanism discussed by Watanabe and Takehisa (1982) suggests methane, ethane, ethylene, ethine, and butadiene as the products of the chain termination steps (Table 8). Consequently, the concentration of these products should increase if there are more termination reactions. It should be noted that all these products except for methane are unstable under the conditions of the decomposition reaction. As a result an increasing initial pressure should cause a higher methane concentration in the gaseous decomposition products. This was the result of earlier investigations (see Figure 11) (Albert and Luft, 1998), and it indicates a greater number of termination reactions as the initial pressure increases.

Figure 12 demonstrates the influence of the comonomers on the maximum rate of pressure increase as a function of the wall temperature. The initial pressure is $p_0 = 50$ MPa. The curves are extrapolated to the x-axis. The intersection corresponds to the limiting temperature of the decomposition boundary at 50 MPa.

The influence of the comonomers on the maximum rate of pressure increase is correlated with the influence on the decomposition boundary. Vinyl acetate and methyl methacrylate shift the ethylene curve in Figure 12 to smaller wall temperatures. Both shift the decomposition boundary to lower temperatures. Comonomers shifting the boundary to higher temperatures increase the curve to higher wall temperatures.

Maximum explosion temperature

We need to know the maximum explosion temperature in order to construct a temperature-proof apparatus. The highest temperatures were reached by the decomposition of pure

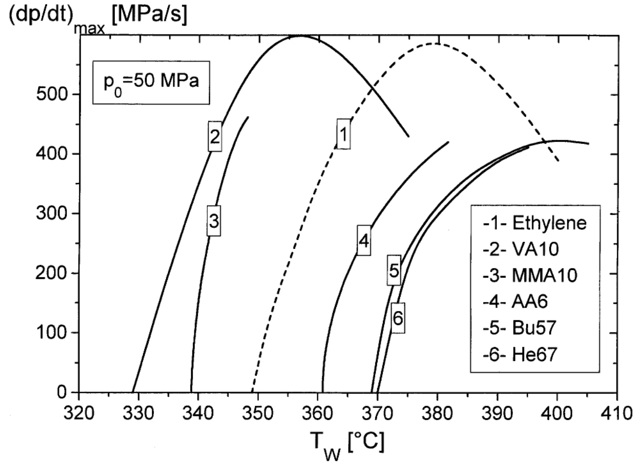

Figure 12. Maximum rate of pressure increase as a function of wall temperature at an initial pressure of $p_0 = 50$ MPa for different mixtures.

ethylene. The addition of a comonomer to ethylene decreases the maximum temperature (Figure 13). Only the mixture with vinyl acetate comes close to the values of ethylene. The lowest values were measured with mixtures of 1-alkenes.

Transfer of the results

Decomposition boundaries and explosion effects are not physical constants, but they are influenced by a lot of variables (Zimmermann, 1994; Neumann, 1975). It still has to be seen if the experimental data can be applied to other apparatus types.

The possibility of transferring the ethylene decomposition boundaries to bigger vessels was verified by Bönsel (1994) and Neumann (1975). The boundary should move to lower temperatures with increasing volume, respectively, surface−volume ratio (Semenov, 1961). Bönsel and Neumann found that the vessel size had little influence if the inner diameter is more than 5 cm. Thus, a transfer to bigger vessels should be possible.

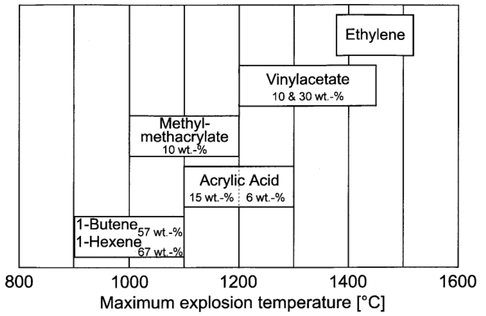

Figure 13. Maximum explosion temperature for ethylene (Bönsel, 1994; Bönsel and Luft, 1995) and ethylene comonomer mixtures.

The value of the maximum explosion pressure depends on the temperatures that occur and the amount of gaseous product. The amount of gaseous product depends mainly on the monomer concentration, and is not dependent on vessel size or shape. Therefore, if the heat loss is small, the maximum explosion pressure is independent of the size and shape of the vessel.

The maximum rate of pressure increase is a function of vessel size (Bartknecht, 1978). It can be described by the "cubic law":

$$\left(\frac{dp}{dt}\right)_{\max} \cdot \sqrt[3]{V} = \text{const.} = K_G,$$

where K_G [MPa·m·s^{-1}] is a constant if the starting conditions like vessel shape, degree of turbulence, ignition source, pressure, and temperature are equal. The maximum rate of pressure increase decreases with rising volume, and therefore conclusions for bigger vessels can be drawn.

Conclusions

1. The thermal decomposition boundary of ethylene is influenced by comonomers. This influence depends on wall temperature, initial pressure, and comonomer concentration. The most important property of the comonomer concerning the influence of the ethylene decomposition boundary is its thermal stability compared to ethylene.
2. The addition of vinyl acetate and methyl methacrylate to ethylene shifts the ethylene boundary of thermal decomposition to lower temperatures. The risk of a decomposition during polymerization grows. The maximum polymerization temperature has to be decreased for safe operations of the reactor.
3. Acrylic acid, 1-butene, and 1-hexene shift the boundary to higher temperatures, thus decreasing the risk of decomposition during polymerization. Polymerization can be carried out at higher temperatures.
4. The maximum explosion pressure can be described as a function of mixture density or of ethylene concentration. In the first case, the graph of pure ethylene describes an upper limit, and in the second case, it describes a lower limit. The maximum explosion pressure can be estimated from the density of comonomer mixture.
5. The maximum rate of pressure increase depends on the initial pressure and wall temperature. It has a maximum value under certain conditions. The value decreases and the explosion is less violent at high initial pressures or wall temperatures.
6. The maximum explosion temperature shows no dependence on initial pressure or wall temperature. The addition of comonomers causes a decrease in the maximum explosion temperature with ethylene describing an upper limit. Therefore, to copolymerize ethylene, no additional constructions are necessary.

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Notation

C_p = isobaric heat capacity, $J \cdot kg^{-1} \cdot K^{-1}$
r_1, r_2 = copolymerization parameters
t = time, s
T_{Bo} = limiting temperature of decomposition, °C
V = volume, m^3
$\Delta_R H_{Po}$ = polymerization enthalpy, $J \cdot mol^{-1}$
η = dynamic viscosity, $kg \cdot m^{-1} \cdot s^{-1}$
λ = heat conductivity, $W \cdot m^{-1} \cdot K^{-1}$
ρ = density, $kg \cdot m^{-3}$

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