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SAFETY ANALYSIS OF A PLANT FOR THE PRODUCTION OF VINYL ACETATE

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***Key Words*:** Systems Engineering, Process System, Safety Analysis, Fault Tree, Failure Rate, Vinyl Acetate

A fault tree is constructed to represent the major failure mechanisms of a plant for the production of vinyl acetate. Component failure rates from different sources are compared and provide input information for its quantitative evaluation. Results with and without inclusion of human error are calculated and proposals for an improvement of the original design are made. The dispersion of failure rate data is described by a log-normal distribution and its effect on the value obtained for system unreliability is assessed.

Introduction

The risk involved in many chemical processes calls for a systematic analysis of their safety. A number of qualitative and quantitative methods are available for this purpose, as discussed in ref. 1. Among them figures fault tree analysis,[2,3] a procedure which is widely used in the assessment of the safety of nuclear power stations and has been applied to chemical installations in some cases, e.g. refs 4–6. In the present work, fault trees for a plant for the production of vinyl acetate are constructed and evaluated numerically in order to assess its safety, taking into account the influence of human error, whose importance for the validity of the results is underlined e.g. by Howland,[7] and the uncertainty of failure rate data.

1. The Plant

1.1 Process description

The plant, whose flow sheet is given in **Fig. 1**, produces vinyl acetate according to the exothermal reaction

$$HC{\equiv}CH + CH_3{-}COOH \xrightarrow{AcZn} H_2C{=}\underset{\substack{|\\H}}{C}{-}O{-}\underset{\substack{\|\\O}}{C}{-}CH_3 \quad (\Delta H = -118\ \mathrm{kJ/g\text{-}mol})$$

which takes place between acetylene and acetic acid in gaseous phase at a pressure of 1 bar and a temperature between 170 and 210°C. The reaction heat is removed by a cooling circuit filled with oil at atmospheric pressure.

The acetic acid is supplied from storage to the evaporation installation. Its temperature is raised to 120°C by heat exchange with process steam in evaporator E_1. After separation of the liquid phase in separator E_2 the saturated acetic acid vapor flows to heat exchanger H_1 where it receives heat from the oil of the reactor cooling circuit. It then enters the mixer M_1 to form a mixture of 8 moles of acetylene per mole of acetic acid. Before reaching reactor R_1 the mixture exchanges heat with the oil of the reactor cooling circuit and attains a temperature between 160°C and 210°C.

The cooling circuit is basically formed by heat exchangers H_2 and H_3 and electric circulation pump P_1. Heat exchanger H_2 only works during start-up, when the cooling circuit is used to raise the reactor temperature to reaction conditions with the help of plant process steam. The reaction heat during stationary plant operation is transmitted in heat exchanger H_3 to an open cooling water circuit.

1.2 Control and safety devices

In order to maintain the reaction temperatures within the prescribed limits the cooling circuit is equipped with a control system composed of temperature indicator and controller TIRC 1 and pneumatic valve C_1. C_1 varies the quantity of coolant recirculated via H_3 to the suction side of the pump according to the oil outlet temperature of the reactor. The valve

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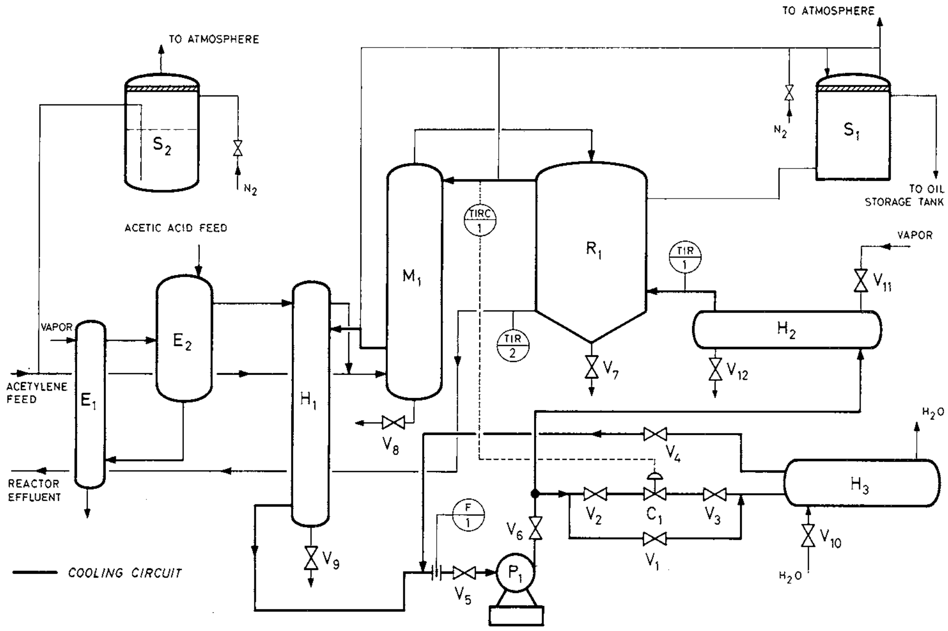

Fig. 1. Flow sheet of plant for production of vinyl acetate.

has the fail-safe property of opening completely on instrument air failure. It can be manipulated from the control room, where readings from TIRC 1 and the oil inlet temperature indicator and recorder TIR 1 are available. Manual control of the cooling circuit is possible on the basis of temperature readings from either of the two instruments if the control system should fail. In this case, manual valve V_1 in the bypass of control valve C_1, which is normally closed, is used. Coolant flow is monitored by flow meter F_1, which permits detection of pump failure or inadvertent closure of valves V_5 or V_6.

Vent S_1 allows pressure relief of the cooling circuit in cases of overpressure which might occur, for example, upon contact of its oil with the reactants due to a perforation of a tube of the reactor. In addition, it provides N_2 blanketing for the coolant. Vent S_2 protects the acetylene supply system, which apart from that is equipped with several other protective devices upstream, from overpressure and furnishes N_2 blanketing.

Except for control valve C_1 all valves are manual and serve either to isolate components during maintenance (V_2, V_3, V_4, V_5, V_6) and therefore are normally open or are used for draining (V_7, V_8, V_9) and hence are closed during operation. Valve V_{10}, which permits cut-off of cooling water supply to H_3, is normally open.

2. Identification of Risks and the Fault Tree

The relevant properties of the substances involved in the process are presented in **Table 1**. All of them can react with air, releasing substantial quantities of energy, and acetylene can detonate as a consequence of spontaneous decomposition. In addition, reaction of the substances with the oil of the cooling circuit is possible. Although the ignition temperatures of the materials are relatively high, an ignition must be considered likely on release.[9] Therefore, it is assumed that contact of any of the substances with air or oil will lead to an explosion. In addition, if the reactor is cooled insufficiently, the possibility of a thermal runaway reaction is to be taken into account. The aforementioned events are combined to form the undesired event "explosion" in the fault tree of **Fig. 2**, which has been elaborated by drawing upon the following hypotheses: (a) contact between acetylene, acetic acid, or vinyl acetate with air invariably causes an explosion; (b) if acetylene is not cut off or N_2 cannot be supplied on failure of electricity, an explosion occurs; (c) insufficient cooling of the reactor cannot be detected from temperature measurement with TIR 2 because of the time lag between an increase of reaction temperature and the corresponding reading; (d) simultaneous failure of TIRC 1 and

Table 1. Safety relevant properties of the materials involved in the production of vinyl acetate[8]

Property	Acetylene	Acetic acid	Vinyl acetate
Ignition temperature in air, °C	305	465	427
Explosion limits in air, % volume	2.5–82	5.4–16	2.6–13.4
Heat of combustion $kJ \cdot g\text{-}mol^{-1}$	1300	870	2072
Decomposition with subsequent detonation	Possible	—	—

TIR 1 causes an explosion, if the plant is not shut down; (e) failure of the N_2 supply causes an explosion only, if pressure relief is impossible; (f) it will always be attempted to open bypass valve V_1 if coolant temperature rises; (g) contact between oil and the reactants owing to a perforation of one or several tubes of reactor R_1, heat exchanger H_1 or mixer M_1 has no dangerous consequences if pressure relief via S_1 is possible, unless a thermal runaway reaction produces a massive tube rupture; (h) the cooling circuit cannot be heated up erroneously by heat exchanger H_2 as process steam is no longer available after start-up and valves V_{11} and V_{12} are closed. Except for (e), (f), (g), which are supported by the plant owner's experience, and (h), which refers to a highly improbable event, all hypotheses are conservative. External and secondary effects are included in the tree in a global fashion with an estimated probability because their detailed analysis would be beyond the scope of this paper.

3. Component Data and Failure Probabilities

The set of failure data used is given in **Table 2** along with the basic events of the fault trees for the original and modified designs. Failure probabilities are calculated according to

$$q_i(t)=1-e^{-\lambda_i t} \quad (t>0) \tag{1}$$

where λ_i is the failure rate for basic event i, or constant probabilities, u_i, are used.

Failure of temperature measuring instruments TIR 1 and TIRC 1 is supposed to be detected easily because readings from both have to bear a definite relation with one another and with the reaction temperature. Therefore, asymptotic unavailabilities are used to describe their behavior, e.g. ref. 15, supposing that the associated downtime is $T_r=3\,\text{h}$

$$u_i=\frac{T_r}{T_i+T_r} \tag{2}$$

Flow meter F_1 is treated in the same way since a mass flow reading outside the range prescribed during plant operation would call for operator intervention, whose possible error in all aforementioned cases is provided for in the fault tree.

A second set of failure data is obtained taking into account the differences between the values indicated in various sources. Each value is considered as an event belonging to a statistical sample from a population distributed according to a log-normal distribution as outlined in ref. 14 with the probability density function, cf. ref. 16.

$$f(\lambda)=\frac{1}{\sqrt{2\pi}s\lambda}e^{-(\ln\lambda-\mu)^2/2s^2} \quad (\lambda>0) \tag{3}$$

The expression of Eq. (3) is characterized by two parameters, the median

$$\lambda_{50}=e^{\mu} \tag{4}$$

and the factor of dispersion

$$K=\frac{\lambda_{95}}{\lambda_{50}}=e^{1.645s} \tag{5}$$

which is chosen such that the probability for a value of λ to be comprised in the interval $[\lambda_{50}/K, \lambda_{50}\cdot K]$ amounts to 90%, its probability to fall below or above the bounds of the interval being 5% each. The parameters required for the application of Eq. (4) are calculated from the failure rates λ_n given in different data collections using the point estimates

$$\mu=\frac{1}{N}\sum_{n=1}^{N}\ln\lambda_n \tag{6}$$

and

$$s=\left[\frac{1}{N}\sum_{n=1}^{N}(\ln\lambda_n-\mu)^2\right]^{1/2} \tag{7}$$

where N denotes the total number of values available. The parameters obtained in this way are presented in **Table 3**.

Human behavior in relation with technical systems depends on a number of factors like training, stress and routine, and therefore is difficult to quantify. In ref. 17 examples of human error which occurred in the chemical industry are given and described by constant probabilities. For actions required in the plant under investigation a value of $u=0.01$ or $u=0.001$ per demand should be adopted, the pessimistic value $u=0.01$ being used in all calculations. Inadvertent opening or closing of valves is treated according to Eq. (1) under the assumption that the probability of such an act is 0.1 after 20 years. In the case of two redundant valves loose coupling is assumed, making use of a relation stated in ref. 18, which leads to a probability of 0.032 after 20 years.

In addition, a lower bound for the unreliability of the plant is calculated supposing that human error does not occur, thus throwing some light on the purely technical aspects of the system.

4. Fault Tree Evaluation

The fault tree is decomposed into its minimal cut sets, each of which comprises the minimal number of basic events—represented by the binary variables x_i—which have to occur simultaneously in order to make the system fail. From the minimal cut sets the multilinear form of the structure function of the system is calculated, as indicated in ref. 5. It allows system unreliability to be assessed, replacing the binary variables x_i by their corresponding probabilities. The analysis is carried out using the computer code ARBOL,[19] which gives an upper bound for system

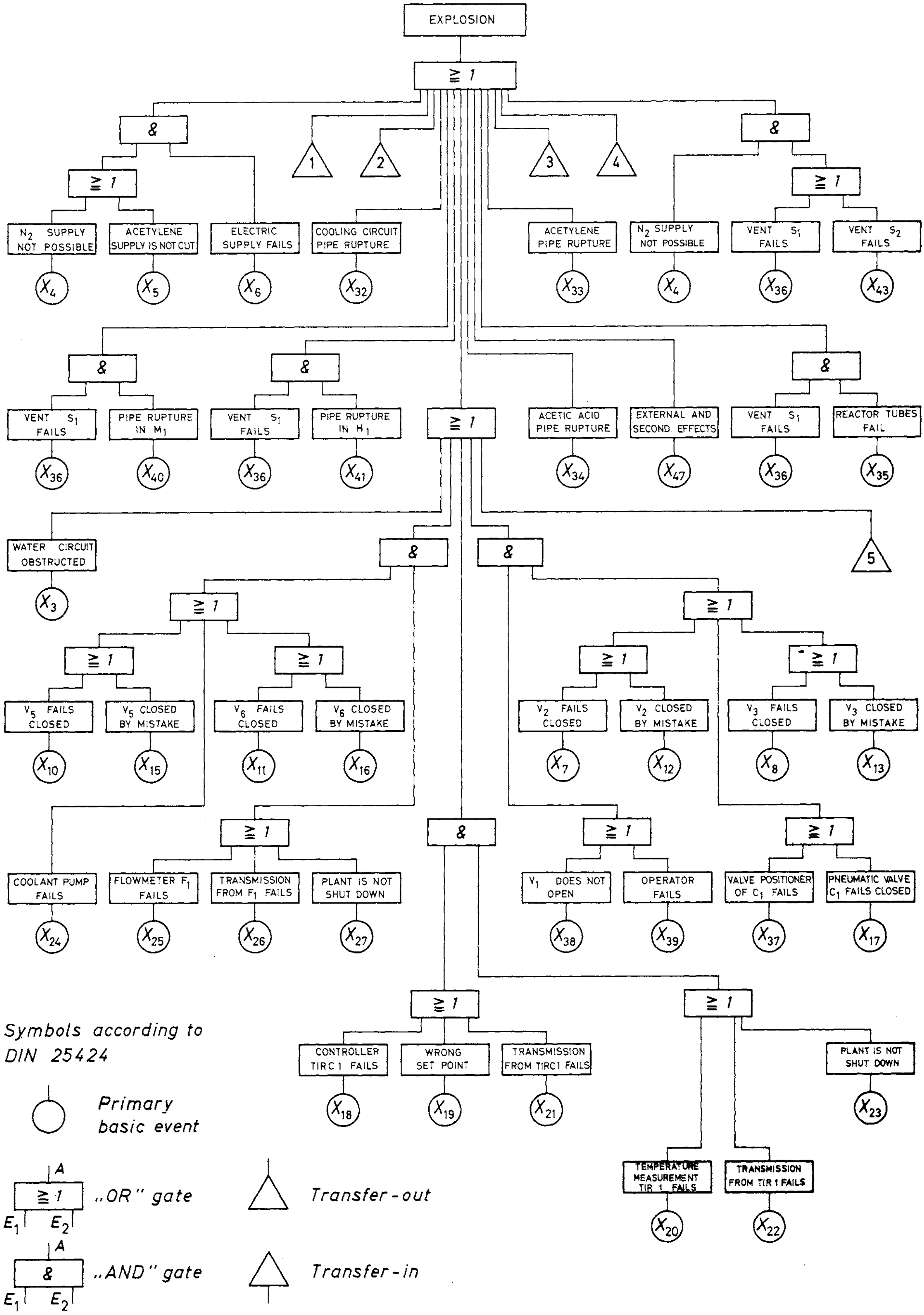
EXPLOSION
≧ 1
&
1
2
3
4
N2 SUPPLY NOT POSSIBLE
ACETYLENE SUPPLY IS NOT CUT
ELECTRIC SUPPLY FAILS
COOLING CIRCUIT PIPE RUPTURE
ACETYLENE PIPE RUPTURE
N2 SUPPLY NOT POSSIBLE
VENT S1 FAILS
VENT S2 FAILS
X4
X5
X6
X32
X33
X4
X36
X43
VENT S1 FAILS
PIPE RUPTURE IN M1
VENT S1 FAILS
PIPE RUPTURE IN H1
ACETIC ACID PIPE RUPTURE
EXTERNAL AND SECOND. EFFECTS
VENT S1 FAILS
REACTOR TUBES FAIL
X36
X40
X36
X41
X34
X47
X36
X35
WATER CIRCUIT OBSTRUCTED
X3
5
V5 FAILS CLOSED
V5 CLOSED BY MISTAKE
V6 FAILS CLOSED
V6 CLOSED BY MISTAKE
V2 FAILS CLOSED
V2 CLOSED BY MISTAKE
V3 FAILS CLOSED
V3 CLOSED BY MISTAKE
X10
X15
X11
X16
X7
X12
X8
X13
COOLANT PUMP FAILS
FLOWMETER F1 FAILS
TRANSMISSION FROM F1 FAILS
PLANT IS NOT SHUT DOWN
V1 DOES NOT OPEN
OPERATOR FAILS
VALVE POSITIONER OF C1 FAILS
PNEUMATIC VALVE C1 FAILS CLOSED
X24
X25
X26
X27
X38
X39
X37
X17
CONTROLLER TIRC 1 FAILS
WRONG SET POINT
TRANSMISSION FROM TIRC1 FAILS
PLANT IS NOT SHUT DOWN
X18
X19
X21
X23
TEMPERATURE MEASUREMENT TIR 1 FAILS
TRANSMISSION FROM TIR 1 FAILS
X20
X22
Symbols according to DIN 25424
Primary basic event
A
≧ 1
E1 E2
„OR" gate
A
&
E1 E2
„AND" gate
Transfer-out
Transfer-in

Fig. 2.

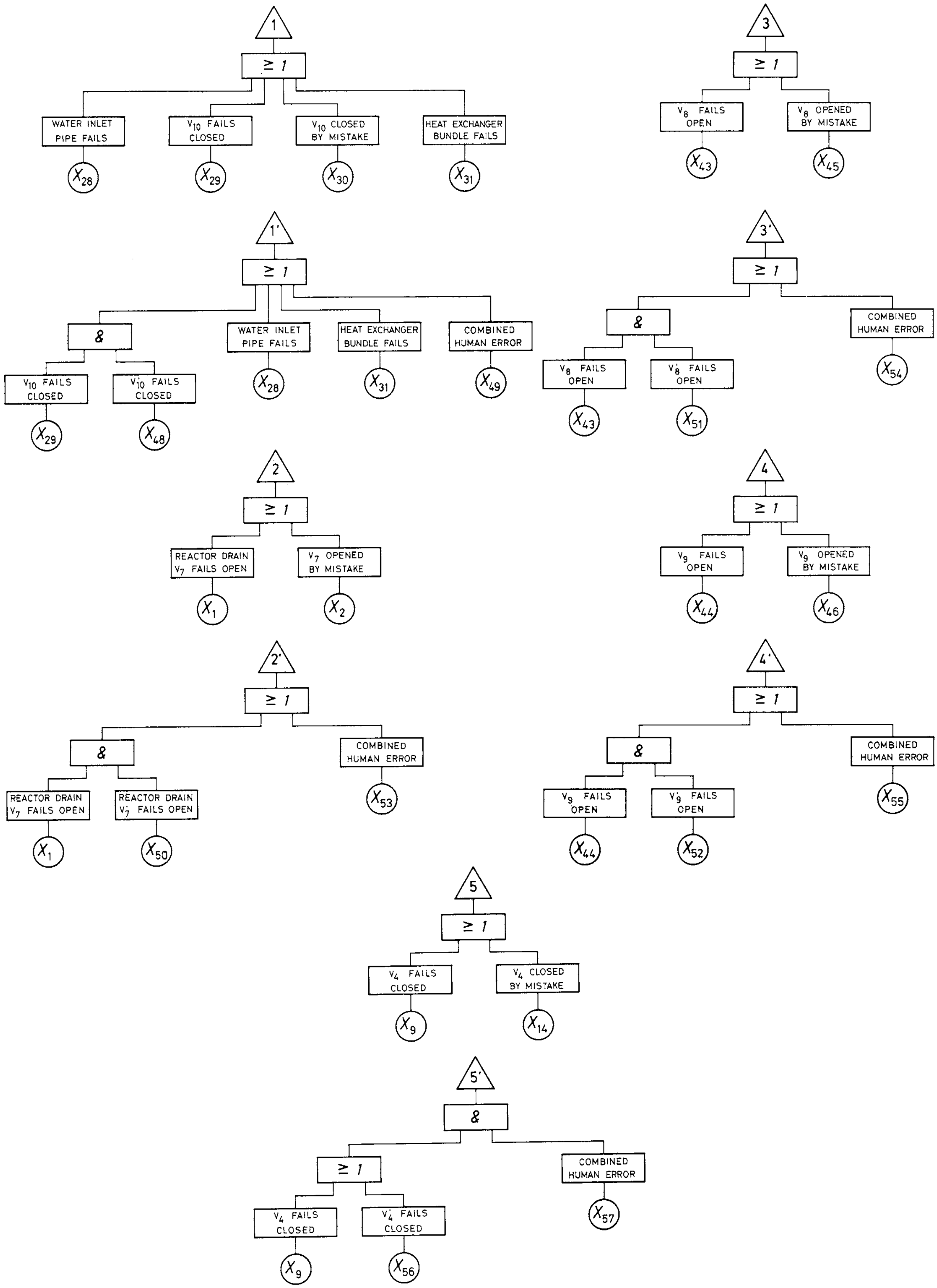

Fig. 2. Fault tree for the plant (primed transfer gates indicate design improvements).

Table 2. Basic events and mean values of their failure rates

Basic event	Variable name	Failure rate $\lambda \times 10^6$, h^{-1}	Unavailability u_i	Remarks
Reactor drain V_7 fails open	x_1	0.11[a]		Ref. 10
V_7 opened by mistake	x_2	0.60		Prob. 0.1 after 20 y
Water circuit obstructed	x_3	0.05[a]		Ref. 11
N_2 supply not possible	x_4	2.28[a]		Est, once in 50 y
Acetylene supply is not cut	x_5		0.01	Human error
Electric supply fails	x_6	11.42[a]		Est, after data ref. 12
V_2 fails closed	x_7	7.96[a]		Ref. 10
V_3 fails closed	x_8	7.96[a]		Ref. 10
V_4 fails closed	x_9	7.96[a]		Ref. 10
V_5 fails closed	x_{10}	7.96[a]		Ref. 10
V_6 fails closed	x_{11}	7.96[a]		Ref. 10
V_2 closed by mistake	x_{12}	0.60		Prob. 0.1 after 20 y
V_3 closed by mistake	x_{13}	0.60		Prob. 0.1 after 20 y
V_4 closed by mistake	x_{14}	0.60		Prob. 0.1 after 20 y
V_5 closed by mistake	x_{15}	0.60		Prob. 0.1 after 20 y
V_6 closed by mistake	x_{16}	0.60		Prob. 0.1 after 20 y
C_1 fails closed	x_{17}	20.50[a]		Ref. 12
Controller TIRC 1 fails	x_{18}		8.90×10^{-4}	Eq. (3) with $T=3.37 \times 10^4$ h from ref. 13
Wrong set point in TIRC 1	x_{19}		0.01	Human error
TIR 1 fails	x_{20}		9.93×10^{-5}	Eq. (3) with $T=3.02 \times 10^4$ h from ref. 13
Transm. from TIRC 1 fails	x_{21}		3.11×10^{-4}	Eq. (3) with $T=9.63 \times 10^3$ h from ref. 13
Transm. from TIR 1 fails	x_{22}		3.11×10^{-4}	Eq. (3) with $T=9.63 \times 10^3$ h from ref. 13
Plant is not shut down	x_{23}		0.01	Human error
Coolant pump fails	x_{24}	29.50[a]		Ref. 10
Flow meter F_1 fails	x_{25}		6.52×10^{-5}	Eq. (3) with $T=4.60 \times 10^4$ h from ref. 14
Transm. from F_1 fails	x_{26}		3.11×10^{-4}	Eq. (3) with $T=9.63 \times 10^3$ h from ref. 13
Plant is not shut down	x_{27}		0.01	Human error
Water inlet pipe fails	x_{28}	0.01		Est
V_{10} fails closed	x_{29}	7.96[a]		Ref. 10
V_{10} closed by mistake	x_{30}	0.60		Prob. 0.1 after 20 y
Heat exchanger bundle fails	x_{31}	0.94		Est, after data ref. 10
Cooling circ. pipe rupture	x_{32}	0.10		Est, after data ref. 13
Acetylene pipe rupture	x_{33}	0.10		Est, after data ref. 13
Acetic acid pipe rupture	x_{34}	0.10		Est, after data ref. 13
Reactor tubes fail	x_{35}	9.43		Est, after data ref. 10
Vent S_1 fails	x_{36}	2.28[a]		Est, once in 50 y
Valve pos. of C_1 fails	x_{37}	46.73[a]		Ref. 13
V_1 does not open	x_{38}	15.00[a]		Ref. 10
Operator fails	x_{39}		0.01	Human error
Pipe rupture in M_1	x_{40}	0.94		Est, after data ref. 10
Pipe rupture in H_1	x_{41}	0.94		Est, after data ref. 10
Vent S_2 fails	x_{42}	2.28[a]		Est, once in 50 y
V_8 fails open	x_{43}	0.11[a]		Ref. 10
V_9 fails open	x_{44}	0.11[a]		Ref. 10
V_8 opened by mistake	x_{45}	0.60		Prob. 0.1 after 20 y
V_9 opened by mistake	x_{46}	0.60		Prob. 0.1 after 20 y
External and second. effects	x_{47}	2.28		Est, once in 50 y
V'_{10} fails closed	x_{48}	7.96[a]		Ref. 10
2 redund. valves closed by mistake	x_{49}	0.18		0.032 in 20 y
R_1 drain V_7' fails open	x_{50}	0.11[a]		Ref. 10
V_8' fails open	x_{51}	·0.11		Ref. 10
V_9' fails open	x_{52}	0.11		Ref. 10
2 redund. valves closed by mistake	x_{53}	0.18		0.032 in 20 y
2 redund. valves closed by mistake	x_{54}	0.18		0.032 in 20 y
2 redund. valves closed by mistake	x_{55}	0.18		0.032 in 20 y
V_4' fails closed	x_{56}	7.96[a]		Ref. 10
2 redund. valves closed by mistake	x_{57}	0.18		0.032 in 20 y

[a] Indicates components to be serviced every 2880 h.

Table 3. Medians of failure rates and dispersion factors for plant components

Basic event	Failure rate $\lambda \times 10^6$, h^{-1}											λ_{50}	K
	Ref. 10							Ref. 11	Ref. 12	Ref. 13	Ref. 16		
Manual valve fails open[a]	0.1	6.8	4.4	1.7	2.0	4.3	5.5					2.19	9.2
Manual valve fails closed[a]	0.0165	1.2	0.765	0.3	0.35	0.75	0.98					0.38	9.5
Pneumatic valve fails closed[a]	10.0							2.2	21.0	34.0	30.0	13.64	5.3
Manual valve does not open[b]												1.7	5.7
Coolant pump fails[b]												25.0	15.0
Heat exchanger bundle fails[c]	0.04	0.02	0.01	0.03								0.022	2.4
Pipe fracture	0.2	0.2	0.12									0.17	1.5

[a] Values have been assigned according to the proportion stated in ref. 11 (0.85 for open failure; 0.15 for closed failure).
[b] Data taken directly from ref. 14.
[c] For heat exchanger H_3, which has a lower charge than the others, data have been divided by a factor of 10.

unreliability. The system unreliability in case of log-normally distributed failure rates is evaluated in a number of trials, each of which uses a different set of failure data selected at random in accordance with Eq. (3). This procedure permits calculation of the arithmetic mean of the unreliability

$$\bar{Q} = \frac{1}{J} \sum_{j=1}^{J} Q_j \tag{8}$$

and its standard deviation

$$\sigma_{\bar{Q}} = \left[\left(\frac{1}{J} \sum_{j=1}^{J} Q_j^2 - \bar{Q}^2 \right) \Big/ J \right]^{1/2} \tag{9}$$

where Q_j is the unreliability resulting from trial j, and J denotes the total number of trials. A further characterization of the result can be obtained by calculating the standard deviation of the values of Q_j and percentiles.

5. Results

The analysis of the tree leads to 60 minimal cut sets, whose composition is stated in **Table 4**. They are made up of one or two basic events only, thus reflecting the low degree of redundancy of the system. Searching the two-event cut sets for potential common mode effects, only a pump failure affecting flow meter F_1 is discovered. Since the influence would have to be such that correct flow is indicated although there is too little or none, the contribution of this event to plant unreliability is considered negligible.

The results obtained from the evaluation of the fault trees of Fig. 2 for the original and modified designs with the data of Table 2 are represented in **Fig. 3** as a function of time until the first inspection, $\theta = 2880$ h. Values are given for two cases: (a) including human error, and (b) assuming that all human interventions are carried out with perfection.

The improvement of the original design is based on an analysis of the minimal cut sets of the system,

Table 4. Minimal cut sets of the system

Minimal cut set	Basic design	Improved design
1 Basic event	17	12
2 Basic events	43	48
Total	60	60

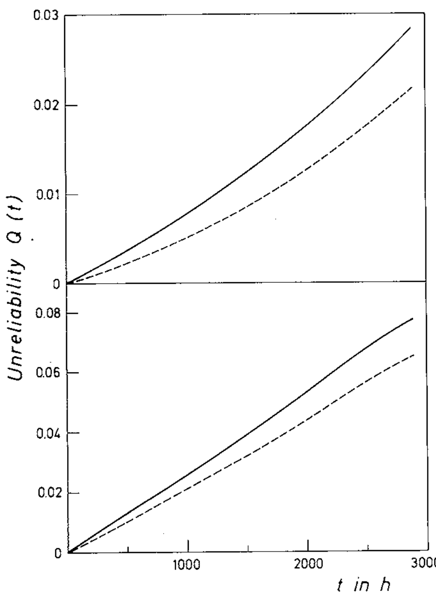

Fig. 3. Unreliabilities for the basic and modified designs. ——, with human error; ----, without human error.

which reveals the following important contributions to system unreliability: (a) mechanical failure of valves V_4 (x_9) and V_{10} (x_{29}), 29% each; (b) rupture of the bundle of heat exchanger H_3 (x_{31}), 3.5%; (c) mechanical failure of drains V_7 (x_1), V_8 (x_{43}), V_9 (x_{44}), 1.2%. The joint contribution of human error amounts to 15% and reflects the relatively low degree of automation of the plant. Human error alone is capable of bringing about the undesired event if valves V_4 or V_{10} are closed by mistake (x_{14}, x_{30}) or valves V_7, V_8 or V_9 are opened inadvertently (x_2, x_{45}, x_{46}). All the other manual valves figure in minimal cut sets which comprise more than one basic event, hence their failure alone cannot make the system fail.

For this reason the proposed modification consists in installing additional valves in parallel to V_4 and V_{10} and in series with V_7, V_8 and V_9. This measure increases plant reliability by a factor of about 2.7 (based on mean values) and reduces the contribution of human failure to about one-half.

Since the system is serviced periodically, the unreliability calculated for the time until the first inspection may be regarded as representative for the entire plant life, although a slight increase is to be expected at later stages due to those components whose possible defects cannot be detected in routine servicing. These components should therefore be subjected to a more profound revision after a certain number of the usual inspection intervals.

An additional calculation gives an unreliability of Q (2880 h) $= 1.92 \times 10^{-1}$ for the plant without flow meter F_1, which has been installed by the owner after commissioning, thus revealing its importance for the safety of the plant. It protects the installation even more efficiently than placing an additional pump in parallel to P_1, a measure which leads to an unreliability of Q (2880 h) $= 7.85 \times 10^{-2}$. The effectiveness of flow measurement, however, depends on quick discovery of its possible defects and their immediate repair; the redundant pump, on the other hand, would improve plant availability.

As can be read from **Table 5**, the unreliabilities obtained when log-normally distributed failure rates are used differ from those which result with mean values for the failure rates. This is due to the fact that mean values of products are formed in evaluating the fault tree in the first case as opposed to products of mean values in the second. The two do not normally coincide. The considerable spread of the results reflects data uncertainties, especially for pumps and the failure of manual valves.

Conclusions

Fault tree analysis has proved useful in revealing weaknesses of the original design of the plant, thus allowing its systematic improvement. Attention has been drawn to components and procedures which are vital to plant safety. The relatively high spread of the values for unreliability when log-normally distributed input data are used indicates that a firmer basis of failure data is desirable. In addition, a number of pessimistic hypotheses had to be made in the elaboration of the fault tree because the underlying phenomena are not yet completely understood. Therefore, the objective of this type of analysis should, at present, be comparison of alternative designs rather than assessment of plant unreliability in absolute terms.

Table 5. System unreliability for $\theta = 2880$ h with and without human failure and using log-normally distributed failure rates

	Basic design	Modified design
With human failure	7.7×10^{-2}	2.8×10^{-2}
Without human failure	6.5×10^{-2}	2.2×10^{-2}
Log-normally distributed failure rates with human failure (Eqs. (8) and (9) with $J = 999$)	7.1×10^{-2} $\pm 1.4 \times 10^{-3}$ 95% of all values in 2.6×10^{-2}, 1.5×10^{-1}	1.8×10^{-2} $\pm 1.1 \times 10^{-4}$ 99% of all values in 1.3×10^{-2}, 3.1×10^{-2}

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Nomenclature

λ_i	= failure rate for basic event i	[h^{-1}]
λ_{50}	= median of failure rate λ	[h^{-1}]
μ	= arithmetic mean of $\ln \lambda$	
θ	= mean time between inspections for the plant	[h]
$\sigma_{\bar{Q}}$	= standard deviation of the mean value of system unreliability $\bar{Q}$	
$f(\lambda)$	= probability density function of the log-normal distribution of failure rates	
K	= factor of dispersion of failure rates	
$q_i(t)$	= unreliability for basic event i	
Q	= system unreliability	
$\bar{Q}$	= mean value of system unreliability	
s	= standard deviation of $\ln \lambda$	
t	= variable "time"	
T_i	= mean time to failure for basic event i	[h]
T_r	= downtime	[h]
u_i	= unavailability for basic event i	
x_i	= binary variable describing basic event i	

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INTERFACIAL TURBULENCE DURING THE PHYSICAL ABSORPTION OF CARBON DIOXIDE INTO NON-AQUEOUS SOLVENTS

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Key Words: Absorption, Mass Transfer, Interfacial Turbulence, Non Aqueous Solvent, Carbon Dioxide, Marangoni Effect, Schlieren Method, Visualization

Interfacial turbulence during the physical absorption of CO_2 into non-aqueous solvents such as methanol and toluene was investigated experimentally from the point of view of the mass transfer rates.

Liquid-phase mass transfer coefficients were measured in the range of gas-liquid contact time $t=0.1$–1000 s, using a wetted-wall column, a two-dimensional source flow cell and a quiescent liquid cell, and were compared with calculated values from the penetration theory. The gas-liquid interface during absorption was observed by schlieren photography.

It was found that interfacial turbulence owing to the Marangoni effect occurs around $t=0.1$ s and succeedingly a density driven convection is superimposed on the turbulence after $t=5$–50 s when CO_2 is absorbed into non-aqueous (organic) solvents. It is also found that Marangoni-type turbulence occurs in the condition of negative Marangoni number.

Introduction

In industrial gas absorption processes, non-aqueous solutions are sometimes preferred to aqueous ones. However, there have been few studies of the absorption mechanism for non-aqueous solutions[10] in comparison with those for aqueous solutions.

It has been known that liquid-phase mass transfer coefficient k_L for organic solvents is larger than that for water and that k_L is apparently inversely proportional to the surface tension of the solvents.[3,4,6] The authors have studied the mechanism of how surface tension affects the mass transfer rate[6] and have found that interfacial turbulence occurs and enhances the mass transfer rate when CO_2 is absorbed into organic solvents.

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The aim of this work is to clarify the behaviour of interfacial turbulence experimentally in a wide range of gas-liquid contact time.

1. Experimental

1.1 Experimental apparatus

To measure liquid-phase mass transfer coefficient k_L in a wide range of contact time, three types of apparatus, a wetted-wall column, a two-dimensional source flow cell[11] and a quiescent liquid cell, were used.

Figures 1 and **2** show the wetted-wall column and the two-dimensional source flow cell.

The quiescent liquid cell is made of a cylindrical glass bottle of 5.2 cm I.D. and 25 cm height, where the liquid depth is 20 cm.

Methanol and toluene were mainly used as the solvents. Water was also used in the source flow cell