

## Risk Based Design of Allyl Chloride Production Plant

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The necessity to identify and quantify the risks for men and the environment, but also the excessive consumption of resources and energy related to the process plants has led to the formulation of analytical methods capable of assessing the reliability and availability of these systems in order to optimize their operation. Integrated Dynamic Decision Analysis (I.D.D.A.), in particular, represents a tool for the logic modeling of the process plants based on “dynamic” event trees able to describe the system both as “logic” concatenation of events and “probabilistic” coherence. This approach was used for reviewing the design of a plant for the production of allyl chloride by chlorination of propylene in exothermic conditions. This paper aims at building an objective and documented reference for the decision making about the design alternatives to be adopted for risk minimization.

### 1. Introduction

In order to have guarantees of consistency and completeness in a risk assessment used as a basis for a proper plant design, the probabilistic model of the system should be completed with a phenomenological interface of the process.

This approach was used for reviewing the design of a plant for the production of allyl chloride by chlorination of propylene in exothermic conditions.

The allyl chloride is product by the chlorination of propylene at high temperature:



$$r_1 = 3301562 \exp(-15118/RT) P_{C_3H_6} P_{Cl_2}; \text{ reaction velocity } [\text{kmole}_{Cl_2,reacted} / \text{h m}^3]$$



$$r_2 = 185,5 \exp(-13811/RT) P_{C_3H_6} P_{Cl_2}; \text{ reaction velocity } [\text{kmole}_{Cl_2,reacted} / \text{h m}^3]$$

At these temperatures (300-600°C), the chlorination occurs through a radical mechanism where the hydrogen atom in allylic position is replaced preferentially by chlorine giving rise to allyl chloride. Below 200°C propylene reacts with chlorine mainly by addition to the double bond to give 1,2-dichloropropane; above 300 °C, this reaction is suppressed and the formation of allyl chloride predominates so that 1,2-

dichloropropane is only a by-product. The compounds cis- and trans- 1, 3-dichloropropene arises from a secondary reaction of allyl chloride, in which a further hydrogen atom is substituted by chlorine (Krähling et al., 2000)

### 1.1 Description of the process

The plant, shown in Figure 1, has been designed for the production of 45000 ton/year of allyl chloride (Anatra and Malandrino, 1980).

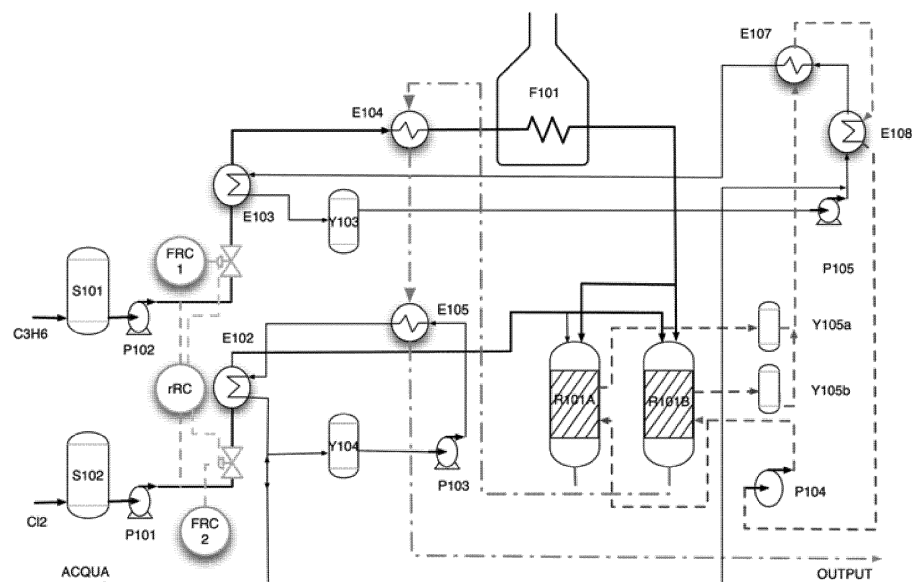


Figure 1: Plant Flow sheet

The plant characteristics are shown in Table 1. The presence in the plant of two reactors (R 101 A, B) is justified by the temperature at which the chlorination reaction takes place, causing pyrolysis phenomena, with the consequent formation of soot compounds in the pipes. In order to have a continuous process, the feed is sent, through a system of valves, at one or the other reactor according whether it can be in the production or cleaning phase. The reactor is cooled up through a circulation of melted salts, that allows realizing also energy conservation through the great heat development generated from the two chlorination reactions, producing the vapor (E 107, E108) necessary to vaporize propylene in C 103 (Anatra and Malandrino, 1980).

Table 1: Plant characteristics

Operative Conditions		Temperature [°C]	Reactor characteristics [m]		
Conversion in allyl chloride	73 %	Reactants inlet	300	Inlet diameter	0.99
Cl <sub>2</sub> conversion	90 %	Melted salts inlet	270	Pipes number	625
Mole C <sub>3</sub> H <sub>6</sub> : Mole Cl <sub>2</sub>	2.5	Max reactor	503	Pipes diameter	0.0125
Pressure	3.2 kg/cm <sup>2</sup>	Outlet products	498	Pipes length	5.1
		Outlet melted salts	300		

## 2. Integrated Dynamic Decision Analysis

Through Dynamic Decision Analysis the representation of the system takes place outlining all its possible behaviors according to the alternative routes that the system can undergo depending from the possible states of relevant components, consistent with a Cause and Effect approach. In fact the scenario of the logical system examined has to be considered complete since the evolution of the probability of occurrence is closely linked with that of the physical phenomena of the process plant.

### 2.1 Logical modeling

Plant operations have been described with I.D.D.A.'s syntax based on the Boolean logic (Galvagni and Demichela, 2003):

1. Identification of the events related to the operation of the system itself and construction of a list of levels, with questions and affirmations, which represents the elementary matter of the logical model and also the nodes in the event tree.
2. Construction of a 'reticulum' indicating the addresses (subsequent level) to be visit after each response in each level, and a comment string that allows the user to read the logical development of a sequence.
3. Association to each of the levels of a probability, which represents the expectation degree of the failure or unwanted event and of an uncertainty ratio, which represents the distribution.
4. Definition of all the constraints, which can modify run time the model, fitting it to the current knowledge status.

An example of the input file regarding the propylene heating phase is reported in Table 2. The software combines the answers to the analyst's questions in all the possible ways, in order to develop all the possible alternative events that may take place in the plant. These are represented as sequence of events that show, step by step, the paths chosen and the probabilities of occurrence assigned (Demichela and Piccinini, 2003). In the present case 12175 alternative sequences have been generated describing alternative behaviours for the system.

Table 2: Description of the propylene's heating phase through IDDA's syntax

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: Does the controller FRC1 work?  
54 0.5, 0., 56 55, 3, 'FRC1' 'Works' 'Does not work'

: How does the controller LRC7 fail?  
55 0.5, 0., 58 58, 3, 'FRC1' 'Partial Signal' 'Absent Signal'

: Does the control valve work?  
56 0.5, 0., 60 58, 3, 'FRCV1' 'Works' 'Does not work'

: How does the valve FRCV1 fail?  
58 0.5, 0., 60 62, 3, 'Failure way FRCV1' 'Open' 'Closed'

: Propylene flow rate at mixing  
60 1., 0., 0 0, 3, 'Flow C2H6' 'Normal' 'Low'

: Propylene flow rate at mixing  
62 1., 0., 0 0, 3, 'Flow C2H6' 'Normal' 'High'

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## 2.2 Probabilistic results

From the alternative sequences set it is possible to extract, through a logical selection, those sequences bringing to TE or to intermediate consequences of interest for the analyst. Table 3 shows the probabilistic results obtained analyzing some of the initiating events and the Top Event.

Table 3: Probabilistic results - initiating events that bring to the Top Event

Ev.	Prob.	Ev.	Prob.
1 Feed flow decrease	$3.8 \cdot 10^{-4}$	5 Melted salts flow decrease	$3.6 \cdot 10^{-5}$
2 Reactor pressure increase	$6.1 \cdot 10^{-6}$	6 Reactants temp. increase	$7.3 \cdot 10^{-4}$
3 Melted salts $T_{in}$ increase	$5.6 \cdot 10^{-5}$	T.E. Reactor heat exhaustion	$4 \cdot 10^{-2}$
4 Reactants ratio decrease	$8.2 \cdot 10^{-3}$	T.E. Mixer explosion	$8.8 \cdot 10^{-4}$

## 2.3 Phenomenological model

It is now possible to complete the probabilistic model of the system with the phenomenological description of the plant, considering as a function of the reactor length: the conversions (Eq. 1, 2), the reactants temperature (Eq. 3) and the melted salts temperature (Eq. 4).

$$\frac{dx_1}{dz} = \frac{A_C}{F} \cdot 3301562 \cdot e^{-\frac{7604}{t} p} \cdot 2^{\frac{a-(1+a)^2(x_1+x_2-x_1^2-x_2^2-2x_1x_2)}{(1+a)(1-x_2)^2}} \quad (1)$$

$$\frac{dx_2}{dz} = \frac{A_C}{F} \cdot 185,5 \cdot e^{-\frac{1918}{t} p} \cdot 2^{\frac{a-(1+a)^2(x_1+x_2-x_1^2-x_2^2-2x_1x_2)}{(1+a)(1-x_2)^2}} \quad (2)$$

$$\frac{dt}{dz} = \frac{a - (1+a)^2(x_1 + x_2 - x_1^2 - x_2^2 - 2x_1x_2)}{(1+a)^2(1-x_2)^2(2,7x_1 - 3,2x_2 + \frac{8,6 + 25,3a}{1+a})} \cdot \frac{P^2 A_c}{F} \cdot (-12853 \cdot e^{-\frac{7604}{t}} \cdot \Delta H_1 - 0,730 \cdot e^{-\frac{1918}{t}} \cdot \Delta H_2) + \frac{U(T-t)A_R}{F(2,7x_1 - 3,2x_2 + \frac{8,6 + 25,3}{1+a})} \quad (3)$$

$$\frac{dT}{dz} = \frac{U(T-t)A_R}{Mc_p} \quad (4)$$

where:  $x_1$ , Allyl chloride conversion;  $x_2$ , 1,2-dichloropropane conversion; P, Design pressure [kg/cm<sup>2</sup>]; F, Feed flow rate for pipe [kmol/h]; a, Mole propylene/Mole chlorine; M, Melted salts flow rate [kg/h];  $A_c$ , Pipe section [m<sup>2</sup>]; z, Reactor length [m];  $A_R$ , Pipe lateral surface [m<sup>2</sup>]; U, Global heat transfer coefficient [kcal/h m<sup>2</sup>];  $c_p$ , Specific heat [kcal/kmol°C];  $\Delta H_1 = -26800$ ,  $\Delta H_2 = -44100$ , Reaction enthalpies [kcal/kmole].

Thanks to integrated modeling, it is possible to obtain, for each sequence initiated by a given event, the trend of the relevant process variable. Figures 2 and 3 show the behaviour of the reactor temperature given a step variation of the inlet flow rate depending on the failure of rRC (reactants ratio control). A full representation of the temperature deviations occurring for the different failures, is given in Table 4, where the bold numbers represent critical  $\Delta T$  ( $T_p - T_{max}$ ), requiring interventions.

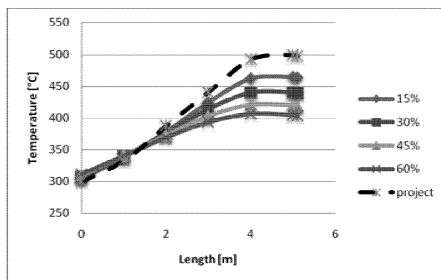


Figure 2: rRC failure closes FRCV1

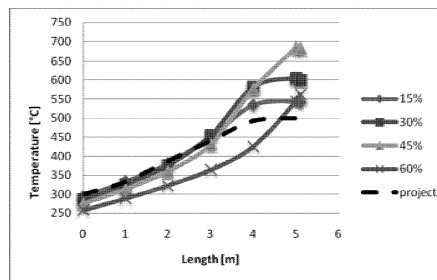


Figure 3: rRC failure opens FRCV1

Table 4: Phenomenological calculations

Temperature		$T_p$	-	$T_{max}$	
Initiator event	Event	15%	30%	45%	60%
FRC2, feed control Cl <sub>2</sub>	4	30	70	<b>100</b>	<b>140</b>
rRC1, reactants ratio control	1,4	40	<b>100</b>	<b>176</b>	<b>57</b>
FRC1 (T), feed control C <sub>2</sub> H <sub>6</sub>	1,4	70	<b>150</b>	<b>230</b>	<b>310</b>
FRC1 (V), feed control C <sub>2</sub> H <sub>6</sub>	1,4	20	45	60	80
TRC2, outlet temperature furnace control	6	70	<b>140</b>	<b>185</b>	<b>250</b>

### 3. Design and Management Improvement

The results in Section 2 have highlighted the critical events requiring interventions in order to reduce risks at a tolerable level. The design and management improvements suggested with the probability assessment for the TE are shown in Table 5.

Table 5: Improvement actions

Configuration	Collapse prob.	Explosion prob.
Initial configuration	$4 \cdot 10^{-2}$	$8.8 \cdot 10^{-4}$
Adding of a high temperature switch (hTS) on the reactor outlet line	$1.2 \cdot 10^{-2}$	$1.4 \cdot 10^{-4}$
Introducing a redundancy of the solenoid valve interlocking Cl <sub>2</sub> flow rate and adding an inerting system in the mixer	$1.3 \cdot 10^{-3}$	$5.7 \cdot 10^{-7}$
Reduction of the intervals between tests of interlock system	$1.6 \cdot 10^{-4}$	$7.2 \cdot 10^{-8}$

### 4. Conclusions

Integrating the probabilistic model of the system with a phenomenological model in a plant which produces allyl chloride has highlighted how a complete approach to the plant safety is able to better support the decision modeling in term of design improvements, such as the installation of systems for prevention/mitigation and changes in the procedural of management/maintenance. Keeping the model updated will make it possible to build an objective and documented reference for the examination of all the solutions proposed gradually in a timely and economically way able to provide the data necessary for monitoring and maintenance of the plant for risk reduction that are required from the modern criteria of Quality, Safety and Risk Guarantee.

### References

- Anatra U., Malandrino G., 1980, Reliability Analysis of a Reactor for the production of Allyl Chloride, Master Thesis, Polytechnic of Turin.
- Demichela M., Piccinini N., 2003, Integrated Dynamic Decision Analysis (I.D.D.A.): a new approach for risk analysis, ICheap-6 AIDIC, Pisa, Italy.
- Galvagni R., Demichela M., 2003, I.D.D.A. (Integrated Dynamic Decision Analysis): a Methodology for the Safety evaluation using Decisional Trees, 3ASI, Association of Environmental Analysts, of Reliability and Industrial Safety, Alghero, Italy.
- Krähling L., Krey J., Jakobson G., Grolig J., Miksch L., 2000, Allyl Compounds, Ullmann's Encyclopaedia of Industrial Chemistry, 7th Edition.