



## Domino Effects Related to Home-Made Explosives

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The present study focuses on the analysis of domino effect triggered by overpressure caused by blast waves due to explosions derived by deliberate attacks to process plants and carried out with home-made explosives. The effects of blast waves caused by home-made explosives were compared with those expected from a net equivalent charge of TNT by using a specific methodology for the assessment of stand-off distances. The methodology was applied to a case study demonstrating the potentiality of home-made explosives in causing accident escalation and severe effects on population and assets, obtaining indications for the importance of adequate management of site security.

### 1. Introduction

According to the US Government Hazardous Substances Database, several substances and mixtures can be used for the realization of home-made explosives, starting from common chemicals sold in markets and pharmacies. Among many, two are often adopted for terrorist attacks, suicide bombing, and other malicious uses: Ammonium Nitrate (AN) - Fuel Oil (ANFO) and Triacetone Triperoxide Peroxyacetone (TATP) (Price & Ghee, 2009). ANFO is a tertiary explosive (TNT is secondary explosive) and is generally composed by 94 % of AN prills and 6% of adsorbed fuel oil. It is extensively used for several authorized purposes as in mine blasting. TNT equivalence is typically 80 %, ideal explosion energy is 3890 J/g, to be compared with the explosion energy of pure AN, 1592 J/g. AN prills for mining applications are however physically different from fertiliser prills used in home-made explosives. Indeed, the commercial AN used for blasting has a 20 % void space and is coated with #2 fuel oil (mainly C10 to C20 linear hydrocarbons) or kerosene. Hence, ANFO has a bulk density of approximately 840 kg/m<sup>3</sup>, starting from AN prills of about 1300 kg/m<sup>3</sup>, whereas pure crystalline AN is 1700 kg/m<sup>3</sup>. On the other hand, homemade explosives made from AN fertilizer do not have high void fraction and are less efficient. This is clearly favored by the new European regulations for fertilizers (EC 2003/2003), which imposes a maximum content of AN (45 % w/w) for general use. Indeed, such fertilizers still may be used to obtain explosives, but require preparation to achieve a detonation. In any case, if commercial AN with 50 % of dolomite - as inert - and diesel fuel are used, a detonation energy of 1071 J/g is obtained, much lower than pure ANFO. For amounts of dolomite higher than 30 % and diesel fuel, no detonation is observed (Buczowski and Zygmunt, 2011).

TATP is a primary explosive, often used as detonator, which is notable for the absence of nitrogen. This peculiarity is essential for avoiding conventional chemical bomb detection systems. Furthermore, TATP is almost undetectable by sniffer dogs. TATP is very unstable: it can be ignited by touch and explode spontaneously. Also it can be obtained from common household as sulphuric acid, hydrogen peroxide, and acetone. TATP is highly volatile and decomposes to form gas phase molecules (i.e. entropic explosion). It is actually composed by isomers and conformers, the dimer being more stable, with lower energy. The density is typically 1220 kg/m<sup>3</sup>. However, home-made TATP formulations are typically in the range of 450-500 kg/m<sup>3</sup> (Kuzmin et al., 2008), and a corresponding detonation velocity of ca 1400 m/s. Thus, TNT equivalence, which is 88 % in ideal conditions, can reach a maximum of 50% for lower densities. Finally,

TATP is often stabilized with carbonaceous liquids and waxes so that the net charge is even lower (Siegel and Saukko, 2012). Nevertheless, Lefebvre et al. (2004) have demonstrated that home-made TATP is very sensitive to impact or friction, although the strength of explosion may strongly vary because the quality of the final product is very sensitive to the temperature during synthesis.

In the general framework of security issues related to explosives, the present study investigates the possibility of using the two cited home-made explosives in order to damage process equipment, and to trigger a domino chain in the process plant due to consequences amplification (Kourniotis et al., 2000). To this aim, the peak overpressures generated by given amount of home-made ANFO or TATP have been calculated by using either Hopkinson-Cranz (mass) or Sachs (energy) scaled distance and TNT equivalence. Results have been adopted in vulnerability functions for domino effects (Salzano and Cozzani, 2005), compared against threshold resistance values (Cozzani et al., 2006), and used for the determination of inherently safe layout of equipment (Cozzani et al., 2007), also in the framework of managing emergency planning (Georgiadou et al., 2010). To this regard, it is worth noting that the proposed methodology has been proved to work accurately with CHN-based high-energy explosives, but rarely proved to be effective with low energy substances, or for the uncertain behaviour of the same explosives with respect to density, composition, humidity and other chemical and physical parameters.

## 2. Methodology

Direct or indirect attack to sensitive target as industrial equipment storing hazardous materials can be performed by using home-explosives. In the case of self-produced ANFO, several kilograms to tons of explosive substances (maximum 10-50 t) can be positioned outside the industrial border in car, or van, or even truck parked in the road adjacent to the industrial installation. On the other hand, TATP is too hazardous to produce, and transport in large quantity. Indeed, it is typically adopted for single-man suicide attack. Hence, we assume that a maximum net-charge of 50 kg can be transported e.g. in backpack. Quite clearly, TATP attack can be only directed to equipment shell, e.g. as in the case of chlorine tank used in swimming pools or public water treatment system. In this work, no confinement (e.g. steel cases) has been considered and the effect of casing fragmentation has been neglected. Several previous publications provide data, references and correlations for the shock wave produced by ANFO (Price and Ghee, 2009) and TATP (Hargather and Settles, 2007). What is relevant here is that: i) the explosion energy gives a good reproduction of the destructive power of the substances at atmospheric pressure, which is the case analysed here; ii) light confinement (even paper) approximately doubles the severity of explosion; iii) the energy output from non-ideal explosives is dependent on charge size, which makes it difficult to define with traditional modelling methods. Table 1 reports the explosion energy and TNT efficiencies ( $TNT_{eff}$ ), expressed as the ratio of the explosion energy with the corresponding value for TNT, for either pure or non-ideal mixture. In the last case, the values have been calculated by using the Chemical Equilibrium Model (CEA) as previously shown for black powder (Salzano and Basco, 2012) and pyrotechnics (Basco et al., 2010).  $TNT_{eff}$  is essential for unconfined explosion, whereas the heat of combustion, which is much larger, has to be included in quasi-static analysis if the case of confinement (Maienschein, 2002).

*Table 1: Experimental heat of explosion ( $\Delta H_{exp}$ ), and combustion ( $\Delta H_{comb}$ ) and TNT efficiencies ( $TNT_{eff}$ ) for the analysed explosives.*

Explosive	$\Delta H_{exp}$ (kJ/kg)	$\Delta H_{comb}$ (kJ/kg)	$TNT_{eff}$ (-)	$\Delta H_{exp}/\Delta H_{exp,TNT}$ (-)
TNT	4680	14961	1.00	1.00
ANFO (94% AN; 6% Fuel Oil)	3890	578	0.60 – 0.88	0.83
TATP (Trimer)	2803	28192	0.30 – 0.92*	0.60
DADP (Dimer)	-	23465	-	1.26
AN/dolomite (90/10) + diesel fuel	3234	-	-	0.69
AN/dolomite (50/50) + diesel fuel	1071	-	-	0.23

The effects of a blast wave on structure or equipment are dependent on its overpressure only, at least in the far field and conservatively. To this regard, Table 2 summarizes the types of equipment and the corresponding overpressure threshold value for structural damage and escalation. Details can be found in Salzano and Cozzani (2005) and Cozzani et al. (2006). These values will be adopted for the vulnerability analysis and land use planning as in Salzano et al. (2013).

For the aims of this study, the peak overpressure ( $\Delta P$  in bar) with respect to the distance for any equivalent mass of TNT, given the  $TNT_{eff}$ , may be calculated by the following correlation (Bounds, 1997):

$$\Delta P = 1.02 \frac{m_{TNT,eq}^{1/3}}{r} + 4.36 \frac{m_{TNT,eq}^{2/3}}{r^2} + 14.00 \frac{m_{TNT,eq}}{r^3} \quad (1)$$

where  $r$  is the distance (in m) and  $m_{TNT,eq}$  is the equivalent TNT mass (in kg) for a given amount of home-made explosive ( $m_{exp}$  in kg) calculated accordingly to the following expression:

$$m_{TNT,eq} = TNT_{eff} \times m_{exp} \quad (2)$$

*Table 2: Escalation thresholds for the escalation due overpressure and heat radiation for different equipment categories (Cozzani et al., 2006).*

Equipment category	Overpressure (bar)	Heat radiation (kW/m <sup>2</sup> )
Atmospheric vessels	0.22	10
Pressurized elongated vessels (toxic materials)	0.16	40
Pressurized elongated vessels (flammable materials)	0.31	40

### 3. Results and discussion

In order to determine the potential impact of a terrorist attack carried out with home-made explosives against process equipment, stand-off distances - here defined as the minimum distance between the asset of interest and the area where an explosive device can be placed without causing damages - have been evaluated. Table 3 shows the calculated stand-off distances for several types of industrial equipment by varying the net explosive mass in the home-made explosive charge, using the value of the  $TNT_{eff}$  reported in Table 1, and considering the threshold values for domino effect (Table 2). As expected, scarce effects are due to the efficiency of detonation for pure "ideal" explosives, whereas the effects of the net explosive mass and the effect of lower efficiency is larger for the home-made explosives. As a rule of thumb we can then say that the non-ideality gives in this case a stand-off distance which is approximately half the value of the correspondent pure explosive.

For the sake of clarity, a case study for a storage section featuring relevant inventories of hazardous chemicals located in an industrial complex surrounded by a residential area has been analyzed (Figure 1). A consequence analysis based on a vulnerability assessment was performed in order to highlight the different potential impact of domino effect triggered by pure process-related causes and escalation scenarios generated by external terrorist attack. In particular, we have considered:

- Primary scenarios only, e.g., associated to each individual tank without considering the possibility of domino effect, as described in Table 4;
- Domino effect triggered by internal process causes;
- "Weak" terrorist attack with limited quantities of explosive (100 kg) inside the industrial complex;
- "Severe" external terrorist attack with a high amount of explosive (50,000 kg) loaded on two trucks outside the industrial complex.

The home-made explosive selected for accidents #3 and #4 is AN/dolomite (50/50) + diesel fuel because its availability may be comparable with the large amounts here considered. We did not consider the scenario where a suicide bomber drives a truck filled with explosives into the industrial complex.

In the case of domino effect caused by internal process malfunctions, the pool-fire following the rupture of tank AT3 is the primary scenario triggering domino escalation. In order to determine the possible escalation targets, the threshold values for thermal radiation as discussed by Cozzani et al. (2013) reported in Table 2 are considered. Figure 1b shows the iso-radiation contours obtained for the pool fire in AT3 catch basin. The flame is tilted by the wind which was supposed to blow towards South direction, thus the contours are not centred on tank AT3. As shown in the figure, all the targets in the tank farm are affected by the pool-fire, with potential fired domino effect escalation. Next, the possibility of external terrorist attack is analysed supposing that the access to the industrial site is not credible with large amounts of explosive.

Thus, only the attack with limited quantities (accident #3) is considered inside the plant, while the one with higher quantities (accident #4) is located at about 130 m from the storage tanks (Figure 1a). In the case of the "weak" attack, the home-made explosive is not able to generate severe damages to the population but it has the potential to damage the equipment inside the storage facility, leading to domino effect escalation. In the case of "severe" attack, even if the considered amount of home-made explosive is large, due to the low efficiency and, thus, high stand-off distance, the escalation is only limited to one piece of equipment, in particular tank AT3. The other units are not affected by the explosion (e.g., stand-off distances reported in

Table 3 are higher than the considered explosive location distance). Table 4 summarizes the escalation scenarios considered. Once determined the possible accidental scenarios, the consequences of overpressure effects are assessed using Eqs. 1, 2), whereas integral models for radiation heat effects are used for the analysis of fire scenarios. Uniform wind direction, 5 m/s wind speed and stability class D were assumed for the consequence assessment.

Table 3: Calculated stand-off distance for different equipment categories by considering the explosives analysed in Table 1. NC = the quantity is Not Credible.

Equipment category	Explosive mass (kg)	TNT (TNT <sub>eff</sub> = 1)	ANFO (TNT <sub>eff</sub> = 0.85)	TATP (TNT <sub>eff</sub> = 0.61)	AN/dolom (50/50)/diesel (TNT <sub>eff</sub> = 0.23)
Atmospheric Vessel	100	37	35	32	18
	1,000	81	76	NC	39
	10,000	174	165	NC	85
	50,000	297	282	NC	145
Pressurised Horizontal Vessel (toxic)	100	46	44	39	23
	1,000	100	95	NC	49
	10,000	215	204	NC	105
	50,000	368	348	NC	179
Pressurised Horizontal Vessel (flammable)	100	30	29	26	15
	1,000	65	62	NC	32
	10,000	140	133	NC	68
	50,000	240	227	NC	117

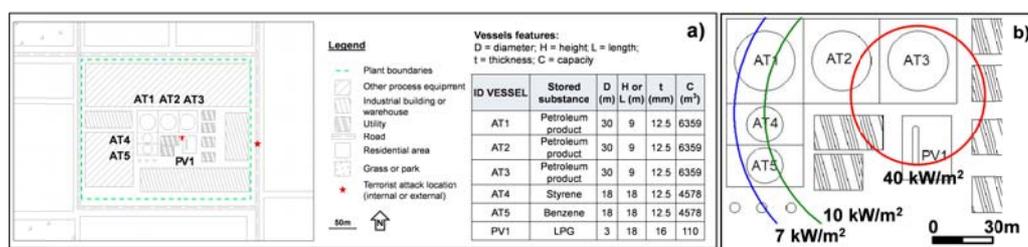


Figure 1: Layout of the analysed plant: a) vessels and map of the surrounding area; b) iso-radiation contours for the pool-fire following the failure of AT3, triggering domino effect.

In order to obtain a homogenous representation of the accidents impact, a vulnerability assessment is also carried out. The results of the vulnerability assessment are reported in Figure 2, which evidences the potential impact by the 1 % lethality contour, as derived by classical probit equations (Salzano et al., 2013). The primary scenarios reported in Table 4 have limited impact and do not affect the area outside the industrial facility. Figure 2a shows the results obtained for the “weak” terrorist attack: The affected area has severe effects outside the plant for the fireball associated with the LPG tank PV1, which is the most severe scenario. In the case of domino effects triggered by internal causes (Figure 2b) the fireball is still the most severe scenario but with a higher impact respect to the previous case. Indeed, in this case, the rupture occurs after the liquid has reached higher pressure and temperature, thus higher energy potential before the rupture, as evidenced by Di Padova et al. (2011) for the identification of fireproofing zones and by Tugnoli et al. (2012) for the establishment of risk mitigation strategies. Finally, Figure 2c reports the vulnerability contour evaluated considering the domino scenarios induced by the external “severe” attack, thus considering the rupture of AT3 only and the associated pool-fire. The escalation scenario has significant effects inside the facility. A higher escalation severity associated to internal process causes is hence evidenced.

#### 4. Conclusions

Security risk assessment in the chemical and process industry is characterised by a systematic approach to organizing information concerning the assets that need to be protected, the threats that may be posed against those assets, and the likelihood and consequences of attacks against them. Hence, security risk assessment serves to audit a chemical company’s understanding of the threats and possible responses to those threats; it forms the basis for establishing an adequate security risk management program to reduce the potential adverse effects of intentionally induced losses upon the company.

Table 4. Primary event and secondary scenarios (domino effect) for the equipment considered in the case-study. \*The rupture of this tank leads to domino escalation. \*\* Bund is present ( $A = 1,000 \text{ m}^2$ ;  $H = 1.5 \text{ m}$ ).

ID	Primary event	Domino effects (process causes)	Domino effects ("weak" attack inside the plant)	Domino effects ("severe" attack outside the plant)
PV1	Jet-fire (1" hole)	Fireball	Fireball	No escalation
AT1	Pool fire**	Pool fire**	Pool fire**	Pool fire**
AT2	Pool fire**	Pool fire**	Pool fire**	No escalation
AT3	Pool fire**	- *	Pool fire**	No escalation
AT4	Pool fire**	Pool fire**	Pool fire**	No escalation
AT5	Pool fire**	Pool fire**	Pool fire**	No escalation

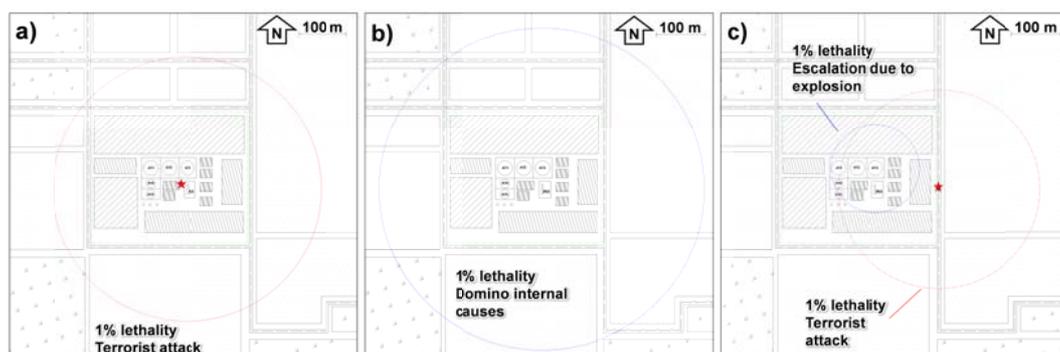


Figure 2: Vulnerability maps (1 % lethality level) obtained for the different accidental scenarios: a) escalation triggered by "weak" terrorist attack; b) domino effect triggered by internal process causes; c) domino effect triggered by "severe" terrorist attack. For scenarios definition, see Table 4.

Before the security risk identification process can take place it is important to undertake a geographical overview of the company. The case study described in this paper illustrates this: not only the 'attractive' installations and storage tanks, but also company installations that may be a target for adversaries to induce domino effects towards those attractive installations, should be identified. Furthermore, the possible nearby roads and access roads from where an adversary may carry out a domino effect inducing attack with home-made explosives, should be determined (depending on the proximity of the installations and storage areas to the plant's fences).

The security hazard and risk identification process should identify all company security risks, including – and especially – domino effects. For more information on security hazard identification in a chemical industrial surrounding, see Reniers et al. (2013). Once the company's security risks have been identified, every risk should be analysed. Typically, it is the responsibility of the security manager, together with the organization's board, to conclude whether the risk is acceptable, tolerable (ultimately with countermeasures), or unacceptable and therefore needs to be mitigated in some way. Every step in the process has to be rigorous and transparent so that changes over time can be captured as well.

The fundamental basis of security management can be expressed in a similar manner to the Layers of Protection used in modern chemical process plants for addressing safety-related, accidental events. In the similar security-related concept of concentric so-called "rings-of-protection" (CCPS, 2003), the spatial relationship between the location of the target asset and the location of the physical countermeasures is used as a guiding principle. Rings-of-protection, also known as 'layered defences', are based on the 'Defence in Depth' principle (IAEA, 1996). An effective countermeasure deploys multiple defence mechanisms between the adversary and the target. Each of these mechanisms should present an independent obstacle to the adversary. Based on the results obtained in our case study, it is important to design rings in a way that domino effect scenarios are taken into account. Every ring is defined and constructed according to the risk sensitivity of the objects inside a zone (e.g. storage of flammable liquids; a reactor that is prone to explode during process disturbances, etc.). The barriers that protect a specific ring are designed with a certain 'resistance against intrusion'. The target in the centre is the asset that is deemed 'attractive' for a potential adversary and therefore requires protection. However, as already mentioned, our case study reveals that if a domino effect can be induced from a nearby installation onto an 'attractive' installation, it may be important to protect this nearby installation as adequately as the 'more attractive' installation, and include it into the zone of this installation. Security management within a

chemical plant should be aware of this. On the one hand, the resistance of a barrier and the time it takes an adversary to get to the target, are important factors in the likelihood of interruption when setting up an analysis of the path an adversary might take to place a home-made explosive. On the other hand, suicide bombers, who are only interested in forced entry, should be considered as well. Hence, it is obvious that a diversity of security countermeasures is needed in a chemical company.

Security management by means of the ring-of-protection concept, translates into a number of measures, as it is a combination of physical security equipment, people and procedures. Elements of all these types are typically needed together in order to offer the best chance of adequate asset protection against a variety of threats, amongst others home-made bombing by terrorists for inducing domino effects.

## References

- Basco A., Salzano E., Cammarota F., 2010, The risk of storage plant of pyrotechnics, *Chemical Engineering Transactions*, 19, 231-236, DOI: 10.3303/CET1019038.
- Bounds W.L., 1997, *Design of Blast Resistant Buildings in Petrochemical Facilities*. ASCE Publications, Reston, VA, USA.
- Buczowski D., Zygmunt B., 2011, Detonation properties of mixtures of ammonium nitrate based fertilizers and fuels, *Central European J. Energ. Mat.* 8, 99-106.
- CCPS, Center for Chemical Process Safety, 2003, *Guidelines for Analyzing and Managing the Security Vulnerabilities of Fixed Chemical Sites*, American Institute for Chemical Engineers, New York.
- Cozzani V., Gubinelli G., Salzano E., 2006, Escalation thresholds in the assessment of domino accidental events, *J Hard Mater*, 28; 1-21.
- Cozzani V., Tugnoli A., Salzano E., 2007, Prevention of domino effect: from active and passive strategies to inherently safe design, *J Hard Mater*, 139, 209-19.
- Cozzani V., Antonioni G., Landucci G., Tugnoli A., Bonvicini S., Spadoni G., 2013, Quantitative assessment of domino and NaTech scenarios in complex industrial areas, *J. Loss Proc. Ind.*, in press DOI: 10.1016/j.jlp.2013.07.009
- Di Padova A., Tugnoli A., Cozzani V., Barbaresi T., Tallone F., 2011, Identification of fireproofing zones in Oil & Gas facilities by a risk based procedure, *J. Hazard. Mat.* 191(1-3), 83-93.
- Georgiadou P.S., Papazoglou I.A., Kiranoudis C.T., Markatos N.C., 2010, Multi-objective evolutionary emergency response optimization for major accidents, *J. Hazard. Mat.* 178(1-3), 792-803.
- Hargather M.J., Settles G.S., 2007, Optical measurement and scaling of blasts from gram-range explosive charges, *Shock Waves*, 17, 215-223.
- IAEA (International Atomic Energy Agency), 1996, *Defence in Depth in Nuclear Safety*, IAEA, Vienna.
- Kourniotis S.P., Kiranoudis C.T., Markatos N.C., 2000, Statistical analysis of domino chemical accidents, *J. Hazard. Mat.* 71(1-3), 239-252.
- Kuzmin V.V., Solov'Ev M.Y., Tuzkov Y.B., 2008, Forensic investigation of some peroxides explosives, *Central European J. Energ. Mat.* 5, 77-85.
- Lefebvre M.H., Falmagne B., Smedts B., Sensitivities and performances of non-regular explosives, *Proc. VII Seminar on New Trends in Research of Energetic Materials*, Pardubice, Czech Republic, 2004.
- Maienschein J.L., 2002, *Estimating Equivalency of Explosives through a Thermochemical Approach*, Report UCRL-JC-147683. US Department of Energy, LLNL, Livermore, CA.
- Price M.A., Ghee A.H., 2009, Modeling for detonation and energy release from peroxides and non-ideal improvised explosives, *Central European J. Energ. Mat.* 6, 239-254.
- Reniers G.L.L., Herdewel D., Wybo J., 2013, A Threat Assessment Review Planning (TARP) decision flowchart for complex industrial areas, *J. Loss Proc. Ind.*, 26, 1662-1669.
- Salzano E., Cozzani V., 2005, The analysis of domino accidents triggered by vapour cloud explosions, *Rel. Eng. and Syst. Saf.*, 90, 271-284.
- Salzano E., Basco A., 2012, A comparison of thermodynamic of explosion of TNT and black powder by means of Le Chatelier diagram, *Prop. Expl. Pyrotech.*, 37, 724-731.
- Salzano E., Antonioni G., Landucci G., Cozzani V., 2013, Domino effects related to explosions in the framework of land use planning, *Chemical Engineering Transactions*, 31, 787-792, DOI:10.3303/CET1331132.
- Siegel J.A., Saukko P., 2012. *Encyclopedia of Forensic Sciences*, 2 Ed., Academic Press, Elsevier, Amsterdam, The Netherlands.
- Tugnoli A., Cozzani V., Di Padova A., Barbaresi T., Tallone F., 2012, Mitigation of fire damage and escalation by fireproofing: A risk based strategy, *Rel. Eng. and Syst. Saf.* 105, 25-35.