SIESO Medal

Can process intensification improve process safety?

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Summary

In 2007 T2 Laboratories Inc. suffered a temperature excursion during the batch manufacture of the fuel additive MCMT (Methylcyclopentadienyl manganese tricarbonyl). The relief valve operated but proved to be inadequate. Subsequently, the 3000-gallon (11 m^3) reactor burst and the highly flammable contents exploded. Four people died and 32 were injured, including 28 members of the public. The plant was destroyed with damage to neighboring property within 400m. Causes of the accident included:

- a lack of understanding of the thermochemistry and hazards associated with the runaway reaction
- absence of 'Management of Change' procedures
- design deficiencies within cooling, venting systems etc.

A more detailed discussion of T2 Laboratories Inc., its process development, the manufacturing process, the accident, and its causes with some lessons learned are given elsewhere[1]. Herein, the safety-related advantages of innovative process engineering technologies developed under the title of process intensification are described and a potential alternative reactor called the spinning disc reactor is discussed.

Keywords: Explosion, exothermic reaction, process intensification

About MCMT

MCMT was used as a fuel additive to boost octane number. Combustion of MCMT releases manganese compounds into the air and exposure is associated with neurological disorders[2]. Overall, the use of MCMT as a fuel additive is said to negatively impact public health and limit the effectiveness of emission control devices[2]. In 2014, the European Parliament amended its Fuel Quality Directive limiting the presence of MCMT in fuel to 2mg of manganese per litre[3]. In the US, facilities and chemical sites which contain EHS (extremely hazardous substances) must submit a Risk Management Plan (RMP) and annual Tier 2 reports to the State Emergency Response Commissions (SERC) explaining the quantities of these chemicals and storage mechanisms. Although T2 laboratories submitted annual Tier 2 reports to the LEPC and SERC, they did not include MCMT as an extremely hazardous substance. This signified a lack of appreciation, within T2 laboratories, of the hazards of the materials they were handling.

A typical chemical data safety sheet further highlights the hazards associated with MCMT[4]:

- Physical hazards
  – H227: Combustible liquid
- Health hazards
  – H300: Fatal if swallowed
  – H311: Toxic in contact with skin
  – H316: Causes mild skin irritation
  – H330: Fatal if inhaled
  – H336: May cause drowsiness or dizziness
  – H370: Causes damage to organs
  – H373: Causes damage to organs through prolonged or repeated exposure
- Serious eye damage, Category 1, H318: Causes serious eye damage.
- Environmental hazards
  – H400: Very toxic to aquatic life;
  – H410: Very toxic to aquatic life with long lasting effects.

The incident

The incident described in this report occurred at the T2 Laboratories Inc. facility in Jacksonville, Florida, USA on 19 December 2007. An operator hand-loaded blocks of sodium metal through a 6-inch gate valve on top of the reactor. The mixture was heated via an oil-based heat exchanger with a process set point of 182°C. Further the reactor pressure process set point was 3.45 bar. Once the temperature of the mixture reached 98°C operators initiated the agitation step. When the mixture had reached 148°C, the operator turned off the oil-based heat exchanger. Heat generated by the reaction continued to raise the temperature inside the reactor until the temperature reached 182°C. The cooling system (a jacket in a single feedback loop) was initiated. At 13:23 hrs a cooling problem was reported by process operators, the two owners who were off-site at the time were requested to return. At 13:33 hrs, the reactor ruptured (see Figure 1), exploding with a 1400 TNT equivalent explosion due to over-pressure and subsequent mechanical failure[5].

A PRV (pressure relief valve) was fitted on a 25 mm secondary

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Figure 1 – Section of the MCMT reactor post-explosion

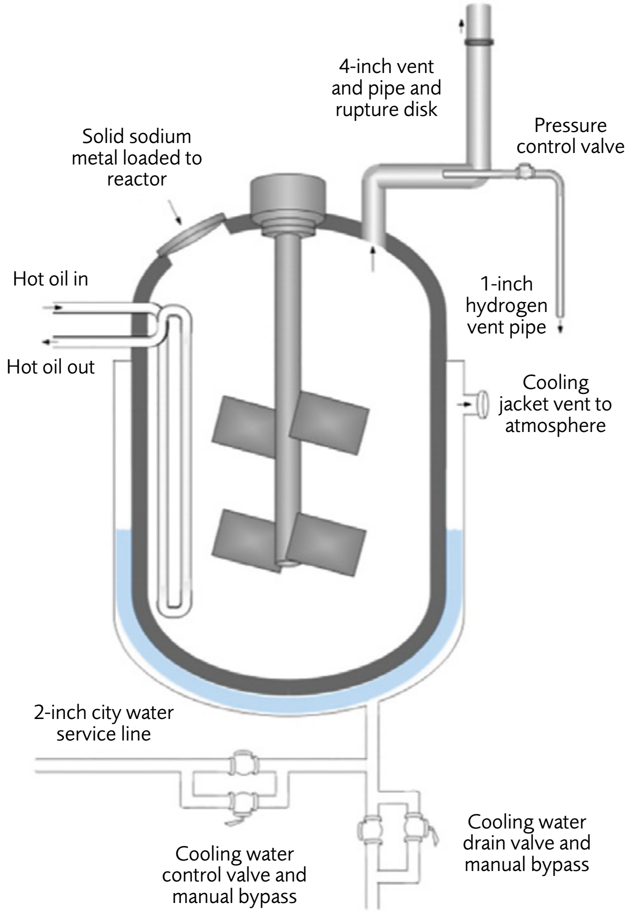

Figure 2 – Layout of the MCMT reactor [1]

vent pipe conjoined to a primary 100 mm vent pipe with a rupture disk set to 400 psi (27 barg), shown in Figure 2. In an over-pressure event, the PRV should have been able to control the excess pressure by venting hydrogen, mitigating any imminent hazards[5]. However, the PRV failed and was designed without acknowledgement of the possibility of a secondary exothermic reaction. This was in part due to the limited knowledge of the MCMT reaction. Regardless, venting is unlikely to be the pivotal issue. Whilst the thermokinetics of the reaction were not fully established, damage suggests it might well be that the required vent-size for a full-scale runaway is larger than the top of the reactor. Even if the vent operated to specification, the material would still be highly flammable and continue reacting. Therefore, discharge to the environment into secondary containment would also be unsuitable as discussed in other studies[5]. In this study, PI (process intensification) for the purposes of dramatically improving process safety becomes an interesting and suitable proposition — specifically the use of spinning disc reactors.

Advancing industry with process intensification

Principles of PI

PI emerged as a concept in the late 1970s at Imperial Chemical Industries (ICI). The initial objective was further defined by Colin Ramshaw in 1995 while opening the 1st International Conference on Process Intensification as achieving significant reduction in the capital cost of process engineering equipment by reducing size and footprint[6]. However, progress in the area soon revealed numerous benefits and the definition of PI evolved to read 'the development of innovative apparatus and techniques that offer drastic improvements in chemical manufacturing and processing, substantially decreasing equipment volume, energy consumption, or waste formation, and ultimately leading to cheaper, safer, sustainable technologies'[7]. PI technologies can be split into two. Firstly, process intensifying equipment includes reactor technologies such as spinning disc reactors, and other equipment such as compact heat exchangers. The second category of PI technologies is process intensifying methods which encompasses multifunctional reactors (e.g. reactive distillation), separation methods (e.g. membrane distillation), and alternative energy such as ultrasound and plasma.

Besides a reduction in size and hence capital costs, the benefits of PI include:

- improved inherent safety through minimised inventory
- greater reaction and heat transfer rates through enhanced mixing
- greater heat transfer and mass transfer rates using thin film technologies
- improved product quality and reduced waste through tighter temperature control and the subsequent prevention of undesirable side reactions.

Unfortunately, many barriers currently exist in the implementation of PI technologies including:

- industry conservatism and risk averse nature
- absence of industry expertise
- time and expertise needed to fully assess the wider implications of any significant change.

Can PI be applied to the T2 Laboratories incident?

As demonstrated in the T2 Laboratories incident, the hazards involved with the scale-up of batch reactors can cost lives if sufficient technical expertise is not present. One important consideration during scale-up is the decrease in the surface area for heat transfer to volume ratio and the subsequent difficulty

knowledge and competence

engineering and design

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in precise temperature control which is essential for the safe operation of exothermic chemical reactions in batch reactors. Additionally, the power required for mixing increases with diameter to the power of five, and the effectiveness of mixing decreases, permitting a more varied temperature profile throughout a larger diameter reactor. The heat pockets present in some areas of a reactor mean that sub-optimal temperatures may be required for exothermic reactions to be carried out safely to avoid thermal runaway. Obvious consequences of this include yield losses and less predictable reaction pathways.

The spinning disc reactor is one of the leading technologies within process intensification having been developed further by Colin Ramshaw whilst working at ICI in the 1970s. Further studies carried out in 1975 at Newcastle University by Colin Bell reiterated the significant enhancement in heat and mass transfer that spinning disc reactors can induce[8]. As shown in Figure 3, spinning disc reactors are composed of several major parts: reactants travel into the reactor via an inlet leading to the centre of a spinning disc, the spinning disc which due to centrifugal force pushes fluids to its circumference, an outlet collects products, whilst a heating element is below the spinning disc.

The principle of operation is to perform reactions on the surface of a rapidly spinning disc of diameter between 0.1 m and 1 m. The high rotational speeds of typically 1000 rpm cause flow to be drawn into extremely thin films under high centrifugal forces of the order of up to one thousand times that of gravitational acceleration. These thin films permit extremely efficient heat transfer and control as well as significantly enhanced mixing. To further improve heat transfer, the spinning disc often has a base of copper, with a chrome plating for chemical resistance. Generally, a spinning disc has an overall heat transfer coefficient of approximately 7–10 kWm^2K. This is typically five to ten times that achieved by most heat transfer device and enables small discs with low process fluid inventory to handle significant thermal duties. Meanwhile mass transfer can be improved by adding grooves to the surface which induces the formation of waves on the thin film whilst the spinning disc reactor is in operation. The overriding benefit is the inherent safety of the reactor due to the vastly reduced inventory compared to the large volume and loading nature of a batch

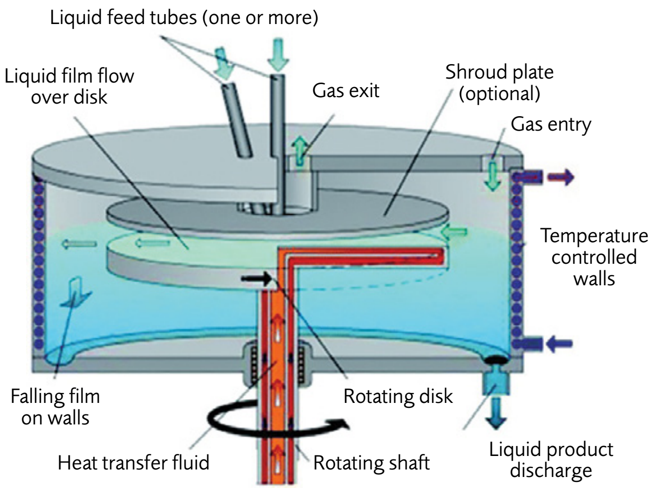

Figure 3 – Schematic of a spinning disc reactor[9]

reactor required for the same duty. Coupled with the benefits of using thin film technologies which provide significantly enhanced heat transfer rates, and tighter temperature control as a result of both this and the improved overall heat transfer coefficient, the risk of thermal runaway would be significantly reduced if not eliminated entirely. Overall, the benefits of spinning disc reactors makes them suited to fast, exothermic reactions.

Limitations of PI

A major issue regarding the use of the spinning disc reactor for the T2 Laboratories incident comes about with the realisation that this reactor is more often used for liquid-liquid phase or gas-liquid phase reactions. This brings about the question as to how sodium could be added to the reactor. A similar reactor which can be used for solid-liquid reactions does exist – the rotor stator spinning disc reactor. However, this reactor is used when the solid is a catalyst. In general, solids handling is a more difficult aspect of process intensification to develop due to the inherent limitations. One of the key features of process intensification is the downsizing of reactors. However, the use of solids in significantly smaller reactors can bring about fouling and blockages where there are large concentrations of solids. Another limitation with respect to the synthesis of MCMT is that, as hydrogen is evolved, it would be difficult and expensive to seal. Overall, although process intensification would be an improved method to help control heat transfer and mitigate thermal runaway, further research and development is needed in order to produce a commercially viable process for solid-liquid phase reactors that also follow the principles of PI.

Conclusion

Techniques developed through process intensification concepts pose many advantages over traditionally scaled-up batch reactors including:

- reduced investment
- smaller plant footprint
- flexibility and speed when changing process conditions
- reduced waste
- increased reaction specificity
- increased process control opportunities
- simplified scale-up
- inherent safety due to a lower inventory.

Understandably, a scrap and start again approach from current plant equipment to modern equipment developed through process intensification concepts would be a great financial cost to any business. Further, some businesses lack the technical expertise to perform such a task — extensive process development programs are required for any alternative technology and its scale-up to optimise conditions and to establish risks and appropriate control measures. Many businesses are simply less open to change. However, in the case of the T2 Laboratories incident the unsafe scale-up method led to a tragic loss of life.

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