API 521 8th Edition Reballot Item

Thermal Cracking
(Work Item 3)

Instructions to Voters/Commenters

- Note that blue indicates modified text included in the previous ballot, while green and red indicates modifications to the previous ballot.
- If you are voting negative with multiple comments, please indicate which comment(s) is the reason for your negative vote, otherwise API's balloting system will categorize all of your comments as negative.

Thanks to Freeman Self and the work group for their efforts.

Melissa Marashi (Chevron)
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API 521 Task Force Chairs

API-521 - 8th Edition - Expected 2025

This is the 7th Ed, 2020 as revised with suggested statements on cracking

3	521 meeting – Spring 2011	4.4.13.2.4.2	New section on thermal cracking (modify previous draft section per comments)	Draft modifications/additions to several sections; See Fall 2020 meeting minutes	F. Self; Z. Kumana; V. Quiroga	Presentation Fall 2020; update Spring 2021

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API-521 Proposed Language for Ballot

New Definition:

Thermal Cracking:

~~Thermal cracking of hydrocarbons entails cracking~~Breaking of carbon-carbon bonds with heat but no catalyst or other reactants (e.g. steam). ~~The free-radical reactions typically include cracking of long chain paraffins, splitting side chains from cycloparaffins, but generally no cracking of ring structures or combining reactions of lower molecular weight compounds to form higher molecular weight compounds.~~ Thermal cracking reactions include breaking of long chain paraffins and splitting of sidechains from cycloparaffins, but generally no breaking of ring structures.

4.4.13 Fire

4.4.13.2 Open Pool Fires

4.4.13.2.1 General

For the purposes of PRD sizing for equipment within the scope of this standard, the design fire scenario has been and continues to be an open pool fire. The recommended method was empirically derived to size PRDs for open pool fires involving hydrocarbons in a refinery environment that is typical for the facilities within the scope of this standard. The method is supported by full-scale test data (see A.2 and C.6 for details).

Both API 521 and API 2000 [111] use open pool fires as the basis for sizing PRDs for the fire case. It is important to apply the appropriate standard when sizing for fire relief because there are differences in assumptions for the fire pool fire intensity, exposed area, and other factors specified in those standards. API 2000 is limited to aboveground liquid-petroleum or petroleum-products storage tanks and aboveground and underground refrigerated storage tanks designed for operation at gauge pressures from vacuum through 103.4 kPa (15 psi).

An open pool fire can affect multiple vessels simultaneously. See 5.3.2 for a discussion.

If the open pool fire involves other types of fuels (e.g. alcohols) that have significantly different radiative fluxes than fuels similar to gasoline, diesel, liquefied petroleum gas (LPG), etc., the method in Annex A can be used with adjusted variables (see Annex A for details).

Relieving temperatures are often above the design temperature of the equipment being protected. If the elevated temperature is likely to cause vessel rupture, additional protective measures should be considered (see 4.4.13.2.6 and 4.4.13.2.7).

High-boiling ~~materials~~ hydrocarbon fluids, such as long chain paraffins, can ~~may~~ exhibit thermal cracking during fire contingencies. Thermal cracking ~~may~~ produces liquids and low-molecular weight gases. As a portion of the fire heat input can be consumed by the endothermic thermal cracking process, less heat would be available for vaporization and for increasing bulk fluid/vapor temperature, ~~The~~ lowering relief temperature ~~may be lowered by this phenomenon. The~~ and required relief rate ~~may also be lowered by the thermal cracking process as a portion of the fire heat input is consumed by the thermal cracking process. This may result in less heat available for vaporization and bulk fluid/vapor temperature increases~~.

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4.4.13.2.4 Fire-relief Loads

4.4.13.2.4.1 General

It is typically assumed that the vessel is isolated during a fire in order to simplify the analysis, although a more detailed analysis can be warranted in certain cases. Crediting for flow paths that remain open during an overpressure event is generally an acceptable practice. However, it should be recognized that operators and/or emergency responders could~~may~~ attempt to isolate certain lines and vessels during a fire condition in order to limit the fire spread and to safely shutdown the unit. There can also be actuated valves that fail in the closed condition when exposed to a fire. It can be difficult to establish with a degree of certainty whether a particular line will indeed remain open under all fire conditions. Further, consideration should be given to the potential that the fire-relief flow in the flow path will overpressure other equipment. Hence, it can be necessary to add the fire-relief load elsewhere. Ultimately, the user shall decide whether a scenario is credible or not.

4.4.13.2.4.2 provides the heat absorption equations for vessels containing liquids, and 4.4.13.2.4.3 provides the equations to determine open-pool-fire-relief requirements for vessels containing only gases/vapors.

Either the vapor thermal-expansion-relief load or the boiling-liquid vaporization-relief load, but not both, should be used. It is a practice that has been used for many years. There are no known experimental studies where separate contributions of vapor thermal expansion versus boiling-liquid vaporization have been determined. When sizing the PRD for fire exposure, the contribution of vaporizing liquid compared with vapor expansion is generally governing unless, for example, the wetted surface has external insulation in accordance with 4.4.13.2.7 and the unwetted surfaces are not insulated. Accounting for thermal cracking could~~may~~ result in lower calculated relief temperatures, changed vapor compositions, and lower required relief rates.

See Annex I for a discussion of thermal cracking of refinery resid from atmospheric and vacuum columns.

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4.4.13.2.5.2 Vapor

For pressure and temperature conditions below the critical point, the rate of vapor formation (a measure of the rate of vapor relief required) is equal to the total rate of heat absorption divided by the latent heat of vaporization. The vapor to be relieved is the vapor that is in equilibrium with the liquid under conditions that exist when the PRD is relieving at its accumulated pressure.

The latent heat and relative molecular mass values used in calculating the rate of vaporization, should pertain to the conditions that can generate the maximum vapor rate.

Consideration for thermal cracking of high-boiling point materials can be included in the analysis. This can result in lower molecular weight gases and liquids, lower relief temperature, and a different latent heat of liquid vaporization. Additionally, a portion of the fire heat input goes into sensible heat to raise the liquid's temperature.

The vapor and liquid composition can change as vapors are released from the system. As a result, temperature and latent-heat values can change, affecting the required size of the PRD. On occasion, a multicomponent liquid can be heated at a pressure and temperature that exceeds the critical temperature or pressure for one or more of the individual components. For example, vapors that are physically or chemically bound in solution can be liberated from the liquid upon heating. This is not a standard latent-heating effect but is more properly termed degassing or dissolution. Vapor generation is determined by the rate of change in equilibrium caused by increasing temperature.

For cases involving vapors physically or chemically bound in solution, multicomponent mixtures that have a wide boiling range, or thermal cracking of high-boiling materials, it could~~may~~ be necessary to develop a time-dependent model where the total heat input to the vessel not only causes vaporization but also raises the temperature of the remaining liquid, keeping it at its boiling range.

The recommended practice of finding a relief vapor flow rate from the heat input to the vessel and from the latent heat of liquid contained in the vessel becomes invalid near the critical point of the fluid, where the latent heat approaches zero and the sensible heat dominates. If no accurate latent heat value is available for these hydrocarbons near the critical point, a minimum value of 115 kJ/kg (50 Btu/lb) is sometimes acceptable as an approximation. If pressure-relieving conditions are above the critical point, the rate of vapor discharge typically depends on the rate at which the fluid expands as a result of the heat input because a phase change does not occur.

Reference [72] gives an example of a time-dependent model used to calculate relief requirements for a vessel that is exposed to fire and that contains fluids near or above the critical range.

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Annex I Thermal Cracking of Refinery Crude Resid in Atmospheric and Vacuum Columns During Fire

This annex describes thermal cracking for fire on vessels containing heavy components (e.g. crude resid in refinery crude atmospheric columns, crude vacuum columns and other equipment). During a fire, the material may experience mild thermal cracking to produce low molecular weight gases and lighter hydrocarbon fluids (e.g. gasoline, distillate and gas oil) in vapor and liquid form.

Two towers typically found in refineries are the crude atmospheric column and crude vacuum column. The atmospheric column is the first major separation of crude oil and operates at the bottom of the column at ~~1 barg [~~100 kPag (15 psig)~~]~~ and approximately 370 °C (700 °F) ~~[370°C]~~. The bottoms from the atmospheric column are fed to the vacuum column, which operates at approximately 0.4 psi-vacuum [0.027 bar-vacuum] and between 400-410 °C (750-770 °F) ~~[400-410°C]~~. The pressure depends on whether steam is used to lower the partial pressure.

During a fire, the column pressure will increase to the relief pressure. For both columns, a typical relief pressure with 21% of external fire accumulation is between 410-620 kPag (60-90 psig) ~~[4.1-6.2 barg]~~. Thermal cracking is a function of time and temperature. If the resid is held at approximately 370 °C (700 °F) ~~[370°C]~~ for 60 minutes, then 1% of the resid could~~may~~ crack. At higher temperatures, 1% of the resid will crack If the resid is held at approximately 400 °C (750 °F) ~~[400°C]~~ for only 10 minutes.

The resid is expected to crack into liquid gas oil, distillate, gasoline and light gases. After cracking begins, some of the fire heat input will be used for the thermal cracking and formation of lower molecular weight products. The remaining fire heat input goes to sensible heat to increase the liquid temperature and vaporization of liquids to form vapor relief. Since the cracked liquid products have lower boiling points, the relief temperature will be reduced compared to direct boiling of uncracked components (Reference [use reference "Quiroga" below]).

In contrast, if no thermal cracking is assumed to occur at 410 kPag (60 psig), the calculated atmospheric crude resid relief temperature can~~may~~ reach ~~approximately~~ 480 °C (900 °F) ~~[480°C]~~. Similarly, the calculated vacuum resid relief temperature can~~may~~ reach ~~approximately~~ 700 °C (1,300 °F) ~~[700°C]~~. Designing for these temperatures can~~may~~ require high-temperature metallurgy and piping stress analysis.

The following factors should be considered when determining the relief rate for fire during a cracking reaction:

- Initial conditions and duration.
- Types of products and yields of products formed by cracking, including gases and liquids
- Calculation of heat of cracking reaction
- Distribution of the fire heat input into heat of cracking, sensible heat and heat of vaporization
- Amount of cracked liquid
- Amount of relief due to gases cracked from the resid and the amount of relief vapor due to vaporization of cracked liquids

For estimation purposes, approximate parameters can~~may~~ be obtained from reference [use reference "Quiroga" below].

Bibliography

[ ] Victor Quiroga, Freeman Self, Gaurav Arora and Debby Sielegar, "Fire Relief Sizing for Heavy Petroleum with Cracking", American Institute of Chemical Engineers AIChE Spring Meeting & Global Congress on Process Safety, April 2021. Available from AIChE Academy <www.aiche.org/academy/>

~~[ ] W.L. Nelson, "Petroleum Refinery Engineering", 3rd Edition, 1949, McGraw-Hill~~

~~[ ] Robert Maples, "Petroleum Refinery Process Economics", 2nd Edition, 2000, Pennwell Press~~