Reappraisal of the role of turpentine vapor in noncondensible gas explosions

RISTO LAUTKASKI

ABSTRACT: Turpentine has been identified as the cause of numerous fires and explosions within the pulp and paper industry. Explosions in the noncondensible gas (NCG) collection systems caused by total reduced sulfur (TRS) compounds have usually been minor and caused minimal damage, but explosions caused by turpentine could be catastrophic. When flammable conditions have been created by insufficient dilution, air leakage into the system, or accumulation and breakthrough of TRS gases or turpentine vapor at a chip bin, it is conceivable that turpentine vapor created near-optimum flammable mixtures more often than TRS gases did. In these cases, the burning velocity would have been close to the maximum. On the other hand, when flammable conditions were created due to insufficient dilution of a stream of high volume, low concentration gases (HVLCs) or due to air leakage into a stream of low volume, high concentration gases (LVHCs), then the flammable mixture formed would be expected to have been off-stoichiometric: lean in the former case and rich in the latter case. In both cases, the burning velocity could have been much lower than in the near-stoichiometric mixture. The violence of explosions caused by turpentine is attributed to its capability to form near-stoichiometric mixtures more easily than the other components of NCGs.

Application: Information in this paper will give designers and users of NCG collection systems insight into the nature of fires and explosions caused by turpentine.

To meet air quality requirements, noncondensible gases (NCGs) generated in the kraft pulping process are collected and disposed of by incineration at the recovery boiler. Noncondensible gases consist of sulfur compounds, referred as total reduced sulfur (TRS) compounds; turpentine (mainly α-pinene); and methanol. **Table I** presents the combustion properties of kraft mill NCGs in air (lower flammability limit [LFL], upper flammability limit [UFL], autoignition temperature [AIT], and fundamental burning velocity S_u).

The data in Table I — except the fundamental burning velocity of hydrogen sulfide [1] — are presented in a number of sources [2–8]. However, the value of the burning velocity of α-pinene — 154 m/s or 506 ft/s — was erroneous in all the sources. This value had already come under criticism: "The value reported for turpentine [154 m/s] is currently being disputed by some experts in the field, who claim that the velocity is much slower" [5].

Compound	LFL, %	UFL, %	AIT, °C	S_u, m/s
Hydrogen sulfide	4.3	45	260	0.46
Methyl mercaptan	3.9	21.8	--	0.55
Dimethyl sulfide	2.2	19.7	206	--
Dimethyl disulfide	1.1	8.0	300	--
α-pinene	0.8	6.0	253	(154) 0.62
Methanol	6.7	36.5	464	0.50

I. Combustion properties of kraft mill NCGs in air.

According to Allen [9], the value 506 ft/s had been taken from a table of combustion properties of hydrocarbon fuels in Perry and Chilton [10]. That table was adapted from the National Advisory Committee for Aeronautics (NACA) [11], where the number 506 was given as the autoignition temperature of α-pinene in degrees Fahrenheit (506°F = 263°C). During the adaptation, this number was entered in the wrong column. It should be noted that NACA gave no value for the fundamental burning velocity of α-pinene. The correct value is 0.62 m/s [12].

EXPLOSION RISKS OF NCGS

Pulp mill NCG sources are divided into four categories [8]:

1. Low volume, high concentration (LVHC) gases, or concentrated NCGs
2. Overhead vapors from foul condensate steam stripping systems, or stripper-off gases
3. High volume, low concentration (HVLC) gases, or dilute NCGs
4. Chip bin vent gases

LVHC gases consist of relatively high concentrations of TRS compounds and air depleted of nearly half of its oxygen content. The TRS compounds are typically present at concentrations between LFL and UFL, which would be flammable in mixtures with air. Because these gases do not contain sufficient oxygen to allow for ignition, LVHC systems are designed to minimize air ingression and thus reduce the hazard of flammability.

Component	Liquid, mass%	Vapor, mole%	LFL–UFL, %
Methyl mercaptan	0.0227	10.9	3.9–21.8
Ethyl mercaptan	0.0714	8.4	2.8–18.0
Dimethyl sulfide	0.408	44.9	2.2–19.7
α-pinene	37.0	18.6	0.8–6.6
β-pinene	62.5	17.4	0.8–6.7

II. Liquid and vapor phase compositions of turpentine.

Stripper-off gases are a mixture of methanol, water vapor, and TRS compounds. Methanol is present at higher concentrations than in LVHC gases. The combustible components in HVLC gases typically are present at levels well below their individual lower flammability limits. Oxygen levels in HVLC gases approach the oxygen level of ambient air.

The combustible components in chip bin vent gases are also present at concentrations below their respective LFLs. However, chip bin vent gases at softwood pulp mills differ from other HVLC gases because they have the potential to contain significant quantities of turpentine, sometimes at concentrations approaching its LFL [8].

Attempts to collect and burn NCGs were first tried in the late 1950s with systems that collected the gases in pipelines and used fans to move the gases. These systems usually diluted the LVHC gases with air below their flammability limits. This approach was not always successful, especially with concentrated gases that came from digesters and evaporators; many early systems experienced fires and explosions.

In the early 1970s, a system was developed in Sweden that kept the LVHC gases undiluted and used steam ejectors to move the gases. This system virtually has eliminated explosions in LVHC systems, and is the accepted method for handling LVHC gases [5].

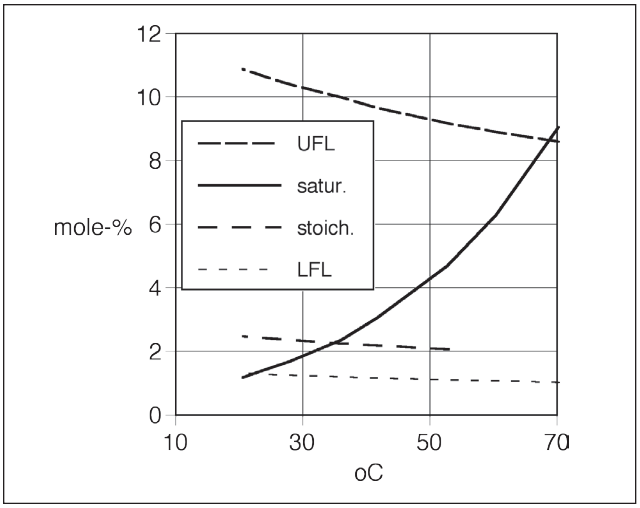
Flammability of turpentine vapors

Woodward and Lygate [12] investigated an explosion in a vapor collecting manifold of three storage tanks for crude sulfate turpentine that occurred in 1995. They made a five-component model in which all heavier components were represented by β-pinene. **Table II** presents the compositions of liquid and vapor phases in equilibrium at 21°C and the flammability range of each component.

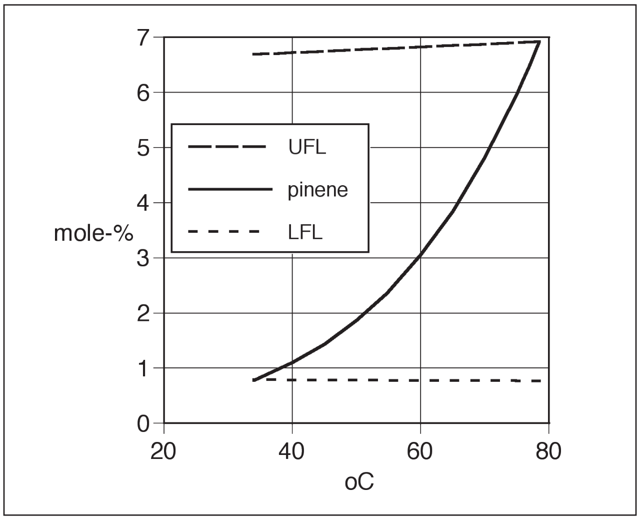
Mashuga and Crowl [13] estimated the flammability limits of crude sulfate turpentine using the Le Chatelier rule (Eq. 1):

$$\frac{1}{LFL} = \sum_{i=1}^{n} \frac{y_i}{LFL_i} \tag{1}$$

where y_i is the mole fraction of the ith component and LFL_i is the lower flammability limit of this component. Equation 1 was also used to estimate the upper flammability limit. The flammability range at 21 °C was estimated to be 1.3%–10.9%. **Figure 1** shows that both flammability limits and the vapor concentration corresponding to stoichiometric mixture decreased with increasing temperature, due to an increase in the mole fractions of the pinenes in the vapor. Figure 1 also shows the saturated vapor pressure curve. In addition, saturated vapor was flammable between 22°C and 69°C and formed stoichiometric mixture with air at 35°C.



1. Saturated vapor pressure, stoichiometric concentration, and flammability limits of crude sulfate turpentine [12].



2. Saturated vapor pressure and flammability limits of turpentine containing no TRS.

The lower temperature limit of flammability LTL (upper temperature limit of flammability UTL) of a flammable liquid is defined as the temperature at which the vapor content of a saturated vapor-air mixture is equal to the lower (upper) flammability limit [14]. Thus, the LTL and UTL of crude sulfate turpentine are 22°C and 69°C, respectively.

In Table II, TRS compounds constituted about 64 mole% of the vapor phase. It is instructive to perform the same calculation for turpentine with no dissolved TRS. According to

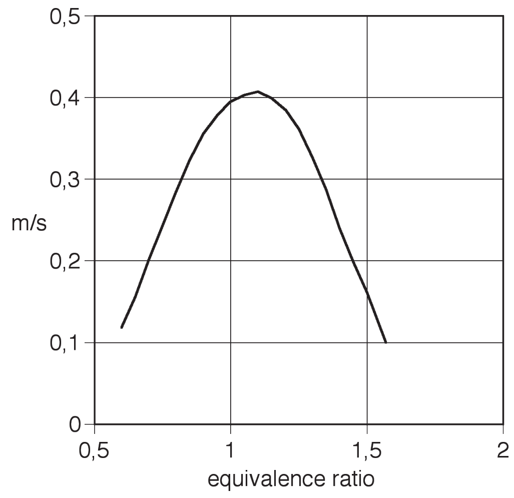
Bodurtha [15], relative decrease of the LFL with increasing temperature is 0.0008/K. This number is also the relative increase of the UFL. The vapor pressures of α-pinene and β-pinene were calculated using information from Hawkins and Armstrong [16].

Figure 2 shows the plots of the resulting flammability limit and saturated vapor pressure curves. From Fig. 2, it can be concluded that the saturated vapor is flammable between 34°C and 78.5°C. Equivalently, the LTL and UTL of pinene are 34°C and 78.5°C, respectively. The stoichiometric concentration of pinene $C_{10}H_{16}$ is 1.86% and corresponds to the saturated vapor pressure at 50°C.

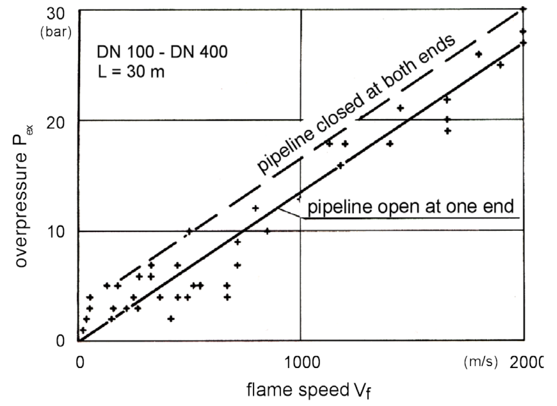
Normal temperatures in a HVLC collection system are 50°C –90°C before cooling or condensing and 40°C–50°C after cooling. Most of the time, temperatures in an HVLC collection system are between the LTL and UTL of turpentine. However, in climates where softwood pulp mills operate, temperature on the top of a chip bin, where gases are collected, is usually below the LTL.

Abnormal situations with temperatures outside these ranges include shutdowns and process failures. During a shutdown, collection system temperature can decrease below normal, and turpentine condensate formation in the system will increase. When the system is started or heated up again, turpentine condensate will evaporate and increase the concentration of turpentine vapor in the HVLC gas stream above LFL.

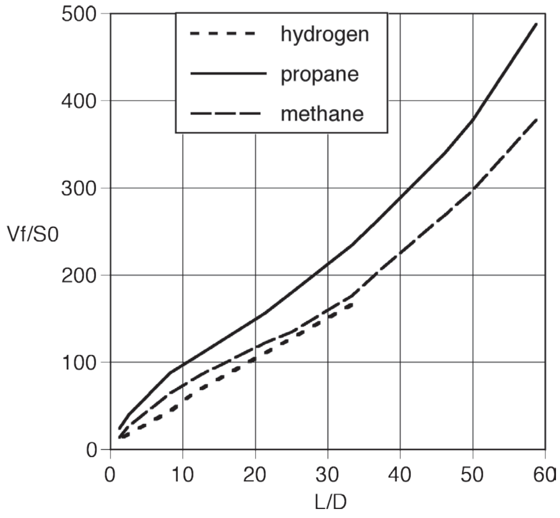
In many installations, the chips in a chip bin are steamed with flash steam. The most critical process failure in a chip bin system is when flash steam passes through the chip layer and finds its way to the HVLC collection system. At that time, turpentine concentration will increase dramatically. The situation becomes even worse when gases are cooled down in an HVLC condensing system, where most of the moisture is condensed away from the gas stream [17].



3. Effect of fuel concentration on burning velocity of propane [18].



4. Explosion overpressure in a pipe of diameter 100 mm–400 mm and length 30 m [20, Fig. 1–63].

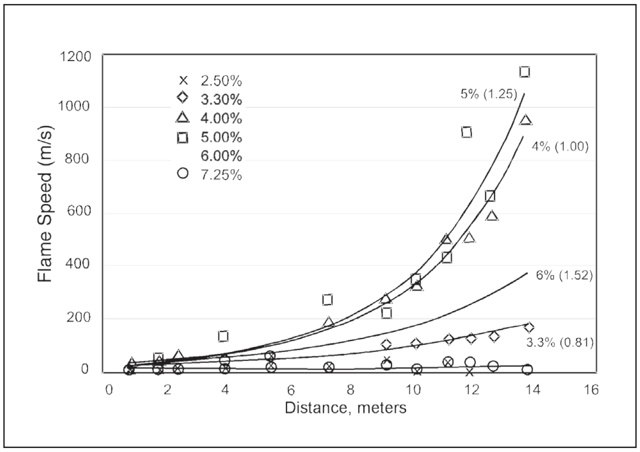


5. Flame speeds in a 400-mm pipe ignited at the closed end by a spark gap [20] for methane, propane, and hydrogen divided by the respective laminar burning velocities.

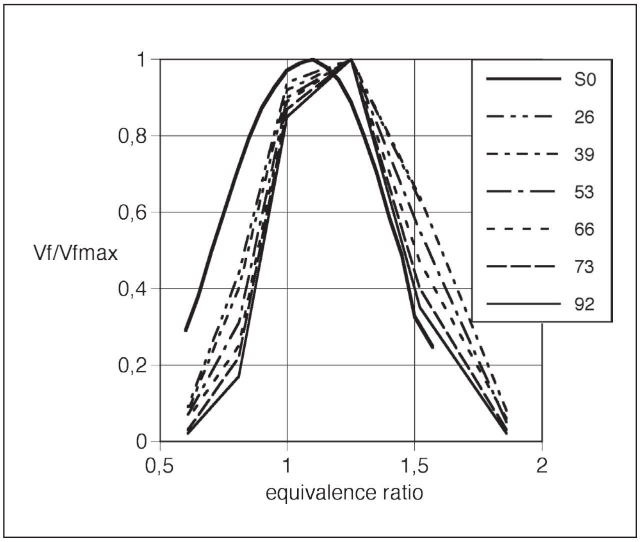
Flame speed and burning velocity in pipe explosions

The laminar burning velocity of a flammable mixture S_0 is defined as the velocity at which the flame zone propagates relative to the velocity of the unburned gas ahead of it. The maximum value of laminar burning velocity corresponding to the so-called optimum mixture is found on the fuel-rich side of the stoichiometric mixture. This value (fundamental burning velocity) S_u is given in Table I for the NCGs.

Laminar burning velocity goes to zero when the fuel concentration approaches either flammability limit. **Figure 3** shows the laminar burning velocity of propane plotted as a function of the equivalence ratio ϕ [18]. The value of the equivalence ratio ϕ is found by dividing the value of the ratio of fuel moles to air moles in the mixture by the correspond-



6. Effect of fuel concentration on flame speed of propane in a 152-mm pipe [21, Fig. 6].



7. Flame speeds at equidistant points of propane-air mixtures with different equivalence ratios in a 152 mm pipe [21] divided by the maximum values of the flame speed. The ratio of burning velocity S_0 [18] to fundamental burning velocity is drawn with a thick line.

ing value of the stoichiometric mixture. For propane, the maximum value of S_0 is 0.41 m/s at $\phi = 1.1$. The LFL (2.2%) and UFL (9.5%) of propane [19] correspond to the values $\phi = 0.54$ and $\phi = 2.50$, respectively.

In fact, the laminar burning velocity of any flammable gas or vapor as a function of ϕ behaves qualitatively the same way as that of propane. When the concentration is near either flammability limit, the burning velocity is much lower than at the optimum mixture.

The speed with which the flame front travels through a flammable mixture, measured with respect to some fixed position, is called the flame speed v_f. In practice, flame speed is not usually the same as burning velocity. During combustion, the flame front is often pushed forward by the effect of gases trapped behind it. This is the case when a flammable mixture is confined in a pipe and ignited at a closed end. The flame speed v_f is the (vector) sum of the burning velocity and the flow velocity u (Eq. 2):

$$v_f = \frac{A_f}{A_0} S_f + u \tag{2}$$

where A_f is the area of the flame, A_0 is the pipe cross section, and S_f is the burning velocity of the mixture. When the flow of unburned mixture is laminar, $S_f = S_0$. In a turbulent flow, the mixing of fuel and air is more effective because of turbulent eddies, and S_f is higher than S_0. The turbulent burning velocity, however, depends upon the degree of flow turbulence, which also increases the flame area A_f.

In practice, there are many difficulties in taking into account the flame area correction in Eq. 2 even when $u = 0$. Because of these difficulties, different fuels and flammable mixtures are compared on the basis of their laminar burning velocities [19].

When a pipe is closed at the ignition end and open at the other, the flow velocity u is parallel to the burning velocity. The flow velocity is high, at 80%–90% of the flame speed. Bartknecht [20] performed flame propagation experiments in straight pipes with diameters of 100 mm, 200 mm, 400 mm, and 1,600 mm. The pipes were filled with optimum propane-air mixtures. Bartknecht concluded that the explosion overpressure acting perpendicular to the pipe wall will change linearly with the flame speed v_f independent of the pipe diameter and the flammable mixture, as illustrated in **Fig. 4**.

Figure 5 shows the flame speeds measured in a 400-mm pipe filled with optimum mixtures of methane, propane, and hydrogen with air [20] divided with the respective fundamental burning velocities (methane 0.37 m/s, propane 0.41 m/s, hydrogen 3.1 m/s). The curves are plotted as functions of the ratio *L/D* where *L* is the length and *D* is the diameter of the pipe. The scaled flame speed curves in Fig. 5 have similar forms and lie close to each other.

Chatrathi and others [21] used straight pipes with a diameter of 152 mm, 254 mm, or 406 mm and an *L/D* ratio of approximately 98. Experiments were performed with mixtures of propane, ethene, and hydrogen with air. Flame speed as well as flame acceleration changed in order of increasing laminar burning velocities: propane (0.41 m/s) < ethene (0.70 m/s) < hydrogen (3.1 m/s). Experiments in the 152-mm and 406-mm pipes also showed similar behavior, thus this behavior was found to be independent of pipe diameter.

Chatrathi and others [21] also investigated the effect of fuel concentration on the flame speed in a pipe ignited at the closed end. **Figure 6** presents the results from tests in a 152-mm pipe filled with different propane-air mixtures [21]. At compositions nearest the optimum one of 4.0% and 5.0% (ϕ = 1.0 and 1.25, respectively), the flame speed accelerated rapidly and exceeded sound velocity at *L/D* of about 75. The next fuel concentrations of 3.3% and 6.0% (ϕ = 0.81 and 1.52, respectively) were approximately midpoint between the flammability limits and the optimum level. Although the flame speeds were reduced by about 75%, the flame propagation was still rapid. Changing the fuel concentration from stoichiometric to 2.5% and 7.25% (ϕ = 0.61 and 1.86, respectively), caused the flame speed to drop significantly and not accelerate. It should be noted that the flame did propagate, although slowly. Arrival times at the end of the 15-m-long pipe exceeded 1 s.

The flame speeds of propane-air mixtures in Fig. 6 at equidistant points of the 152-mm pipe have been divided by the maximum flame speed at each point. The maximum flame speeds were measured for the 5% mixture with an equivalence ratio of 1.25. **Figure 7** presents the resulting curves plotted with the burning velocity of propane from Fig. 3. The curves of the scaled flame speeds lie close to one another. This means that the ratio of the flame speed corresponding to a given value of equivalence ratio ϕ to the flame speed of an optimum mixture does not change much as the flame propagates along a pipe.

Figure 7, however, does not show the behavior of flame speed near the optimal mixture since no experiments were performed between ϕ=1.0 and ϕ=1.25. The curves of scaled flame speeds have the same form as the curve of burning velocity, but are shifted to higher values of ϕ.

These conclusions can be extended to any flammable mixture burning in a pipe closed at one end or at both ends. The consequences of a pipe explosion can be predicted based on the equivalence ratio ϕ of the mixture and length to diameter ratio L/D of the pipe. Provided that the ratio L/D is large enough, rapid flame acceleration will occur at near-optimal compositions ($\phi \approx 1$), leading to high flame speeds and explosion overpressures. If, however, the pipe fails, combustion gases are vented and explosion overpressure is reduced. On the contrary, if the mixture is near either flammability limit, the flame will propagate slowly with only a small overpressure, causing little or no damage to the pipe.

Explosion risks of turpentine

The following are some observations from several authors who have discussed the explosion risks caused by turpentine contained in the NCGs:

"Most explosions or fires in foul-gas systems can be traced to turpentine collecting in the system by condensing in low spots or to a slug of turpentine vapor entering the system because of an upset in the turpentine condensing system" [2].

"Many of the flashbacks that are attributed to noncondensible gas systems may actually be fine aerosols of turpentine that ignite in the line just prior to the incineration point" [22].

"Turpentine has been identified as the cause of numerous fires and explosions within the pulp and paper industry. One of the main concerns with turpentine is its immiscibility with water and thus its ability to decant as a floating layer on foul condensates. Any reheating or excessive splashing, such as in a fan casing, of a system containing pools of turpentine can immediately create high levels of combustibles. ... It is normally assumed that turpentine will be present in saturation concentrations at the collected temperatures. This may not always be the case, but for a safe design the conservative assumption should be taken" [23].

"The burning velocity of sulfur gases is relatively slow. However, the burning velocity for turpentine ... is extremely fast ... Explosions caused by TRS are usually minor, with minimum damage, while explosions caused by turpentine can be catastrophic. While noncondensible gas systems are designed to handle the burning velocity of TRS, it is not practical to design against the burning velocity of turpentine. For this reason, it is very important to minimize the amount of turpentine entering the NCG system" [5].

CONCLUSIONS

Burgess attributes the violence of explosions caused by turpentine vapor to the erroneous value of the burning velocity of α-pinene [5]. As concluded by Chatrathi and others [21], flame speed and, consequently, the overpressure in pipe explosions depend significantly on the fuel concentration. Indeed, explosions of NCGs can be violent if the equivalence ratio ϕ is close to the optimum one. The conclusion by Burgess [5] can be explained if the presence of turpentine vapor caused the content of flammable gases to be near the optimum one.

This is related to process conditions in the collection systems. In the actual explosion incidents, flammable conditions were created by insufficient dilution, air leakage into the system, changes of temperature during shutdown and startup, or accumulation and breakthrough of turpentine vapor at a chip bin.

When the flammable conditions were created due to insufficient dilution of a stream of HVLC gases, or due to air leakage into a stream of LVHC gases, the flammable mixture formed is expected to have been off-stoichiometric: lean in the former case and rich in the latter case. In both cases, the value of burning velocity could have been much lower than in the near-stoichiometric mixture case.

On the other hand, changes of collection system temperature during shutdowns and startups, as well as accumulation and breakthrough of turpentine vapor at a chip bin, are expected to have created near-optimum mixtures more often than in the two situations mentioned previously. Then, the burning velocity would be close to the maximum one.

This explains why high concentrations of turpentine vapor have caused violent explosions in NCG systems. It also underscores the necessity to avoid the various mechanisms resulting in such concentrations. **TJ**

ACKNOWLEDGEMENTS

The author thanks R&D Manager Mikko Anttila for supervising the study on explosion risks of NCG collection systems on behalf of Metso Power Oy, Tampere, Finland, and Product Manager Tuomo Hilli for information about the process conditions of NCG collection systems. He is also indebted to Travis Allen of Weyerhaeuser Company, Federal Way, WA, USA, for his aid in tracing the original error on the burning velocity of turpentine.

LITERATURE CITED

1. Vervisch, L., Labegorre, B., and Réveillon, J., *Fuel* 83: 605(2004).
2. Burgess, T., Kjerolf, E.B., and Tenn, T.L., *Tappi J.* 67(9): 92(1984).
3. Burgess, T. and Young, R., *1992 Environmental Conference Proceedings, Book 1*, TAPPI Press, Atlanta, GA, USA, p. 81.
4. Bell, M., *Pulp Paper* 70(6): 127(1996).
5. Burgess, T., 1996 *Kraft Recovery Short Course Proceedings*, TAPPI Press, Atlanta, p. 4.2-1.
6. Allen, T., *Pulp Paper* 75(4): 39(2001).
7. Black Liquor Recovery Boiler Advisory Committee (BLRBAC), "Thermal oxidation of waste streams in black liquor recovery boilers," BLRBAC, 2002, pp. 9, 12. Available [online] *www.blrbac.org/Recommended Practices/Waste_Streams.pdf.*
8. Varma, V. K., "Experience with the collection, transport, and burning of kraft mill high volume low concentration gases," Special Rept. No. 03-03, National Council for Air and Stream Improvement, Southern Regional Center, Gainesville, FL, USA, 2003. Available [online] *plaza.ufl.edu/callie/special.report.03-03.pdf.*
9. Allen, T., personal communication.
10. Perry, R.H. and Chilton, C.H., *Chemical Engineers' Handbook*, 4th edn., McGraw-Hill, New York, NY, USA, 1963, p. 9–33.
11. National Advisory Committee for Aeronautics (NACA), "Basic considerations in the combustion of hydrocarbon fuels with air," Rept. 1300, NACA, Washington DC, 1957. Available [online] *naca.central.cranfield.ac.uk/reports/1957/naca-report-1300.pdf.*
12. Woodward, J.L. and Lygate, J., *Proc. Saf. Prog.* 21(3): 171(2002).
13. Mashuga, C.V. and Crowl, D.A., *Proc. Saf. Prog.* 19(3): 112(2000).
14. Britton, L.G., Cashdollar, K.L., Fenlon, W., et al., *Proc. Saf. Prog.* 24(1): 12(2005).
15. Bodurtha, F.T., *Industrial Explosion Prevention and Protection*, McGraw-Hill, New York, 1980, p. 19.
16. Hawkins, J.E. and Armstrong, G.T., *J. Am. Chem. Soc.* 76: 3756(1954).
17. Hilli, T., personal communication (2009).
18. Bosschaart, K.J., "Analysis of the heat flux method for measuring burning velocities," Ph.D. thesis, Technical University of Eindhoven, The Netherlands, 2002, pp. 65–76, Appendix D. Available [online] *alexandria.tue.nl/extra2/2003/0699.pdf.*
19. Harris, R.J., *The Investigation and Control of Gas Explosions in Buildings and Heating Plant*, London, E & FN Spon, 1983, pp. 8–14.
20. Bartknecht, W., *Explosions, Course, Prevention, Protection*, Springer, Berlin, 1981, pp. 56–65.
21. Chatrathi, K., Going, J.E., and Grandestof, B., *Proc. Saf. Prog.* 20(4): 286(2001).
22. Johnston, J., *1993 Kraft Recovery Operations Short Course Proceedings*, Book 1, TAPPI Press, Atlanta, p. 147.
23. Wright, J.M. and Lund, G., *1994 International Environmental Conference Proceedings*, Book 1, TAPPI Press, Atlanta, p. 285.

ABOUT THE AUTHORS

Metso Power Oy asked VTT to perform a literature study on explosions in collection systems of noncondensible gases. I have performed several literature studies and consultations on gas explosions, but this was the first one for the pulp and paper industry. My biggest challenge was to identify and describe situations with high concentrations of turpentine vapor, so I consulted an expert to provide insights on those situations.

While conducting the literature study, I found the most surprising thing to be the persistence of a misconception deriving from a misprint on the burning velocity of turpentine.

The information in this paper should be useful in avoiding explosions due to high concentrations of turpentine vapor. For a future step, the erroneous burning velocity of turpentine and the conclusions deriving from it should be rectified in documents such as "Thermal Oxidation of Waste Streams in Black Liquor Recovery Boilers" by the Black Liquor Recovery Boiler Advisory Committee (BLRBAC) [7].

Lautkaski

Lautkaski is senior research scientist with VTT, Technical Research Centre of Finland in Espoo, Finland. E-mail Lautkaski at risto.lautkaski@vtt.fi.