COMMENTARY ON THE PROPOSED USE OF LNG AS A COOLING AGENT CONCURRENTLY WITH ITS EVAPORATION

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Having made a fairly close study of the physical chemistry which forms section 2 of the paper on LNG ‘cold energy’ [1] in a recent issue of this journal, I have some questions to put to the authors.

The PR equation of state bears some similarity to the classical van der Waals model, details of which are in any textbook on physical chemistry. The authors again follow classical principles by utilising critical quantities to obtain an equation of state in reduced variables: that at any rate is the impression one forms on perusal.

All of this is unexceptionable, but the subsequent application of the PR equation does leave a reader unclear. The above is an equation of state for a gas. The expression ‘pressure of the LNG’ is used in [1], and this presumably means the pressure of vapour in equilibrium with the liquid phase. This is a fairly important point which ought to be clarified. If the term ‘pressure of the LNG’ is so interpreted, we have a basis for examining the numbers which follow in [1].

On this basis, the temperature of LNG at 100 kPa is given as −162°C (111K) which is actually the value for pure methane, so notwithstanding the invocation of a fairly advanced equation of state and a detailed analysis of the composition of natural gas imported into Taiwan the authors, at this point, appear to have approximated it to pure methane. The authors then refer to pressurisation from atmospheric to 80 bar. Here, though the authors do not explicitly say so, it is superheated methane which is under discussion. This can in fact be established from the statement considerably later in the article:

At 8 MPa LNG would have an enthalpy of 786 kJkg⁻¹...

From Tables [2], superheated methane at 80 bar has an enthalpy of 786 kJmol⁻¹ at 221 K (−52°C) and this represents a stage long after evaporation. The following points of criticism in relation to [1] can therefore be made:

- The comparison of LNG at atmospheric pressure with the ‘pressurised’ form is not of like with like: in the former case, the methane is in a phase equilibrium situation and in the latter, it is superheated at a temperature in excess of 100 K above its normal boiling point.

- The statement quoted above in italics is completely misleading. The figure of 786 kJkg⁻¹ is for saturated methane, not for LNG. To give a specific enthalpy for LNG, one would have to sum enthalpies for the two phases and therefore have to know the proportion of the mass in each phase. The specific enthalpy of LNG, understood as a phase equilibrium, is not single valued at any temperature because of its dependence on the mass distribution in the phases. It is for exactly the same reason that one cannot talk of ‘the enthalpy’ of saturated steam at any temperature and corresponding pressure: it depends on the dryness fraction.

Examining now the statement that:

‘... 786 kJkg⁻¹ only amounts to 88% of its [LNG’s] value at atmospheric pressure’

The following points can be made. At atmospheric pressure under phase equilibrium conditions (i.e., at −162°C), the specific enthalpy of liquid methane is 716.3 kJkg⁻¹. One might well assume, with justification, that almost all of the mass is in the liquid, in which case this is the value of the specific enthalpy of LNG at atmospheric pressure and 786 kJkg⁻¹ is not 88 but 110% of ‘its value at atmospheric pressure’. The specific enthalpy of the vapour at −162°C is of course higher than that of the liquid so the assumption that the material is entirely in the liquid phase provides a lower bound on the actual specific enthalpy of the LNG. So the 88% is difficult to understand, though clarification might be obtained if the precise composition of the LNG is considered. There is of course the difficulty that one cannot sum tabulated enthalpies for different hydrocarbons because a different arbitrary zero will apply in respect of each. If the authors of [1] somehow went along the path of calculating an enthalpy on the basis of the composition of the LNG, that needs to be fully explained.

The paper under discussion appears to be flawed in respect of elementary thermodynamics. A two-
A phase system is discussed alongside a single-phase one with no note of the distinction and the term LNG is applied to superheated methane. A statement on the relative values of the enthalpies under different conditions cannot, at least without further information, be reconciled with tabulated data from an authoritative source. The abstract refers to latent heat yet all of the enthalpies quoted appear to be sensible heats. The equation of state introduced in some detail appears not to have been used and there is an entirely irrelevant graph of predicted LNG usage in Taiwan at the centre of an article which otherwise purports to be technically focused.

Much clarification is needed if a reader is to have confidence in the subsequent technological arguments in the paper.

REFERENCES
