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Compositional Fractionation Studies of R410A Alternative R452B or DR55 and Their Impact on Flammability Behavior and Safety Implications

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ABSTRACT

Today air conditioning product and applications designers, as a result of climate change contribution concerns for high direct global warming potential (GWP) refrigerants, are being asked to consider lower GWP refrigerants with various degrees of flammability. In recent years, the HVACR industry has been actively investigating the safety of flammable refrigerants by determining their risks, potential occurrences and severity of events. Today R410A is used to cover most air conditioning applications and all lower GWP alternatives presented to date have some degree of flammability with most being ASHRAE 34 flammability class 2L.

A novel R410A alternative refrigerant blend, R452B or DR55, has recently been studied in a 4 ton RTU to determine the potential for compositional fractionation in various modes of operation. In addition, the ASHRAE flammability process needed to classify refrigerant flammability and flammability classification data for R452B will be presented in this paper. The unit compositional data and the ASHRAE classification process and data will be compared and contrasted to show differences in potential flammability interpretations and design safety implications.

1. INTRODUCTION

One of the main societal drivers for the development of chlorofluorocarbons (CFCs) in the 1930s was the need to reduce both personal and property safety risks, primarily from the flammability and toxicity safety issues presented by hydrocarbons, ammonia (R717), sulfur dioxide and other chemicals like methyl chloride (R40). CFCs and later hydrochlorofluorocarbons (HCFCs) such as R22, provided over 60 years of reduced flammability and improved toxicity safety with refrigerants. In the 1970s, it was determined that CFCs cause ozone depletion. Society demanded solutions to eliminate this environmental risk while maintaining the safety requirements developed in the 1930s. Hydrofluorocarbons (HFCs) and blends of HFCs were developed that met the flammability and toxicity requirements demanded by society in the 1930s. Today, R410A is used to cover most air conditioning applications and more specifically in direct expansion refrigerant systems in occupied space applications. R410A is a nonflammable blend of R32, which is ASHRAE 34 Class 2L flammable, and R125, which is nonflammable and is added to R32 as a flammability suppressant.

Maintaining nonflammability and low toxicity is not without challenges when developing lower GWP refrigerants to replace R410A. In most instances, to meet the demands of a low GWP refrigerant world, society will have to evaluate flammable refrigerants and their risks to personal and property safety compared to the relative benefits to the environment. New unsaturated HFCs (HFOs), R1234yf and R1234ze(E), have been developed that have very low GWPs (<1 per AR5) and offer the opportunity for blending with existing HFCs, like R32 and R125, to form new R410A alternatives. All new HFC/HFO alternatives proposed to date are ASHRAE 34 Class 2L with varying degrees of flammability. Determining the safety of flammable and slightly flammable refrigerants, their risks and
potential occurrences is being heavily debated with research and risk assessments sponsored by the HVAC&R industry on going. Unfortunately, there is limited baseline application data of flammability risks and occurrences for HVAC&R or other similar products since in most applications refrigerants are nonflammable.

Kujak and Schultz (2015, 2016) described a blend labeled DR55 (now designated as R452B) that balances flammability, performance, and GWP. Table 1 describes the composition, GWP and temperature glide of R452B as compared to R410A. R452B was selected because of its prospects for being a more design compatible and lower flammable alternative to replace R410A than R32. The thermodynamic properties of R452B indicate capacities within a few percent of R410A while offering ~1% higher thermodynamic efficiency. R452B’s burning velocity (~3 cm/s for the as formulated composition) is lower than R32’s (6.7 cm/s) while matching R32’s GWP (675). The performance of a 4 RT, 13 SEER commercial unitary rooftop heat pump was measured with R410A as a baseline and with the alternative refrigerants R452B (Kujak and Schultz, 2015, 2016). During the performance characterization work, this unit was used to conduct a series of refrigerant leak scenarios while operating and while turned off. R452B refrigerant composition was measured at specific points during this study to determine any shift in composition. This paper focuses on the R452B compositions measured during cooling mode testing while conducting various leak tests and compares them to R452B compositional requirements to classify under ASHRAE 34.

Table 1. Compositions, GWPs and temperature glide of the R410A and R452B.

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>R32 % wt</th>
<th>R125 % wt</th>
<th>R1234yf % wt</th>
<th>Tolerances % wt</th>
<th>GWP$_{AR4}$</th>
<th>GWP$_{AR5}$</th>
<th>glide $^\circ$Fd / $^\circ$Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>R410A</td>
<td>50</td>
<td>50</td>
<td>–</td>
<td>+0.5, -1.5/+1.5, -0.5</td>
<td>2088</td>
<td>1924</td>
<td>0.2 / 0.1</td>
</tr>
<tr>
<td>R452B/DR55</td>
<td>67</td>
<td>7</td>
<td>26</td>
<td>+/-1.5/+/1.5, +/-2.0</td>
<td>698</td>
<td>675</td>
<td>2.2 / 1.2</td>
</tr>
</tbody>
</table>

2. ASHRAE STANDARD 34 FLAMMABILITY CLASSIFICATIONS

When considering a flammable refrigerant for use, one has to realize that flammability is a continuum and specific limits are difficult to assign for varying degrees of flammability. The ASHRAE 34 refrigerant designation and safety standard attempts to classify refrigerants into three classes (1, 2 or 3) and one optional subclass (2L) based on lower flammability limit (LFL) testing, calculation of heat of combustion (HOC), and the optional burning velocity (BV) measurement (Figure 1). Currently, BV is a subclass of Class 2 and is an optional classification that can be obtained through ASHRAE 34. ISO 817 treats the 2L class as a separate class and it is a mandatory requirement. ASHRAE 34 will likely be modified to harmonize with the ISO 817 methodology.

Figure 1. ASHRAE Standard 34 safety classification for refrigerants.

The four flammability classes are: Class 1 – no flame propagation, Class 2L – lower BV class 2’s with burning velocities less than or equal to 10 centimeters/second, Class 2 – lower flammability, and Class 3 – higher flammability. A LFL of <100 g/m3 and HOC of >19,000 kJ/kg mark the boundaries between Class 3 and Class 2 refrigerants. Historically, ASHRAE 34 contained only flammability classes 1 through 3. The new 2L class was added in the late 2000s to express the unique lower flammability properties of the new HFOs, like R1234yf and R1234ze(E), and older refrigerants like R32, R143a and R717. Figures 2 and 3 provide graphical summaries of
various refrigerants by their ASHRAE classification boundaries for LFL by BV and HOC by BV, respectively. Obtaining the values for LFL and BV in the Figures below is a complex and rather expensive task, while the HOC is a calculated value. How the HOC is calculated and determined is not part of this discussion; it is presented here only for comparison purposes. In general, LFLs for Class 3 refrigerants are 6 times lower than Class 2L refrigerants and HOCs are about 5 times higher for Class 3 refrigerants than Class 2L refrigerants.

ASHRAE 34 flammability classification requires determining the lowest LFL (most flammable condition) under various leak scenarios and conditions per ASTM E681 using a 12 liter spherical flask. Refrigerants are determined to be nonflammable (Class 1) if they don’t show flame propagation that exceeds the limits described in the ASTM method. Testing is conducted at elevated temperature conditions of 140°F (60°C) in air with an absolute humidity of 0.00875 lbm/w/lbmDA (kgw/kgDA) (determined from the condition of 50% relative humidity at 73.4°F (23.0°C) and 14.7 psia (101.3 kPa)). This limit is labeled by the standard as the elevated temperature flame limit (ETFL_{60}). The ETFL_{60} is the minimum concentration of refrigerant in air that is capable of propagating a flame at 14.7 psia (101.3 kPa) above 73.4°F (23.0°C). For those refrigerants that show flame propagation at these conditions, flammability testing is also conducted with air at the same absolute humidity of 0.00875 lbm/w/lbmDA (kgw/kgDA) to report the LFL. In the particular case of R1234ze(E), the LFL is reported at the ETFL_{60} since it does not exhibit flame propagation at 73.4°F (23.0°C). The authors expect in the future that more refrigerants will be developed that are non-flame propagating at near room temperature because of the regulatory advantages of handling, shipping and storage of refrigerants as non-flammable.

For single component refrigerants, like R32, required flammability testing by ASHRAE 34 is straight forward. For zeotropic refrigerant blends, the situation is complicated by the fact that the liquid and vapor phases do not have the same composition. The blend can fractionate while circulating through a piece of equipment or during a leak. ASHRAE 34 requires that the flammability be determined at both a worst case formulation for flammability (WCF) and a worst case fractionation for flammability (WCFF). WCF is defined as the formulation within the compositional tolerances that results in the concentration of components with the lowest LFL. WCFF is defined as the composition produced during fractionation of the worst case formulation for flammability (WCF) that results in the highest concentration of flammable component(s) in either the vapor or liquid phases.

The most flammable WCF and WCFF compositions must be determined under varying leak scenarios that simulate potential slow leaks from cylinders under storage and shipping, one time slow leaks from equipment, and multiple successive slow leakages and recharges with the WCF blend. A detailed description of these leak scenarios is summarized in Table 2. These leak scenarios, however related to real life risk conditions, add additional complexity and expense to determining the flammability of a blend. Note that a fractionation analysis for flammability is not required if the individual components of the blend are all in one class; in this case, the blend is assigned the same class. For example, if the blend contains only Class 3 hydrocarbons, the blend is classified Class 3.

The leakage scenarios are carried out to determine if classification boundaries are crossed. The LFL is determined for the most flammable composition after completing the fractionation testing laid out in Table 2 for both the WCF
and WCFF blends. This LFL is used only for classification purposes. The LFL for a blend is typically reported at the WCF composition. From this, a flammable concentration limit (FCL) is determined as 25% of the LFL. The output of Standard 34 is a refrigerant concentration limit (RCL). The RCL for a refrigerant is the lower value of the FCL or the acute toxicity exposure limit (ATEL) concentrations. In general, the RCLs for refrigerants classified as flammable are controlled by the FCL and the RCLs for nonflammable refrigerants are controlled by the ATEL. One exception is ammonia (R717) where the ATEL is much lower than the FCL.

If a refrigerant is determined to be Class 2, the above WCF and WCFF data are used to determining the refrigerant blend composition to run the BV testing. BV is defined as the maximum velocity at which a laminar flame propagates in a normal direction relative to the unburned gas ahead of it. ASHRAE 34 does not specify a specific burning velocity test methodology at this time since no standardized test methods exist. However, the standard does specify that the BV test for R32 and R152a be conducted as evidence to support the accuracy of the testing method. One acceptable BV method is the vertical tube method as detailed by Jabbour (2004) and summarized by Jabbour and Clodic (2004).

<table>
<thead>
<tr>
<th>Leak Scenario</th>
<th>Cylinder Fill</th>
<th>Leak Rate and Analysis</th>
<th>Tests Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow Storage/Shipping Leak</td>
<td>Container shall be filled with the WCF to 90%, by mass, of the maximum fill</td>
<td>The blend is vapor leaked at 2% by mass per hour. Composition of vapor and liquid measured after 2%, and then at successive 10% mass losses until the cylinder reaches atmospheric pressure or no liquid remains in the cylinder.</td>
<td>Tests conducted at: (1) 130°F (54.4°C) (2) -40.0°F(-40.0°C) or the bubble point at 14.7 psia (101.3 kPa) plus 18.0°F (10.0°C), whichever is warmer. (3) The temperature that results in the WCFF between (1) and (2) if the WCFF does not exist at either (1) or (2). If no temperature exists between (1) and (2), then instead conduct test at 73.4°F (23.0°C).</td>
</tr>
<tr>
<td>Slow Equipment Leak</td>
<td>Container shall be filled with the WCF to 15%, by mass, of the maximum fill</td>
<td>Same as Storage/Shipping.</td>
<td>Same as Storage/Shipping.</td>
</tr>
<tr>
<td>Slow Equipment Leak to 20% loss with 5X Recharges</td>
<td>Container shall be filled with the WCF to 15%, by mass, of the maximum fill</td>
<td>A vapor leak at a rate of 2% by mass of the starting charge per hour and maintained at 73.4°F (23.0°C) until 20% mass leaked. The composition of the head space gas shall be determined by analysis.</td>
<td>Conducted at 73.4°F (23.0°C).</td>
</tr>
</tbody>
</table>

The BV value determination differs from the LFL value determination in that the maximum value of BV is typically obtained at slightly higher than stoichiometric concentration, while the LFL is the lowest concentration mixture that will show flame propagation. The BV measurements are conducted starting from the LFL to at least 125% of the stoichiometric concentration to determine the maximum burning velocity. This difference is significant since most safety standards are using a fraction of the LFL concentration to determine the maximum refrigerant concentration.
limit (RCL) and thus refrigerant charge to be allowed in a product. If the LFL is reached within a space, the BV of this mixture is significantly lower than the value of BV reported by ASHRAE 34. The other complicating factor in interpreting the flammability characteristics of BV is that the BV is determined at a fractionated mixture not typical of a product leak scenario that could lead to a flammable event. Product leak scenarios are based on fast leaks, not slow leaks stated in ASHRAE 34. Fast leaks are better represented by the as formulated blend or WCF and not the worst case fractionated or WCFF blend. It should also be recognized that fractionation testing results in an amount of refrigerant remaining in many of these ASHRAE 34 leak scenarios that is too small to allow for a sizeable flammable mixture to form.

4. R452B ASHRAE 34 FLAMMABILITY CLASSIFICATION DATA

This section summarizes the flammability data obtained to classify R452B as a Class 2L refrigerant. Figure 4 and Figure 5 summarize the compositions determined as the result of the various leak scenarios conducted as summarized in Table 2, along with the final fractionation of the blend with both the WCF and WCFF of R452B as the starting composition. The nominal composition of R452B, the WCF and WCFF to determine the LFL and the WCF and WCFF to determine the maximum BV are shown in Table 3.

It becomes readily apparent wide variations in refrigerant compositions are obtained as a result of the leak scenarios required by ASHRAE 34 to determine the flammability classification. Focusing on the R32 content, concentrations range from a high of 76.8% by mass in the vapor of the WCFF mixture to a low of 13.4% in the liquid at the -40.0ºF(-40.0ºC) slow equipment leak scenario. R125 and R1234yf vary similarly from highs of 5.5% and 83.1%, respectively, to lows of 3.5% and 17.7%, respectively.

![Figure 4: Measured WCF compositional data obtained for Standard 34 classification of R452B.](image)

![Figure 5: Measured WCFF compositional data obtained for Standard 34 Classification of R452B.](image)

<table>
<thead>
<tr>
<th>Table 3. Summary of R452B flammability classification results</th>
<th>R32/R125/R1234yf Compositions (% by Mass)</th>
<th>LFL, % v/v (g/m³)</th>
<th>BV, cm/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal</td>
<td>67/7/26</td>
<td>3.0 cm/sec</td>
<td></td>
</tr>
<tr>
<td>at 73.4F (23ºC)</td>
<td></td>
<td></td>
<td>12.2% (316)</td>
</tr>
<tr>
<td>at 140ºF (60ºC)</td>
<td></td>
<td></td>
<td>11.5% (299)</td>
</tr>
<tr>
<td>WCF - LFL</td>
<td>66.5/5.5/28.0</td>
<td>11.9% (310)</td>
<td></td>
</tr>
<tr>
<td>at 73.4F (23ºC)</td>
<td></td>
<td></td>
<td>11.0% (287)</td>
</tr>
<tr>
<td>at 140ºF (60ºC)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WCFF - LFL</td>
<td>13.4/3.5/83.1</td>
<td>7.5% (300)</td>
<td></td>
</tr>
<tr>
<td>at 73.4F (23ºC)</td>
<td></td>
<td></td>
<td>7.0% (282)</td>
</tr>
<tr>
<td>at 140ºF (60ºC)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WCF - maximum BV</td>
<td>69.0/5.5/25.5</td>
<td>3.5 cm/sec</td>
<td></td>
</tr>
<tr>
<td>WCFF - maximum BV</td>
<td>76.8/5.5/17.7</td>
<td>4.2 cm/sec</td>
<td></td>
</tr>
<tr>
<td>FCL</td>
<td>66.5/5.5/28.0</td>
<td>3.0% (78)</td>
<td></td>
</tr>
</tbody>
</table>
5. UNIT LEAK STUDIES

Refrigerant leak studies were conducted using a 4 ton RTU to determine the potential for compositional fractionation during full load operation. The unit was run at the AHRI Standard 210/240 “A” rating condition (95°F/35°C ambient) when conducting the leak testing and was part the testing conducted to characterize the performance of R452B (Kujak and Schultz, 2016). A vapor leak was simulated by extracting approximately 2 lbm (0.9 kg) of refrigerant from the compressor discharge line into an evacuated cylinder over a one hour period; this equates to about a 25% per hour leak rate of 0.03 lbm (0.014 kg) per minute. This leak rate is about 12 times faster than the 2% per hour leak rate prescribed by ASHRAE 34. However, it is only 0.3% of the 635 lbm/hr (288 kg/hr) refrigerant circulating through the unit during operation. Extracting vapor at this rate should not cause departure from the isothermal nature of an ASHRAE 34 slow leak at 2% per hour. In contrast, risk assessments have typically been using a scenario in which the whole unit charge is released in a four minute period. In the unit tested, this would equate to about a 2 lbm (0.9 kg) per minute leak rate, about 60 times faster than the leak rate used in this testing. After the completion of each “leak” (collection) step, the unit was recharged back to its nominal refrigerant charge of 8.2 lbm (3.7 kg). The leak and recharge process was repeated four times.

The unit was initially charged with 8.2 lbm (3.7 kg) of R452B from the “small” (15 lbm/6.8 kg) cylinder with liquid composition shown in Figure 6, within the tolerances for nominal R452B. The unit was then recharged from the “large” (30 lbm/13.6 kg) cylinder with a very similar initial liquid composition. After each leak period, a refrigerant sample was collected from the liquid line at the condenser/subcooler outlet. The compositions measured for those samples are shown in Figure 7.

The composition circulating through the unit was observed to be very close to the composition charged into the unit. This suggests that the liquid and vapor were moving through the heat exchangers with the same velocity as the refrigerant changed phases in both evaporation and condensation. Therefore, refrigerant leaks from the single-phase vapor or liquid lines would produce no change in composition and the leaked composition would match the unit bulk composition, that is, a composition near the nominal R452B formulation.

A second leak scenario was also checked. The unit was first charged with 8.2 lbm (3.7 kg) of refrigerant with composition within R452B tolerances. The unit was then run at the “A” rating condition and a refrigerant sample extracted from the condensate line. The composition of this sample was very similar to the charged composition, consistent with the experience above. The unit was then turned off. One-half of the charge was extracted (leaked as vapor) from the compressor discharge line while holding the facility at 95°F (35°C) over a two hour period. In theory, this should be similar to the ASHRAE 34 slow equipment leak in Table 2. The unit was then recharged and run at the “A” condition. A liquid sample was again pulled for analysis. A REFLEAK (Dideon, et al, 2012) simulation of this scenario suggests the R32 mass fraction remaining in the unit should have dropped by 0.036 due to fractionation. The measured R32 mass fraction was lower by only 0.003. This indicates that the leaked vapor had
lower R32 content than expected and would have a lower burning velocity than determined by the WCFF methodology.

This scenario was repeated with a refrigerant blend of 76% R32 / 15% R1234yf / 9% R1234ze(E) which has a slightly larger temperature glide of 3.1°Fd (1.7°Cd) compared with R452B’s glide of 2.2°Fd (1.2°Cd) and should therefore exhibit a larger amount of fractionation. In this case, a REFLEAK simulation suggests the R32 mass fraction remaining in the unit should have dropped by 0.038. The measured R32 mass fraction was lower by only 0.012. Together, these results suggest that the ASHRAE 34 methodology for determining the flammability of blends might be overly conservative.

6. COMPARISON OF ASHARE 34 CLASSIFICATION AND UNIT LEAK DATA

The authors have previously reported a relationship of BV and minimum ignition energy as a function of R32, R1234yf and R125 concentration as shown in Figure 8 (Kujak and Schultz, 2016) based on several data sources. Points are plotted for R452B at 73.4°F (23°C) at the nominal, WCF-LFL, WCFF-LFL, WCF-BV and WCFF-BV compositions. Good agreement is seen between the previously determined lines of constant BV with the BV values listed in Table 3. Interestingly, the WCF-LFL and WCF-BV burning velocities are not much different than the nominal R452B BV and is likely more representative of a fast leak scenario that would lead to a potentially flammable event. WCFF-LFL and WCFF-BV compositions both poorly represent potential flammable leak events. The WCF-LFL composition is determined at a very low temperature with refrigerant mass remaining insufficient to lead to a flammable event. The WCFF-BV is the initial fractionation of a slow leak. As such a leak progressed, the integrated composition in the surrounding space moves back toward the starting composition (by conservation of species mass) and is therefore not representative of a fast leak that could lead to a flammable event. In the end, ASHRAE 34 tries to determine when a refrigerant blend may change classification over a wide range of slow leak and temperature scenarios which do not represent well real life situations that could lead to a significant flammable event. On the other hand, the WCF-LFL and WCF-BV are more realistic of real life compositions that could be seen during a potential fast leak scenario that could lead to a flammable event.

![Figure 8: Fractionation compositions for WCF-LFL, WCFF-LFL, WCF-BV and WCFF-BV plotted on a composition by BV relationship plot for refrigerants blends that contain R32, R125 and R1234yf. Nominal compositions for R410A, R452A and R452B shown for reference.](image)

7. CONCLUSIONS

A novel R410A alternative refrigerant blend, R452B or DR55, has recently been studied in a 4 ton RTU to determine the potential for compositional fractionation. Analysis of refrigerant samples showed no compositional
shifts of the R452B during a leak of that was 25%/hr, but only 0.3% of the refrigerant circulation rate, from the compressor discharge line. The composition remained unchanged after four leak/recharge steps. On the other hand, the slow leak scenarios specified in ASHRAE 34 result in extreme compositional shifts that represent an instant in time and are not representative of scenarios that could lead to potentially flammable events. A number of product safety standards are considering using a fast leak scenario of basically the entire charge leaking out in four minutes. Such a scenario results in a leaked refrigerant composition that is closer to the bulk composition in the unit. This brings into question whether ASHRAE 34’s slow leak rate and resulting compositional shifts are overly conservative and thus does not represent real life situations when determining flammability classification.

Many of the nonflammable refrigerants, such as R125, R134a, and R227ea, that are used to suppress flammability have elevated GWPs and add significantly to the GWP of a blend. The authors suggest that the GWPs of nonflammable blends are needlessly being elevated at the expense of flammability safety risks that are low or nonexistent. The WCF-LFL and WCF-BV conditions represent the flammability behavior of R452B well. However, the WCFF-LFL and WCFF-BV scenarios produce extreme (instantaneous) compositions not likely to represent realistic situations. ASHRAE 34 should consider changing the leak rate of 2% of refrigerant per hour leak rate for its slow leak rate scenarios to potentially better align with real life leak that can lead to flammability safety risks. This change would allow for more flexibility in the design new lower GWP refrigerants with lower real flammability characteristics. In addition, a review of the temperature scenarios should also be considered to improve alignment with reality. In doing so, the refrigerant designer would then have an opportunity to offer more optimized refrigerants for flammability, GWP and HVACR equipment performance.

**NOMENCLATURE**

- $\text{GWP}_{\text{AR4}}$: Global Warming Potential according to IPCC (2007)
- $\text{GWP}_{\text{AR5}}$: Global Warming Potential according to IPCC (2013)

**REFERENCES**


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