1996

A Refrigerant Producer's Experience in Manufacturing Zeotropic Blends

H. M. Hughes
AlliedSignal Inc.

W. P. Dulaney
AlliedSignal Inc.

R. L. Broussard
AlliedSignal Inc.

A REFRIGERANT PRODUCER'S EXPERIENCE IN MANUFACTURING ZEOTROPIC BLENDS

H. M. Hughes
W. P. Dulaney
R. L. Broussard

AlliedSignal Inc.

Abstract

This paper addresses the issues associated with blending the components of zeotropic mixtures and subsequent packaging. It does not deal with the manufacture of the individual components. Several mixtures are considered but more attention is focused on one particular blend. The specific mixture chosen for this assessment is a blend of HFC-32, HFC-125 and HFC-134a with a nominal composition by weight percent of 23, 25, 52 respectively. This particular mixture has been designated by ASHRAE as R-407C[1]. In general, this blend has been proposed as an alternative for HCFC-22. The main emphasis is placed on maintenance of product within specification. Issues related to this include blending equipment and techniques, the number and quantity of components and the temperature of the blend.

Introduction

Refrigerant blends, in the form of azeotropes, have been used for air conditioning and commercial refrigeration applications for approximately 40 years. There have been only very limited use of zeotropic refrigerants, e.g. R-400, which is a specialty binary mixture of CFC-12 and CFC-114, until recently. The first commercial zeotropes to find greater acceptability than specialty products were the ternary mixtures of R-22, R-152a and R-124, designated by ASHRAE as R-401A and R-401B.

These refrigerants were announced in 1989 and introduced as a commercial products in 1992. Since that time, several blends have been commercialized. The introduction of blends, particularly those with three or more components, has introduced new manufacturing problems to the refrigerant producers.

Blending Methods-Large Scale

For well established commercial blends such as R-507 or R-404A, the mixtures are made on a large scale using mixing tanks that are hard-piped from the component tanks. The measurements of the amounts of individual components are made with mass flow meters. The large blending tanks use eductors (stationary mixing devices) as well as dynamic pumping mixing to facilitate attaining a uniform blend in the tank. Dynamic mixing is accomplished by recirculation of the blend by pumps.

A typical blending scenario is to introduce the individual components of the mixture serially starting with the lowest vapor pressure component and progressing to the highest. There are exceptions to this progression which will be discussed later. The refrigerant blend is then mixed for a period of time. A liquid phase sample is then drawn off and sent to the laboratory for analysis. If the analysis is within the manufacturing specification, the mixture is available for packaging. If not within the manufacturing specification, the mixture is adjusted by adding calculated amounts of the deficient component(s). The process is then repeated, starting with the mixing, then the analysis, followed by readjustment if required.

The sampling procedure is very critical and if not done carefully can result in significant errors. Through experience, we have found that a flow-through sampling procedure yields the best results. The sampling cylinder (bomb) has valves at both ends and is located in a recirculating line downstream from the pump discharge. With the pump running, the downstream valve is closed followed by closing of the upstream valve. It is very important that the cylinder be completely filled with liquid. Fractionation into a vapor head space will give erroneous results, particularly for zeotropic blends with significant temperature glides.

For azeotropic binary mixtures such as R-507, adjustment is rarely needed, and when required the blend can almost always be brought within specification with a single adjustment. Near-azeotropic ternary mixtures like R-404A are somewhat more difficult, but the first mix is within specification about 80 percent of the time. The 80 percent rule seems to apply for this particular mixture, therefore 80 percent of the remaining 20 percent are brought within acceptable tolerances in the first adjustment. This means that 96 percent can be brought into specified tolerance with one or less adjustments and 99.2 percent with two or fewer adjustments.

Blending Methods-Small Scale

There are some commercial products that are either still in a transitional developmental stage or will only see limited usage because of specialized application. A product that falls into the developmental category is R-407C. This product has been identified as an alternative for HCFC-22 but does not appear to be the preferred replacement for the majority of applications. It is not an ideal match, but does offer approximately equal capacity in a system optimized for HCFC-22. The vapor pressure of R-407C in a typical air cooled condenser would be about 10 percent higher than that of HCFC-22. Due to the moderately high temperature glide, the heat transfer is negatively impacted. In retrofitted HCFC-22 systems, the operating efficiency tends to be about 5-10 percent lower than with the original refrigerant.

There are, however a limited number of products in the market which use R-407C. There is also some interest in retrofitting existing HCFC-22 systems to an HFC refrigerant, at least on a trial basis. As a result, there is a small, slowly emerging market for this refrigerant. In addition, there are other interim retrofit fluids which have limited acceptance but are requested by customers. For these products, the capital expense associated with large, hard-piped blending systems is not justified, and smaller, modular systems are preferred.

In order to meet the market needs without major capital expenditures and with an appropriately sized system **the authors use** relatively small, portable mixing tanks which allow movement around the plant grounds. These tanks have oversized mixing pumps but no stationary mixing devices. The mixing tank is moved to the area of the component storage and the components are added from ton tanks mounted on digital scales. Large hoses are used to connect the component tanks to the mixing tank. As market demand increases, these systems are replaced by permanent hard-piped systems.

It was mentioned earlier that the preferred sequence of blending is by vapor pressure of the components starting with the lowest pressure. This is done partially to reduce the pumping requirement of the addition of subsequent components, but more importantly to minimize the risk of reverse flow into the component tank. This backflow could render the component unusable for other mixtures or as a single component refrigerant because of contamination. An exception to this procedure is made when a minor component is used in a blend of three or more components. In this case the minor component is normally introduced last.

In the case of R-407C, the components are added starting with the lowest vapor pressure component (HFC-134a) followed by the HFC-125 and finally the HFC-32. Except for the initial mixture, one of the issues to be dealt with in making a subsequent batch is the amount and composition of the residual heel in the tank. As will be discussed later, this heel can be impacted significantly by temperature. The mixing process is performed by circulation of the product. The pumps draw the material from one end of the tank and return it to the other end. Experiments were conducted to determine the required mixing time. These studies led to the conclusion that a mixing time of 4 hours is close to optimum. Shorter mixing times resulted in unacceptable scatter in the analysis of the mixture, indicating incomplete mixing, and longer times offered no real improvement. Another system of a different design might require different mixing times. The use of oversized pumps facilitates the mixing procedure by creating higher velocities and a higher rate of product changes. Unfortunately, the large pump on a small tank adds heat at a high rate. Higher temperatures exacerbate the segregation of the product in terms of the liquid and vapor phase since the liquid density tends to decrease and the vapor density to increase with increasing temperature. Fluorocarbons tend to have high liquid coefficients of thermal expansion thereby it is important that adequate head space is provided at low temperatures so that the heat added in circulation doesn't result in 100 percent liquid fill, which can have catastrophic consequences.

Impact of Amount and Number of Components

The manufacture of binary blends is relatively simple. If analysis indicates that the composition needs to be adjusted, the procedure is straightforward, e.g. if a blend (A+B) is 59 percent of component "A" rather than the desired 60 percent it is easy to determine the amount and add it to achieve the desired ratio. In this example, it would be necessary to add 2.5 percent of the original targeted mixture weight, i.e. 59+2.5=61.5 which relative to the 41 percent of component "B" would yield a 60/40 ratio.

In the case of a blend containing three or more components, the addition of one component which is low can force another one which is within the specification to an unacceptable level. Consider 100 lb. of a three component blend where the desired ratio of components A, B and C is 30/40/30. Assume that analysis shows the actual composition of the blend to be 29/40/31. It is obvious that it is necessary to increase the amount of component A, but if 1.43 lb. of component A is added, the new ratio would be 30/39.44/30.56. The sum of B and C is correct but the quantities of each material deviate from the original requirement. In order to achieve the exact ratio desired, it would be necessary to add either individually or a mixture of 2 percent A plus 1.33 percent B which will result in a total amount 3.33 percent greater than the original targeted amount but in the correct ratio.

In general, the rule for addition of components is to (1) determine which component has the highest percentage of excess (component C in the above example); then (2) calculate the ratio of the actual percent to the desired percent for this maximum excess component (31/30=1.033). The sum of the additions of the other components must equal the difference in percentage, e.g. 3.3 percent of the original target quantity. Next (3) for each component multiply this percentage as a fraction times the difference between the desired percentage and the actual measured percentage. The following numerical example for a theoretical 4 component blend illustrates this procedure:

	Component A	Component B	Component C	Component D	Total
1) Desired Composition	10	20	30	40	100
2) Measured Composition	15	18	33	34	100
3) Ratio of Measured/Desired	1.5*	.9	1.1	.85	(* greatest excess)
4) Fraction (0.5) X Row 1	5	10	15	20	
5) Desired Minus Measured (1-2)	-5	2	-3	6	
6) Amount to Add Row 4 + Row 5	0	12	12	26	
7) New Total Row 2+ Row 6	15	30	45	60	150

Table 1

Tolerances

In the previous paragraphs, we have discussed blend ratios as if the objective were to manufacture refrigerant mixtures at exactly the nominal composition. In commercial practice, it is necessary to have realistic tolerances on the composition. By realistic, we mean that the composition variability should be small enough that performance variations are imperceptible and the allowable range of compositions is large enough that the product can be manufactured economically. Performance variation is not limited solely to refrigeration system capacity and efficiency. It also includes safety characteristics such as flammability and toxicity properties and reliability characteristics such as lubricant miscibility and compressor discharge temperature.

There are more than one set of tolerances which apply to refrigerants. ARI[2] specifies acceptable levels of contaminants, e.g. water, acidity etc. which apply to all types of refrigerants, whether single component, azeotropic or zeotropic. ASHRAE[1] includes composition tolerances for mixtures although historically they were not included for azeotropes. Individual manufacturers however, frequently have sales specifications which incorporate tolerances which are more restrictive than those permitted by the ASHRAE standard. These tighter tolerances may be governed by customer requirements or other marketing concerns. Furthermore, it is common for a producer to have manufacturing tolerances which are held even closer to the nominal composition than the sales specification permits. This is done to insure that the product that is sold meets the sales specification allowing for some composition shifting during packaging and variability in instrumentation and measurement techniques.

Historically, ASHRAE did not specify composition tolerances for blends, but Underwriters Laboratories required producers to specify sales tolerances of mixtures for Classification. Until recently these blends were limited to binary azeotropic mixtures with the exception of minor amounts of R-400, which is also a binary mixture but not an azeotrope. As ternary mixtures were submitted to ASHRAE, specifications including tolerances were established. Manufacturers of refrigerants have the option of establishing internal specifications which are tighter than the limits defined by ASHRAE. The degree of fractionation will impact the composition of the liquid which is used to fill individual packages for sale. For example, R-401A and 401B were somewhat difficult to produce because of the moderate temperature glide combined with the use of three components. As a result the tolerance band for each component was set at 2.0 percent. In this case the composition tolerance for the flammable component (HFC-152a) was set at +0.5, -1.5 percent. It became common practice to set tolerances of ± 2.0 for non-flammable components and ± 1.0 for any flammable components. In the case of refrigerants with a minor component, such as R-402A, where the nominal propane composition is only 2 percent, it seems reasonable that producers would self impose tighter tolerances than the ASHRAE limits.

Initially, the tolerances for R-407C were established based on the common practice cited above. It appears that there was some difficulty in producing this particular refrigerant and that the problem was not endemic to one producer because it was proposed and consensus reached that the ASHRAE tolerance be relaxed to ± 2 percent on all components. The justification was that the impact on performance was minimal and there was adequate safety factor with regard to flammability. This proposal was approved by the Standing Standard Project Committee and is out for public review at the time of this writing. As discussed in the subsequent paragraphs, the fractionation characteristics of this refrigerant require more stringent manufacturing tolerances to insure that the final product is within specification. To minimize performance variations due to composition variance, it is reasonable to suggest that the final product sales specification should be held closer than the ASHRAE limits. Compared to the 80 percent initial composition within tolerance for R-404A, this refrigerant has an initial hit rate of closer to 35 percent. This means that the time to produce a single batch can range from less than one day up to a week based on having to mix, analyze, adjust and reanalyze etc.

As mentioned above, one of the additional issues to deal with in the production of zeotropes is the composition shift as the refrigerant is removed from the mixing tank. Since, at the present time, R-407C is not used on a large scale, most of the requirements are for small packages of the type used by service personnel. As the mixing tank is depleted by withdrawal of liquid into the small packages, the composition of the residual refrigerant continually changes toward one richer in the lowest vapor pressure component (in this case, HFC-134a). This means that if one starts with a full tank of a blend that is within the specified tolerance, at some point the liquid being withdrawn will no longer be within the specification. The composition shifting effect is related to the difference between the liquid and vapor composition in equilibrium. This is also related to the temperature glide of the mixture. The higher the glide, the more composition shifting occurs during drawdown.

A method to predict this shifting of composition was developed by Kim and Didion[3]. Using this technique allows prediction of the point at which drawdown should be terminated. During packaging, the process is closer to isothermal than adiabatic and therefore the modeling should simulate an isothermal liquid leak. The modeling of the shifting of the composition leads to the conclusions that the yield can be increased by deliberately starting with a composition rich in the low boiling constituents. An effective technique is to start with a composition which is about 0.5 percent high in both HFC-32 and HFC-125 with a corresponding reduction of 1 percent in the HFC-134a component.

The remaining mixture (heel) which is left in the mixing tank also creates problems since it is essentially a partial batch of the zeotropic mixture which is out of specification and the composition must be adjusted to bring it back within the tolerances. This is further complicated by the uncertainty of the exact weight of the heel. This weight can be calculated by the difference between the estimated weight of the original batch and the estimated weight of the amount withdrawn in the packaging process.

Conclusions

The introduction of zeotropic refrigerants in significant quantities has introduced new issues for refrigerant producers. The issue of greatest concern in the production of these blends is maintenance of product composition within specifications. R-407C has demonstrated this particular issue to a greater extent than most of the other zeotropes although any mixture with a comparable glide would be expected to have similar characteristics. Specific items that need to be addressed include:

- The complexity of blend formulation is increased substantially with increased number of constituents. Binary blends are much easier to control than ternary mixtures.
- Higher glide of zeotropic mixtures increases the difficulty of controlling the composition.
- Careful selection of tolerances is critical. Composition must be consistent enough that performance is not impacted, yet specifications must be realistic so that the product can be made economically.
- A significant impact on yields can be realized by carefully selecting a deliberate offset from the nominal composition. This offset is such that the composition shifting initially moves toward the nominal composition.
- The heel left in the mixing tank after drawdown for packaging creates another concern for the manufacturing plant to address.

All of these concerns are solvable problems, but they definitely add complications to the manufacturing plant that, only a few years ago, were not even minor issues.

References

1. ANSI/ASHRAE Standard 34-1992, *Number Designation and Safety Classification of Refrigerants,* American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc., Atlanta, Georgia, 1992.

2. ANSI/ARI Standard 700-95, *Specifications for Fluorocarbon Refrigerants,* Air-Conditioning and Refrigeration Institute, Arlington, Virginia, 1995.

3. Kim, M.S. and Didion, D.A., *Simulation of Isothermal and Adiabatic Leak Processes of Zeotropic Refrigerant Mixtures,* International Journal of Heating, Ventilating, Air-Conditioning and Refrigerating Research, January, 1995, p. 3-20.