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PRELIMINARY ASSESSMENT OF CONDENSATION BEHAVIOR
FOR HYDROCARBON-VAPOR EXPANSIONS WHICH CROSS
THE SATURATION LINE NEAR THE CRITICAL POINT

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I. SUMMARY

1. Background

Previous analyses of binary cycles for conversion of geothermal energy from moderate temperature resources to electrical energy (Reference 1) have shown potential gains in net geofluid effectiveness of on the order of 8%, resulting from selection of turbine-expansion processes whose equilibrium states pass through the two-phase region (assuming major condensation does not occur). If condensation occurs, this gain could be reduced or eliminated by the resulting loss in turbine efficiency. Experience with many fluids, however, indicates that vapor supersaturation (or subcooling) permits metastable pure-vapor states to exist at temperatures considerably below the saturation temperature at a given pressure; thus, by better understanding the condensation process, and properly structuring the cycle, substantial performance gains may be achievable.

The purpose of the present study was to assess, qualitatively, the probability for attaining this performance gain.

2. Approach

Overall, the study adopted a bounding approach intended to "bracket" effects and check magnitudes. The first step was to estimate the extent of condensation which might be expected during the expansion of isobutane (or similar hydrocarbon) vapor if the equilibrium state points describing the process cross the saturation line within a few percent of the critical temperature. Second, the probable effects on turbine performance of such expansion processes were examined.

The specific approach for predicting the onset of condensation during hydrocarbon turbine expansion processes entailed utilizing existing vapor supersaturation data obtained for other fluids, and based on differences in fluid properties, assessing the behavior of working fluids of interest here. Isobutane was selected as a typical working

fluid, and turbine expansion processes were considered which start at 280°F (a slightly supercritical temperature) and at entropies near the critical entropy. Predictions of condensation were made based on two points of view. The first of these consisted of a droplet-vapor equilibrium assessment using the observed "Wilson Line" for steam condensation in describing the limiting values of water vapor subcooling. For this approach the Kelvin-Helmholtz expression, relating vapor pressure and fluid properties to the droplet size which is in equilibrium with the vapor (Reference 2) was modified and applied to isobutane vapor. Second, a corresponding states correlation of the vapor subcooling behavior of a number of fluids, by Lienhard and Karimi (Reference 4), was used.

The effects on turbine performance of an expansion process whose equilibrium states "pass through" the two-phase region were estimated, assuming no condensation, using thermodynamic properties for the metastable vapor region based on extrapolations from equilibrium properties both near the beginning and near the end of the expansion process. Further, it was reasoned that if an isentropic expansion begins and ends at state points corresponding to stable equilibrium for pure vapor, and no condensation occurs, the change in enthalpy for the process is not influenced by passage of the equilibrium states through the moisture region.

3. Conclusions

Several conclusions have been reached as a result of the preliminary assessments made.

- a) Turbine expansion processes which cross the saturation line at the critical point are expected to show some condensation. As the entropy at which the process state points cross the saturation line increases, the tendency for maintaining a pure-vapor expansion increases.

- b) Condensation may not occur (except on the channel walls) during expansion processes of interest for binary geothermal cycles using hydrocarbon working fluids; these processes would cross the saturation line at entropies somewhat above the critical value. If condensation does occur, it is expected to occur early in the process (near the saturation line), and remain in the form of very fine droplets (fog), which tend to evaporate as the expansion continues.
- c) Turbine performance should not be degraded significantly as a result of equilibrium states of the turbine expansion passing through the moisture region if condensation does not occur, and should remain acceptable even if limited amounts of early condensation occur. Thus, a large fraction, or perhaps essentially all, of the gain in geofluid effectiveness of 8%, identified previously, is potentially achievable by proper structuring of the thermodynamic cycle.
- d) Nozzle condensation experiments and turbine performance testing are recommended for more quantitative evaluations of hydrocarbon turbine expansions in the metastable region of interest for binary geothermal cycles.

II. INTRODUCTION

Binary thermodynamic cycles used in the conversion of geothermal to electrical energy commonly utilize hydrocarbon working fluids (pure fluids or mixtures); the cycles generally have been structured such that equilibrium states in the turbine expansion processes avoid the two-phase region. Such a cycle is represented schematically by the temperature-entropy diagram in Figure 1 as state points 1, 2, 3, 4, 5, 1. It has been recognized that if no condensation occurs during expansion through the turbine, plant net geofluid effectiveness (watt-hours net plant output/lbm geofluid), and therefore cost of power, might be improved by allowing the equilibrium states for the turbine expansion process to "pass through" the moisture region with the turbine exhaust state falling on the saturation line or in the pure vapor region. This modified cycle is also shown in Figure 1 as points 1, 2, 3', 5, 1. Analyses of mixed-hydrocarbon binary cycles (Reference 1), for example, predicted an increase in net geofluid effectiveness of about 8% for a 96% isobutane/4% heptane mixture with this type of turbine expansion. (For that expansion the equilibrium states crossed the saturation line near the critical point.) Relative thermal efficiencies for cycles utilizing these two types of turbine expansion depend on the working fluid, but for the example cited, thermal efficiencies were essentially equal. Geofluid effectiveness, however, being proportional to thermal efficiency times the enthalpy change of geofluid, was improved because of the ability to remove more energy from the geofluid when the expansion "passes through the moisture region". This situation is illustrated by the temperature-heat exchanged diagram in Figure 2 which shows that for a given pinch point in the working-fluid vaporizer, the cycle whose turbine expansion passes through the moisture region requires less heat addition and allows the geofluid to be exhausted at a lower temperature with a greater enthalpy change. The cycle was correspondingly improved since turbine-exhaust desuperheating was not required, and less energy had to be rejected to the atmosphere.

A major question which must be addressed relative to attaining this improvement in performance is: "Can the stable-equilibrium states of a turbine expansion process pass through the two-phase region without resulting in sufficient condensation to reduce turbine performance,

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Figure 1. Binary Cycles Showing Two Types of Turbine Expansion

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Figure 2. Temperature Versus Heat Exchanged During Working Fluid Vaporization For Two Types of Turbine Expansion

measurably, and/or to produce turbine damage?"

Water condensation in steam turbines has been moderately well characterized; a so-called "Wilson Line" has been used frequently for estimating the extent to which supersaturated water vapor can be maintained (without condensation) in a near-isentropic expansion. For water, the Wilson Line is displaced in enthalpy about 55 Btu/lbm below the saturation line on an enthalpy-entropy diagram as sketched schematically below. (This line is actually a "band" since the supersaturation limit, even for a "clean" vapor, has been found to be influenced by the time rate of vapor expansion.)

WILSON LINE FOR STEAM

The Wilson Line is normally of interest, and accordingly, is presented at conditions well below the critical temperature. The prediction of hydrocarbon vapor supersaturation limits at conditions of interest can be expected to entail major uncertainties since those conditions (for hydrocarbon turbines in geothermal plants) are different from normal steam-turbine conditions in several respects, and in general, are less well defined. First, for a steam turbine, condensation generally takes place at temperatures and pressures far from the critical values; the hydrocarbon turbine expansion would "cross" the saturation line near the critical point (perhaps within two or three percent of the critical temperature). Second, for an expansion process in a steam turbine, the water tends toward higher moisture content as the expansion proceeds, whereas for some of the more commonly considered hydrocarbons, such as

isobutane, the moisture content first tends to increase, but then tends to decrease and vanish as the expansion proceeds. This behavior is illustrated by the turbine expansion line 3', 5 in Figure 1. Third, properties of the hydrocarbons are different from those of water, and particularly in the region near the critical point, are less well known.

Four types of fluid behavior can be considered for turbine expansions in which the equilibrium states enter the two-phase region:

1. The fluid maintains its metastable, pure-vapor state while in the turbine (no condensation, vapor is supersaturated); the stable-equilibrium turbine-exhaust state is pure vapor.
2. The fluid maintains its metastable pure-vapor state while in the turbine, but the stable-equilibrium turbine-exhaust state is two-phase.
3. Some condensation occurs in the turbine; the stable equilibrium turbine-exhaust state is pure vapor.
4. Some condensation occurs in the turbine; the stable equilibrium turbine-exhaust state is two-phase.

By examining these types of fluid behavior, the present effort is intended to serve as an initial step toward the evaluation of gains in cycle performance attainable with such turbine expansions, relative to potential gains suggested in Reference 1. Favorable conclusions would provide support for subsequent evaluation steps which might include nozzle expansion experiments, and small scale turbine testing. Specific objectives of this effort are:

- (1) to qualitatively assess the likelihood and extent of condensation occurring during the expansion of isobutane vapor through a turbine in which the state points describing the process cross the saturation line within a few percent of the critical temperature, and

- (2) to consider the probable effects on turbine performance of expansion processes in which the stable-equilibrium state points enter the moisture region.

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III. PREDICTION OF ONSET OF CONDENSATION

The basic approach adopted for prediction of the onset of condensation during the hydrocarbon turbine expansions of interest involves the extension of experimental vapor supersaturation (or subcooling) information obtained for other working fluids (water, for example). As far as is known sufficient thermophysical and condensation-kinetics properties do not exist for direct prediction of supersaturation limits for hydrocarbon vapors, particularly near the critical point. For this initial evaluation, isobutane was selected as a good candidate for a hydrocarbon working fluid; for the present, other hydrocarbons represented by similar equations of state are assumed to behave qualitatively the same relative to condensation. Ultimately, of course, condensation behavior and its consequences must be evaluated for hydrocarbon mixtures, which are of prime interest because of their ability to produce high cycle performance.

The condensation question was addressed here from two somewhat different viewpoints: (1) consideration of droplet-vapor equilibrium conditions, and (2) use of corresponding states correlations of existing condensation data.

1. Droplet-Vapor Equilibrium Assessment

The change from the metastable (pure vapor) state (which exists just after the vapor expanding in the turbine crosses the saturation line) to the stable-equilibrium state (which contains both vapor and liquid phases in equilibrium) must begin with the formation of a small amount of the liquid phase. This initial liquid phase can form by vapor condensing on existing foreign solid or liquid surfaces, but for the homogeneous nucleation process being considered here, it has been stated by Keenan (Reference 2) in describing initiation of condensation: "It is probably that chance groupings of two or more molecules are the nuclei for condensation".

Kelvin-von Helmholtz Relationship - To estimate the mass of a

liquid droplet that will serve as a nucleation site for continued condensation, Keenan presents an approach due to Kelvin and von Helmholtz relating the pressure of the vapor which is in equilibrium with a curved droplet surface (at a given temperature) to the fluid and droplet characteristics (radius, surface tension, saturation pressure, and ratio of saturated liquid to saturated vapor specific volumes). One form of this relationship, given in Reference 2, is:

$$\ln \left(\frac{P_{\text{cond}}}{P_{\text{sat}}} \right) = \frac{2 \sigma v_{\text{SL}}}{P_{\text{sat}} r v_{\text{SV}}} \quad (1)$$

where: P_{cond} is the pressure of the vapor in unstable equilibrium with the liquid droplet at a given temperature.

P_{sat} is the saturation pressure of the vapor at the given temperature.

σ is the surface tension of the liquid in equilibrium with its vapor at the given temperature.

v_{SL} and v_{SV} are the specific volumes of the saturated liquid and vapor of the fluid at the given temperature.

r is the droplet radius.

This relationship (with an added correction to surface tension accounting for the pressure drop across the liquid-vapor interface) along with the observed condensation behavior for water, formed the basis for Keenan's conclusion, that for water, the droplets which have served as nucleation sites for condensation are sufficiently small to contain only a very few (on the order of two) molecules.

Some Probabilistic Considerations - Equation (1) predicts that at a given temperature, condensation will occur closer to the saturation pressure (resulting in less vapor subcooling) as the droplet size increases. Probabilistic considerations, however, suggest that

the rate of chance grouping of larger numbers of molecules (forming larger drops for nucleation sites) should be slow relative to the formation of drops containing two or three molecules. If Keenan's phenomenological description of the homogeneous nucleation and condensation process for metastable vapors is valid, one must conclude that for the observed condensations of water vapor (by homogeneous nucleation), rates of subcooling, generally, have been sufficiently fast that the vapor pressure required for condensation on the smallest nucleation droplets is reached before significant numbers of larger groupings of vapor molecules occur. In other words, the most probable droplet resulting in homogeneous nucleation of the condensation process contains only a few (on the order of two) molecules as opposed to a large number.

Condensation Predictions for Isobutane - To predict the super-saturation (or vapor subcooling) limit for isobutane near the critical point, Equation (1) was used first to estimate the droplet size which would have provided nucleation sites for water corresponding to a typical point on the Wilson Line (about 55 Btu/lbm lower than the saturation enthalpy at a given entropy). A droplet radius of 2×10^{-8} in was calculated.

Next, the relationship described by Equation (1) was rederived to include a term involving the ratio of liquid specific volume to vapor specific volume. Generally, this term can and has been neglected, but for condensation conditions near the critical point where the specific volume ratio can reach 0.5, the effect on the required pressure for condensation is not negligible; Figure 3 shows the results of the modified derivation. Equation (1) corresponds to the curve on Figure 1 labelled $\frac{v_{SL}}{v_{SV}} = 0$. The quantities and notation shown on the figure are the same as discussed for Equation (1).

**Figure 3. Effects of Fluid Properties
and Droplet Radius on Condensation Pressure**

At this point in the prediction of condensation, the amount by which the condensation pressure for the expanding metastable vapor exceeds the saturation pressure, can be estimated at a given temperature (from Figure 3). It remains to determine the pressure of the vapor as a function of temperature during its isentropic expansion, based on estimated metastable-vapor properties, and then at each of several temperatures, to compare these pressures with the pressures at which condensation is expected. The specific procedure followed was to select four initial vapor states for the expansion processes. These states were defined by a temperature of 280°F (slightly supercritical) and four entropies (1.1725, 1.1667, 1.642, and 1.612 Btu/lbm°F) which correspond to saturated vapor temperatures of 150, 110, 90 and 60°F. The expansions examined followed these isentropes from the initial states into the two-phase region as illustrated, conceptually, on the left-hand half of Figure 4. The isentropes leave the two-phase region at the four saturated vapor temperatures listed above. Along each of the four isentropes several temperatures were selected, and corresponding pressures calculated (assuming no condensation occurred) using the relationship

$\frac{P}{P_i} = \left(\frac{T}{T_i}\right)^{k/(k-1)}$, where P_i and T_i are the initial pressure and temperature, and P is the pressure corresponding to one of the selected temperatures, T . The exponent $k/(k-1)$ was estimated from the variation of pressure with temperature along each of the isentropes near the initial state points using properties predicted by THERPP (Reference 3). At each temperature, the vapor pressure at which condensation would be predicted to occur was also found using the modified Kelvin-Helmholtz relationship shown on Figure 3. In applying Figure 3, values of v_{SL} , v_{SV} , P_{sat} and surface tension were found for isobutane for each temperature selected, and the value of the isobutane droplet radius, r , was determined which contains the same number of molecules as does the 2×10^{-8} inch radius water droplet (found to correspond approximately to the Wilson Line observed for water).

Figure 4. Estimates of Pressure Increments
Below Condensation Pressure For
Dry Isentropic Expansions of Isobutane

Results of Condensation Estimates - The right-hand half of Figure 4 shows two sets of pressure differences. The first set ($P_{\text{sat}} - P$) consists of estimates of the difference between the saturation pressure at a given temperature and the pressure of the metastable pure vapor at that temperature calculated using the exponents, $k/(k-1)$. The second set ($P_{\text{cond}} - p$) shows estimates of the difference between the pressure required for condensation at the given temperature, and the pressure of the metastable vapor calculated at that same temperature. Both sets of pressure differences were estimated for each of the four isentropes listed in the previous paragraph.

The values of $\Delta P = 0$ for the $P_{\text{sat}} - P$ curves should correspond to the intersections of the four isentropes with the saturation line (left-hand half of Figure 4). The apparent discrepancy in this regard is believed to be the result of describing the four isentropic expansion processes as $P = T^{k/(k-1)}$ assuming that $k/(k-1)$ remains constant along each expansion. Near the critical point, as is the case here, the extrapolation used is not adequate for accurate state point calculations. The $P_{\text{sat}} - P$ curves illustrate, however, that during each of the four isentropic vapor expansions, the vapor pressure starts somewhat below the saturation pressure level, next reaches the saturation pressure (entering the metastable range of state points), and finally for the portion of the expansion shown, tends to keep increasing slightly relative to the saturation pressure. The vapor pressure would eventually be expected to approach the saturation pressure again as the expansions continue toward the saturation temperatures. Overall, the curves suggest that the vapor pressure remains relatively close to the saturation pressure during these expansions.

The $P_{\text{cond}} - P$ curves shown in Figure 4 indicate that the values of vapor pressure remain lower than the pressure required for condensation during the entire expansion processes for the four

initial states chosen. This result suggests that condensation may not occur at all; the curves indicate that the tendency for condensation reduces as the expansion proceeds. Note that this predicted behavior is quite different from that of water in conventional steam turbines.

Interpretation of Results of Estimates - The interpretation reached for these results is that if a turbine expansion process crosses the saturation line at the critical point, some condensation might be expected. If the process crosses the saturation line at a higher entropy (lower temperature) than critical (see Figure 4) condensation may not occur. If some condensation does form early in the expansion, it would be in the form of very fine droplets which will immediately begin to lag in temperature, relative to the continuously decreasing vapor temperature, as the expansion continues. The droplets, being higher in temperature than the vapor, will no longer be able to serve as condensation sites, and new sites would have to form if additional condensation were to occur. Thus, any droplets formed should remain very small, as in a very fine fog. Figure 4 suggests that the tendency for condensation decreases markedly as the temperature drops farther from the critical temperature, and so only a very limited amount of condensation (or no condensation) may occur for the turbine expansions of interest here. As will be discussed later, expansion processes whose final equilibrium states fall in the single-phase vapor region would be expected to include some evaporation of existing droplets during the final portions of the expansions.

2. Corresponding States Correlations

Lienhard and Karimi (Reference 4) have conducted corresponding states correlations of a large number of experiments in which vapor subcooling and condensation occurred for different fluids under different experimental conditions. The fluids include water, ammonia, nitrogen, chloroform, freon, ethanol, benzene

alkanes, and alkylbenzenes. The condensation processes occurred in nozzles, shock tubes, and diffusion cloud chambers. Condensation temperatures ranged up to about 60 percent of the critical temperatures. (Reference 4 points out that several kinetic theories describing homogeneous nucleation exist, but to apply the theories, experimentally determined nucleation rates are needed. These rates are stated to range from 10^2 to $10^{18}/\text{cm}^3\text{sec}$ for conditions where no condensation occurs to conditions where condensation is certain to occur. This range is large, and as far as is known, experimental values do not exist for isobutane vapor, or similar hydrocarbons, near the critical point.) One topic addressed in Reference 4 was to see how closely the most severe transients, tending to produce condensation, approach the limit of the metastable range for vapor subcooling. This metastable range of state points can be visualized on a pressure-volume-temperature surface as falling between the temperature of saturated vapor at a given pressure and the temperature at that pressure, defined by $\frac{\partial p}{\partial v} = 0$, $\frac{\partial^2 p}{\partial v^2} < 0$ where the temperature, T , is held constant for both partial derivatives.

Description of Vapor Subcooling Correlation - The correlation of vapor subcooling limits is shown in Figures 2 and 3 of Reference 4 as the difference between the reduced temperature (T/T_{critical}) at which condensation occurred and the reduced saturated vapor temperature at the same pressure, plotted as a function of reduced saturated vapor temperature. Also shown on these figures, and plotted in the same form, is the lower temperature limit of the metastable range for vapor subcooling, $\left. \frac{\partial p}{\partial v} \right|_{T = \text{const}} = 0$, as calculated

using the van der Waals equation of state. (This line is referred to as a locus of "spinodal" points in Reference 4.) The correlation shows all of the data points falling between the lines defining the temperature limit for the metastable range and the saturation temperature, but closer to the saturation line. (Reference 4

suggests that a possible reason for these condensation data points not appearing to lie closer to the limit of the metastable region may be related to imperfect reduction of data because of incomplete knowledge of thermophysical properties in the metastable region.)

Interpretation of Correlation - Figure 2 of Reference 4 illustrates that the temperature range of the metastable region vanishes at the critical point; the correlation shown suggests that if the vapor expansion process in a turbine passes through the critical point, no vapor subcooling should occur, and condensation should start immediately. If the expansion crosses the saturation line at an entropy higher than (but near) the critical entropy, then some vapor subcooling might be expected. These interpretations are in general agreement with those based on the droplet-vapor equilibrium assessment discussed in the previous section.

IV. EFFECTS ON TURBINE PERFORMANCE

The second objective of the present effort was to consider the possible impact on turbine performance of utilizing the class of turbine expansions whose equilibrium states pass into the moisture region. As discussed earlier, it is believed that condensation (by homogeneous nucleation) may not occur if the expansion crosses the saturation line at entropies higher than the critical entropy (the vapor would pass through a range of metastable states during the process). Some condensation would be expected on the walls of the flow passages; however, the major fraction of the fluid does not interact directly with the walls, and in the absence of solid or liquid contaminants, could remain in a pure vapor state. It is the effect on turbine performance of the behavior of the fraction of the turbine flow not directly contacting the walls which is being considered here. Several conditions are considered and discussed below.

1. No Condensation in Turbine

Two situations come to mind for which condensation does not occur within the turbine. First, the equilibrium state at the turbine exit may be two-phase, and second, the equilibrium exit state may be pure vapor (saturated or superheated).

Equilibrium Exit State is Two-Phase - For this condition the actual turbine exit flow (assumed to be pure vapor in a metastable state at a pressure established by the condenser) would be expected to have a higher enthalpy than would exist for the stable equilibrium condition since no reduction in enthalpy associated with condensation would have occurred. Therefore, for the same turbine inlet enthalpy, the turbine work (Δh) would be smaller for the metastable vapor expansion than for an equilibrium expansion (two-phase). Accurate assessments of turbine work under these conditions (metastable vapor expansion) require knowledge of thermodynamic properties in the metastable region, and have not been made. An indication of the high

sensitivity of turbine work to the method of estimating properties is illustrated by Table 1 in the following section. Superficial consideration has not revealed reasons to expect major benefits to be realized with this category of turbine expansion; therefore, it has not received further consideration in this study.

Equilibrium Exit State is Single-Phase Vapor - An example of this expansion process is one in which the equilibrium state at the turbine exit lies on the saturated vapor line. Isobutane or hydrocarbon mixtures which are predominately isobutane, would constitute working fluids for which this type of turbine expansion shows potential benefits. As mentioned in the introduction, a 96% isobutane/4% heptane mixture employing this expansion process has shown a potential increase in net geofluid effectiveness of about 8%, relative to a turbine expansion which "avoids" the two-phase region (Reference 1). This comparison assumed no condensation and no penalty to turbine work associated with "passing through the two-phase region".

A question which must be answered for this case is "How would the work produced by a turbine expansion process (Δh) which remains single phase (metastable vapor states) compare with the work produced by a hypothetical isentropic process which follows stable equilibrium states (two-phase), and terminates at the saturation line?" Both processes start at the same turbine inlet state, and expand to the same downstream pressure. No penalty in efficiency associated with the presence of moisture in the two-phase equilibrium expansion is to be applied.

The first approach taken to answer this question was to estimate ideal turbine work based on an expansion of metastable isobutane vapor, and to compare the work with that of a corresponding stable-equilibrium expansion.

Properties for the metastable region were estimated by "extrapolating" equilibrium properties from the initial state

point ($P = 535.47$ psi, $T = 380^\circ\text{F}$) and separately from the terminal point ($P = 59.66$) of the two-phase equilibrium expansion. (It was subsequently concluded, as discussed in the next section, that for this specific comparison the turbine work for the two processes should be identical. The results shown here (Table 1) have been included primarily to provide an indication of, and to document, the sensitivity of turbine work to the specific properties estimated for the metastable region.)

Three approaches were used for the extrapolation of the thermodynamic properties and calculations of enthalpy changes. These are:

$$(1) \quad \frac{P_2}{P_1} = \left(\frac{v_1}{v_2} \right)^k \quad \text{where } k \text{ was evaluated from:}$$

$$k = \left. \frac{\partial \ln p}{\partial \ln v} \right|_{S = \text{const}} = \frac{c_p}{c_v} \left. \frac{v}{p} \frac{\partial p}{\partial v} \right|_{T = \text{const}},$$

$$\text{and } h_1 - h_2 = \int_{P_2}^{P_1} v dp$$

$$(2) \quad \frac{P_2}{P_1} = \left(\frac{h_2}{h_1} \right)^{k/(k-1)} \quad \text{where } k/(k-1) \text{ was evaluated from:}$$

$$\frac{k}{k-1} = \left. \frac{\partial \ln p}{\partial \ln h} \right|_{S = \text{const}} = \frac{h}{p} \left. \frac{\partial p}{\partial h} \right|_{S = \text{const}} = \frac{h}{p} v,$$

$$\text{and } h_1 - h_2 = h_1 \left[1 - \left(\frac{P_2}{P_1} \right)^{(k-1)/k} \right]$$

$$(3) \quad \frac{P_2}{P_1} = \left(\frac{T_2}{T_1} \right)^{k/(k-1)} \quad \text{where } k/(k-1) \text{ was calculated from:}$$

$$\left. \frac{k}{k-1} = \frac{\partial \ln p}{\partial \ln T} \right|_{S = \text{const}} = \left. \frac{T}{p} \frac{\partial p}{\partial T} \right|_{S = \text{const}} = \left. \frac{T}{p} \frac{\partial s}{\partial v} \right|_{p = \text{const}}, \text{ and}$$

$$h_1 - h_2 = h_1 - h_{\text{sat vap at } p_2} - C_{p \text{ sat vap at } \bar{T}_2} \left[T_1 \left(\frac{p_2}{p_1} \right)^{(k-1)/k} - T_{\text{sat vap at } p_2} \right]$$

$$\text{where } \bar{T}_2 = \frac{T_2 + T_{\text{sat vap at } p_2}}{2}.$$

This value of $h_1 - h_2$ is equivalent to the enthalpy change of the two-phase equilibrium isentropic process ($h_1 - h_{2 \text{ sat vap at } p_2}$),

corrected for the enthalpy difference corresponding to the difference in temperature between the saturated vapor at the final pressure (p_2) and the metastable vapor at the same pressure. The enthalpy correction (at constant pressure) was estimated based on saturated vapor specific heat at an average of the two final temperatures ($\bar{T}_2$).

The various partial derivatives used in the three approaches were evaluated from tabular output of the computer program THERPP (Reference 3) for isobutane. Values of Δh based on the three approaches are tabulated below, in Table 1, along with exponents k and $k/(k-1)$ as determined from equilibrium vapor properties at the initial and final states of the two-phase equilibrium expansion. (Note that for the isentropic expansions of a perfect gas, k corresponds to the ratio of specific heats for the three approaches described above).

Table 1. Enthalpy Changes for Three Approximations to a Metastable Isentropic Expansion Process for Isobutane

	Definition of Process		
	$\frac{p_2}{p_1} = \frac{v_1^k}{v_2^k}$	$\frac{p_2}{p_1} = \frac{h_2^{k/(k-1)}}{h_1^{k/(k-1)}}$	$\frac{p_2}{p_1} = \frac{T_2^{k/(k-1)}}{T_1^{k/(k-1)}}$
Exponent Determined at Initial Condition (280°F)			
Exponent	0.718	15.28	5.78
k	0.718	1.07	1.21
$\Delta h(\text{Btu/lbm})$	34.0	19.9	50.3
Exponent Determined at Final Condition (90°F)			
Exponent	0.874	7.04	10.11
k	0.874	1.17	1.11
$\Delta h(\text{Btu/lbm})$	25.2	39.9	10.55
Δh_{ave}	29.6	29.9	30.4

Note: Δh for the corresponding two-phase equilibrium isentropic expansion is 31.8 Btu/lbm.

Table 1 suggests that the exponent describing an isentropic expansion of the type shown (starting near the critical point) varies substantially during the process, and even at a given pressure and temperature, must take on greatly different values when expressing the relationships between different thermodynamic variables for the process. Corresponding values of Δh are sensitive to the different exponents, and cannot be used with confidence for estimation of turbine performance. A better approach, if needed, would be to use properties based on extending the range of application the equation of state (Starling's modified Benedict-Webb-Rubin equation of state is used in THERPP, Reference 3) beyond the saturation line and approaching, as a limit, the line of $\frac{\partial p}{\partial v} \Big|_{T = \text{const}} = 0$,

$$\frac{\partial^2 p}{\partial v^2} \Big|_{T = \text{const}} < 0. \text{ It might be noted in passing that averages}$$

of the two values of Δh shown in Table 1 (Δh_{ave}) for each of the three approaches illustrated, are in moderate agreement with each other and with the Δh for the comparable two-phase stable equilibrium isentropic expansion.

Effects on Turbine Performance of Expanding "Through the Moisture Region" - A problem and/or question which might be suggested by the results of Table 1 is as follows: Hypothesize an isentropic expansion process for a 100% efficient turbine which starts in a pure vapor state, passes through the two-phase region, maintaining stable equilibrium conditions, and ends on the saturated vapor line. In the two-phase region some condensation occurs for this process, followed by evaporation until no liquid remains at the final point of the expansion. Does a second isentropic (reversible adiabatic) expansion maintaining metastable equilibrium conditions (having no condensation), which starts at the same pressure and temperature and ends at the same pressure as did the first expansion, reach the same final temperature as for the first expansion? Does the second expansion experience the same enthalpy change as did the first process?

If the expansion (for the 100% efficient turbine) through the metastable region does not experience condensation, that process will be reversible (and adiabatic); therefore, the entropy as well as pressure at the final state should be the same for the two processes (since the initial entropies were equal). The given substance, isobutane vapor for this example, must have unique values of temperature, enthalpy, volume, etc., for given values of pressure and entropy. The enthalpy change for the two processes, therefore, must be the same. The significance of this conclusion is that turbine expansion processes which "pass through the moisture region" without condensation, but whose equilibrium states terminate in the vapor region, should not experience degradations in turbine work (relative to those expansions which "avoid the moisture region"). Therefore, if no condensation occurs, turbine performance can be estimated by correcting the isentropic Δh as determined from the stable-equilibrium initial and final state points, and applying a turbine efficiency in the conventional manner. Under these conditions the entire 8% performance gain, discussed in the Introduction, would be attainable.

2. Condensation Occurs in Turbine

Two cases were considered, qualitatively, in which condensation occurs in the turbine: first, the turbine exit condition at equilibrium falls in the pure vapor region, and second, the equilibrium exit condition falls in the two-phase region.

Dry Turbine Exit Condition at Equilibrium - The more important of these two cases is the one in which the turbine expansion is selected such that the process crosses the saturation line near the critical point and some condensation occurs, but the equilibrium state for the turbine exit falls in the pure vapor region.

Under these conditions the condensation which occurs should take place near the saturation line. As discussed earlier, the condensate should exist as a very fine "fog", since once the droplets form their temperature should lag behind the falling vapor temperature, and further condensation on the initial droplets would not occur. New nucleation sites could form, but again, droplets would remain minute. As the expansion proceeds, droplet vaporization will tend to occur. The difference in temperature between the liquid and vapor phases will remain small because of the small droplet size, so that heat can be transferred from the drops to the vapor nearly reversibly. Entropy increases in the liquid-vapor system due to the evaporation, therefore, should remain small. It is recognized that for this situation, the turbine exit entropy (at the exhaust pressure), being increased a small amount due to condensation, vaporization, and phase temperature differences, theoretically will result in a somewhat lower turbine Δh than for a corresponding process without condensation at the same pressure ratio. Turbine testing will ultimately be required to demonstrate whether or not overall "turbine performance" is degraded significantly by the condensation and revaporization which may occur in this type of turbine expansion.

Turbine Exit Condition Falls Well within Two-Phase Region - This case is similar to the more conventional steam turbine situation. The exhausts of steam turbines (final stages) commonly contain moisture, and the turbine stage efficiency is degraded by about 1% for each percent of "average" moisture predicted for that stage. One difference between isobutane and steam turbine two-phase expansions, however, is that the steam tends to become wetter as the expansion proceeds, whereas the isobutane (in a two-phase equilibrium expansion) first forms moisture, but then tends to dry as the expansion continues (see Figure 1). Generally, it might be expected that if the turbine exhaust state

falls well into the moisture region for isobutane, and condensation occurs, turbine performance estimates similar to those made for steam turbines would be reasonable as a first approximation; again, turbine testing would be required for final evaluation. This case, however, was not given major attention in the present review.

V. CONCLUSIONS

The following preliminary conclusions have been reached relative to the probable extent and effects on performance of condensation occurring during the turbine expansion processes being considered for advanced binary geothermal cycles.

1. The study has indicated that condensation will not necessarily occur in turbine expansion processes of interest here, whose equilibrium states pass through the two-phase region.
2. Turbine expansion processes which cross the saturation line close to the critical point, and finally leave the two-phase region, may show some condensation, initially, in the form of very fine droplets (fog); however, this condensation should be limited in extent. Estimates made here suggest that as the expansions proceed, further condensation will not occur, and any early-formed fog will tend to evaporate. As the entropy at which the expansion process crosses the saturation line increases, the tendency for condensation to occur decreases.
3. Turbine performance should not degrade significantly as a result of the turbine expansion process (equilibrium states) passing through and leaving the moisture region if no condensation occurs, and should still be acceptable even if some early condensation occurs near the saturation line. Part, or nearly all, of the potential 8% increase in geofluid effectiveness, identified in earlier studies, may be achievable through proper selection of cycle state points.
4. In view of (1) the potential cycle-performance and cost-of-power benefits from allowing turbine expansions to "pass through the moisture region", (2) the lack of fluid properties and condensation-kinetics information for the hydrocarbon working fluids of interest, and (3) the moderately favorable conclusions regarding

condensation and turbine performance resulting from the present assessment, nozzle experiments to investigate condensation behavior near the critical point and tests to evaluate turbine performance in the metastable region are recommended.

VI. REFERENCES

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