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ANALYSES OF MIXED HYDROCARBON BINARY THERMODYNAMIC CYCLES

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Abstract

A number of binary geothermal cycles utilizing mixed hydrocarbon working fluids were analysed with the overall objective of finding a working fluid which can produce low-cost electrical energy using a moderately low temperature geothermal resource. Both boil-ing and supercritical shell-and-tube cycles were considered. The performance of a dual-boiling isobutane cycle supplied by a 280F hydrothermal resource (corresponding to the 5MW pilot plant at the Raft River site in Idaho) was selected as a reference. To investigate the effect of resource temperature on the choice of working fluid, several analyses were conducted for a 360F hydrothermal resource, which is representative of the Heber resource in California. The hydrocarbon working fluids analysed included methane, ethane, propane, isobutane, isopentane, hexane, heptane, and mixtures of those pure hydrocarbons. For comparison, two fluorocarbon refrigerants were also analysed. These fluorocarbons, R-115 and R-22, were suggested by Milora and Tester as resulting in high values of net plant geofluid effectiveness (watt-hr/lbm geofluid) at the two resource temperatures chosen for the study. Preliminary estimates of relative heat exchanger size (product of overall heat transfer coefficient times heater surface area) were made for a number of the better performing cycles.

For the 280F resource, a mixture of 90% propane and 10% isopentane in a supercritical cycle showed the highest value of net geofluid effectiveness of the working fluids assessed. This working fluid showed improvements of about 42% relative to the highest performing single-boiling isobutane cycle, and 20% relative to the reference dual-boiling isobutane cycle. For the 360F resource, with the plant outlet geofluid kept above 160F (to prevent silica precipitation), mixtures of 96% isobutane/4% heptane, 65% isobutane/35% isopentane, and 95% propane/5% hexane, all resulted in improvements in geofluid effectiveness of about 6% relative to a 90% isobutane/10% isopentane mixture at 580 psia heater pressure (conditions approximating those which have been considered for a 50MW plant at the Heber site). The more promising of the cycles employing mixed hydrocarbon working fluids require heaters which are estimated to range from seven to approximately 50% larger in total surface area than those for the reference cycles.

BACKGROUND

A dual-boiling isobutane cycle was selected for the present 5-megawatt (5MW) Raft River Pilot Plant to utilize the lower-temperature geothermal resources near 300F). This study represents a second effort directed toward the design of an improved binary geothermal electric plant suitable for utilization of the lower temperature resources. Earlier studies (1)

DiscLAIMER This book was prepared as an account of work sponsored by an agency of the United States Government, Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or impled, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, appartus, product, or or oncess discload, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof. have considered cycle improvements by way of introducing multiple boiling and condensing, and employment of direct contact heat exchangers. Those studies included a small effort investigating use of hydrocarbon mixtures as working fluids. Consistent with findings of K. Starling, for example, work of Reference 1 indicated that the mixtures showed promise. The intent of the present effort was to expand the earlier analyses of binary cycles using mixtures of pure fluids, and to assess corresponding improvements in net geofluid effectiveness.

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BINARY GEOTHERMAL CYCLES

The working fluid in a binary geothermal electric plant undergoes the processes of a Rankine thermodynamic cycle. Figure 1, which is a schematic diagram of a simple binary geothermal cycle, illustrates these processes as well as the major components of the binary plant. Starting at the condensate storage tank, working fluid is pumped from the condenser to the heater pressure at nearly constant entropy. The working fluid is then heated and vaporized at constant pressure in the heater as heat is transferred from the geothermal fluid. The working fluid vapor expands through the turbine at nearly constant entropy, producing work on the turbine wheel. The turbine exhaust vapor is then condensed (following desuperheating if necessary) by rejecting heat to the cooling water in the condenser.



Figure 1: Simple Binary Geothermal Cycle

This rejected heat, in turn, is transferred to the atmosphere in the cooling tower. The condensed working fluid finally passes into the condensate storage tank, and the cycle is repeated.

For a cycle which utilizes energy from a

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geothermal fluid at a given initial temperature and rejects heat to a given sink temperature, a theoretical maximum exists for the amount of work that can be produced by the cycle per unit mass of geofluid. This maximum corresponds to the change in thermodynamic availability of the geothermal fluid between its initial state and its state corresponding to the heat sink temperature. Actual net work is less by the amount of the thermodynamic irreversibilities generated during each of the real processes in the cycle.

To illustrate the principle behind the present approach, the general thermodynamics of two simple binary cycles are illustrated in the T-Q (temperatureheat exchanged) diagrams shown in Figure 2. A single boiling isobutane cycle is shown with solid lines, and a cycle using a mixed hydrocarbon working fluid, consisting of 90% propane and 10% isopentane, is shown using dashed lines. Recognizing that the irreversibility generated in a heat exchange process is directly related to the total increase in entropy of the two fluids involved, it can be shown that the average difference in temperature between the two fluids is a measure of the thermodynamic irreversibility introduced. To help minimize this temperature difference, both cycles use counterflow heat exchangers for heating and condensing. Figure 2 shows that the constant tempera-ture boiling and condensing behavior of isobutane at constant pressure (characteristic of pure fluids) results in substantial departures of the geofluid and cooling water temperature profiles from the isobutane temperature profiles, and in turn significant irreversibilities, with losses in plant performance. The mixed hydrocarbon working fluid cycle (dashed lines) shows a reduced average temperature difference relative to the pure fluid for heating and condensing, and therefore, reduced thermodynamic irreversibilities. This mixed fluid cycle incorporates a supercritical heating process (boiling as such does not occur because heating is accomplished at a pressure above the critical pressure); however, the change in temperature during boiling for a mixed fluid would show a similar reduction in irreversibility relative to a pure fluid.



Figure 2: Temperature - Heat Exchanged Diagrams for Binary Geothermal Cycles

CYCLE ANALYSIS APPROACH

A number of single heating cycles were analysed for both pure and mixed hydrocarbon working fluids for a resource temperature (T_{GF}) of 280F. (For reference, similar calculations were made for a dual-boiling isobutane cycle corresponding to the 5MW Raft River Pilot Plant.) Working fluids considered included methane, ethane, propane, isobutane, isopentane, hexane and two-component mixtures of those hydrocarbons. For compar-

ison, a fluorocarbon refrigerant, R-115, was investigated. R-115 has been shown (2) to result in very good geofluid utilization efficiency at the 280F resource temperature. The general approach taken for each working fluid investigated was to conduct cycle calculations which included determination of turbine power, working-fluid pumping parasitic loss, and an estimate of the parasitic loss introduced by a wet cooling tower. The calculations were made for a number of turbine-inlet (or heater) pressures until a maximum net plant power was found. A different working fluid or mixture composition was then selected and the process repeated. More specific "ground rules" were adopted as follows:

- 1. Shell-and-tube heat exchangers were assumed.
- Geofluid pumping requirements (at a given geofluid flow rate) were assumed the same for all cases, and those parasitic losses were not included.
- Component and piping frictional pressure drops were neglected.
- Pump and turbine efficiencies were assumed to be 80 and 85%. For simplicity, electrical motor and generator efficiencies were taken as 100%.
- 5. Except in several special cases for T_{GF} = 360F, heater outlet state points were selected to avoid two-phase equilibrium conditions throughout the turbine expansion process and to minimize desuperheating of the turbine exhaust.
- Pinch points (minimum approach temperature differences) in the heaters were 10F. Countercurrent flow was assumed. (For the 360F resource temperature, additional cases were calculated as discussed in the next paragraph.)
- Wet cooling towers were assumed which provide cooling water to the condensers at 70F. Countercurrent cooling water flow was selected to maintain condensing approach temperature differences of 10F (see Figure 2).
- 8. As discussed in References 1 and 3, total cooling tower parasitic losses in watts were estimated from earlier work as 0.077 times the cooling water flow in lbm/hr for a cooling water temperature rise (ΔT_{CW}) = 20F. For $\Delta T_{CW} \neq$ 20F small adjustments in this factor were made to account for changes in pumping power required for the modified cooling water flow.
- Water and fluorocarbon refrigerant properties were taken from References 4 and 5. Mixed hydrocarbon working fluid properties were obtained using Computer Program THERPP (6), which utilizes Starling's modified Benedict-Webb-Rubin equation of state.

To evaluate the effect the geofluid resource temperature on the choice of working fluid, additional cycles were calculated for a resource temperature of 360F. For this temperature two component mixtures of propane, isobutane, isopentane, hexane, and heptane were considered. Also included was R-22, which is a fluorocarbon refrigerant suggested in Reference 2 as showing relatively high geofluid utilization efficiency at 360F. The basic approach and assumptions used for the 360F resource were the same as for 280F, but with two additional considerations. First, at the higher resource temperature sufficient silica is assumed to be dissolved in the geofluid that precipitation (possibly causing well-bore damage) may occur if untreated plant discharge geofluid is allowed to reach temperatures less than 160F. Accordingly, cycle performance was calculated for cases having plant outlet temperatures of 160F as well as those which maintained 10F pinch points in the heaters. Second, as an example illustrating the magnitude of the performance penalty associated with avoiding the two-phase region during turbine expansion, cycle calculations were repeated for 96% isobutane/4% heptane for several cases in which the working fluid entered the two-phase region as it expanded through the turbine (assuming equilibrium conditions), and exited the turbine as saturated vapor. (This working fluid was chosen for the example because it exhibited good geofluid effectiveness at moderate heater pressures both with and without the temperature restraint imposed on the discharged geofluid.) With the same pure-vapor conditions at the turbine inlet and exit, sufficient departure from equilibrium may exist to allow a real expansion process to occur without condensation, resulting in improved cycle performance.

EVALUATION OF WORKING FLUIDS FOR $T_{GF} = 280F$

Net plant power in watt-hr/lbm geofluid, (net geofluid effectiveness), is plotted in Figure 3 versus turbine inlet temperature for several of the working fluids selected. The cycles are generally single boiling cycles or single heating supercritical cycles shown schematically in Figure 1. Vertical dashed lines between boiling and supercritical cycles. It is seen that for a given working fluid, the maximum performance can occur for either supercritical or boiling cycles; the transition occurs in a smooth continuous fashion as the pressure is changed. Turbine inlet pressures are shown for each of the working fluids at the turbine inlet temperature corresponding to maximum performance. Mixtures of the pure fluids can be seen to provide higher performance than either of the two parent fluids, a result consistent with Figure 2. Net plant power for a dual-boiling isobutane cycle is shown as a dashed line to provide a comparison with the performance of the reference 5MW pilot plant. The dual-boiling cycle shows about 18% improvement relative to a single-boiling isobutane cycle.

intersecting the curves represent approximate boundaries

Figure 4 shows the maximum net plant power plotted versus the mass percent of the heavier hydrocarbon for the different mixed hydrocarbon systems considered. For comparison, the maximum performance of R-115 is shown with the dashed line. The highest net plant power found was for a supercritical cycle utilizing a mixture consisting of 90% propane and 10% isopentane, and occurred at 660 psia turbine inlet pressure. An approximate power balance for the cycle consists of (1) turbine = 5.64, (2) working fluid pump = 0.86, (3) cooling tower = 0.47, and (4) net power = 4.32 watt-hr/ lbm geofluid. This net performance is 42% higher than for pure isobutane in a single boiling cycle, and about 20% higher than for the optimum dual-boiling isobutane cycle. The net plant power of 4.32 represents approximately 44% of the thermodynamic availability of 9.73







watt-hr/lbm geofluid for a 280F resource temperature and an assumed sink temperature of 70F. (This sink temperature corresponds to the assumed temperature of the cooling water entering the condensers.)

EVALUATION OF WORKING FLUIDS FOR TGF = 360F

Results of the cycle analyses for a 360F resource temperature are summarized in Figure 5, which again shows maximum values of net power for each working fluid mixture, plotted versus the mass percent of heavier hydrocarbon. The solid lines correspond to cases in which the heater outlet geofluid temperature was held at 160F (to prevent silica precipitation), and the dashed lines represent cases in which the outlet geofluid was allowed to fall below 160F, but the pinch point temperature difference in the heater was held at 10F. The two different restraints result in different values of maximum performance which occur, in general, at different values of composition and pressure for a given working fluid system. Relaxing the 160F temperature limit results in higher values of net power of up to 14% depending on the working fluid; the highest net plant power found was for 95% propane/5% hexane, but the required turbine inlet pressure was 1400 psia. As a reference point, net power was calculated and plotted for 90% isobutane and 10% isopentane at 580 pisa turbine inlet pressure. This point shows net plant power for conditions approximating those considered for a 50MW plant at the Heber site in California. Also included in Figure 5 are corresponding performance values for R-22. Mixtures of 96% isobutane/4% heptane, 65% isobutane/35% isopentane, and 95% propane/5% hexane



Figure 5: Maximum Effectiveness for Single-Heating Cycles, T_{GF} = 360°F



fluids considered for a 360F resource when the 160F plant outlet geofluid temperature was imposed. For 96% isobutane/4% heptane, as an example, the maximum performance then occurred at about 800 psia heater pressure; an approximate power balance consists of: (1) turbine power = 11.05, (2) working fluid pump = 1.56, (3) cooling tower = 0.85, and (4) net power = 8.64watt-hr/lbm geofluid. Curves for that mixture showing net power versus turbine inlet temperature for a heater outlet geofluid temperature of 160F (open symbols) and for a heater pinch point temperature difference of 10F (shaded symbols) are presented in Figure 6. This figure includes curves both for turbine expansions which avoid the moisture region (solid lines) and those which enter the turbine in the vapor phase, expand into the two phase region, and then leave the turbine as saturated vapor (dashed lines). Figure 6 shows that for this working fluid a loss in performance of 7% is caused by imposing the 160F outlet geofluid temperature for those turbine expansion processes which avoid the moisture region; for cycles which maintain a heater pinch point of 10F, passing through the moisture region provides a potential improvement in net power of about 8%. The thermodynamic availability corresponding to the 360F resource temperature and a sink (or heat rejection) temperature of 70F is 17.5 watt-hr/lbm geofluid. The maximum net plant power for the 96% isobutane/4% heptane mixture, in a cycle which maintains 10F heater pinch points, represents approximately 53% of the availability at 360F if the turbine expansion avoids the moisture region. This value increases to about 57% if the turbine expansion has intermediate equilibrium states which fall within the two phase region.



Figure 6: Net Geofluid Effectiveness for 98% Isobutanel 4% Heptane Supercritical Cycles, TGF = 360°F

RELATIVE HEATER SIZES

To provide a preliminary assessment of relative magnitudes of surface areas for the working fluid heaters, estimates of UA, the product of overall heat transfer coefficient and heat-transfer surface area, were made for each of the working fluid systems considered. The approach taken for estimating UA was first to divide the heat exchanger into two regions; one region was for temperatures above the pinch point or "knee" in a curve of working fluid temperature versus enthalpy, and the other for temperature below the knee. In each of these regions the heat load (Q) in Btu/lbm geofluid and the "log mean temperature difference," (ΔT_m) were determined. UA, in Btu/°F lbm geofluid, was estimated as (Q/ ΔT_m). The UA value for the heater was then taken as the sum of the values of UA for each region.

Values of UA were calculated for the maximum net power conditions shown in Figures 4 and 5 for each of the working fluid systems, and are plotted versus net plant power for the 280F resource temperature in Figure 7. As a reference point, a comparable value of UA is shown for the dual-boiling isobutane cycle. A comparison of dual and single boiling isobutane cycles shows, for example, that the additional 18% net power attainable with the dual-boiling cycle requires 40 to 50% more heater surface, which at this low resource temperature should more than "pay for itself" in terms of final cost of electricity. The 90% propane/10% isopentane mixture is estimated to provide the 20% improvement in net power, relative to the dual-boiling



Figure 7: Heater UA for Maximum Effectiveness Single-Heating Cycles, T_{GF} = 280°F

isobutane cycle (mentioned earlier), with only a 9% increase in UA. It is seen that the R-115 cycle (supercritical) produced about the same net power as the dual-boiling isobutane cycle, but requires a value of UA approximately 60% higher.

Figure 8 shows values of heater UA, similarly plotted, for the 360F resource temperature. The open symbols are for cycles whose plant outlet geofluid temperatures were maintained at 160F; the shaded symbols denote the cycles whose heater pinch points were held at 10F. For the plant outlet geofluid temperature of 160F, the 96% isobutane/4% heptane cycle requires about 45% higher UA to achieve the 6% increase





in net plant power, relative to the reference 90% isobutane/10% isopentane 50MW cycle, whereas a mixture of 65% isobutane/35% isopentane achieves the same improvement with an increase in UA of only 15% relative to the reference plant. The maximum performance R-22 cycle can be seen to require a value of UA over twice as large as does the reference cycle (with 160F outlet geofluid temperature) while producing about the same net plant power.

SUMMARY OF RESULTS AND CONCLUSIONS

Results and conclusions of the study can be summarized as follows:

- For a given working fluid and resource temperature, the maximum net geofluid effectiveness may occur for either a boiling or supercritical Rankine cycle, depending on the particular combination of working fluid and resource temperature. The higher values found in this study occurred for supercritical cycles. These results generally support the work of Pope, et al. (7), which indicates that when the "optimum working fluid" is found for a conventional binary geothermal Rankine cycle utilizing a given hydrothermal resource, the optimum turbine inlet state will fall close to the Transposed Critical Temperature line.
- At the 280F resource temperature, the maximum net geofluid effectiveness found was for a working fluid consisting of 90% propane and 10% isopentane. Improvements in effectiveness of 42 and 20% were found relative to single and dual-boiling isobutane reference cycles.

- 3. For the 280F resource, the value of UA (representing a preliminary indication of relative heater surface area) for the 90% propane/10% isopentane working fluid was found to be slightly larger (9%) than the UA for the reference dual-boiling isobutane cycle.
- 4. At the 360F resource temperature, when the temperature of the plant outlet geofluid was held at 160F (to prevent silica precipitation), the maximum net geofluid effectiveness values found were for 96% isobutane/4% heptane, 95% propane/5% hexane, and 65% isobutane/35% isopentane. Those values were about 6% higher than for the 90% isobutane/10% isopentane reference cycle.
- For the 96% isobutane/4% heptane cycle (360F resource), imposing a lower limit of 160F on the geofluid outlet temperature penalized the net geofluid effectiveness by about 7%.
- Permitting equilibrium states for the turbine expansion process to pass through the two phase region for the 96% isobutane/4% heptane mixture (without the restraint on outlet geofluid temperature) resulted in a potential improvement in net geofluid effectiveness of approximately 8%.
- For the 360F resource temperature, mixtures of propane and isopentane may produce net geofluid effectiveness as high or higher than those fluids analysed.
- Mixed hydrocarbon working fluids appear promising, and warrant experimental evaluation.

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