

USE OF MIXTURES AS WORKING FLUIDS IN OCEAN THERMAL ENERGY CONVERSION CYCLES

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Mixtures offer potential advantages over pure compounds as working fluids in ocean thermal energy conversion cycles. Power plant capital costs per unit of energy output can be reduced using mixtures because of increased thermal efficiency and/or decreased heat exchanger size requirements. Mixtures also potentially offer the advantage of improved performance characteristics under conditions of progressive fouling of heat exchangers.

Potentially, a significant portion of the world's future energy needs can be supplied by ocean thermal energy conversion (1). In ocean thermal energy conversion schemes, the objective is to utilize the 30 to 40 F temperature differences between warm surface sea water and cold (1000 to 2000 feet deep) sea water which occur in numerous regions in the oceans. The utilization of these ocean temperature differences for power generation was proposed before 1900 by D'Arsonval (1). An open steam cycle for ocean thermal energy conversion was proven technically but not economically feasible in 1926 by Claude (1). Currently, the closed cycle proposed by Anderson and Anderson (2) is being given major consideration for ocean thermal cycles, partly owing to the fact that use of working fluids such as propane or ammonia leads to small turbine sizes relative to turbine sizes for the open steam cycle. Noteworthy conceptual designs for ocean thermal energy conversion plants have been proposed by Heronemus *et al.* (3) and Zener (4). In a recent proposal, "Uses of Mixtures as Working Fluids in Ocean Thermal Energy Conversion Cycles" (K. E. Starling, principal investigator) submitted to the National Science Foundation by the University of Oklahoma in May 1974, it is argued that the use of mixtures offers advantages over the use of pure compounds as working fluids in OTEC (ocean thermal energy conversion) cycles. The purpose of the present paper is to discuss the principal advantages of mixtures over pure compounds as working fluids in OTEC cycles, in terms of improved cycle efficiency, heat exchanger performance, and OTEC system cost effectiveness.

The OTEC Closed Cycle

Figure 1 shows a schematic diagram of the OTEC closed cycle, essentially as proposed by Anderson and Anderson (2). Propane is shown in Figure 1 as the working fluid for subsequent use in example calculations. In this cycle, Q_H is the heat transferred in the evaporator from the warm sea water to the working fluid. The working fluid exits from the evaporator as a gas near its dew point. The high-pressure, high-temperature gas then is expanded in the turbine to yield turbine work, W_T . For the cycle shown in Figure 1, the working fluid is slightly superheated at the turbine exit if the working fluid is propane and the turbine has an efficiency of 90% based on reversible, adiabatic expansion. From the turbine exit, the working fluid enters the condenser where it rejects heat, $-Q_C$, to

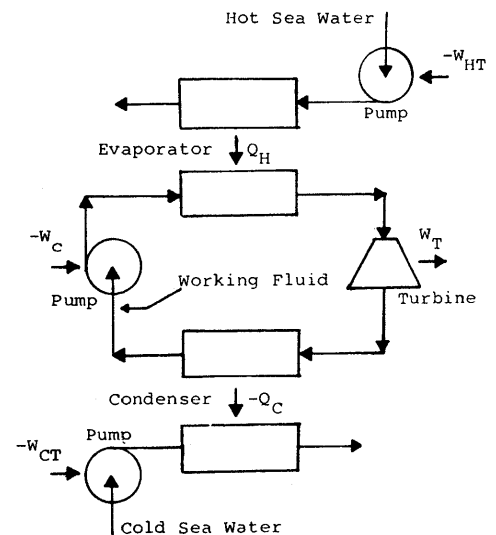


FIGURE 1. Schematic diagram of OTEC cycle.

the cold sea water. The condensate is then compressed to the highest pressure in the cycle, requiring condensate pump work, W_C . Thus, the Anderson closed cycle is a Rankine-type cycle similar to the conventional power plant steam cycle except that in the Anderson cycle the working fluid is never superheated more than a few degrees Fahrenheit. It is realized that owing to viscous effects there must be working fluid pressure drops in both the evaporator and the condenser. These pressure drops, which are dependent on the types of heat exchangers used, must be considered in final design calculations but can be ignored here to simplify the analysis for comparing mixtures with pure compounds as working fluids without risk of erroneous conclusions. Thus, the parasitic condensate pump work, W_C , computed here will be lower than if the heat exchanger pressure drops were included. The major additional parasitic energy requirements in the OTEC plant are the cold water pump work, W_{CT} , and the warm water pump work, W_{HT} . Denoting all other parasitic energy requirements by W_A , the net work from the OTEC plant, W_{NP} , is

$$W_{NP} = W_T + W_C + W_{CT} + W_{HT} + W_A \quad \text{Eq. 1}$$

The thermodynamic cycle undergone by the working fluid can be analyzed without detailed consideration of the parasitic energy requirements. According to the first law of thermodynamics, the energy balance for the working fluid as the system is

$$W_N = Q_H + Q_C \quad \text{Eq. 2}$$

where $W_N = W_T + W_C$ is the net work for the thermodynamic cycle (5). For the special idealized case in which there is no working fluid pressure drop in the heat exchangers,

$$Q_H = \int_H T_H ds \quad \text{Eq. 3}$$

and

$$Q_C = \int_C T_C ds \quad \text{Eq. 4}$$

so that the net thermodynamic cycle work becomes

$$W_N = \int_H T_H ds + \int_C T_C ds \quad \text{Eq. 5}$$

Figure 2 shows, on a temperature-entropy diagram, the changes of state undergone by propane in the OTEC cycle is Figure 1. Turbine and pump efficiencies of 85% based on adiabatic reversible expansion and compression were utilized to obtain the results shown in Figures 1 and 2. From Equation 5 it can be realized that the net thermodynamic work in the cycle is the difference in the areas beneath the heating and cooling curves for the working fluid when plotted on a temperature-entropy diagram, regardless of the working fluid choice, but shown in Figure 2 for propane. The temperature profiles of the warm and cold sea water relative to the working fluid temperature also are shown in Figure 2. It should be noted, however, that the abscissa in Figure 2 is the specific entropy of propane, not sea water, as the sea water profiles in Figure 2 are only intended to show the driving force for heat transfer as a function of working fluid temperature within each heat exchanger. The heat exchangers were considered to be adiabatic for these calculations.

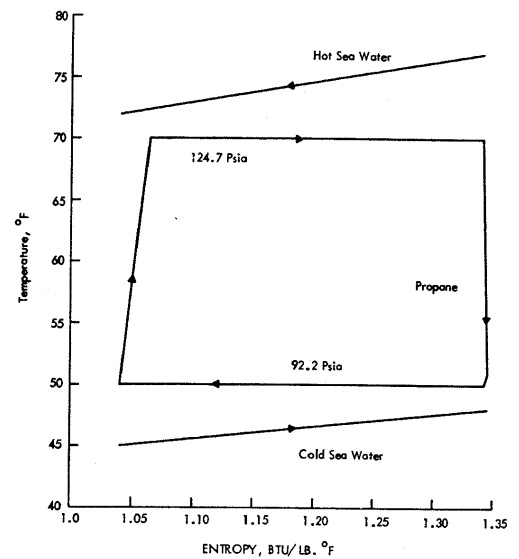


FIGURE 2. Temperature-entropy diagram for propane cycle.

Heat Exchanger and Efficiency Considerations

Heat exchanger sizes required for OTEC power plants are much larger than for conventional power plants and constitute the major cost items in OTEC plants (3). In addition, corrosion and biofouling problems are exaggerated in OTEC plants relative to conventional power plants. Thus, there is great incentive to reduce costs and improve performance of the OTEC heat exchangers.

Consider first the heat exchanger duty requirements, Q_A and Q_C , for a given net thermodynamic cycle work W_N ,

$$Q_H = W_N/\eta$$

Eq. 6

$$Q_C = W_N(\eta-1)/\eta$$

Eq. 7

where η , which is defined by Equation 6, is the net thermal efficiency of the thermodynamic cycle (5). For a conventional power plant with $\eta = 0.40$, Equations 6 and 7 yield $Q_H = 2.5 W_N$ and $Q_C = -1.5 W_N$ (where the fact that Q_C is negative is a result of the convention that heat transferred from the working fluid as the system is negative). The maximum efficiency possible for any cycle is the Carnot efficiency (5),

$$\eta_c = (T_H - T_C)/T_H$$

Eq. 8

where T_H and T_C are the warm and cold source absolute temperatures. For warm sea water at 77 F and cold sea water at 45 F, the Carnot efficiency is $\eta_c = 0.0596$. Because roughly half of the temperature difference, $T_H - T_C$, is used to transfer heat between the working fluid and sea water in OTEC plants, efficiencies attainable are only roughly half of the Carnot efficiency. Using $\eta = 0.03$ yields $Q_H = 33.3 W_N$ and $Q_C = 32.3 W_N$ for an OTEC cycle. Thus, for a given net work, W_N , from the thermodynamic cycle, the OTEC condenser must transfer about $32.3/2.5 = 12.9$ times as much heat as a condenser in a conventional plant.

Consider next heat exchanger size requirements. We can use the conventional formula for forced convection heat transfer (6),

$$Q = UA\Delta T$$

Eq. 9

where Q is the heat exchanger duty, A is the area across which heat transfer occurs, ΔT is the log mean temperature difference between the sea water and the working fluid, and U is the overall heat transfer coefficient (defined in terms of the log mean temperature difference).

$$A_C = Q_C/(U_C\Delta T_C) = ((\eta-1)/\eta) (W_N/(U_C\Delta T_C))$$

Eq. 10

Equations 7 and 9 can be combined to obtain the relation

for the condenser surface area, A_C . For a conventional power plant shell and tube heat exchanger with one-inch diameter tubes, using $\eta = 0.4$, $\Delta T = -15$ F, and a cooling water velocity of 7 feet per second, U is roughly 1000 Btu/hr-ft²-°F and $A_C = 0.0001 W_N$. For an OTEC power plant, using $\eta = 0.03$, $T = -5$ F, and a cold sea water velocity of 2 feet per second, U is roughly 380 Btu/hr-ft²-°F and $A_C = 0.017 W_N$. Thus, the condenser heat transfer area requirements for the OTEC plant considered are about $0.017/0.0001 = 170$ times as great as for the conventional power plant. Obviously, any means for reducing OTEC heat exchanger size requirements will improve the cost effectiveness of OTEC systems.

Next consider the problem of heat exchanger fouling. It is convenient to express the convective heat transfer formula in Equation 9 in the form

$$\Delta T = Q/UA = RQ$$

Eq. 11

where the overall resistance R is the sum

$$R = \sum_{i=1}^5 r_i$$

Eq. 12

the individual resistances r_1, r_2, \dots, r_5 are due respectively to (a) the water film, (b) water-side fouling, (c) the wall of heat transfer surface, (d) working-fluid-side fouling and (e) the working fluid film. The film resistances are convective, $r_i = 1/A_i h_i$, $i = 1, 5$, while the fouling and wall resistances are conductive, $r_i = t_i/A_i k_i$, $i = 2, 3, 4$, where A is the heat transfer area, h_i is the convective heat transfer coefficient (either water or working fluid film), k_i is the thermal conductivity, and t_i is the thickness (of fouling material or heat transfer wall). A major problem in OTEC plants is progressive fouling of heat exchangers, mainly on the water side. The temperature difference across the thickness t_2 of the water-side fouling is

$$\Delta T_2 = r_2 Q = (t_2/A_2 k_2) Q$$

Eq. 13

When the heat exchanger is new there is no fouling and $t_2 = 0$, so that $\Delta T_2 =$

0, but as fouling occurs, t_2 and therefore ΔT_2 progressively increase. This situation is illustrated in Figure 3, in which ΔT_1 is the temperature difference between the mixing cup temperature of the cold sea water and the water-side fouling and ΔT_2 is the temperature difference across the water-side fouling. The working fluid cycle in Figure 3 has been simplified to correspond to an internally reversible

cycle for purposes of illustration, with attention focused on the condenser. As progressive fouling takes place, the overall resistance R increases, so the overall heat transfer coefficient U and therefore the heat transferred Q decrease. The most convenient means for maintaining the heat transfer duty Q is to increase the sea water flow rate so as to increase h_1 and thereby reduce r_1 by an amount equal to the increase in $(r_2 + r_4)$ caused by fouling. However, eventually the additional parasitic pump work requirements become intolerably large and the heat exchangers must be cleaned or replaced. Continuous or periodic mechanical cleaning or chemical treatment methods may be used but the fouling problem probably cannot be completely solved.

Advantages of Mixtures in OTEC Cycles

Two of the major advantages of using mixtures instead of pure compounds as working fluids in OTEC plants can be noted by reference to Figure 4. For purposes of illustration, the pure-fluid cycle is shown in Figure 4 by dashed lines as the internally reversible cycle with heat transfer at constant temperature (at the pure-fluid vapor pressure). The mixture cycle is shown in Figure 4 by solid lines as the internally reversible cycle with heat transfer along paths (essentially between the mixture bubble and dew points) which parallel the warm and cold sea water temperature profiles, a situation which can be approached for real mixtures but is impossible for pure fluids. Because both the pure-fluid cycle and mixture cycle are reversible, the areas enclosed by each cycle represents the work from the cycle. These areas are equal and therefore the work from each cycle in Figure 4 is identical. On the other hand, for a pure-fluid inlet temperature difference of 10 F and exit temperature difference of 3 F for both the evaporator and condenser, the log mean temperature differences for the cycles in Figure 4 are 5.85 F for the pure-fluid cycle and 6.5 F for the mixture cycle, so that the heat transfer surface area required for the mixture is only 90% of the heat transfer surface area required for the pure fluid (for equivalent fluid properties). This translates almost directly as a 10% reduction in the cost of the heat exchangers. It should be noted that it is the fact that mixtures vaporize and condense at varying temperatures in constant-pressure processes while pure fluids vaporize and condense at constant temperature in constant-pressure processes that gives rise to the opportunity for the improved heat transfer performance idealized in Figure 4.

An additional potential advantage of mixtures over pure fluids evident from Figure 4 is the fact that under conditions

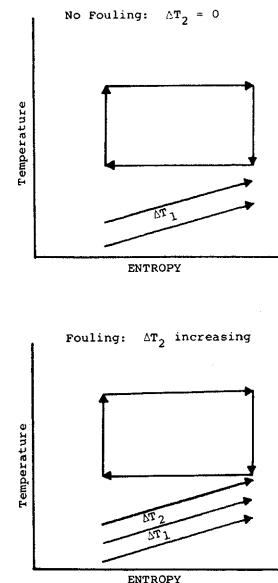


FIGURE 3. Effects of progressive heat exchanger fouling.

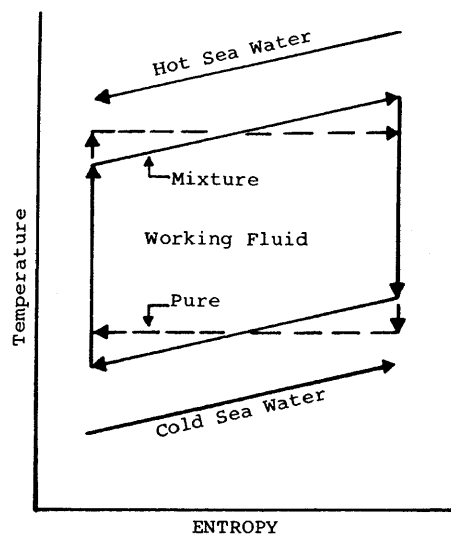


FIGURE 4. Comparison of mixture (solid lines) and pure fluid (dashed lines) idealized cycles.

of progressive fouling, the mixture cycle possibly can be maintained operative for a longer time with increased water flow rates. This is because the driving force for heat transfer is uniform throughout the heat exchanger for the mixture cycle, while a "pinch point" tends to occur with fouling in the pure-fluid cycle, at the point of entrance to the heat exchanger of the pure working fluid.

It is axiomatic that a trade-off exists between overall power plant efficiency and heat exchanger size in virtually any thermal power conversion method. Thus, if the same heat exchanger surface areas were considered for the pure-fluid and mixture cycles, then for the case considered above, the efficiency of the internally reversible mixture cycle would be 9% greater than the internally reversible pure-fluid cycle. For irreversible cycles, the efficiency improvement will vary, depending on the differences in behavior of the mixtures considered compared to pure fluids. It is beyond the scope of the present work to demonstrate the advantages of mixtures over pure compounds based on optimized mixture compositions and operating conditions, but an unoptimized mixture cycle calculation has been performed to illustrate the differences for an actual mixture.

Comparison of Mixture and Pure-Fluid Cycles

The advantages of using mixtures rather than pure compounds as working fluids in ocean thermal-difference cycles can be demonstrated with reference to the differences in pure-compound and mixture cycle design calculations summarized in Table 1 and temperature-entropy diagrams, shown in Figures 2 and 5. The pure-compound cycle in Figure 2 is for propane while the mixture cycle in Figure 5 is for a three-component mixture which approximates the characteristics of propane in the single-phase gas and liquid regions but exhibits mixture phase behavior. The composition of this mixture is 1% ethane, 98% propane, and 1% normal butane, on a mole percentage basis. The temperature-pressure conditions for Table 1 and Figures 2 and 5 are for the case of warm sea water at 77 F and cool sea water at 45 F with expansion

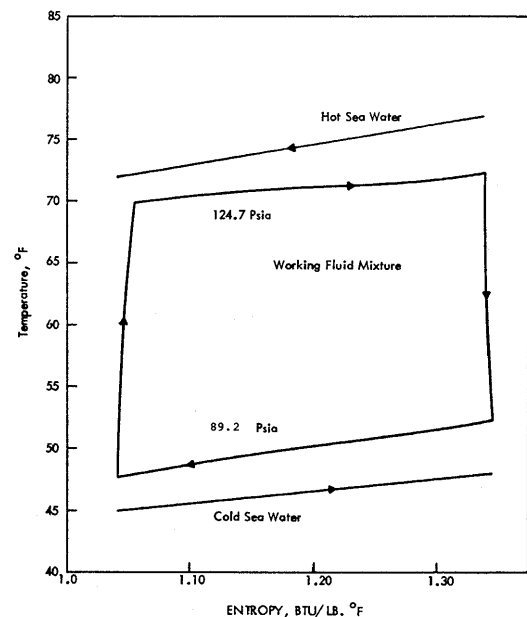


FIGURE 5. Temperature-entropy diagram for mixture cycle.

TABLE 1. Comparison of propane and mixture ocean thermal difference cycles.

	Working Fluid	
	Propane	Mixture ^a
Warm sea water inlet temp. (F)	77.0	77.0
Warm sea water outlet temp. (F)	72.0	72.0
Cool sea water inlet temp. (F)	45.0	45.0
Cool sea water outlet temp. (F)	48.0	48.0
Cool sea water reqd. (lb per lb of warm sea water)	1.55	1.6
Condenser outlet temp. (F)	50.0	47.7
Turbine inlet temp. (F)	70.0	72.1
Turbine inlet press. (psia)	124.7	124.7
Turbine outlet temp. (F)	51.0	50.1
Turbine outlet press. (psia)	92.2	89.2
Turbine outlet liquid (vol. %)	0.0	0.1
Net work (BTU per 100 lb warm sea water)	13.1	15.1
Cycle net thermal efficiency (%)	2.62	3.02

^aMixture composition, in mole percent: 1% ethane, 98% propane, 1% n-butane.

of the working fluid from 124.7 psia to 92.2 psia for propane and 89.2 psia for the mixture. Turbine and pump efficiencies of 85% compared to adiabatic reversible expansion and compression were used. In Figures 2 and 4 the difference between the areas under the cycle heating and cooling curves for the working fluid represents the work obtained from the cycle for equal amounts of warm sea water used before accounting for work required for pumping sea water. Pertinent information from the calculations for both the propane and mixture cycles is summarized in Table 1. Predictions of enthalpies, entropies, densities, dew points, bubble points, and vapor-liquid equilibria for the working fluids were made using a correlation known to be accurate for the fluids considered (7).

The turbine exit pressure of 92.2 psia is chosen for the propane cycle to insure complete condensation in the condenser at 50 F, where the vapor pressure of propane is 92.2 psia. The condensation temperature of 50 F for propane is required in order to maintain at least a 2 F driving force for heat transfer between the working fluid and cool sea water in the case where the cool sea water enters at 45 F and exits at 48 F. For the case of the mixture, the fact that at 89.2 psia the dew point temperature is 50.2 F, while the bubble point temperature is 47.7 F, allows expansion to a lower pressure than is possible for pure propane and thus, more work is obtained in the mixture cycle. The principal difference between the behavior of mixtures and pure fluids in this Rankine-type cycle is the fact that the warming and cooling curves for mixtures in the two-phase region are sloped rather than horizontal, as for pure fluids. This difference between mixture and pure-fluid behavior can be noted easily by comparing the temperature-entropy diagrams in Figures 2 and 5. Thus, with proper selection of its composition, the working fluid mixture's warming curve can be made to nearly parallel the cooling curve of the warm sea water, while the mixture cooling curve can be made to nearly parallel the warming curve of the cool sea water, behavior which is impossible to achieve with pure working fluids. For specified log mean temperature differences between fluids in countercurrent heat exchange, the thermal efficiency and the work obtained from the cycle potentially can be made larger for mixtures than for pure fluids. Although the test composition of the mixture used for this comparison is not an optimized composition with respect to its warming curve at 124.7 psia or its cooling curve at 89.2 psia, considerably more work is obtained per pound of warm sea water in the mixture cycle than the propane cycle, and thus the thermal efficiency of the mixture cycle is 3.02% compared to 2.62% for the propane cycle.

In summary, the calculations for even the unoptimized mixture considered here demonstrate potential advantages in using mixtures as working fluids in ocean thermal gradient cycles. In particular, near paralleling of working fluid heating and cooling curves with the warm and cool sea water cooling and heating curves increases the net work and cycle efficiency, reduces the heat transfer surface required, and improves performance under conditions of progressive fouling.

CONCLUSIONS

The major conclusion from the study presented here is that mixtures potentially can be used to advantage in ocean thermal energy conversion cycles to achieve the following results, compared to pure-fluid cycles: (a) decreases in heat exchanger sizes, with a corresponding reduction in plant capital costs and/or (b) increase in power plant efficiency, and (c) improved heat exchanger performance under conditions of progressive fouling.

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