Proceedings of the ASME 2009 3rd International Conference of Energy Sustainability
ES2009
July 19-23, 2009, San Francisco, California, USA

ES2009-90220

A DUAL-SOURCE ORGANIC RANKINE CYCLE (DORC) FOR IMPROVED EFFICIENCY IN CONVERSION OF DUAL LOW- AND MID-GRADE HEAT SOURCES

F. David Doty and Siddarth Shevgoor

Doty Scientific, Inc., 700 Clemson Road, Columbia SC 29229 USA

ABSTRACT

Detailed thermodynamic and systems analyses show that a novel hybrid cycle, in which a low-grade (and low-cost) heat source (340 K to 460 K) provides the boiling enthalpy and some of the preheating while a mid-grade source (500 K to 800 K) provides the enthalpy for the final superheating, can achieve dramatic efficiency and cost advantages. Four of the more significant differences from prior bi-level cycles are that (1) only a single expander turbine (the most expensive component) is required, (2) condenser pressures are much higher, (3) the turbine inlet temperature (even with a low-grade geothermal source providing much of the energy) may be over 750 K, and (4) turbine size is reduced.

The latent heat of vaporization of the working fluid and the differences in specific heats between the liquid and vapor phases make full optimization (approaching second-law limits) impossible with a single heat source. When two heat sources are utilized, this problem may be effectively solved – by essentially eliminating the pinch point. The final superheater temperature must also be increased, and novel methods have been investigated for increasing the allowable temperature limit of the working fluid by 200 to 350 K. The usable temperature limit of light alkanes may be dramatically increased by (1) accommodating hydrogen evolution from significant dehydrogenation; (2) periodically or continually removing undesired reaction products from the fluid; (3) minimizing the fraction of time the fluid spends at high temperatures.

Detailed simulation results are presented for the case where (1) the low-grade heat source (such as geothermal) is 400 K and (2) the mid-grade Concentrated Solar Power (**CSP**) heat source is assumed to be 720 K. For an assumed condensing temperature of 305 K and working fluid flow rate of 100 kg/s, preliminary simulations give the following: (1) low-grade heat input is 25 MW_T; (2) mid-grade heat input is 24 MW_T; (3) the electrical output power is 13.5 MW_E; and (4) the condenser rejection is only 35 MW_T. For comparison, with a typical bi-level ORC generating similar power from this geothermal source alone, the low-grade heat requirement would be ~100 MW_T.

1. INTRODUCTION

A large number of different Organic Rankine Cycles (**ORC**s) for the production of mechanical and then electrical power from a single thermal source (either low-grade or mid-grade) have been highly developed over the past century, but still they typically achieve only 35% to 55% of Carnot efficiency limits. (The debates on exactly how this limit should be defined come down largely to assumptions about the distributions of temperatures in the sources and sink.)

Our motivation for taking a fresh look at ORCs came from the need to do a better job with conversion of waste heat in a novel carbon-neutral-fuels process we are developing – a method for synthesizing renewable fuels of all types (ethanol, gasoline, jet fuel...) from waste CO_2, H_2O, and off-peak wind energy [*1*]. The process we've proposed, dubbed *WindFuels*, ends up with two large sources of waste heat – one at about 420 K (from the hot-water electrolyzer) and one at about 580 K (from the Fischer Tropsch reactor). It seemed from simple exergy considerations that it should be possible to design a single cycle that took much better advantage of the 'availability' of two separate (each essentially isothermal) heat sources than could be achieved with two heat engines, each operating from its own source. An obvious additional application for a cycle that achieves higher conversion efficiency when two heat sources are simultaneously available would be a geothermal-CSP hybrid, and that is the specific application we'll address in this paper.

Most commercial power conversion cycles, even low-grade until quite recently, have ended up as conventional steam cycles. However, other – organic – working fluids have been used, in Organic Rankine Cycles (**ORC**s). The appeal of the ORC comes from the much lower heat of vaporization of organic fluids compared to steam and the possibility of much higher condenser pressure, which reduces the size of the expander turbines and condensers. Still, the latent heat of vaporization of the working fluid and the differences in specific heats between the liquid and vapor phases make full optimization (approaching second-law limits) impossible with a single heat source. (New fluids that eliminate these problems are not likely to be found.) Problems also arise from

Copyright 2009 by ASME

limited long-term stability of the organic fluid: It dehydrogenates into coke precursors and hydrogen gas – which kills the expansion ratio, as it stays trapped in the condenser.

Many low-grade ORCs, such as for geothermal, have utilized isobutane, as it has a fairly high vapor pressure at the typical condensing temperature (~300 K) and has a relatively low latent heat of vaporization at the typical boiler temperature, ~400 K [*2*]. Some ORCs have utilized multi-component fluids, including propane/ethane mixtures, and some have used synthetic refrigerants such as R-22B1, $CHBrF_2$, or ammonia, NH_3. These have all been designated as Organic Rankine Cycles (**ORC**s), as distinguished from conventional water steam cycles.

For mid-grade heat sources, cascaded cycles have been utilized in which a higher boiling fluid, such as benzene, water, or toluene, is heated to the maximum available temperature; and its condenser, typically ~430 K, drives the boiler for a loop utilizing a lower-boiling fluid such as isobutane [*3*]. Pressure ratios are typically about 10 in each loop, and recuperation is usually utilized, as the expander temperature ratio ($T_R=T_{IT}/T_{OT}$, turbine inlet temperature divided by turbine outlet temperature) is only about 1.15 in such fluids – because γ, the ratio of C_P to C_V, is under 1.1 at the typical expander conditions. Others have utilized mixtures of ammonia and water in ways that permit the condensing to take place with reduced temperature differences and hence improved efficiency, albeit with increase in complexity [*4*].

The trend toward higher peak temperatures has pushed the fluid choice toward aromatics, such as benzene and toluene, because of their very low susceptibility to dehydrogenation. However, their low vapor pressures at ambient temperatures require the use of costly, cascaded cycles to avoid sub-atmospheric condensers. Sub-atmospheric condensers (though fine with steam cycles) are unacceptable in ORCs because the ingress of air and moisture through unavoidable minute leaks catalyzes degradation reactions in the working fluid.

When two heat sources are utilized, the pinch-point problem associated with the boiling enthalpy may be effectively solved. In the novel hybrid cycle, a low-grade heat source provides the boiling enthalpy and some of the preheating while a mid-grade source provides the enthalpy for the final superheating.

The Dual-source ORC (or **DORC**) is markedly different from prior cycles, such as hybrid-flash steam, bi-level and cascaded recuperated ORCs, and combined cycles. Four of the more significant differences are that (1) only a single expander turbine (the most expensive component) is required, (2) the turbine inlet temperature (even with a low-grade geothermal source) can be over 750 K, (3) condenser pressures are much higher (always above 1 bar, even on cold nights), (4) the size of the turbine and condenser are reduced (because of the higher vapor pressure in the condenser). Of course, the final superheater temperature must be increased (compared to what is normally seen when using low-boiling liquids), and methods are presented for increasing the allowable temperature limit of light alkanes.

We present detailed analyses for a proposed application using a combination of a Concentrated Solar Power (**CSP**) source and a geothermal source (400 K). The CSP heat transfer fluid (**HTF**) is assumed to leave the solar field at 720 K and return to the field at about 650 K, which is much higher than normally seen, but essential for high thermal efficiency. The low-grade heat source is assumed re-injected at ~370 K (much warmer than might make sense for geothermal) to make the point that this option is possible for an industrial process where it does make sense (as in *WindFuels*). In this example, condenser heat rejection is seen to be less than 3 times the electrical output power, which compares to more than 6 times for a conventional bi-level ORC operating from this geothermal source alone.

Some of the gain comes from advances assumed in novel gas-to-gas recuperators [*5*]. Some of the efficiency gain also comes from the simple fact that energy five years from now will be worth an order of magnitude more than it was a decade ago, and this justifies exchangers with higher effectiveness and turbines with higher polytropic efficiencies. However, the biggest gains come from (A) appreciating the potential for minimization of exergy destruction using a doubly-recuperated dual-source cycle, and (B) approaching the working fluid selection problem from both a systems and a catalysis perspective.

The analysis shows that the optimum working fluid for the DORC should (a) have at least 0.1 MPa vapor pressure at the minimum condenser nighttime temperature (which will generally be between 250 K and 285 K), (b) have exceptional chemical stability in the super-heater (which will usually be 600 to 800 K, and 0.5 to 3 MPa), (c) be sub-critical at the temperature of the lower-grade heat source (usually 360-460 K), (d) be environmentally safe, (e) have high thermal conductivity in the vapor phase, (f) have high autoignition temperature, (g) have high $\gamma=C_P/C_V$, and (h) have reasonably low cost Most prior discussions of optimum fluid selection have focused largely on only one or two of the above criteria, or on another – the slope of the saturated vapor line on the T-S diagram, which now is irrelevant in the DORC.

Our searching has concluded that the best fluids will be mixtures of mostly light alkanes – propane, butanes, pentanes, and especially isobutane. This mixture could obviously satisfy all but two of the above desired requirements (high γ and high chemical stability), and we will show that solutions appear available for the critical requirement – chemical stability in the superheater.

Misconceptions have not been uncommon related to chemical stability, and these include the notion that higher boiling points generally correlate with high thermal stability and that the upper temperature limit of a working fluid is mostly determined by the fluid chemistry itself. We show there are methods for increasing the practical temperature limit for a given light alkane by 200 to perhaps 350 K, primarily from some combination of the following, in typical order of significance:

(1) accommodation of substantial hydrogen evolution,
(2) minimization of high-temperature residence time,
(3) incorporation of on-line HHC separations processes,
(4) deactivation of catalytically active surfaces,
(5) eliminating deleterious catalytic contaminations,
(6) choosing a more stable lubricant,
(7) operating (high side) at 50-95% of the critical pressure.

Copyright 2009 by ASME

In the conventional ORC, the loss of expansion ratio that results from a non-condensable partial pressure in the condenser has a very detrimental effect on expander shaft power and efficiency, as the increased turbine outlet enthalpy is not useable. In the DORC, where recuperation above the boiling point may be very effectively utilized, the increased turbine outlet temperature means that less final superheating is required. Hence, the efficiency of utilization of the heat sources is much less affected by high H_2 partial pressure in the condenser or by degraded expander efficiency. The mass flow rate of the working fluid must be increased for a given output power, and the expander must continue to work efficiently at a lower expansion ratio; but these are minor technical issues. While it is still preferable to maintain fairly low H_2 partial pressure in the condenser, high enough H_2 partial pressures (~0.1) are acceptable such that the task of separating light-gas reaction products becomes quite practical in the DORC. Several methods for both minimizing fluid chemical reactions and achieving the needed removal of reaction products (both light and heavy) from the working fluid are discussed.

2. THE DORC, IN A GEOTHERMAL-CSP EXAMPLE

Detailed simulations were carried out for the case where (1) the low-grade heat source (such as geothermal) was 400 K and (2) the mid-grade heat source was 720 K (such as advanced CSP). Small pressure drops across equipment were included in the simulations; and only real-gas properties, obtained from NIST REFPROP 8, were used [*6*]. **Figure 1** shows the T-S diagram for the typical cycle.

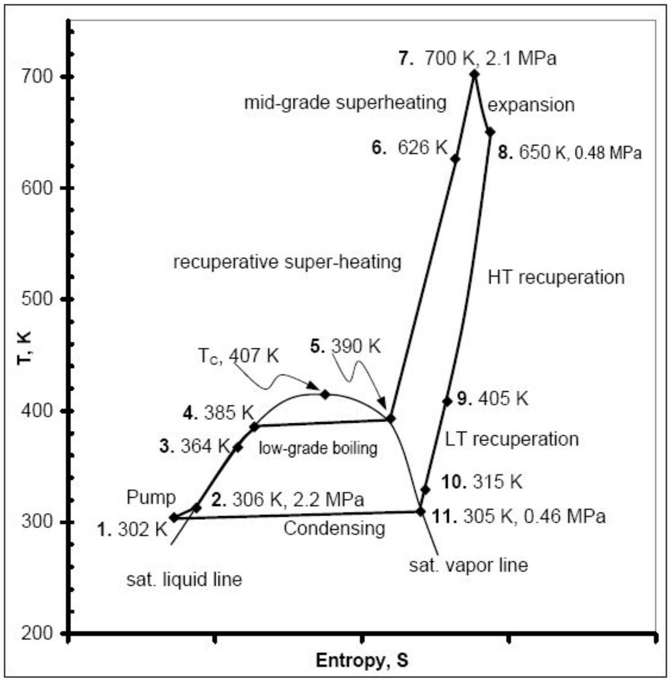

Figure 1. The T-S diagram for the DORC.

For the assumed condensing temperature of 305 K and working fluid flow rate of 100 kg/s, preliminary simulations give the following: (1) low-grade heat input is 25 MW_T; (2) mid-grade heat input is 24 MW_T; (3) the electrical output power is 13.5 MW_E; and (4) the condenser rejection is only 35 MW_T. For comparison, with a typical bi-level ORC generating similar power from this geothermal source alone, the low-grade heat requirement would be ~100 MW_T and the condenser would be rejecting ~85 MW_T.

A more detailed system flow diagram for the doubly recuperated dual-source ORC (DORC) is presented in **Figure 2** for this case. (Two streams of heat transfer fluids, not shown, transport heat from the two heat sources to the boiler and superheater.) Component reference numerals are shown in braces and boldface in the text.

Here, the working fluid is assumed to be pure isobutane, which we will show is a suitable choice for mid-latitude winters, where the minimum night-time lows may often reach 260 K and the daytime highs are about 290 K. The example presented here assumes 10% mean non-condensable gas partial pressure (mostly H_2) in the condenser. (The H_2 partial pressure elsewhere in the cycle will be under 0.01%.)

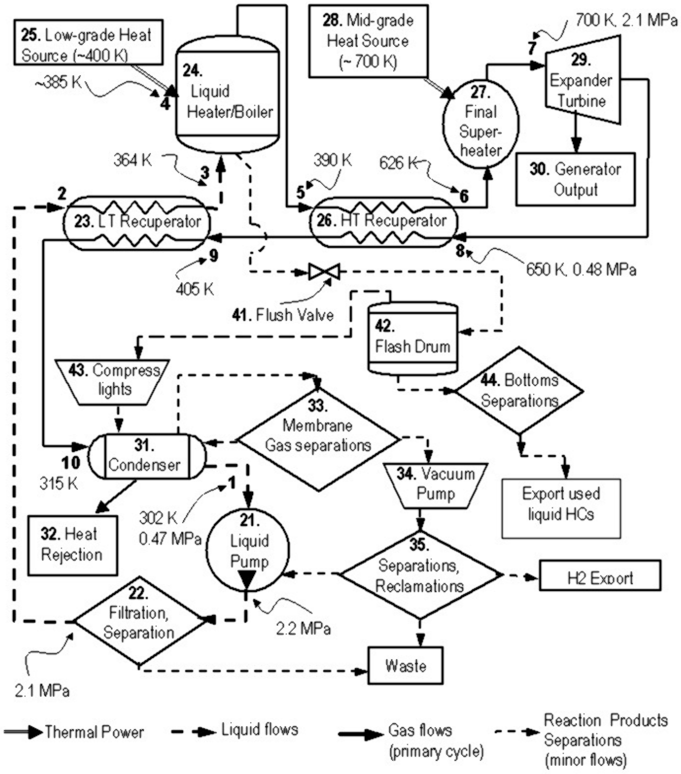

Figure 2. A detailed system flow diagram for the DORC.

The condensed and slightly sub-cooled fluid at point 1, pressure p_1, temperature T_1, assumed here to be 302 K and 0.46 MPa, is pumped {**21**} to the desired high pressure of ~2.5 MPa. The high-pressure liquid passes through filters {**22**} to remove any particulates to prevent turbine damage. An excess fluid inventory tank (not shown) may be placed between the condenser and the pump. See also the T-S diagram in Figure 1, where the same node numbers, 1-11, are used.

The pressurized liquid is then preheated against the returning low-pressure vapor and leaves the LT recuperator {**23**} at point **3** on the T-S diagram. In this example, the enthalpy from cooling the returning low-pressure vapor between points **9** and **10** (150 kJ/kg) is sufficient to heat the liquid to about 364 K prior to entering the liquid heater/boiler {**24**} at point **3**. The low-grade source {**25**} supplies: (a) the

Copyright 2009 by ASME

final liquid heating (~40 kJ/kg) to point **4** (385 K), (b) the heat of vaporization (207 kJ/kg), and (c) a little superheating. The vapor then enters the high-temperature (**HT**) recuperator (or recuperative superheater) {**26**} at point **5**, temperature T_5, where it is superheated to T_6 against the returning turbine exhaust vapor. If a mixture were used rather than pure isobutane, the temperature at point **5** would be above that at point **4** by more than the boiling glide amount.

As the temperature difference between the mid-grade source and the low-grade source is much greater than the difference between the boiling and condensing temperatures, most of the heat from the returning turbine exhaust is available between nodes **8** and **9**. This 690 kJ/kg preheats the pressurized vapor to 626 K at node **6** before the vapor enters the compact final superheater {**27**}. The mid-grade source {**28**} supplies the 235 kJ/kg then needed to further superheat the preheated vapor to the 700 K turbine inlet temperature T_{IT}, or T_7, at point **7**.

It is essential that the volume of working-fluid in the upper half of the final superheater {**27**}, and especially within the manifolds at its hot end and the duct **7** from there to the expander turbine inlet be minimized. This is needed to minimize HT relative residence time to minimize thermal dehydrogenation and cracking, a point we return to in more detail later. Hence, a liquid heat transfer loop (not shown in Figure 1) is required between the mid-grade heat source and the final superheater.

The vapor is then expanded through turbine {**29**} essentially to the condenser total pressure (plus minor pressure drops through the recuperators), which is the sum of the condenser vapor pressure (e.g., 0.425 MPa for isobutane at 305 K) and the partial pressures of the non-condensable reaction products, mostly H_2, C_2H_6, and CH_4. The vapor leaves the expander {**29**} at point **8** at 651 K after delivering ~15 MW of shaft power (for 100 kg/s). (We assumed non-condensable partial pressure of 0.04 MPa and expander polytropic efficiency of 0.89.) About 96% of the shaft power gets converted to electrical power in the generator {**30**}.

The hot turbine exhaust proceeds through the HT recuperator and exits at point **9** at about 15 K above the boiling temperature. It then proceeds through the LT recuperator, from which it exits at point **10** at about 10 K above the condensing temperature. The vapor is then further cooled (~20 kJ/kg), condensed (322 kJ/kg), and slightly sub-cooled (~4 kJ/kg) in the condenser {**31**} to prevent cavitation in the pump {**21**}. The light stable reaction products (H_2, CH_4, C_2H_6) mostly remain trapped in the condenser until removed, as discussed in section **4.2**.

The power per flow rate in this example is lower than often seen in CSP ORCs for two reasons: γ is quite low for an extremely superheated organic vapor, and the pressure ratio is rather low – mostly because of the low ratio of the boiling to condensing temperatures, but also because of the non-condensable gas in the condenser. This makes the effectiveness of the HT recuperator quite important. Side benefits of this recuperator are that expander efficiency becomes much less critical and moderately high non-condensable gas pressures can be accommodated in the condenser with little loss in efficiency. While it is still preferable to maintain fairly low H_2 partial pressure in the condenser, the task of separating the light gases from the isobutane vapor is not practical at very low gas partial pressures.

For comparison, the efficiency of prior geothermal ORCs from a similar source temperature has usually been ~12%, and CSP has usually seen peak efficiencies of 26-32%. In this example, about 25 $\mathrm{MW_T}$ of low-grade heat is needed, along with about 24 $\mathrm{MW_T}$ of mid-grade heat. After powering pumps and fans (including the separations processes discussed shortly), over 13 $\mathrm{MW_E}$ of net electrical power is produced from a single, small, inexpensive, expander turbine. Hence the efficiency of utilization of the combined sources is 27.5%. Alternatively, if the low-grade heat is regarded as free, the efficiency of utilization of the mid-grade heat would be 56%. So the performance of the DORC appears to be 35% to 60% better than the weighted average of prior ORCs, depending on how one does the weighting.

The biggest advantage of the DORC is that two independent sources are used in a way that permits minimization of exergy loss from each. Each heat source is delivered by a separate heat transfer fluid that is returned to its source with only a small temperature drop. This is critical for the case where the mid-grade heat is from concentrated solar and efficiency of utilization of low-grade exergy is also important, as with flat-plate solar. Whether or not this is the most cost-effective approach for the geothermal-solar hybrid is not yet clear, as it does increase demands on both recuperators. However, it has recently been shown that gas-to-gas recuperation at over 97% effectiveness may be possible with an order-of-magnitude reduction in costs [*5*], though in the above simulation we assumed only about 92%.

3. MINIMIZING FLUID REACTIONS

Chemical stability of the working fluid is ultimately the limiting factor for DORC performance, at least when the higher-grade heat source is concentrated solar. Butanes have previously not been recommended for use above 480 K [*3*, *7*], but only partly because it is assumed there may be some moist-air ingress leading to formation of organic acids and other oxygenates. (The combination of copper and water very strongly catalyzes oxidation of alkanes). Heavier alkanes have often been mistakenly thought to be better suited for higher temperatures.

We show that a two-pronged approach – firstly, doing what is possible to reduce reaction rates, and secondly, doing what is necessary to accommodate much higher reaction rates – should permit long-term operation with light alkanes at 200 to 350 K higher than has previously been thought advisable. It begins by recognizing that reaction rates (at least for endothermic reactions) are not delta functions.

3.1 Minimizing Dehydrogenation

The most detrimental reaction of light alkanes in ORCs has been endothermic dehydrogenation to an alkene of the same carbon number. For butane, for example,

$$C_4H_{10} \rightleftarrows C_4H_8 + H_2\ , \quad \Delta H_{f\,600K} = 47\ \mathrm{kJ/mol} \qquad (1)$$

The alkenes then (relatively quickly) may crack to a lighter alkene or metathesize, homologate, dimerize, or polymerize in combination with other hydrocarbons (**HC**s) to heavier hydrocarbons [*8*]. The primary problem is that the hydrogen doesn't condense, and therefore it soon kills the expansion pressure ratio, maximum output power, and efficiency. Also, the heavier alkenes rather quickly dehydrogenate to dienes, aromatics, and alkenylarenes. The alkenylarenes especially will polymerize and gum up the pump or coke up the superheater if not quickly removed from the fluid.

The equilibrium constant K_P for dehydrogenation of isobutane to butene is 4.9E-5 at 600 K, and 2.5E-3 at 700 K. However, the activation energies for dehydrogenation of propane and butanes are very high. Even on platinum catalysts, for example, they have been estimated to be about 126 and 113 kJ/mol for propane and isobutane respectively [*8*]. Hence, below about 700 K, dehydrogenation of these species at pressures of several MPa essentially occurs only on catalytic surfaces. The most effective catalysts for dehydrogenation are the noble metals, which obviously would not be present in the system. The next most effective catalyst may be Cr_2O_3, which covers the surfaces of all stainless steels and superalloys if not deactivated. Even though the concentration of coke precursors in the working fluid will be kept as low as practical, the Cr_2O_3 will eventually become coated with enough coke (under 0.1 microns is sufficient) to be well deactivated. However, more than enough hydrogen can be released to stop effective system operation before adequate surface deactivation if the gas is not removed fast enough. Clearly, the surfaces of the turbine blades, nozzles, HT ducts, and HT recuperator should be deactivated prior to use to eliminate strong catalytic dehydrogenation at startup.

With catalytic dehydrogenation essentially eliminated, only thermal (un-catalyzed) dehydrogenation remains. Isobutane thermal dehydrogenation rates in the absence of oxygen or water are extremely low below 900 K at pressures above 0.1 MPa [*9*, *10*]. One reference indicates ~35% of isobutane at ~0.05 MPa is thermally dehydrogenated in ~30 minutes at ~920 K [*11*]. While quantitative data are scarce, several sources [*9-14*] indicate dehydrogenation rates for isobutane under the conditions of interest (2-3 MPa, 700-800 K, near-zero H_2O and oxygenates), are probably lower than the thermal cracking rates, as discussed in section **3.3**.

3.2 Minimizing Catalytic Cracking

At temperatures above 650 K, endothermic cracking may occur – to lighter alkenes, and eventually to CH_4. Again for butane, for example,

$$C_4H_{10} \rightleftarrows 2C_2H_4 + H_2 \,, \quad \Delta H_{f\,600K} = 73 \text{ kJ/mol} \tag{2}$$

The activation energies for these reactions are also very high, so they primarily occur on catalytic surfaces. Hydrocracking catalysts include oxides of Co, Ni, Mo, and W, supported on acid-treated Al_2O_3. The alumina acid sites catalyze the initial cracking (which is endothermic for isobutane even at 800 K), and the base-metal oxide catalyzes the subsequent exothermic hydrogenation [*8*]. These base-metal oxides may initially be present as very low coverage on many HT metallic component surfaces. The presence of even a minute amount of moisture can increase cracking catalytic activities by orders of magnitude (hence the imperative of avoiding sub-atmospheric pressure in the condenser).

At the very low H_2 and H_2O partial pressures that will be present, the catalytically active sites will eventually be deactivated with coke from reactions subsequent to dehydrogenation and cracking. Obviously, the use of catalytically active materials should be minimized, and surfaces should be deactivated prior to installation. After the internal surfaces of all the HT flow passages are well deactivated, catalytic cracking will essentially cease.

3.3 Minimizing Thermal Cracking

Above some temperature, thermal cracking proceeds faster than thermal dehydrogenation for alkanes higher than ethane. This crossover is ~750 K for isobutane and lower for higher alkanes. Thermal cracking will ultimately limit the maximum operating temperature, as alkane thermal cracking K_P's and rates increase by about three orders of magnitude for a 100 K increase in temperature. While thermal cracking of alkenes and normal alkanes beyond C5 occurs quite readily above 700 K, this limit is higher for n-pentane, isopentane, n-butane, isobutane, and propane (in that order). Thermal cracking of normal alkanes begins by homolysis of a C-C bond to form two alkyl radicals. Each of these radicals must then abstract hydrogen from another alkane, as this is favored over other possibilities [*9*, *14*]. The radicals can then undergo cleavage to form an ethylene or propylene. The thermal cracking activation energy for isobutane is higher because of the molecule's symmetry.

One reference reported ~2% thermal reactions for nearly pure isobutane in several seconds at 900 K, 0.1 MPa [*12*]; and others (with very low activity catalysts, giving almost thermal cracking) showed ~1% cracking (in a similar time) to propylene at 840 K, 0.4 MPa [*12*, *13*]. On the other hand, thermal cracking of naphtha (mostly C5-C9 alkanes with little branching) proceeds well over an order of magnitude faster under these conditions [*9*, *14*]. (Another stability clue is seen from the autoignition temperature, which is over 210 K higher for isobutane than for n-hexane and higher alkanes.)

Table 1 summarizes some calculated reaction equilibrium constants where the reactants are all isobutane. (The K_Ps are higher with n-butane than with isobutane.) Few thermal activation energies for these reactions have been reported, but they are very high for un-catalyzed cracking of isobutane, so those rates are much lower than their K_P's might suggest. The equilibrium constants for the methanation

Table 1. Calculated equilibrium constants (K_P) for some isobutane reactions

Primary Reactions	Product	K_P, 600 K	K_P, 700 K
$i\text{-}C_4H_{10} \rightleftarrows C_4H_8 + H_2$	butene	4.9E-5	2.5E-3
$i\text{-}C_4H_{10} \rightleftarrows 2C_2H_4 + H_2$	ethylene	4.5E-7	4.4E-4
$2\ i\text{-}C_4H_{10} \rightleftarrows C_8H_{18} + H_2$	octane	3.5E-5	2.3E-4
Secondary Reactions			
$C_6H_6 + C_2H_4 \rightleftarrows C_8H_{10}$	ethylbenzene	380	190
$C_4H_8 + C_2H_4 \rightleftarrows C_6H_6 + 3H_2$	benzene	6.6E4	2.2E5
$C_3H_8 \rightleftarrows C_3H_6 + H_2$	propylene	1.3E-4	5.2E-3
$C_2H_6 \rightleftarrows C_2H_4 + H_2$	ethylene	4.4E-6	2.4E-4
$i\text{-}C_4H_{10} \rightleftarrows C_2H_4 + C_2H_6$	ethane	0.1	1.8
$i\text{-}C_4H_{10} \rightleftarrows C_3H_6 + CH_4$	methane	11	1.9E3

Copyright 2009 by ASME

reaction listed on the last line look alarmingly high; but thermal methanation of isobutane first requires cracking [*14*], so its rate is still quite slow.

The single most effective measure that can be taken to reduce thermal cracking (and other un-catalyzed reactions) is to minimize the relative residence time in the HT regions. The high-temperature relative residence time is proportional to the ratio of the fluid mass in the HT zones to the total fluid mass. It is the residence time in the upper half of the final super-heater and the ducts from there to the expander turbine that really matter. (Note we sometimes denote the HT recuperator as the "first super-heater", as that is an accurate moniker; so the final "heater" in the DORC is also denoted the "final super-heater".) With proper attention to flow optimization details, the volume of the ducts from the final super-heater to the expander turbine can be reduced by two orders of magnitude compared to a recently published CSP example without a significant increase in viscous losses – a factor of 10 reduction in length and a factor of 3 reduction in diameters are often possible.

Alkane cracking and dehydrogenation increase the number of moles by a factor of two to three. Hence, although many reaction rates are proportional to concentrations, the rates of the critical reactions in the DORC are inverse with pressure over a very wide range [*9, 14*]. Hence, the reaction rates increase more slowly than might initially be expected from constant-pressure superheating if the pressure is sub-critical. At pressures much above the critical pressure, the effects of the increased density in the superheated gas outweigh the pressure effects. Thus, it is beneficial to stay sub-critical. Keeping the boiler sub-critical is also essential for simple and effective heavy hydrocarbons (**HHC**s) separations by the method discussed in section **4.3**.

From the isobutane cracking data mentioned earlier, we estimate about 0.8% isobutane thermal cracking in 1000 hours at 750 K and 3 MPa (with ppm-level moisture). If the HT relative residence time (between 730 and 760 K) is 1% (which seems quite practical with proper HT duct optimization and novel exchangers [*5*]), then about 0.07% of the fluid inventory would crack in one year. If the inventory (in kg) is 2000 times the magnitude of the engine flow rate (in kg/s), then the cracking rate is approximately 5E-8 of the engine fluid-flow rate. With a similar thermal dehydrogenation rate and a similar rate from residual catalytic reactions, the total primary reaction rate is expected to be ~1.5E-7 of the fluid flow rate for $T_{IT} = 760$ K. Of this, about one-fifth is H_2 and most of the balance would be CH_4, light alkenes, and other unstable HCs that may form coke or gum after a few more steps.

3.4 Preferred Working-fluid Mixtures

Table 2 lists some relevant properties of 12 fluids of relevance, including 4 high-boiling organics that could be used as heat transfer fluids (**HTF**s) from the CSP field.

Propane, as noted earlier, is more stable than isobutane, but using too much of it results in operating pressures being inconveniently high and critical temperature being lower than optimum in most cases. Benzene is nearly immune to dehydrogenation, and it is not easily cracked at low hydrogen pressures. However, its vapor pressure is much too low for it to be a large constituent of the fluid in a DORC, but it could be a minor component and thereby allow the addition of more propane with acceptable total vapor pressure and glide range.

A mixture of propane, isobutane, and benzene – with isobutane constituting most of the mixture – may have another advantage, as the benzene could help trap light alkenes for easier separation. Benzene hydrogenation to cyclohexane at the very low H_2 pressure present (outside the condenser, which is too cool) is much less likely than alkylation with the alkenes present to ethylbenzene, butylbenzene, etc. [*9, 14*]. The alkylated benzenes, and the octanes from butanes alkylated with butenes, can easily be removed from the fluid by the same process that removes all the heavy HCs (see section **4.3**) before they are likely to polymerize or have a major effect on vapor pressures. For 0.05, 0.9, and 0.05 molar fractions respectively for propane, isobutane, and benzene, the thermodynamic behavior in the DORC is similar to that for pure isobutane. For such a mixture, the condensing temperature at 0.4 MPa is 309 K (with a 15 K glide range from saturated vapor to saturated liquid), the mean boiling temperature at 2 MPa is 378 K (with an 8 K glide range), and the vapor pressure is above 0.12 MPa at 270 K. The boiler and condenser can readily be designed to handle these boiling and condensing temperature glides [*15*]. Unlike the ORC, the effect of glide on efficiency is negligible in the DORC.

An additional benefit of using mixtures with significant glides is that this makes it possible to achieve optimum performance over the large change in condensing temperatures seen between summer and winter operation in many areas [*16*]. Improved performance can be obtained by increasing the propane in the winter and the benzene or isopentane in the summer.

By keeping those HCs above C4 at a very low level (preferably below 2%, except for benzene and perhaps pentanes), coke and gum build-up beyond that desired for catalytic deactivation is minimized.

3.5 Minimizing De-isomerization

It is useful to minimize isomerization reactions – transformations of isobutane into other, less preferred isomers. Such reactions are most effectively catalyzed by acid sites (including aluminas) and especially superacids (such as HSO_3F and many halides) [*14*]. However, in the absence of active surfaces, isobutane isomerizations generally proceed more slowly than thermal cracking for the temperature range of interest [*12, 14*]. The thermodynamics favor isobutane over n-butane at low temperatures, so it may be desirable to include an isomerization reactor into the liquid stream, either before or after the preheating, to promote conversions of n-butane to isobutane. However, the isobutane/butane ratio then would be about 3 if the isomerization reactor is near 373 K or about 5 if near room temperature.

Even with effective on-line separations, the more rapid depletion of the isobutane relative to propane will require its periodic addition to restore the inventory to the desired amount and boiling point. (The benzene level may remain quite stable, as it may be created by some reactions, as seen in Table 1, about as fast as it is removed in alkylates in the HHCs.) Periodic fluid changing may still be desired, as this may be more cost-effective than separations processes for some less preferred isomers that are produced a low rates.

Copyright 2009 by ASME

4. ACCOMMODATING HIGHER REACTION RATES

A guideline on fluid stability requirements in prior CSP ORCs, where there have usually been no provisions to deal with gas evolution, is that working fluid loss *from reactions* be limited to approximately 0.03% per year, or about 1E-11 of the inventory per second. (Note that fluid leakage rates are often over two orders of magnitude higher than this.) The HT fluid inventory (benzene or toluene) in a conventional 5 MW_{PE} cascaded ORC may be ~100,000 kg. Light-gas production is about one tenth of total reaction products, or about 0.1 mg/s in this case. The partial pressure of the light gases would then build to ~6 kPa in the condenser (2% of total) in one year.

The other components of the reactions are predominately alkenes, which then could lead to gum and coke precursors if the concentrations of intermediates are allowed to build up. However, coke and gum are never primary or secondary products (and seldom even tertiary reaction products, at least from alkanes below C6) [*8*]. If their precursors are kept to a low enough concentration in the boiler, they should not be a problem. Their concentrations in the superheaters and condenser will be at least a factor of 20 lower than in the boiler, as shown in section **4.3**.

4.1 Acceptable Fluid Reaction Rates

Gas production is quite endothermic, so at some point it must be limited to avoid loss in system efficiency. Still, gas production three to four orders of magnitude beyond the limit that has previously been deemed necessary – an H_2 production rate per second equal to about 1E-12 of the fluid inventory mass – can be accommodated if the reaction products can be removed fast enough (and preferably reprocessed). The inventory magnitude in ORCs has often been ~3000 times the cycle flow rate per second, so an acceptable H_2 production rate has been seen as ~3E-9 of the engine fluid flow rate.

With efficient removal of all the reaction products but without their reclamation, a maximum reaction rate might be such that the energy lost in chemical reactions is about 0.5% of electrical output, as the increased T_{IT} enabled with higher reaction rates allows higher cycle efficiency. A 0.5% efficiency loss is equivalent to a fluid-loss rate equal to about 1E-5 of the flow rate in the engine. Cost-effective reclamation of the reaction products (both the gases and the HHCs) should be practical in large installations, in which case fluid loss rates three times higher could still be acceptable. This would be 10,000 times higher gas evolution than has been recommended in CSP ORCs.

4.2 Light-Gas Separations

From section **3.3**, we would expect an H_2 production rate of 3E-6 kg/s for T_{IT} =760 K with a fluid flow rate of 100 kg/s. Assuming a total vapor volume in the condenser of 200 m^3, an H_2 pressure of 40 kPa amounts to 6 kg H_2. This is approximately the amount of H_2 produced in 20 days at the above rate. Hence, a weekly gas venting process might be adequate, but the amount of isobutane lost in each condenser venting could be over 500 kg. There is a better option for the light-gas removal.

With a high-pressure condenser (as desired for other reasons), selective membranes {33} can easily keep the light-gas relative partial pressure below 0.1 with low loss of the working fluid. For example, the glassy polymer polyvinyltrimethylsilane has about 100 times the molar permeance to H_2 as to isobutane, and other membranes may have even better separation factors [*17*]. Hence, in removing 3E-6 kg/s H_2 at 10% partial pressure with a single membrane

Table 2. Relevant Fluid Data

Name	Formula	m.m.	pour point, K	n.b.p. K	T_C, K	p_c, MPa	Auto-ignition temp., K	ΔGf, 700 K, kJ/g	v. pres., 300 K, kPa	gas *k*, 500 K, W/m-K	γ, C_P/C_V, 600 K, 1 MPa
propane	C_3H_8	44.10	90	231.0	369.9	4.25	723	2.20	1000	0.0476	1.076
isobutane	C_4H_{10}	58.12	125	261.4	407.8	3.63	733	2.48	370	0.0442	1.059
n-butane	C_4H_{10}	58.12	150	272.7	425.1	3.80	678	2.51	258	0.0441	1.060
isopentane	C_5H_{12}	72.15	150	301.0	460.4	3.38	673	2.63	98	0.0408	1.051
n-pentane	C_5H_{12}	72.15	160	309.2	469.7	3.37	533	2.64	73	0.0385	1.052
benzene	C_6H_6	78.11	285	353.2	562.1	4.89	771	2.58	14	0.0289	1.070
toluene	C_7H_8	92.14	190	383.8	591.8	4.13	808	2.47	4.16	0.0308	1.067
water	H_2O	18.02	273	373.1	647.1	22.1		-11.6	3.54	0.0388	1.323
dioctyl phthalate	$C_{24}H_{38}O_4$	390.6	250	657	806	11.8	780	1.02	1E-4	-	-
1-n-dodecyl-naphthalene	$C_{22}H_{32}$	296.5	305	676	862	13	790	3.1	~1E-5	-	-
TBBP-100 phosphate			270	708			795		~1E-6	-	-
polyphenyl ether 5P4E	$C_{30}H_{26}O_4$	450	285	749	~900	~3	880	~2	~1E-10	-	-

Copyright 2009 by ASME

stage, one could achieve isobutane mass flow in the light-gas permeate also ~3E-6 kg/s. A small vacuum pump {**34**} is needed on the permeate stream, as the pressure there must be well below the H_2 partial pressure in the condenser. The permeate, possibly 10% molar fraction C_4H_{10} with the balance mostly light gases, would be vented in very small DORCs, but it could also easily be further separated. Most of the permeate's chemical energy is in the H_2, which could be compressed and sold. Of course, the isobutane and other components desired in the working fluid could be reused. With reclamation of these products, 5-30 times higher fluid reaction rates may be preferred to enable operation at 20-50 K higher T_{IT} and 2-4% higher cycle efficiency.

The theoretical minimum power required for pumping 6E-6 kg/s light-gas permeate from 10 kPa to 200 kPa is about 15 W. In practice, this may require 200 to 1000 W, but that is still a very minor loss relative to 13 MW_E. Obviously, hydrogen production rates up to two orders of magnitude higher could be acceptable from this perspective, which would then be similar to the limit deduced earlier in section **4.1**.

The *K*-values (ratios of vapor phase molar fraction to liquid phase molar fractions) for the primary non-condensables in isobutane at 0.4 MPa and 300 K are about 2000, 40, 10, and 6.7 for H_2, CH_4, C_2H_4, and C_2H_6 respectively. So, an H_2 molar fraction of 0.1 (or partial pressure of 40 kPa) in the condenser vapor implies an H_2 molar fraction of 5E-5 in the liquid. A C_2H_4 molar fraction of 1E-4 in the condenser vapor implies a C_2H_4 molar fraction of 1E-5 in the liquid. The process that addresses the hydrogen buildup would also probably accommodate the other gases, as they are produced at lower rates. The relative H_2 partial pressure on the high-pressure vapor side (between points **5** and **6**) is the same as the H_2 molar fraction in the liquid, and of little effect. The same is true of the CH_4 and C_2H_6. The alkenes will alkylate with the benzene or isobutane and come out in the HHC separations, as discussed next.

4.3 Lubricants and HHC Separations

The pump {**21**} could probably be designed to operate satisfactorily without a lubricant in the working fluid (by using MoS_2, teflon, or wear-resistance composite coatings), but the use of high-stability soluble lubricants may improve lifetime and reduce costs. A soluble lubricant would have much higher boiling point than isobutane, so it, like the other HHCs, would quickly concentrate in the boiler – and hence be depleted elsewhere.

If the lubricant is sufficiently stable, there would be no concern from it vaporizing in the boiler and continuing on through the cycle. A very minor vapor flux of the lubricant through the cycle would be sufficient to maintain adequate pump lubrication. Most common lubricants, anti-wear additives, antioxidants, and stabilizers could be disastrous at the temperature of the final superheater [*19*], but very low vapor concentrations of some pure HCs such as light alkylated aromatics or light poly-α-olefins should be acceptable [*19, 20*]. Soluble lubricants may significantly decrease the boiler vapor pressure (and hence pressure ratio) for a given boiling temperature. The cycle analysis becomes more complex, as the fluid composition is then very different in the boiler than elsewhere, but the effect on efficiency is small.

The *K*-value for the lightest usable lubricants in isobutane would likely be below 0.03 and their molecular mass would probably be above 150, so their concentration in the boiler would be over 30 times their concentration elsewhere. However, lubricant molar concentrations in the pump below 0.01% should be adequate, as good lubricants bind tightly to cool metal surfaces, and a lubricant film thickness of 0.1 to 0.4 microns is sufficient on precision surfaces [*19*]. The lower the normal boiling point of the working fluid, the greater the tendency of the HHCs to concentrate in the boiler. Most direct precursors of coke and gum (heavy n-alkanes, naphthalenes, higher polynuclear aromatics) in an oxygen-free fluid will have *K*-values similar to or lower than that of the lightest lubricants.

The easiest way to deal with the heavy reaction products is to periodically or continually drain the boiler liquid through drain valve {**41**} (while operating), and then cool, separate, and reclaim its constituents. The pentanes, butanes, and other lights can easily be flashed from the drained cooled fluid in flash drum {**42**}, and the remaining boiler concentrate (bottoms product) would be sent to a bottoms separation process {**44**}. The flash gas (perhaps 99% of the total flush stream) could simply be compressed {**43**} back into the condenser, or it could be further processed to a more preferred mixture, either locally or elsewhere, before reuse.

The (minute) bottoms product would consist mostly of pump lubricants if such are being used, and they would be separated for reuse. Separations may be done with a combination of selective membranes, selective absorbents, distillation, and freezing [*17*]. Boiler draining and the subsequent separations associated therewith are not a significant part of the thermodynamic cycle as the mean flow rate is extremely low, but they are critical to its lifetime.

The draining rate need only be sufficient to keep the total vapor pressure in the boiler within desired limits and to keep the concentration of direct coke precursors at very low levels in the vapor. Earlier, we estimated the production rate of unstable light precursors to be about 1E-7 of the fluid flow rate for T_{IT} = 760 K. Most of these precursors would lead to rather stable alkylates that would be removed along with the less stable HHCs. Since the direct coke and gum precursors will have low *K*-values in the boiler liquid, reasonable concentrations there would be allowed before there would be enough in the vapor to matter. With the alkylations and other secondary reactions, the total HHC production rate may be 3E-7 of the flow rate.

If the boiler drain rate is 3E-4 of the fluid flow rate, then the equilibrium concentration of new HHCs (not including the lubricant, assumed to be very stable) in the boiler would be 1E-3, assuming an HHC production rate of 3E-7. If their mean *K*-value is 0.03, the mean concentration of new HHCs in the vapor would be 3E-5, which should be more than low enough to keep the coke and gum formation rates acceptable. A boiler flushing rate of 3E-4 of the cycle flow rate could require about 0.15% of the electrical output power if the bottoms separations {**44**} and flash-gas recompression {**43**} are well implemented.

We note there is considerable uncertainty with respect to the level of unstable HHCs that could be allowed in the vapor without leading to excessive rates of coke and gum formation. Rough estimates suggest their vapor concentration

Copyright 2009 by ASME

might be able to exceed the level expected from the above assumptions (3E-5) by more than an order of magnitude without problems. If so, then T_{IT} at least to 800 K should be acceptable. The T_{IT} limits estimated in the previous section for accommodating hydrogen evolution were similar.

We also note there is considerable uncertainty in the limits imposed on H_2O contamination. It is not clear if it will be necessary to keep it below 2 ppm, or 10 ppm, or perhaps even 100 ppm for its role in catalyzing deleterious reactions to be negligible with respect to thermal reactions. If moisture ingress is not sufficiently minimized, it may be necessary to incorporate a process that steadily removes water from the fluid inventory. Undoubtedly, the H_2O limit will depend on many factors, including the exchanger materials, $T_{IT,}$ HT relative residence time, and the working-fluid maintenance program.

A 50 K decrease in T_{IT} may make the difference between needing continuous or monthly boiler flushes for adequate HHC separations, but it may also decrease cycle efficiency by 4%. The optimum temperature and fluid maintenance program will depend on (a) the higher-grade source temperature, (b) the size of the DORC, and (c) developments in separations technologies, especially membranes. Complete fluid changes may still eventually be needed to take care of buildup of less desired isomers (n-butane, n-pentane, hexanes, and others) that are not easily separated by simple methods. With highly effective HHC separations, complete fluid changes at 5- or even 20-year intervals may be adequate.

5. ANTICIPATED APPLICATIONS

Excellent solar resources are often present near many good geothermal resources. In these cases, much more economical resource utilization can be achieved by using a DORC in which the low-grade geothermal resource (360-460 K) drives the boiler while concentrated solar drives the super-heater, perhaps up to 800 K.

To quadruple a 20 MW_E geothermal power plant (~150 MW_T) to an 80 MW_E geo-CSP hybrid using the DORC would require ~140 MW_T of mid-grade heat. The geothermal is available continuously, while the concentrated solar is cyclic. Hence, some mid-grade thermal storage would be justified – perhaps enough to keep the plant running above 40 MW_E overnight after a typical day. The solar field may need to have about 500 MW_T peak capacity to provide about 110 MW_T mean heating, depending on the location and the tracking system. The solar field need not be constructed very close to the geothermal plant, as the mid-grade solar heat could easily be piped cost effectively at least 30 km to the existing 20 MW_E geothermal plant, or the new plant could be constructed quite some distance from either heat source. The condenser heat rejection requirement for the new 80 MW_E DORC would be only 60% more than that of the 20 MW_E geothermal ORC it replaces.

An existing 65 MW_{PE} (peak electrical output) CSP plant (~200 MW_{PT}, peak thermal power) might be able to be tripled to a 200 MW_E geo-CSP hybrid with much higher capacity factor (ratio of mean to peak electrical output) by drilling down a few miles and adding ~200 M_{WT} of geothermal. An industrial plant with a large amount of low-grade waste-heat will be more motivated to add micro-CSP to the roof-top of their plant (or in a nearby field) if they know they can now convert both with much higher efficiency.

The assumed mid-grade source temperature of 720 K is somewhat higher than current trough-CSP technology, which has been limited to ~660 K by available, low-cost, organic HTLs [*7*]. Salts have been used as HTLs in Tower-CSP to at least 840 K, and organic HTL advances appear likely to permit trough-CSP to reach at least 720 K before long [*21*].

Preliminary simulations also showed the potential for exceeding 50% of Carnot limits with low-grade heat sources as low as 320 K using pure propane as the working fluid [*22*], again with CSP superheating. Nonetheless, the practicality of using such a cycle with oceanic thermal gradients still looks doubtful, partly because of the distances involved between the sink and the low-grade and mid-grade sources. However, these simulations do suggest that low-cost flat-plate solar for the low-grade source, combined with CSP for the mid-grade, driving a propane-butane-DORC is worth more investigation.

Finally, we return to what motivated us to begin this development – using off-peak wind energy to synthesize standard transportation fuels (ethanol, gasoline, jet fuel...) from waste CO_2 and water [*1, 22*]. Preliminary simulations indicated that with enough innovations and advances, it should become practical to achieve about 60% net system efficiency from input electrical energy to chemical energy in the products. One of the important prerequisites for this level of efficiency is more efficient conversion of the enormous amounts of waste heat produced by the electrolyzer and the Fischer Tropsch reactor in the proposed process, and the DORC appears able to do that. Recent system simulations indicate that these synthesized *WindFuels* will be more competitive and much more carbon neutral than most biofuels in the economy of the future [*1, 23*].

6. CONCLUSIONS

A single system efficiency for the DORC for a given set of conditions is less meaningful than for conventional cycles, as the DORC uses two heat sources, one of which is not only of higher thermodynamic quality, but also more valuable. In the geo-CSP example simulated, the electrical output was 27.5% of the total input heat. Approximately half of the input was from a 400 K geothermal source, and approximately half from a 720 K CSP source. If the low-grade source is nearly free, as with some industrial waste heat, then one can consider efficiency of utilization of the CSP source to be over 50%.

Another of the major benefits of the DORC is that the condenser operates at ~0.4 MPa (assuming isobutane) rather than 0.004 MPa (as for water). This permits an enormous size reduction in the expander turbine – the most expensive component of the thermal conversion system.

Seven measures are essential to increase the turbine inlet temperature from 480 K to 600-800 K for working fluids that are mixtures of mostly light alkanes. In likely order of importance, they are:

1. Accommodate two to four orders of magnitude higher light-gas evolution.

Copyright 2009 by ASME

2. Minimize the fraction of time the fluid spends at high temperatures.
3. Use mixtures of mostly isobutane, propane, benzene, and isopentane for the working fluid such that the total vapor pressure is above 0.1 MPa at the minimum, cold-night, condenser temperature.
4. Remove all HCs above C5 and all alkenes to the extent practical, either continually or periodically, except for benzene and perhaps very low levels of highly stable lubricants.
5. Minimize catalytic activity of all surfaces in contact with the hot vapors.
6. Keep oxygen and moisture levels in the ppm range.
7. Operate at high-side pressures of 40% to 95% of the boiler critical pressure.

Coke and gum are not primary or secondary reaction products from light alkanes. If HHC separations processes are utilized to keep direct coke and gum precursors to a low enough concentration in the boiler, they should not cause problems, as their concentrations in the superheaters and condenser will be lower than in the boiler by a factor of 20 to 100. The lower the normal boiling point of the working fluid, the easier it is to separate the deleterious precursors from it.

We estimated the hydrogen production rate from thermal cracking of isobutane to be about 3E-8 of the engine fluid-flow rate for a peak temperature of 760 K at 3 MPa for an HT relative residence time of 1%. Methods for removal of reaction products (both light and heavy) at rates well over an order of magnitude larger should be quite practical with very little energy consumption. This suggests peak temperatures up to 800 K may be manageable with working fluids consisting of mostly isobutane.

The geo-CSP hybrid using a dual-source organic Rankine cycle with isobutane as a major component of the working fluid shows enormous promise for reducing the cost of renewable energy.

REFERENCES

[1] FD Doty and S Shevgoor, "Securing our Transportation Future by Using Off-Peak Wind to Recycle CO_2 into Fuels", ES2009-90182, ASME Joint Conferences, San Francisco, 2009.

[2] R DiPippo, "Geothermal Power Plants: Principles, Applications and Case Studies", Elsevier Ltd, Oxford U.K., 2005.

[3] E Prabhu, "Solar Trough Organic Rankine Electricity System (STORES)", NREL/SR-550-39433, 2006. http://www.nrel.gov/docs/fy06osti/39433.pdf

[4] D Dejfors, G Svedberg, "Second Law Analysis of Ammonia-Water Power Cycle for Direct-fired Cogeneration Application", Intern J of Applied Thermodynamics, Vo2 2, pp 125-131, 1999.

[5] FD Doty and S Shevgoor, "Compact, High-Effectiveness, Gas-to-gas Compound Recuperator with Liquid Intermediary (CRLI)", HT2009-88372, ASME Joint Conferences, San Francisco, 2009.

[6] NIST REFPROP 8, http://www.nist.gov/srd/nist23.htm , 2007.

[7] H Price and V Hassani, "Modular Trough Power Plant Cycle and Systems Analysis" NREL/TP-550-31240, 2002.

[8] CH Bartholomew and RJ Farrauto, *Industrial Catalytic Processes*, Wiley, 2006.

[9] K Weissermel and HJ Arpe, *Industrial Organic Chemistry*, 4th ed., Wiley, 2003.

[10] SS Bharadway, LD Schmidt, "Oxidative Dehydrogenation Process", US Pat 5,639,929, 1997.

[11] JV Heyse, PG Johnson, BF Mulaskey, "Dehydrogenation Processes, Equipment and Catalyst Loads Therefor", US Pat 5,723,707, 1998.

[12] JD Kemp and RP Sieg, "Gasoline Production", US Pat 4,046,520, 1977.

[13] CD Chang, JE Penick, RF Socha, "Conversion of LPG Hydrocarbons to Distillate Fuels or Lubes using Integration of LPG Dehydrogenation and MODGL", US Pat 4,678,645, 1987.

[14] G Olah and A Molar, *Hydrocarbon Chemistry*, 2nd ed., Wiley, 2003.

[15] A Borsukiewicz-Gozdur, W Nowak "Comparative analysis of natural and synthetic refrigerants in application to low temperature Clausius-Rankine cycle", *Energy*, **32**, 344-352, 2007.

[16] BT Liu, KH Chien, CC Wang, "Effect of working fluids on organic Rankine cycle for waste heat recovery", *Energy*, **29**, 1207-1217, 2004.

[17] JD Seader and EJ Henley, "Separation Process Principles", 2nd ed., Wiley, 2006.

[18] FD Doty, "High-Temperature Dual-source Organic Rankine Cycle with Gas Separations", PCT to be published soon.

[19] LR Rudnick, "Synthetics, Mineral Oils, and Bio-based Lubricants, CRC, Boca Raton, 2006.

[20] TR Lynch, "Process Chemistry of Lubricant Base Stocks", CRC Press, Boca Raton, 2008.

[21] FD Doty, pending patent, "Compact, High-Effectiveness, Gas-to-gas Compound Recuperator with Liquid Intermediary", PCT to be published soon.

[22] FD Doty, "Hydrocarbon and Alcohol Fuels from Variable, Renewable Energy...", PCT WO 2008/115933, http://windfuels.com/PDFs/WO2008115933.pdf.

[23] GN Doty, FD Doty, LL Holte, D McCree, S Shevgoor, "Securing Our Energy Future by Efficiently Recycling CO_2 into Transportation Fuels – Driving the Off-peak Wind Market", Proceed. WindPower 2009, paper 175, Chicago, 2009.

Copyright 2009 by ASME