WASTE HEAT RECOVERY FLUIDS FOR HEAVY-DUTY TRANSPORTATION BOTTOMING CYCLE SYSTEMS: A SUMMARY REPORT

by

J. L. Krasinski, K. L. Uherka, R. E. Holtz, and J. E. Ash

Components Technology Division

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ABSTRACT

This report examines working fluids used in Rankine bottoming cycle systems for heat recovery from long-haul trucks, marine vessels, and railroad locomotives. Rankine bottoming cycle systems improve fuel economy by converting the exhaust heat from the prime mover into useful power. The report assesses fluid property requirements on the basis of previous experience with bottoming cycle systems. Also, the exhaust gas characteristics for the transportation modes of interest are summarized and compared. Candidate working fluids are discussed with respect to their potential for use in Rankine bottoming cycle systems. Analytical techniques are presented for calculating the thermodynamic properties of single-component working fluids. The resulting equations have been incorporated into a computer code for predicting the performance of Rankine bottoming cycle systems. In evaluating candidate working fluids, the code requires the user to input only a minimal amount of fluid property data.
I. INTRODUCTION

This is a summary report describing Argonne National Laboratory's (ANL) work on waste heat recovery fluids for heavy-duty transportation bottoming cycle systems.

Bottoming cycles improve fuel economy by converting exhaust heat from the prime engines into useful power. The major objective of Argonne's work is to determine the optimum working fluids for candidate Rankine bottoming cycle (RB) systems for installation on long-haul trucks, marine vessels, and railway locomotives. The purpose of the work is to advance scientific knowledge and establish the foundation for future technology development by the private sector or government agencies involved in implementing more fuel-efficient transportation systems.

Although the emphasis of the project is on working fluids for organic Rankine bottoming cycle (ORB) systems, non-organic fluids (e.g., steam, inorganic fluids, etc.) are included in the scope of work for RB applications involving high-temperature exhaust streams, such as those associated with advanced adiabatic diesel engines. (In the adiabatic diesel, the cooling system is eliminated and certain metallic components are replaced with ceramic materials; the resulting exhaust gas temperatures of adiabatic diesels are thus significantly higher than those of standard diesel engines [1,2].)

The major project efforts are focused on three tasks:

- **Task 1 - Bottoming Cycle Requirements.** Determine fluid property and other critical requirements for transportation bottoming cycle systems on the basis of industrial R&D experience to date. This involves collecting data from present and former contractors on fluid characteristics, materials, thermodynamic requirements, and other pertinent factors.

- **Task 2 - Characterization of Fluids.** Identify candidate fluids, derive fluid selection criteria based upon the bottoming cycle requirements established in Task 1, and characterize the working fluids for long-haul trucks, railway locomotives, and marine push-tow vessels. Task 2 includes participation by chemical manufacturers and other industries involved in the development and characterization of working fluids.

- **Task 3 - Fluids Comparative Evaluation.** Establish the methodology and simulation models necessary for thermodynamic and economic analysis of transportation bottoming cycle systems. This will enable a cost/benefit assessment of the candidate fluids to be performed and allow a ranking of heat recovery fluids for each transportation system of interest.

For Task 1, data were obtained from the following sources: a literature search, telephone conversations with researchers working in related areas, and site visits to present and former Department of Energy (DOE) contractors. Task 1 has been completed and the results are presented in Section II of this document. These results are pertinent to the Task 2 and Task 3 efforts.
Task 2 involves the identification and characterization of working fluids for heavy-duty transportation bottoming cycle systems. Adequate thermophysical property data is generally available for the more commonly used organic fluids which include methanol, toluene, Refrigerant 11, Refrigerant 113, and Fluorinol 85. These fluids all have stability temperatures below about 750°F. A technology gap exists for fluids that have stability temperatures beyond about 750°F; such fluids would be appropriate for RBC systems integrated with adiabatic diesel engines. In conjunction with Task 2, additional data on working fluids were acquired by ANL from industrial organizations. This effort will be discussed in Section III.

Task 3 involves the development of the methodology and simulation models necessary for the thermodynamic and economic analysis of transportation bottoming cycle systems. The work includes modification and updating of Argonne's RBC Performance Code (originally developed for analyzing RBC systems for stationary power generation applications) to include improved component models, variable duty-cycle operation, etc. A single-component fluid property subroutine has been developed and integrated into ANL's RBC Performance Code. Current efforts focus on documenting and integrating a multicomponent fluid property subroutine into the RBC Performance Code. Future work will include improving Rankine bottoming cycle component models and simulating transportation duty cycles. Additional details of the Task 3 effort are given in Section IV.

II. BOTTOMING CYCLE REQUIREMENTS FOR HEAVY-DUTY TRANSPORTATION SYSTEMS

A. Characteristics of Rankine Bottoming Cycle Systems

The RBC systems installed on long-haul trucks, railroad locomotives, and push-tow boats will convert heat from the exhaust gases into shaft power. The major components of an RBC system are shown in Fig. 1 [3,4]. Although the system shown in Fig. 1 is designed for a truck application, the components are similar to those required for the locomotive and marine applications.

The working fluid in the RBC system is in the liquid state on entering the vapor generator. In the vapor generator, the fluid is heated, vaporized, and (possibly) superheated by the hot exhaust gas. The temperature of the exhaust gas stream decreases as it passes through the vapor generator. The point of closest approach between the working fluid temperature and the exhaust gas temperature is referred to as the pinch point of the vapor generator. As the pinch-point temperature difference between the exhaust gas and the working fluid becomes smaller, the size of the vapor generator generally increases.

After leaving the vapor generator, the working fluid then enters the turbine. The fluid expands through the turbine, producing mechanical work. The turbine delivers power to the diesel output shaft through a gearbox. After expanding through the turbine, many of the organic fluids used in RBC systems are still superheated. To recover some of this energy, the organic vapor flows through the regenerator (see Fig. 1), where heat is transferred to the working fluid entering the vapor generator. After leaving the
regenerator, the working fluid then passes through the water-cooled condenser, feedpump, and the regenerator (liquid-side) prior to entering the vapor generator and completing the cycle.

The RBC system illustrated in Fig. 1 was installed on a long-haul truck. The systems installed on railroad locomotives and push-tow boats would contain similar components, although the hardware would be larger in size. The relative power outputs of RBC systems for long-haul trucks, railroad locomotives, and push-tow boats are shown in Table 1; the expected power outputs for locomotive and marine RBC systems are an order of magnitude larger than the power output for truck RBC systems.

Table 1. Comparison of Rankine Bottoming Cycle Systems

<table>
<thead>
<tr>
<th>System Application (Reference)</th>
<th>Prime Mover/Heat Source Size, hp</th>
<th>Heat Source Temperature, °F</th>
<th>Bottoming System Size, hp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long-haul trucks (3,4)</td>
<td>285</td>
<td>950</td>
<td>40-45</td>
</tr>
<tr>
<td>Locomotives (5)</td>
<td>3950</td>
<td>800</td>
<td>475</td>
</tr>
<tr>
<td>Push-tow boats (6)</td>
<td>5600</td>
<td>700</td>
<td>510</td>
</tr>
</tbody>
</table>
In the Task 1 effort, both present and former DOE contractors were consulted to determine bottoming cycle requirements for the prime engines used in heavy-duty highway, railway, marine, and pipeline transportation systems. The objective was to establish baseline data concerning size and configuration constraints, engine exhaust temperature and pressure limitations, materials requirements, operational (full and part-load) specifications, safety considerations, and other aspects.

The industrial organizations visited in conjunction with Task 1 included the Electro-Motive Division of General Motors Corporation, the Advanced Energy Programs Department of General Electric Company, the Thermo Electron Corporation, and the Sundstrand Corporation. Typical design information for ORBC heavy-duty transportation systems, as well as for stationary ORBC systems, is tabulated in Table 2.

**B. Working Fluids for Rankine Bottoming Cycle Systems**

One of the major decisions in the design of an RBC system is the selection of an appropriate working fluid. Consideration must be given to the fluid thermophysical properties, materials compatibility, safety requirements, and cost. The temperature range of the waste heat source also affects the choice of a working fluid. In addition, there may be site-specific restrictions (e.g., toxicity and flammability requirements) that preclude the use of a given fluid. Consequently, the fluid selected for one RBC system may not be the optimum choice for all heat-recovery applications.

For electric utility power generation systems, steam is the working fluid of choice. Over the ranges of power outputs and heat source temperatures characteristic of RBC systems, however, fluids other than steam have been used. Typically these fluids have been organic fluids that can use single-stage turbines and still achieve higher efficiencies than steam systems. The organic fluids have been either pure fluids or components in a mixture with other organic fluids or with water.

In developing a set of fluid selection criteria for a given application, each of the above factors should be considered. Selection criteria are needed to identify potential working fluids for heat recovery from heavy-duty transportation systems. Examples of selection criteria that could be used for heavy-duty transportation systems are given in the 1973 Monsanto Study [7]. In the Monsanto Study, selection criteria were developed to identify promising working fluids for automotive Rankine cycle engines. In general, the size and weight constraints for heavy-duty transportation systems will be less severe than those for the automotive system. Therefore, the criteria established in the Monsanto Study need to be appropriately modified for heavy-duty transportation systems. Table 3 lists the fluid selection criteria established in the Monsanto Study. Also given in Table 3 is a preliminary list of selection criteria for heavy-duty transportation systems. The criteria for the heavy-duty transportation systems are similar to those used for automobiles, although changes have been made to reflect differences between the two types of applications.

Examples of fluids selected for previous organic Rankine cycle (ORC) systems are shown in Table 4. The categories of application are primarily mobile
Table 2. Design Information for Representative Bottoming Cycle Systems

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>System Application</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>System Power Output (HP)</td>
<td>510</td>
<td>40-45</td>
<td>900</td>
<td>900</td>
</tr>
<tr>
<td>Exhaust Gas Inlet Temp. (°F)</td>
<td>700</td>
<td>950</td>
<td>821</td>
<td>752</td>
</tr>
<tr>
<td>Exhaust Gas Exit Temp. (°F)</td>
<td>277</td>
<td>280-300</td>
<td>~360</td>
<td>~300</td>
</tr>
<tr>
<td>Working Fluid</td>
<td>Fluorinol 85</td>
<td>Fluorinol 85</td>
<td>Toluene</td>
<td>Toluene</td>
</tr>
<tr>
<td>Turbine Inlet Temp. (°F)</td>
<td>600</td>
<td>550</td>
<td>465</td>
<td>465</td>
</tr>
<tr>
<td>Turbine Inlet Pressure (psia)</td>
<td>700</td>
<td>800</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Condensing Temperature (°F)</td>
<td>98</td>
<td>~50-150 (varies with ambient temp.)</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>Condensing Pressure (psia)</td>
<td>3</td>
<td>~1-10</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Coolant Inlet Temp. (°F)</td>
<td>75</td>
<td>---</td>
<td>86 (Design)</td>
<td>86 (Design)</td>
</tr>
<tr>
<td>Coolant Exit Temp. (°F)</td>
<td>---</td>
<td>---</td>
<td>111 (Design)</td>
<td>111 (Design)</td>
</tr>
<tr>
<td>Approximate Fluid Inventory (gal)</td>
<td>360</td>
<td>5</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Materials of Construction</td>
<td>Vapor Generator/Regenerator---Carbon Steel (SA-210A-1); Condenser-Cupronickel (90% Cu/10% Ni)</td>
<td>Vapor Generator--321 Stainless Steel and Carbon Steel Fins; Condenser/Regenerator--Aluminum</td>
<td>Carbon Steel and Copper</td>
<td>Carbon Steel and Copper</td>
</tr>
</tbody>
</table>

*AEPD - Advanced Energy Programs Department*
Table 3. Comparison of RBC Fluids Selection Criteria

<table>
<thead>
<tr>
<th>Fluid Selection Criteria</th>
<th>Monsanto Study (1973, Ref. 7)</th>
<th>Heavy-Duty Transportation Systems (1983, ANL)</th>
</tr>
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<tbody>
<tr>
<td>Allowable fluids</td>
<td>Known and available fluids as of 1973.</td>
<td>Known and available fluids as of 1983.</td>
</tr>
<tr>
<td>Fluid flow point (freezing point) restrictions</td>
<td>Flow point ≤ -20°F; liquid or non-damaging to engine at -40°F.</td>
<td>Similar restrictions apply.</td>
</tr>
<tr>
<td>Boiling point (to limit condenser pressure to 5-50 psia at condensing temp. of 220°F)</td>
<td>Normal boiling points of 150-250°F.</td>
<td>Similar restrictions apply except for lower condensing temp. (typically 100-200°F) and lower pressures (could be &lt; 5 psia). For condensing pressures of 1-50 psia, normal boiling points could be 100-300°F.</td>
</tr>
<tr>
<td>Fluid stability limits</td>
<td>Stable in carbon steel at 720°F for &gt; 200 hr.</td>
<td>Could be lower (500-600°F), depending on heat source; for adiabatic diesels, Tstab could exceed 1000°F.</td>
</tr>
<tr>
<td>I-factor restrictions (to limit regenerator size)</td>
<td>I-factor between 0.75 and 1.5.</td>
<td>Probably less restrictive--less severe size/weight constraints.</td>
</tr>
<tr>
<td>Minimum cycle efficiency</td>
<td>30%</td>
<td>Depends on system economics, i.e., payback period.</td>
</tr>
<tr>
<td>Limits on regenerator size—UAk/ (system hp)</td>
<td>125 $\frac{Btu}{hp\cdot hr\cdot F}$</td>
<td>Probably less restrictive, although smaller regenerators are desirable.</td>
</tr>
<tr>
<td>Turbine enthalpy drop limitation for single-stage turbines</td>
<td>$\Delta h \leq 200 \frac{Btu}{lbm}$</td>
<td>Turbine probably should be single-stage because multistage turbines are expensive.</td>
</tr>
<tr>
<td>Maximum fluid cost over a 5-yr period</td>
<td>$$100.00$</td>
<td>Depends on system economics.</td>
</tr>
<tr>
<td>Health, fire, and safety aspects</td>
<td>Negligible environmental impact.</td>
<td>May be somewhat less severe, depending on the number of systems in operation.</td>
</tr>
<tr>
<td>Materials and lubrication constraints</td>
<td>Working fluids must be compatible with low-cost materials and available lubricants</td>
<td>Low-cost materials are desirable, but stainless steel may be justified, depending on the system cost.</td>
</tr>
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Table 4. Fluids Selected for Previous ORC Systems

<table>
<thead>
<tr>
<th>Organization [Reference]</th>
<th>ORC Application</th>
<th>Working Fluid</th>
<th>Maximum Fluid Temperature, °F</th>
<th>Condensing* Temperature, °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerojet Corp. [8]</td>
<td>Automobile</td>
<td>AEF-78</td>
<td>650</td>
<td>241(A)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(hexafluorobenzene/perfluorotoluene)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>General Electric Co.</td>
<td>Locomotive</td>
<td>Fluorinol-50</td>
<td>600</td>
<td>180(W)</td>
</tr>
<tr>
<td>(AEFD)** [5]</td>
<td></td>
<td>(trifluoroethanol/water)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>General Electric Co.</td>
<td>Gas pipeline</td>
<td>Toluene</td>
<td>500</td>
<td>150(A)</td>
</tr>
<tr>
<td>(AEFD) [9]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>General Electric Co.</td>
<td>Push-tow boat</td>
<td>Fluorinol-85</td>
<td>600</td>
<td>98(W)</td>
</tr>
<tr>
<td>(AEFD) and Thermo</td>
<td></td>
<td>(trifluoroethanol/water)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electron Corp. [6]</td>
<td>Automobile</td>
<td>RC-1</td>
<td>720</td>
<td>220(A)</td>
</tr>
<tr>
<td>Monsanto Research Corp.</td>
<td></td>
<td>(hexafluorobenzene/pentafluorobenzene)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monsanto Research Corp.</td>
<td>Automobile</td>
<td>RC-2</td>
<td>720</td>
<td>220(A)</td>
</tr>
<tr>
<td>[7]</td>
<td></td>
<td>(2-methylpyridine/water)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sundstrand Corp. [10]</td>
<td>Stationary</td>
<td>Toluene</td>
<td>465</td>
<td>140(W)</td>
</tr>
<tr>
<td>sources</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermo Electron Corp.</td>
<td>Automobile</td>
<td>Fluorinol-85</td>
<td>550/625</td>
<td>217(A)</td>
</tr>
<tr>
<td>[8]</td>
<td></td>
<td>(trifluoroethanol/water)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Long-haul</td>
<td>Fluorinol-85</td>
<td>550</td>
<td>150(W)</td>
</tr>
<tr>
<td></td>
<td>trucks</td>
<td>(trifluoroethanol/water)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* (A) - air-cooled condenser; (W) - water-cooled condenser  
** AEFD - Advanced Energy Programs Dept.
systems (automobiles, heavy-duty transportation systems), although gas pipeline and stationary systems are included for purposes of comparison. The ORC systems in Table 4 are systems in which the maximum temperature of the working fluid generally exceeds 500°F. For lower-temperature designs in which the maximum fluid temperature is below 500°F, fluids other than those listed in Table 4 (e.g., Refrigerant 11, Refrigerant 113) often are selected. The condensers for the ORC systems in Table 4 were either water-cooled condensers or air-cooled units. The condensers used in ORC systems for heavy-duty transportation applications have typically been water-cooled units operating at condenser temperatures of 100–200°F.

The vapor pressure of a working fluid at the condenser temperature has been used in developing the fluid selection criteria. Too high a condensing pressure results in a heavy, bulky condenser undesirable for transportation applications. Too low a condensing pressure poses difficulties in providing the necessary net positive suction head to avoid feed pump cavitation, as well as increasing the possibility of air leakage into the system [7]. The condenser pressures selected are those which do not vary significantly from atmospheric pressure (see Table 3).

Inorganic fluids are additional potential candidates for RBC systems. The 1973 Monsanto Study identified approximately 30 inorganic fluids with boiling points in their range of interest [7]. These inorganic fluids were considered by Monsanto because of their potential for good thermal stability at the maximum temperature specified for the automotive system (720°F). Unfortunately, the inorganic fluids were so reactive (corrosive) and/or noxious that they could not be used with materials ordinarily found in automotive applications (in particular, low-carbon steel). No promising inorganic fluids were identified by Monsanto for automotive systems.

Additional information was acquired by ANL on some of the more common, commercially available inorganic fluids identified by the 1973 Monsanto Study. Product data sheets were obtained for the inorganic fluids listed in Table 5; of particular interest is their materials compatibility and reactivity. In general, the fluids in Table 5 are toxic fluids that must be handled carefully. It is important that the fluids not contact moisture; they react with water, sometimes violently, to form strong acids that are corrosive to most metals. This preliminary information indicates that there could be serious handling and safety problems associated with the widespread use of such inorganic fluids in bottoming cycle systems. Additional R&D is required to determine the compatibility of inorganic fluids with stainless steels and materials other than low-carbon steel.

If promising inorganic fluids were available, they could be used for heat recovery from heavy-duty transportation systems with high exhaust gas temperatures, such as those in adiabatic diesel engines (≥ 1000°F). In the adiabatic diesel engine, now under development, the exhaust gas temperatures are significantly higher than those of standard diesel engines. Working fluids being considered for RBC systems installed on adiabatic diesels should have relatively high thermal stability temperatures, i.e., in the range of 700–1000°F or higher. The specific inorganic fluids identified in the 1973 Monsanto Study appear to have handling and materials compatibility problems. If other inorganic fluids could be found that were both stable at high temperatures and more benign in nature, then those fluids could be attractive candidates for RBC systems designed for adiabatic diesel engines.
<table>
<thead>
<tr>
<th>Fluid Name</th>
<th>Chemical Formula</th>
<th>Source of Information</th>
<th>Melting Point, °F (°C)</th>
<th>Boiling Point, °F (°C)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon tetra-chloride</td>
<td>SiCl$_4$</td>
<td>Air Products and Chemicals, Inc. Allentown, PA</td>
<td>-94 (-70)</td>
<td>136 (58)</td>
<td>Highly corrosive; reacts violently with water to form hydrochloric acid and clear gelatinous silox-ane. System must be kept free of moisture. Stainless steel (304 or 316), teflon, pyrex, or quartz are compatible materials.</td>
</tr>
<tr>
<td>Germanium tetrachloride</td>
<td>GeCl$_4$</td>
<td>Powell Metals &amp; Chemicals, Inc. Rockford, IL</td>
<td>-58 (-50)</td>
<td>181 (83)</td>
<td>No corrosion data obtained.</td>
</tr>
<tr>
<td>Titanium tetrachloride</td>
<td>TiCl$_4$</td>
<td>Staufer Chem. Co. Westport, CT</td>
<td>-22 (-30)</td>
<td>277 (136)</td>
<td>Exposure to moisture generates hydrochloric acid, titanium oxides, and titanium oxychloride. Carbon steel can be used only if system is kept free of moisture.</td>
</tr>
<tr>
<td>Vanadium oxytrichloride</td>
<td>VOCl$_3$</td>
<td>Staufer Chem. Co. Westport, CT</td>
<td>-112 (-80)</td>
<td>261 (127)</td>
<td>When exposed to moisture, decomposes to form hydrochloric acid and vanadium pentoxide.</td>
</tr>
<tr>
<td>Phosphorus oxychloride</td>
<td>POCl$_3$</td>
<td>Monsanto Chem. Intermediates Co. St. Louis, MO</td>
<td>34 (1)</td>
<td>225 (107)</td>
<td>Reacts violently with water, forming hydrochloric and phosphorous acids; POCl$_3$ is corrosive to most metals except nickel and lead.</td>
</tr>
<tr>
<td>Phosphorus trichloride</td>
<td>PCl$_3$</td>
<td>Monsanto Chem. Intermediates Co. St. Louis, MO</td>
<td>-170 (-112)</td>
<td>167 (75)</td>
<td>Reacts violently with water, forming hydrochloric and phosphorous acids. Corrosive to most common metals except nickel and lead; not corrosive to iron if protected from moisture.</td>
</tr>
<tr>
<td>Klarus 1717 — a chloro- sulfurized hydrocarbon</td>
<td>17.5% S 19.0% Cl</td>
<td>Keil Chem. Div. of the Ferro Corp. Hammond, IN</td>
<td>&lt; 0 (-18) (Pour Point)</td>
<td>&gt; 550 (288)</td>
<td>No corrosion data obtained (Monsanto Study listed pure S$_2$Cl$_2$ as a candidate inorganic fluid).</td>
</tr>
</tbody>
</table>
C. Diesel Engine Exhaust Gas Characteristics

As part of the Task 1 effort, data were obtained on the performance of diesel engines used as prime movers on long-haul trucks, railroad locomotives, and marine push-tow vessels. In particular, information was gathered on the exhaust gas characteristics (e.g., temperatures, flow rates) of these particular prime movers. Such data are needed to define the design requirements of RBC systems and to determine the maximum operating temperatures of the working fluids. Exhaust gas temperatures and flow rates were obtained for both full-load and part-load conditions. The part-load data are needed to evaluate the performance of the RBC systems over the characteristic duty cycles of the prime movers.

Table 6 compares the exhaust gas temperatures and flow rates for the applications of interest. The marine and locomotive engines have similar ranges of exhaust gas temperatures and flow rates. The exhaust gas flow rates for both the standard and adiabatic truck engines are about an order of magnitude less than those for locomotives and marine vessels. The exhaust gas temperatures for trucks, on the other hand, vary widely, depending on the type of engine under consideration. The temperatures for standard truck engines are similar to those for locomotives and marine vessels. However, the exhaust gas temperatures for adiabatic diesels, now under development, are greater than 1000°F and depend on whether the engine includes a turbocompound unit. In the turbocompound diesel engine, a turbine driven by the exhaust gas stream transfers power to the drive train of the engine. The presence of this power turbine, in addition to the turbocharger, results in the lower exhaust gas temperatures of the turbocompound adiabatic diesel.

Figures 2-4 are profiles of exhaust gas flow rates and temperatures as a function of engine load for a number of diesel engines. The figures contain two sets of curves. On each figure, the solid lines represent one diesel engine model and the dashed lines represent a different diesel engine model. The marine and locomotive engines (Figs. 2 and 3) are standard diesel engines, while the long-haul truck data (Fig. 4) include information for a standard diesel engine as well as an adiabatic diesel engine. The exhaust gas flow rates increase with engine load. The variation of the exhaust gas temperatures with engine load differs from one engine design to another. Figures 2-4 show significant differences in the exhaust gas characteristics within each category of heavy-duty transportation systems. Consequently, the curves are intended to illustrate only general trends in the variation of exhaust gas temperatures and flow rates with engine load. The data shown are for turbocharged engines. The exhaust gas temperatures are the temperatures at the turbocharger outlet, i.e., the temperatures of the exhaust gas streams available for heat recovery by a Rankine bottoming cycle system.

Duty cycles for the locomotive and marine applications are given in Table 7. The locomotive data are an average of medium-duty cycle and heavy-duty cycle data. The marine duty cycles are typical of those vessels which operate on the Lower Mississippi River. No comparable duty cycle data were obtained for long-haul trucks. The fraction of time at which a long-haul truck engine operates at full power will vary with the route terrain (level, hilly, or mountainous) [12].
Fig. 2. Exhaust Gas Temperatures and Flow Rates for Two Marine Diesel Engines
--- GE Model 7FDML2A3; --- EMD Model 20-645E5/E7)
Fig. 3. Exhaust Gas Temperatures and Flow Rates for Two Locomotive Diesel Engines
(--- GE 16-CYL Engine for U36 Locomotive; --- EMD Model 16-645E3B)
Fig. 4. Exhaust Gas Temperatures and Flow Rates for Two Truck Diesel Engines
(— Data from Ref. 11; --- Mack Model ENDT676)
Table 6. Comparison of Diesel Engine Exhaust Gas Characteristics

<table>
<thead>
<tr>
<th>Application</th>
<th>Exhaust Gas Temp. at Full Power, °F</th>
<th>Exhaust Gas Flow Rate at Full Power, lb/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Locomotive</td>
<td>700-850</td>
<td>30,000-50,000</td>
</tr>
<tr>
<td>Marine</td>
<td>700-800</td>
<td>30,000-50,000</td>
</tr>
<tr>
<td>Truck</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard turbocharged diesel</td>
<td>700-950</td>
<td>2000-5000</td>
</tr>
<tr>
<td>Turbocharged adiabatic diesel with turbo-compounding</td>
<td>1000-1150</td>
<td>2000-5000</td>
</tr>
<tr>
<td>Turbocharged adiabatic diesel without turbocompounding*</td>
<td>1300-1400</td>
<td>2000-5000</td>
</tr>
</tbody>
</table>

*More recent information shows the exhaust gas temperatures of the turbocharged adiabatic diesel, without turbocompounding, to be in the range of 1100-1250°F at the turbine exit (at full power), depending on whether or not the engine is aftercooled [11] (see Fig. 4).

Table 7. Duty Cycles for Heavy-Duty Transportation Systems

<table>
<thead>
<tr>
<th>Application</th>
<th>Idle (% of time)</th>
<th>Part-Load (% of time)</th>
<th>Full-Load (% of time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Locomotive</td>
<td>50*</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Marine</td>
<td>10</td>
<td>0**</td>
<td>90</td>
</tr>
</tbody>
</table>

*Includes dynamic braking          **80% of full-load
III. CHARACTERIZATION OF FLUIDS

The major objective of Task 2 was to obtain information on potential working fluids for RBC systems used in the heavy-duty transportation sector. Fluid property data were acquired in order to select and characterize the most promising fluid candidates for heavy-duty transportation applications. The information acquired in Task 2 also will be available for use in the ANL RBC Performance Code (discussed in Section IV). The Task 2 effort was carried out with the assistance of companies in the chemical industry.

In conjunction with an earlier study, ANL already had acquired some property data on the fluids methanol, toluene, Refrigerant 11, Refrigerant 113, Fluorinol 85, and 2-methylpyridine/water [13]. As part of Task 1 of the current project, additional preliminary information was obtained by ANL on a number of commercially available inorganic fluids, as shown in Table 5. The inorganic fluids were considered as possible candidates for heat recovery from the high-temperature exhaust streams of adiabatic diesel engines. Task 2 itself involved acquiring more detailed fluid property data to complement existing information for the more common working fluids, as well as providing data on new fluids that could be of interest for heat recovery with RBC systems. Such data are especially needed to evaluate suitable working fluids for heat recovery from adiabatic diesel engines.

A wide variety of fluid properties is needed to assess the adequacy of a specific working fluid for an RBC system. The key fluid properties needed for such an evaluation are summarized below in Section A. Section B discusses specific fluids for which ANL obtained information from industrial organizations.

A. Properties Needed to Evaluate Rankine Bottoming Cycle Working Fluids

Adequate characterization of a working fluid for an RBC system requires a wide variety of information about that fluid. For this discussion, that information is divided into four major categories:

- Thermophysical Properties
- Stability/Compatibility
- Fluid Safety
- Availability/Cost

The fluid thermophysical properties (e.g., density, specific heat, vapor pressure, etc.) have a direct impact on RBC system design and performance. A fluid that has a property outside the desirable range (for example, too high a freezing point) can be eliminated immediately from further consideration. Fluid transport properties (i.e., viscosity and thermal conductivity) affect the system pressure drop, as well as the heat exchanger design (and cost). Similarly, the properties of the superheated vapor (e.g., enthalpy drop and specific volume) directly affect the design of the turbine.

Other fluid properties, such as molecular weight, critical pressure, and critical temperature, are needed for the mathematical models (e.g., equation of state) used in designing the RBC system and in analyzing its performance. Selecting a specific working fluid from a group of fluid candidates depends on
accurate thermophysical properties over the temperature and pressure ranges of interest. A further discussion on the impact of specific fluid properties on RBC system design is given in Section IV.

Because a working fluid in an RBC system contacts a variety of different materials, the compatibility of the fluid with these materials is an important consideration. The fluid stability restricts the maximum operating temperature (and hence the system efficiency) and affects the fluid replacement rate. The fluid must be compatible with any metals, sealing materials, and lubricants encountered in the system. The fluid stability at the maximum operating temperature is also of concern. Provision must be made for fluid decomposition products (e.g., venting of noncondensables or filtration of the working fluid) that could degrade system performance or even lead to a shutdown of the unit. Fluid additives may be required for enhancing the stability of a fluid or for mitigating the effects of products of decomposition on the system. Fluid decomposition is a complicated process that requires an experimental program (generally done statically in sealed capsules and dynamically in test loops) to assess the extent of the problem and to investigate various methods of solution.

Safety and handling requirements also must be known when a working fluid is selected. Hazards from the fluid can arise during normal system operation, system maintenance or changing of the fluid, or a system boundary failure resulting in the loss of most (or all) of the fluid inventory. Fluid toxicity data, such as the Threshold Limit Value of the fluid vapor,* are needed to evaluate the hazard potential of both the working fluid itself, as well as any decomposition products that may be regularly vented from the system.

The flammability of a working fluid, characterized by its flash point, fire point, autoignition temperature, and flammability limits, is an important safety consideration that has an impact on fluid handling, system design, and system operation. Fluids that are highly flammable or toxic may require additional safety systems or special handling and disposal methods; such fluids may even be precluded from use in a specific RBC application. The above characteristics need to be identified in order to assess their impact on the design and cost of an RBC system.

The cost of the working fluid not only affects the initial cost of an RBC system, but also its operating cost due to periodic fluid replacement. The replacement rate depends on the rate of fluid decomposition at the operating temperatures of the RBC system. Fluids selected for a specific application must also be available in sufficient quantities to meet the projected demand. Making accurate cost estimates may be difficult for new fluids under development that are not widely available. Consequently, fluid cost should probably be a secondary factor in initial fluid selection, with more emphasis placed on the other fluid properties discussed earlier.

*The Threshold Limit Value - Time Weighted Average (TLV-TWA) of a substance, published by the American Conference of Governmental Industrial Hygienists (ACGIH), is the time-weighted average concentration for a normal 8-hour workday (40-hour workweek), to which nearly all workers can be repeatedly exposed, day after day, without adverse effect.
B. Fluid Property Data Obtained from Industrial Organizations

As discussed in Section A, a wide variety of fluid property data is needed to adequately characterize a particular fluid and to evaluate its usefulness for a specific RBC application. Some data, such as the fluid boiling point, can be readily measured in the laboratory. Other information, such as that related to fluid safety and toxicity, may require expensive, long-term testing. A comprehensive testing program for a working fluid would not be warranted unless a preliminary evaluation indicated potential advantages of the fluid for the RBC system under consideration.

A number of working fluids that have been selected for use in RBC systems are listed in Table 4. These particular fluids were chosen on the basis of selection criteria established by the respective organizations involved in the various projects. Property data for the fluids in Table 4 are available, although the extensiveness of the data varies from fluid to fluid. In conjunction with Task 2 of the current project, ANL attempted to obtain data on additional fluids that could be considered for use in heavy-duty transportation RBC systems. Data on several fluids were received from various chemical companies. The fluids for which information was obtained, including their potential for use in heavy-duty transportation RBC systems, are discussed briefly below.

- Data were obtained from the Dow Chemical Company on methylene chloride [14]. An earlier study examining heat recovery from sources at "moderate" temperature; (i.e., 320-375°F) had recommended methylene chloride as one of the fluid candidates that merited additional consideration [15]. Methylene chloride is attractive with regard to its flammability properties; it has no flash point or fire point measurable by standard laboratory test methods. Unfortunately, the initial thermal degradation temperature of methylene chloride is 250°F. Because the exhaust gas temperatures for heavy-duty transportation systems exceed 700°F, methylene chloride would not be a viable candidate for this application.

- Data were obtained on "Fluid B" from E. I. duPont de Nemours and Company [16]. "Fluid B" is an informal designation for an isomeric mixture of trichlorodifluorobenzene. "Fluid B" was investigated with regard to rotating heat exchangers in Rankine cycle engines [17]. Tests carried out at 620°F with anhydrous borax (an inhibitor added to improve thermal stability) indicated good compatibility with a variety of Cr/Mo steels. Unfortunately "Fluid B" has a very high boiling point—397°F; this is outside the range of desirable values given in Table 3. Consequently, "Fluid B" has a very low vapor pressure over the range of typical condensing temperatures for heavy-duty transportation systems. (The vapor pressure of "Fluid B" is 0.02 psia at 100°F and 0.36 psia at 200°F.) Such low pressures increase the possibility of air leakage into the condenser, which may result in enhanced fluid decomposition due to fluid/air reactions in the high-temperature sections of the RBC system.

A wide variety of heat transfer fluids are commercially available for industrial applications. These fluids are marketed, for example, under the
tradenames Therminol®, Dowtherm®, and Syltherm® [18-20]. Such fluids are frequently used as liquid-phase heat transfer fluids in high-temperature applications. Because of their high boiling points (typically above 350°F), these fluids can be used in the liquid phase at much lower pressures than can water. The recommended operating range for these fluids can also be quite large: -60 to 600°F for Therminol® 60, -100 to 575°F for Dowtherm® J, and -40 to 750°F for Syltherm® 800 [19,20]. Like "Fluid B", however, such fluids have low vapor pressures (generally < 1 psia at 200°F) over the range of typical condensing temperatures of heavy-duty transportation systems. Even Dowtherm® A, intended for use as a liquid or vapor heat transfer agent, has a vapor pressure of only ~ 0.05 psia at 200°F [21]. In addition, some of these fluids would require auxiliary heating systems to eliminate freezing and startup problems at low temperatures (below 0°F). Based on this information, these families of heat transfer fluids do not appear to be good candidates for heavy-duty transportation RBC systems.

- Data were received by ANL on water-pyridine working fluids from the Union Carbide Corporation. These fluids could be used at up to ~ 750°F, although the Rankine cycle system would first have to be preconditioned with the fluid to ensure maximum stability [22]. In addition, operation at this temperature could require some type of fluid purification, including the purging of noncondensables. Operating the system at 550-650°F would result in considerably less decomposition of the fluid.

Pyridine is miscible with water in all proportions. As discussed in Chapter IV, mixing two single-component fluids can result in a fluid that has certain advantages for a specific RBC application. The addition of water lowers the toxicity and flammability of pyridine, as well as the fluid cost. In addition, the two fluids could be mixed such that expansion of saturated (or somewhat superheated) vapor through a turbine produces an exhaust fluid having neither too much liquid nor excess superheat [23]. Unlike the commercial heat transfer liquids discussed earlier, pyridine-water mixtures would have reasonable condenser pressures. The vapor pressure of a 60 wt% pyridine/40 wt% water mixture, for example, varies from 1.1 psia at 100°F to 14.2 psia at 200°F [22].

Pyridine was an initial fluid candidate in an earlier study examining working fluids for automotive Rankine engines [7]. One of the final two candidates eventually selected, RC-2, is a mixture of 2-methylpyridine and water. The 2-methyl derivative was selected, rather than the 3-methyl and 4-methyl derivatives, or pyridine itself, for the following reasons [7]:

- The 2-methyl derivative is the most effective water freeze point depressant.

*Therminol is a registered trademark of the Monsanto Company, Dowtherm is a registered trademark of The Dow Chemical Company, and Syltherm is a registered trademark of the Dow Corning Corporation.
- It has, in a water solution, a thermal stability comparable to pyridine/water and slightly higher than the other pyridine derivatives.

- The ideal cycle efficiency of 2-methylpyridine is equal to, or slightly higher than, that of its other family members in the range of 0-40 mole percent of the organic fluid. This range of low organic concentrations was preferred, because the presence of larger amounts of water would reduce the fluid toxicity and flammability.

- Its flash point, although significantly lower than those of the 3- and 4-methylpyridines, is higher than that of pyridine itself at equal molal concentrations of the fluids with water.

A mixture of 35 mole percent 2-methylpyridine was selected for the candidate RC-2 to place the flow point at ~ -40°F. This temperature was specified as the highest permissible cold-damage fluid temperature.

The advantages of 2-methylpyridine/water mixtures over pyridine/water mixtures do not appear significant enough to immediately eliminate pyridine as a fluid candidate. Consequently, pyridine/water mixtures, in addition to the fluid RC-2, could be considered as possible candidates for heavy-duty transportation RBC systems, at least for systems with standard diesel engines.

Heat recovery from systems with adiabatic diesel engines will require fluids with higher thermal stability temperatures, due to the high exhaust gas temperatures. It is difficult to identify fluids that are stable at ~ 750-800°F, or higher, and that satisfy the additional selection criteria outlined in Table 3. Inorganic fluids, some of which are listed in Table 5, could be potential candidates for this application, although further investigation is needed to determine if such fluids can be found that are less corrosive to materials of construction and safer to handle. The fluid RC-1 (a mixture of 60 mole percent pentafluorobenzene and 40 mole percent hexafluorobenzene) is being tested for thermal stability at 700-1000°F [24]. A working fluid that is thermally stable in this temperature range is needed, if an RBC system is to be developed that more fully utilizes the high temperature exhaust gas streams available from adiabatic diesel engines.

IV. FLUID COMPARATIVE EVALUATION

A. Simulation Modeling

Simulation modeling is necessary for the thermodynamic and economic analysis of transportation bottoming cycle systems. A computer code was developed at ANL for examining organic Rankine cycle power systems in stationary applications [13]. The RBC Performance Code included thermodynamic property data for seven working fluids and calculated Rankine bottoming cycle system performance (efficiency, power output, etc.) for systems in the size range of 600-2400 kW. This initial model provides a foundation for the simulation modeling of transportation bottoming cycle systems.
The accomplishments in Task 3 for transportation bottoming cycle systems include:

- Development of a single-component fluid properties subroutine (e.g., toluene),
- Integration of this subroutine into the Rankine Bottoming Cycle Performance Code, and
- Development of a multicomponent fluid property subroutine (e.g., ethanol/water).

The single-component fluid property subroutine is described briefly in Section IV-B. Details of the methodology and thermodynamic analysis are given in Appendix A.

The development of the multicomponent fluid property subroutine is discussed briefly in Section IV-C. The results of this effort will be reported separately [25].

The future ANL development of computer simulation models and the performance of cost/benefit assessments of selected fluids for long-haul trucks, marine vessels, and locomotives are directed towards accomplishing the following goals:

- Documentation of the multicomponent fluid property subroutine and integration of this subroutine into ANL's RBC Performance Code,
- Improvement of Rankine bottoming cycle component models (vaporizers, etc.) for use with transportation system modeling, and
- Development of a transportation duty cycle simulation model.

B. Thermodynamic Evaluation of Rankine Bottoming Cycle Working Fluids

For optimal, useful energy recovery with a Rankine bottoming cycle (RBC) system, the working fluid should be tailored to the characteristics of a particular waste-heat source. Consideration of the significant thermodynamic properties of the fluid should include:

- The boiling point temperature,
- Condensing pressure,
- Expansion ratio through the turbine,
- Enthalpy drop through the turbine, and
- Shape of the vapor saturation curve.

In addition to influencing the cycle thermodynamic efficiency, each of these attributes has a bearing upon the size and cost of the mechanical components of an RBC system. The items listed above are directly related, respectively, to:
For heat sources in the temperature range of 700-800°F or less, the use of steam as a working fluid results in RBC system efficiencies lower than the efficiencies of systems using organic fluids. So at these heat-source temperatures, organic fluids become attractive. For example, toluene has been used in a stationary bottoming-cycle generating system manufactured by the Sundstrand Corporation [10]. For a wider range of applications, including the higher temperatures associated with the adiabatic diesel engine, a wider spectrum of possible working fluids should be investigated. For example, Monsanto Corporation recommended the fluids RC-1 and RC-2 for an automotive application after an extensive screening of candidate organic fluids [7]. The composite RC-1 is a pentafluorobenzene/hexafluorobenzene mixture; RC-2 is a 2-methylpyridine/water mixture. The screening process used in Ref. 7 included consideration of physical properties such as freezing points, vapor pressures, liquid densities, viscosities, specific heats, and thermal conductivities. Many candidate fluids were eliminated by failure to pass preliminary constraints imposed on the cost, toxicity, operating stability, flammability, and materials compatibility with mechanical components. Candidates that survive the screening process need to be evaluated for their Rankine-cycle thermodynamic performance.

The original ANL computer program was developed to comparatively analyze working fluids for Rankine bottoming cycles [13]. Evaluation was based on system performance and cost. The thermodynamic properties of the fluid must be provided as input to perform the calculations. The required properties have to be supplied as tabulated data. Because such data for many fluids are rarely available in sufficient detail, analytical expressions for thermodynamic properties of single-component fluids (see Appendix A) were used to modify and generalize the original RBC Performance Code developed by ANL. In the modified code, the thermodynamic and physical properties of a wide range of single-component fluids can be computed directly for inclusion into the Rankine-cycle performance and cost-analysis code.

The fluid thermodynamic properties have a significant impact on the RBC system design and performance. The manner in which five of the major fluid characteristics influence the selection of cycle components is outlined below:

1. The working fluid boiling point (in relation to the waste-heat source temperature) directly influences the size and cost of the boiler (vapor generator), which is a major factor in the overall system cost. As heat is supplied to the Rankine-cycle working fluid, the temperature of the heat source drops with passage through the heat exchanger; the dropping temperature is shown by the dashed line in Fig. 5. Relative to this line, the working fluid boiling point generally determines the pinch point and must provide a sufficiently large, positive temperature increment to avoid excessively large heat exchanger surface requirements.
Fig. 5. Minimum Temperature Pinch-Point Difference Between the Heat Source and the Rankine-Cycle Working Fluid
2. The condenser pressure range should be restricted to avoid air-leakage problems at the lower limit and structural integrity problems at the upper limit. The condenser pressure range is indirectly influenced by the working fluid boiling temperature. For example, to bound the condenser pressure between 5 and 50 psia for a condenser temperature of 220°F (the temperature may be lower if water-cooling rather than air-cooling is used), the normal (1 atm) boiling point can be specified (e.g., see Ref. 7) to fall between 150 and 250°F. The associated fluid constraints are illustrated in Fig. 6 based on the (approximate) straight-line relationship between ln p and 1/T.

3. The expansion ratio directly affects the turbine size. A large discharge specific volume of the working fluid will require a correspondingly larger through-flow turbine exit area.

4. Also related to the turbine size and cost is the magnitude of the enthalpy change. The gas velocity (squared) increases directly with the enthalpy drop. With high gas velocities, the corresponding blade tip speeds will also be high for efficient turbine performance. The enthalpy drop across a stage is limited by the maximum allowable blade tip speed and a large drop may require multistaging.

5. The slope of the vapor saturation curve is important in two respects: (a) to avoid entering the condensation ("wetting") region during expansion through the turbine, and (b) to avoid excessive enthalpy "loss" between the turbine exit state and the saturation line. The enthalpy "loss" may be partially recovered through the use of a regenerator which, however, entails an additional equipment expense. These two design considerations are somewhat conflicting and are controlled by the slope of the vapor saturation curve, as illustrated in Fig. 7. The slope depends on the ratio of the fluid latent heat of vaporization ΔH and vapor specific heat capacity C_p as measured by an "I-factor", defined below [7]:

\[
I = \frac{\Delta H}{C_p T}
\]

<table>
<thead>
<tr>
<th>I Value</th>
<th>Saturation Curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 1</td>
<td>Retrograde (positive)</td>
</tr>
<tr>
<td>Equal to 1</td>
<td>Isentropic (vertical)</td>
</tr>
<tr>
<td>Greater than 1</td>
<td>Wetting (negative)</td>
</tr>
</tbody>
</table>

C. Thermodynamic Analysis of Multicomponent Working Fluids

Because of the constraints imposed on eligible working fluids, the spectrum of acceptable single-component fluids is rather limited. Considerable adaptability in working fluid characteristics can be achieved by blending two (or three) pure components into a binary (or ternary) composite mixture. Improvements, such as a reduction in the freezing point of a fluid, can be achieved by mixing two components. Cost and flammability can be reduced by mixing an organic fluid with water. Because the range of fluid properties can be significantly extended by the mixing of pure components, an effort is underway to extend the computational capability of the ANL RBC Performance Code to include multicomponent fluids.
Fig. 6. Relationship of Normal (1 atm) Boiling Point Constraints for a Specified Acceptable Condenser Pressure Range.

Acceptable Range of Cond. Press.

Envelope of Acceptable Organic Working Fluids

Decreasing

Normal Boiling Point Range

150 F

220 F

250 F

1 atm

50 psig

5 psig

In p
a) Retrograde saturation curve (positive slope); no condensation but enthalpy "loss"

b) Negative saturation curve slope; no enthalpy "loss" but condensation

Fig. 7. Effect of the Saturation-Curve Slope on Working Fluid Performance
The discussion in Section IV-B illustrates the influence of the working fluid thermodynamic characteristics on the selection of ORBC system hardware and its resulting performance. For specified design conditions (power output, heating and cooling temperatures), there is a potential for improved cycle efficiency if working fluids can be synthesized to possess optimum saturation curve shapes, (critical points, boiling and condensation lines), latent heats, specific heats, etc. Guidelines for the selection and synthesis of such fluids are being provided through incorporation of a subroutine into ANL's RBC Performance Code for calculating the thermodynamic properties of multi-component fluids. The subroutine permits the computation of the thermophysical properties pertinent to a Rankine cycle performance analysis; in particular, the enthalpy drop through the turbine, the change in the specific volume of the fluid, and the prediction of possible condensation within the turbine. The dew-point and bubble-point curves are determined from an iterative solution of the vapor/liquid equilibrium equation (equality of the vapor and liquid fugacities). This condition is expressed in terms of semi-empirical expressions for the fugacity and activity coefficients [25]).

A sample computation was performed with the code for a binary mixture of ethanol and water using the Redlich-Kwong equation of state, the Antoine equation for the pure-component vapor pressures, and the Van Laar expressions for the activity coefficients. The multicomponent fluid property subroutine also could be easily adapted to examine mixtures with a higher number of components. Performing computations over a spectrum of component concentrations will quickly provide the information needed to determine an optimum mixture composition for a specific Rankine cycle application.
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APPENDIX A. ANALYTICAL EXPRESSIONS FOR THERMODYNAMIC PROPERTIES OF SINGLE-COMPONENT ORGANIC WORKING FLUIDS USED IN RANKINE BOTTOMING CYCLE SYSTEMS
A.1 INTRODUCTION

Rankine bottoming cycle (RBC) systems, previously designed for heat recovery from low temperature sources, have used working fluids other than water. Organic fluids, either in the pure state or in mixtures, have been used in order to improve the system efficiency. A computer code was developed in an earlier study at ANL to compare the performance of candidate working fluids [13]. The tabulated physical and thermodynamic properties of the selected fluids were input into the code. Utilization of the data to compute cycle performance involved interpolation procedures. To improve the code versatility, as well as to facilitate a more detailed study of the effects of fluid properties on RBC design/operation, analytical expressions for pertinent fluid properties were incorporated into the code.

The following discussion outlines the analytical procedures developed to treat single-component working fluids in the performance analysis of the Rankine cycle. Sample computational results are presented for toluene. The methods developed provide a basis for the more extended analysis required for multicomponent working fluids.

A.2 ENTHALPY AND ENTROPY CHANGES IN THE TURBINE

A.2.1 The General Problem

The basic Rankine cycle system involves a heat source (vaporizer or boiler), heat sink (condenser), and a heat engine (turbine). A pump supplies the condensate to the boiler. The cycle may include various refinements to improve efficiency, such as a regenerator to recover some of the heat at the turbine discharge. Of primary interest is the magnitude of the turbine work output measured by the enthalpy drop \( \Delta h_{12} \) between the inlet and outlet shown in Fig. A1, i.e.,

\[
\Delta h_{12} = h_1 - h_2.
\]

For specified inlet conditions and discharge pressure, the problem is to find the exit conditions. In exploratory, overall cycle-performance computations, the internal details of the turbine flow processes can be lumped into an assumed thermodynamic efficiency

\[
\eta_T = \frac{\Delta h_{12}}{h_1 - (h_2)_s}.
\]

This efficiency is defined as the ratio of the actual enthalpy drop divided by the theoretical enthalpy drop for an isentropic expansion. Because both the discharge entropy and pressure are known at state \((2)_s\), i.e., the thermodynamic state \((s_2, P_2)_s\) where \((s_2)_s = s_1\) is known, the isentropic enthalpy \((h_2)_s\) can be determined. For an assumed turbine efficiency, the actual discharge enthalpy \(h_2\) can be calculated from Eqs. 1 and 2.
Fig. A1. The Real Nonisentropic Expansion Process in the Turbine where (1) is the Inlet and (2) is the Outlet
The procedure for finding the turbine discharge state is conceptually very simple. Complications could be introduced if the expansion process were to enter the two-phase region. An advantage of many organic fluids over steam is that they are "nonwetting" or "retrograde" because the vapor-liquid saturation curve doubles back on itself, thereby avoiding expansion into the wet region with its undesirable condensate formation.

For the following discussion, the working fluid is assumed to be a pure substance (i.e., a single-component fluid) which remains completely in the vapor phase throughout the turbine.

A.2.2 Real Gas Considerations

For a perfect gas, the end state of an isentropic expansion is a simple function of the initial state. But in the region of the saturation curve, the thermodynamic processes of a real working fluid deviate significantly from the behavior of an ideal gas. The procedure developed here for treatment of the real gas effects of a pure, single-phase working fluid is to be incorporated into a computer subroutine. The method is based on the classical thermodynamic principles reviewed briefly below.

Deviations from ideal gas behavior can be represented by a "compressibility factor" $z$ (for an ideal gas $z = 1$):

$$ z = \frac{pV}{RT}, $$

where $R$ is the individual gas constant (the universal gas constant $R_u$ divided by the molecular weight $M$ of the selected fluid), i.e.,

$$ R = \frac{R_u}{M}. $$

Real gas deviations can be expressed by a power series ("virial expansion") in either pressure $p$ or the specific volume $v$. The "virial coefficients" are functions of the temperature $T$ alone:

$$ z = 1 + \sum_n A_n(T)p^n, $$

or

$$ z = 1 + \sum_n B_n(T)v^n. $$

Numerical values of the coefficients are estimated by combinations of various means (experiments, molecular statistical mechanics concepts, etc.).

Generalized correlations are sought for specific classes of working fluids by introducing "scaling" or "reducing" parameters. The classical scaling parameters which were originally used are $T_c$ and $p_c$, the critical temperature and pressure (i.e., values at the peak of the vapor-liquid dome), from which "reduced" temperatures and pressures are defined:
The assumption that $z$ is a common function of these two reduced parameters is the classical "principle of corresponding states." An improved expression for the class of organic fluids is a three-parameter extension of this classical principle by the introduction of an "acentric factor" $\omega$ [26]:

$$z = z(T_r, p_r, \omega)$$

This correlation, together with a truncated virial expansion, provides the basis for the Pitzer expansion used in the computer subroutine.

### A.2.3 Departure Functions

A convenient procedure for computing the change in thermodynamic properties between two equilibrium states, such as between the turbine inlet (1) and outlet (2) shown in Fig. A1, is to connect the points by two isothermal real-gas paths (at $T_1$ and $T_2$) and by a non-isothermal path in the ideal gas region. Variations of this concept are exemplified by methods involving either "residual properties" [27] or "departure functions" [28] which measure deviations between the real and ideal gas property values. The method involving departure functions used in the computer code is explained below.

For a gas temperature $T$ at a sufficiently small pressure $p^*$, the gas may be assumed to obey the ideal gas law

$$p^* = \frac{RT}{v^*}$$

As is well known from classical thermodynamics, the assumption that the entropy is a thermodynamic state function implies an ideal gas to be "calorically perfect"; that is, the internal energy $u^*$ is a function of temperature only:

$$u^* = u^*(T)$$

A gas state variable is by definition a function of two other state variables, e.g., pressure and temperature, and so the entropy function is given by

$$s = s(p, T)$$

The enthalpy is defined as

$$h = u + pv$$

and hence, for a calorically perfect, ideal gas,

$$h^* = u^*(T) + RT$$

or

$$h^* = h^*(T)$$
It follows that the perfect gas isotherms are vertical lines in an \((h,p)\) state diagram as shown in Fig. A2.

For a real gas, the enthalpy is a thermodynamic function of two variables, e.g., the pressure \(p\) in addition to the temperature \(T\):

\[
h = h(p,T) .
\]

The isotherms passing through points (1) and (2) may then deviate from the perfect-gas vertical lines, as shown in Fig. A3.

The departure of the enthalpy along an isotherm of the real gas from the perfect gas values is expressed in terms of "departure functions"

\[
Dh_1 = h^\circ_1 - h_1
\]

and

\[
Dh_2 = h^\circ_2 - h_2 .
\]

If the two isotherms are extended to the ideal gas region and then connected by an isobar, the enthalpy change along this isobar is the ideal gas difference

\[
\Delta h^{\circ}_{12} = h^\circ_1 - h^\circ_2 .
\]

The total enthalpy change between points (1) and (2) representing, say, the turbine inlet and outlet states, is the net change along each of the three paths (the two isotherms and the isobar):

\[
\Delta h_{12} = h_1 - h_2
\]

\[
= Dh_2 + \Delta h^{\circ}_{12} - Dh_1 .
\]

A differential form of the enthalpy change is derived from Eq. 11:

\[
dh = du + pdv + vdp .
\]

Along an isobar the differential is

\[
dh|_p = du + pdv .
\]

The right-hand side is recognized as an "equivalent heat" \(\delta q\) (from the first law of thermodynamics), which may be expressed in terms of the specific heat capacity at constant pressure:

\[
dh|_p = C_p dT .
\]

Hence, along the ideal gas \(p^\circ\)-isobar,

\[
\Delta h^{\circ}_{12} = h^\circ_1 - h^\circ_2
\]

\[
= \int_{T_2}^{T_1} C^\circ_p(T) dT .
\]
Fig. A2. Perfect Gas Isotherms in a (p,h) Diagram
Fig. A3. Departure $Dh$ of the Real Gas Enthalpy from Perfect Gas Values
The ideal gas specific heat may be approximated by a power series in $T$:

$$C_p^o = A + BT + CT^2 + DT^3 .$$  \hspace{1cm} (21)

In general, the differential enthalpy from Eq. 13 is

$$dh = \frac{\partial h}{\partial p} dp + \frac{\partial h}{\partial T} dT .$$  \hspace{1cm} (22)

The departure functions are the path integrals along the isotherms:

$$Dh_1 = h^o_1 - h_1$$

$$= \int_{p_1}^{p_1^o} \left. \frac{\partial h}{\partial p} \right|_{T_1} dp$$

and

$$Dh_2 = h^o_2 - h_2$$

$$= \int_{p_2}^{p_2^o} \left. \frac{\partial h}{\partial p} \right|_{T_2} dp .$$  \hspace{1cm} (23)

Substitution of the forms given by Eqs. 20 and 23 into Eq. 16 gives the enthalpy difference between the gas state points (1) and (2).

The difference in entropy $\Delta s_{12}$ between the two points can be represented by the same form as Eq. 16 for the enthalpy:

$$\Delta s_{12} = s_1 - s_2$$

$$= Ds_2 + \Delta s_1 - Ds_1 .$$  \hspace{1cm} (24)

The entropy differential is defined in terms of the equivalent heat $\delta q$,

$$ds = \delta q/T ,$$  \hspace{1cm} (25)

and is related to the enthalpy through Eq. 17 and the first law of thermodynamics:

$$dh = du + pdv + vdp$$

$$= \delta q + vdp$$

$$= Tds + vdp .$$  \hspace{1cm} (26)

Hence, along the $p^o$-isobar, the perfect-gas entropy change between the isotherms is
\[ \Delta s_{12}^* = s_1^* - s_2^* \]

\[ = \int_{T_1}^{T_2} \frac{C_v^o(T)}{T} \, dT . \]  

A.2.4 Derivation of the Departure-Function Forms from the Helmholtz Function

The derivation of the enthalpy and entropy departure functions involves differentiation with respect to temperature at constant volume. It is convenient (and conventional) to introduce the Helmholtz function

\[ A = A(T,v) \]  

because \( T \) and \( v \) are the "natural coordinates" for this function. The Helmholtz function is defined as

\[ A = u - Ts \]  

and the differential is

\[ dA = du - Tds - s \, dT . \]  

Recall that the first law (for an infinitesimal, reversible process and a closed system) relates the internal energy \( u \) as a thermodynamic function (an "exact differential") to the heat \( \delta q \) and work \( \delta w \) terms (as "inexact differentials") through

\[ du = \delta q + \delta w \]

\[ = Tds - pdv . \]  

Hence, Eq. 30 becomes

\[ dA = -sdT - pdv . \]  

(This, incidentally, illustrates the basis for referring to \( T \) and \( v \) as the natural coordinates for \( A \)).

The general differential form for Eq. 28 is

\[ dA = \frac{\partial A}{\partial T} \, dT + \frac{\partial A}{\partial v} \, dv \]  

and comparison with Eq. 32 shows that the entropy is derived from the derivative of the Helmholtz function

\[ s = -\frac{\partial A}{\partial T} \bigg|_v . \]  

Combining the definitions for the enthalpy and the Helmholtz functions (Eqs. 11 and 29) gives
\[ h = A + Ts + pv . \]  
\[ (35) \]

The differential form is given by

\[ dh = dA + Tds + sdT + d(pv) . \]  
\[ (36) \]

Integration along an isotherm (from base pressure \( p^o \)) gives

\[ h^o - h = A^o - A + T(s^o - s) + p^o v^o - pv . \]  
\[ (37) \]

In the perfect gas region (at \( p^o \)) we have

\[ p^o v^o = RT \]  
\[ (38) \]

and in terms of departure functions

\[ Dh = DA + TDs + RT - pv , \]  
\[ (39) \]

where

\[ Dh = h^o - h , \]
\[ DA = A^o - A , \text{ and} \]
\[ Ds = s^o - s . \]  
\[ (40) \]

The Helmholtz departure function is derived from Eq. 32 as the path-integral along an isotherm* (see Fig. A4):

\[ DA = - \int_{v}^{v^o} pd\tilde{v} . \]  
\[ (41) \]

The value \( v^o \) (shown in Fig. A4) corresponding to the pressure \( p^o \) is in the ideal gas region, since the arbitrary \( p^o \) is considered to be sufficiently small. Another point \((i)\) is chosen on the isotherm where

\[ v_i > v^o . \]  
\[ (42) \]

That is, \((i)\) is another arbitrary point in the ideal gas region for which \( v_i \) will be allowed to increase indefinitely as \( p_i \) approaches zero. The path integral Eq. 41 can be formally resolved into

\[ DA = - \int_{v}^{v_i} pd\tilde{v} - \int_{v}^{v^o} pd\tilde{v} \]  
\[ (43) \]

(i.e., the integration simply traces and retraces the path from \( v^o \) to \( v_i \), cancelling itself out). The path segment between \( v^o \) and \( v_i \) is in the perfect gas region, so for the condition given by Eq. 42,

*The notation \((-)\) emphasizes that \( \tilde{v} \) is the integration dummy, not to be confused with the variable \( v \). Care must be taken when forming the limiting process, as is discussed later.
Fig. A4. An Isotherm in the (A,v) Plane with Perfect Gas in the Region Between $v^*$ and $v_1$. 

Ideal Gas Region (Low p, high $\tilde{v}$)

Helmholtz Function, A
\[
p = \frac{RT}{v}
\]  

and

\[
DA = - \int_{v_i}^{v} p \, dv - \int_{v_i}^{v^0} \frac{RT}{\tilde{v}} \, d\tilde{v}.
\]  

By adding and subtracting the integral of RT/\tilde{v} between v_i and v, the following expression is obtained:

\[
DA = - \int_{v_i}^{v} \left( p - \frac{RT}{v} \right) dv + \int_{v_i}^{v^0} \frac{RT}{\tilde{v}} \, d\tilde{v}.
\]  

Because the entropy is the derivative of A (see Eq. 34), we have

\[
s = - \left. \frac{\partial A}{\partial T} \right|_v = - \lim_{\Delta T \to 0} \frac{A(v, T + \Delta T) - A(v, T)}{\Delta T}
\]

and

\[
s^0 = - \left. \frac{\partial A^0}{\partial T} \right|_{v^0} = - \lim_{\Delta T \to 0} \frac{A(v^0, T + \Delta T) - A(v^0, T)}{\Delta T}.
\]  

The entropy departure function is obtained by the direct combination of the above two limits to give

\[
Ds = - \left. \frac{\partial A}{\partial T} \right|_{v, v^0}.
\]  

Conceptually, the limiting process is a rigid horizontal translation of the (T + \Delta T)-isotherm into the T-isotherm, as shown in Fig. A5.

The specific volumes v, v^0, and v_i appearing in the limits of the two integrals in Eq. 46 are held fixed for the differentiation. Consequently, the derivative operator \partial/\partial T can be "passed under" (i.e., commuted with) the integration operator so that

\[
Ds = \int_{v_i}^{v} \left( \frac{\partial p}{\partial T} \right)_v - \frac{R}{\tilde{v}} \, d\tilde{v} - \int_{v_i}^{v^0} \frac{R}{\tilde{v}} \, d\tilde{v}.
\]  

The integrals Eqs. 46 and 49 can be evaluated for a given equation of state, as explained below.

A.2.5 Evaluation of the Enthalpy and Entropy Changes Based On the Redlich-Kwong Equation of State

To demonstrate the procedure for computing the enthalpy and entropy changes, the working fluid is assumed to be described by the Redlich-Kwong equation of state (an extension of van der Waals equation of state):
Fig. A5. Limiting Process for the Evaluation of $\frac{\partial A}{\partial T}$ as $\Delta T \to 0$
This expression for \( p \) can be substituted into the integrand of Eq. 46 to evaluate the Helmholtz departure function. Taking the limit \( (v_1 \to \infty) \) gives

\[
DA = RT \ln \left( 1 - \frac{b}{v} \right) + \frac{a}{b \sqrt{T}} \ln \left( 1 + \frac{b}{v} \right) + RT \ln \frac{p^0v}{RT} .
\]  

Substitution of \( p \) from Eq. 50 into the integrand of the expression for the entropy departure function (Eq. 49) gives

\[
Ds = -R \ln \left( 1 - \frac{b}{v} \right) + 0.5 \cdot \frac{a}{bT^{1.5}} \ln \left( 1 + \frac{b}{v} \right) - R \ln \frac{p^0v}{RT} .
\]  

These expressions for \( DA \) and \( Ds \) can be substituted into Eq. 39 to give the enthalpy departure function

\[
Dh = 1.5 \cdot \frac{a}{b \sqrt{T}} \ln \left( 1 + \frac{b}{v} \right) + RT - pv .
\]  

The enthalpy and entropy changes across the turbine, \( \Delta h_{12} \) and \( \Delta s_{12} \), are obtained by substitution of the departure functions and the perfect gas differences \( \Delta h^0_{12} \) and \( \Delta s^0_{12} \) into Eqs. 16 and 24.

A.7.6 Computation of the Turbine Exit State for an Isentropic Expansion

The turbine inlet state \( (p_1, v_1, T_1) \) is specified. Also specified is the exit pressure \( p_2 \). The problem is to compute the exit specific volume \( v \) and temperature \( T \), from which the exit enthalpy (and hence the enthalpy drop across the turbine) is determined. One equation for the two unknowns \( (v, T) \) is the Redlich-Kwong equation of state (Eq. 50), which can be expressed as

\[
0 = f_1(v, T) = \frac{RT}{v-b} - \frac{a}{\sqrt{T} v(v+b)} - p_2 .
\]  

The equation is expressed in this form to emphasize the fact that we are seeking a root \((v, T)\) of the function \( f_1 \). Because there are two unknowns, a second equation is required to make the problem determinate. The condition of constant entropy provides a second equation. The entropy change \( \Delta s_{12} \) given by Eq. 24 is a function of the turbine exit state, i.e.,

\[
\Delta s_{12} = f_2(v, T) .
\]
Substituting the entropy departure functions (Eq. 52) into this expression (see Eq. 24) gives the function \( f_2(v,T) \):

\[
\begin{align*}
 f_2(v,T) &= R \ln \left[ \frac{(1-b/v_1)}{(1-b/v)} \frac{(v_1/T)}{(v/T)} \right] \\
 &+ 0.5 \frac{a}{b} \left( \ln \left( \frac{1+b/v}{T^{1.5}} \right) - \ln \left( \frac{1+b/v_1}{T_1^{1.5}} \right) \right) + \Delta s_{12}^o
\end{align*}
\] (56)

The ideal gas entropy change \( \Delta s_{12}^o \) is given by the integral in Eq. 27 which, with the specific heat given by the T-series in Eq. 21, gives

\[
\Delta s_{12}^o = A \ln(T_1/T) + B(T_1 - T) + C(T_1^2 - T^2)/2 + D(T_1^3 - T^3)/3 .
\] (57)

The isentropic condition is

\[
0 = f_2(v,T) .
\] (58)

The solution for the system of two equations (54 and 58) is the matrix root \((v,T)\) of the matrix function \((f_1, f_2)\).

There are many numerical schemes for finding roots for systems of equations. The Newton-Raphson iterative method, which starts from a first guess, was found to converge rapidly. The concept of the iteration is illustrated schematically in Fig. A6 for a one-dimensional root \(x\) of the function \(f(x)\).

Based on the first guess \(x_1\), the values \(y_1\) of the function \(f(x_1)\) and of the derivative \(f'(x_1)\) are computed. The increment \(\Delta x\) (shown in Fig. A6) is

\[
\Delta x = -y_1/f'(x_1) .
\] (59)

The resulting second approximation is

\[
x_2 = x_1 + \Delta x
\] (60)

and the procedure is repeated to find the third approximation \(x_3\). The iteration is continued until the absolute value of two successive approximations is less than some preassigned number, \(\varepsilon\).

In general, \(x\) can be a finite \(n\)-dimensional root for a system of \(n\) equations. For the two-dimensional matrix \((f_1, f_2)\) given by Eqs. 54 and 58, the root \((v,T)\) is given by the analog of Eq. 59:

\[
- f_1 = \frac{\partial f_1}{\partial v} \Delta v + \frac{\partial f_1}{\partial T} \Delta T
\]

and

\[
- f_2 = \frac{\partial f_2}{\partial v} \Delta v + \frac{\partial f_2}{\partial T} \Delta T .
\] (61)
Fig. A6. The Iterative Newton-Raphson Numerical Procedure
The solution \((\Delta v, \Delta T)\) for this system is

\[
\Delta v = \left( \frac{\partial f_2}{\partial T} - \frac{\partial f_1}{\partial T} \right) / J
\]

and

\[
\Delta T = \left( \frac{\partial f_2}{\partial v} - \frac{\partial f_1}{\partial v} \right) / J,
\]

where \(J\) is the Jacobian determinant

\[
J = \left( \frac{\partial f_2}{\partial v} - \frac{\partial f_1}{\partial v} \right) \left( \frac{\partial f_1}{\partial T} - \frac{\partial f_2}{\partial T} \right).
\]

The derivatives of the functions are

\[
\frac{\partial f_1}{\partial v} = -\frac{RT}{(v-b)^2} + \frac{a}{\sqrt{T}} \frac{2v+b}{\sqrt{v(v+b)}},
\]

(64.1)

\[
\frac{\partial f_1}{\partial T} = \frac{R}{v-b} + 0.5 \frac{a}{v(v+b)T^{1.5}},
\]

(64.2)

\[
\frac{\partial f_2}{\partial v} = -\frac{\partial f_1}{\partial T},
\]

(64.3)

and

\[
\frac{\partial f_2}{\partial T} = \frac{R}{T} - 0.75 \frac{a}{b T^{2.5}} \ln \left(1 + \frac{b}{v}\right) - \frac{C_0(T)}{T}.
\]

(64.4)

In terms of the first guess \((v(1), T(1))\), the second approximation is

\[
v(2) = v(1) + \Delta v
\]

and

\[
T(2) = T(1) + \Delta T.
\]

(65)

The procedure is repeated until the error is sufficiently small—say, for a preassigned \(\varepsilon\),

\[
\max \left( \frac{\Delta v}{v}, \frac{\Delta T}{T} \right) < \varepsilon.
\]

(66)

After the computation of the turbine exit-state values \((v, T)\), the isentropic enthalpy drop \(\Delta h_s\) can be computed from Eq. 16 for the departure functions given by Eq. 53. The ideal gas enthalpy change is computed by the integral in Eq. 20 for the specific-heat power series in Eq. 21, i.e.,

\[
\Delta h_{12}^s = A(T_1 - T) + B(T_1^2 - T^2)/2 + C(T_1^3 - T^3)/3 + D(T_1^4 - T^4)/4.
\]

(67)
A.2.7 Computation of the Turbine Exit State for a Nonisentropic Expansion

The actual working gas flow process through the turbine is nonisentropic, as illustrated in Fig. A1. The enthalpy drop representing the thermodynamic work output is less than that for an ideal isentropic expansion. The isentropic change \( \Delta h_{Is} \) is the maximum theoretical output and is the basis for the turbine thermodynamic efficiency defined by Eq. 2. Computation of this efficiency requires a detailed analysis of the internal flow processes in the turbine. It is not necessary to perform such an analysis for preliminary comparative studies of various working fluids. Rather, it is sufficient to assume a typical value for the turbine efficiency. For such an assumed \( n_T \) and the computed isentropic \( \Delta h_{Is} \), the exit enthalpy \( h_2 \) is given by

\[
h_2 = h_1 - n_T \Delta h_{Is},
\]

enabling computation of the thermodynamic work output of the turbine.

From the specified exit pressure \( p_2 \) and the computed enthalpy \( h_2 \), the exit state \((v,T)\) can be determined. The equation of state Eq. 54 provides one equation and the enthalpy drop Eq. 16 a second equation, which can be expressed as

\[
0 = f_3(v,T) = \Delta h^{o}_{12} - \Delta h_{12} - n_T \Delta h_{Is}.
\]

The solution is the root \((v,T)\) of the function \(f_1,f_3\). The enthalpy departure functions appearing in Eq. 69 are given by Eq. 53 and the ideal gas enthalpy drop \( \Delta h^{o}_{12} \) by Eq. 67. The Newton-Raphson method again can be used to compute the root by the same procedure* as represented by Eqs. 61 through 66. The derivatives of \( f_1 \) are given by Eq. 64 and the derivatives of \( f_3 \) are

\[
\frac{\partial f_3}{\partial v} = -1.5 \frac{a}{\sqrt{T} v(v+b)} - p_2
\]

and

\[
\frac{\partial f_3}{\partial T} = R - 0.75 \frac{a}{bT^{1.5}} \ln \left( 1 + \frac{b}{v} \right) - C_p(T).
\]

A.3 COMPUTATION OF THE THERMODYNAMIC PROPERTIES FOR TOLUENE

To illustrate the application of the above procedures, computations are performed for a selected organic working fluid, toluene. Comparison with results obtained from previous studies serve to validate the computational procedures [13,28-30].

A.3.1 Parameters for the Redlich-Kwong Equation of State

The Redlich-Kwong equation of state (Eq. 50) is used as the model for

*Simply replace the function \( f_2 \) by the function \( f_3 \).*
toluene. The equation involves two parameters \((a\) and \(b\)) in addition to the ideal gas constant \(R\). The parameters are determined from the two conditions imposed on the isotherm at the critical point (peak of the liquid-vapor dome) in the \((p,v)\) diagram: (i) the isotherm is tangent to the saturation curve, and (ii) the isotherm has an inflection point. Therefore,

\[
\left(\frac{\partial p}{\partial v}\right)_c = 0
\]

and

\[
\left(\frac{\partial^2 p}{\partial v^2}\right)_c = 0 .
\]

These two conditions lead to the following expressions for \(a\) and \(b\):

\[
a = \Omega_a \frac{R^2 T_c^2}{p_c}
\]

and

\[
b = \Omega_b \frac{RT_c}{p_c},
\]

where

\[
\Omega_a = 0.42748023
\]

and

\[
\Omega_b = 0.08664035 .
\]

Because the numerical values of the coefficients in some of the empirical equations to be discussed later are unit-dependent (an undesirable practice), some care is exercised here to indicate units explicitly. The least ambiguous procedure is to reduce all variables to dimensionless quantities; however, for consistency with an earlier study [13] an "engineering system" of units is followed here.

For engineering units, the universal gas constant is

\[
R_u = 10.73 \frac{\text{ft}^3}{\text{lb-mol} \text{ R}} .
\]

The molecular weight of toluene is

\[
M = 92.13 \text{ lb/lb-mol} .
\]

It follows that the toluene gas constant \(R\) is

\[
R = R_u / M = 0.11646 \frac{\text{ft}^3}{\text{lb} \text{ psia}} .
\]

The critical temperature and pressure for toluene are

\[
T_c = 1065.1^\circ\text{R}
\]

and

\[
p_c = 596.8 \text{ psia} .
\]

Evaluation of the parameters \((a,b)\) and \(R\) permits the computation of toluene properties from the equation of state (Eq. 50).
A.3.2 Computation of the Vapor Saturation Line

Methods for determining the vapor saturation line are based on extensions of the Clausius-Clapeyron equation (see Refs. 26 and 27). One such extension is the Pitzer expansion (see Eq. 7 and its accompanying discussion):

\[ \ln(p_v^r, T^r) = f^{(0)}(T^r) + \omega f^{(1)}(T^r). \]  

(78)

The subscript 'r' indicates the reduced values (see Eq. 6) and 'v' indicates the vapor value. For higher-molecular-weight hydrocarbons, the non-sphericity of molecules, or "acentricity," has an influence upon the vapor saturation line. A semi-empirical acentricity factor \( \omega \), expressed as a function of the critical reduced boiling temperature \( T_b^r \) (called the Lee-Kesler vapor-pressure relation), has been applied to hydrocarbons:

\[
\omega = \frac{-\ln p_c - 5.92714 + 6.09648(T_b^r) - 1.28862 \ln(T_b^r) - 0.169347(T_b^r)^6}{15.2518 - 15.6875(T_b^r) - 13.4721 \ln(T_b^r) + 0.43577(T_b^r)^6}. 
\]

(79)

Care must be taken to express the pressure in this equation in atmospheres; the critical pressure and the boiling temperature at 1 atm for toluene are

\[ p_c = 40.6 \text{ atm} \]
\[ T_b = 691^\circ R. \]

The Lee-Kesler expressions for the functions \( f^{(0)} \) and \( f^{(1)} \) are

\[ f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln T_r + 0.169347 T_r^6 \]

and

\[ f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln T_r + 0.43577 T_r^6. \]

(81)

For selected saturation temperatures, the saturation pressures can be computed for the above expressions. Values computed for toluene are shown in Table A1. The values of the vapor specific volume listed in the table are computed from the equation of state (Eq. 54). Since \( v \) is involved implicitly in the equation, the Newton-Raphson method is used to find the roots of \( f_1(v, T) \) for specified \((T, p)\) values. The one-dimensional procedure follows the form of Eqs. 59 and 60 where the derivative \( \delta f_1/\delta v \) is given by Eq. 64.1.

A.3.3 Computation of the Saturated Liquid Line

Liquid thermodynamic properties are relatively independent of pressure, facilitating the determination of values by experimental methods. Properties important to engineering include the coefficients for volume expansion and for heat capacity. Commonly used parameters are listed below:
Table Al. Toluene Properties on the Saturation Dome

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>610.000</td>
<td>3.284</td>
<td>0.020</td>
<td>21.447</td>
<td>170.020</td>
<td>238.854</td>
<td>0.403</td>
</tr>
<tr>
<td>635.000</td>
<td>5.472</td>
<td>0.020</td>
<td>13.339</td>
<td>166.863</td>
<td>251.288</td>
<td>0.413</td>
</tr>
<tr>
<td>660.000</td>
<td>8.716</td>
<td>0.020</td>
<td>8.652</td>
<td>163.514</td>
<td>264.313</td>
<td>0.423</td>
</tr>
<tr>
<td>685.000</td>
<td>13.343</td>
<td>0.021</td>
<td>5.821</td>
<td>159.947</td>
<td>277.597</td>
<td>0.434</td>
</tr>
<tr>
<td>710.000</td>
<td>19.723</td>
<td>0.021</td>
<td>4.043</td>
<td>156.145</td>
<td>291.109</td>
<td>0.445</td>
</tr>
<tr>
<td>735.000</td>
<td>28.261</td>
<td>0.022</td>
<td>2.886</td>
<td>152.093</td>
<td>304.815</td>
<td>0.457</td>
</tr>
<tr>
<td>760.000</td>
<td>39.391</td>
<td>0.022</td>
<td>2.111</td>
<td>147.780</td>
<td>318.684</td>
<td>0.468</td>
</tr>
<tr>
<td>785.000</td>
<td>53.574</td>
<td>0.023</td>
<td>1.576</td>
<td>143.199</td>
<td>332.681</td>
<td>0.480</td>
</tr>
<tr>
<td>810.000</td>
<td>71.289</td>
<td>0.023</td>
<td>1.197</td>
<td>138.337</td>
<td>346.773</td>
<td>0.492</td>
</tr>
<tr>
<td>835.000</td>
<td>93.037</td>
<td>0.024</td>
<td>0.924</td>
<td>133.179</td>
<td>360.920</td>
<td>0.504</td>
</tr>
<tr>
<td>860.000</td>
<td>119.342</td>
<td>0.024</td>
<td>0.722</td>
<td>127.696</td>
<td>375.080</td>
<td>0.516</td>
</tr>
<tr>
<td>885.000</td>
<td>150.759</td>
<td>0.025</td>
<td>0.569</td>
<td>121.808</td>
<td>389.202</td>
<td>0.528</td>
</tr>
<tr>
<td>910.000</td>
<td>187.886</td>
<td>0.026</td>
<td>0.452</td>
<td>115.458</td>
<td>403.222</td>
<td>0.540</td>
</tr>
<tr>
<td>935.000</td>
<td>231.386</td>
<td>0.027</td>
<td>0.361</td>
<td>108.509</td>
<td>417.057</td>
<td>0.552</td>
</tr>
<tr>
<td>960.000</td>
<td>282.008</td>
<td>0.028</td>
<td>0.288</td>
<td>100.725</td>
<td>430.587</td>
<td>0.563</td>
</tr>
<tr>
<td>985.000</td>
<td>340.625</td>
<td>0.029</td>
<td>0.229</td>
<td>91.694</td>
<td>443.621</td>
<td>0.573</td>
</tr>
<tr>
<td>1010.000</td>
<td>408.274</td>
<td>0.031</td>
<td>0.180</td>
<td>80.622</td>
<td>455.812</td>
<td>0.583</td>
</tr>
<tr>
<td>1035.000</td>
<td>486.211</td>
<td>0.034</td>
<td>0.137</td>
<td>65.627</td>
<td>466.351</td>
<td>0.591</td>
</tr>
<tr>
<td>1060.000</td>
<td>575.982</td>
<td>0.042</td>
<td>0.092</td>
<td>37.858</td>
<td>471.384</td>
<td>0.594</td>
</tr>
</tbody>
</table>

volume expansion: \[ \beta = \frac{1}{v} \frac{\partial v(p,T)}{\partial T} , \]

compressibility: \[ k = - \frac{1}{v} \frac{\partial v(p,T)}{\partial p} \text{ (isothermal)} , \]

specific heats: \( c_p, c_v \) (at constant \( p \) and \( v \)).

The ratio of specific heats \( \gamma \) can be shown to be

\[ \frac{c_p}{c_v} = \frac{k}{k_s} , \]

where \( k_s \) can be determined directly from measurements of the sonic speed \( c_s \):

\[ k_s = \frac{v}{c_s^2} . \]

The difference in the specific heats is

\[ c_p - c_v = T \beta^2 / \kappa \]
and
\[ k_k = T v_b^2 / c_p \]  
(86)
The latent heat is approximated by the Clapeyron equation
\[ h_{lg} = T v_{lg} \frac{dp}{dT} \]  
(87)
where for a constant saturation temperature \( T \) and pressure \( p \), the differences between the liquid line (\( l \)) and the vapor line (\( g \)) are
\[ h_{lg} = h_g - h_l \]
and
\[ v_{lg} = v_g - v_l \]  
(88)

A.3.3.1 Liquid Specific Volume

Expansion coefficients are determined from empirical (or semi-empirical) relations of specific volume to temperature. Semi-empirical expressions employ some variation of the principle of corresponding states (see Eq. 7 and the discussion for scaling parameters and reduced values). The Gunn-Yamada method, involving the acentric factor \( \omega \), is used in the ANL computer code for the computation of the saturated liquid line [28]:

\[ \frac{v_l}{v_{sc}} = v_r^{(0)} (1 - \omega T) \]  
(89)
The scaling parameter \( v_{sc} \) is given by
\[ v_{sc} = \frac{RT_c}{P_c} (0.292 - 0.0967 \omega) \]  
(90)
The subscripts in Eqs. 89 and 90 are defined as follows:
- '\( l \)', the saturated liquid,
- 'sc', a scaling parameter,
- 'r', a reduced value, and
- 'c', the critical value.
The function \( v_r^{(0)} \) depends upon the temperature range:
for \( 0.2 \leq T_r \leq 0.8 \):

\[ v_r^{(0)} = 0.33593 - 0.33953 T_r + 1.51941 T_r^2 \]

\[ - 2.02512 T_r^3 + 1.11422 T_r^4 \]  
(91.1)
and for $0.8 < T_r < 1$:

$$v_r^{(0)} = 1.0 + 1.3 \sqrt{1-T_r} \log (1-T_r) - 0.50879 (1-T_r) - 0.91534 (1-T_r)^2 .$$  \hfill (91.2)

The function $\Gamma$, given for $0.2 \leq T_r < 1$, is

$$\Gamma = 0.29607 - 0.09045 T_r - 0.04842 T_r^2 .$$  \hfill (92)

Values of the saturated liquid specific volume (for toluene) have been computed from the Gunn-Yamada equation (Eq. 89) and are listed in Table A1.

### A.3.3.2 Latent Heat of Vaporization

The latent heat (or enthalpy) of vaporization $h_{lg}$ is derived from extensions of the Clapeyron equation (87). In terms of the compressibility factor $z$, the increase in specific volume from the liquid to the vapor saturation line is

$$v_{lg} = \frac{RT}{p} z_{lg}$$  \hfill (93)

and the Clapeyron equation (87) becomes

$$\frac{dp}{p} = \frac{h_{lg}}{Rz_{lg}} \frac{dT}{T^2} .$$  \hfill (94)

Introducing the temperature and pressure as reduced values, the Clapeyron equation can be expressed in terms of a dimensionless parameter $\Psi$ defined as

$$\frac{h_{lg}}{RT_c z_{lg}} = - \frac{d \ln(p_T)}{d \left( \frac{1}{T_r} \right)} = \Psi .$$  \hfill (95)

Differentiating the Pitzer expansion (Eq.78) and using the Lee-Kesler expressions (Eq. 81) gives

$$\Psi = 6.09648 - 1.28862 T_r + 1.016 T_r^7$$

$$+ \omega (15.6875 - 13.4721 T_r + 2.615 T_r^7) .$$  \hfill (96)

Based on the above expressions, the computed values of $h_{lg}$ for toluene are given in Table A1.

### A.3.4 Computation of the Enthalpy and Entropy on the Saturated Vapor Line

#### A.3.4.1 Selection of a Reference Base Point

The reference base point for the zero enthalpy and entropy values is
arbitrarily selected to be the saturated liquid state at 32°F. The corresponding liquid density (or specific volume) is computed from the Gunn-Yamada equation (Eq. 89). The acentric factor \( \omega \) in this equation, computed for toluene from Eq. 79 is
\[
\omega = 0.262
\]
The scaling parameter \( v_{sc} \), given by Eq. 90, is
\[
v_{sc} = \frac{(0.11646)(1065.1)}{596.8} [0.292 - (0.0967)(0.262)]
\[
= 0.05542 \text{ cu ft/lb}.
\]
The reduced temperature is
\[
(T_r)_{base} = \frac{(32 + 459.67)}{1065.1}
\[
= 0.4616
\]
for which the \( \Gamma \)-function (Eq. 92) has the value
\[
\Gamma = 0.244
\]
The function \( v_r(0) \) from Eq. 91.1 has the value
\[
v_r(0) = 0.3544
\]
With the above values substituted into Eq. 89, the saturated liquid specific volume at 32°F is
\[
(v_{s})_{base} = 0.01838 \text{ cu ft/lb}
\]
For the specified base temperature, the reference base pressure can be determined from the saturated vapor-line Pitzer expansion (Eq. 78), where the Lee-Kesler expressions (Eq. 81) yield
\[
f(0) = -6.282
\]
\[
f(1) = -8.314
\]
and
\[
(p_v)_{base} = (596.8) \exp (f(0) + \omega f(1))
\[
= 0.126 \text{ psia}
\]
The corresponding saturated vapor specific volume is obtained from the Newton-Raphson solution of the equation of state (Eq. 54):
\[
(v_g)_{base} = 454.2 \text{ cu ft/lb}
\]
corresponding to a compressibility
\[ (z_g)_{\text{base}} = 0.99946. \]

The change in compressibility is
\[ z_{lg} = \frac{p_v - v_k}{RT} = 0.99942. \]

The latent heat of vaporization is given by Eq. 95 where the \( \psi \)-function Eq. 96 has the value
\[ \psi = 7.99. \]

The latent heat is thus
\[ h_{lg} = RT_c z_{lg} \psi \]
\[ = (0.11646)(1065.1)(0.99942)(7.99) \]
\[ = 990.52 \frac{\text{cu ft}}{\text{lb}} \text{ psia} \]
\[ = 990.52 \frac{144}{778.16} = 183.30 \text{ Btu/lb}. \]

The entropy increase of vaporization is then
\[ s_{lg} = \frac{h_{lg}}{T} \]
\[ = \frac{183.30}{491.67} \]
\[ = 0.373 \text{ Btu/lb-R}. \]

The values of the enthalpy and entropy for any vapor point (1) with respect to point (2) can be computed from Eqs. 16 and 24, where
\[ h_2 = h_{lg} = 183.30 \text{ Btu/lb} \]
and
\[ s_2 = s_{lg} = 0.373 \text{ Btu/lb-R}. \]

The computed values are listed in Table A1.
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