STATUS REPORT ON COLD-VAPOR STUDIES

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INTRODUCTION

Studies of cold-vapor systems at the Oak Ridge National Laboratory and elsewhere are aimed at efficient practical production of mechanical work from relatively low-temperature heat. Sources of low-temperature heat for this purpose include solar radiation, geothermal sources, gas-turbine exhausts, and steam at above-atmospheric pressure withdrawn from steam power stations. Also, since work is obtained from heat by combining a warmer heat source with a cooler heat sink, cold heat absorbers, such as water at the deeper levels of the ocean may allow practical power production with heat from ambient air or from surface ocean levels, as proposed by numerous investigators over the course of more than a century.

Some of the heat sources listed above are sources of sensible heat, which means that the heat is available over a range of temperatures; geothermal hot water and gas turbine exhausts are examples. Supercritical cold-vapor systems appear to be more efficient than Rankine cycles for obtaining mechanical work from that kind of heat.

Cold vapors are excellent vehicles for low-temperature heat, as well as good working fluids. This fact provides power plant designers with new options for disposal of waste heat and new opportunities for power plant siting.

At present, we are limiting our investigation to fluids that boil below 32°F (0°C) and whose critical temperature is above 110°F. We are not considering olefins or unusually toxic or corrosive fluids.

Our current program consists of four parts: fluid properties, component studies, system studies, and cost studies.

Although we are collecting data on 19 different fluids, and we are considering a variety of heat sources, our present detailed effort is on an ammonia system to replace the subatmospheric portion of a nuclear power station. By keeping a specific application in mind, we can proceed

with economic considerations and we are forced to resolve some of the small details that divide a real problem from a more hypothetical problem. We can then apply the methods we develop to other fluids and other types of systems.

Our initial choice of ammonia is partly historical and partly because ammonia appears to require the smallest equipment and ducting. In the systems considered on our program, the relative velocity of a working fluid in a duct of a given size is approximately proportional to the volume of vapor that contains a given amount of latent heat — e.g., in $\text{ft}^3/1000 \text{ Btu}$. Except under special conditions, the velocity of a gas in a duct cannot exceed sonic velocity and gas velocities in modern turbines are usually kept below sonic velocity. Since at a given temperature the sonic velocity in an ideal gas is roughly proportional to $\sqrt{1/M}$ where M is the molecular mass, $\sqrt{M} \cdot \text{ft}^3/(1000 \text{ Btu of latent heat})$ is an approximate measure of the relative size of turbines, ducts, and other components for different working fluids in a given application.

The following table lists, alphabetically, values of $\text{ft}^3/1000 \text{ Btu}$ and $\sqrt{M} \cdot \text{ft}^3/1000 \text{ Btu}$ for some candidate vapors in the condenser-temperature range where the vapors will have the highest specific volume.

Vapor	M	125°F		100°F		75°F	
		$\frac{\text{ft}^3}{1000 \text{ Btu}}$	$\frac{\sqrt{M} \text{ ft}^3}{1000 \text{ Btu}}$	$\frac{\text{ft}^3}{1000 \text{ Btu}}$	$\frac{\sqrt{M} \text{ ft}^3}{1000 \text{ Btu}}$	$\frac{\text{ft}^3}{1000 \text{ Btu}}$	$\frac{\sqrt{M} \text{ ft}^3}{1000 \text{ Btu}}$
Ammonia	17	2.2	9	3.0	12	4.2	17
Freon 12 ($\text{Cl}_2\text{F}_2\text{C}$)	121	4.2	46	5.6	62	7.5	83
Isobutane	58	5.8	44	7.0	53	8.9	68
Propane	44	3.2	21	4.1	27	5.5	36
Water	18	180.0	760	340.0	1400	700.0	3000

These data indicate that the cold vapors will require much smaller systems than will steam for power production and transport of heat in this temperature range, and that ammonia systems will be somewhat smaller than systems for other fluids.

However, other criteria may control the final choice of working fluid for a given low-temperature application. For example, the efficiency of turbines can be seriously reduced if the vapor becomes markedly wet and, because of its lower molal heat capacity, ammonia tends to become wetter during expansion than fluids with more complex molecules at the same reduced temperature. In addition, unusually small turbines tend to be less efficient because of the proportionately larger leakage through blade clearances.

Once we have developed and evaluated our methods with ammonia, we will apply them to other fluids in a variety of potential applications.

PHYSICAL PROPERTIES

One phase of our work in the Cold Vapor Technology Program is directed toward locating, collecting, and correlating values for the thermophysical properties of those compounds that could find application as working fluids in low-temperature heat utilization systems. Low-boiling-point fluids are superior to steam in low-temperature applications because of their inherently lower vapor specific volumes. Thus, the size of the final turbine stages does not limit the temperature to which a cold vapor can be expanded, and advantage can be taken of low ambient temperatures to improve cycle efficiencies. As an additional advantage, if the particular fluid used has a normal boiling point that is lower than the lowest operating temperatures, then operation under partial vacuum in the low-temperature part of the cycle is avoided. To take advantage of this situation locally, compounds with boiling points above some minimum temperature would be excluded. For the present, we have arbitrarily chosen this temperature to be 32°F. However, higher boiling point compounds will be considered for specific applications in which the lowest anticipated temperatures are higher than 32°F or other considerations outweigh the disadvantages of subatmospheric pressures.

Since most of the applications envisaged will require heat rejection by condensation, an additional fluid property limitation will be that the compound have a critical temperature that is greater than the maximum

anticipated temperature at which the heat is rejected. At present, we are assuming a maximum heat rejection temperature of 110°F. By selecting compounds with critical temperatures greater than 110°F, this requirement will automatically be satisfied for all applications of interest. If it appears desirable at some later time, our coverage can be expanded to include fluids with lower critical temperatures.

Table 1 is a listing of the more common compounds that meet the boiling point and critical temperature requirements mentioned above. The compounds have been listed in order of increasing boiling point. The numbers presented in column 2 refer to the standard refrigerant designation of the American Society of Heating, Refrigerating and Air Conditioning Engineers. In compiling the list, unsaturated hydrocarbon compounds were not considered because of possible chemical interaction. Still, there are 19 compounds that meet the general requirements. Although many of these compounds have such low critical temperatures that they would be impractical for use in subcritical Rankine cycles, they are attractive for use in supercritical cycles where heat is supplied by the source over a range of temperatures.

Thermophysical Properties of Ammonia

Presently, we are in the process of collecting relevant thermophysical properties data for each of the compounds listed in Table 1. As an example, Tables 2 and 3 represent a typical "skeleton chart" of the available thermodynamic and transport properties data for ammonia. These properties include pressure-volume-temperature data, enthalpy, entropy, specific heat, thermal conductivity, viscosity, surface tension, and Prandtl number for the subcooled liquid, saturated liquid, saturated vapor, and superheated vapor regions. The sources of data used in preparing the charts were obtained in considerable part through the services of the Thermophysical Properties Research Center of Purdue University, and the services of TPR are being used in accumulating data for the other compounds of interest.

Table 1. Low Temperature Rankine Cycle Working Fluids

Compound Name	ASHRAE Designation	Molecular Weight	Normal Boiling Point (°F)	Critical Temperature (°F)	Critical Pressure (psia)
Methyl Fluoride	R41	34	-104	112	852
Bromotrifluoromethane	R13B1	148.9	- 72	152.6	575
Methylene Fluoride	R32	52.03	- 61	173	846
Propane	R290	44.1	- 44.2	206.3	617.4
Chlorodifluoromethane	R22	86.5	- 41.44	204.8	721.9
Chloropentafluoroethane	R115	154.5	- 37.7	175.9	458
Octafluoropropane	R218	188	- 34.1	160	390
Armonia	R717	17.03	- 28	271.4	1657
Ethyl Fluoride	R161	48	- 25	216	685
Dichlorodifluoromethane	R12	120.9	- 21.62	233.6	597
Difluoroethane	R152a	66.05	- 12.4	236.3	652
Methyl Chloride	R40	50.48	- 10.8	289.6	968.7
Pentafluoropropane	R245	134	0	224.5	455
Isobutane	R600a	58.13	10.3	274.8	529.1
Sulfur Dioxide	R764	64.07	14	315.4	1143
Chlorodifluoroethane	R142b	100.5	14.4	278.8	599
Methyl Amine	R630	31.06	20.3	314.4	1082
Octafluorocyclobutane	RC318	200.04	21.5	239.6	403.6
n-Butane	R600	58.13	31.3	305.6	550.7

Table 2. Available Thermodynamic Properties of Liquid and Gaseous Ammonia^a

Molecular Weight = 17.032 Normal Boiling Point = -28.12°F (Ref. 1) Critical Constants (Ref. 2): Temperature = 270.1°F Pressure = 111.3 atm Volume = 0.06811 ft ³ /lb				
Property	Subcooled Liquid	Saturated Liquid	Saturated Vapor	Superheated Vapor
P-V-T	0°C (10°) 130°C } Ref. 3 100 (100) 1100 atm } 30°C (10°) 130°C } Ref. 5 20 to 500 atm }	30°C to 132°C ^c Ref. 4 -60°F (5°) 125°F ^f Ref. 7 15°K to B.P. ^d Ref. 8	-60°F (1°) 125°F ^f Ref. 7	140°C (10°) 210°C } Ref. 3 100 (100) 1100 atm } 50°C (25°) 325°C } Ref. 4 ^e 20 to 95 atm } 140°C to 300°C } Ref. 6 20 to 1000 atm } Saturation to 400°F } Ref. 7 5 to 300 psia } -35°C to 300°C } Ref. 9 1 to 28 atm }
Enthalpy	30°C (10°) 130°C } Ref. 5 20 to 500 atm }	-60°F (5°) 125°F ^f Ref. 7	-60°F (1°) 125°F ^f Ref. 7	150°C (25°) 300°C } Ref. 6 20 to 1000 atm } Saturation to 400°F } Ref. 7 5 to 300 psia }
Entropy	30°C (10°) 130°C } Ref. 5 20 to 500 atm }	-60°F (5°) 125°F ^f Ref. 7	-60°F (1°) 125°F ^f Ref. 7	150°C (25°) 300°C } Ref. 6 20 to 1000 atm } Saturation to 400°F } Ref. 7 5 to 300 psia }
Specific Heat ^b		-60°F (5°) 125°F ^{c,f} Ref. 7 15°K to B.P. Ref. 8	-45°C (5°) 45°C ^c Ref. 12	150°C (25°) 300°C } Ref. 6 20 to 1000 atm } Saturation to 150°C } Ref. 11 0 atm (1) 20 atm }
Ideal Gas Specific Heat ^b				50°K to 5000°K Ref. 10

^aComplete tables and charts incorporating all available data are presented in Ref. 13 and Ref. 14.^bRefers to constant pressure specific heat, unless otherwise noted.^cRefers to saturation conditions.^dRefers to vapor pressure measurement only.^eDetermines constants of the Beattie-Eridgeman equation of state.^fPresents values extrapolated to the critical point by means of a correlating equation.

Table 3. Available Transport Properties of Liquid and Gaseous Ammonia.

Property	Subcooled Liquid	Saturated Liquid	Saturated Vapor	Superheated Vapor
Thermal Conductivity	40°F (60°) 220°F } Ref. 1 200 to 5000 psia 290°K (10°) 400°K } Ref. 3 ^{b,c} 50 to 1000 atm	40°F (60°) 220°F Ref. 1	40°F (60°) 220°F Ref. 1	50°C (50°) 150°C } Ref. 2 0 to 9 atm 40°F (60°) 400°F } Ref. 1 14.7, 200 to 5000 psia 290°K (10°) 480°K } Ref. 3 1 to 1000 atm 300°K to 475°K } Ref. 4 1 atm 38°C (20°) 200°C } Ref. 5 3.48 psia
Viscosity	100°F (60°) 220°F } Ref. 6 400 to 5000 psia 40°F (30°) 220°F } Ref. 7 200 to 6000 psia	100°F (60°) 220°F Ref. 6 40°F (30°) 220°F Ref. 7 5°C (15°) 25°C Ref. 9 0°C (10°) 70°C Ref. 10	100°F (60°) 220°F Ref. 6	100°C (50°) 200°C } Ref. 8 ^a 250 to 5000 psia 100°F (60°) 400°F } Ref. 6 14.7, 200 to 5000 psia 20°C (10°) 30°C } Ref. 11 1 to 6 atm 25°C (25°) 125°C } Ref. 12 1 atm to saturation
Surface Tension	-33°C to -56°C Ref. 13 ^d -50°C to 50°C Ref. 14			
Prandtl Number				-100°C to 400°C } Ref. 15 "zero" pressure

^aIncludes a reduced viscosity correlation for the high density gas and liquid regions.

^bIncludes a correlation for the thermal conductivity of liquid and high density gas regions.

^cIncludes data in the vicinity of the critical point.

^dEmpirical equation covering the temperature range indicated.

Determination of Equation-of-State Parameters for Ammonia

The heat capacity (and hence the increase in enthalpy and entropy with increasing temperature) of most gases at zero pressure can be predicted from the molecular structure of the gas within about 1% or less over the entire temperature range of interest for working fluids. The change in thermal properties (enthalpy, entropy, and heat capacity) with change in pressure at a constant temperature is a function only of the relationship between pressure, specific volume, and temperature. Hence, an accurate and analytically or numerically tractable generalization (equation of state) that relates the pressure, specific volume, and temperature of a working fluid will allow calculation of all thermodynamic properties of interest in our program. This will be useful in generating tables and charts of properties, and it will obviate the introduction of tabulations of property data into computer programs for analyzing power cycles that use a particular fluid.

An immediate objective of our Cold-Vapor Technology Program is to select from the literature a suitable equation of state that will apply to all fluids of interest. With a general equation, we need only introduce the specific constants for the equation of state and for the zero-pressure heat capacity equation to provide all the needed information on thermodynamic data in computer calculations for each fluid.

It would be desirable to choose an equation of state for which the constants have already been evaluated for some of the compounds of interest in our program. This is the case of the Martin-Hou equation which has been applied to many of the commercial refrigerants (R115, R40, RC318, R218, R23, etc.). In its latest revised form, this equation contains 21 adjustable constants that must be chosen to fit accurately the pressure-volume-temperature data of the compounds being studied. As a test of its accuracy, we have applied this equation to the P-V-T data for ammonia along the critical isotherm and the results are encouraging in that the calculated pressures deviate from the experimental data by at most 1% for values of density up to twice the critical density. This preliminary fit provides values for eight of the equation-of-state constants. We are in the process now of extending the fit to other isotherms, and thereby obtaining the values of the remaining 13 constants.

If the results of the complete fit are favorable, the analysis will be applied to the other fluids, and we will find or write appropriate computer routines for use in our power-cycle program and for generating tables of the thermodynamic properties of cold vapors where our literature search indicates that they may be needed.

COMPONENT DEVELOPMENT

Fluted Condensers and Evaporators

Preliminary analysis discloses no reason why fluted surfaces that have been found superior to flat surfaces for condensing and evaporating water should not also be superior for evaporating and condensing cold-vapor fluids. Data with water imply slight if any sensitivity to surface tension over a wide range of conditions, and any effect due to poor thermal conductivity is expected to be at least as pronounced on smooth surfaces.

The principal difference we expect in extending our water experience with fluted surfaces in distillation systems to similar operations in cold-vapor power cycle systems will be increased volumetric condensation and evaporation rates because of higher heat fluxes and lower latent heats. This may require shorter tubes than the 20 ft specified in some aqueous distillation systems.

Turbines

The principles of designing cold-vapor turbines are the same as for steam turbines. At present, we are assuming that wetness in cold vapor reduces efficiency to about the same degree as wetness in steam (about 1% point for each percent of liquid). We also assume that liquid separation using grooves on the backs of the blades will, as in the case of steam, not be particularly effective above a reduced temperature of about 0.65. We hope to check these assumptions with experience elsewhere and perhaps with small-scale experiments of our own if we find condensation is a problem in optimum systems.

Safety and Compatability

We have held preliminary discussions with G. P. Wachtell of the Franklin Institute regarding the possibility of their helping us to compile information on safety and compatible structural materials for use with ammonia.

KROV Tests

At the request of the AEC, we are planning to test the Keller Roto Oscillating Vane vapor expander. We are negotiating with the Oak Ridge Mobile Steam Society which has developed a boiler that is particularly suited for these tests, and we believe we can capitalize on their interest in this type of device to save time and cost in the testing.

At present, the tests are scheduled to begin sometime between the 7th and 14th of May. The machine is expected to develop about 10 hp with saturated steam at 400 psi.

CYCLES AND COST STUDIES

For our first study, we are comparing TVA's Watts Bar nuclear steam system with a corresponding binary steam ammonia system. We have calculated the reduction in power from the steam system caused by removing the steam at 240°F, and we have examined the efficiency of a saturated ammonia system operating from 225°F.

The results indicate relative insensitivity to the exact temperatures for regenerative feed heating.

We find, as might be expected, that our turbine efficiency is seriously reduced by condensation during expansion. As a result, we recover only about 50% of the Carnot work available across our temperature range, and we must use a sink temperature of 70°F to get the same thermodynamic efficiency as obtained from a single steam cycle that condenses at 100°F.

In practice the ammonia might be superheated using steam from other turbine stages or by using steam at the final temperature in ammonia reheat cycles and we are currently revising our computer program to include subroutines that can provide the properties of superheated ammonia so that we can calculate heat balances and efficiencies using superheat.

We will then introduce cost figures so we can determine the costs of generating power in optimum systems.

At present, we have found no really reliable data on the cost of large steam turbines designed to operate with back pressures of several tens of pounds per square inch gage. It appears overly conservative to assume that the saving in turbine cost with increased back pressure is proportional to the reduction in power output by the turbine, because in increasing the back pressure we remove larger stages. On the other hand, simply assuming the cost of the turbine to be proportional to its weight may underestimate the cost. To date the manufacturers have not been helpful on this question.

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