United States Patent

Bechtold

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[54] **POWER FLUIDS FOR RANKINE CYCLE ENGINES**

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[52] **U.S. Cl.** **60/36**
[51] **Int. Cl.** **F01k 25/00**
[58] **Field of Search** 60/36

[56] **References Cited**

UNITED STATES PATENTS

3,282,048 1/1972 Murphy et al. 60/36

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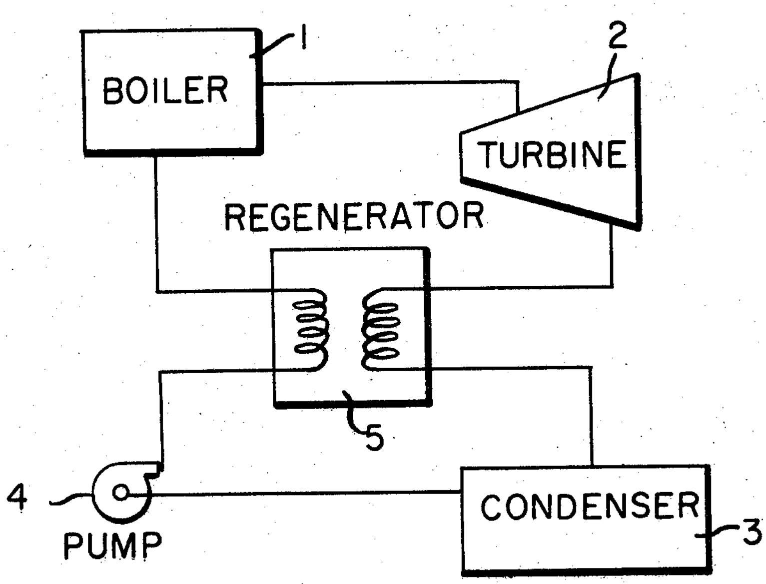
[57] **ABSTRACT**

Perhalogenated benzenes of the formula $C_6Br_xCl_yF_z$ where x is 0–2, y is 0–4, z is 2–4 and $1.5x + y$ is from 2.5 to 4, their isomers and mixtures thereof have a combination of properties which render them suitable for use in small Rankine cycle engines.

7 Claims, 2 Drawing Figures



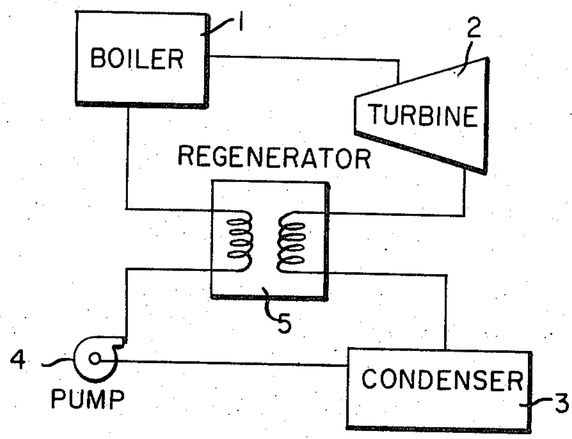


FIG. 1

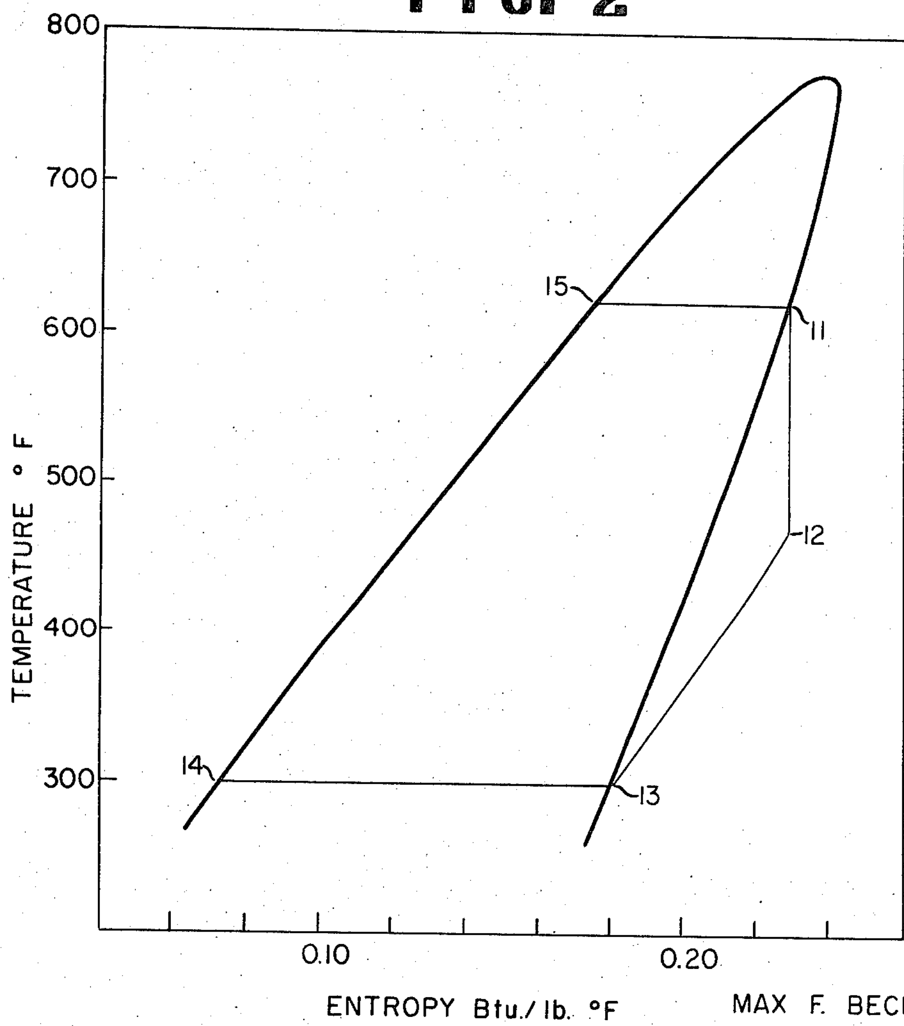


FIG. 2

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POWER FLUIDS FOR RANKINE CYCLE ENGINES

FIELD OF THE INVENTION

This invention relates to the use of novel power fluids in Rankine cycle engines.

BACKGROUND OF THE INVENTION

External combustion engines offer a number of advantages over internal combustion engines such as a broader selection of fuel sources. Such engines are generally more readily adapted to low pollution operation in part due to the choice of fuel and in part to the choice of combustion conditions which can be employed. The greater number of engines operating on the Rankine cycle at the present time are conventional steam engines including piston engines and turbines. Screw expanders have also been proposed. While water is an inexpensive and readily available power fluid, it is not without disadvantages such as expansion upon freezing. Also, because of the nature of the temperature entropy diagram, it is generally necessary to use superheated steam at high pressure and temperature in order to obtain acceptable efficiency and to avoid "-wet" vapor upon expansion. Further, when turbines are employed it is necessary to employ multiple stages. For these reasons, steam engines operating on the Rankine cycle are generally large stationary engines such as those employed for the production of electric power.

The present invention is, therefore, directed to providing novel fluids useful in Rankine cycle engines and particularly in small portable engines with efficient air-cooled condensers.

SUMMARY OF THE INVENTION

The present invention can be defined as a method of generating power in which a working substance is heated and vaporized, does work in a prime mover, and after doing said work is condensed and recycled, wherein said working substance consists essentially of at least one perhalogenated benzene having the formula

$$C_6Br_xCl_yF_z$$

in which

x is from 0 to 2

y is from 0 to 4

z is from 2 to 4 and

$1.5x+y=2.5$ to 4 inclusive.

In particular, the substances of the present invention are suited to use in Rankine cycle engines wherein the working substance is subjected to centrifugal force during the steps of heating and condensation and is recycled by centrifugal force.

The working fluids employed in the present invention thus include

$C_6Cl_3F_3$

$C_6Cl_4F_2$

$C_6Br_2F_4$

C_6BrClF_4

$C_6BrCl_2F_3$

$C_6Br_2ClF_3$

The above compounds all have position isomers. While the pure isomers can be employed in the practice of this invention, all isomers of a given compound have been found to boil in a range of about ± 2°C. and mixtures of such isomers, as well as mixtures of the compounds, can be employed and in many instances are preferred to the pure isomers since such mixtures have lower melting points.

THE DRAWINGS AND DETAILED DESCRIPTION OF THE INVENTION

This invention will be better understood by reference to the drawings which accompany this specification. In the drawings:

FIG. 1 is a diagram showing the various stages of a Rankine cycle including an optional regeneration step to optimize the efficiency.

FIG. 2 is a temperature-entropy diagram for trichlorotrifluorobenzene.

Turning now to FIG. 1, the working substance is evaporated in the boiler 1. This boiler can be any conventional form of boiler. Boilers of the rotating type wherein the liquid is distributed over a large surface by centrifugal force are particularly efficient thermally and produce high quality vapor. Such boilers are preferred for use with the working substances of the present invention. The vapor then passes to a prime mover such as a turbine 2 where it expands in the turbine nozzles and is employed to run an impulse turbine. The vapor can then be passed to a condenser 3 where it is condensed back to the liquid phase. The liquid is then pumped back to the boiler 1 by pump 4 and thus recycled. With the liquids of the present invention, small air-cooled condensers of high efficiency can be employed. It is, therefore, desirable to employ a condenser of smaller diameter attached to and rotating with the boiler. The liquid can then be pumped from the condenser to the boiler by centrifugal force.

Expansion of the vapor in the prime mover is essentially isentropic. The vapors of the working substances of this invention become superheated upon expansion. The efficiency of the cycle can, therefore, be improved by passing the exhaust from the turbine employed as a prime mover through a regenerator 5 wherein the excess heat is removed from the vapor and transferred to the boiler feed as taught by U.S. Pat. No. 3,040,528.

In FIG. 2 there is shown the temperature-entropy diagram for trichlorotrifluorobenzene, one of the working fluids of the present invention. Power is generated by the expansion of the trichlorotrifluorobenzene from vapor at a pressure of 149.7 p.s.i.a. and temperature 620°F., point 11 on the diagram, in a turbine. Expansion is essentially isentropic and the working fluid, therefore, is cooled following the line from 11 to 12 to a temperature of 463°F. at the condensing pressure of

3.07 p.s.i.a. The vapor is cooled from 463° to 299°F., preferably in a regenerator but optionally in the condenser, to point **13** on the diagram. The vapor is then condensed to liquid at 299°F. and 3.07 p.s.i.a. following the path **13** to **14** in the figure. The liquid at point **14** is pumped to 149.7 p.s.i.a. and heated by the boiler, and also by regeneration, if that is employed, to point **15** and thereafter evaporated to vapor at 620°F. and 149.7 p.s.i.a. to point **11** thereby completing the cycle.

For the above cycle, the following enthalpy values relative to the liquid at the condenser temperature and pressure have been calculated.

Point	Pressure p.s.i.a.	Temperature °F.	Enthalpy Btu/lb.
11	149.70	620	153.57
12	3.07	463	123.03
13	3.07	299	82.97
14	3.07	299	0
15	149.70	620	96.49

Without regeneration, this Rankine cycle thermal efficiency is about 20 percent. For 70 percent regeneration, the efficiency is about 24 percent.

Similar calculations for 1,3-dibromotetrafluorobenzene operating at a boiler temperature of 613°F. (149.8 p.s.i.a.) with a condenser temperature of 289°F. (3 p.s.i.a.) show that the thermal efficiency is about 21 percent without regeneration and 25 percent with 70 percent regeneration.

From the above, it can be seen that useful thermal efficiency can be achieved with the fluids of the present invention at modest, subcritical pressures and at condenser temperatures sufficiently great to render possible the use of small, air-cooled condensers.

The above results are typical of the fluids of the present discovery. All of the compounds defined hereinabove boil in the range of 175° – 250°C. Lower boiling points lead to larger pressures in the engine and to the need for larger condensers. Higher boiling points require boiler temperatures so great in attaining an efficient cycle that the thermal stability limits of organic compounds are exceeded. Further, the creep resistance of metals commonly employed for engine construction is frequently insufficient for use with such high boiling materials.

A preferred range of boiling points is from 175°–225 °C. The perhalobenzenes defined above when $1.5X + y$ is 2.5 to 3.5 fall in this desirable range and form a preferred class of materials. In addition to the necessary thermal properties, a number of other properties are highly desirable for working fluids in Rankine cycle engines. These properties are:

THERMAL STABILITY DURING ENGINE OPERATION

This is necessary to permit prolonged operation in a closed system. In particular, any decomposition generating noncondensible gases would blanket and inactivate the condenser or require a constant purging device. Further, decomposition of the working fluid should not produce insulating solid deposits in valves, nozzles, seals or on heat exchanging surfaces.

LOW TOXICITY

The working fluids are preferably such that inhalation of vapors from accidental breakage or spills should not be damaging to health.

LOW FLAMMABILITY

The flammability of the fluids should be as low as possible to minimize the risks of fire.

LOW CORROSIVITY

The liquids should not attack metals employed for engine construction.

HIGH MOLECULAR WEIGHT

High molecular weight is particularly beneficial in the construction of low horsepower (i.e., < 1000 h.p.) turbine engines, since it permits operation with a single stage turbine at reasonable speeds. For this purpose the molecular weight should be at least 150. The liquids employed in the present invention all have molecular weight greater than 235.

HIGH LIQUID DENSITY

As mentioned above, rotary boilers in which the working substance is maintained in the liquid state on an extended cylindrical surface by centrifugal force are particularly useful for small Rankine cycle engines. Rotary condensers which have a smaller diameter than the boiler and rotate therewith can be employed with advantage, and the centrifugal force employed to pump the liquid (optionally through a regenerator) from the condenser to the boiler. The greater the liquid density of the working substance, the smaller the diameter of the boiler (and consequently the smaller engine) which is required at a given speed of rotation or conversely, for a given size of boiler and condenser the slower the rate of rotation required to achieve efficient operation. The construction of a particularly preferred system employing a rotating boiler and condenser is taught in the copending commonly assigned patent application of William A. Doerner, U.S.S.N. 25,587 filed Apr. 6, 1970 and now abandoned, and U.S. Pat. No. 3,590,786 and U.S. Pat. No. 3,613,368.

LOW FREEZING POINT

The freezing point of fluids employed in Rankine cycle engines must be well below the operating condenser temperature. Even more preferably, the fluids should be liquid at ambient temperatures, although, in contrast to water, freezing of organic fluids, which contract on freezing, will not cause breakage of condenser tubes, etc.

The perhalobenzenes of the present invention are surprisingly stable thermally, particularly in the presence of aluminum, aluminum-alloys, or aluminized steel which are desirable materials of engine construction, at temperatures in excess of about 100°C. The compounds are essentially nontoxic. Further, the compounds do not support combustion. The various position isomers of a given perhalobenzene also boil within about ± 2°C. of each other so that mixed isomers can be employed with advantage. Such mixtures have a lower freezing point than the pure isomers. The density of the liquids about (1.7 to 2.3) is also suited for use with rotating boilers and condensers.

The compounds of the present invention can be made by a variety of techniques known in the art. For example, the chlorofluorobenzenes can be made by heating hexachlorobenzene with potassium fluoride, preferably in a polar medium such as sulfolane, dimethylsulfone, dimethylformamide, N-methylpyrrolidone and the like. This process ordinarily produces a mixture of compositions and isomers thereof, the predominant composition being determined both by the relative amounts of potassium fluoride and hexachlorobenzene employed and the length of time the reactants are held at elevated temperatures.

For example, 2,718 grams of potassium fluoride were added to 5,400 ml of redistilled sulfolane. Water was removed from the system by distilling off 300 ml of the sulfolane at ordinary pressure. The mixture was then cooled to 200°C. in a dry nitrogen stream and 2,566 gm of hexachlorobenzene were added. The mixture was then heated to reflux with stirring for 3 hours. The initial pot temperature slowly dropped to 220°–230°C. The product was distilled and then purified from sulfolane by steam distillation. A composite of such runs was then fractionally distilled. The product boiling in the vicinity of 198° consisted largely of a mixture of position isomers of $C_6Cl_3F_3$. A minor amount of hydrogen containing impurities were present, which could be removed by further careful fractionation. The mixture of compounds, however, is suitable for use as the working substance in Rankine cycle engines.

Bromofluorobenzenes can be made by bromination of partially fluorinated benzene with bromine in oleum as described in British Pat. No. 996,496. The bromine atoms of the bromofluorobenzenes can be partially or wholly replaced by reaction with chlorine to obtain bromochlorofluorobenzene or chlorofluorobenzene. For example chlorine gas is passed at the rate of 100 cc/minute through 100 cc of 1,3-dibromotetrafluorobenzene illuminated with a 25 watt electric light bulb. After 45 minutes a 53 percent yield of 1-bromo-3-chlorotetrafluorobenzene is obtained which can be isolated by distillation. Likewise C_6BrCl_2BJ3 and $C_6Br_2ClF_3$ can be obtained by passing chlorine gas through $C_6Br_3F_3$ dissolved in trichlorobenzene and maintained at 120°C. as described by N. N. Vorozhtsov, G. G. Yakobsen and N. I. Krizhechkovskaya, Zhurnal Obshchei Khimii 31 1674 (1961), followed by purification of the mixture by distillation.

The foregoing detailed description has been given for clarity of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described for obvious modifications will be apparent to those skilled in the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The method of generating power by heating and vaporizing a working substance, expanding said vapor in a prime mover to do work, and after doing said work condensing said vapor and recycling said working substance, wherein said working substance consists essentially of at least one perhalobenzene of the formula

$C_6Br_xCl_yF_z$

where

x is from 0 to 2

y is from 0 to 4

z is from 2 to 4 and

$1.5x+y$ is from 2.5 to 4.

2. The method of claim 1 in which said liquid is maintained in contact with aluminum or an aluminum alloy at temperatures greater than 100°C.

3. The method of claim 1 wherein said working substance consists essentially of a mixture of isomers of trichlorotrifluorobenzene.

4. The method of claim 1 wherein said working substance consists essentially of 1-bromo-3-chlorotetrafluorobenzene.

5. The method of claim 2 wherein the working substance is subjected to centrifugal force during the steps of heating and condensing and is recycled by centrifugal force.

6. The method of claim 5 wherein said working substance consists essentially of a mixture of isomers of trichlorotrifluorobenzene.

7. The method of claim 5 wherein said working substance consists essentially of 1-bromo-3-chlorotetrafluorobenzene.

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