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Tullock

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[54] **GENERATION OF POWER USING TRICHLOROBENZENE IN A RANKINE-CYCLE ENGINE**

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[52] **U.S. Cl.** **60/649,** 252/67

[51] **Int. Cl.** **F01k 25/00**

[58] **Field of Search** 60/36; 252/67

[56] **References Cited**

UNITED STATES PATENTS

3,040,528	6/1962	Tabor et al.	60/36
3,234,734	2/1966	Buss et al.	60/36
3,516,248	6/1970	McEwen	252/67
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FOREIGN PATENTS OR APPLICATIONS

21,127	9/1912	Great Britain	60/36

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The Condensed Chemical Dictionary, 6th Edition, (page 1160) Copyright 1961, 5th Printing 1965 by Reinhold Pub. Corp.

Primary Examiner—Edgar W. Geoghegan
Assistant Examiner—H. Burks, Sr.

[57] **ABSTRACT**

1,2,4-Trichlorobenzene is an inexpensive and useful working fluid for use in Rankine-cycle engines. Thermal stability at high temperatures is enhanced by constructing the engine, particularly the boiler, with ferritic alloy steels.

1 Claim, 2 Drawing Figures

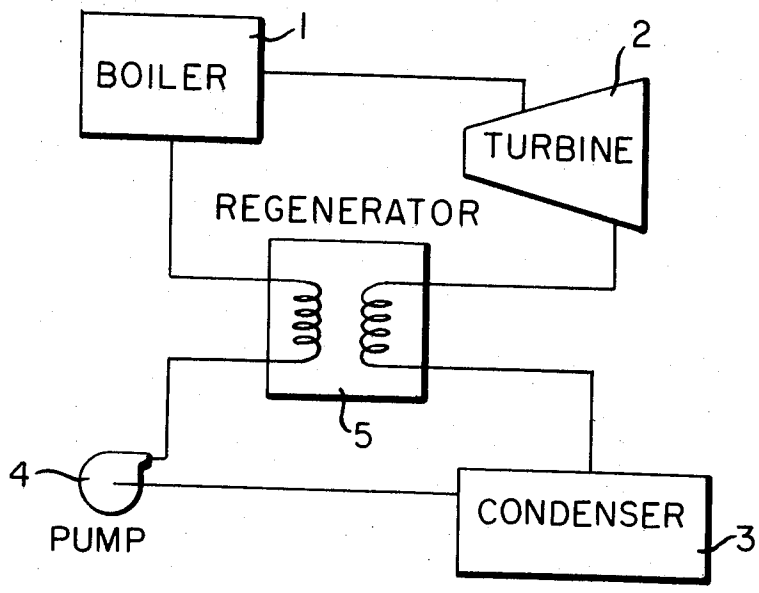


FIG. 1

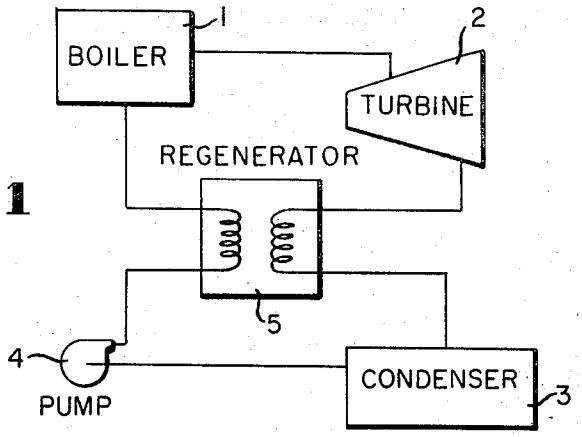
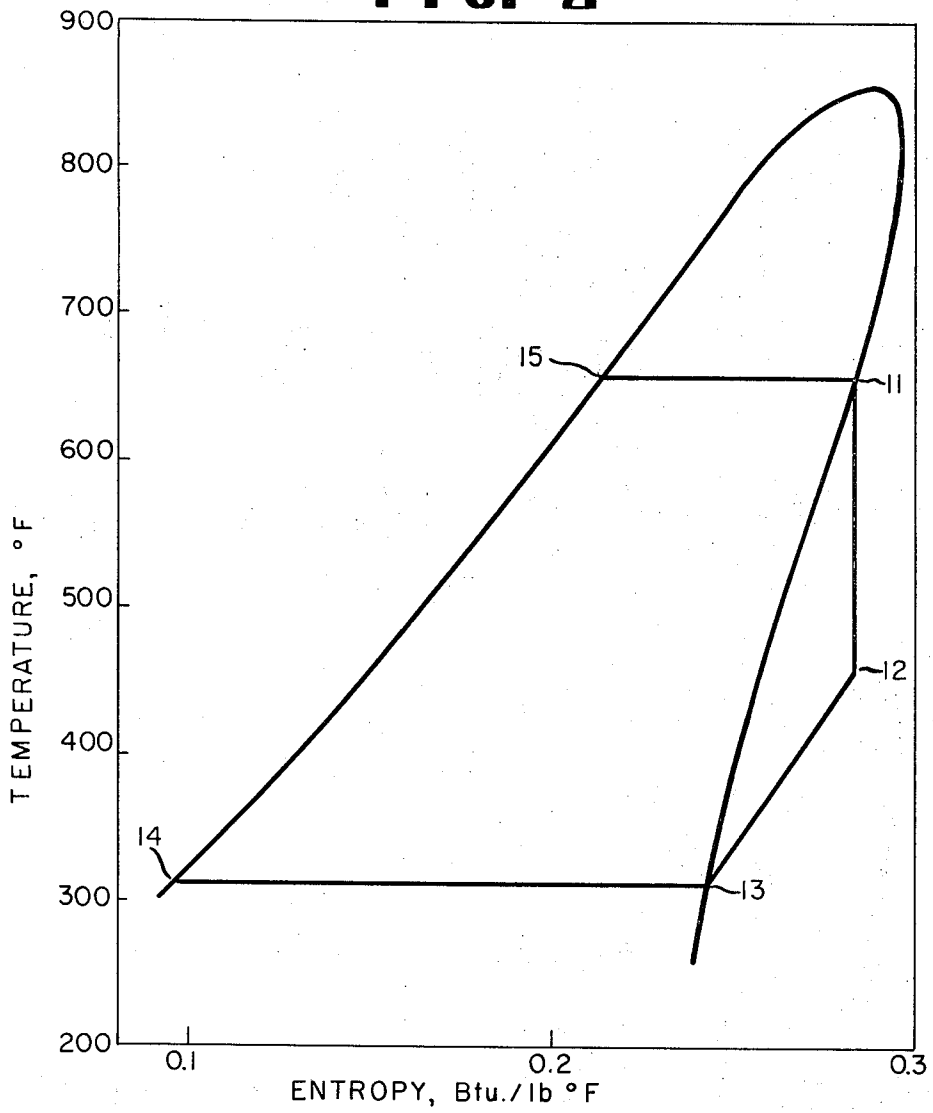

BOILER
1
2
TURBINE
REGENERATOR
5
4
PUMP
CONDENSER
3

FIG. 2


900
800
700
600
500
400
300
200
TEMPERATURE, °F
15
11
12
14
13
0.1
0.2
0.3
ENTROPY, Btu./lb °F

GENERATION OF POWER USING TRICHLOROBENZENE IN A RANKINE-CYCLE ENGINE

FIELD OF THE INVENTION

This invention relates to the use of a novel power fluid 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 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 super-heated 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 Rankin cycle are generally large stationary engines such as those employed for the production of electric power.

The present invention is, therefore, directed to providing a novel fluid 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 1,2,4-trichlorobenzene.

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 optical regeneration step to optimize the efficiency.

FIG. 2 is a temperature-entropy diagram for 1,2,4-trichlorobenzene.

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 when it expands in the turbine nozzles and is employed to run an impulse turbine. The vapor can then be passed to a condenser 3 when it is condensed 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 by pumped from the condenser to the boiler by centrifugal force.

Expansion of the vapor in the prime mover is essentially isentropic. The vapor of the working substance of this invention becomes 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 1,2,4-trichlorobenzene, the working fluid of the present invention. Power is generated by the expansion of the trichlorobenzene from vapor at a pressure of 148.7 p.s.i.a. and temperature 655° 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 459° F at the condensing pressure of 3.02 p.s.i.a. The vapor is cooled from 459° F to 312° F, preferably in a regenerator but optionally in the condenser, to point 13 on the diagram. The vapor is then condensed to liquid at 312° F and 3.02 p.s.i.a. following the path 13 to 14 in the figure. The liquid at point 14 is pumped to 148.7 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 655° F and 148.7 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	148.7	655	186.076
12	3.02	459	145.603
13	3.02	312	111.841
14	3.02	312	0
15	148.7	655	108.427

Without regeneration, this Rankine cycle thermal efficiency is about 22 percent. For 70 percent regeneration, the efficiency is about 25 percent.

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

In addition to the necessary thermal properties, a number of other properties are highly desirable for working flud 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 inslulating 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 of 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.

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 particuarly 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 boilder (and consequently of the small 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 condener is taught in the copending commonly assigned patent applications of William A. Doerner, U.S. Ser. No. 110,748 filed Jan. 28, 1971 as a continuation-in-part of U.S. Ser. No. 24,857 filed Apr. 6, 1970 and now abandoned U.S. Ser. No. 231,232 filed Feb. 3, 1972 and U.S. Ser. NO. 227,902 filed Feb. 22, 1972; also U.S. Pat. No. 3,590,786 and U.S. Pat. No 3,613,368 to William A. Doerner.

LOW FREEZING POINT:

The freezing point of fluids employed in Rankine-cycle engines must be well below the operating consenser temperature.

The 1,2,4-trichlorobenzene which is employed as the working fluid in the present invention has a boiling point of 214° F (417° F) which renders it suitable for use in small Rankine-cycle engines employing an efficient air-cooled condenser. The thermal stability is surprisingly good in contrast to the 1,2,3-isomer which is found in mixture with 1,2,4-trichlorobenzene in commercial trichlorobenzene. Accordingly, commercial trichlorobenzene sould be purified to removed the 1,2,3-trichlorobenzene which can be achieved by known methods, e.g., by partial freezing of the commercial trichlorobenzene, followed by isolation of the liquid, unfrozen material which is enriched in the 1,2,4-isomer. In particular, 1,2,4-trichlorobenzene is especially stable in ferritic steels such as 1018 steel. The stability is less in alloy steel such as stainless steel which appears to catalyze decomposition of the trichlorobenzene. The melting point of 1,2,4-trichlorobenzene, 17°C (63°F), is the lowest of the three possible trichlorobenzene isomers.

The high molecular weight (181.4) renders trichlorobenzene particularly useful in small, single stage turbines operating at relatively low speeds. 1,2,4-Trichlorobenzene has a relatively low toxicity as determined by tests with rats. The Toxic Substances Annual List 1971, Herbert E . Christensen. National Institute for Occupational Safety and Health, U.S. Department of Health, Education and Welfare gives a value of LD_{50} = 756 mg/kg rat for toxicity by ingestation.

The acute inhalation toxicity measured with room temperature air saturated with 1,2,4-trichlorobenzene vapor (418ppm) showed no deaths in 6 rats exposed for four hours. During the exposure lachrymation, salivation, pink ears, labored breathing and discoordination were observed. The body weight after exposure dropped to 84 percent of the initial weight the first day after exposure followed by normal weight gain for two weeks. 1,2,4-Trichlorobenzene is a mild skin irritant but does not, however, sensitize guinea pigs.

With respect to flammability, 1,2,4-trichlorobenzene has a flash point of about 230° F. However, although a swab of glass wool impregnated with 1,2,4-trichlorobenzene is ignited in a flame, the ignited material extinguishes itself upon removal from the flame.

Finally, 1,2,4-trichlorobenzene can be obtained in large quantities at relatively low cost.

Since obvious modifications and equivalents in the invention will be evident to those skilled in the arts, I propose to be bound solely by the appended claims.

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 to a vapor in a ferritic steel container, 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 1,2,4-trichlorobenzene.

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