Review of Experimental Research on Supercritical and Transcritical Thermodynamic Cycles Designed for Heat Recovery Application

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Abstract: Supercritical operation is considered a main technique to achieve higher cycle efficiency in various thermodynamic systems. The present paper is a review of experimental investigations on supercritical operation considering both heat-to-upgraded heat and heat-to-power systems. Experimental works are reported and subsequently analyzed. Main findings can be summarized as: steam Rankine cycles does not show much studies in the literature, transcritical organic Rankine cycles are intensely investigated and few plants are already online, carbon dioxide is considered as a promising fluid for closed Brayton and Rankine cycles but its unique properties call for a new thinking in designing cycle components. Transcritical heat pumps are extensively used in domestic and industrial applications, but supercritical heat pumps with a working fluid other than CO2 are scarce. To increase the adoption rate of supercritical thermodynamic systems further research is needed on the heat transfer behavior and the optimal design of compressors and expanders with special attention to the mechanical integrity.

Keywords: supercritical ORC; supercritical cycle; CO2; heat-pump; power cycle; steam cycle; waste heat recovery; heat-to-power; heat-to-upgraded heat

1. Introduction

Utilizing low grade heat as an energy source and recovering waste heat from various processes provides avenues for sustainable energy in the future with fewer environmental problems. Low grade heat is defined by its low temperature often combined with low capacity and intermittent availability. Examples are waste heat (i.e., excess industrial heat, rejected heat of combustion engines), solar heat and geothermal heat. A recent study showed that for the EU alone, waste heat potential in industry amounts to 304.13 TWh/year [1]. The fundamental technology to convert low-grade heat to electricity or to upgrade it to a higher temperature is available [2]. One of the most mature technologies, which
is offered commercially, is the organic Rankine cycle (ORC). The working principle is analogous to the classical water/steam cycle. However, instead of working with water/steam, alternative working fluids are used with beneficial thermophysical properties to cope with low temperature heat. It is important to recognize that these working fluids can also have an environmental impact. As such an important effort is put in the development of new generation working fluids with low global warming potential (GWP) and zero ozone depletion potential (ODP) [3,4]. While the basic concept of an ORC is well accepted in industry, there is huge potential to increase performance by adapting the operating regime or the cycle layout. One of the most promising concepts is the supercritical ORC (SCORC) with performance improvements up to 10% [5]. Instead of evaporating the working fluid at a constant temperature the working fluid is heated at supercritical state while gradually increasing the temperature.

One of the immediate benefits is a better match with the heat source profile resulting in a higher thermal efficiency and more heat being captured from the heat source [6,7]. It is interesting to note that there was a similar evolution with the classical Rankine cycle shifting to supercritical operation to increase thermal efficiency. The benefit in supercritical fossil fuel power plants is mainly seen in a superior efficiency due to the higher work availability of the steam entering the turbine. The main challenge was the development of new materials that could withstand the high pressures and temperatures [8]. Currently both, supercritical and ultra-supercritical plants, are the standard.

The first supercritical CO\textsubscript{2} power cycle was proposed in the late 1940s, but Angelino and Feher [9,10] initiated the interest by presenting theoretical fundamentals and possible configurations of the cycle. Interest in the topic dwindled mainly due to the limited amount of suitable heat sources. After the development of compact heat exchangers and materials in the 1990s, interest renewed in the topic. Nonetheless, most studies have focused on a cycle with a nuclear reactor as a heat source and hence the employment of such a cycle for low grade waste heat is relatively new. Recent times have seen more research in transcritical CO\textsubscript{2} cycles utilizing low grade heat.

Another interesting application is heat upgrading with the use of heat pump technology. CO\textsubscript{2} is a natural refrigerant that is used in heating and cooling applications. It was one of the early refrigerants to be used in a commercially feasible vapor compression system for refrigeration. Examples of some other refrigerants that were used early on include ether, ammonia, sulphur dioxide and methyl chloride. Very high operating pressures caused difficulties in the wide use of CO\textsubscript{2} as the primary choice for a refrigerant. Ammonia systems were preferred over CO\textsubscript{2} systems as they had good efficiency, however, CO\textsubscript{2} systems are smaller in size and did not pose toxicity risks. In a subcritical heat pump, the refrigerant always remains under the critical point and heat rejections takes place via condensation. Whereas, in a transcritical cycle, the heat rejection occurs at a supercritical pressure by single-phase sensible cooling. The difference in the pressure levels in a transcritical CO\textsubscript{2} system is much higher compared to a conventional subcritical system. This brings in additional thermodynamic and throttling losses. However, the large difference in pressure allows for the use of an expansion work recovery device which partially compensates for the losses in a transcritical CO\textsubscript{2} heat pump [11]. In what follows the supercritical/transcritical heat pump will be discussed besides the supercritical/transcritical ORC as many of the characteristics are shared.

**Characteristics and Benefits of Supercritical Energy Conversion**

A working fluid achieves a supercritical state (i.e., becomes a supercritical fluid) when the pressure and temperature is at or above its critical pressure and temperature. In the vapor generator of an ORC the working fluid at critical pressure is heated from subcooled conditions through the critical point ending in a supercritical state. During this process the temperature of the working fluid increases and during the subcooling phase it closely follows the saturation liquid curve. This property is exploited when recovering energy from sensible heat streams. It is known that closely matching heat profiles (see Figure 1) are beneficial to increase the thermal efficiency (higher mean temperature of the working fluid) and to increase the energy recovered (waste heat stream cooled to a lower temperature) [6]. For water,
both the critical temperature (647.096 K) and the critical pressure (22.064 MPa) are high while for CO₂ the critical temperature (304.36 K) is low and the critical pressure (7.38 MPa) is moderate. These high pressures result in technical challenges and additional material cost [12]. Furthermore, complex multistage pumps are required to reach those pressures. If the efficiencies of the pumps are low, their used power will amount to a large share of the gross power produced [13].

Many studies theoretically investigate the performance benefit of supercritical ORCs. Li et al. [14] investigated the use of supercritical ORCs applied to the desalination of seawater using low grade heat sources. They concluded that for applications like waste heat recovery, a supercritical cycle is much more efficient and is capable of operating in a wider range when compared to a conventional ORC. Yaugli et al. [15] carried out an exergy analysis with the aim of comparing the performance of a sub- and supercritical ORC for the recovery of waste heat from the exhaust of a biogas fueled combined heat and power (CHP) system. Lecompte et al. [5] found that the second law efficiency of supercritical cycles was up to 10% higher compared to subcritical ORCs depending on the waste heat temperature. For lower heat source temperatures the performance gain was higher.

For the generation of power, where condensation takes place at constant temperature, while liquid to vapor transition phase occurs at a continuously varying temperature the supercritical cycle is sometimes referred to as transcritical cycle. If such a transcritical cycle is reversed, heat supply results in isothermal vaporization and condensation occurs at variable temperature with the heat rejected being used for heating applications. Such applications do not always require heat at a constant temperature. Examples are found in district heating and sensible heat storage systems. Because in the phase change region, pressure and temperature are directly linked, an increase in the cycle temperature inevitably increases the overall pressure ratio. Supercritical vapor compression cycles are inherently free from this limitation.

Supercritical heat pumps for application in industry are mostly studied on a theoretical basis in the literature. Li et al. [16] proposed a supercritical heat pump with two evaporators with CO₂ as working fluid for drying application. Klocker et al. [17] performed a comparison between the performances of a supercritical CO₂ heat pump with an electric heating system and found that savings in energy of up to 65% can be achieved on using an optimized supercritical heat pump. Diaby et al. [18] used a transcritical CO₂ heat pump cycle to evaluate the performance of two heat pumps in (i) heating, cooling and domestic hot water and (ii) simultaneous cooling and desalination applications, achieving a coefficient of performance (COP) between two and three.

After the curtailment of fluorinated fluids in the refrigeration sector in Europe interest in CO₂ as refrigerant has grown. When compared to other commonly used working fluids, CO₂ is a natural working fluid with low GWP (=1) and no ODP. It is also non-flammable, nonexplosive and inexpensive in comparison.

**Figure 1.** Rankine cycle architectures for (a) subcritical and (b) supercritical modes of operation.
It is clear that there is still a gap for working fluids that have both low critical temperature and pressure. In Table 1 some refrigerants with zero ODP are listed showing potential for supercritical ORC operation. However, most organic fluids exhibit low fluid stability, high flammability and corrosiveness near or at supercritical pressure operation [19].

From the above analysis it is clear that supercritical and transcritical cycles provide possibilities for improving the performance of heat-to-power and heat-to-heat systems. However experimental results are scarce in literature and to the authors knowledge no thorough review is available. Therefore, in what follows, an overview will be given on experimental research on supercritical and transcritical heat-to-x cycles.

Table 1. Working fluids suitable for supercritical operation.

| Fluids | Mol. Wt. | NBP (°C) | P_c (bar) | t_c (°C) | GWP |
|--------|----------|----------|-----------|----------|-----|
| R744   | 44.01    | −56.6    | 73.8      | 31.1     | 1   |
| R170   | 30.07    | −88.6    | 48.7      | 32.2     | 3   |
| R744a  | 44.01    | −88.5    | 72.4      | 36.4     | 298 |
| R41    | 34.03    | −78.1    | 59.0      | 44.1     | 97  |
| R32    | 52.02    | −51.6    | 57.8      | 78.1     | 550 |
| R1270  | 42.08    | −47.7    | 46.6      | 92.4     | 2   |
| R290   | 44.09    | −42.1    | 42.5      | 96.7     | 3   |
| R152a  | 66.05    | −24.0    | 54.20     | 113.3    | 120 |
| C3H4   | 40.06    | −23.2    | 56.3      | 129.2    | 150 |
| R717   | 17.07    | −33.3    | 113.3     | 132.2    | 0   |
| R600a  | 58.12    | −11.8    | 36.30     | 134.6    | 3   |

2. Heat-to-Power Applications

Power generation from waste heat is usually economically feasible when the temperature of the heat source is higher than 150 °C. The main heat-to-power systems can be classified in conventional mechanical power cycles (Rankine-based), direct power conversion (turbo-compounding) and advanced technologies (TEG among others). Among the mechanical power cycles, the steam Rankine cycle (SRC) and organic Rankine cycle (ORC), both following the same configuration, are widely developed; they only differ in the working fluid [20].

2.1. Supercritical Steam Rankine Cycles

There are several methods to improve the thermal efficiency of a Rankine cycle. One way frequently used to increase the cycle’s efficiency is to increase the temperature of the steam entering the turbine. However, this temperature is restricted by metallurgical limitations imposed by the materials and design of the components and primary piping. The equipment and piping must withstand high pressures and great stresses at elevated temperatures. With new material development it is possible to go to higher temperatures during superheat and reheat. To balance that with the wetness at the last turbine stages, higher boiler pressure is required. Most thermal power plants are currently designed to operate on the supercritical Rankine cycle (i.e., with steam pressures exceeding the critical pressure of water 22.1 MPa, and turbine inlet temperatures exceeding 374 °C). Supercritical fossil fuel power plants present efficiencies of around 43%. Moreover, efficiencies of 48% are reached for very complex coal-fired power plants that operate at “ultra-critical” pressures (i.e., around 30 MPa) and use multiple stage reheat (see Figure 2) [21].
This step change proved that solar has the potential to compete with the peak performance capabilities of fossil fuel sources. Even though most supercritical units are coal-fired, in 2014, the Commonwealth Scientific and Industrial Research Organization (CSIRO) of Australia set a world record in generating “supercritical” steam using solar power with a field of more than 600 directional mirrors (heliostats) directed at two towers housing solar receivers and turbines, generating steam at a pressure of 23.5 MPa and 570 °C [22]. This step change proved that solar has the potential to compete with the peak performance capabilities of fossil fuel sources.

One very efficient way to ameliorate the performance of classic thermal power plants is the combined cycle gas turbine (CCGT) system configurations. Attaining higher overall thermal efficiency of the CCGT necessitates optimizing the entire plant and the three major components: the gas turbine (GT), the heat recovery steam generator (HRSG) and the steam turbine (ST). However, among the three components of the CCGT plants, the performance of the GT comes into first as the predominant influencer on the performance; with which plant efficiency can approach the 55% target and even more [23].

Another concept, proposed by Xu et al. [24], investigates an improved 1000 MW supercritical coal-fired power generation system incorporating a supplementary regenerative supercritical CO₂ cycle. The overall system efficiency of the proposed system reached as high as 46.0%, 0.4% higher than that of the reference power plant and could soar to 46.9% when the exhaust flue gas temperature dropped to 100.0 °C.

2.2. Supercritical Organic Rankine Cycles

As mentioned in the previous section, the supercritical organic Rankine cycle (ORC) presents the exact same configuration as the supercritical steam Rankine cycle (see Figure 3), however the working fluid is an alternative fluid rather than water. The organic fluids that can be used in temperatures below 400 °C do not need to be highly superheated in most of the cases, a fact that leads to higher cycle efficiency [25]. This allows to exploit low-grade heat sources that otherwise would be wasted. However, unlike large-scale utility steam power plants where the use of supercritical cycles has been accomplished, in small/medium-scale systems using a supercritical ORC, the selection of the appropriate components becomes very challenging. Moreover, low-temperature operation (below 100 °C) brings some additional restrictions, since a limited number of fluids can be used for such purposes and the cycle configuration does not allow any flexibility.

Supercritical ORC systems are studied in several publications [26–31] especially for geothermal and industrial heat recovery applications, where the temperature of heat source is adequate for a supercritical transition. The number of experimental references can be a good track of R&D progress on the supercritical ORC technology. Even though the theoretical investigation is becoming important...
in this field, only few ORC units running at supercritical conditions are reported so far [32], due to the excessive pressure levels and safety concerns. Most experimental systems refer to a low temperature operation and an accordingly low production, however the results concerning the cycle’s efficiency are very promising. Some experimental investigation has also been carried out for larger systems as presented below.

![Basic Rankine cycle layout.](image)

**Figure 3.** Basic Rankine cycle layout.

### 2.2.1. Various Layouts

The various theoretical studies focusing on supercritical ORC provide an overview concerning the performance potential of such cycles or the fluid selection under such conditions [6,33,34]. This kind of research provides few details about the performance and operation of some of the cycle key components—such as the pump and expander—at off-design conditions, while heat transfer at supercritical conditions is at the center of interest. Such aspects however are very important, especially in small-scale systems, in order to evaluate and compare the performance of a supercritical ORC.

One of the most important components in ORC engines is the expander. There is intensive research effort to find the optimal design to operate safely and efficiently in supercritical ORC conditions. Kosmadakis et al. [35] have developed and experimentally evaluated an ORC engine of a net capacity of 3 kW, with R-404a heated by concentrated PV/thermal collectors, to operate at both subcritical and supercritical conditions, with a temperature range of 65 to 100 °C. For their prototype, they have modified a market available scroll compressor to an appropriate scroll expander, re-designing many of its parts for better matching its operation as an expander. Moreover, they have developed a dedicated evaporator for this application, following a helical-coil design with a capacity of 41 kW [36].

Landelle et al. [37] have designed, constructed and tested, in transcritical conditions, an ORC prototype of a net capacity of 1.5 kW, using R-134a as a working fluid and operating at a temperature range of 55 to 120 °C. They have also used a modified scroll expander and their prototype includes four heat exchangers; apart from the evaporator and the condenser, they have included a pre-heater before the evaporator and an economizer to recover the heat from the expander outlet in order to reduce the requested heat load.

Hsieh et al. [38] have tested a 20 kW transcritical ORC using R-218 as a working fluid and operating at a temperature range of 90-100 °C. In their prototype, they have used two multistage centrifugal
pumps, a preheater, an evaporator, an oil injected twin-screw expander integrated with an induction generator, an oil separator, and a condenser.

Demierre et al. [39] tested a new concept of combined ORC and heat pump, using supercritical R-134a as the ORC working fluid. Their investigation concerns an oil-free compressor-turbine unit (CTU) used for a thermally driven heat-pump based on the combination of a heat pump compression cycle and an ORC. The CTU consists of a radial inflow turbine and a centrifugal compressor of the order of 2 kW each, directly coupled through a shaft supported on gas lubricated bearings.

Finally, Wang et al. [40] have made a different investigation, developing a prototype that helped them evaluate the heat transfer of supercritical R134a in a horizontal micro-fin tube, for conditions related to the supercritical heater in transcritical ORC systems. The experimental facility consists of a main circulating loop, including a circulating pump, a mass flowmeter and a U type preheater. The test section consists of the micro-fin tube and a plate heat exchanger. The supercritical R134a was circulated by the pump through the loop. A cooling tower was used for the condensation of R134a. In their experiment, focus was given on the refrigerant properties and performance and not on the cycle’s operation, however their research greatly contributes in the field of transcritical ORC engines.

Experimental activities have also been performed in larger scale electricity production. In Livorno, Astolfi et al. [41] report the construction of supercritical cycle of a capacity of 500 kWel using R134a for geothermal applications by Enel, Turboden and Politecnico di Milano. The experimental results have proved the important flexibility of these cycles, along with a very stable operation. The variation of the pump’s rotational speed helps in monitoring the operation in off-design conditions as well as the smooth transition from a supercritical to a subcritical operation following the heat source maximum temperature and mass flow rate without instability presence.

Spadacini et al. [42] have developed a 1 MWel high efficiency supercritical cycle for heat recovery or biomass combustion application. The particular features of this cycle are the use of an innovative radial outflow turbine and the use of a new high complexity per fluorinated working fluid never used before in the ORC field.

Finally, Atlas Copco and Mistral Power [13] have designed and installed a 7.5 MW ORC using waste-heat-recovery from a gas turbine installed in a natural gas pipeline pumping station. It drives butane supercritical cycle with a maximum temperature of 250 °C and a pressure of 45 bar. A customized two-stage turboexpander with the two wheels rotating at different velocities is used in this plant in a very advanced configuration.

2.2.2. Experimental Results

The experimental work on small-scale supercritical ORC, although limited, has provided some important results concerning the cycle’s efficiency and power production in transcritical conditions.

Several tests conducted by Kosmadakis et al. [35] in the laboratory have shown a cycle efficiency of 4.4% at supercritical conditions, when in subcritical operation it reached a value of 7%. However, supercritical operation was difficult to achieve and only when the cooling water flow rate was decreased, could the engine operate and maintain such conditions. At these conditions, the expander frequency/speed was low, keeping a pressure ratio close to the designed one, but leading to a low expansion efficiency. Nevertheless, the real test data and their study provide good arguments whether a supercritical ORC can be indeed more efficient than a subcritical cycle, and if the theoretical results can be verified. The thermal efficiency results in the field of CPV-T system showed that the ORC operated only in subcritical conditions. The most important conclusions from the laboratory tests were that such ORC engine with a capacity of just 3 kW can reach an adequate thermal efficiency, when operating at very low temperature.

In Landelle et al. [37] tests, the ORC scroll expander was able to produce up to 6 kWe gross, with supercritical R-134a supply and has shown good performance, however, the ORC engine performance was insufficient, with a net thermal efficiency of only 1%. Nevertheless, it showed a good potential for
waste heat recovery application since it performed better than 2/3 of the same power scale ORC for gross exergetic recovery efficiency.

Hsieh et al. [38] experimental results showed that their attempt in using a screw expander in a transcritical ORC was successful, since it converted low-grade heat into approximately 20 kW of power. The experimental results also demonstrated a net thermal efficiency (gross thermal efficiency) of 2.75% (5.7%), 2.66% (5.38%), and 2.63% (5.28%) for heat source temperatures of 90 °C, 95 °C, and 100 °C respectively.

Demierre et al. [39] have proven the feasibility of thermally driven heat pump based on small-scale turbomachinery demonstrated and the turbine used reached an efficiency of 0.75 as well as the compressor. However, the exergy losses between the turbine and the compressor reached ~30%. In Table 2, a summary of the aforementioned experimental prototypes is presented.

Table 2. Experimental prototypes in small and large-scale systems.

| Small Scale Systems                                      | Application                                                                 | T Range [°C] | Power Production [kWel] | Refrigerant |
|---------------------------------------------------------|----------------------------------------------------------------------------|--------------|-------------------------|-------------|
| CPV-T ORC with scroll expander and heat exchange development, Kosmadakis et al. [35] | 65–100 | 3 | R-404a |
| Transcritical ORC with scroll expander and four heat exchangers, Landelle et al. [37] | 55–120 | 1.5 | R-134a |
| Transcritical ORC with two multistage centrifugal pumps and a twin-screw expander with induction generator, Hsieh et al. [38] | 90–100 | 20 | R-218 |
| Supercritical ORC with oil-free compressor-turbine unit for a thermally driven heat-pump, Demierre et al. [39] | 95–123 | 2 | R-134a |

| Large Scale Systems                                      | Application                                                                 | T Range [°C] | Power Production [kWel] | Refrigerant |
|---------------------------------------------------------|----------------------------------------------------------------------------|--------------|-------------------------|-------------|
| Supercritical ORC for geothermal applications, variable operation according to heat available, Astolfi et al. [41] | 120–180 | 500 | R-134a |
| Supercritical ORC with radial outflow turbine and PP1 working fluid, Spadacini et al. [42] | 130–170 | 1000 | PP1 |
| Supercritical ORC with two-stage turbocharger for waste-heat recovery from a gas turbine in a natural gas pipeline, Atlas Copco and Mistral Power. [13] | 250 | 7500 | Butane |

The main layouts of the supercritical ORC engine, as described in the aforementioned prototypes.

2.3. Supercritical CO$_2$ Power Cycles

2.3.1. Transcritical CO$_2$ Rankine Cycle

Carbon dioxide has interesting properties for waste heat recovery with many beneficial features as displayed in Table 3 [43–45]: very low critical point, non-toxic, non-ignitable, widely available, zero ODP, low GWP of 1 by definition, etc. A screening of the archives shows large amounts of studies on this topic, therefore CO$_2$ Rankine cycles will be discussed separately here.

Table 3. Physical properties of the supercritical carbon dioxide.

| M (g/mol) | BP (°C) | CP (°C/MPa) | ASHRAE | ODP | GWP 100 Year | Atm. Life (Year) | LFL % |
|-----------|---------|-------------|--------|-----|--------------|-----------------|-------|
| 44        | -78.4   | 31/7.38     | A1     | 0   | 1            | >50             | none  |
2.3.2. Various Layouts

Experimental investigations on small scale transcritical CO$_2$ Rankine cycle have been carried out since the 2000s. Early attempts were carried out at the Doshisha University, Japan and regarded a solar driven medium-temperature system. And since then, few other systems have been built and tested, mainly for waste heat recovery applications. A list of various layouts is given in Table 4 and commented in following paragraphs.

Zhang et al. [43–46] conducted experimental research on a solar driven CO$_2$ transcritical cycle. In principle, their system uses a solar collector array and direct evaporation, a microturbine, a condenser, a CO$_2$ feed pump and is designed to operate in CHP mode. Due to lack of appropriate turbine/expansion machine, they installed an expansion valve and implemented an equation to estimate the power output of the system. Two heat exchangers connected in series configuration serve as condenser, cooled by a cooling tower. A piston pump was integrated to move the working fluid across the cycle.

Pan et al. [47] proposed a small scale transcritical system in which they integrated a 2 kW rolling piston expander coupled to a generator, shell and tube heat exchangers that can stand a pressure of 20 MPa as evaporator and regenerator and another one that can stand lower pressure as 8 MPa as condenser. A plunger pump with a rated pressure of 20 MPa was used as feed pump. A 34 kW cooling unit providing 5 °C cold water was connected to the condenser. An oil loop with an electric heater produced hot fluid at an approximate temperature of 210 °C.

A test facility was built for investigation on small-scale transcritical CO$_2$ Rankine cycles by Ge et al. [48]. It comprises an 80 kW micro-turbine CHP unit, an oil loop, a Rankine engine with integrated recuperator, and a dry cooling system. The CO$_2$ turbine was an axial, with single stage and a reaction ratio of 0.5. It was designed for 5 kW electronic power output, 0.281 kg/s mass flow rate and has a diameter of 144 mm. The CO$_2$ feed pump was a triplex plunger pump. Hot oil temperature and mass flow rate were varied through CHP power output and variable pump speed, respectively. As their system was designed, four two-way valves were installed so as to bypass the recuperator whenever necessary. System parameters could therefore be measured in both configurations: with and without recuperator.

Li et al. [49] decided to build, test and compare a small scale transcritical CO$_2$ Rankine cycle using R245fa. The system investigated by Ge et al. [50] was then complemented with an ORC engine. The ORC engine uses copper pipes instead of stainless steel as for the CO$_2$ test rig. The ORC turbine was also an axial one with single stage. The working fluid pump was a diaphragm pump coupled to a 1.1 kW asynchronous motor, and two air condensers mounted separately and controlled by variable speed fans. As both engines were driven by the same heat source, two valves were installed for cycle’s selection for comparing their performance at similar conditions.

Shi et al. [50] designed a small scale highly flexible CO$_2$ transcritical Rankine system in which they could study several cycle configurations: basic cycle, cycle with regenerator, cycle with preheater, and cycle with both regenerator and preheater. Heat was recovered from a heavy-duty diesel engine (exhaust flue gas and coolant water), the gas heater was a double pipe heat exchanger, and other plate heat exchangers type were used for the rest of heat transfer systems. A plunger pump was integrated to pressurize the liquid fluid in the condenser, and a needle type expansion valve was integrated instead of a turbine.

Li et al. [51] constructed a small test rig in which they used a 243 kW heavy duty diesel engine as heat source, a gas heater (tube-in-tube) for heat transfer, an expansion valve because of lack of appropriate turbine, a plunger type pump as CO$_2$ feed pump and brazed plate heat exchangers as condenser and pre-cooler. The system would be cooled by R22 refrigeration unit.

Shi et al. [52] conducted theoretical and experimental research on a kW transcritical system. Their aim was to maximize engine waste heat recovery after the integration of a preheater. In their study they used a test bench which comprises a heavy-duty diesel engine, preheater and gas heater, an expansion valve, a condenser and pre-cooler cooled by a refrigeration unit. This system is similar to the one of Shi et al. [50].
Table 4. A list of experimental studies and main layouts.

| Author            | Heat Transfer                                      | Evaporator/Gas Heater | Turbine/Expansion Device                  | Fluids | Fluid Pump | Cooling System | Application          |
|-------------------|-----------------------------------------------------|-----------------------|-------------------------------------------|--------|------------|----------------|----------------------|
| Li et al. [49]    | Flue gas from a 80 kWe CHP unit/thermal oil          | Plate heat exchanger  | Single stage axial (Reaction), 5 kWe      | R245fa, CO₂ | Diaphragm pump (R245fa), and triplex plunger pump (CO₂) | Air cooled          | Heat recovery         |
| Ge et al. [48]    | Flue gas from a 80 kWe CHP unit/thermal oil (124–144 °C) | Plate heat exchanger  | Single stage axial (Reaction), 5 kWe      | CO₂    | Triplex plunger pump | Air cooled          | Heat recovery         |
| Pan et al. [47]   | Oil heater/thermal oil/                            | Shell and tube HX     | 2 kW Rolling Piston expander              | CO₂    | Plunger pump (2/20 MPa) | Shell and tube HX/cold water/refrigeration unit | Waste heat recovery  |
| Shi et al. [50]   | Flue gas from diesel engine                        | Gas heater/double pipe| Expansion valve                           | CO₂    | Plunger pump                               | Cold water (7–13 °C) from a refrigeration unit | Heat recovery         |
| Li et al. [51]    | Flue gas from four-stroke six cylinders heavy duty diesel engine (water cooled) | Tube in tube HX      | Expansion valve                           | CO₂    | Reciprocating plunger pump                | Brazed plate HX, Cold water (7–13 °C) from a refrigeration unit | Heat recovery         |
| Shi et al. [52]   | Engine coolant water and flue gas from diesel engine | Preheater and gas heater/double pipe | Expansion valve                           | CO₂    | Plunger pump                               | Cold water (7–13 °C) from a refrigeration unit | Heat recovery         |
| Zhang et al. [43], Zhang and Yamaguchi [44] | Direct evaporation/Evacuated tube solar collectors | Evacuated tube solar collectors | Pressure relief valve                     | CO₂    | Piston pump                                | Shell and tube HX/Cold water from a cooling tower | Solar energy harvesting |
2.3.3. Experimental Results

Experimental work carried out by Zhang et al. [43–45,53] was first of its kind and provided significant results. A strong correlation between variation of solar irradiation and thermophysical properties of the cycle working fluid was demonstrated. Collector outlet temperature and pressure increased with the amount of radiation recovered. Collector efficiency performed well, and displayed a thermal efficiency above 50% and comparison with water proved supercritical carbon dioxide had better heat transfer characteristics [44]. The estimated power output was 820 W. The maximum temperature and pressure of around 187 °C and 9.26 MPa were reached and the system yield an overall efficiency of around 9%, well above that of a solar cell, 8.2% [43].

Pan et al. [47] used light bulbs as electrical load and the system investigated produced around 1 kW electrical power, and yielded an efficiency of 5%. They found that the piston expander performed poorly and displayed an isentropic efficiency as low as 22%, and concluded it wasn’t suitable. They furthermore indicated that an increase in the mass flow rate causes the pressure in the evaporator to increase.

Ge et al. [48] evaluated experimental performances of a low-grade heat driven CO₂ transcritical cycle and few results were obtained. Tests results showed a correlation between CO₂ cycle mass flow rate and turbine’s inlet and outlet pressures and subsequently with the generated power. Power output varied with working fluid and thermal oil mass flow rates, and reached a maximum around 500 W. System overall efficiency exceeded 10% and increased with the mass flow rate. The maximum turbine isentropic efficiency was 45% and showed poor performance when CO₂ mass flow rate was increased. From the experimental results obtained these authors were able to develop and implement a model in TRNSys to predict the impact of ambient air temperature on the system.

Li et al. [49] tested CO₂ transcritical and R245fa subcritical cycles driven by the same heat source in view of performance comparison. Input parameters were kept in closed ranges, 50–70 kW thermal heat, 0.2–0.3 kg/s working fluid flow rate, oil temperature of 139 °C and 130 °C for CO₂ and R245fa, and ambient air temperature of 24 °C and 17 °C, respectively. Test results on both configurations showed that pressure at different parts of the system, power generated, and turbine efficiency increased with working mass flow rate while cycle temperatures decreased with an increase in mass flow rates and poor performances of the turbines were observed. Maximum cycle pressure recorded was around 90 bar for the transcritical cycle, i.e., more than seven-fold that of the subcritical one, 12 bar. Heat transfer analysis in the evaporator/gas heater showed that the transcritical cycle has the potential to perform better than the subcritical configuration. Positive variation of heat input, a effect both cycle temperature and pressure. Measured isentropic efficiencies of expanders were below 40%. However, the authors failed to bring out important results such as cycle power output and system efficiency of both systems in similar conditions for meaningful comparison.

Shi et al. [50] aimed at improving trans-critical operation by cycle architecture modification and compared four configurations: basic cycle (B), cycle with regenerator (R), cycle with preheater (P), and cycle with both regenerator and preheater (PR). They were able to show that integrating a regenerator and a preheater is the best option as it provided best performances: 34 kW power output, a thermal efficiency of 7.8% and an exergy efficiency of 17.1%. It should be noted that of all configurations, the basic cycle showed lowest performances. However, results obtained were not realistic as the system did not produce any work, and performances were overestimated.

Li et al. [51] proposed to evaluate the dynamic behavior of a trans-critical system by mass flow rate and expansion ratio variation. Fluid mass flow rate variation was obtained by means of pump speed variation, while the pressure ratio variation could be achieved through expansion valve opening. Decreased mass flow rate induced an increase in pressure at the valve inlet and an increase in temperature. A decreasing valve opening led to an increase in pressure and temperature at the valve’s inlet, a decrease in mass flow was also observed despite fixed pump rpm. Overall, the system showed good dynamic response with average time response below 62 s.

Heat transfer optimization is an important issue in CO₂ transcritical cycles. Shi et al. [52] in their research tackled the issue by integrating a preheater in their system. They kept different pumps at
fixed speeds and varied the pressure in the gas heater, in the range 7.57–10.35 MPa and obtained a gas heater efficiency of 73–80% and a preheater efficiency of about 90%. They suggested further work to improve the gas heater, and proposed engine coolant pump frequency selection as way of optimizing preheater’s operation.

2.4. Supercritical CO\(_2\) Brayton Cycles

A Brayton cycle can be implemented with working fluids such as carbondioxide (CO\(_2\)), air, helium (He), ethane (C\(_2\)H\(_4\)), sulphur hexafluoride (SF\(_6\)), xenon (Xe), methane (CH\(_4\)) and nitrogen (N\(_2\)). The standard configuration can be modified to give birth to other layouts with the aim of increasing the cycle efficiency. More than a dozen layouts have been investigated so far throughout the literature [54–59]: standard Brayton, pre-compression, recompression, split expansion, partial cooling, cascade, simple reheat, double reheat, etc. These architectures are meant to be applied for power generation from various heat sources including coal combustion, thermonuclear reaction, solar radiation harvesting and waste heat recovery [49,60].

Mecheri and Le Moullec [61] investigated the possibility of applying Brayton cycles for heat recovery in coal power plants. Several possibilities with supercritical carbon dioxide were screened of which the recompression cycle emerged as the best option with an efficiency increase of about 4.5%pt in comparison with the standard Brayton cycle.

Concentrating solar power developers are also seeking for competitive designs, and efficiency increase through Brayton cycle have been proposed. Enríquez et al. [62] investigated Brayton cycles for line-focusing solar power plants with various working fluids. Ma and Turchi [63] argue that replacing steam Rankine by sCO\(_2\) Brayton in tower plants has many benefits: compactness, modularity and efficiency. Stein and Buck [64] compared several options for solar power, and Brayton appeared as a promising option but is yet to be confirmed by demo plants.

The Brayton cycle is being intensely investigated and attracts a lot of interest in the nuclear industry for use in the fourth generation nuclear power reactors [54,65–67]: sodium-cooled fast reactor, lead-cooled fast reactor, gas-cooled fast reactor, super-critical water-cooled reactor, very high temperature gas-cooled reactor and molten salt reactor. It could be well adapted for temperature in the range of 500–600 °C, with efficiency around 50%.

Brayton cycle performance is affected by several factors including the turbine inlet temperature and the pressure ratio. Performance may vary also depending upon the cycle architecture, and the recompression cycle was proposed as a suitable option for maximum cycle temperature around 500–600 °C, pre-compression and partial cooling being the right choices for processes over 600 °C.

2.4.1. Various Layouts

Since the 1960s a number of test facilities have been constructed in the world, with power output ranging from kW up to MW scale with the aim of investigating heat transfer and turbomachinery related to supercritical CO\(_2\) operation but research in this area has been frozen for decades [68]. However, since 2000s there has been a steady increase in experimental research regarding components developments, fluid behavior and systems integration. In the US, the Department of Energy (DOE) has been supporting efforts to develop highly efficient power conversion systems, and now more than a dozen of companies (Echogen, GE, Net power, etc.) and research centers (Sandia National Lab, Oak Ridge national Lab, National energy technology lab, etc.) are involved in research around supercritical CO\(_2\). In Europe, the European commission under the framework of H2020 program recently funded two major projects related to the development of supercritical Brayton: the sCO\(_2\)-HeRo and the sCO\(_2\)-Flex. The goal of the sCO\(_2\)-HeRo was to develop a small-scale Brayton cycle to be incorporated in a PWR glass model [69] and the sCO\(_2\)-flex project aims at developing a scalable, modular and flexible 25 MWe coal power plant utilizing a supercritical CO\(_2\)-based Brayton cycle. Ahn et al. [54]. In a survey reported experimental studies being carried out in South Korea. Several research centres are involved, and include the KAIST (Korea Advanced Institute of Science and Technology), the KAERI (Korean
Atomic Energy Research Institute) and the Korea Institute of Energy Research (KIER). Many other research centres based in China, Japan, India, Canada, UK and Australia are reported to be involved in the development of Brayton cycles.

Under the Sunshot initiative \cite{70,71}, the South West Research Institute (SwRI) along with its partners General Electric (GE), Thar Energy LLC (Thar), Bechtel Marine Propulsion Corporation, operator of Knolls Atomic Power Lab (KAPL), Aramco Services Co., and Electric Power Research Institute (EPRI) have developed a first MW size Brayton recuperated cycle. The project aimed at designing and engineering cycle components as well as testing the closed loop. Held \cite{72} reported ongoing R&D at Echogen Power Systems LLC where they compared several cycle architectures based on supercritical Carbone dioxide Brayton cycles. They came out with a “dual rail s-CO\textsubscript{2} cycle” that was further tested in a simple version \cite{61}. It is a modified standard recuperated Brayton cycle which utilizes multiple stages of recuperation and heat recovery. The cycle architecture integrates two turbines, the main one being decoupled from the compressor. The working fluid stream is split into two streams, and directed in both turbines. The power producing turbine bear the highest share while the other coupled to the compressor receives enough flow to drive the compressor.

2.4.2. Experimental Results

Wright et al. \cite{73} developed models of closed recuperated Brayton cycle driven by heat from a nuclear reactor and these models were subsequently validated. For the model validation, they used nitrogen as working fluid and a capstone C-30 microturbine power generator to provide a small-scale closed Brayton cycle, the SBL-30. The 30 kW microturbine operated at 1144 K turbine inlet temperature with a shaft speed of 96 kRPM and was modified to integrate an electrical heater and a water-cooled chiller.

Iverson et al. \cite{74} later on investigated a split flow recompression Brayton cycle based on previous research carried by Wright et al. \cite{75,76} during which they designed and tested the cycle components. In the proposed architecture two separate turbines receive separated flows. The system design integrates two TACs of 123 kW rated power each (hermetically sealed pressure vessels), two recuperators (610 and 2232 kW), electrical heaters (780 kW), and a pre-cooler (531 kW). Efficiencies of turbines and compressors were 87% and 68%, respectively. The experiment aimed at simulating the operation of a solar thermal power plant. The split flow recompression Brayton cycle configuration tested by Iverson et al. \cite{75} showed poor performance. For a turbine inlet temperature of 404 °C (9.89 MPa), a power output of 16.6 kW, and a cycle efficiency of 4.9% were obtained. At design conditions, the system was expected to produce 135 kW power output and a cycle efficiency of 15.2%. During the experiment, thermal losses at various parts of the system were detected and quantified, about 40% of total heat input. Rotating losses also contributed to system inefficiency. In fact, the high density of the working fluid and the high-speed environment led to turbulent flow at the shaft.

Vojacek et al. \cite{68} at CVR, Czech Republic, built a small-scale test facility in the framework of the SUSEN project. The facility is intended to be used for components testing at temperature up to 550 °C and pressure up to 30 MPa. The test rig built at CVR, aimed at testing heat exchangers and turbomachinery. Compressor operated as expected while closed loop operation of the simple Brayton cycle was not possible because of excess pressure losses. The 1 MW recuperated cycle built at SwRI \cite{72} saw its firsts tests, and the turbine reached a temperature of 550 °C at 21 kRPM. Future experimental investigations are planned and will focus on taking the temperature up to the design point set at 715 °C/25 MPa.

Anselmi et al. \cite{77} reported the development of a test rig at the university of Cranfield (UK) were they intend to test various components integrated in a CO\textsubscript{2} loop.

In South Korea, KAERI, KAIST and POSTECH have teamed up to carry out investigation on supercritical Brayton cycles. They have developed a s-CO\textsubscript{2} integral experiment loop (SCIEL) test facility with the aim of testing cycle operation and components. Two projects were put in place for high and low compression ratio \cite{54,78}. The first test rig was a recuperated Brayton with two stage
compression and two stage expansion. The turbines were designed for low pressure ratio (<2) and could stand a temperature as high as 500 °C, well suited for an SFR. The second one was a simple Brayton cycle. At the KIER, a research plan was set to investigate transcritical Rankine and Brayton cycles. Several cycle architectures with different power output were to be tested and evaluated [79]. Selected Brayton architectures were standard closed Brayton and dual Brayton. In the course of their experiment they designed and built a small-scale high speed turbo-generator (1 kWe, 200 kRPM) for a multi-purpose test loop which could operate at high temperature (500 °C) as simple Brayton and at low temperature (200 °C) as a transcritical Rankine cycle [80].

The first system designed by Echogen was a 10 MW sCO2 plant based on an innovative recuperated cycle. Tests were carried out on their EPS100 installation, which integrates printed circuit heat exchangers (PCHE) as recuperator and cooler, heater of fine tube design, a turbopump that consists of a hermetically sealed unit, and a power turbine coupled to a four-pole synchronous generator [72]. Initial testing took place without the power turbine, and off-design performance of components were measured and data recorded in comparison with model predictions showed in good agreement. At the KAERI, a simple Brayton was tested [79,80]. The test rig comprises an oil loop, a double low-pressure motor-compressor unit, a power turbine (200 kW power output) and a pre-cooler. The turbine was designed to stand a pressure up to 12.5 MPa, a temperature around 435 °C, and has a shaft speed of 80 kRPM. Compressor performance maps were drawn, transient analysis and cycle operation performed. After recording cycle parameters, they were able to draw the thermodynamic cycle in a TS diagram and succeeded in producing 1.2 kW output power.

3. Heat-to-Heat Applications

Heat pumps have been proposed for heat recovery applications, upgrading their heat supply to temperatures up to 150 °C or higher [81]. Most of the commercial and experimental units are based on subcritical cycles, with few examples available in the literature operating at transcritical conditions. A typical cycle design of a transcritical heat pump employing an internal heat exchanger for increasing the cycle performance and the corresponding pressure-enthalpy chart are shown in Figure 4. Most of the relevant applications concern a heat pump with CO2 as its working fluid, with few more using alternative ones. These are presented next.

![Figure 4. CO2 transcritical heat pump (left) and its cycle in a pressure-enthalpy chart (right).](image)

3.1. Transcritical CO2 Heat Pump Cycles

Heat pumps operating at a transcritical cycle with CO2 as the working fluid are attracting much attention especially in the domestic sector. The main reason is the high temperature lift of these type of heat pumps and their high volumetric heating capacity, making them suitable for hot water heating applications. This large lift is possible even with a single-stage cycle, reducing the system complexity and cost. However, they need low temperature in the evaporator side, so as to keep the boiling process within the two-phase region (practically lower than about 25–30 °C), which is usually supplied by
ambient air. This restricts their use in the industrial sector for heat recovery in cases where the heat source is from low-temperature wastewaters or from the rejected heat of refrigeration units [81].

In general, heat production of CO\textsubscript{2} transcritical heat pumps is limited to a temperature below 100 °C, being suitable for a limited number of industrial processes, such as for drying applications [16,17,82]. Their performance is greatly increased when the CO\textsubscript{2} temperature at the gas coolers is reduced as much as possible [83], exploiting most of the thermal content of the high-pressure gas. Heat production at different temperatures in the gas coolers is also possible. At the same time, it is ensured that the working fluid after the expansion process is within the two-phase region.

The experimental studies of this type of heat pumps for the production of process heat are limited. Although there are numerous experimental test-rigs for hot water heating mostly for buildings [84–86], its industrial application has not been examined so extensively [87]. This has mostly to do with the heat recovery process, requiring lower temperatures as the ones available in most waste heat recovery applications, as previously explained. Moreover, the maximum heat sink temperatures usually restricted below 100–120 °C, limit the possible applications [88] mostly for air preheating or drying purposes [16]. It should be mentioned that heat pumps based on subcritical cycles and with other refrigerants, both HFCs and HFOs, can reach higher temperatures of process heat well above 100 °C, reaching even 150 °C, enlarging their possible integration in industrial units [81,89,90].

The CO\textsubscript{2} heat pump for heat recovery can be an air-source one, utilizing the thermal content of the outlet air from drying processes or from rejected heat from refrigeration units (possibly within the same unit for simultaneous heating and cooling production). Water/brine-source ones are scarcer due to the need to keep the evaporation temperature below the critical one. Ground-source systems have been also examined [91], showing a good potential for both heating and cooling applications, once they recover the heat from the ground [92].

3.1.1. Various Layouts

For reaching a temperature lift of about 80–100 °C, a single-stage configuration is adequate, for keeping the system complexity low, which is one of the main advantages of CO\textsubscript{2} transcritical heat pumps. An internal heat exchanger can be also used, as shown in Figure 4, for exploiting the heat content of the pressurized gas, with smaller performance improvements as in subcritical heat pump cycles. Moreover, the large pressure difference reaching even 80–100 bar, makes the compression process very demanding in terms of compressor technology and performance. Relevant to this feature of this kind of heat pumps, different technologies are developed and tested at lab-scale units, mostly applicable for heat pumps in the domestic sector, with the aim to increase the flexibility and the COP [93]. However, these can be applied even in larger heat pumps for heat recovery, with heat supply from sources other than air. These two configurations leading to layout variants are briefly presented next, without restricting the use of additional (standard) variations, such as the use of internal heat exchanger, cascade cycles, or economizers [94,95].

Expansion Machine at the Gas Cooler Exit:

The large pressure difference makes it appropriate to use expansion devices for recovering some power from the expansion process of CO\textsubscript{2} at the gas cooler exit. This power covers a fraction of the necessary power input for the compression process. Even if this device operates with low efficiency of 19% [96], due to the two-phase operation and other losses (e.g., mechanical), the work recovery potential is significant. Baek et al. [97] reached an even lower isentropic efficiency of 11% using a reciprocating piston expander, probably due to the internal leakages, resulting however to a COP increase of 10%. Li et al. [98] used a rolling piston expander, reaching an isentropic efficiency of 58% and a COP increase by over 10%, without having any effect on the cooling capacity. Similar findings have been also reached by Tian et al. [99]. Even higher improvement was experimentally observed with larger expansion machines based on scroll types by Kohsokabe et al. [100], making it possible to increase the COP by 30%. The different expansion devices that have been proposed, as well as the
coupling methods of the expander with the compressor, are reviewed with detail in a recent work by Zhang et al. [101], highlighting the benefits of this layout.

Ejector for Assisting the Compression Process:

The second layout for enhancing the cycle performance that is under development is to use an ejector for increasing the pressure of the superheated CO$_2$. This layout is often called the thermo-compression cycle and the performance improvement greatly depends on the features of the ejector [102]. The ejector efficiency is usually restricted to lower than 30–35% [103,104], leading to a COP improvement of up to 10% [105], or even higher under varying operating conditions [106] and the use of multiple ejectors [107]. Detailed operational issues with this layout have been examined by Minetto et al. [108], highlighting the lubrication aspects as well.

Comprehensive review works relevant to the use of ejectors in CO$_2$ transcritical vapor compression cycles have been recently prepared by Sarkar [109], also focusing on other refrigerants, and by Elbel [110].

3.1.2. Experimental Results

There are numerous test results of domestic CO$_2$ heat pumps [95]. For heat recovery applications, the experimental facilities of CO$_2$ heat pumps are rather limited, as explained previously, having mostly to do with the limitations of its heat supply temperature to below 30 °C. However, there are few drying applications for which this kind of heat pumps has been tested and even commercially applied. The available test results were based on a limited number of experimental studies [16,99] and data provided by system manufacturers [111,112]. The main relevant results are shown in Figure 5, depicting the COP as a function of the temperature lift.

![Figure 5](image)

**Figure 5.** Coefficient of performance (COP) of CO$_2$ heat pumps for heat recovery as a function of the temperature lift.

The test results with a COP of 6.5, shown in Figure 5 to deviate from all other results, concern an air-source heat pump drier with small differences between the gas cooler and heated air temperatures, favoring its performance. In the same figure, a fitted (exponential-type) correlation is also presented, with its R$^2$ greatly reduced due to the aforementioned test result. In general, the heat pump performance can reach a COP of four for a temperature lift of about 40 K, while even for a lift of 90 K, the COP was still high and equal to three, achieved with a single-stage cycle. Similar performance at such high lifts is not possible to be achieved with a subcritical vapor compression heat pump that would require a two-stage cycle [81].
3.2. Supercritical Heat Pumps with Various Working Fluids

There are limited works on the use of other working fluids than CO\textsubscript{2} in transcritical heat pumps. The thorough literature research has identified only three relevant works based on different working fluids. Yu et al. [113] studied theoretically the use of the azeotropic mixture R32/R290 in a transcritical heat pump for heat production at 90 °C. The numerical results show that by using this mixture the COP can be about 10% higher as in a CO\textsubscript{2} transcritical heat pump under the same heat source/sink temperatures. On the other hand, Dayma et al. [114] simulated a transcritical heat pump using N\textsubscript{2}O, which has similar properties as CO\textsubscript{2}. The resulting COP is about 5% higher as with CO\textsubscript{2}, showing however lower volumetric heating capacity and thus requires larger component for delivering the same useful heating.

Except from the two above theoretical works, Wang et al. [115] tested in the laboratory under controlled conditions a heat pump using R125, operating at either subcritical conditions or near the critical point. Its main advantage over CO\textsubscript{2} heat pump is the lower working pressures and the potential to reach higher performance.

All these studies are mostly intended for cooling or heating applications supplied with ambient air. However, this is a small sample of the features of this technology, mostly fitting other applications than heat recovery.

4. Development and Market Status of Supercritical Energy Conversion

Energy demands are ever growing, and methods of the past no longer prove viable. Power production through the use of coal has been prevalent and was reported to produce 41% of all the electricity produced globally in 2013 [116]. The International Energy Agency’s (IEA) ‘World Energy Outlook 2015’ reports that the source of highest percentage of CO\textsubscript{2} emission are coal power stations.

With the European Union determined in phasing out coal to reduce its carbon footprint, new technologies harnessing cleaner sources of energies like solar, wind and geothermal are emerging in response. Meanwhile, attempts are being made to improve existing technologies and finding new ways to produce power that satisfies the demand. Supercritical power plants are an example of such technological improvements.

4.1. Operational Pilot-Plants and Commercial Systems

The first commercial supercritical unit in operation was the steam generator from the American Electric Power’s (AEP) Philo Plant Unit 6, installed in 1957. It could deliver 120 MW of power operating at 85 kg/s and 31 MPa and was supplied by The Babcock and Wilcox Co. Philadelphia Electric Co. developed a dual reheat steam generator that could deliver 325 MW at 252 kg/s and 34.5 MPa. This equipment was manufactured using stainless steel materials and helped pave the way for supercritical boilers. It is evident by now that supercritical (SC) and ultra-supercritical (USC) power plant technologies are very efficient techniques of generating power [117].

There are some supercritical ORCs in commercial use as well, some of which have been enumerated in Table 5. Even though highly efficient in theory, it is difficult to demonstrate the operation and exercise control over CO\textsubscript{2} supercritical power plants. Hence, supercritical pilot power plants with long operational background that can display cycle feasibility are scarce. Data available to the research community are produced by very few labs as discussed in Sections 2.3 and 2.4.
With an interest in CO₂ as a working fluid, a number of heat pump systems have been in use in commercial operation and research studies. Mayekawa [118] and Mitsubishi Electric [119], for example, produce commercial heat pump systems that operate on waste water sources and provide hot and cold water.

4.2. Pathways in Future Development

The use of water as a working fluid in supercritical power plants is the largest application of any fluid at supercritical pressures in an industry. However, there are a number of areas where other supercritical fluids are used currently, or can show performance benefits in the near future [120–122] as given below:

- Supercritical carbon dioxide as a refrigerant in air conditioning, refrigerating systems and power systems.
- Supercritical refrigerants in thermodynamic cycles for heat and power conversion.
- Supercritical carbon dioxide, near-critical helium and liquid hydrocarbon used as cooling media.

However, at the moment there is no general adoption of supercritical fluids in thermodynamic cycles. This is primarily due to the unknown behavior of the supercritical fluid in the heat exchangers at design and during operation. It is known that in the supercritical region the thermophysical properties change drastically with temperature and pressure. The near-critical point is actually a region around the critical point where all thermophysical properties of a pure fluid exhibit rapid variations. In contrast to the refrigerants used in ORCs or heat pumps, supercritical heat transfer has only been investigated in some detail already for CO₂ and water [123,124]. An example of data found for water is given in Figure 6. These unknowns now pose a high risk for potential manufacturers which are typically small to medium sized companies.

Table 5. Selected supercritical ORC plants in operation.

| Plant/Company Name | Country  | Type         | Working Fluid | Output (kW) | Year of Commissioning |
|--------------------|----------|--------------|---------------|-------------|-----------------------|
| Granite Power      | Australia| Solar        | GRANEX⁰       | 30          | 2014                  |
| TAS                | USA      | Geothermal   | R134a         | 22,000      | 2012                  |
| Atlas Copco        | Canada   | Waste Heat   | Butane        | 7500        | 2012                  |
| Turboden           | Italy    | Geothermal   | -             | 500         | 2012                  |
| San Emidio         | USA      | Geothermal   | R134a         | 8000        | 2013                  |

Figure 6. Variations of selected thermophysical properties of water near pseudo-critical point: pseudo-critical region at 25 MPa is about ±25 °C around pseudo-critical point.
In addition, there are regions of heat transfer enhancement (HTE) and heat transfer deterioration (HTD) [125]. However, even for CO$_2$ and water, there is no consensus on the physical explanation. Yet, it is clear that these effects lead to flow instabilities during operation and they complicate the design of heat exchangers. For ORCs this becomes even more of an issue as the heat source frequently shows intermittent behavior as waste heat availability and solar irradiation changes. As such, understanding the flow behavior during heat transfer to supercritical refrigerants is a crucial step to design supercritical ORCs and to avoid unstable operation. Unfortunately, this specific research is mostly lacking in scientific literature.

Another technology that influences the economy, safety and reliability of a high-pressure plant and sits at its core are the high-pressure pumps and compressors [126]. The challenge in designing pumps operating at high pressure include proper sealing, fatigue, wear, installation and vibration which come up in such applications. In these conditions, high stresses and strains are generated in the liquid containing parts leading to fatigue and hence, non-conventional materials and techniques of design and manufacturing are required. From the point of view of increasing efficiency of the power plant by increasing steam inlet pressure and temperature, there is a reduction in the power demand from almost all auxiliary equipment except the boiler feed pump. The reason behind this is the linear dependence of the power needed to drive the feed pump on pressure. This results in a substantial increase in the feed water pumping power, even though there is increase in the pump efficiency [126]. When compressors are employed to work in a transcritical or supercritical heat pump cycle, due to extremely high-pressure differences leakage becomes a major issue and affects the performance of the compressor.

Although much is known about turbine design and technology, there is limited information and operational experience of supercritical CO$_2$ power turbines. Operating with CO$_2$ at critical point with rapidly varying properties is a relatively new, unexplored regime for turbomachinery design. The design challenges faced here are somewhat similar in nature with the ones encountered during pump design, for example, materials reliability and coatings, seals, bearings, corrosion, erosion and blade cooling, especially in applications with an elevated turbine inlet temperature. Challenges about material reliability include carburization and sensitization, high-temperature corrosion, erosion, creep and thermal fatigue. Even though below temperatures of 500 °C CO$_2$ is inert, studies have suggested corrosion and carburization of steel and Nickle alloys in the presence of CO$_2$ at elevated temperatures, especially when water is present even in small amount, or any other contaminant for that matter [127–129]. Degradation mechanisms and the long-term behavior of corrosion and carburization needs to be investigated in further detail.

5. Conclusions

Concerns about climate change, future oil depletion and growing energy demand are fostering ways for advanced and efficient power systems. New paths are thus being investigated for next generation heat and power systems. Supercritical thermodynamic cycle systems including Rankine, Brayton and heat pumps have been reviewed from experimental and commercial viewpoints, focusing on their application for heat recovery. Several conclusions can be drawn from the study.

First of all, supercritical operation is already well accepted in specific situations. These include supercritical Rankine cycles (e.g., classical steam power plant) and to a lesser extend also supercritical heat pumps and Brayton cycles working with CO$_2$. Although CO$_2$ appears as a promising fluid, a lot of research is still needed as it calls for new engineering design.

Secondly, very few working fluids are considered suitable for supercritical operation. Either the critical temperature doesn’t match the application or the working fluid is not stable at high pressure and temperature or there are other (i.e., environmental, safety, cost) constraints.

Specifically for low-temperature transcritical cycles, experiments in literature are scarce and available results display poor performances mainly due to non-optimized turbomachinery. Supercritical Brayton cycles are intensely researched for its higher efficiency but experiments show we
are still far from expected performances. Furthermore research is lacking in heat transfer behavior of supercritical fluids, especially for the refrigerants used in ORCs and heat pumps.

Supercritical thermodynamic cycles have the potential to increase energy efficiency but at the moment high performing experimental test-rigs are missing to demonstrate this. In the future an integrated design is needed where all of the main components are optimized for supercritical operation (e.g., pump, expander, compressor, heat exchanger). The results of this could allow to increase the adoption rate of supercritical thermodynamic systems and to increase energy efficiency.

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