

**ČESKÉ VYSOKÉ
UČENÍ TECHNICKÉ
V PRAZE**

**FAKULTA
STROJNÍ**



**TEZE
DISERTAČNÍ
PRÁCE**

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ÚSTAV ENERGETIKY

TEZE DISERTAČNÍ PRÁCE

Studie Tepelného Oběhu s Nadkritickým CO₂

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1. CURRENT STATE OF THE S-CO₂ POWER CYCLES

The research on the S-CO₂ power cycles is intensive in the last 20 years. However, a commercial S-CO₂ power systems still does not exist. The research is largely theoretical, focusing on cycle analysis and the design of new cycle layouts for applications from Table 1 [1]. However, the research moves to the practical verification of proper functioning of the components in the operating conditions and detailed design of components, especially compressors and heat exchangers.

The use of CO₂ cycles begun in the last century [2]. However, parameters of cycles were under the critical point. With the advent of new technologies and materials, the use of cycles with critical parameters began to be considered. Initially, the use of cycles for nuclear power applications was considered [3]. The S-CO₂ power cycle is considered for new generation of nuclear reactors, due to previous experience with CO₂ in the field of nuclear power. The development of the S-CO₂ power cycle directed to applications other than nuclear energy started to appear as well. Earlier, the basic cycle layouts were considered. However, with growing interest in S-CO₂ power cycle, the development of new cycle layouts for different application begun.

The new applications of S-CO₂ power cycles includes, the waste heat recovery systems [5], solar power plants [6, 7], geothermal power plants or application to fossil fuel power plants [8].

Table 1. Applications of S-CO₂ power cycles. [9]

Application	Power	Operation Temperature	Operation Pressure
	[MWe]	[°C]	[MPa]
Nuclear	10-300	350-700	20-35
Fossil Fuel	300-600	550-1500	15-35
Geothermal	1-50	100-300	15-35
Solar	10-100	500-1000	35
Waste heat recovery	1-10	200-650	15-35

The research is done for example in the Naval Nuclear Lab [10], Southwest Research Institute [11], Argonne National Laboratory [12], Tokyo Institute of technology [13] or Korea Institute of Energy Research [14] and University of Wisconsin, Madison [15]. The research of a heat exchangers is focused on

heat transfer and design of channels for the PCHEs (Printed Circuit Heat Exchangers). [10, 13–15] However, the research also focuses on the shell and tube heat exchangers, plate fin heat exchangers or ceramic heat exchanger (application for direct-fired S-CO₂ cycle) [16] depending on the application and utilization. Because, the gas cycle has at least three different types of heat exchangers, the cooler, the heater and the recuperative heat exchanger, each type of the heat exchanger has a different operating parameters. Therefore, different types of the heat exchangers can be used.

The important part of the power cycle is the compressor. University of Wisconsin carried out research and developed a compressor and other component of the S-CO₂ cycle. [17] The Sandia National Laboratories (SNL) is conducting research of S-CO₂ power cycle for solar power plants, as well as testing components of the power cycle since 2007. The research is focused on testing of compressor near the critical point of CO₂. The radial compressor with power of 50 kW was used. The compressor speed was 75 000 rpm and mass flow rate was 3.51 kg/s. The compressor efficiency was found to be 66% [18]. The experimental loop was used for testing of turbo compressors, dynamic behaviour of compressors, verification of control elements and dynamic codes. The turbine for 10 kW was developed. The maximal turbine temperature was 600 K. [19]

Other experimental loop is at the Tokyo Institute of Technology and Institute of Applied Energy in Japan. As already mentioned, research on heat exchangers is being carried out there as well as turbine and compressor testing. [20] The power of the experimental loop is 10 kWe, mass flow rate is 1.2 kg/s, the turbine inlet temperature is 550 K and pressure is 12 MPa. The compressor speed is 100000 rpm. The research is focused on the fast nuclear reactors (SFR). The research in Delft University of Technology is focused on CFD simulation of compressor, turbulent flow and study of CO₂ properties. [21] The research of the S-CO₂ power cycle is also carried out in the Czech republic. The Research Center Rez built an experimental loop for testing of components of S-CO₂ power cycle. [22]

Research of the S-CO₂ power cycle is done all over the world. As can be seen the research is focused on the behaviour of the cycle layout and components testing. Development of the S-CO₂ power cycle is done from demonstrable benefits. Research is focused on many application, different cycle layouts and for each component is the system. However, the research is mostly done for pure CO₂. The pure CO₂ will most likely not be used in the real cycle. It is much more likely that the working medium will be a mixture with CO₂. Therefore the research of the effect of mixtures on the cycles and the components of the cycles is necessary.

The research of the effect of mixtures on the S-CO₂ power cycle is in progress but, only on a marginal scale [23–25], which is focused on the specific application of the S-CO₂ power cycle, for example direct-fired S-CO₂ power cycle [7, 26, 27]. Another research is being done for CCS. The research is focused on the impact of impurities on compression, liquefaction and transportation [28–31].

2. GOALS

The main goal is the detail description of the effect of mixtures on the S-CO₂ power cycle, to identify the substances with negative or positive effect on the cycle and the components and to define the maximum amount of the second substance in CO₂, with still acceptable impact on the cycle. The other goals of the research are following:

- The physical description of the effect of mixtures on the components (compressor and turbine).
- The description of the effect of mixtures on the pinch point.
- The description of the effect on the heat exchanger type (cooler, heater and recuperative heat exchanger).
- The description of the effect of the compressor inlet temperature on the cycle efficiency and cooling of the cycle.
- The techno-economic evaluation for specific application.

This work will give an overall insight on the issue of impurities on S-CO₂ power cycle. It is an initial research of the effect of mixtures on the S-CO₂ power cycle. The results will be used as the input information for the future applications of the S-CO₂ power cycle. Especially, the S-CO₂ power cycle with working medium from different application, which produces CO₂ or from the direct-fired S-CO₂ power cycles.

3. METHODS OF PROCESSING

The research in this thesis was oriented on the description of the effect of the mixtures on the S-CO₂ power cycle. Namely, the binary mixtures of CO₂ with He, Ar, CO, N₂, O₂, H₂S, H₂, CH₄, Xe, Kr and SO₂. The research is divided into several parts with theoretical description of the effect on the cycle. The parts are connected to each other and give the complex overview and description of the effect of the mixtures on S-CO₂ power cycle. The parts of the research are following:

- The first part focuses on the description of the effect of mixtures on the S-CO₂ power cycle performance. It evaluates the overall cycle efficiency and the net power.
- The second part is focused on the detail description of the effect on each component in the cycle, especially on the turbine, the compressor and the heat exchangers.
- The third part of the research is focused on the optimization of the S-CO₂ power cycle, mainly the compressor inlet temperature. The results for this part of research are calculation and optimization for the specific cycle layouts for different binary mixtures.
- The fourth part is the technical-economic evaluation for the S-CO₂ power cycle with different binary mixtures for different applications.

Each parts have the theoretical part, where the theoretical background for understanding of the S-CO₂ power cycle and the components is described. The other part is oriented on the description of the calculation, the boundary conditions and the input parameters which are used in the research. The last part is focused on the analysis of the results and conclusions drawn for each part of the research.

4. RESULTS

Several conclusions can be made based on the results from each parts of the research. The main conclusion is that each mixture has an effect on the power cycle and the components. The mixtures have generally negative effect which increases with the amount of impurities in CO₂. Although, this is not true for all investigated substance. The research showed that at lease three substance have the opposite effect.

- The negative effect is caused by: He, Ar, CO, N₂, O₂, H₂, Kr, CH₄
- The positive effect is caused by: H₂S, Xe, SO₂

H₂S has the highest positive effect and He has the highest negative effect among investigated substances. However, for mixtures with CO₂ purity over 99 % the effect is negligible (The effect of the mixtures on the cycle efficiency, respectively on the net power.).

The cycle efficiency and the net power depends on the compressor and the turbine power and input and output heat. For this reason, the definition of the effect of mixtures on the components is necessary. The conclusions for the turbine and the compressor are following:

- The compressor performance:
 - The Compressor input power dramatically increases with the increase of amount of the investigate substance in CO₂.
 - All the investigated mixtures have the negative effect on the P_c, expect H₂S, SO₂ and Xe.
 - The effect of H₂S, SO₂ and Xe is only marginally positive.
- The turbine performance:
 - All the investigated mixtures have the slightly increases the Turbine power output.
 - He has the biggest effect.

These results are very important for the design of the compressor, the turbine and selection of operating parameters. However, it should be noted that decreasing the compressor inlet temperature could reduce the effect of mixtures on the compressor power. This is an important information for the design of the cooling system and selection of the cooling medium. Also, this may affect the already designed cycle when the condition of the cooling medium changes.

The compressor power increase is the most important negative effect on the cycle efficiency and the net power. The same problem can be observed in other systems with CO₂, for example the compression stage for transport of CO₂ to the storage or heat pumps with CO₂. The decrease of the cycle efficiency appears to be linear, for concentration of CO₂ from 100 % to 99 %. The decrease of the cycle efficiency from 99 % to lower mol % can be approximated by exponential function. The increase of cycle efficiency is observed for H₂S, SO₂ and Xe and appears to be linear for all concentration of CO₂. Conclusion is that the optimum amount of the second substance is up to 1 %. For this amount the negative effect of binary mixture is small.

The S-CO₂ power cycle has three different type of heat exchanger. The mixtures have different effect on each HEX type. The conclusions for the heat exchangers are following:

- The recuperative heat exchanger:
 - The pinch point can be completely removed by the use of mixtures.
 - The substances with a positive effect on the cycle has a positive effect on the ΔT (increase of ΔT) and the substances which has a negative effect on the cycle has a negative effect on the ΔT (decrease of ΔT).
- The cooler:
 - The substances with a positive effect on the cycle has a negative effect on the ΔT (decrease of ΔT) and the substances which has a negative effect on the cycle has a positive effect on the ΔT (increase of ΔT).

The effect of the mixtures on heater is similar as for cooler. However, the effect may vary depending on the composition of the working medium and it is not possible to clearly say what will be the effect of the mixture on the heater.

From the techno-economic evaluation of a hypothetical power plant with the S-CO₂ power cycle several conclusions can be made based on the presented results. The conclusions for the techno-economic evaluation are following:

- The mixtures with negative effect on the cycle, reduces effectively the project capital cost.
- The mixtures with negative effect have a negative effect on the specific cost as they lower the net power which leads to a higher specific cost.
- The mixtures with negative effect have a negative effect on the IRR and NPV. However, the negative effect on the profit is negligible in the long term operation for working medium with 99 % pure CO₂.
- The mixtures with negative effect have a negative effect on the LCOE. However, the effect is negligible.

5. CONCLUSION

From the results, it is evident, that mixtures have a very important effect the S-CO₂ power cycle, operating parameters and components. However, with good optimization and design of the cycle which uses mixtures, marginal negative effect on the cycle efficiency and the net power output can be achieved. This is an important information for the design of the cycle layout and components. Regardless of the CO₂ purity, the same cycle layouts can be used, however in order to achieve good performance with the impurities the cycle operating conditions and components design must be re-optimized.

Future research will be focused on the detail description of effect of another potential mixtures on the S-CO₂ cycle, for the close S-CO₂ power cycle and the Direct-Fired S-CO₂ power cycle or other application S-CO₂ power cycle for fossil fuel power plant, for specific application. Because, these system is currently very popular, for increase of total efficiency of power plant, as waste heat recovery systems. But, the effect of the mixtures will be higher. The mixture will be product of combustion or impurities from the primary loop.

At the same time, research about impact on materials of components and chemical effect is necessary. The each substance has some effect on the materials, for example H₂S, is very interesting substance for increase the cycle efficiency and the net power. On the other hand, effect on materials of the turbine and the compressor is enormous, especially on blades. Research of the new materials is therefore necessary.

NOMENCLATURE

S-CO ₂	Supercritical carbon dioxide
HEX	Heat exchanger
PCHE	Printed circuit heat exchanger
SNL	Sandia National Laboratories
CFD	Computational Fluid Dynamics
SFR	Sodium cooled fast reactor
P _{tu}	Turbine power output
P _c	Compressor input power
ΔT	Temperature difference
LCOE	Levelized cost of electricity
NPV	Net Present Value
IRR	Internal Rate of Return

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ANOTACE

S rostoucím zájmem o solární a geotermální elektrárny a systémy využívající odpadního tepla z mnoha technologií se celý svět více orientuje na využívání plyných cyklů. Tepelné oběhy s nadkritickým CO_2 (S-CO_2) jsou velmi zajímavé tepelné oběhy pro tyto aplikace. S-CO_2 cykly mají mnoho výhod, ale i nevýhod v porovnání s dalšími tepelnými oběhy, jako je parní nebo Heliový. Výhodou S-CO_2 cyklu je, že je kompaktní a velmi jednoduchý, výkon kompresoru je nižší než pro cyklus využívající helium jako pracovní medium. Jednou z nevýhod je vliv reálných vlastností, které mohou být významně ovlivněny přítomností nečistot v pracovním mediu. Je zřejmé, že nečistoty ovlivňují tepelný oběh, konstrukci komponentů, celkovou účinnost a výkon, z důvodu změn termodynamických a transportních vlastností. Výzkum byl zaměřen na popis vlivu směsí na S-CO_2 cykly. Výzkum je rozdělen na několik oblastí, které jsou vzájemně propojeny pro komplexní přehled a popis účinku směsí na S-CO_2 cykly. Výzkum byl proveden pro binární směsi CO_2 s He, Ar, CO, N_2 , O_2 , H_2S , H_2 , CH_4 , Xe, Kr a SO_2 . Všechny zkoumané látky, s výjimkou H_2S , Xe a SO_2 mají negativní vliv na cykly a jejich účinnost. Vliv směsí na příkon kompresoru je nepříznivý. Vliv směsí na výkon turbíny je nepatrně pozitivní. Vliv směsí na výměníky tepla je rozdílný pro různé druhy výměníků tepla. Optimální množství sekundární látky je do 1 %. Vliv směsí musí být zohledněn při návrhu S-CO_2 cyklu. Optimalizace je velmi důležitá při návrhu S-CO_2 cyklu pro každou jeho aplikaci a rozvržení cyklu. Je možné dosáhnout minimálního vlivu směsí na S-CO_2 cykly při dobré optimalizaci a návrhu tepelného oběhu. Bez ohledu na čistotu CO_2 může být použito stejné rozložení tepelného oběhu, nicméně jsou, pro dosažení maximálního výkonu S-CO_2 cyklu s nečistotami, provozní parametry a konstrukce komponentů opakovaně optimalizovány.

SUMMARY

With the increasing interest in solar and geothermal power plants as well as waste heat recovery systems from many technologies, the whole world is more focused on the gas power cycles. Especially, the supercritical carbon dioxide (S-CO₂) cycles are very interesting for these applications. The S-CO₂ power cycles have a many advantages and disadvantages over the other cycles such as a steam-water cycle or helium Brayton cycle. The advantages are the cycles are compact systems, the compressor power is lower than for helium Brayton cycle, the cycles are very simple. One of the disadvantages is the effect of real properties, which can be significantly altered by the presence of impurities in the working fluid. Because, it is obvious that impurities through the change of thermodynamic and transport properties affect the cycle as they influence cycle component design and thus the overall efficiency of the power cycle and the net power. The research was oriented on the description of the effect of the mixtures on the S-CO₂ power cycle. The research has focused on the several areas, which are connected to each other for the complex overview and description of the effect of the mixtures on S-CO₂ power cycle. The research was conducted for the binary mixtures of CO₂ with He, Ar, CO, N₂, O₂, H₂S, H₂, CH₄, Xe, Kr and SO₂. The all investigated substances, except for H₂S, Xe and SO₂ have a negative effect on the cycle and the cycle efficiency. The effect of the mixtures on the compressor performance is negative. The effect of the mixtures on the turbine performance is negligibly positive. The effect of mixtures on the heat exchangers is different for different type of the heat exchangers. The optimum amount of the second substance is up to 1 %. The effect of mixtures must be taken into account when designing the S-CO₂ power cycle. The optimization for each application of the S-CO₂ power cycle is very important when designing of the S-CO₂ power cycle. With good optimization and design of the cycle which uses mixtures, marginal negative effect on the cycle efficiency and the net power output can be achieved. Regardless of the CO₂ purity, the same cycle layouts can be used, however in order to achieve good performance with the impurities the cycle operating conditions and components design must be re-optimized.