

Zvečanje učinkovitosti krovnega procesa z zvišanjem tlačnega nivoja uparjanja

Improvement of Topping-Cycle Efficiency with an Increase in Evaporation Pressure Level

Boštjan Cerkvenc - Alojz Poredoš - Felix Ziegler

Zahteve po klimatizaciji poslopij so iz leta v leto večje. Ponavadi se za pripravo hladu uporabljajo kompresorske hladilne naprave, za katere je značilna zgoščenost in ugodne cene. Sorpcijske hladilne naprave se uporabljajo samo v posebnih primerih in pokrivajo le manjši tržni delež na področju hlajenja.

V našem prispevku je predlagan tristopenjski kaskadni sorpcijski hladilni proces, sestavljen iz osnovnega absorpcijskega procesa z dvojnimi učinkom in delovnim parom $\text{LiBr}/\text{H}_2\text{O}$ ter krovne procesa, ki deluje z delovnim parom $\text{CaO}/\text{H}_2\text{O}$. Zaradi uporabe vode kot hladiva v krovnem procesu je tlačna raven uparjanja nizka, kar ima za posledico nezadostno intenzivnost faze sinteze glede na fazo razpada. Za rešitev sta predlagani dve spremembi krovne procesa, pri katerih z dvigom tlačne ravni uparjanja pospešimo proces sinteze v reaktorju. Ugotovili smo, da lahko dosežemo hladilno število ($H\dot{S}$ - COP, Coefficient of performance) do 1,6 kljub temu, da s spremenjenim krovnim procesom ne moremo več pridobivati hladu. Ta vrednost pomeni izboljšanje za približno 30 odstotkov glede na učinkovitost industrijskih $\text{LiBr}/\text{H}_2\text{O}$ absorpcijskih hladilnih naprav na trgu.

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(Ključne besede: sorpcija, hlajenje, procesi kaskadni, procesi krovni, učinkovitost)

The demand for better air conditioning in buildings is increasing from year to year. Compression machines are normally used for cold-air production, due to their compactness and favourable price. Sorption machines are used in special cases only, covering small niches of the cooling market.

In our paper a three-stage cascading sorption cycle is proposed, consisting of a bottoming double-effect absorption cycle with a $\text{LiBr}/\text{H}_2\text{O}$ working pair and a topping solid-gas cycle with $\text{CaO}/\text{H}_2\text{O}$ as the working pair. Because water is used as the refrigerant in the topping cycle the evaporation pressure level is low, what results in the insufficient intensity of the synthesis phase relative to the decomposition phase. As a solution, two modifications of the topping cycle are proposed in which the evaporation pressure level is increased to intensify the synthesis phase. It is shown that coefficient of performance (COP) values of 1.6 could be reached, despite the fact that the topping cycle is not used as a cooling cycle anymore. This COP value represents an improvement of about 30% compared to industrial double-effect $\text{LiBr}/\text{H}_2\text{O}$ absorption chillers currently on the market.

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(Keywords: sorption, cooling, cascading cycles, topping cycles, efficiency)

0 UVOD

Komercialne, na trgu dostopne absorpcijske naprave z dvojnimi učinkom lahko dosežejo hladilno število ($H\dot{S}$) okoli 1,25. To pa dostikrat ni dovolj za konkurenčnost kompresorskim hladilnim napravam. Ob uporabi visokotemperaturne toplote, npr. zgorevanja plina, za pogon naprave lahko $H\dot{S}$ absorpcijske hladilne naprave izboljšamo z dodajanjem dodatnih absorpcijskih stopenj. Kapljeviti delovni pari, ki se trenutno uporabljajo v absorpcijskih napravah, povzročajo pri

0 INTRODUCTION

Commercial double-stage absorption chillers can reach a cooling COP of about 1.25, which is often not high enough to compete with compression chillers. Using high-temperature driving heat, i.e. the combustion of gas, the COP of absorption chillers can be improved by multi-staging. But the currently used liquid working pairs tend to cause heavy corrosion of the construction materials at high temperatures. These corrosion problems can

visokih temperaturah močno korozijo vgrajenih materialov. Problemom s korozijo se lahko izognemo z uporabo sorpcijskih procesov s trdnimi sorbenti kot visokotemperaturnimi krovni procesi. S pojmom krovni proces je označen del kaskadnega sorpcijskega procesa, ki je postavljen nad osnovni del procesa glede na temperaturno raven delovanja. Za razliko od osnovnega dela naprave, ki je ponavadi absorpcijska hladilna naprava, so krovne naprave navadno enostopenjske, trdno - plin sorpcijske naprave ali v določenih primerih absorpcijske naprave z delovnimi pari, ki so bolj odporni proti koroziji.

Poleg teoretičnega dela o kaskadnih procesih ([1] in [2]) je bilo na področju sorpcijskih kaskadnih naprav opravljeno tudi eksperimentalno delo. Pri kaskadnih napravah se za pogon osnovne sorpcijske naprave uporabi vsaj del toplote, ki jo odvedemo krovni napravi. Prva kaskadna eksperimentalna naprava je bila dvostopenjska hladilna naprava [3]. Sestavljena je bila iz enostopenjske LiBr/H₂O hladilne naprave in adsorpcijske hladilne naprave z delovno dvojico zeolit/H₂O. Dosegala je HŠ okoli 1,2, kar se je v tistih časih štelo za veliko. V zadnjem času je bila v nemško-francoskem sodelovanju razvita in preskušena nova kaskadna naprava ([4] do [6]). V tem primeru je osnovna naprava LiBr/H₂O absorpcijska naprava z dvojnimi učinkom in kot krovna naprava hladilna naprava s trdnim sorbentom in delovno dvojico NiCl₂/NH₃. Uporaba amoniaka kot hladiva v krovnem procesu je bila ugodna, zato ker visok tlak uparjanja NH₃ zmanjša probleme prenosa toplote in snovi v sorpcijskem procesu s trdnim sorbentom.

V primeru uporabe vode kot hladiva v krovnem procesu postane problem nizkega tlaka v reaktorju pomembnejši pri omejevanju moči krovne procesa kakor v primeru amoniaka. Po drugi strani pa lahko v primeru, da uporabimo vodo v osnovnem in krovnem procesu, sistem deluje samo z enim skupnim uparjalnikom, kar pomeni zmanjšanje stroškov. Še več lahko dosežemo s pametno združitvijo med obema procesoma [7].

V tem prispevku nadaljujemo delo pri zelo učinkovitih kaskadnih procesih, z LiBr/H₂O absorpcijsko napravo z dvojnimi učinkom kot osnovno napravo in krovni procesom s trdnim sorbentom CaO/H₂O [8]. Prejšnje delo je bilo namenjeno kot izhodišče za vrednotenje možnosti uporabe kovinskih soli v kaskadnih sorpcijskih napravah. Da lahko uporabimo vodo v krovnem procesu s trdnim sorbentom, moramo fazo sinteze, ki poteka pri tlaku uparjanja hladiva, pospešiti. To lahko storimo z dvigom tlaka v reaktorju ali z dvigom celotnega uparjalnega tlačne ravni. V nadaljevanju želimo temeljiteje predstaviti dve rešitvi z dvigom tlačne ravni uparjanja, ki ju lahko v praksi izvedemo.

1 KASKADNI SORPCIJSKI PROCES Z VODO KOT HLADIVOM

V našem prejšnjem delu [8] smo predstavili tri mogoče LiBr/CaO/H₂O kaskadne sorpcijske

be avoided by the use of solid sorption cycles as the high-temperature topping cycles. With the topping cycle we refer to the part of the cascading sorption cycle which is set above the bottoming cycle in terms of operational temperature levels. In contrast to bottoming cycles, where absorption cycles are usually appropriate, topping cycles are usually single-stage solid-gas cycles, or in some cases, absorption cycles with corrosion-resistant working pairs.

In addition to the theoretical work on cascading cycles ([1] and [2]), experimental work in the field of sorption cascading cycles has also been undertaken. In such a cascade at least a part of the heat rejected from the topping cycle is used as driving heat for the bottoming sorption cycle. The first experimental two-stage cascading cycle [3] was a combination of a single-effect LiBr/H₂O chiller and a zeolite/H₂O adsorption cooling device. It had a COP of around 1.2, which was considered high at that time. In recent years a new cascading chiller has been developed and tested in a French/German co-operation ([4] to [6]). In this case a double-effect LiBr/H₂O chiller is the bottoming cycle with a NiCl₂/NH₃ solid sorption chiller working as the topping cycle. The use of ammonia as the refrigerant in the topping cycle was favourable, because the high evaporation pressure of NH₃ alleviates the problems with heat and mass transfer in the solid sorption cycle.

In the case of using water as the refrigerant in the topping cycle the problem of low pressure in the reactor becomes more significant in restricting the power of the topping cycle, as in case of ammonia. On the other hand, when water as the refrigerant is utilised in both, bottoming and topping stages, the whole system can operate with only one evaporator, which brings about a reduction in the initial costs. Moreover, there are other opportunities to increase performance by intelligent integration [7].

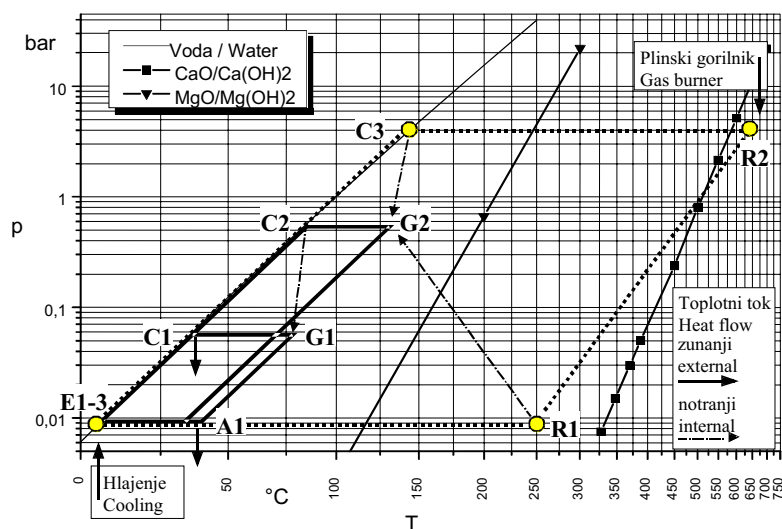
In this paper we continue our work on highly efficient cascading cycles with a bottoming LiBr/H₂O double-effect cycle and CaO/H₂O topping cycle [8]. Our previous study served as a starting point for the evaluation of possibilities for the application of metal salts in our cascading sorption cycles. To enable the application of topping cycles with water as the refrigerant its synthesis phase, which runs at the evaporation pressure, has to be intensified. This can be done with a rise in the reactor pressure or a rise in the whole evaporation pressure level. In the following we want to elaborate on two solutions involving a rise in the evaporation pressure level which can be practically realised.

1 CASCADING SORPTION CYCLE WITH WATER AS A REFRIGERANT

In our recent paper [8] three possible LiBr/CaO/H₂O cascading sorption cycles were presented.

proces. Hladilni proces je označen kot kaskadni proces, kadar poteka med obema deloma naprave samo notranji prenos toplote. Notranji prenos snovi je omejen na oba posamezna dela naprave. Kakor smo omenili, je naša kaskadna hladilna sorpcijska naprava sestavljena iz osnovne LiBr/H₂O absorpcijske naprave z dvojnimi učinkom (polna črta na sliki 1) ter krovnim procesom s trdnim sorbentom CaO/H₂O (črtkasta črta na sliki 1). Zaradi istega hladiva v obeh delih naprave (sl. 1) obstaja možnost združitve obeh uparjalnikov. Kljub temu bomo naš proces označevali kot kaskadni proces.

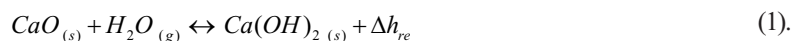
The cooling cycle is denoted as the cascading cycle in the case where there is only internal heat transfer between both parts of the cycle. The internal mass transfer is limited to separate parts of the cycle. As mentioned before, our cascading sorption cycle consists of a bottoming double-effect absorption LiBr/H₂O cycle (solid line in Fig.1) and a topping solid-gas CaO/H₂O reaction cycle (dashed line in Fig.1). Because the same refrigerant is used in both parts of the cycle, presented in (Fig.1), there is a possibility of integrating both evaporators. Nevertheless, we will denote our cycle as a cascading one.



Sl. 1. Tristopenjski LiBr/CaO/H₂O proces (E1,3 - uparjalnika, A1 - absorber, G1,2 - generatorja, C1,2,3 - kondenzatorji, R1,2 - reaktorja)

Fig. 1. Three-stage LiBr/CaO/H₂O cycle (E1,3 - evaporators, A1 - absorber, G1,2 - generators, C1,2,3 - condensers, R1,2 - reactors)

Proces na sliki 1 je sorpcijski, gnan s toploto zgorevanja plina. Pogonska toplota je dovedena v sistem pri visoki temperaturi 650 °C in se uporablja za razpad Ca(OH)₂ v reaktorju R2 po reakciji:



Pri reakciji sproščena vodna para kondenzira pri dovolj visoki temperaturi, da lahko toploto kondenzacije prenesemo v generator G2 osnovnega procesa. Podobno se zgodi v reaktorju R1, kjer poteka sinteza Ca(OH)₂ pri 250 °C. Toplota reakcije, ki se sprošča med fazo sinteze, se tudi prenese v G2 osnovnega procesa. Na strani hladiva se v uparjalniku, pri zadostnem tlaku za proizvodnjo hladu, uparja voda. Osnovni proces je standardni dvostopenjski absorpcijski proces z dvojnimi učinkom, pri katerem se toplota kondenzacije iz kondenzatorja C2 uporabi znotraj procesa za pogon generatorja G1.

HŠ tristopenjskega kaskadnega procesa (sl. 1) lahko določimo z metodo superpozicije [2]. Metoda da možnost določitve približka HŠ zapletenih

The cycle in Fig.1 is a gas-driven sorption cycle. Driving heat is brought into the system at high temperature of 650°C and is used to decompose the Ca(OH)₂ in reactor R2 following the reaction:

Water vapour released from the reactor condenses at a temperature high enough to transfer the heat of condensation into the generator G2 of the bottoming cycle. A similar situation occurs in reactor R1, where the synthesis of Ca(OH)₂ occurs at 250°C. The heat of reaction, which is released during the synthesis phase is also transferred to the G2 of the bottoming cycle. On the side of the refrigerant the water evaporates in the evaporator at a pressure low enough for cold production. The bottoming cycle is a standard two-stage double-effect absorption cycle, where the heat of condensation in condenser C2 is used internally to drive the generator G1.

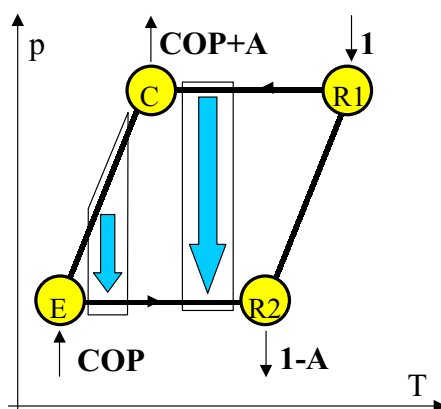
The COP of the three-stage cascading cycle (Fig.1) can be estimated with the superposition method [2]. It gives us the possibility to approximate

sorpcijskih naprav s superpozicijo učinkovitosti elementarnih enostopenjskih procesov ζ , ki so znani iz meritev ali izračunov. Učinkovitost enostopenjskih absorpcijskih procesov ζ je ponavadi okoli 0,75.

Na sliki 2 je prikazan elementarni enostopenjski absorpcijski proces. Štirje glavni prenosniki toplote, uparjalnik E, absorber A, generator G in kondenzator C so vrisani v diagram odvisnosti tlaka in temperature. Smeri toplotnih in masnih tokov so označene s puščicami. Če dovedemo eno enoto toplote generatorju G, proizvedemo ζ enot hladu v uparjalniku E. Toplota, ki jo iz procesa odvajamo v absorberju A in kondenzatorju C, znaša $1+\zeta$. Širšo razlago in analizo metode lahko najdemo v literaturi [2].

the COP of a complex sorption cycle by the superposition of elementary single-stage cycle efficiencies ζ , which are known from experiments or calculation. The efficiencies of single-stage absorption cycles (ζ) are usually around 0.75.

In Fig.2 an elementary single-stage absorption cycle is presented. The four main heat exchangers, evaporator E, absorber A, generator G and condenser C, are drawn in a pressure-temperature diagram. The heat flows and the refrigerant mass flow direction are denoted with arrows. If we supply one unit of heat to generator G, we produce ζ units of cold in evaporator E. Heat is rejected from the cycle in absorber A and condenser C and amounts to $1+\zeta$. Further explanation and analysis can be found in the reference [2].



Sl. 2. Shematski prikaz elementarne sorpcijske stopnje [2]
Fig. 2. Schematic representation of the elementary sorption stage [2]

Metodo superpozicije bomo predstavili na primeru kaskadnega procesa na sliki 1. Ena enota pogonske toplote je dovedena v sistem prek reaktorja R2 krovnega procesa. Posledično se pridobi ζ_{TC} hladu v uparjalniku E3. Toplota, odvedena iz krovnega procesa ($1+\zeta_{TC}$), se prenaša v osnovni proces. Tako je za pogon osnovnega procesa na voljo več ko ena enota toplote, kar lahko prispeva k večjemu HŠ kaskadne naprave.

Za določitev približka HŠ osnovnega procesa, moramo le-tega deliti v dve elementarni stopnji [2]. Zgornja stopnja osnovnega procesa je sestavljena iz uparjalnika E1, absorberja A1, generatorja G2 in kondenzatorja C2 ter spodnja iz uparjalnika E1, absorberja A1, generatorja G1 in kondenzatorja C1 (sl. 1). Zgornja stopnja pridobi ζ_2 hladu ob ($1+\zeta_{TC}$) dovedene toplote v generator G2. Kondenzacijska toplota zgornje stopnje ζ_2 se znotraj procesa prenaša v spodnjo stopnjo, kjer rabi kot pogonska toplota. S spodnjo stopnjo tako pridobimo $\zeta_1 \cdot \zeta_2$ hladu. Celotno hladilno toploto, ki jo pridobimo z osnovnim procesom kaskadne naprave ζ_{BC} , lahko ocenimo z naslednjo enačbo:

The superposition method will be presented on the cascading cycle in Fig.1. One unit of driving heat is brought into the system in reactor R2 of the topping cycle. As a result, ζ_{TC} of cold is produced in evaporator E3. The heat rejected from the topping cycle ($1+\zeta_{TC}$) is transferred into the bottoming cycle. Therefore, for driving the bottoming cycle, more than one unit of heat is available, which could bring a higher COP for the cascading cycle.

To approximate the COP of the bottoming cycle, it has to be divided into two elementary stages [2]. The upper stage of the bottoming cycle consists of evaporator E1, absorber A1, generator G2 and condenser C2 and the lower stage consists of evaporator E1, absorber A1, generator G1 and condenser C1 (Fig.1). The upper stage gains ζ_2 amount of cold, at the ($1+\zeta_{TC}$) brought to the generator G2. Further, the heat of condensation in the upper stage ζ_2 is transferred internally to the lower stage of the bottoming cycle. This heat serves as the driving heat for the lower stage, which produces $\zeta_1 \cdot \zeta_2$ of cold. Thus the cold produced with the bottoming cycle ζ_{BC} can be estimated with the equation:

$$\zeta_{BC} = (1 + \zeta_1) \cdot \zeta_2 \quad (2).$$

HŠ kaskadne sorpcijske naprave je seštevek celotne hladilne toplote, ki jo pridobimo v treh stopnjah kaskadne naprave (3):

$$COP_{CS} = \zeta_{TC} + (1 + \zeta_{TC}) \cdot \zeta_{BC} \quad (3).$$

Ocena učinkovitosti krovnega procesa je bolj zapletena zaradi dejstva, da so tovrstni sistemi še v razvojni fazi. Z uporabo termodinamične analize procesa lahko določimo učinkovitost povračljivega sorpcijskega procesa z enojnim učinkom, podobno kakor je to storjeno v primeru absorpcijskega procesa [9]:

$$COP_{\max} = \frac{q_{ev}}{\Delta h_{re}} \quad (4).$$

Učinkovitost povračljivega procesa je določena kot razmerje med uparjalno in reakcijsko toploto ter je odvisna od lastnosti delovnega para, ki je uporabljen v krovnem procesu, npr. razdalje ravnotežne krivulje od krivulje nasičenosti hladiva (sl. 1) ter hladiva, uporabljenega v procesu.

Razlike v COP_{\max} med različnimi delovnimi pari so predstavljene v preglednici 1. Nedvomno je, da sistemi z vodo kot hladivom dosegajo višje COP_{\max} kakor sistemi z amoniakom. Kljub večji reakcijski toploti Δh_{re} kakor pri delovnih parih z amoniakom, dosegamo zaradi večje uparjalne toplote vode višje vrednosti COP_{\max} .

Preglednica 1. Primerjava učinkovitosti povračljivega krovnega procesa z različnimi delovnimi pari. Uparjalna toplota hladiv q_{ev} je bila vzeta pri 20°C.

Table 1. Comparison of the reversible efficiency of the topping cycle with different working pairs. Heat of evaporation q_{ev} for refrigerants at 20°C

Sol Salt	Hladivo Refrigerant	Δh_{re} (kJ/kg)	COP_{\max} COP_{\max}
Mg(OH) ₂ / MgO	H ₂ O	4500	0,55
Ca(OH) ₂ / CaO	H ₂ O	6070	0,40
Sr(OH) ₂ / SrO	H ₂ O	6940	0,35
NiCl ₂ *(NH ₃) ₆ / NiCl ₂ *(NH ₃) ₂	NH ₃	3480	0,34
NiCl ₂ *(NH ₃) ₂ / NiCl ₂ *NH ₃	NH ₃	4680	0,25
NiCl ₂ *NH ₃ / NiCl ₂	NH ₃	5280	0,22

V našem prispevku se bomo omejili na procese s CaO in MgO solmi in z vodo. Za njih smo ugotovili, da so zaradi primerne delovne temperature območja najbolj primerni za uporabo v reakcijskih hladilnih procesih [8].

Za določitev mejnih učinkovitosti plinsko gnanih kaskadnih procesov moramo gledati prek porabe primarne energije. Primarna energija je v našem primeru energija, dovedena v sistem z zgorevanjem plina. V primeru plinskega sorpcijskega hlajenja je zelo pomembno, da vključimo učinkovitost zgorevanja plina v plinskem gorilniku, ko določamo učinkovitost plinsko gnane procesa. Razmernik primarne energije (RPE - PER) upošteva izgube pri zgorevanju in je

The COP of the cascading cycle is the total amount of cold which is produced in the three stages of the device:

The estimation of the efficiency of the topping cycle is more complex because they are still in the development phase. With a thermodynamic analysis of the cycle, a reversible efficiency for the single-effect device can be determined, similar to the absorption cycle [9]:

The efficiency of the reversible cycle is defined as the ratio of the heat of evaporation to the heat of reaction and it depends on the properties of the working pair used in the cycle, e.g. the distance of the equilibrium line from the refrigerant saturation line (Fig.1) and the refrigerant used.

Differences in the COP_{\max} between the working pairs are presented in Table 1. It is obvious that the systems with water as the refrigerant can reach higher COP_{\max} values, than those with ammonia. Despite the higher heat of reaction (Δh_{re}) for ammonia working pairs, the higher heat of evaporation for water leads to the higher COP_{\max} values.

In our paper we will focus on topping cycles with CaO and MgO as salts and water. They have been found to be the most interesting for use in reaction cooling cycles due to their operating temperature range [8].

To define the efficiency limits for a gas-driven cascading cycle we have to look at the consumption of primary energy. Primary energy is, in our case, energy brought into the system by the combustion of gas. In the case of gas-cooling sorption cycles it is very important to include the efficiency of the gas combustion in a gas burner for the gas-fired cycle performance. The primary energy ratio (PER) considers the losses due to gas consumption and it

določen kot poraba primarne energije za pridobivanje hladu [10]:

$$PER = \frac{Q_{gb}}{Q_{ev}} = \frac{1}{COP \cdot \eta_{gb}} \quad (5).$$

To omogoča primerjavo sorpcijskih hladilnih procesov s kompresorskimi na nivoju porabe primarne energije.

V našem primeru smo bolj zainteresirani za HŠ, ki je reducirano na porabo primarne energije kakor za standardno HŠ procesa. Zato moramo uvesti reducirano HŠ (RHŠ - $COP^{\#}$), ki ga izračunamo po enačbi (6):

$$COP^{\#} = \frac{1}{PER} \quad (6).$$

RHŠ predstavlja učinkovitost hladilnega procesa na enoto energije, dovedene v plinski gorilnik. V primeru idealnega zgorevanja plina $\eta_{gb}=1,0$ in učinkovitosti krovnege procesa $COP_{TC}=0,2$ do $0,4$, COP_{CS} kaskadnega procesa lahko doseže vrednosti do $2,0$. Z realističnimi učinkovitostmi plinskega gorilnika ($0,7$ do $0,9$) lahko dosežemo vrednosti $COP^{\#}$ prek $1,5$.

Učinkovitost plinskega gorilnika je v veliki meri odvisna od uporabe grelnika zraka za predgretje vstopnega zraka. V primeru brez predgrevanja zraka (polne črte na sliki 3) se RHŠ z višjimi temperaturami pogonske toplote T_{eg} izrazito zmanjša. S slike 3 je razvidno, da je uporaba krovnege procesa z višjimi temperaturami odveč. Celoten RHŠ je lahko pri višjih temperaturah v določenih primerih celo manjši od COP_{BC} osnovnega procesa (črtkasta črta na sliki 3). Pozitivni učinek je neizkoriščena toplota, ki zupušča reaktor R2 in jo lahko uporabimo v osnovnem procesu kot dodatno pogonsko toploto.

V primeru uporabe predgretja zraka [11] so vrednosti RHŠ blizu vrednosti učinkovitosti kaskadnega procesa COP_{CS} . Z učinkovitimi plinskimi

is defined as the consumption of primary energy for cold production [10]

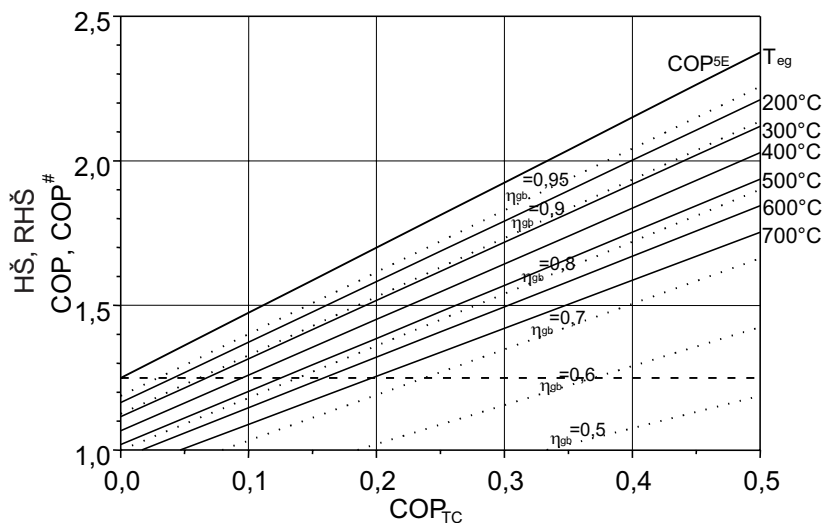
It makes it possible for as to compare the sorption cooling cycles with the compression cycle on a primary energy consumption level.

In our case we are more interested in the COP value reduced to the primary energy consumption than in the standard cycle COP. Therefore, the reduced $COP^{\#}$ has to be introduced, which is calculated as:

It represents the efficiency of the cooling cycle per unit of energy supplied to the gas burner. In the case of ideal gas burning $\eta_{gb}=1.0$ and $COP_{TC}=0.2$ to 0.4 , the COP_{CS} of the cascading cycle could reach values as high as 2.0 . With realistic burner efficiencies (0.7 to 0.9), $COP^{\#}$ values over 1.5 can be reached.

The burner efficiency depends to a great extent on whether a preheater is used for warming the inlet air. In the case of no air-preheating (solid lines in Fig.3) the $COP^{\#}$ reduces drastically with a higher driving heat temperature level T_{eg} . It can be seen in Fig.3 that the use of the topping cycle reduces with higher temperatures. At high temperatures the total $COP^{\#}$ could be, in some cases, as high as the COP_{BC} of the bottoming cycle (dashed line in Fig.3). A positive effect is the unused heat of the hot exhaust air leaving the reactor R2, which can be further used as additional driving heat in the bottoming cycle.

In the case where an air-preheater is used [11], values of the $COP^{\#}$ are close to the COP_{CS} of the cascading cycle. Gas burners with efficiencies of 0.9 to 0.95 (dotted lines in Fig.3) bring about a rise in the



Sl. 3. HŠ in reducirani RHŠ kaskadnih sorpcijskih procesov
Fig.3. COP and reduced $COP^{\#}$ for cascading sorption cycles

gorilniki $\eta_{gb}=0,9$ do $0,95$ (pikćaste ćrte na slici 3) vplivamo na dvig RHŠ celotnega kaskadnega procesa na vrednosti med $1,5$ in $1,9$.

Samo približek ućinkovitosti kaskadnega procesa ni dovolj, kadar želimo narediti korak dlje k praktićni izvedbi naprave. V prejšnjem prispevku [8] problema nezadostne reakcijske kinetike pri nizkem tlaku uparjanja vode nismo upoštevali.

Problem je bil že opazen pri analizi meritev na majhni sorpcijski napravi s trdnim sorbentom in delovnim parom $\text{CaO}/\text{H}_2\text{O}$ [12]. Meritve so bile izvedene v različnih tlačnih in temperaturnih razmerah v reaktorju. Pokazano je bilo, da je trajanje faze odvisno od razdalje od ravnotežne krivulje reakcije, ki poteka v napravi. Na slici 1 je vidno, da se temperatura reakcije ne ujema z ravnotežno temperaturo pri tlaku v reaktorju. Za začetek reakcije je potrebna sprožilna energija, ki jo moramo dovesti oz. odvesti v ravnotežnem stanju. Sprožilno energijo si lahko predstavljamo kot majhno temperaturno razliko glede na ravnotežno stanje reakcije. Vsako nadaljnje povećanje temperaturne razlike pospeši reakcijo. Zaradi majhne intenzivnosti pri nizkih tlakih uparjanja je temperaturna razlika v reaktorju R1 veća kakor v reaktorju R2 (sl. 1). Kljub temu je najveća mogoća temperaturna razlika premalo za krožno delovanje krovnega procesa [12].

Notranje temperature v reaktorju R1 na slici 1 morajo med fazo sinteze ostati razmeroma nespremenljive, zaradi prenosa reakcijske toplote v G2 osnovnega procesa. Za pospešitev faze sinteze lahko zato spremenimo le tlak uparjanja. Na drugi strani je med fazo razpada v reaktorju R2 tlak doloćen s temperaturo kondenzacije v kondenzatorju C3. Zato lahko fazo razpada pospešimo le z dvigom temperature pogonske toplote. V našem delu se bomo omejili le na fazo sinteze.

2 DVGUPARJALNE TLAĆNE RAVNI

Hitrost reakcije sinteze lahko izboljšamo z dvigom:

- tlaka v reaktorju ali
- celotne uparjalne tlačne ravni.

Prvi naćin lahko izvedemo z uporabo mehanskega kompresorja, s katerim stisnemo vodno paro v reaktor. Podobno je bilo že raziskano pri absorpcijskih procesih, pri katerih dvig tlaka v absorberju povzroći padec temperaturne ravni pogonske toplote ([13] do [15]). Zaradi preobširnosti tega naćina dviga tlačne ravni v nadaljevanju ne bomo obravnavali.

Drugi naćin je, zaradi preprostosti potrebnih sprememb na začetnem procesu (sl. 1), zanimivejši. Z dvigom tlačne ravni uparjanja krovnega procesa pospešimo reakcijski proces v reaktorju R1. Ker je

COP[#] of the total cascading system to between 1.5 and 1.9 .

Only an estimation of the cascading cycle efficiency is not enough, when we want to go one step further to the practical realisation of a device. In the earlier paper [8], the problem of insufficient reaction kinetics at the low evaporation pressure of water was not considered.

The problem was already observed in the analysis of measurements on a small-scale solid-gas reaction device with $\text{CaO}/\text{H}_2\text{O}$ as the working pair [12]. Measurements were performed under different pressure and temperature conditions in the reactor. It was shown that the duration of the phase depends on the distance from the reaction equilibrium line. This fact is also included in our study. It can be seen from Fig.1 that the reaction temperature does not coincide with the equilibrium temperature at pressure in the reactor. To start the reaction an activation energy is needed which has to be brought or rejected at the equilibrium state. The activation energy can be presented with a small temperature difference with respect to the reaction equilibrium state. Any additional increase in temperature difference intensifies the reaction. Due to the low intensity at low evaporation pressures the temperature difference in reactor R1 is bigger than in R2 (Fig.1). Still, the temperature difference is not enough for the cyclic operation of the topping cycle [12].

For our cycle in Fig.1 internal temperatures have to be sufficiently constant during the synthesis phase, because the heat of reaction is transferred to the G2 of the bottoming cycle. Therefore, only pressure can be changed to speed up the synthesis reaction. On the other hand, the pressure during the decomposition phase is fixed with the condensation temperature in condenser C3, so that the decomposition can be intensified with an increase in the temperature level of the driving energy. In our work we will focus only on the synthesis phase.

2 INCREASE IN THE EVAPORATION PRESSURE LEVEL

An improvement of the synthesis reaction rate can result from an increase in:

- the pressure in the reactor only,
- the whole evaporation pressure level.

The pressure in the reactor can be increased with the inclusion of a mechanical compressor to compress the water vapour into the reactor. A similar situation has already been studied in absorption cycles, where an increase in the absorber pressure causes a decrease in the driving heat temperature level ([13] to [15]). This method is beyond the scope of our work and will not be discussed further.

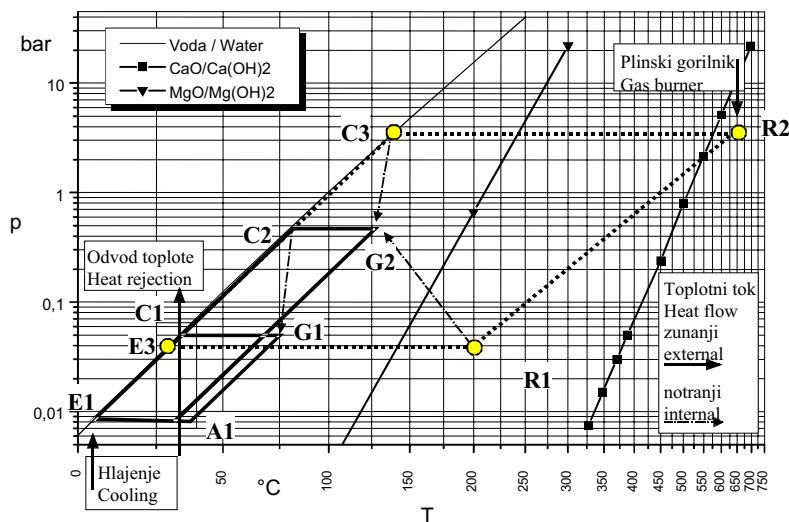
The increase in the evaporation pressure level is more interesting because of the simplicity of the changes which have to be made to the basic cycle presented in Fig.1. With an increase in the evaporation

tlačna raven višja, krovni proces ne pridobiva več hladu. V tem primeru je krovni proces namenjen kot prenosnik toplote za osnovni del kaskadnega procesa. Da je dvig tlačnega nivoja mogoče izvesti, potrebujemo dodaten vir toplote za uparjalnik krovnega procesa. V našem primeru bomo obravnavali dva vira toplote znotraj procesa, toploto kondenzacije iz kondenzatorja C1 in podobno iz C2. Drugih možnosti, na primer dodaten zunanji vir toplote ali proces zgorevanja plina brez predgrelnika zraka, ne bomo obravnavali.

2.1 Primer 1 – Uparjanje na tlačnem nivoju C1

Analiza meritev [12] je pokazala, da je pri 30 mbar in 200 °C dolžina faze sinteze primerljiva z dolžino faze razpada $\text{Ca}(\text{OH})_2$. Če torej povišamo tlak na isto tlačno raven kakor v kondenzatorju osnovnega procesa C1, lahko toploto, odvedeno iz C1 in A1, delno uporabimo v uparjalniku krovnega procesa E3 (sl. 4). Ker krovni proces v tej postavitvi ne more pridobivati hladu, predstavlja COP_{TC} razmerje med dovedeno toploto v uparjalnik E3 in pogonsko toploto. COP_{CS} kaskadnega procesa lahko določimo z naslednjo enačbo:

$$\text{COP}_{\text{CS},1} = (1 + \zeta_{\text{TC}}) \cdot \zeta_{\text{BC}} \quad (7)$$



Sl. 4. Kaskadni sorpcijski hladilni proces – Primer 1: (polna črta – osnovni proces, črtkasta – krovni proces)
Fig.4. Cascading sorption cooling cycle – Case 1. (solid line – bottoming cycle, dashed line – topping cycle)

2.2 Primer 2 – Uparjanje na tlačni ravni C2

Če uparjalno tlačno raven dvignemo še višje na tlačno raven kondenzacije v C2, lahko za uparjalnik krovnega procesa E3 uporabimo kondenzacijsko toploto C2 (sl. 5). Zaradi dejstva, da toploto kondenzacije že uporabljamo za pogon generatorja G1, njena delitev na G1 in E3 povzroči znižanje COP_{CS} . Za določitev COP_{CS} moramo uporabiti metodo superpozicije, tako za zgornjo kakor tudi za spodnjo stopnjo osnovnega procesa.

pressure level of the topping cycle, the reaction in reactor R1 is intensified. Because the pressure level is higher the topping cycle does not produce cold anymore, it serves as a heat transformer for the bottoming cycle only. To make the increase in pressure possible we need an additional heat source for the topping cycle evaporator. In our case we will discuss the two internal heat sources, the heat of condensation from condensers C1 and C2. Other possibilities, e.g. additional external heat sources or the gas-burning process without air-preheater, will be excluded from the discussion.

2.1 Case 1 – Evaporation at C1 pressure level

An analysis of the measurements showed that the length of the synthesis phase at 30 mbar and 200°C is comparable with the length of the $\text{Ca}(\text{OH})_2$ decomposition phase [12]. Therefore, if the pressure is increased to the same level as it is in the C1 condenser of the bottoming cycle, heat rejected from C1 and A1 could be partly used in the topping cycle evaporator E3 (Fig.4). Because the topping cycle cannot produce cold in this case, COP_{TC} represents the heat ratio between the heat evaporator E3 and the driving heat. The COP_{CS} of the cascading cycle can easily be estimated as follows:

2.2 Case 2 – Evaporation at C2 pressure level

If the evaporation pressure level is further increased to the condensation pressure level of C2, the heat of condensation can be transferred to the evaporator E3 (Fig.5). Because this heat is already used to drive the generator G1, its division between the E3 and G1 brings about to a lower COP_{CS} . To determine the COP_{CS} we have to use the superposition method for both upper and lower stages in the bottoming cycle.

Prispevek zgornje stopnje 2 h COP_{BC} osnovnega procesa je zmnožek pogonske toplote za generator G2 in učinkovitosti zgornje stopnje $(1 + \zeta_{TC}) \cdot \zeta_2$.

Podobno lahko storimo za spodnjo stopnjo osnovnega procesa. Pogonska toplota za generator G2 je zmanjšana za del toplote, ki je prenesena v uparjalnik E3 krovnega procesa ζ_{TC} . COP_{CS} kaskadnega procesa zato zapišemo z enačbo:

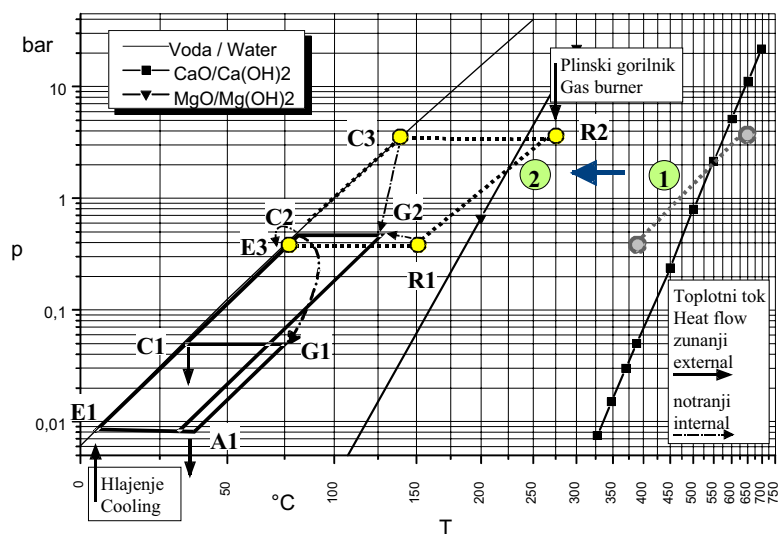
$$COP_{CS,2} = (1 + \zeta_{TC}) \cdot \zeta_2 + ((1 + \zeta_{TC}) \cdot \zeta_2 - \zeta_{TC}) \cdot \zeta_1 \quad (8).$$

Pozitiven vpliv je viden na sliki 5. Z dvigom tlaka na tlačno raven C2 je omogočeno, da namesto CaO uporabimo MgO kot delovno snov krovnega procesa. V tem primeru delujeta oba reaktorja blizu ravnotežne krivulje reakcije MgO/H₂O (točka 2 na sliki 5). Velika prednost pred procesom CaO/H₂O je ta, da je temperaturna raven pogonske toplote opazno nižja (300 °C). Zaradi tega je tudi učinkovitost gorilnika večja. Dodatno lahko v primeru MgO v krovnem procesu, zaradi manjše reakcijske toplote MgO/H₂O kot v primeru CaO/H₂O (preglednica 1), dosegamo večja HS.

The contribution of the upper stage 2 to the COP_{BC} of the bottoming cycle is a product of driving the heat for the generator G2 and the efficiency of the upper stage $(1 + \zeta_{TC}) \cdot \zeta_2$.

The same can be done for the lower stage in the bottoming cycle. Driving heat for generator G1 is decreased by the part of the heat used in evaporator E3 of the topping cycle ζ_{TC} . Therefore, the COP_{CS} of the cascading cycle can be written as:

The positive effect is shown in Fig.5, with the increase in pressure to the C2 pressure level there is the possibility of using the MgO salt instead of CaO in the reaction with water. In this case both reactors would operate near the equilibrium line for the MgO/H₂O reaction (Position 2 in Fig.5). The major advantage over the CaO/H₂O cycle is that the driving temperature level is noticeable lower (300 °C) which also brings about a higher burner efficiency. Further more, by using MgO in the topping cycle a higher COP can be obtained because of the lower heat of reaction than in the case of CaO (Table 1).



Sl. 5. Kaskadni sorpcijski hladilni proces – Primer 2: točka 1 - CaO/H₂O kot delovni par; točka 2 - MgO/H₂O kot delovni par (polna črta – osnovni proces, črtkasta črta – krovni proces)

Fig.5. Cascading sorption cooling cycle – Case 2. Positions: 1. CaO/H₂O working pair; 2. MgO/H₂O working pair. (solid line – bottoming cycle, dashed line – topping cycle)

3 PRIMERJAVA REZULTATOV

Rezultati učinkovitosti obeh primerov, ki smo ju obravnavali zgoraj, so predstavljeni na sliki 6. Kot izhodišče je vključena tudi učinkovitost začetnega kaskadnega procesa s slike 1. Primerjava je narejena za učinkovitosti krovnega procesa $COP_{TC}=0,35$.

Vidimo lahko, da se ocenjena vrednost učinkovitosti v primeru 1 zniža z 2,0 na 1,7 v primerjavi z izhodiščnim procesom na sliki 1. V primeru 2 je mogoče doseči učinkovitosti okoli 1,4. Vrednosti RHS (pikčaste

3 COMPARISON OF THE RESULTS

The values of the efficiencies for both cases discussed above are presented in Fig.6. As a starting point the efficiency of the basic cycle COP_{CS} (Fig.1) is included also. The comparison will be made for the efficiency of the topping cycle $COP_{TC}=0.35$.

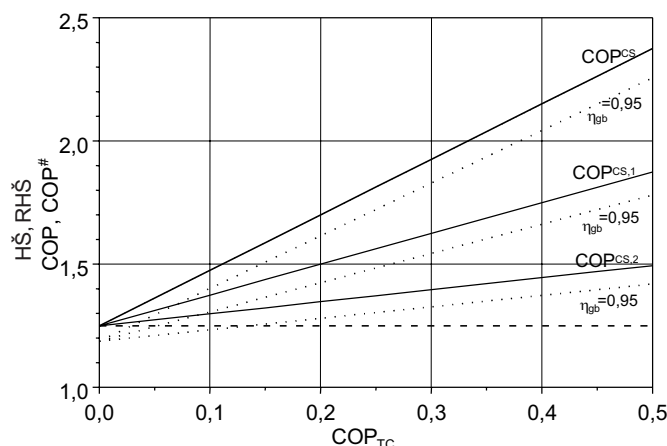
It can be seen that the estimated efficiency in Case 1 lowers from an ideal 2.0 to 1.7. In Case 2 it is possible to reach an efficiency of about 1.4. Values of the reduced $COP^{\#}$ (dotted lines in Fig.6) are a little bit

črte na sliki 6) so malo nižje, zaradi upoštevanja učinkovitosti plinskega gorilnika $\eta_{gb}=0,95$.

Pri manjših učinkovitostih krovnege procesa so ocenjene vrednosti COP_{CS} blizu vrednostnim COP_{BC} (črtkasta črta na sliki 6) osnovnega procesa. Zato je uporaba krovnege procesa pri nizkih COP_{TC} tako s praktičnega kakor tudi gospodarnega vidika že vprašljiva.

lower due to the consideration of the burner efficiency $\eta_{gb}=0,95$.

At lower efficiencies of the topping cycle the estimated COP_{CS} values are close to the COP_{BC} (dashed line in Fig.6) of the bottoming cycle. Therefore, the application of the topping cycle at lower COP_{TC} is already questionable from both the practical and economic point of view.



Sl. 6. Primerjava ocenjenih vrednosti HŠ in RŠ za različne izvedbe kaskadnih procesov
Fig.6. Comparison of estimated COP and COP# values for different cases of the cascading cycle

4 SKLEP

Iz rezultatov meritev [12] je bilo povzeto, da moramo za uporabo CaO v krovnem delu kaskadnega sorpcijskega procesa [8] upoštevati še eno dodatno omejitev. Zaradi nizkega tlaka uparjanja v krovnem procesu je faza sinteze opazno počasnejša od faze razpada in tako preprečuje stabilno in optimalno dinamiko procesa. Rezultat je nižji COP_{TC} krovnege procesa in posredno tudi COP_{CS} kaskadnega procesa. Za rešitev problema počasne faze sinteze smo predstavili dve spremembi procesa, pri katerem smo dvignili tlak uparjanja krovnege procesa na različna tlačna nivoja, odvisna od razmer v osnovnem procesu.

Iz rezultatov na sliki 6 je razvidno, da lahko s spremembo krovnege procesa kakor v primeru 1 dosežemo 10 do 30 odstotno povečanje učinkovitosti v primerjavi z industrijsko absorpcijsko napravo z dvojnimi učinkom. Slabše je v primeru 2, zaradi delitve toplote kondenzacije iz C2 med uparjalnik E3 in generator G1. Termodinamično je primerno graditi krovno napravo kakršna je predstavljena v primeru 2, ker lahko dosežemo do 10% večje učinkovitosti kakor v primeru standardne absorpcijske naprave. Z gospodarnega vidika pa je dvig učinkovitosti premajhen za dejansko izvedbo kaskadne naprave.

Dejansko je dodatek krovnege procesa standardni absorpcijski napravi upravičen v primeru 1, vendar le pod pogojem zadostne učinkovitosti

4 CONCLUSION

It can be concluded from the experimental results [12] that in order to use CaO in the topping cycle of a cascading sorption cycle [8] an additional limitation has to be considered. Due to the low evaporation pressure in the topping cycle the synthesis phase is noticeably slower than the decomposition phase and this prevents stable and optimum process dynamics. As a result, the COP_{TC} of the topping cycle is lowered and, as a consequence of this, also the COP_{CS} of the cascading cycle. To solve the problem of a slow synthesis phase, two modifications were presented which increase the evaporation pressure of the topping cycle to different levels dependent on the conditions in the bottoming cycle.

It can be seen from the results in Fig.6 that with the modification of the topping cycle as described in Case 1, efficiencies of about 10-30% higher than those of the industrial double-effect absorption machines can be reached. The values are not as good for Case 2 due to the division of the heat of condensation in C2 to the evaporator E3 and generator G1. Thermodynamically, it does make sense to build the topping machine as described in Case 2, because up to 10% higher efficiencies than for standard absorption machines can be attained. But from the economic point of view the rise in efficiency is too small for the actual construction of the cascading device.

Therefore, to add a topping cycle to the standard absorption device is justified in Case 1, but

krovnega procesa. Učinkovitost krovnega procesa je trenutno majhna v primerjavi s povračljivim procesom (pregl. 1), tako da bo treba še veliko storiti na področju dinamike toplotnih reakcijskih procesov in notranjega prenosa toplote.

Ocena učinkovitosti ni dovolj za potrditev primernosti krovnega procesa s solmi kovinskih oksidov za aplikacijo v kaskadnih procesih. Zaradi specifičnih lastnosti delovnih parov mora biti vsaka reakcija testirana s preskusi, da se določijo različne lastnosti reakcije, na primer kinetika, stabilnost, ponovljivost ipd.

only for the condition of sufficient topping cycle efficiency. The efficiency of the topping cycle is low in comparison with the reversible cycle (Table 1) so that a lot still has to be done, especially in the field of reaction cycle dynamics and internal heat transfer.

The estimation of the efficiency is not enough if we want to verify the suitability of the topping cycle with metal-oxide salts for application in a cascading cycle. Due to the specific properties of the working pair each reaction has to be experimentally tested to measure different characteristics of the reaction, e.g. kinetics, stability, repeatability, etc.

5 OZNAČBE 5 NOMENCLATURE

hladilno število	HŠ-COP	-	coefficient of performance
reducirano hladilno število	RHŠ-COP [#]	-	reduced coefficient of performance
specifična toplota	q	J/kg	specific heat
toplota	Q	J	heat
tlak	p	bar	pressure
razmernik primarne energije	PER	-	primary energy rate
temperatura	T	°C	temperature
specifična entalpija	h	J/kg	specific enthalpy
učinkovitost	η	-	efficiency
HŠ elementarne, enojne sorpcijske stopnje	ζ	-	COP of elementary, single sorption stage
razlika	Δ		difference

Podpisi

spodnja in zgornja stopnja procesa z dvojnimi učinkom

osnovni, krovnji in kaskadni proces

izpušni plini

uparjanje

plinski gorilnik

največji

Subscripts

1,2	lower and upper stage of double-effect cycle
BC, TC, CS	bottoming cycle, topping cycle and cascading cycle
eg	exhaust gases
ev	evaporation
gb	gas burner
max	maximum

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Naslova avtorjev: mag. Boštjan Cerkvėnik
prof.dr. Alojz Poredoš
Univerza v Ljubljani
Fakulteta za strojništvo
Aškerćeva 6
1000 Ljubljana

Felix Ziegler
ZAE Bayern
Walther-Meissner-Str.6
85748 Garching, Nemćija

Authors' Addresses: Mag. Boštjan Cerkvėnik
Prof.Dr. Alojz Poredoš
University of Ljubljana
Faculty of Mechanical Eng.
Aškerćeva 6
1000 Ljubljana, Slovenia

Felix Ziegler
ZAE Bayern
Walther-Meissner-Str.6
85748 Garching
Germany

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