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Sorption-enhanced reforming of bioethanol in dual fixed bed reactor for continuous hydrogen production

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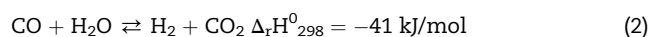
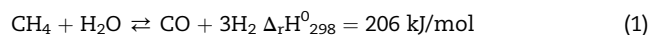
ABSTRACT

The sorption enhanced reforming (SER) of ethanol over an admixture of CaO sorbent and Ni reforming catalyst has been experimentally studied in a periodically operated dual fixed bed reactor. The optimal parameters for SER process were calculated from thermodynamic data. The experiment was carried out in cyclic mode; temperature swing adsorption and pressure swing adsorption (PSA) modes were used for periodic sorbent regeneration. It was shown that the continuous hydrogen production and the purity of hydrogen during the sorption-catalytic ethanol reforming maintained at the constant level and were 50 L/min and 97–99 vol.% respectively. The dual fixed bed SER reactor worked fine during 2 months on stream and more than 250 cycles. Both the sorbent and the catalyst maintained the sufficient activity during experiment. The obtained results suggest that sorption enhanced reforming may be a perspective approach for hydrogen production in fuel cell powered cogeneration systems.

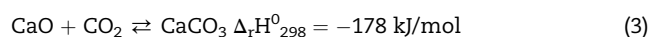
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Introduction

Sorption-enhanced reforming (SER) of hydrocarbons is an emerging technology which is especially advantageous for low scale on-site hydrogen generation [1–3]. In SER the reforming of hydrocarbons occurred in presence of a carbon dioxide acceptor, for example, calcium oxide. Since carbon dioxide is a byproduct of the hydrogen in the reforming reactions:



its removal by the reaction



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results both in the higher conversion extent and better hydrogen purity.

Several studies on the sorption enhanced steam reforming of alcohols [4] and methane [2], [5], [6] demonstrated that the single-step process can directly produce the 95–98% purity hydrogen having both CO and CO₂ concentrations below 100 ppm and the balance methane. Introduction of the CO₂ acceptor into reaction zone eliminates the need for downstream water gas shift and preferential oxidation reactions that, in turn, considerably simplifies the fuel processor design.

One of the most important demands to SER for practical applications is not only the purity of hydrogen but also its continuous production. Continuous reforming with CO₂ removal requires either that there is parallel fixed bed reactors operated alternatively and out of phase in reforming and sorbent regeneration modes, or that sorbent is continuously transferred between the reformer/carbonator and regenerator/calciner in fluidized regime [7–10]. However, experimental investigations for SER have mainly been conducted in small-scale fixed bed reactors, and we consider, fixed bed is more appropriate for low-scale hydrogen in-site production. In this case, overall scheme of the SER processor should include at least two periodically operated fixed bed reactors which ensure continuous hydrogen delivery to the fuel cell stack. During the first phase of the cycle the first reactor is fed with a hydrocarbon/steam mixture and Reactions (1)–(3) take place over the fixed bed layer producing hydrogen for a fuel cell. At the same time the second reactor is purged with the air or steam to facilitate CO₂ desorption from the sorbent by reaction (reversible 3). During the second phase the first reactor is purged and the second reactor produces hydrogen. Several issues should be analysed (researched/studied) during developing the SER fuel processor. The first is the behaviour and the stability of the steam reforming catalyst and the CO₂ sorbent in multiple carbonation–calcination cycles. Grasa [11] and Lysikov [12] confirm that after initial decrease the sorption capacity of CaO reaches a residual value of 7–12 wt.% that is stable over hundreds of cycles. The stability of the supported Ni reforming catalysts in SER process was not so extensively studied; however, Ortiz and Harrison [13] reported that after 25 cycles the decay of catalytic activity was negligible. It was also shown that in model conditions without sorbent, continuous change of reduction and oxidation atmosphere partially prevents sintering of the Ni catalyst active component and stabilizes the activity at a higher level as compared with the conventional steady state reforming [14].

Another issue is the selection of the optimal conditions for the SER process applied on practice. On the one hand, the process should provide clean hydrogen for fuel cells feed and on the other hand, it must be energy effective [15–17]. Application of pressure swing adsorption (PSA), is considered to be the most energy efficient way of the SER process operation, when the regeneration of the sorbent is provided at the same temperature as reforming stage [18–20]. One of the challenges of using CaO as carbon dioxide sorbent is the following: the regeneration of this sorbent is easy to provide at elevated temperatures, significantly higher than reforming stage. Thus, the SER process with CaO traditionally is carried out in temperature swing adsorption (TSA) mode [21].

In our work described below a sorption reforming process of ethanol with continuous hydrogen production was investigated. Ethanol was selected because it presents several advantages related to natural availability, storage and handling safety, ethanol can be produced renewably from several biomass sources, including energy plants, waste materials from agro-industries or forestry residue materials, organic fraction of municipal solid waste, etc [22–24].

Our previous article was focused on SER reforming stage [2]. The study mentioned above was performed in quasi-adiabatic mode at one value of operating pressure. Due to the lack of experimental data on the performance of the overall process, in current study special attention was given to the study of PSA and TSA modes of both regeneration and reforming stages in multi-cycle process under SER circumstances with precisely controlled reactor temperature profile. The work presented is devoted to search of optimal conditions for high temperature sorption-enhanced reforming process in dual fixed-bed reactor with continuous one-step pure hydrogen production at different pressures and to the determination of the stable experimental setup and catalyst in repetitive cycles with additional start-stop tests that is crucial for practical applications.

Materials

The CaO sorbent was prepared from the micron sized CaCO₃ powder (>98.5% pure, “SoyuzChim- Prom”, Russia). The powder was calcined for 1.5 h at 1300 °C in a muffle oven in air [25].

A standard commercial Ni based catalyst NIAP-03(OAO NIAP, Novomoskovsk Russia) containing 11 wt % of NiO was used in this work which was early studied at SER conditions [14]. Prior to use, sorbent and catalyst were crushed and sieved into particles of 1–2 mm size. Amounts of 9,09 wt.% of catalyst and 90,9 wt.% of CaO sorbent were carefully mixed and further used in the experiments. A mixture of rectified ethanol with distilled water (C₂H₅OH was 29 vol.%, where H:O:C = 18:7:2) was used for alcohol-vapour steam generation.

Experimental

The laboratory-scale fixed bed dual reactor shown in Fig. 1 was used for reaction tests.

The scheme of the process was designed in the way that allowed to produce hydrogen continuously [26]: Alcohol/water mixture was fed using a Grundfos DME 2–18 plunger pump equipped with a digital actuator. After evaporation the ethanol/water steam fed into the first reactor to produce hydrogen. Another reactor was purged by air for regeneration of the sorbent and then by hydrogen for catalyst reduction (Fig 1). As a next step, the flow of steam and air was forwarded to the second and first reactors respectively by switching the valves. Reactor was operated periodically in this way cycle to cycle.

The SER cycle for each reactor comprised the following steps:

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