Dual-stage vacuum pressure swing adsorption for green hydrogen recovery from natural gas grids

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A shift to renewable energy sources is crucial to mitigating climate change. Fossil fuels, such as petroleum, natural gas, and coal, mainly contribute to the economy's growth. However, their use is also the main contributor to global warming. According to the IPCC report, in 2019, the combined energy supply, industry, and transport sectors represented 73% of the total net anthropogenic emissions, which means approximately 42.7 $GtCO_2$ was released into the atmosphere by these sectors [1]. Green Hydrogen (GH), produced from the electrolysis of water, has the potential to play a significant role in reducing CO_2 emissions from fossil fuel systems. Additionally, GH can serve as an intersectoral bridge by storing and utilizing intermittent renewable energy sources (such as wind and solar) for later use in the energy supply, industry, and transport sectors [2]. Following the production of GH, it can be injected into existing natural gas grids (NGG) for cost-effective transportation, thus eliminating the need for extensive infrastructure investments [3]. However, when GH is blended into the NGG, it is necessary to recover and purify it to a high purity level to facilitate applications such as fuel cells (H_2 > 99.97%). One challenge associated with separating and purifying GH blended in NGG is the low H_2 feed concentration (<20%), which is significantly lower than that required for traditional H_2 adsorption purification processes, for example, H_2 produced from steam methane reforming (>70%).

In this work, we develop a conceptual dual-stage vacuum pressure swing adsorption (VPSA) process to separate and purify H_2 blended into the natural gas grids with low H_2 feed

concentration (<20%). Figure 1A shows the dual-stage VPSA coupled in the NGG diagram. Stage 1 consists of a VPSA filled with a carbon molecular sieve (CMS-3K-172), which adsorbs preferentially H_2 and blocks CH_4 from entering its pores. In this way, CH_4 is produced in the feed step, while H_2 is enriched in the blowdown vacuum depressurization step. In our previous work [4], we showed that the VPSA filled with CMS-3K-172 can enrich the H_2 molar fraction from about 20% to 60 – 70%, with a recovery higher than 90%. This is highlighted by the green circle in Figure 1C, which shows the trade-off between H_2 purity and recovery for stage 1. In this way, to feed stage 2, two H_2 concentrations were considered, namely 55% and 65%. Stage 2 consists of a conventional VPSA filled with binder-free zeolite 13X (13XBFK) with a greater affinity towards CH_4 than H_2, as shown in our previous work [5]. Oppositely to stage 1, in stage 2, H_2 is produced in the feed step, while CH_4 is recovered in the blowdown vacuum depressurization step.

Each stage has its independent cycle configuration; that is, they have a different sequence of elementary steps through which the column undergoes, as seen in Figure 1B. Stage 1 VPSA consists of 5 steps, namely (1) pressurization with feed, (2) feed, (3) H_2 purge, and (4) countercurrent vacuum blowdown. Stage 2 consists of a VPSA with 11 steps including 3 pressure-equalization steps, namely (1) feed, (2) depressurization-equalization 1, (3) depressurization-equalization 2, (4) depressurization-equalization 3, (5) countercurrent vacuum blowdown, (6) re-pressurization 1, (7) idle 1, (8) re-pressurization 2, (9) idle 2, (10) re-pressurization 3, and (11) re-pressurization with product. Stage 1 was optimized previously [4], therefore, only stage 2 is optimized in the present work. Stage 2 performance, i.e., H_2 purity and recovery, was evaluated by changing the process variables such as feed step time, blowdown vacuum pressure (Pv), and H_2 feed molar fraction. The trade-off between H_2 purity-recover for stage 2 can be seen in Figure 1D. From a feed of 55% H_2, stage 2 allows obtaining an H_2 purity higher than 98% with a recovery up to 80% as highlighted by the green circle in Figure 1D. The CH_4 purity in both stages is higher than 88%.

In this work, we reported a conceptual dual-stage VPSA to separate and purify GH from NGG. Stage 1 is a VPSA with a CMS-3K-172 that kinetically separates CH_4 from H_2, intending to pre-concentrate H_2 from a value in the feed of 20% to a value around 60%, and stage 2 is a conventional VPSA using benchmark zeolite 13X from thereof 60% to a final H_2 purity higher than 98%. With this strategy, it was possible to enrich GH mixed in NGG from 20 to c.a. 99% with a high recovery rate (>80%). In conclusion, the developed dual-stage VPSA process can provide a technically viable way to recover and purify H_2 blended into the natural gas grids. We are currently working on an economical evaluation of the dual-stage VPSA process.

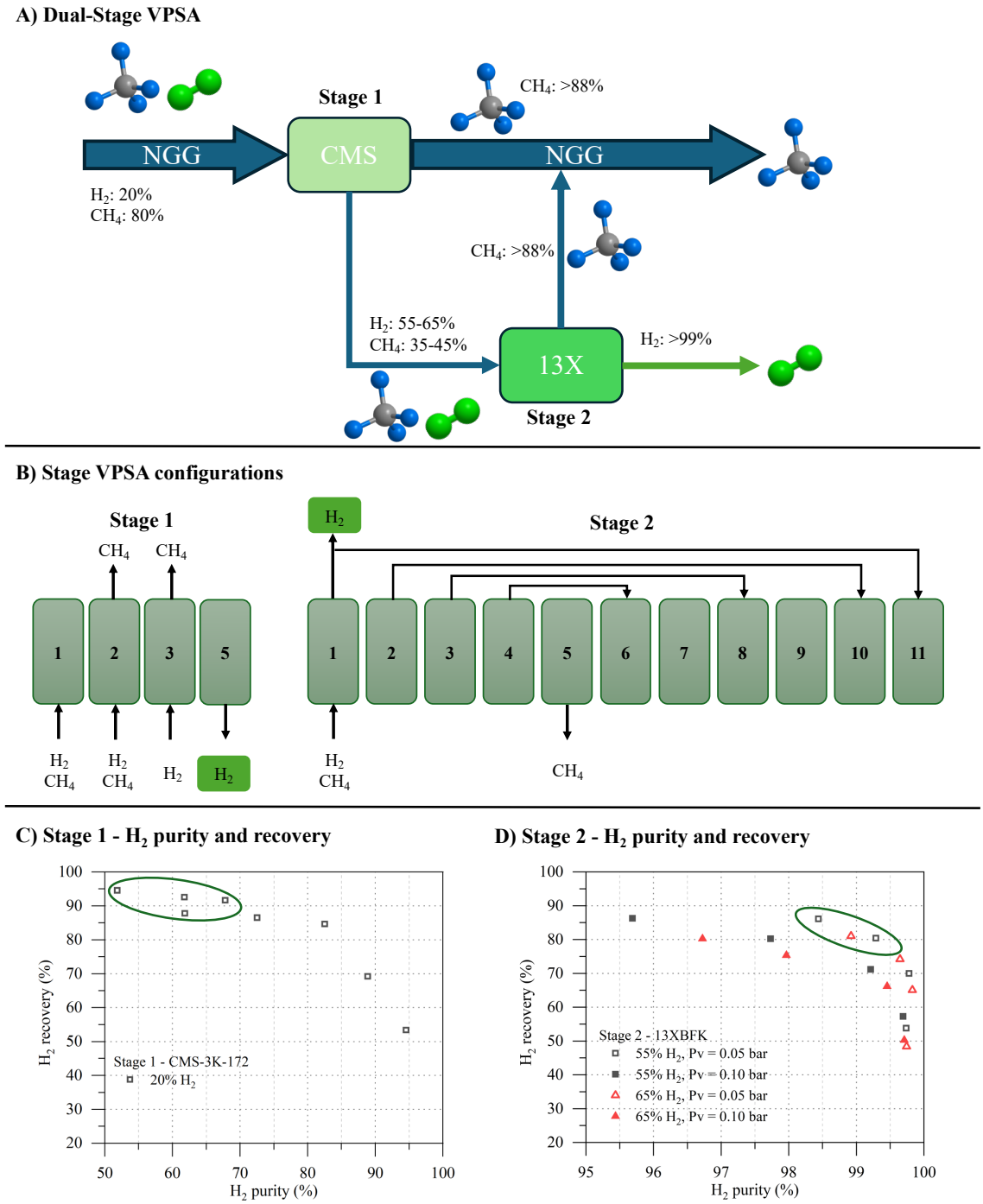

Figure 1. A) Diagram of dual-stage VPSA coupled in the natural gas grids (NGG); B) Stage VPSA cycle configurations (steps are defined in the main text); C) Trade-off between H_2 (20% in the feed) purity and recovery for stage 1; and D) Trade-off between H_2 (55-65% in the feed) purity and recovery for stage 2.

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