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Analysis of the Isotopes Hydrogen Mixtures from Cryogenic Distillation Separation using Gas Chromatography

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A gas chromatographic system for the analysis of gas species of hydrogen is very important for the separating of hydrogen species by cryogenic distillation, catalyst isotopic exchange and another processes. This paper will present the analysis of gas species of hydrogen samples which had been taken from the top and the bottom of the cryogenic distillation column at different pressures of the column.

Key Words: Gas chromatography, Cryogenic distillation, Isotopic separation of hydrogen.

INTRODUCTION

Separation procedures are probably the most important techniques that are commonly employed in the scientific activities of both academic and industry today. All chromatographic separations are carried out using a mobile and a stationary phase. As a result of this prerequisite, the primary classification of chromatography is based on the physical nature of the mobile phase. Thus, all separation processes that utilize a gas as the mobile phase are classed as a gas chromatography[1].

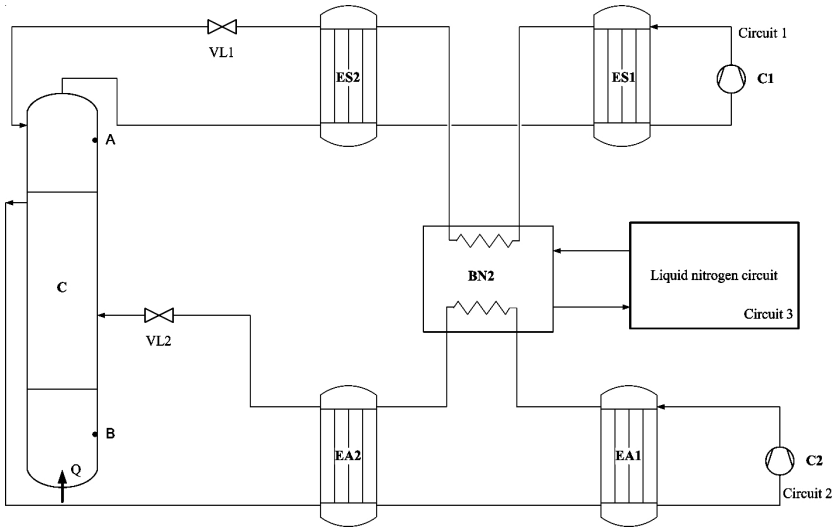
The two important characteristics of every chromatographic process are: the velocity at which the zone of component travels in the column and the broadening of the zone during this process. Under given conditions, at constant temperature, pressure and carrier gas velocity, the migration rate of the zone is a simple function of the thermodynamic equilibrium of partition of the component between the moving and the stationary phase[2].

There are three isotopes of the element hydrogen: hydrogen, deuterium and tritium. They each have one single proton (Z = 1), but differ in the number of their neutrons. Their nuclear symbols are therefore 1H, 2H (D-deuterium) and 3H (T-tritium). Also, there are two isomeric forms of molecular hydrogen, namely with its two proton spins aligned either parallel (orthohydrogen) or antiparallel (parahydrogen).

Cryogeny represents the ensemble of technologies available for liquidated gases production, utilization and storage, both with technological and laboratory processes which there are developed at very low temperatures. The processes from a hydrogen isotopes separation plant occur at low temperatures. This domain begins with the methane liquefaction temperature, about 111.7 K and be equal to absolute zero with reference points nitrogen (77.36 K), hydrogen (20.39 K) and helium (4.224 K).

The separation processes by cryogenic distillation there were developed in parallel with gases liquefaction processes and there were contingent by the manufacture of some specific devices in order to obtain the necessary temperatures. The characteristics of the cryogenic distillation plants are determined by the way of the realization of gases liquefaction together with the possibility to maintain of the temperature and pressure in a small range, corresponding to the liquid-vapour equilibrium zone.

The separation by cryogenic distillation (Fig. 1) is realized by masic and termic transfer between vapour and liquid phases which are flow in countercurrent on a separation medium. A cryogenic distillation column has in its composition a boiler for the conversion of the liquid phase in vapours, a separation medium, plates or packages and a condenser for the vapour condensation and the production of the liquid phase which participate to the exchange on the separation medium.



The main circuits of the diagram are: Circuit 1-Cooling circuit for the column condenser; Circuit 2-Feed circuit, Circuit 3-Liquid nitrogen circuit. These circuits have the following components: C1, C2-compressors; C-cryogenic distillation column; EA1, EA2-feed heat exchangers; ES1, ES2-cooling heat exchangers; BN2-liquid nitrogen vessel; VL1, VL2-throttle valves.

Fig. 1. Cryogenic distillation plant

EXPERIMENTAL

The gas chromatograph employed in this work was a type CP 3800 from Varian Analytical Instrument. It is equipped with a capillary molecular sieve 5A column with following characteristics:

- The length of the gas chromatograph column is: 50 m;
- The inside diameter of the gas chromatograph column is: 0,32 mm;
- The film thickness of the gas chromatograph column is: 30 mm.

The operating temperature of the gas chromatograph column was -99 ºC. The temperature of the oven of the gas chromatograph column was maintained in the range of 0 to -99 ºC, by spraying liquid nitrogen into the oven. A temperature controller to control the liquid nitrogen flow and the heater was used[3].

As detector, we used a Pulsed Discharge Helium Ionization Detector (PDHID). The carrier gas used was: Helium (99.999 % purity). It is recommended that a quality grade of helium 5.0 (99.999 % pure or better) be used at all times. The sample loops of gas chromatograph: 5 µL. The gas chromatograph column was conditioned before to use this for the separate of the hydrogen isotopes mixtures.

RESULTS AND DISCUSSION

The method described in this paper was based on using a capillary molecular sieve 5 A column which has been operated at only 174 K.

The gas chromatograph column was conditioned before to use this for the separate of the hydrogen isotopes mixtures. A small flow of helium (1.2 mL/min) was maintained through the column during conditioning. The method used was calibrated with standard gas of protium and deuterium by external standard calibration type. The retention times were relatively short, about 9-11 min. The sample in the 5 µL sampling volume is injected into system which uses helium as carrier gas. The carrier flow rate was 3.7 mL/min at a pressure of 10 psi. The samples had been taken from the top and the bottom of the cryogenic column at the next pressures of the cryogenic column: 0.5 bar, 1 bar and 1.5 bar.

Figs. 2 and 3 presented the results and the chromatograms at 0.5 bar. The concentration of the mixture gas at 0.5 bar in the top of the cryogenic column was: 30.458 % *p*-H2 (*para*-H2) ; 68.163 % *o*-H2 (*ortho*-H2); 1.379 % D2 and the concentration of the mixture gas at 0.5 bar in the bottom of the cyiogenic column was: 11.873 % *p*-H2; 46.975 % *o*-H2; 41.152 % D2.

Figs. 4 and 5 presented the chromatograms obtained at 1 bar. The concentration of the mixture gas at 1 bar in the top of the cryogenic column was: 37.217 % *p*-H2; 62.425 % *o*-H2; 0.359 % D2 and the concentration of the mixture gas at 1 bar in the bottom of the cyiogenic column was: 14.358 % *p*-H2; 31.159 % *o*-H2; 0.11 % HD; 54.374 % D2.

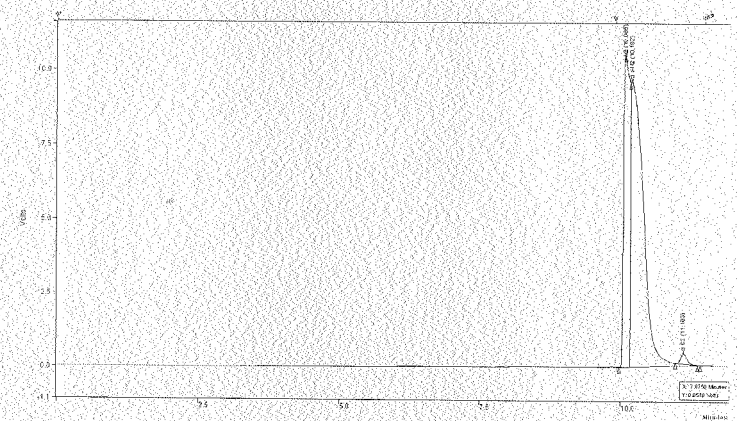


Fig. 2. Sample-0.5 bar-top-30.458 % *p*-H2; 68.163 % *o*-H2; 1.379 % D2

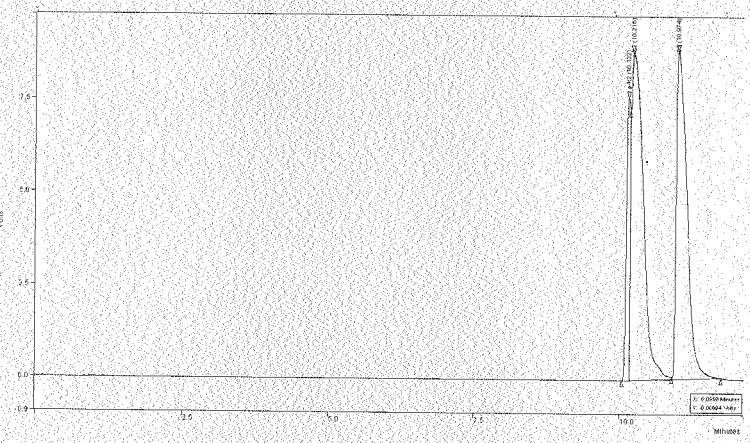


Fig. 3. Sample - 0.5 bar - bottom - 11.873 % *p*-H2; 46.975 % *o*-H2; 41.152 % D2

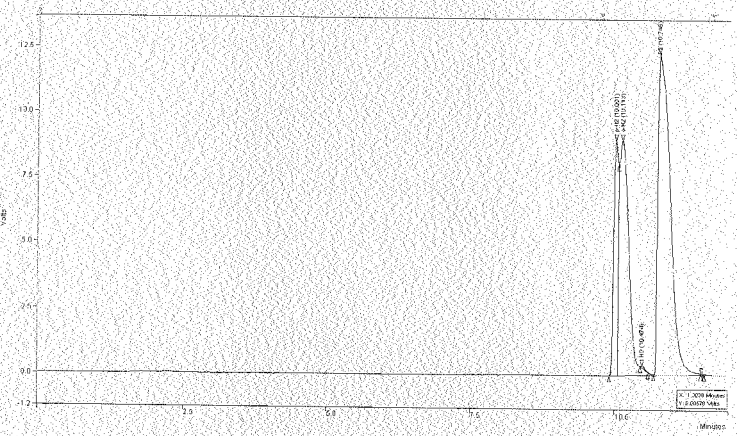


Fig. 4. Sample - 1 bar - top- 37.217 % *p*-H2; 62.425 % *o*-H2 ; 0.359 % D2

Fig. 5. Sample - 1 bar - bottom - 14.358 % *p*-H2; 31.159 % *o*-H2; 0.11 % HD; 54.374 % D2

Figs. 6 and 7 are presented the chromatograms obtained at 1.5 bar. The concentration of the mixture gas at 1.5 bar in the top of the cryogenic column was: 99.566 % *p*-H2; 0.434 % D2 and the concentration of the mixture gas at 1.5 bar in the bottom of the cryogenic column was: 10.584 % *p*-H2; 17.058 % *o*-H2; 1.984 % HD; 70.374 % D2.

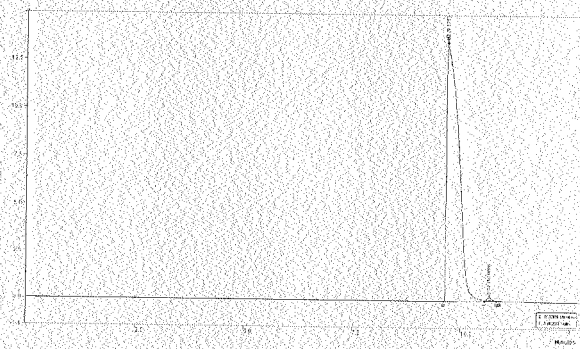


Fig. 6. Sample - 1.5 bar - top - 99.566 % *p*-H2; 0.434 % D2

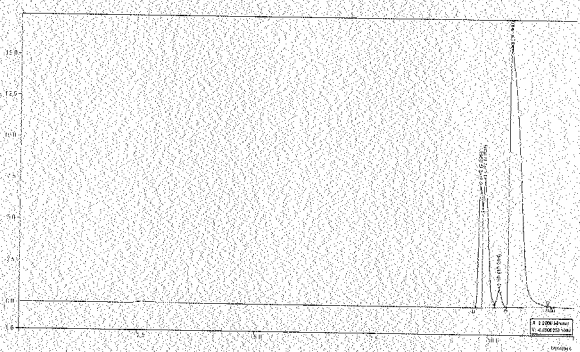


Fig. 7. Sample-1.5 bar-bottom - 10.584 % *p*-H2; 17.058 % *o*-H2; 1.984 % HD; 70.374 % D2

The results show a good separation of the cryogenic column in the cryogenic distillation process. Also, a good separation of the two isomeric forms of hydrogen, orthohydrogen and parahydrogen is observed.

Conclusion

The analysis using GC is useful in order to study the performances of the catalysts which is equipped the cryogenic distillation column. These studies are helpful to choose the adequate catalyst to obtain the separation requested.

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