

# A THEORETICAL STUDY OF THE IMPACT OF HEAVY IMPURITIES ON THE PERFORMANCE OF NATURAL GAS ADSORPTIVE STORAGE SYSTEMS

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## Introduction

Natural gas (NG) is a potentially attractive fuel for vehicle use. It is cheaper than gasoline and diesel, it is abundant compared to the much more limited reserves of crude oil, the feasibility of NG vehicles is well established, and they have a less adverse effect on the environment than liquid-fueled vehicles, emitting less CO<sub>2</sub> as well as several other air pollutants [1].

The most promising alternative to the traditional high-pressure compression (20 MPa) storage method is adsorption storage, which at relatively low pressure (3.5 MPa) can provide nearly the same capacity of compressed NG [2]. This new technology may change the economics leading to the wide acceptance of NG as a transportation fuel [3].

Several problems that affect the success of adsorption storage have been addressed in the literature [4]. The one of concern here is the gradual deterioration of storage capacity due to the cumulative adsorption of the heavier hydrocarbons, which are present in small amounts in NG. These have a higher adsorption potential than methane and are not easily desorbed during fuel use [5].

In this work, the impact of impurities on NG adsorption storage is assessed by studying the performance of adsorption storage on a model NG consisting of a binary mixture of methane and an hypothetical impurity obtained from thermodynamic mixture combination rules applied to the composition of a typical natural gas.

## Model formulation

The behavior of an on-board storage reservoir is simulated by a series of consecutive cycles, each consisting on the isothermal charge of a storage cylinder with the gas mixture, followed by discharge at a fixed slow rate.

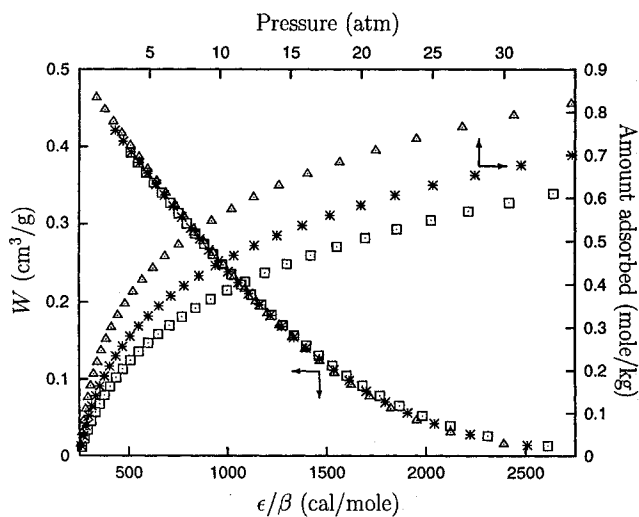
The heavier hydrocarbons present in NG are grouped in a single species, whose physical and thermodynamic properties are predicted from mixture combination rules applied to the gas mixture listed in table 1. The model employed for the discharge phase is the extension to a binary mixture of previous theoretical work [4] on pure methane that has been validated experimentally [6].

Experimental isotherm data, reported by Chang and Talu [6], for methane adsorption on an activated carbon with a good adsorption capacity was analysed on the basis of the

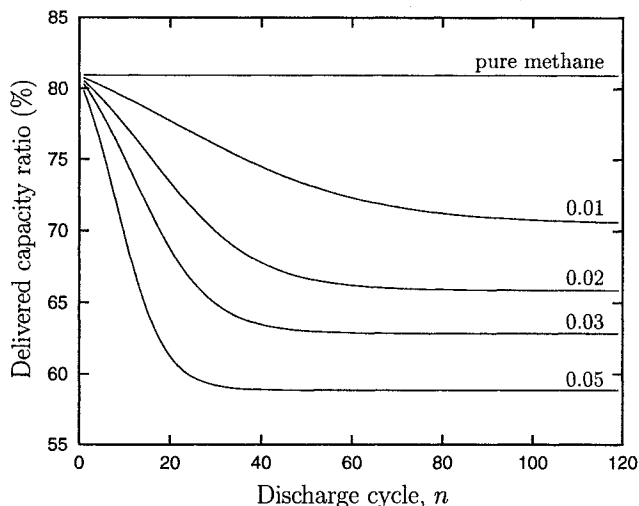
**Table 1.** Composition of gas containing hydrocarbons higher than methane taken from a typical natural gas.

Component	Mole fraction	Component	Mole fraction
Ethane	0.622	<i>n</i> -pentane	0.011
Propane	0.233	Isopentane	0.011
<i>n</i> -butane	0.067	Hexane and higher	0.022
Isobutane	0.033		

adsorption potential theory. A characteristic curve of adsorption on the carbon was obtained (Figure 1), whose temperature independence corroborates the applicability of the theory. The characteristic curve can be employed to predict pure-component adsorption equilibrium on the carbon if the affinity coefficient of the adsorbate is known. The value for the impurity was obtained from the correlation based on the critical volume of the adsorbate, proposed by Ozawa *et al.* [7]. The binary mixture adsorption equilibrium was predicted by using the model of Grant and Manes [8], who applied the equipotential concept to mixed-gas adsorption.



**Figure 1.** Experimental adsorption equilibrium data for methane and characteristic curve of adsorption on activated carbon. *W*, volume adsorbed;  $\epsilon/\beta$ , scaled adsorption potential;  $\Delta$ , 0°C; \*, 25°C;  $\square$ , 45°C.



**Figure 2.** Delivered capacity ratio (%) as a function of discharge cycle,  $n$ , for various mole fractions of the impurity in the charge gas.

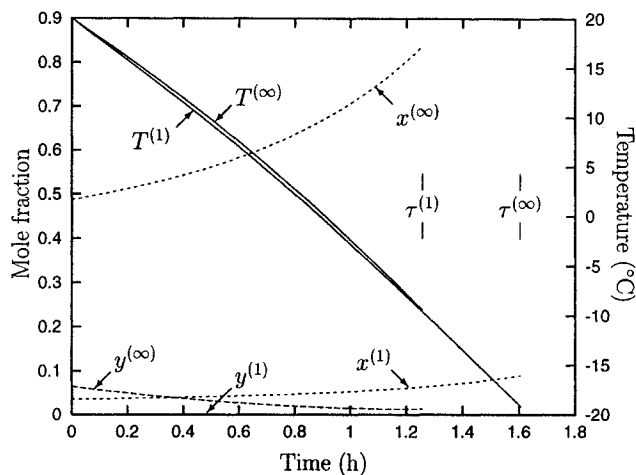
### Results and discussion

Due to lack of space only a very limited amount of results is presented. Charge pressure is 35 atm while depletion pressure is 1.2 atm. The discharge flow rate considered produces an isothermal discharge duration of 2 hours if the storage cylinder, whose radius is 12 cm, is filled with pure methane.

The delivered capacity, expressed in figure 2 as a fraction of the net capacity of an isothermal storage with pure methane, reduces gradually with the number of cycles due to the presence of the impurity. The adverse impact of the impurity increases with its mole fraction in the charge gas.

The discharge history for the first and steady cycles is compared in figure 3 for a mole fraction of impurity in the charge gas of 0.03. Each lumped value results from averaging the variable over the cross section of the cylinder. The discharge duration is reduced as the number of cycles increases since the of active sites are gradually occupied by the impurity which remains adsorbed at depletion pressure. The temperature history is insensitive to the number of cycles and to the impurity mole fraction, because the discharge is carried out at a fixed rate and both heats of adsorption have similar magnitudes. Notice the significant increase of the adsorbate mole fraction of impurity from the first cycle to the steady one.

In a real system, the higher hydrocarbons present in NG originate a similar qualitative behavior. Thus, some kind of economical mean of controlling the contaminants which enter the on-board storage system is needed. The solution could be either a gas clean-up system installed at the NG refueling station [9] or a guard bed placed in front of the on-board storage reservoir [5].



**Figure 3.** Temperature and mole fractions histories during discharge for the first (1) and steady ( $\infty$ ) cycles.  $T$ , cylinder temperature;  $y$ , gas mole fraction of impurity;  $x$ , adsorbate mole fraction of impurity;  $\tau$ , discharge duration.

### Acknowledgements

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