

Computer Simulation Studies of Adsorption of Binary and Ternary Mixtures of Gasoline Components in Engine Deposits

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ABSTRACT

Carbonaceous deposits can accumulate on various surfaces of the internal combustion engine and affect its performance. The porous nature of these deposits means that they act like a "sponge", adsorbing fuel components and changing both the composition and the amount of fuel in the combustion chamber. Here we use a previously developed and validated model of engine deposits to predict adsorption of normal heptane, isooctane, toluene and their mixtures in deposits of different origin within a port fuel injected spark ignition engine (Combustion Chamber Deposits, or CCDs, and Intake Valve Deposits, or IVDs) and under different conditions. We explore the influence of molecular structure of adsorbing species, composition of the bulk mixture and temperature on the uptake and selectivity behaviour of the deposits. While deposits generally show high capacity toward all three components, we observe that selectivity behaviour is a more subtle and complex property.

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INTRODUCTION

It has now been widely recognised that the accumulation of carbonaceous deposits on the internal surfaces of the sparkignition engines can lead to engine performance deterioration and higher emissions [1,2,3,4]. Several mechanisms have been proposed for why these adverse effects happen and these mechanisms depend on the location and origin of the deposits. However, one mechanism that seems to be both universal for all types of deposits and also is the most important contributor to their adverse influence is the adsorption of fuel components [1,2,3,4]. According to this mechanism, deposits, due to their porous structure, act as a "sponge" within which fuel components and combustion products (in case of the combustion chamber deposits) tend to accumulate. In the case of IVDs this has the result that the engine operates under transient conditions with a lower amount of fuel in the combustion chamber than is intended by the vehicle's engine management system, while the adsorbed

chemicals can be released (desorbed) at other stages of the cycle, contributing to higher emissions. Finally, if adsorption is selective towards a particular type of species, it may change the composition of the fuel-air mixture prior to ignition possibly changing its knock resistance.

In a series of recent publications we aimed at establishing the significance and extent of this adsorption mechanism [5,6,7,8]. Transient processes in the engine, which involve rapidly changing temperature and pressure conditions, as well as chemical reactions, can not be reproduced in a laboratory setup. In order to focus specifically on adsorption processes we considered interaction of fuel components with engine deposits under static temperature and pressure conditions, in the absence of chemical reactions. Even in this case, measurement of adsorption from mixtures remains an experimentally challenging task. Hence the emphasis of this and previous studies has been on predictive molecular simulation models. The key idea of these models is to

represent a porous material as a system of independent slit pores. Although deposits are in general very complex materials, this is not a completely unreasonable assumption as the transmission electron microscopy (TEM) images by Zerda et al do show regions of lamellar structure within the deposits [9]. This is also an approach widely adopted in the adsorption studies of related porous carbon materials [10]. Behavior of a real sample of the material can be then viewed as a collective behavior of the ensemble of slit pores. Depending on the sample, pores of different width will occur with different frequency within the sample and the property that describes this frequency is called pore size distribution (PSD).

The idea of the approach is to obtain adsorption isotherms on real deposit samples using species and conditions amiable for the experimental measurements. Adsorption in individual slit pores is linked to the adsorption in whole sample through the Adsorption Integral Equation (AIE):

$$N(P_i) = \int_0^{\infty} \rho(w, P_i) f(w) dw$$

$$i = 1, \dots, n \quad (1)$$

where $N(P_i)$ is the experimentally determined adsorption isotherm at pressure P_i , $\rho(w, P_i)$ is the single-pore adsorption isotherm in a model slit pore of a characteristic width w , and $f(w)$ is the pore size distribution, or PSD. Thus, if adsorption isotherms in individual slit pores of particular widths are known (forming so-called adsorption kernel), the AIE equation can be inverted to obtain PSD and this PSD can then be used for prediction of adsorption in this material at other conditions or for other species and mixtures of species.

In our previous studies we used ethane to measure adsorption at ambient temperature in IVD and CCD samples [5,6]. Grand Canonical Monte Carlo simulations were used to obtain adsorption isotherms in individual pores. Details of the parameters of the simulation and required model optimization are published elsewhere [5,6]. The model was calibrated to reproduce adsorption behavior of ethane and was validated by comparison with the experimental data for adsorption of normal and iso- butanes.

Employed in the predictive capacity, the model indicated that both CCDs and IVDs should adsorb substantial amounts of alkanes under temperature conditions of interest [6,7]. These observations clearly supported the adsorption mechanism of engine performance deterioration.

So far our studies have focused on a single component adsorption. The key advantage of molecular simulations is that adsorption of multi-component mixtures can be considered as easily as the single component adsorption, in contrast to experiments. In addition, one family of components that has

not been considered in our previous publications is aromatic hydrocarbons. Yet they are an important, high octane component of the gasoline.

Hence, this article extends our previous studies in two important aspects. Firstly, in addition to isooctane and normal heptane considered previously as components of the fuel with extreme values of octane number (100 and 0 respectively), we also consider adsorption of toluene as a representative of aromatic species. Secondly, we consider for the first time adsorption of binary and ternary mixtures of these components.

METHODOLOGY

This study is based on the same methodology employed in a series of our previous publication [8]. In particular, a model slit pore in this study consists of two walls, where each wall is made of six graphene layers. Within the walls the layers are separated from each other by 3.35Å.

Single component adsorption of normal heptane (n-heptane), isooctane (i-octane) and toluene, binary and ternary mixtures of these components are considered. These species are modeled using the TraPPE united atom forcefield [11,12]. For the atoms constituting the walls of the slit pores we adopt parameters from the previous work of Pinto da Costa et al [5,6]. Standard Lorentz-Berthelot rules are applied to generate Lennard-Jones parameters for the interactions between the adsorbing species and the atoms of the slit pore walls. For adsorbate-adsorbate interactions potential cut-off distance of 15Å is imposed. The system is placed in periodic boundary conditions in x and y directions.

All Grand Canonical Monte Carlo simulations are performed using the Multipurpose Simulation Code, MuSiC [13] and using the protocol described in our previous publication [8].

An adsorption simulation takes fugacity of adsorbing species as an input parameter and returns the absolute amount adsorbed (in terms of number of molecules per simulation cell) as a result. In the results section the isotherms are reported as the excess amount adsorbed versus pressure of adsorbing species. We use the Peng-Robinson equation of state to relate the fugacity and pressure of adsorbing species, and the following expression to obtain the excess amount [14]:

$$n^{ex} = n^{abs} - \rho_{bulk} V_p \quad (2)$$

where n^{ex} and n^{abs} are excess and absolute amounts adsorbed, respectively (number of molecules per simulation cell), ρ_{bulk} is the density of the bulk phase at the conditions of interest, calculated using the Peng-Robinson equation of state, and $V_p = L_x \cdot L_y \cdot (L_z - 6.1\text{\AA})$ is the pore volume, with L_x and L_y being the dimensions of the pore in x and y directions, L_z its width in z direction and 6.1Å being the smallest width of the