

## Adsorptive Denitrogenation of Liquid Hydrocarbons on Carbon Materials: A Fundamental Study

Almarri M.<sup>1</sup>, Ma X. L.<sup>2</sup> and Song C. S.<sup>3\*</sup>

Clean Fuel and Catalysis Program, Department of Energy and Geo-Environmental Engineering, The Energy Institute, The Pennsylvania State University, University Park, PA, 16802, USA

\*csong@psu.edu

### Introduction

Hydrodesulfurization process (HDS) is one of the most important processes in the modern refinery due to the requirement of environmental regulations for low sulfur fuels. A lot of researchers worldwide are seeking more efficient way for deep desulfurization. As well known, the refractory sulfur compounds in diesel fuel, such as 4-methyl and 4,6-dimethyl dibenzothiophenes, are difficult to be removed by the conventional HDS [1]. The coexisting nitrogen-containing compounds (NCC) make the deep desulfurization even more complicated and difficult, as these NCC inhibit the HDS reaction significantly [2,3]. Consequently, the removal of NCC prior to HDS can improve the HDS performance significantly [4]. The reactivity of the NCC in hydrotreatment is low in comparison with the sulfur compounds. When NCC are adsorbed on the catalyst surface, they stay on the surface due to their strong adsorption affinity and low reactivity, and block the way for adsorption of the sulfur compounds on the active sites. Especially, the basic nitrogen compounds can be adsorbed easily on the acidic sites of the HDS catalyst, and poison the sites. Moreover, hydrogenation of both basic and non-basic nitrogen compounds during the hydrotreatment process produces ammonia as an intermediate product, which has been confirmed to be an inhibitor for deep HDS [2]. As a result, an approach to the removal of NCC prior to HDS is important.

Using specific adsorbents to remove nitrogen compounds from liquid hydrocarbons is one of the promising approaches [5]. As adsorption can be accomplished at low operating temperature without using hydrogen, it is a promising method for improving the deep HDS performance. Zeolite [5], activated carbon [4], activated alumina [6], and silica gel [7] were reported to have a good selectivity for the removal of NCC from gas oil. For example, SK Company has developed a pretreatment adsorption process that is able to remove over 90 % of nitrogen compounds from diesel fuel [7]. The total amount of fuel adsorbed was found to be around 2 % of the total diesel feed treated, which comprises a large quantity of polar compounds having such functional groups, such as -COOH (naphthenic acids), -OH (phenols), -N (pyridines) and -NH (pyroles), and aromatic compounds, according to 85% of the polar compounds in the initial feed. It was found that the degree of improvement in the subsequent HDS is directly proportional to the degree of nitrogen removal [7]. Mochida's group published several studies in adsorptive denitrogenation of real gas oil over activated carbon materials [4,8]. They found that MAXSORB-II, an activated carbon prepared from petroleum coke through KOH activation with an apparent surface area of 3000 m<sup>2</sup>/g, was effective for adsorptive denitrogenation of gas oil at ambient temperature. They attributed this to the oxygen functional groups on the carbon surface; in particular those evolve CO in the temperature range of 600 – 800 °C. However, the paper [8] did not provide sufficient evidence for their claim. In addition,

the mechanism of the interaction between carbon surface functionalities and nitrogen compounds in liquid hydrocarbons is still unclear.

The objective of the present study is to fundamentally understand the adsorption mechanism of nitrogen compounds on activated carbon through the evaluation of the adsorption capacity, selectivity of the various activated carbons for different compounds. The different adsorption conditions on the adsorption performance are also examined.

### Materials and Methods

A series of commercial activated carbons with surface area of 650-2200 m<sup>2</sup>/g and average pore diameter of <30 μm were tested to evaluate their performance for adsorptive desulfurization and denitrogenation of the model diesel fuel (MDF). The adsorbent materials were dried under a vacuum condition at 110 °C for 2 h before use.

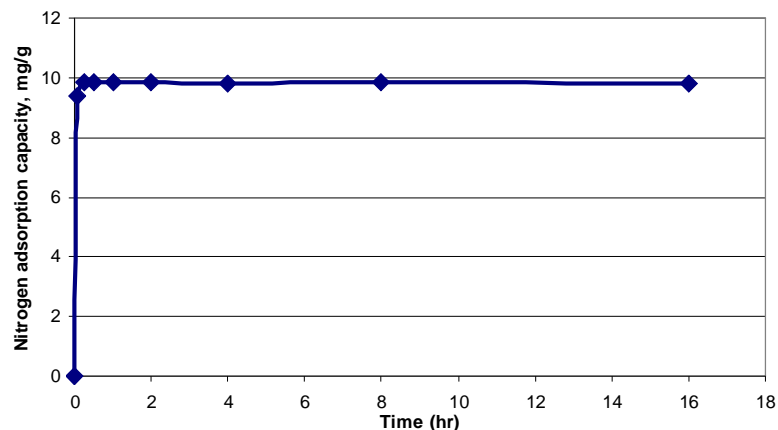
In order to compare the adsorption selectivity, a model diesel fuel (MDF) was prepared by adding the same molar concentration of sulfur, nitrogen, and aromatic compounds into liquid alkanes. MDF contained 10.0 μmol/g of dibenzothiophene (DBT), 4,6-dimethyl-dibenzothiophene (4,6-DMDBT), indole, quinoline, naphthalene (NA), and 1-methyl-naphthalene (1-MNA). The total sulfur and nitrogen content in MDF was 641 ppmw and 280 ppmw, respectively. All compounds added in MDF were purchased from Aldrich Chemical Co. and used as such without further purification.

The adsorption experiments were conducted in a batch system with a magnetic stirrer at desired temperature and contacting time. After adsorption, the treated MDF was separated from the spent adsorbent by filtration, and the sulfur and nitrogen concentration in the treated MDF were quantitatively analyzed. A series of adsorption experiments were performed in a batch system to estimate and compare adsorption capacity and selectivity. Two activated carbon materials that exhibit different behavior toward adsorption of sulfur and nitrogen compounds were selected for further examination.

The total nitrogen and sulfur concentration of the treated fuel samples was analyzed by using an ANTEK 9000 series analyzer. The concentration of various compounds in the treated MDF was quantitatively analyzed by a HP 5890 gas chromatograph with a capillary column (XTI-5, Restek, 30 m in length, 0.25 mm in internal diameter) and a flame ionization detector (FID), using n-tetradecane as an internal standard.

### Results and Discussion

Figure 1 shows the effect of contacting time on adsorptive denitrogenation of model fuel at room temperature using AC1 adsorbent. The results indicate that the adsorption rate was fast and the adsorption equilibrium was reached within the first fifteen minutes. The effect of temperature on adsorption capacity of nitrogen compounds was also examined. It was found that maximum adsorption capacity was obtained at room temperature as expected.



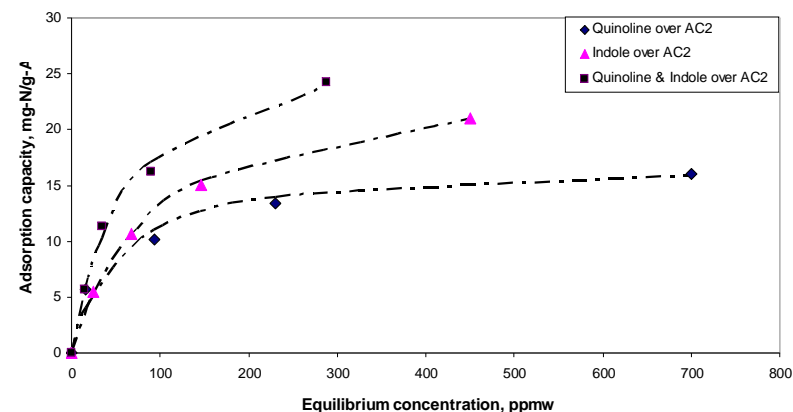
**Figure 1.** Adsorption capacity of AC1 for the nitrogen compounds as a function of adsorption time.

In order to better understanding the adsorption mechanism, adsorption capacity and selectivity for each compound (DBT, 4,6-DMDBT, quinoline, indole, NA, and 1-MNA) in the model fuel was evaluated in a batch system at room temperature for two hours, and the results are listed in Table 1. AC2 gave the highest adsorption capacity for both basic and non basic nitrogen compounds (i.e. quinoline and indole respectively), while AC3 clearly showed better adsorption capacity for sulfur compounds, especially the 4,6-DMDBT. In comparison of the adsorptive selectivity, AC2 also showed the highest selectivity for both nitrogen compounds especially for the basic one. For example, AC2 selectivity factor is around 5 times greater than AC3, which has the second highest adsorption selectivity factor among the tested ACs. AC3 was found to have the highest adsorption selectivity for 4,6-DMDBT. To achieve deep desulfurization of gas oil, removal of the refractory sulfur compounds (i.e. 4,6-DMDBT) and co-existing nitrogen compounds from gas oil is essential. Since AC2 and AC3 are relatively highly selective for nitrogen compounds and 4,6-DMDBT respectively. Therefore, further investigation in AC2 AC3 was carried out to fundamentally understand the adsorption mechanism.

Various amounts of quinoline, indole, and a mixture of quinoline and indole were separately added to decane to prepare nitrogen containing solution in order to study adsorption isotherm of nitrogen compounds over AC2 and AC3. For example, the adsorption capacity over AC2 as a function of the equilibrium concentration of quinoline, indole, and a mixture of both in liquid phase is shown in Figure 2. It is clear that the adsorption capacity increases with increasing equilibrium concentration of the nitrogen in the liquid phase. The results show that AC2 has very higher affinity for indole than for quinoline. The active sites density, adsorption constant and coverage% for AC2 and AC3 were estimated by a curve fitting on the basis of Langmuir isotherm, and an adsorption model for explaining the interaction between the active sites on carbon surface and the basic and non-basic nitrogen compounds is proposed.

**Table 1.** Adsorptive capacity and selectivity for nitrogen, sulfur, and aromatic compounds over various activated carbon at room temperature using a stirred batch system; stirring time: 2h; fuel/adsorbent ratio: 20 wt/wt

	Comps	NA	1MNA	DBT	4,6-DMDBT	Indole	Quinoline
AC1	Ads. Cap.	47.65	55.22	146.35	171.08	164.15	154.96
	Conc.	7.59	7.21	2.60	1.35	1.70	2.17
	Select.	1.00	1.22	7.34	20.15	15.36	11.39
AC2	Ads. Cap.	47.65	56.34	136.16	162.31	190.65	195.51
	Conc.	7.63	7.20	3.23	1.93	0.51	0.27
	Select.	1.00	1.25	5.39	13.50	59.29	114.71
AC3	Ads. Cap.	95.97	112.21	183.28	192.91	180.38	190.30
	Conc.	5.16	4.34	0.75	0.27	0.90	0.40
	Select.	1.00	1.39	9.41	38.80	10.78	25.65
AC4	Ads. Cap.	85.70	24.87	96.95	121.94	148.28	121.49
	Conc.	5.72	8.76	5.16	3.91	2.59	3.93
	Select.	1.00	0.19	6.62	2.08	3.82	2.06
AC5	Ads. Cap.	29.43	38.58	129.27	169.03	116.66	83.83
	Conc.	8.53	8.07	3.52	1.53	4.16	5.80
	Select.	1.00	1.39	7.67	31.97	8.13	4.19



**Figure 2.** Adsorption isotherm for Quinoline, Indole and a mixture of (quinoline & indole) at room temperature on AC2. The experimental data are fitted to the Langmuir isotherm

### **Significance**

Adsorptive denitrogenation/desulfurization of the model diesel fuel, over 5 activated carbon adsorbents was conducted in a batch system. AC2 was found to have highest adsorption capacity and selectivity for basic and non-basic nitrogen compounds, while AC3 was the best for removing 4,6-DMDBT. The high capacity and selectivity of the activated carbon for both the nitrogen compounds and the refractory sulfur compounds indicate the activated carbon is a promising adsorbent for adsorptive denitrogenation/desulfurization of liquid hydrocarbons. Quite different adsorption performance of different the activated carbons imply that the activated carbons can be further designed and modified to improve their adsorption performance. The present study provides some new insight into the fundamental understanding of adsorption of nitrogen compounds on carbon surface, which benefits the design and preparation of better activated-carbon-based adsorbent for the adsorptive denitrogenation/desulfurization.

### **References**

1. Song, C. *Catalysis Today*. 86, 211 (2003).
2. Kwak C., Lee J., Bae J., Moon S. *Applied Catalysis B* 35, 59 (2001).
3. Uday T., Ma X., Song C. *Catalysis Today* 86, 265 (2003).
4. Sano Y., Choi K., Korai Y., Mochida I. *Applied Catalysis B* 49, 219 (2004).
5. Hernandez-Maldonado A., and Yang R. *Angewandte Chemie* 43, 1004 (2004).
6. Kim J. H., Ma X., Zhou A., Song C. *Catalysis Today* 111, 74 (2006).
7. Min W. *Korean J. Chem. Eng.* 19, 601 (2002).
8. Sano Y., Choi K., Korai Y., and Mochida I. *Energy & Fuel* 18, 644 (2004).