ACTIVATED CARBONS FROM BIOMASS FOR METHANE AND HYDROGEN STORAGE

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The search for alternative transportation fuels has been actively pursued in recent years due to the instability in the oil markets and the increase in environmental concerns. One alternative to gasoline is natural gas, which consists primarily of methane (85-95%) with small amounts of ethane, heavier hydrocarbons, nitrogen, and carbon dioxide (Perry and Chilton, 1974). The advantages of natural gas include its abundance and environmental compatibility. Specifically, natural gas burns cleaner than gasoline, emitting appreciably less hydrocarbons and 90% less carbon monoxide. A considerable and steadily growing worldwide market exists for natural gas-fuelled vehicles (NGV) equipped with storage cylinders for compressed natural gas (CNG) at pressures up to 25 MPa (ca 3600 psig). The cylinders' sizes and costs, however, are substantial deterrents to the large-scale utilization of CNG as a motor vehicle fuel. If the gas could be stored at much lower pressures, e.g., 2-4 MPa (ca 300-600 psig), the competitiveness of NGVs to their liquid-fuelled counterparts would be greatly improved. An alternative method of storing natural gas is through adsorption. Adsorbed natural gas (ANG) storage at ambient temperature under pressures as low as 500 psig has been proposed as a means of fueling motor vehicles (Talu, 1992). The attractive feature of ANG storage is that the storage tank can be filled with an inexpensive single-stage compressor (Parkyns and Quinn, 1995). It has been reported that break-even ANG storage factors (volume of methane adsorbed at STP / total volume of the tank) are 78 for light-duty vehicles and 120 for heavy-duty vehicles (Talu, 1992). In ANG storage, natural gas is usually stored in a lightweight cylinder filled with highly porous carbons. Activated carbons have long served as effective adsorbents. In recent years, the development of an economical carbon adsorbent has been widely attempted for natural gas storage. The ideal adsorbent would possess limited macropore volume and a high adsorption capacity for methane, the predominant component of natural gas. Activated carbons have been prepared from a vast number of precursors with a wide variety of activation methods (Quinn and MacDonald, 1992; Lewis, et al., 1993; Lozano-Castelló et al., 2002; Zhang et al., 2004; Zhang et al., 2005, 2005). Apparently, cereal grains, such as sorghum and wheat, primarily consisting of starch, have not yet been explored as the precursors for the production of activated carbon adsorbents for methane storage.

This study aimed at establishing the technical feasibility of preparing activated carbons by chemical activation from sorghum and wheat for ANG storage. A comparative study was also carried out with commercial activated carbons from traditional sources. Precursors for generating chars, which were eventually converted into activated carbons through activation, include two types of grain. One was sorghum, with a moisture content of 15% and a grain diameter between 3 and 4 mm; grains of sorghum are nearly spherical. The other was hard red winter wheat, with a moisture content of 8.4%, a grain length of about 6 mm and a grain diameter of about 2 mm. The activating agents added to the chars were ortho-phosphoric acid (H_3PO_4), zinc chloride ($ZnCl_2$), and potassium hydroxide (KOH) (Fisher Scientific, ACS certified). The aqueous solutions of phosphoric acid were 35, 50, and 85 wt%. The concentrations of aqueous zinc chloride and potassium hydroxide solutions were both 50 wt%. All activating agents are dehydrating agents that influence the pyrolytic decomposition and inhibit the formation of tar. They also reduce the formation of by-products, e.g., acetic acid and methanol, thus enhancing the yield of activated carbons (Bansal et al., 1988). An inert gas atmosphere was maintained with compressed nitrogen with a purity of 99.995% for both carbonization and activation. Liquid nitrogen served as the coolant; and ultra-pure carrier grade compressed nitrogen with a purity of 99.9995%, as the adsorbate for N_2-adsorption characterization. The methane adsorption capacity of activated carbons was measured with ultra high purity (UHP) methane. Carbonization and activation were performed in a custom-fabricated tubular furnace under a steady flow of gaseous N_2. The electrical-resistance furnace had an inner diameter of 10.2 cm and a length of 55.0 cm. The samples were contained in cylindrical baskets made from 60 mesh stainless steel gauze. This mesh size was sufficiently small to prevent sample loss. Both grain-based and commercial activated carbons were characterized with a gas sorption analyzer, Quantachrome Autosorb-1-MP Analyzer. The absorption of UHP methane was measured at ambient temperature (25 °C) and 500 psig with activated carbons in a custom fabricated adsorption cell.

Experiments were also conducted to investigate the influence of compaction on methane storage. Compaction leads to an increase in the bulk density of the activated carbons. It was carried out by tapping the adsorption cell by hand or pressing the activated carbon sample by finger. Subsequent studies resorted to a hydraulic press to compact the activated carbons so that pressures up to 8000 psig could be attained. In addition, an attempt was made to investigate the mixtures of both granular and powdered commercial activated carbons to prepare an optimum mixture for gas storage. Note that the granular activated carbons have a much higher density than the powdered ones. By mixing granular and powdered activated carbons, it was possible to form an activated carbon blend suitable for natural gas storage.

Our study indicated that most of the activated carbons examined had BET surface areas ranging between 900 and 2000 m^2/g, and the ratio of micropore volume to total pore volume ranging between 0.26 and 0.65. In addition, the pore-size distributions (PSD's) of activated carbons were narrow and peaked around 1.1 to 1.2 nm, implying the PSD's of these activated carbons were suitable for ANG storage. The highest storage factor (volume of methane adsorbed at STP/total volume of the tank) attained was 89 for compacted activated carbons from grain sorghum with a bulk density of 0.65 g/cm^3, and the highest storage factor attained was 106 for compacted commercial activated carbons with a bulk density of 0.70 g/cm^3. Thus, both the sorghum-based and commercial activated carbons would be effective for ANG storage in the fuel tanks of motor vehicles at 25 °C and 500 psig: The reported ANG break-even points are 78 for light-duty vehicles and 120 for heavy-duty vehicles. The storage factor was found to increase approximately linearly with increasing bulk density. Additional experiments were carried out to modify the activated carbons from biomass to generate molecular-sieve like carbon adsorbents. The preliminary estimation indicates that such carbon adsorbents can be highly effective for hydrogen storage.

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