Chapter 1

Mobile Energy

1.1 Introduction

The worldwide appetite for energy grows while energy-dense resources diminish and the threat posed by the negative environmental consequences of their use is no longer contested.[1] In particular, observations of increased levels of CO_2 in the Earth's atmosphere and a correlated rise in global temperatures since the advent of the widespread use of fossil fuels by humans has motivated the effort to reduce or eliminate the dependency on such fuels to fulfill future energy demands. At present, more than 80% of global energy consumption is met by burning fossil fuels,[2] primarily coal, oil, and natural gas, and their eventual physical depletion is certain. Total world consumption of energy will continue to increase, motivating the need to investigate alternative, sustainable means of energy transfer, use, and storage.

The two most impactful ways to effect a significant change to global carbon emissions are to 1) change the mobility fuel and 2) change the method of electricity generation.[3] Each accounts for ~40% of the total anthropogenic emission of CO_2 and the fuel of choice is highly segregated, mobility demands dominantly met by oil and electricity generation dominantly by coal. In this work, we focus on mobility; a portable fuel system capable of providing energy on demand and in a nonpolluting manner is needed. The essential quality of an ideal mobility fuel is high energy density, but it must also meet other standards of availability, low cost, safety, and convenience of use.

Hydrogen is an ideal mobility fuel since it has the highest specific energy content of any chemical fuel, its constituent element (H) is highly abundant, it is readily synthesized by renewable methods, and it can be oxidized efficiently without the production of CO_2. However, numerous obstacles remain to realizing hydrogen as the primary mobility fuel beyond those associated with its inherent demands on infrastructure. Petroleum-based fossil fuels do not need to be synthesized, require relatively minor processing to be used, and are easily transported (due to their high volumetric energy density) whereas hydrogen must be synthesized and effectively stored, both steps that require substantial energy in themselves. Nonetheless, the superlative properties of hydrogen ensure that it will have importance in the global energy market in years to come.

1.2 Hydrogen and Energy

Hydrogen is the simplest and lightest element in the periodic table, is the most abundant element in the universe, and exhibits many unique properties due to its quantum-mechanical nature. Its liquid and solid state at ambient pressure are limited to very low temperature, a result of weak intermolecular forces. Supercritical hydrogen also exists at relatively low temperatures and pressures: above 33 K and 1.3 MPa (see Figure 1.1). At standard conditions, hydrogen is a near-ideal gas of diatomic molecules.

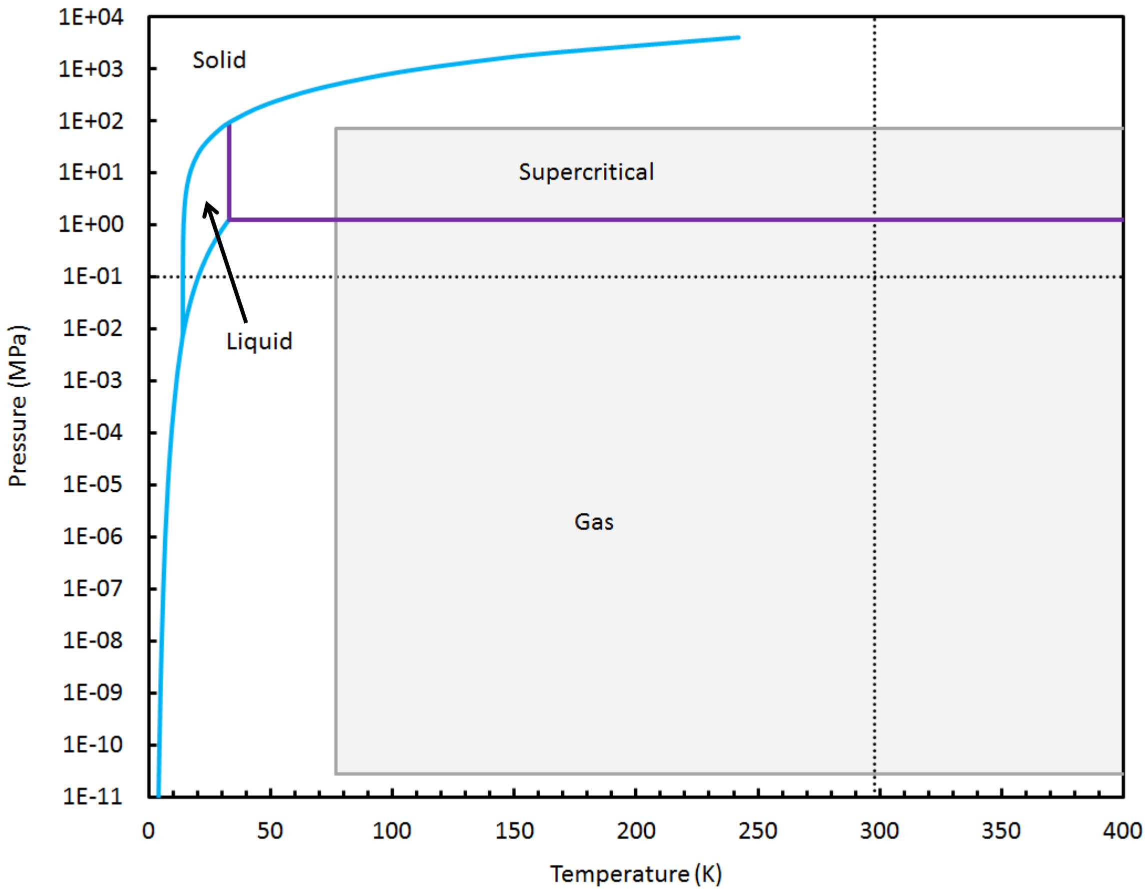

Figure 1.1. The phase diagram of hydrogen, calculated using REFPROP standard reference data. The equilibrium boundaries between the primary phases are shown: blue lines indicate the melting, boiling, and sublimation transitions and the purple lines indicate the boundary of the supercritical region. The dotted lines indicate standard conditions (0.1 MPa and 298 K) and the gray shaded region indicates the temperature and pressure limits of adsorption experiments in our laboratory.

Each molecule is bound by a single nonpolar covalent bond. While H_2 is not a particularly reactive molecule, H atoms will react with each other and all other elements (except noble gases); the H-H bond has a dissociation energy of +436 kJ mol^{-1} (dissociation is highly endothermic), and the heat of recombination leads to extremely high temperatures (e.g., 10^4 K during solar flares).[4] In the oxygen rich atmosphere on

Earth, it is practical to take advantage of a different reaction: the oxidation of molecular hydrogen to produce water:

$$H_{2\,(g)} + \frac{1}{2}O_{2\,(g)} \rightarrow H_2O_{(l)} \qquad \Delta H^{\circ} = 141.8\ kJ\ (g\ H_2)^{-1}$$

Hydrogen has the highest gravimetric energy of any combustible species, a factor of three greater than gasoline (see Table 1.1). This chemical energy can be harnessed by thermal conversion to mechanical energy, such as in an internal combustion engine, or by electrochemical conversion to electrical energy, such as in a fuel cell. The latter method is not limited by Carnot efficiency, and typically reaches efficiencies twice that of traditional combustion. Using sunlight and a photovoltaic cell to drive the reverse reaction (electrolysis), the cycle of hydrogen production and consumption can be carried out entirely carbon-free.

A comparison of hydrogen's thermal energy properties with hydrocarbon fuels is given in Table 1.1. The standard enthalpy of combustion is also referred to as the "higher heating value" (HHV) since it represents the thermodynamic maximum energy that can be harnessed from combustion if all products are brought back to standard conditions after the reaction. It is more practical in engineering applications to assume that the water produced is not cooled back to 298 K, and the "lower heating value" (LLV) is a more accurate description of the energy gained in, for example, an internal combustion engine. In a fuel cell, the HHV is applicable. We also see the most obvious disadvantage of hydrogen as a fuel; gravimetric energy density is extraordinarily high, but the volumetric energy density of hydrogen is much lower than gasoline, even under conditions far from standard temperature and pressure (STP), due to its very low density. In fact, the hydrogen content in liquid water or gasoline at STP is actually higher, per volume, than that found in pure liquid hydrogen at 20 K. This is an important caveat of hydrogen as an ideal fuel.

Table 1.1. Heat energy properties of hydrogen, methane, propane, and gasoline for engineering considerations.

Energy Carrier	ρ_{STP} ($g\ L^{-1}$)	HHV ($kJ\ g^{-1}$)	LHV ($kJ\ g^{-1}$)	Volumetric HHV ($MJ\ L^{-1}$)	
Hydrogen	0.0813	141.8	120	20 MPa, 298 K:	2.05
				80 MPa, 298 K:	6.09
				0.1 MPa, 20 K:	10.1
Methane	0.649	55.3	50	20 MPa, 298 K:	8.7
				80 MPa, 298 K:	17.8
Propane	1.809	48.9	46	0.95 MPa, 298 K:	24
Gasoline	~720	46.7	45	STP:	34

*standard state is defined as: T = 298 K, P = 0.1 MPa

The large heat of combustion of hydrogen has been known since well before liquid hydrocarbons were established as mainstream chemical energy carriers, and energy conversion technologies using hydrogen as a fuel have been pursued for over two centuries. For example, Figure 1.2 shows a large inflatable hydrogen storage container behind the Echo Mountain House, a remote (now defunct) mountain resort overlooking Pasadena, in 1893.[5] Hydrogen was used as a fuel for lighting and heating until it was replaced by electricity. Hydrogen was considered as an engine fuel for early vehicles as well, with the first known experiments carried out in 1820 by W. Cecil.[4] Some examples[6] of coal gas (containing hydrogen and other fuels) fuelled mobile vehicles are shown in Figure 1.3, predominantly used by civilians during World War I when petroleum-based fuels were in high demand for the war effort. Hydrogen and coal gas vehicle experiments continued until approximately World War II when they were almost universally discarded in favor of the vastly denser energy available in liquid petroleum-based fuels. Liquid hydrogen-liquid oxygen mixtures became the primary propellant in chemical rocket engines starting in the 1960s and are still used today.

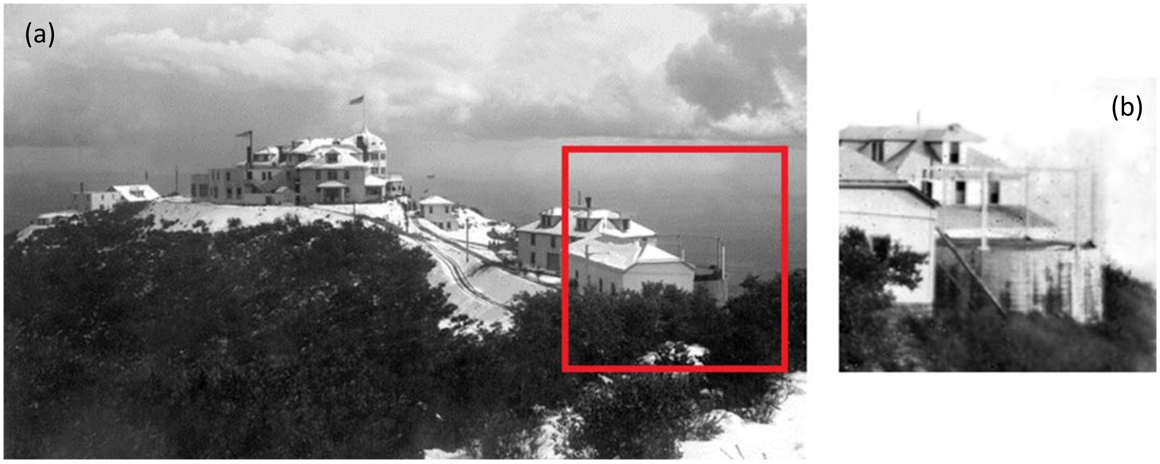

Figure 1.2. (a) The Echo Mountain House and Mt. Lowe Railway shown in 1893. An inflatable hydrogen storage container is shown in the red box. (b) A close-up view shows the framework used to support the gas reservoir which would expand upon filling.

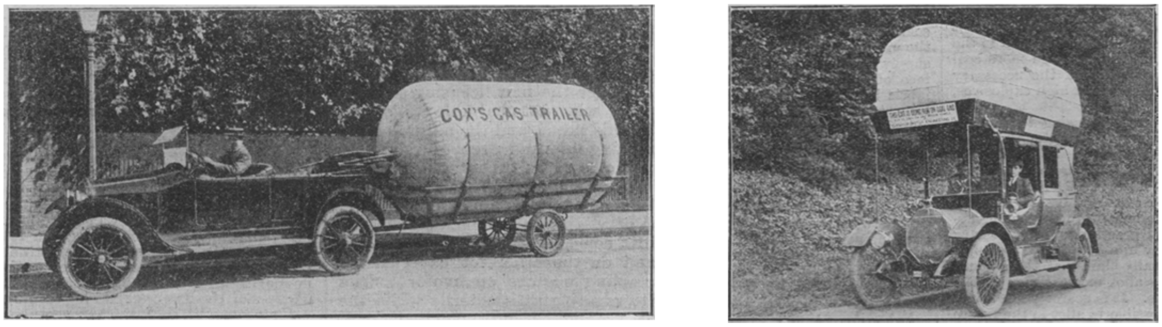

Figure 1.3. Early mobile vehicle gas storage concepts. On the left, ~6 cubic meters of coal gas is towed in a trailer to be used in the vehicle's internal combustion engine. The stated range of such a vehicle is ~20-30 km.

1.3 Methane and Energy

Energy density aside, hydrogen has another obstacle to achieving mainstream viability as a mobility fuel. Despite being the most abundant element in the universe, hydrogen on Earth is rarely found in pure molecular form, existing mainly in the form of water. Restoring molecular hydrogen via electrolysis is costly and itself the cause of significant carbon emission if the electricity used is generated in coal-burning power plants. A majority of the demand for hydrogen today is met by the steam reforming of natural gas, an economical method but one that inherently cannot take advantage of most of hydrogen's advantages over hydrocarbon fuels (carbon emission is still prevalent, though it is limited to the stationary location of the production facility rather than the remote location of the vehicle).

Until renewable hydrogen production is realized in a clean and economical way, other alternative fuels will maintain a significant role in the energy economy. Natural gas, the primary component of which is methane, is stated to be the premium fuel after hydrogen for numerous reasons.[7] While methane is itself a greenhouse gas (in fact 23 times more effective at trapping heat than CO_2[8]), it burns relatively cleanly, producing far less pollutant gases and particulate matter, and ~30% less CO_2 per unit energy than oil. Methane can also be derived by renewable means (referred to as biogas or biomethane) and is significantly more economical than producing longer-chain synthetic hydrocarbons.

Methane has a higher heating value of 55.3 kJ g^{-1}, the second highest (following hydrogen) of all chemical fuels. The phase diagram of methane is shown in Figure 1.4.

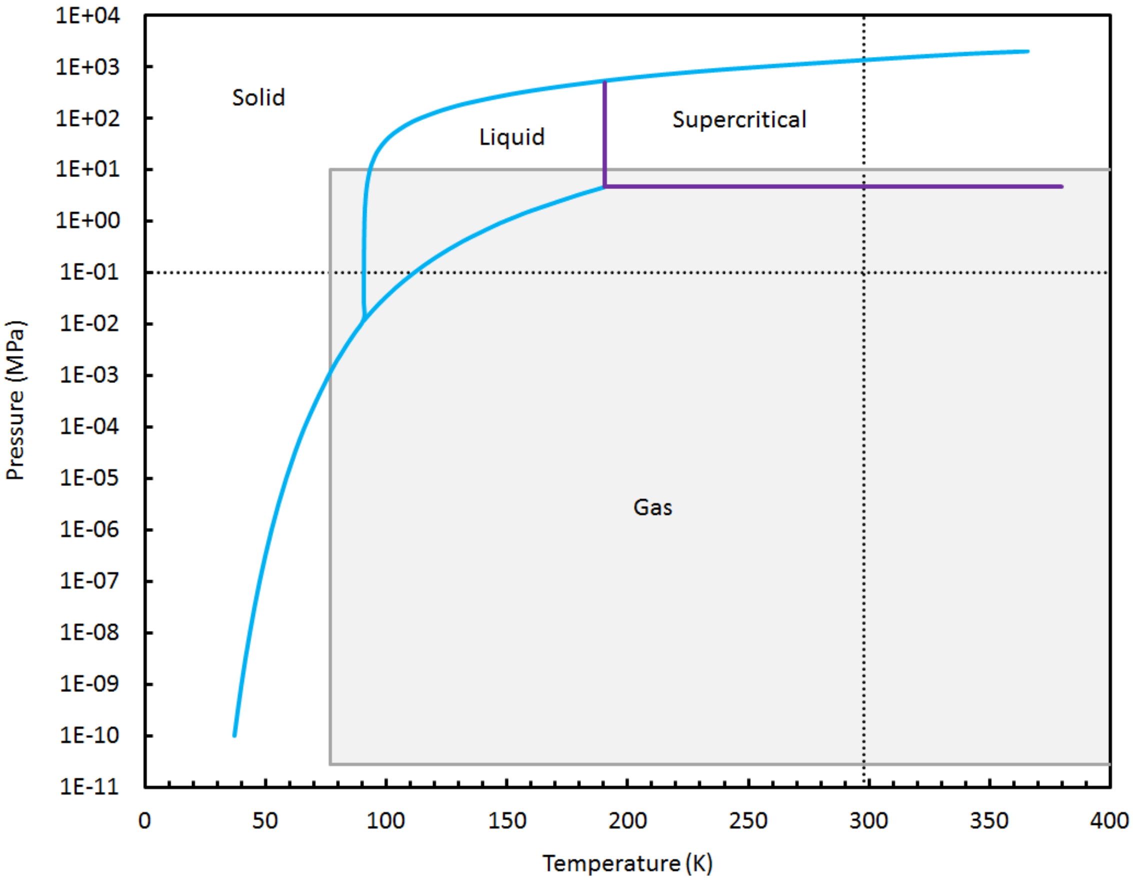

Figure 1.4. The phase diagram of methane. The equilibrium boundaries between the primary phases are shown: blue lines indicate the melting, boiling, and sublimation transitions and the purple lines indicate the boundary of the supercritical region. The dotted lines indicate ambient conditions (0.1 MPa and 298 K) and the gray shaded region represents the temperature and pressure limits of adsorption experiments in our laboratory.

Methane has significantly different properties than hydrogen, which can be observed from the shift of the phase boundaries nearer to the ambient regime. Strong interactions between methane molecules are responsible for this shift, and the gas is far from ideal within the pressure and temperature conditions applicable to storage. Thus, methane is interesting from both an engineering and fundamental science perspective.

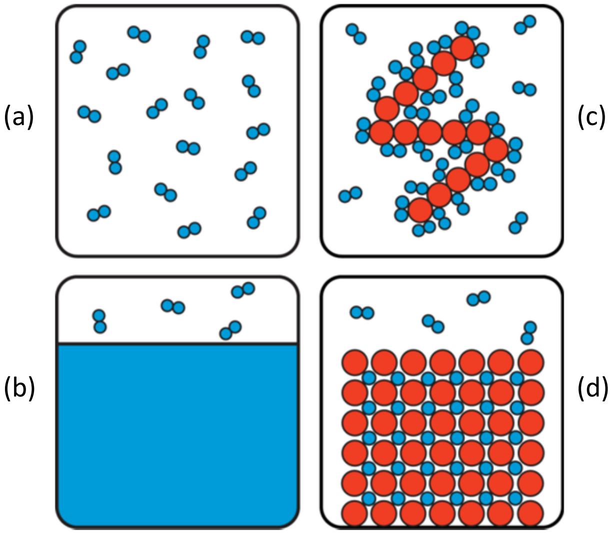

Figure 1.5. A schematic portraying four typical approaches to compact hydrogen storage: (a) pure gas compression, (b) liquefaction, (c) adsorption, and (d) absorption.

1.4 Hydrogen Storage

A serious obstacle to realizing a hydrogen-based energy economy is compact storage.[9] The problem is even more apparent for applications as a mobility fuel where volumetric energy density is of utmost importance. Numerous approaches for compact storage of hydrogen have been investigated (see Figure 1.5). As a pure substance, hydrogen can be contained as a gas or liquid (solidifying hydrogen is not considered a realistic storage approach). A secondary material, while adding mass to the system, can also be used to increase the volumetric density of hydrogen. Some metal hydrides reversibly store large amounts of hydrogen, chemically bound (*absorbed*) within their crystal structure, but generally suffer from poor kinetics and practicality is only achieved at elevated temperatures. Light-element hydrides such as $LiBH_4$ contain among the highest gravimetric capacities of known materials, but hydrogen sorption is not fully reversible except under extreme conditions, and there are many complications to safety and practicality. There are many technologies being explored in these categories of storage materials and others such as complex hydrides. Hydrogen can also be effectively stored by *adsorption* on the surface of a material. For example, carbonaceous (i.e., predominantly carbon) sorbent materials are particularly attractive because they are lightweight, abundantly available, simple to produce, and can effectively increase the volumetric density of stored gases.[10-14] Another promising class of materials for adsorptive hydrogen storage is metal-organic frameworks (MOFs),[15, 16] which can achieve extremely high surface area and contain exposed metal sites which act as preferential adsorption sites at low pressure. Synthesis and characterization of MOFs as physisorptive storage materials is under active investigation, but is not the focus of this work. Representative isotherms of gas adsorption on a large variety of carbonaceous materials measured during the course of this thesis work are shown in Figure 1.6.

A main challenge for carbon (and other) adsorbent materials is that room temperature reversible hydrogen storage capacities are too low for effective use in mobile vehicle applications. Total system gravimetric capacities are better for pure compression than adsorptive compression except at very low temperatures; hydrogen adsorption at 77 K is a more promising solution, but requires significant additional system complexity to maintain such a low temperature. As compression containers achieve high strength to weight ratios, pure compression is favored over adsorption, but compaction of the adsorbent is a potential avenue favoring adsorption and could impart significant improvement to volumetric capacities.[17] The complications associated with cryogenic containment temperatures and thermal management are also under assessment, but appear to be acceptable compared to other storage solutions. High-pressure hydrogen delivery is currently available to the public, for example up to 70 MPa, favoring pure compression storage as well as physisorption over other solutions.

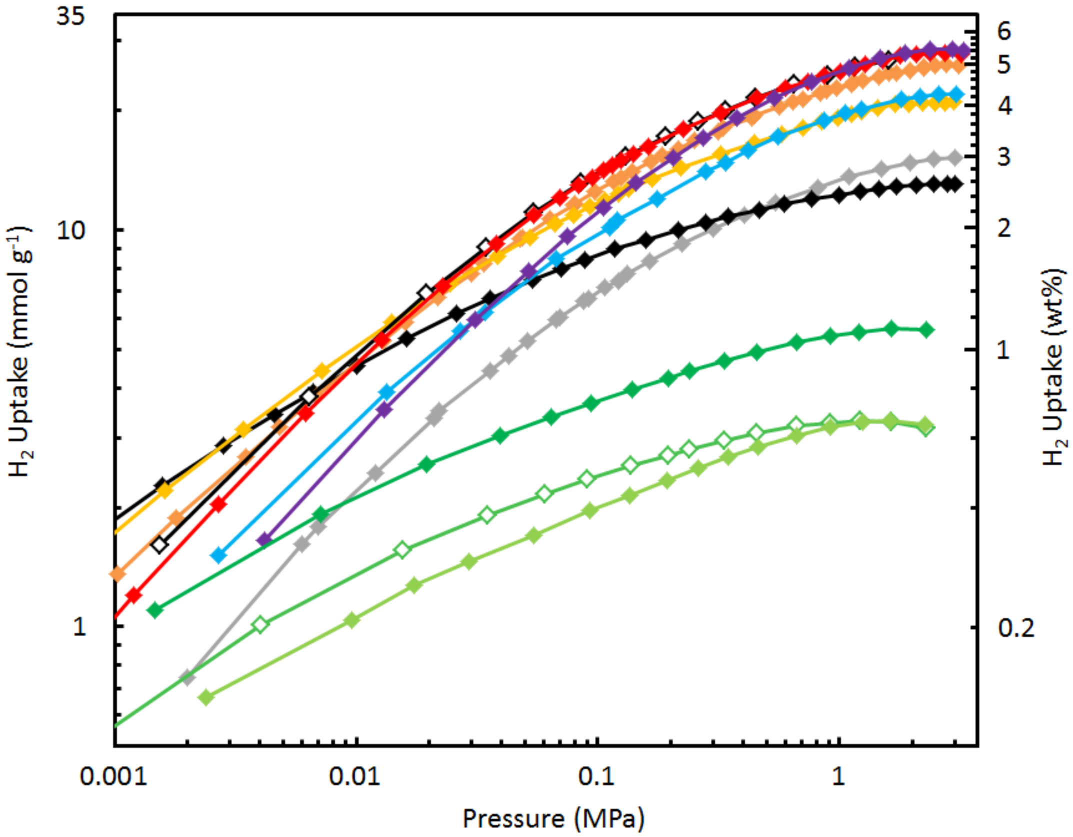

Figure 1.6. Equilibrium hydrogen adsorption isotherms (77 K) of a variety of carbonaceous samples measured during the present study:

Activated Carbon: (black) CNS-201, coconut shell-, (black, open) MU3K, corncob-, (yellow) CO2-9-60, PEEK-, (orange) CO2-9-80, PEEK-, (red) MSC-30, petroleum pitch-derived carbon

Aerogel Carbon: (gray) LLNL AD1

Templated Carbon: ZTC-2 (blue), ZTC-3 (purple)

Hetero-atom Substituted Carbon: (dark green) P-, (green, open) B-, (light green) N-doped carbon scaffolds

1.5 References

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