c. Identification and Significance of the Problem

Increased concerns over air pollution and whether the Middle East will be a reliable source of oil have made natural gas an interesting alternative to conventional liquid transportation fuels. On an equivalent energy basis, natural gas costs much less than gasoline and has a clean air advantage since the hydrocarbon emissions from automobiles are considerably lower resulting in less ozone formation by photochemical reactions. Furthermore carbon monoxide contamination is reduced and a significant benefit is obtained with zero evaporative emissions that can more than equal tailpipe emissions. More specifically, the CO emissions from a natural gas-fueled vehicle are one half to one tenth of those from a gasoline-powered vehicle.[1] There are currently about 700,000 natural gas vehicles (NGV) in operation in the world with about 30,000 of those in the United States. The majority of these applications use compressed natural gas (CNG) and store it in high pressure tanks at 3000 psi (200 atm). Peoples Gas, Light and Coke Company in Chicago has a fleet of 400 CNG trucks and vans. A typical application has a natural gas storage capacity equivalent to 12-13 gallons of gasoline. Although CNG provides more energy than gasoline on a weight basis, the compressed volumetric efficiency is one sixth that of an equal volume of gasoline. Thus to hold an energy content equal to a given amount of gasoline, a CNG storage tank must be six times as large as a gasoline tank. This typically results in a weight penalty of 400 pounds for a CNG vehicle.

Absorbed natural gas (ANG) is an interesting alternative to CNG since the same amount of natural gas can be stored at much lower pressure (500 psi or 30 atm) in a thinner walled tank filled with activated carbon adsorbent. Possible uses of adsorbed natural gas are numerous. These include transportation vehicles as an alternative to compressed natural gas (CNG), stationary sources where a ready access to back-up energy is required, and ocean tankers carrying natural gas. Similar arguments and technology apply to all cases but the emphasis in this proposal will be placed on transportation vehicles. Capillary condensation of the natural gas (primarily methane) in the small micropores of the carbon adsorbent permits significantly more natural gas to be stored than that possible by gas phase storage. IGT in Chicago[2] has been pursuing this ANG technology and point out that an adsorbent storage system has the potential to improved the economics of natural gas storage. IGT has looked a numerous adsorbents and concluded that carbon adsorbents are the leading candidates for low pressure storage. Schwarz[3] has also concluded that activated carbon is effective for storage of hydrogen in hydrogen-fueled vehicles. One of the biggest factors in improved economics is a lighter and safer storage cylinder which reduces compressor and operating costs for filling. Additionally the lighter tank means less vehicle weight than the CNG counterpart and ultimately better fuel economy.

Previous studies of natural gas storage on activated carbon have compared performance on equivalent weights of material. Quinn and MacDonald[4] have clearly shown that comparing storage capacity on a unit volume basis is more appropriate. The storage tank volume is fixed on a transportation vehicle and adsorption capacity determines how much energy can be stored in the tank. A goal frequently mentioned for storage capacity of ANG systems, is to be able to store 150 volumes of natural gas per volume of tank capacity at 500 psi. So far, this goal has been reached in only a few isolated cases in which a high density carbon precursor is specially treated to create micropores and ultimately, a high adsorption capacity per unit volume[5]. The general conclusion is that the carbon must be in the form of a solid monolith or briquette when loaded into the storage tank to maximize the micropore volume. As illustrated below in the bar charts, granular carbon wastes space due to the voids between the granules. Furthermore the mesopore(10-500 pore radius) and macropore volume (radius > 500) contribute little to the storage capacity of the carbon.

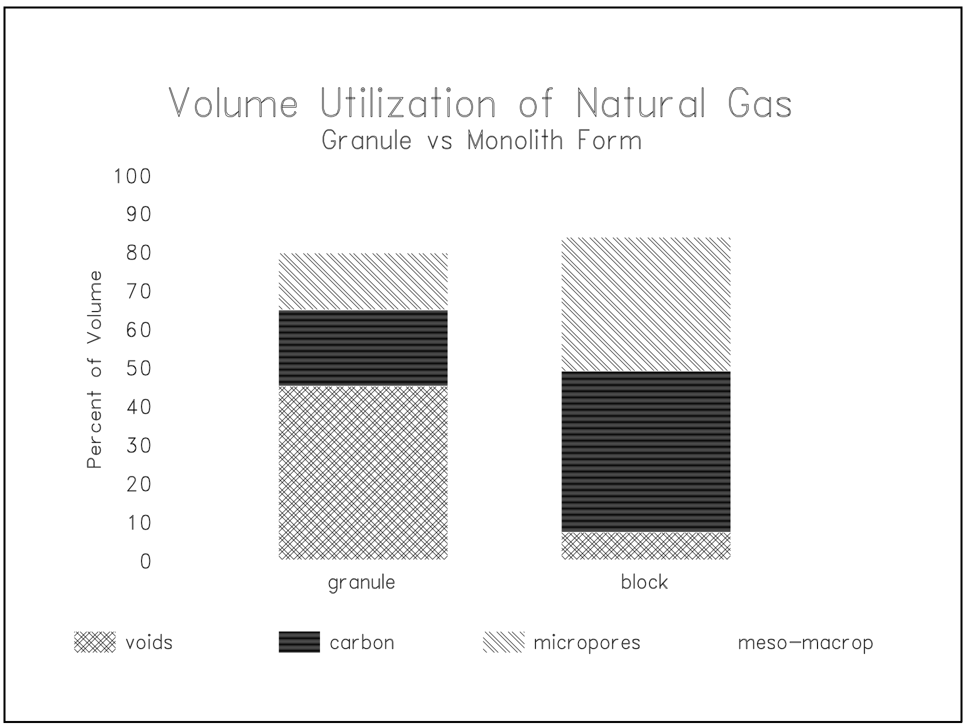


Figure 1 A Comparison of Storage Efficiencies for Granules and Blocks

Mega-Carbon Company believes it has the capability to solve the present technical shortcomings which are impeding commercialization of adsorbed natural gas. The basic problem is to transform carbon powder with exceptional gas adsorbing properties to a highly dense form (i.e. monolithic block) without significantly decreasing its adsorption capacity. Mega-Carbon believes it can successfully do this for the following reasons:

* Mega-Carbon plans to use the Amoco superactivated PX-21 carbon powder[6,7] as a cornerstone for this project and has obtained a license from Amoco for commercial production of their high performance superactivated carbon.

* Mega-Carbon is obtaining a license for granulation of the carbon powder which was developed by Robinson[8] for drinking water treatment.

* Mieville has successfully developed ways to fuse AX-21 superactivated carbon powders with polymer binders with virtually no decrease in adsorption properties.

* Mega-Carbon has entered into an agreement with Research Corporation Technologies (RCT) in Tucson, AZ for a unique surfactant technology which reduces electrostatic charge of carbon powders and allows them to pack at very high densities. This process was developed at the Center for Applied Energy Research, Lexington, KY under contract research to RCT.

For reference, the properties of two grades of the Super A activated carbon powder are shown below and will be used in this proposed project. There is considerable controversy on which is more effective and both have been referenced in the technical literature for methane adsorption studies[9,10].

Property	**Super A, AX-21**	**Super A, AX-24**
BET Surface Area, m^2/g	3000	1300
Iodine Number, mg/g	2800	2000
Methylene Blue, mg/g	500	250
Total pore Volume, cc/g	1.6	0.6
Bulk density, g/cc	0.3	0.6

In summary, Mega-Carbon has a unique mix of technologies and materials which will allow us to develop a carbon adsorbent with high volumetric storage efficiency for storing natural gas.

d. Background, Technical Approach and Potential Uses

d1. Background and Technical Approach

The main purpose of this proposal is to develop a system that utilizes the high adsorption capacity of Super A Carbon (also known as Amoco or Anderson Carbon) for the storage of natural gas (mostly methane). Compressed natural gas at 3000 psi has a ratio of ~210 storage volumes at STP per volume of container and this is the ultimate goal of an adsorbed natural gas system which can operate at some convenient lower pressure. This pressure has been suggested to be 500 psi since this is within the ratings for modified propane cylinders, a ready available and cheaper version of the higher pressure cylinders. At this pressure, ratios approaching 150 volumes of gas per volume of container at ambient temperature have been claimed using Super A carbon. This comparison of adsorbed and compressed natural gas is show above in Figure 2 and points out that most of the advantage of the adsorbent system is gained at 500 psi and then levels off. At the 150 volume ratio, the adsorbent system is marginally attractive. Other carbons have been tried and none have superseded this figure. Any future development that can raise this ratio value has to take several technical aspects into consideration.

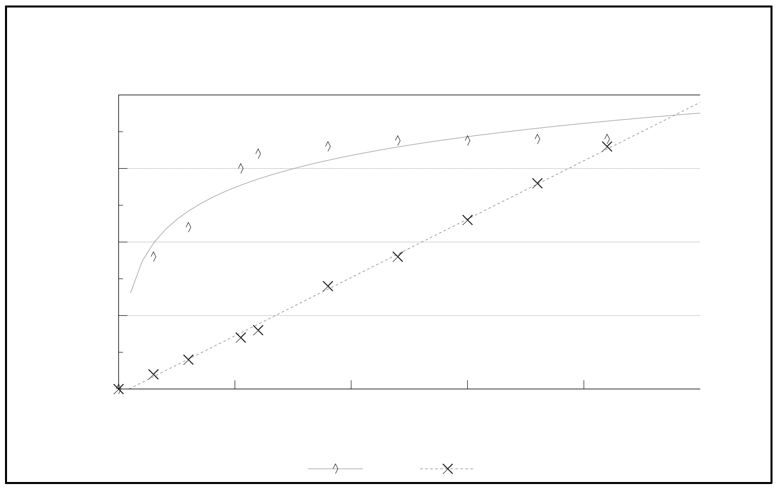


Figure 2 Volumetric Storage as a Function of Pressure

- Storage of methane in the adsorbed state occurs primarily in the micropores of the carbon (< 10 A radius) where the mechanism is generally termed "micropore filling". In the meso-, macropore, and void volumes, methane exists in the compressed gas state where the volume ratio at 500 psi is only ~35. Therefore, it is necessary to maximize the micropore volume and minimize the other contributing volumes occupying the methane container.

- Micropore filling is an exothermic process requiring heat dissipation to allow for maximum adsorption and rapid charging of gas to fill empty storage tanks.

- Micropore emptying (i.e. methane discharging) is conversely endothermic requiring heat input to maintain adequate discharge of methane during vehicle periods of acceleration and start-up.

These latter two problems have been addressed by either the design of storage vessels with heat exchange capabilities or by the use of eutectic materials placed within the body of the carbon to counteract temperature changes. This proposal is primarily concerned with the first problem of maximization of the micropore volume within the volume of the container cylinder. To help further understand this problem, the different types of volume occupation that contribute to the bulk density of carbon have to be considered.

- <u>Carbon</u>, itself, can be regarded in its graphitic form which has a density of 2.25 g/cc although in its disordered crystal state it probably is closer to 2.1 g/cc. The most desirable quality needed in a carbon for the purpose of ambient methane temperature adsorption is a high ratio of micropores to solid carbon.

- As previously mentioned, <u>micropores</u> are the single most important factor in methane adsorption. In this regard, Super A has the highest volume ratio of micropores to dense carbon (~1:1).

- <u>Mesopores</u> (10-500 radius) in general, contribute little to the added presence of methane over and above the compressed state. However, down near the micropore range, adsorption in the mesopores probably occurs to some extent depending on the ambient temperature. This is an ill-defined area and still needs better understanding and characterization. Mesopores can exist within and between particles. Intraparticle mesopores exist in most carbons although there is some doubt that they actually are present in Super A carbon. Interparticle mesopores occur when the primary particles are very small e.g. micron range. This occurs for Super A carbon.

- Similar to mesopores, <u>macropores</u> (> 500 radius) exist both within and between particles depending on the size of the particle and the nature of the carbon. Above about 70,000 radius, these pores can be regarded as void space. They also contribute only their compressed gas share to the storage.

- The void spaces between the particles can be equivalent to half the volume of the particles themselves depending on the size and packing distribution. Filling of the container with carbon particles typically results in a bulk density two thirds that of the particles themselves.

Evidently from the above, the minimization of meso-, macro- and void volumes needs to occur for the maximization of methane adsorption in a given volume. Several possible ways exist for this to occur.

1. Intraparticle meso- and macropore volumes are dependent on the way the carbon is formed. Most carbons start off as larger granules of solid carbon sources such as coal or coconut shells etc; they are then activated by heating in controlled atmospheres of certain gases. This activation process creates the porous system and the integrity of much of the original particle is maintained. So far microporosity at the expense of meso- and macroporosity has not been sufficiently realized. The Super A carbon is activated by chemical means i.e. fusion with KOH. This results in a highly microporous material with a very fine particle size completely different from the original starting material.

2. Interparticle meso- and macropore volume is most likely to occur with the smaller particle Super A (average particle size ~ 5 microns). It is estimated that this interparticle porosity occupies ~10% of the total void volume between two particles, touching one another. High pressure crushing may decrease this and the void volume although it may have a deleterious effect on the mass transfer properties.

3. Much of the void volume can be eliminated by using a carbon monolith system to fit the container cylinders. This requires the molding or extruding of a mixture of the existing particles with a suitable binder.

The order in which these tasks are performed will be initially adhered to as outlined but as in all studies of this nature, feedback information may require some divergence. For example, if it is discovered that the property of one of the carbons does not meet our expectations then further work on mixtures with this material may be discontinued.

d2. Anticipated Results

The successful completion of the Phase I program will mean that the low storage density problem for compressed natural gas has been eliminated by the development of an adsorbed natural gas system. Most importantly, this means that natural gas can be seriously considered as a key alternative fuel for cars and trucks. It will minimize air pollution problems associated with gasoline-powered vehicles and position the United States better for energy resources. The Clean Air Act Amendments (CAAA) have put a relatively short timetable on U.S. cities to improve their air quality for ozone, carbon monoxide, and other toxics. Natural gas vehicles will allow that timetable to be met. Since the North American continent, and particularly the U.S. has vast natural gas reserves, this should put our nation in a much more favorable position for energy independence. Natural gas utilization will counteract the undesirable balance of trade associated with imported oil and reduce the U.S. reliance on oil supplies from unreliable sources in the Mid-East.

Phase II can then proceed to examine full sized natural gas storage tanks for vehicles and the best way to deal with rapid fill and discharge problems. Better tank designs may be necessary to allow heat to be transferred to the atmosphere effectively as discussed by Komodromos et al[11]. and the use of energy storage systems suggested by Jasionowski et al[12]. As part of Phase II, Mega-Carbon will proceed with the design and evaluation of a commercial plant to 1. produce the Super A carbon powder and 2. monolith forming facility to make the fused blocks of the carbon adsorbent. Mega-Carbon believes there will be considerable application of the Super A powder beyond natural gas storage and plans to market it in areas of chemical warfare, and as a adsorbent for the semiconductor industry to trap and contain arsine gas used in manufacturing epitaxial devices via MOCVD.

In Phase II, Mega-Carbon expects that the major automobile companies will be eager to collaborate on the development of an ANG system for evaluation of alternative fuels with strong pressure probably being in California to address the severe air pollution problems in Los Angeles, San Diego and adjoining cities. Also, the natural gas companies will, most likely, be anxious to collaborate on Phase II effort, since it has the potential to rapidly expand their market. Furthermore, many of the states seriously impacted by the Clean Air Act Amendments will probably be anxious to evaluate this system to identify how it can be implemented for the general public.

d3. Significance of Phase I Effort

Phase I is critical in establishing the technical feasibility of fusing the high capacity Super A carbon powders into a dense monolithic block for natural gas storage. A number of researchers and organizations have tested the Super A carbon for natural gas storage but none have really tried to solve the problem of low volumetric storage efficiency. The problem cannot be simply designed around, but instead requires some fundamental changes in the forming technology for the adsorbent. Mega-Carbon has identified the critical pieces of this puzzle and believes it can successfully develop a solution. The concepts can be shown in proof of concept tests in Phase I with relatively small and inexpensive equipment to test out the various adsorbent specimens. Phase II will require much bigger samples to measure heat effects, tank designs and how best to fill and discharge the storage tank.

e. Technical Objectives - Phase I

Although natural gas has significant advantages over other hydrocarbon fuels in terms of air pollution and domestic supply, its large scale application to transportation vehicles is impeded due to its low volumetric storage efficiency. There is a strong need to address this deficiency since it could be used in cars and trucks in urban areas and provide relief to air pollution problems, particularly ozone and carbon monoxide. Adsorbed natural gas will allow this scenario to happen. Mega-Carbon will develop the technology for storage of natural gas on carbon adsorbent blocks which will have an energy storage density sufficient to give a acceptable driving range. A combination of high performance activated carbon powder with improved packing and forming technology will be used to accomplish this goal. The following questions will be addressed through this effort:

* What is the preferred activated carbon powder or mixture of powders to use for the natural gas adsorbent?

* What geometric and physical factors are important in maximizing the packing density of carbon powders?

* How can the carbon powders be fused into a monolithic block without impairing the adsorption properties?

* What is the maximum volumetric storage capacity that can be achieved with the natural gas-carbon adsorbent block system?

* Are there severe limitations to fast-fill tank charging and how can these be alleviated?

* What types of carbon block geometries lend themselves to successful application and how can the adsorption-desorption heat problem be solved?

Objectives

The following objectives for Phase I will address the questions listed above:

1. Develop an understanding of methane adsorption on activated carbons and the role of pore size distribution with different versions of the superactivated Super A carbon (AX-21 and AX-24) and commercially available powders.

2. Identify how a combination of polymeric or inorganic binders in combination with surface active agents can lead to a highly dense carbon adsorbent block.

3. Define the equilibrium adsorption capacity of the carbon specimen blocks at

room temperature(70^{O}F) and the maximum storage value at 500 psi.

4. Define the limiting rate of methane adsorption on carbon adsorbent blocks with a dynamic adsorption test to simulate a "fast-fill" situation.

5. Examine the effect of geometric shape and size and how this impacts on the dynamics of methane adsorption relative to "fast-fill" and heat transfer.
6. Develop a carbon adsorbent block which will have a volumetric adsorption density in excess of 200 volumes natural gas/tank volume at 500 psi.

f. Work Plan- Phase I

Task 1. Development of Carbon Monolithic Blocks

The fabrication of carbon monolith specimens for subsequent testing requires several steps that are covered under the subtask categories. For experimental ease and convenience, the samples will be considerably smaller from the actual commercial size. Scale-up to commercial size blocks will be accomplished by judicious extrapolations of results with several different sizes.

Subtask 1.1 Characterization of Carbon Starting Materials

There are three carbon powders that will be used in the experimental formulations:

1. PX-21 (highest suraface area version)
2. PX-24 (medium surface area version)
3. Calgon BL

The first two carbons are both Super A carbons, the first having more BET surface area than the second; both can be characterized as gas adsorbing carbons. Calgon BL is a standard commercial carbon powder with less surface area but more open structure than the Super A type and therefore may have better transport properties. We plan to develop surface area and pore size distribution (PSD) data on each of these carbons using nitrogen sorption techniques. Each carbon will be tested by itself and then the PSD data mathematically combined based on various hypothetical mixtures to get an idea of how the PSD would be altered by blending of these carbon sorbents in various ratios. Also, since a surfactant will be used to reduce the surface charge between the small carbon particles, the impact of the surfactant treatment on surface properties will be established for these carbons to be sure that pore "blinding" is not taking place. In addition to the nitrogen sorption data, we will also obtain an estimate of adsorption capacity with an Iodine Number test.

Subtask 1.2 Development of Block Forming Technologies

Before molding or extruding the monolith block, the right combination of carbon, binder, dispersant and other additives need to be established to produce the right rheological and green strength properties. In-house technology has been developed in this area for carbon granules for drinking water treatment under an EPA contract. For example, Mega-Carbon has found that the one of the keys to maintaining surface area/adsorption properties is to protect the interior of the small carbon particles by pre-wetting with water or water in combination with a water-soluble dispersant. This seems to prevent the binding agent from entering the small micropores and plugging them. We have already explored some binding agents and dispersants in the EPA supported studies but this aspect still needs to be better defined. We will examine the following variables in the experimental grid as shown below.

Possible Binding Agents for Monolithic Blocks

Binder	**Comments**
Latex Enamel(LE)	Polymer binder with medium compressive strength of the extrudate
Polyurethane latex (PUL)	Polymer binder with high compressive strength of the extrudate
Polyacrylic latex (PAL)	Polymer binder with very high compressive strength of the extrudate
Polyacrylic acid (PAA)	
Mixtures of PAA, PUL and PAL	Similar to PUL binder
Betonite clay	Inorganic binder with medium compressive strength

Subtask 1.3 Formulation of Carbon Monolith Specimens

Extrusion, molding and casting will be used to form different shapes and sizes of samples for testing. Bonded blocks of carbon have been described by Redfarn et al[13] for purifying fluids. A perforated metal open block mold was used to mix the carbon powders first with a solvent, then draining and subsequently mixing with a dry solid soluble polymer. It was then finally evaporating off the remaining solvent to form a carbon block. The mold designs and techniques from their work may prove helpful in forming the various carbon blocks based on the high capacity Super A carbon powders. Discussions with IGT personnel indicate that extreme compressive forces were necessary to achieve a density of 0.7 g/cc in the carbon-filled cylinders used in their tests. This fact suggests that it is imperative to understand packing physics of small particles and how surface forces can be reduced to achieve maximum packing density. Mieville has been able to achieve densities of 0.6 g/cc in initial attempts using only the binder and no surfactant. Mega-Carbon is optimistic that with the aid of the surfactant technology plus some further compression in a press, the 0.7 g/cc density can be surpassed. The following approaches will be explored:

Parameter	**Experimental Approach**
Carbon blends	Varying ratios of PX-21.PX-24 and Calgon BL
Binder types	Polymer and Inorganic binders
Surface treatment	Surfactants to reduce surface charge
Particle size distribution	Bimodal size mix to increase packing density
Forming technology	Extruder, molds, and presses

Task 2. Characterization of Adsorption Properties

This work task will test out the various samples previously prepared and determine how suitable each sample is for adsorbing methane at 500 psi and room temperature. Follow-up experiments will then measure the rate that methane is adsorbed and desorbed and the corresponding adsorption heat effects.

Subtask 2.1 Equilibrium Adsorption Tests

Measurement of N_2 BET surface area and Iodine numbers will be performed on each sample. Equilibrium methane adsorption isotherms up to a pressure of 500 psig and at ambient temperature will then be measured. The experimental apparatus envisioned for the methane adsorption tests is shown below and has been used in other natural gas adsorbent studies[14]:

Figure 3 Apparatus for Methane Adsorption Tests

Subtask 2.2 Dynamic Adsorption Tests

The rates of adsorption of methane in each carbon sample will be measured in a manner to try and duplicate the filling of an empty adsorbent cylinder with a low pressure compressor(i.e. measurements to be conducted at a constant pressure of 500 psi). Particular attention will be paid to the rates of adsorption and at the same time the temperature of the carbon block will be monitored. Desorption rates will also be measured to simulate fuel delivery during vehicle acceleration and start-up. Block cooling occurs on methane desorption.

Task 3. Scale-Up Aspects and Application

After identifying the top performing carbon monoliths in small scale experiments, a few larger samples will be prepared and evaluated at conditions approximating those in a storage tank. The smaller samples are appropriate for isothermal tests since any heat for adsorption/desorption is rapidly transferred to the surrounding environment. However, the larger samples can be used to simulate actual tank filling on a vehicle. Also different shaped particles will be prepared to better understand how the natural gas can be transported into the interior of the carbon block. It is conceivable that small bore holes might be needed to provide access of natural gas to the block interior.

Subtask 3.1 Size Effects of Storage Blocks

Larger scale molds and presses will be used to prepare a larger block specimen (2 and 3 inch diameter pellets). These will then be evaluated and the rate of methane transport to the pellet interior established. We expect to insert a small 1/16" needle probe into the middle of the pellet and then sample the gas concentration inside following a sharp step change in methane pressure both in an increasing and decreasing step. Temperature will also be measured in the larger pellet at various points to determine "hot spots" during adsorption, etc. The diagram on the right gives an idea of how the larger carbon block specimen will be instrumented.

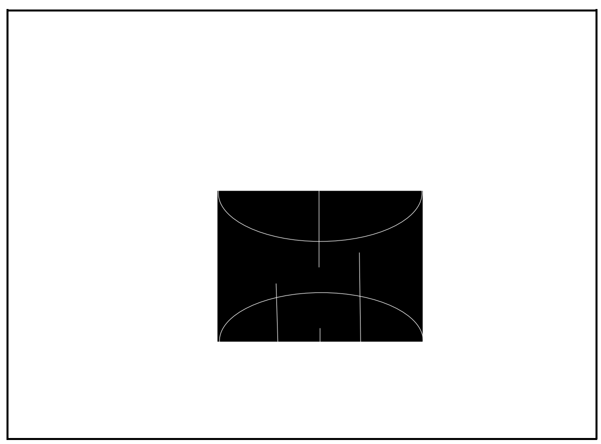


Figure 4 Larger Pellet of Carbon for Heat/Mass Transfer Effects

Subtask 3.2 Geometry Effects of Storage Blocks

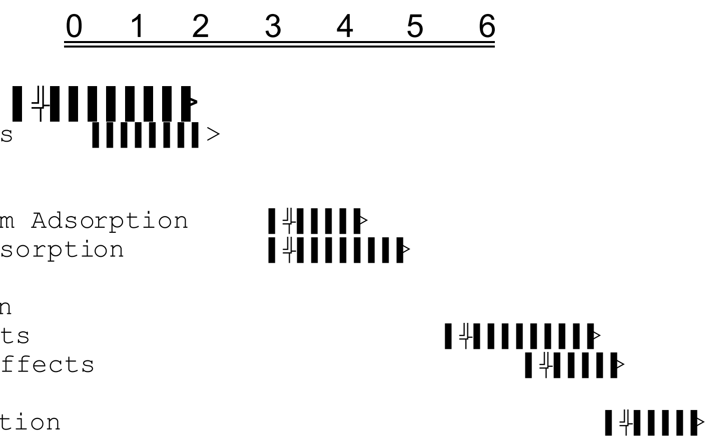
The fuel tank shape may not be a simple cylindrical tank as this has a relatively low surface to volume ratio and is not a preferred geometry for efficient heat transfer. Consequently, other carbon block shapes such as triangular prisms, pie shapes will be examined, and also the implanting of high thermal conductivity rods in the carbon block to enhance heat transfer. IGT used low melting point salt to control temperature rise but this has the disadvantage of occupying adsorption volume and lowering the overall energy storage density for natural gas. It is quite possible that heat transfer fins can be molded into the block which occupy less volume than the thermal energy storage (TES) device evaluated by IGT[15].

Task 4 Final Report Preparation

A final report will be prepared summarizing and analyzing the data for the carbon forming and natural gas adsorption tests. We plan to keep the analysis and monthly reporting very current so that this task will not involve excessive time.

Project Schedule

Month



Task 1: Forming of Blocks
- Subtask 1.1 Binders
- Subtask 1.2 Surfactants

Task 2: Adsorption Tests
- Subtask 2.1 Equilibrium Adsorption
- Subtask 2.2 Dynamic Adsorption

Task 3: Scale-Up/ Application
- Subtask 3.1 Size Effects
- Subtask 3.2 Geometry Effects

Task 4: Final Report Preparation

g. Project Description- Phase I

1. Project Objective

The applicant will investigate natural gas storage on high capacity carbon adsorbents for application to natural gas vehicles. Superactivated carbon powders will be fused into high density carbon blocks to achieve a volumetric energy storage density higher than has yet be attained for natural gas. The objective is to achieve a volumetric storage density in excess of 200 vol methane/volume of storage tank at 500 psig and ambient conditions.

2. Project Description

The work to be performed consists of the following tasks and subtasks:

Task 1. **Development of Carbon Monolithic Blocks**
Subtask 1.1 Characterization of Carbon Starting Materials
Subtask 1.2 Development of Block Forming Technologies
Subtask 1.3 Formulation of Carbon Monolith Specimens

Task 2. **Characterization of Adsorption Properties**
Subtask 2.1 Equilibrium Adsorption Tests
Subtask 2.2 Dynamic Adsorption Tests

Task 3. **Scale-Up Aspects and Application**
Subtask 3.1 Size Effects of Storage Blocks
Subtask 3.2 Geometry Effects of Storage Blocks

Task 4. **Final Report Preparation**

3. Performance Schedule

Task 1 to be completed 2 1/2 months after start of work.
Task 2 to be completed 4 1/2 months after start of work.
Task 3 to be completed 5 1/2 months after start of work.
Task 4 to be completed six months after start of work.

4. Reporting Requirement

The applicant shall provide a Final Report containing the data from the experiments performed according to Tasks 1, 2, and 3 along with analyses and conclusions based on these data.

h. Related Research

Dr. Ken Robinson, principal investigator of the proposed project, has been deeply involved in developing drinking water treatment carbons for the last 5 years. He has been successful in obtaining a patent based on the granulation of the Amoco superactivated carbon powder so that it can be used in granular form. This background is very helpful as spin-off applications of the superactivated carbon will be for gas masks, air filters, and of course, natural gas adsorption for the use in transportation vehicles.

Dr Rodney Mieville, the other key team member, has been intimately involved in the science of adsorption, since the start of his technical career. He has studied adsorption on reforming catalysts, molecular sieves and more recently was involved in a unique adsorbent system emission control of automobiles during cold-start. He is well qualified to participate on the research team on this project and is currently involved on developing drinking water carbons under an SBIR grant from the EPA.

Dr. John Butt, Walter P. Murphy professor of Chemical Engineering at Northwestern University is our other consultant on this project. Dr. Butt has a high distinguished career in catalysis and has been involved in a myriad of projects on adsorption. He is a member of the Catalysis Center at Northwestern and has access to all of its equipment. Additionally he has unique equipment in his personal laboratories at Northwestern for measuring active site population on catalytic surfaces by CO and NH_3 adsorption.

Mr. Walter Jasionowski, another consultant to Mega-Carbon, has spent the last seven years of his career at IGT working on gas adsorbent technology and its application to natural gas fueled vehicles. He evaluated adsorption, solution, clatheration, and microencapsulation; he determined that carbon-based adsorbents would store ore natural gas that achieved by compression only. His assistance and review on the more practical aspects of natural gas adsorption will be invaluable to moving Mega-Carbon's proposed project forward to a successful conclusion.

i. Key Personnel

Dr. Ken Robinson (Principal Investigator)

D.Sc. Ch.E. 1970, Washington University-St. Louis
M.S. Ch.E. 1964, University of Michigan
B.S. Ch.E. 1963, University of Michigan

Experience-
11/89 to 4/92: Amoco Corporation
Manager, Technical University Relations
Technical liaison with major universities in the United States. Technology transfer and coordination of external research.

11/84-01/89: Amoco Oil Company, Research and Development
Research Associate
Exploratory process research on heavy oil conversion, asphaltene solubility-solids formulation, and coal-resid coprocessing.

01/80-11/84: Standard Oil (Indiana)
Director, Coal Utilization

01/73-01/80: Amoco Oil Company, Research and Development
Project Manager
Petroleum Refining Research and Synfuels

1/65-1/73: Monsanto Company
Senior Development Engineer

Member of AIChE, ACS, Chicago Catalysis Society
Professional Engineer in Illinois
5 Patents, 14 Publications

Publications:

1. K. K. Robinson, and D. E. Briggs, "*Isothermal Pressure Drop Across Banks*

of Finned Tubes," Heat Transfer-Los Angeles, Chemical Engineering Progress Symposium Series, Vol. 62, No. 64, 177 (1966).

2. K. K. Robinson, A. Hershman, F. E. Paulik, and J. F. Roth, "*Catalytic Vapor Phase Hydroformylation of Propylene Over Supported Rhodium Complexes*," JOURNAL OF CATALYSIS, Volume. 15, No. 3, 245 (1969).

3. A. Hershman, K. K. Robinson, J. H. Craddock, and J. F. Roth, "*Continuous Propylene Hydroformylation in a Gas Sparged Reactor*," INDUSTRIAL AND ENGINEERING CHEMISTRY, PRODUCT R&D, Vol. 8, No. 4, 372 (1969).

4. K. K. Robinson, and E. Weger, "*High Temperature Pyrolysis of Propylene-Propane Mixtures*," INDUSTRIAL AND ENGINEERING CHEMISTRY FUNDAMENTALS, Vol. 10, No. 2, 198 (1971).

5. K. K. Robinson, A. Hershman, J. H. Craddock, J. F. Roth, "*Kinetics of the Catalytic Vapor Phase Carbonylation of Methanol to Acetic Acid*," JOURNAL OF CATALYSIS, Vol. 27, No. 3, 389 (1972).

6. E. C. Meyers, and K. K. Robinson, "*Multiphase Kinetic Studies with a Spinning Basket Reactor*," ACS Symposium Series No. 65, Chemical Reaction Engineering 37 (1978).

7. J. A. Mahoney, K. K. Robinson, and E. C. Myers, "*Catalyst Evaluation with the Gradientless Reactor*," CHEMTECH, 758 (December 1978).

8. R. J. Bertolacini, L. C. Gutberlet, D. K. Kim and K. K. Robinson, "*Catalyst Development for Coal Liquefaction*," EPRI, AF-574 (1977).

9. R. J. Bertolacini, L. C. Gutberlet, D. K. Kim, and K. K. Robinson, "*Catalyst Development for Coal Liquefaction*," EPRI AF-1084 (1979).

10. D. K. Kim, R. J. Bertolacini, J. M. Forgac, R. J. Pellet, and K. K. Robinson, "*Catalyst Development for Coal Liquefaction*," EPRI AF-1233 (1979).

11. D. F. Tatterson, K. K. Robinson, T. L. Marker, and R. Guercio, "*Coal Flash Pyrolysis in a Free-Jet Reactor*," I&EC RESEARCH, 27 1606 (1988).

12. K. K. Robinson "*Molecular Structure of Heavy Coal Liquids*," EPRI ER-6099-SR (1988).

13. R. J. Bertolacini, J. M. Forgac, D. K. Kim, R. J. Pellet, and K. K. Robinson "*Catalytic Functionality for Cool Hydroliquefaction*," Third International Conference--The Chemistry and Uses of Molybdenum (1979).

14. D. F. Tatterson, K. K. Robinson, R. Guercio, and T. L. Marker, "*Feedstock Effects in Coal Flash Pyrolysis*," Communication, I&EC, (1990).

Patents:

1. F. E. Paulik, K. K. Robinson, and J. F. Roth. "*Vapor Phase Hydroformylation Process*," US 3,487,112-British Patent 1,228,201.

2. D. K. Kim, R. J. Bertolacini, L. C. Gutberlet, and K. K. Robinson, "*Process for Coal Liquefaction and Catalyst*," US 4,257,922.

3. D. K. Kim, R. J. Bertolacini, L. C. Gutberlet, and K. K. Robinson, "*Process for Coal Liquefaction and Catalyst*," US 4,294,685.

4. J. S. Meyer, K. K. Robinson, J. M. Forgac, and D. F. Tatterson, "*Rapid Hydropyrolysis of Carbonaceous Solids*," US 4,326,944.

5. K. K. Robinson, "*Granulated Activated Carbon for Water Treatment*," US 4,954,469.

Dr. Rodney L. Mieville

Ph.D. Physical Chemistry, 1964, University of Western Ontario, Canada, Thesis: Photo-Addition of Methyl Mercaptan to Olefins
ARIC Chemistry, 1953, Northern Polytechnic London University, England

Experience:

1964-1992: Amoco Oil Research and Development
Associate Research Scientist

Worked on a variety of projects including combustion kinetics, oil additives and catalysis, petroleum processes, adsorption, and inorganic membranes. The catalytic work involved all aspects of catalysis including reaction kinetics, coke and poisoning deactivation, synthesis and characterization and assessment of adsorbent and catalytic materials.

1954-1961: British Petroleum Research and Development
Research Chemist

Member of the ACS, RSC (Royal Society of Chemistry), NATAS (Thermal Society), and the Catalysis Society of North America. Chairman of Surface Acidity Task Group of D.32 Committee ASTM
6 Patents, 25 Publications

Publications:

1. D. M. Graham, R. L. Mieville, R. H. Pallen, and C. Sivertz, "*Photo-Initiated Reactions of Thiols and Olefins, I. The Thiyl Radical Catalyzed Isomerization of Butene-2 and 1,2-Ethylene-d2*," <u>CANADIAN JOURNAL OF CHEMISTRY</u>, Volume 42 (1964).

2. D. M. Graham, R. L. Mieville, R. H. Pallen, and C. Sivertz, "*Photo-Initiated Reactions of Thiols and Olefins, II. The Addition of Methanethiol to Unconjugated Olefins*," CANADIAN JOURNAL OF CHEMISTRY, Volume 42 (1964).

3. R. L. Mieville and Garbis H. Meguerian, "*Mechanism of Sulfur-Alkyllead Antagonism*," IND. & ENG. CHEMISTRY, Volume 6, No. 4, December 1967.

4. R. L. Mieville "*Measurement of Microporosity in the Presence of Mesopores*," JOURNAL OF COLLOID & INTERFACE SCIENCE, Vol. 41, No. 2, November 1972.

5. R. L. Mieville "*Measuring Acidity by Temperature-Programmed Desorption*," JOURNAL OF CATALYSIS 74, 196-198 (1982).

6. R. L. Mieville "*Studies on the Chemical State of Cu during Methanol Synthesis*," JOURNAL OF CATALYSIS 90, 165-172 (1984).

7. R. L. Mieville "*Platinum-Rhenium Interaction: A Temperature-Programmed Reduction Study*," JOURNAL OF CATALYSIS 87, 437-442 (1984).

8. H. Deligianni, R. L. Mieville, and J. B. Peri, "*State of Pd in Active Methanol Synthesis Catalysts*," JOURNAL OF CATALYSIS 95, 465-472 (1985).

9. B. L. Meyers and R. L. Mieville, "*Reducibility of Ni-W Hydrocracking Catalysts*," APPLIED CATALYSIS, 14 (1985) 207-213.

10. R. L. Mieville, "*Coking Characteristics of Reforming Catalysts*," JOURNAL OF CATALYSIS 100, 482-488 (1986).

11. R. L. Mieville, "*The Chemical State of Copper during Methanol Synthesis*," JOURNAL OF CATALYSIS 97, 284-286 (1986).

12. R. L. Mieville, "*N_2 Adsorption Method for Measuring Certain Acid-Base Sites on Alumina*," JOURNAL OF CATALYSIS 105, 536-539 (1987).

13. David F. Tatterson and Rodney L. Mieville, "*Nickel/Vanadium Interactions on Cracking Catalyst*," I&EC RESEARCH (1988), 27, 1595.

14. R. L. Mieville and M. G. Reichmann, "*Temperature-Programmed Desorption Study of CO on Pt-Reforming Catalysts*," AMERICAN CHEMICAL SOCIETY (1989).

15. R. L. Mieville, "*Coking Kinetics of Reforming*," CATALYST DEACTIVATION (1991).

16. B. L. Meyers, R. S. Kurek, and R. L. Mieville, "*Microchemisorrption*," JOURNAL OF CATALYSIS, Volume 127, No. 2, (February 1991).

17. R. L. Mieville, presentation at the Symposium on Effect of Pore Size on Catalytic Behavior Presented before the Division of Petroleum Chemistry,

Inc., American Chemical Society in Miami Beach on September 10-15, 1976, entitled "*Temperature-Programmed Desorption Studies of Cracking Catalysts. Relationship with Microporosity and Activity*."

18. R. L. Mieville, presentation at the Symposium on Multimetallic Catalysts Presented before the Division of Petroleum Chemistry, Inc., American Chemical Society in Seattle on March 20-25, 1983, entitled "*Platinum-Rhenium Interaction: A Temperature-Programmed Reduction Study*."

19. R. L. Mieville, presentation at the Symposium on Zeolite and Shape Selective Catalysis Presented at the AIChE Annual Meeting in Houston on March 29-April 2, 1987, entitled "*Interacrystalline Zeolite Diffusion*."

20. R. L. Mieville and M. G. Reichmann, presentation at the Symposium on Preparation and Characterization of Catalysts Presented Before the Division of Petroleum Chemistry, Inc., American Chemical Society, Los Angeles Meeting on September 25-30, 1988, entitled "*Temperature-Programmed Desorption Study of CO on Pt Reforming Catalysts*."

21. R. L. Mieville, D. M. Trauth, and K. K. Robinson, General Papers (Poster Session) Presented Before the Division of Petroleum Chemistry, Inc., American Chemical Society in Miami Beach on September 10-15, 1989, entitled "*Asphaltene Characterization and Diffusion Measurements*."

22. R. L. Mieville, D. M. Trauth, and K. K. Robinson, presentation at the Symposium on Convection and Diffusion in Porous Catalysts at the AIChE Annual Meeting in San Francisco on November 5-10, 1989, entitled "*Asphaltene Characterization and Diffusion Measurements*."

23. B. L. Meyers and R. L. Mieville, "A Comparative Study of TGA and TPR on Ni-W Hydroprocessing Catalysts," (Paper # 111, ACS Meeting).

24. H. Deligianni, R. L. Mieville and J. B. Peri, "*Possible Relationships of Sites for CO Adsorption with Methanol Synthesis Activity of Supported Pd Catalysts*."

Patents:

1. R. L. Mieville, "*Improvements in or Relating to the Production of Oxygenated Organic Compounds*," US 882,863.

2. R. L. Mieville, "*Middle Distillate Fuel Oil Compositions Having Improved Pumpability*," US 3,807,975.

3. R. L. Mieville, "*Middle Distillate Fuel Oil Compositions Having Improved Pumpability*," US 3,807,990.

4. R. L. Mieville, "*Catalyst for Selective Hydrocracking of Alkylbenzenes*," US 4,171,290.

5. R. L. Mieville, "*Reforming with a Catalyst Comprising Iridium, Zirconia,*

and Alumina," US 4,297,205.

6. R. L. Mieville, "*Methods to be Used in Reforming Processes Employing Multi-Metallic Catalysts*," US 4,048,058.

j. Facilities/Equipment

Mega-Carbon has their laboratory and corporate offices in St. Charles, IL. The research facilities provide a full service organization in which all resources are under one roof: chemical engineering, computer technology, process assembly, and maintenance. Additionally Mega-Carbon has a full complement of chemical research equipment including UV spectrometers gas chromatographs, analytical balances, temperature controllers, furnaces, and test rigs. Presently Mega-Carbon is conducting research on an improved drinking water carbon for the Environmental Protection Agency through a Phase I SBIR grant. Additionally Mega-Carbon is located near Northwestern University, in Evanston IL, where it is possible to have analyses run on the adsorbents to determine surface area, examine its microstructure via scanning microscopy, and measure its adsorption capacity.

k. Consultants

Mr. Walter J. Jasionowski

B.S. Chemical Engineering, 19550, Illinois Institute of Technology

Present Position: Private Consultant

Experience:
1/76-9/92: Institute of Gas Technology
Senior Engineer
Conducted R&D on adsorption and storage of natural gas of vehicular applications, distribution of natural gas, assessment of gas distribution equipment, catalytic combustion and nonconventional gases.

2/68-12/75 CHEMTRIC, Inc.(subsidiary of AMGLO Industries)
Program Manager
Managed and supervised engineering staff and technical support on internal projects and contract work for government agencies including NASA, Air Force, EPA, and Rockwell International.

39 Publications

Publications:

1. Blazek, C.F., and W.J. Jasionowski, "*Charge/Discharge Characteristics of High Capacity Methane Storage Systems*", Proceeding of the 25th Intersociety Energy Conversion Engineering Conference, Reno, NV, August 12-17 (1990).
2. Blazek, C.F., and W.J. Jasionowski, "*Gaseous Fueled Vehicles: A Role for Natural Gas and Hydrogen*", National Hydrogen Association's 2nd Annual

U.S. Hydrogen Meeting, Washington, D.C. March 13-15, (1991).

3. Jasionowski, W.J. et al, "*A Thermal Energy Storage System for Adsorbent Low-Pressure Natural Gas Storage*," 1992 International Gas Research Conference, Orlando FL, November 16-19, (1992).

4. Jasionowski, W.J., and C.F. Blazek, "*Technical Support for Commercialization: Natural Gas-Fueled Cutting Torch Equipment*", IGT Final Report for Project 46029, Chicago, IL, Institute of Gas Technology, March (1990)

Walter Jasionowski has met with Mega-Carbon and agreed to serve as a consultant on the Phase I proposal described, herein. He has agreed to the salary indicated in the budget sheet and also the number of hours listed. A letter confirming his involvement is included as page 23.

Dr. John B. Butt

D.Eng. Ch.E. 1960, Yale University
M.Eng. Ch.E. 1958, Yale University
B.S. Ch.E. 1963, Clemson University

Academic Experience-

1969 to Present: **Northwestern University**, Department of Chemical Engineering, Professor. Walter P Murphy Professor

1964-1969: **Yale University**, Department of Engineering and Applied Science, Associate Professor

1963-1964: **Yale University**, Department of Engineering and Applied Science, Assistant Professor

1961: **University of Texas**, Visiting Professor of Chemical Engineering

Member of AIChE, ACS, Chicago Catalysis Society
New York Academy of Sciences
American Association for the Advancement of Science
Associate Editor, "Catalysis Reviews-Science and Engineering"
168 technical publications, 1 patent and 2 textbooks

John Butt has met with Mega-Carbon and agreed to serve as a consultant on the Phase I proposal described, herein. He has agreed to the salary indicated in the budget sheet and also the number of hours listed. A letter confirming his involvement is included as page 24.

l. Similar Grant Applications, Proposals, or Awards

No prior, current, or pending support for proposed work.

References

1. Field, Stanford, "1991 Oil Report, Chapter 13, Motor Vehicles of the Future", SRI International

2. "Natural Gas: A Solution To Vehicle Fuel Problem", Midwest Engineer, December (1990)

3. Schwarz, J.A. "Hydrogen on the Horizon ?", Chemical Engineering Progress, February (1993)

4. Quinn, D. F., and J.A. MacDonald, " Natural Gas Storage" *Carbon*, Vol. 30, No. 7, pp 1097-1103, (1992)

5. Kasuh, T. K. Okawa, and T. Maeda, "Low Pressure Storage Concept for Natural Gas Fueled Vehicles", 1992 International Gas Research Conference, November (1992)

6. Wennerberg, A.N. and T.M. O'Grady, U.S. Patent 4,082,694

7. Wennerberg, A.N. and T.M. O'Grady, "High Surface Area Activated Carbon, Petroleum-Derived Carbons, ACS Symposium Series 303, 302-309

8. Robinson, K.K., "Granulated Activated Carbon for Water Treatment", U.S. Patent 4,954,469, Sept 4, (1990)

9. Barton, S.S., J.R. Dacey, and M.J.B. Evans, "Experimental Evaluation of Selected Adsorption Media for Storage of Compressed Natural Gas", Transportation Energy Management Program, AF84-01, April (1984)

10. Aukett, P.N., N. Quirke, S. Reddiford, and S.R. Tennison, "Methane Adsorption on Microporous Carbons-A Comparison of Experiment, Theory, and Simulation", Carbon, Vol. 30, No.6, pp 913-924, (1992)

11. Komodromos, C. S. Pearson, and A. Grint, "The Potential of Adsorbed Natural Gas (ANG) for Advance On-Board Storage in Natural Gas-Fuelled Vehicles" 1992 International Gas Research Conference pp 588-597 (1992)

12. Jasionowski, W.J., K.J. Kountz, C.F. Blazek, and A.J. Tiller, "A Thermal Energy Storage System for Adsorbent Low-Pressure Natural Gas Storage", 1992 International Gas Research Conference, pp 598-611 (1992)

13. Redfarn, C.A., and J. Bedfrod, U.S. Patent 4,000,236

14. Barton, S.S., "Proposal for 'Experimental Evaluation of Selected Adsorption Media for Storage of Compressed Natural Gas'," Royal Military College of Canada, Kingston, October 20, (1981)

15. Blazek, C.F., and W. Jasionowski, "The Institute of Gas Technology's Adsorbent Research Program", GRI NGV Gas Storage Workshop, Chicago IL, July 1, 1992