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CATALYTIC CRACKING OF DIESEL FUEL FOR ARMY FIELD BURNERS

Part III

Study of Catalytic Cracking and Steam Reforming

by
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and
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December 1999

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December 1995 - December 1997

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This is one of three reports of a study to develop an advanced fuel conversion process to produce gaseous fuel for field burners. In this process, a gaseous mixture of light hydrocarbons is produced via the catalytic cracking of logistic fuels like diesel and JP-8. This innovative concept leads to a new generation of field burners which are relatively simple, reliable, easy to start and environmentally favorable. This report (Part III) documents an intense study of both catalytic cracking and steam reforming of diesel. Along with exploring commercially available catalysts, Aspen Systems also designed and synthesized diesel cracking/reforming catalysts, and tested their performance for application. The technical approach of the centralized fuel processing unit was modified to be a combination of catalytic cracking and steaming reforming, instead of a single catalytic cracking as proposed originally. The first report (Part I, NATICK/TR-00/004) documents and demonstrates the feasibility of a catalytic cracking process to produce hydrogen and light hydrogen molecules from diesel with a minimal yield of heavy hydrocarbon residues. A second report (Part II, NATICK/TR-00/005) contains results of objectives to demonstrate the long-term peprformance (durability/reliability) of a catalytic cracking process developed during Phase I and to produce a prototype catalytic burning unit.

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Preface

The study reported here was conducted under U.S. Army Soldier and Biological Chemical Command (SBCCOM), Soldier Systems Center, contract No. DAAK60-94-C-0030. The work was performed by Hamed Borhanian , Jae Ryu, and Alan Zhou of Aspen Systems, Inc., Marlborough, MA. Mr. Donald Pickard of the Soldier Systems Center was the project officer for the contract.

This report is one of a series of three. The references for the other reports are:

Rye, J., (1994). *Catalytic Cracking of Diesel Fuel for Army Field Burners. Part I Feasibility of Producing Gaseous Fuel from Diesel Fuel via a Catalytic Cracking Process.* (Tech. Rep. NATICK/TR-00/004). Natick MA: Soldier Systems Center, U.S. Army Soldier and Biological Chemical Command (SBCCOM).

Borhanian, H., Ryu, J., Zhou, A., (1995). *Catalytic Cracking of Diesel Fuel for Army Field Burners. Part II: Demonstration of Long Term Performance and Production of a Prototype Catalytic Cracking Unit* (Tech. Rep. NATICK/TR-00/005). Natick, MA: Soldier Systems Center, U.S. Army Soldier and Biological Chemical Command (SBCCOM.

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CATALYTIC CRACKING OF DIESEL FUEL FOR ARMY BURNERS

PART III
Study of Catalytic Cracking and Steam Reforming

Executive Summary

The overall objective of this project was to develop an advanced fuel conversion process to produce gaseous fuel for field burners. In this process, a gaseous mixture of light hydrocarbons is produced via the catalytic cracking of logistic fuels like diesel and JP-8. This innovative concept leads to a new generation of field burners that are relatively simple, reliable, and easy to start. Furthermore, the gaseous light hydrocarbons promote clean combustion, which is environmentally favorable.

The entire project was divided into four phases. In Phase I, Aspen System successfully identified a commercial catalyst, Zeolite HZSM-5, as the diesel cracking catalyst. In Phase II, Aspen Systems modified the M-2 gasoline burner with a new catalytic generator, transforming it into a multi-fuel blue flame burner. Aspen Systems further investigated the diesel cracking phenomenon during Phase III, to provide design criterion for a centralized fuel processing unit, which converts liquid fuel to gaseous fuel. The proposed technical objective of Phase Iii was to design and fabricated a prototype of the centralized fuel processing unit. But the HZSM-5 could not provide a high enough conversion efficiency of liquid to gaseous fuel, so intensive research was carried out during Phase III, to find a new type of diesel cracking catalyst efficient enough for the centralized fuel processing unit.

During Phase III, both catalytic cracking and steam reforming of diesel were studied intensively. Along with exploring commercially available catalysts, Aspen Systems also designed and synthesized diesel cracking/reforming catalysts, and tested their performance for this application. As a result, Molybdenum Carbide was identified to be the most promising candidate for catalytic cracking and steam reforming of diesel. The technical approach of the centralized fuel processing unit was modified to be a combination of catalytic cracking and steaming reforming, instead of a single catalytic cracking as proposed originally.

The advantage of steam reforming is that a significant amount of hydrogen can be produced and supplied to a fuel cell system to generate electrical power in the field. Thus, based on this technology, an integrated co-generation system can be developed that produces gas and electricity in the same unit. The system can use several kinds of logistic fuel such as gasoline, diesel and JP-8, with a small amount of water, to provide gaseous fuel and electricity for field operations. This integrated co-generation system will be highly efficient and environmental friendly, with numerous applications both in the military and commercial sectors.

1. PHASE IV TECHNICAL OBJECTIVES

The overall objective of this project was to develop an advanced fuel conversion process to produce gaseous fuel for field burners. By the end of Phase III, it was found that the conversion efficiency of liquid to gaseous fuel had to be further increased to realize a viable centralized fuel processing unit. Thus, the primary goals of Phase III of this three phase program were rearranged to maximize the yield of the gaseous hydrocarbons produced by the catalytic cracking process, or a combination of catalytic cracking and steam reforming processes. For a centralized fuel processing unit, a liquid to gas conversion efficiency of 85% (based on HHV) or higher is needed. For multi-burner operation, the required fuel flow rate is 20 lb./hr. As a results of these requirements, the additional set of Phase III objectives were developed as follows:

- To maximize the yield of light hydrocarbons by optimizing the catalytic cracking process. Parameters to be studied include catalyst temperature, residence time, feedstock to catalyst ratio, and catalyst specifications such as transition metal-based, transition metal carbide-based, zeolite-based, etc.;

- To study the efficiency of steam reforming to generate gaseous fuel. Parameters to be studied include steam ratio, catalyst temperature, feedstock to catalyst ratio, and catalyst specifications such as transition metal-based, transition metal carbide-based, etc.;

- To design and synthesize steam reforming catalyst particularly for the purpose of gaseous fuel generating; and

- To conceptualize a prototype centralized fuel processing unit for field burners with multi-burner capability utilizing the optimized catalytic cracking and steam reforming process.

The achievements during Phase III (December 1996 to December 1997)) are discussed in the following sections.

2. INTRODUCTION

2.1 Catalytic Cracking of Hydrocarbons

Cracking of heavy hydrocarbons to produce light hydrocarbons has been practiced for almost two hundred years, and may be classified into two categories: thermal cracking and catalytic cracking. Thermal cracking involves many chemical reactions, including dehydrogenation, polymerization, and isomerization. However, the primary chemical reaction involves the formation of free radicals by the random loss of hydrogen atoms to other free radicals, followed by a carbon chain rupture at the hydrogen deficient carbon atom. Thus, many different carbon chain lengths are possible in the final product as a result of thermal cracking.

The use of catalysts to modify the yield and quality of cracked products was initiated as early as 1915 and was successfully commercialized in the 1930's. Since then, major efforts have been focused on the development of highly efficient catalysts and economical cracking processes [1-4] in the petroleum industry to increase the yield of valuable products, such as high octane gasoline. In parallel, there has been a continued effort to produce synthetic fuel from coal utilizing the catalytic cracking process. Both syngas and liquid fuels have been commercially produced via catalytic cracking of tar. [5-8] The exact mechanism involved in catalytic cracking of hydrocarbons is not precisely known, although a staggering amount of research has been published on product yields of catalysts, and effects of operational variables and feedstock quality.

When cracking occurs, there is a hydrogen deficiency in the reaction, and complex reactions follow to reconcile the unsaturated light hydrocarbons (light olefins). Reactions that may occur include polymerization, formation of aromatic hydrocarbons, and coking. Most of these secondary reactions of light olefins are undesirable and reduce the yield of gaseous products. The degree of these secondary reactions, which will determine the product distribution in the cracking process, depends heavily upon process conditions. Furthermore, the addition of various cracking promoters or product stabilizers, such as water, air, or hydrogen (recycled from the product stream), can significantly suppress the above-mentioned secondary reactions. However, supplying water to the fuel conversion process may be logistically unfavorable for certain Army field operations, and air injection or recycling hydrogen product may require a power source.

As mentioned above, catalytic cracking of heavy hydrocarbons to produce light hydrocarbons is a well established process in the petroleum and coal industries. However, the specific process of catalytic cracking of diesel to produce light hydrocarbons has not yet been investigated. There have been intensive but less than fruitful research efforts within the U.S. military to produce hydrogen via reforming of diesel. The purpose of these programs was to provide electricity utilizing phosphoric acid fuel cell (PAFC) technology at remote sites.[9, 10] As a result of these efforts, various reforming processes have been successfully developed to produce hydrogen-containing gas mixtures from diesel through slight modifications to well-developed industrial processes.

Independently, there has been a worldwide effort to develop an onboard fuel processing unit for the production of gaseous fuels from liquid hydrocarbons in order to minimize air pollution from internal combustion engines for automobiles.[11] For this application, the gaseous product was typically comprised of mostly hydrogen with a small amount of hydrocarbon impurity. As a result of this program, advanced catalysts and catalytic cracking processes were successfully developed. However, for the internal combustion engine, the requirements in fuel product distribution were rather stringent, and, therefore, the onboard fuel processor for automobiles has not yet been realized. Currently, worldwide concerns for a clean environment have re-ignited the interest in the development of onboard fuel processors for the production of zero emission vehicles.

2.2 *Steam Reforming of Hydrocarbons*

In early twentieth century, the process of steam reforming was developed as an economical method to supply hydrogen for the direct synthesis of ammonia. Originally, coke was used as the feedstock. Besides hydrogen, carbon monoxide and carbon dioxide were also generated as byproducts. Subsequently, in the areas where natural gas was available in large quantities, interest centered around steam reforming of methane as the feedstock. The feedstock for steam reforming varies widely from methane to larger paraffins (C_nH_{2n+2}), or to more complex compounds sharing empirical formulae which lie between $CH_{1.9}$ and $CH_{2.4}$. It may contain sulfur or chlorine compounds as well.

In the industry, the objective of the catalytic steam reforming process is to extract the maximum quantity of hydrogen held in water and the hydrocarbon feedstock. The reforming of natural gas utilizes two simple reversible reactions: the reforming reaction (1) and the water-gas shift reaction (2).

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2 \qquad \Delta H = +206\ \text{kJ mol}^{-1} \qquad (1)$$
$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad \Delta H = -41\ \text{kJ mol}^{-1} \qquad (2)$$

The reforming reaction is strongly endothermic, so the forward reaction is favored by high temperature as well as by low pressure. The shift reaction is exothermic and is favored by low temperature but is largely unaffected by changes in pressure. Another important factor in steam reforming of hydrocarbons is the steam ratio. Steam ratio is defined as the mole ratio of water to carbon atoms in the feed. As a rule of thumb, steam ratios of 3.5 to 4.5 are adopted in the industry. At low steam ratios, the methanation reaction begins to dominate.[12] Since methane is the desired product for the burner system in this research, the steam ratio used in this study was much lower than that used in the industry. When diesel was used as the feedstock, a steam ratio ranging from 0.1 to 0.2 was used (this was coincidentally equivalent to the volume ratio of water to diesel in the feed).

2.3 Fuel Processing Research at Aspen Systems, Inc.

During Phase I of this program (March 23 to November 23, 1994), Aspen Systems successfully demonstrated the feasibility of producing gaseous fuel from diesel via a catalytic cracking process.[13] Both the clean combustion of diesel and a wide range of firing rate controllability were clearly demonstrated using the M-3 burner head. The total energy required to crack one gallon of diesel fuel was determined to be 730 Btu and 680 Btu (with and without the heat loss incurred during the operation, respectively), which is less than the energy required for the vaporization of diesel (theoretical value of 781 Btu/gallon).

During Phase II of this project (December 27, 1994 to August 14, 1995), Aspen Systems, Inc. successfully demonstrated the durability and reliability of the catalytic cracking technology by operating a prototype catalytic cracking burner on diesel for 300 hours.[14] Clean combustion of diesel and wide ranges of firing rate were clearly demonstrated on a slightly modified M-2 burner during the entire 300-hour test. There was no sign of coking and sulfur poisoning in the catalyst (which consumed about 970 pounds of diesel fuel). Sulfur was detected only in an insignificant portion of the catalyst. This result indicated that fuel-bound sulfur was not accumulating in the catalyst as a solid and/or liquid by-product of the reaction.

Also in Phase II, Aspen Systems, Inc. successfully fabricated a well-functioning prototype of a catalytic cracking burner unit by slightly modifying an existing M-2 burner unit. For the prototype burner, we developed many types of the catalytic cracking vaporizers utilizing nickel coated copper tubing. The new design allowed for a preheating time of less than 5 minutes. Two catalytic cracking vaporizers were fabricated and delivered to Army Natick RD&E Center for performance evaluation. Multi-fuel capability of the catalytic cracking burner system was successfully demonstrated by operating the burner on Exxon No. 2 diesel (0.025% sulfur), Army No. 2 diesel (maximum 0.5% sulfur), JP-8, and gasoline.

Under a ARO/ARPA program, Aspen Systems successfully developed an advanced fuel conversion process to produce gaseous fuels, such as hydrogen and light hydrocarbons, from logistic fuels, such as cetane, diesel and JP-8, utilizing the innovative catalytic cracking technology.[15] The overall objective of the ARO/ARPA program was to develop a new fuel conversion process which operated at relatively low temperatures and pressures at high conversion efficiencies. In the program, we found that about 75 % and 63 % of the high heat value (% HHV) of the feedstock was recovered as C_4 and lighter hydrocarbons from the catalytic cracking of cetane reference fuel ($C_{16}H_{34}$) and No. 2 diesel, respectively. The hydrogen concentration in the effluent gas stream was more than 64 mole % (about 20 % HHV of the feedstock). In addition, we found that hydrogen sulfide (H_2S) was the only sulfur-bearing compound in the effluent gas stream.

During the ARO/ARPA program, Aspen Systems established a new base of technology and process for developing a compact, reliable, and relatively simple diesel reformer. Several crucial technical obstacles involved in current diesel reforming processes can be resolved by employing our innovative technologies, such as the following:

- Fuel bound sulfur can be readily removed from the gas phase at relatively low temperatures (below 700°C) and near ambient pressures without using air or water in the feedstock;
- The entire reforming process can be established at low temperatures (below 700°C) and with far less demand of air and water; therefore, reformer system peripherals can be greatly reduced in size and complexity. This technology offers a very wide turn down ratio; and
- The heavy petroleum distillates in diesel, which usually lead to coking in ordinary diesel reforming processes, can be converted to light hydrocarbons without coking. We believe that reforming light hydrocarbons (C_4 or lighter) should be easier than reforming diesel.

In another project supported by advanced Research Project Agency, Aspen System is developing an advanced onboard high purity hydrogen production subsystem for fuel cell vehicles. High purity hydrogen will be produced from liquid hydrocarbons utilizing both catalytic cracking and steam reforming. In the latest effort of this project, Aspen System tested a mixture of hydrocarbons with the molecular size between C_{10} to C_{12} as the feedstock for steam reforming. The conversion efficiency of liquid to gaseous fuel was 100% at a reactor wall temperature as low as 500°C. The effluent steam consisted of hydrogen, methane, carbon monoxide, carbon dioxide and water.

3. PHASE IV EXPERIMENTS

3.1 Test Setup and Materials

During the Phase IV, we slightly modified the experimental set-up and testing procedures used during Phase III [16]. Figure-1 is a Schematic of the Catalytic Cracking Experiment Setup.

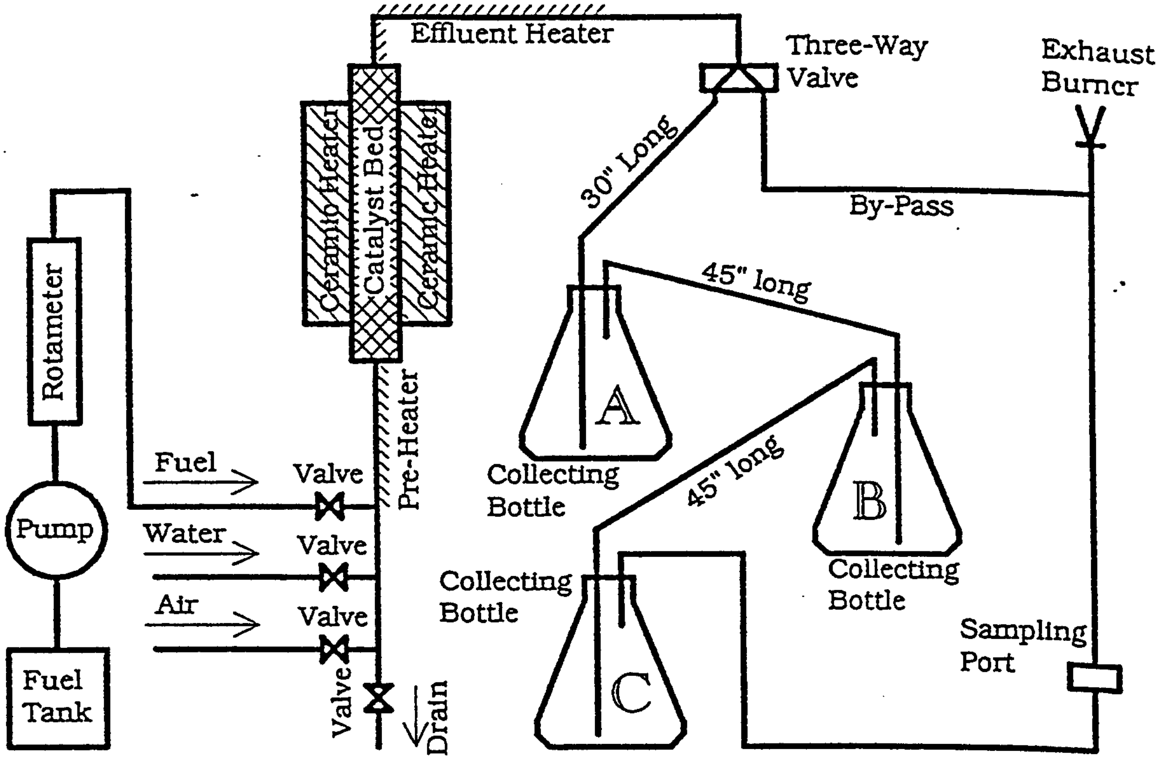


Figure- 1: Schematic of the Catalytic Cracking Experiment Setup

A in-line liquid phase sample collecting port was install between the three-way valve and the collecting bottle A. This new device allowed the collection of an instantaneous sample of the liquid phase in the effluent, without interrupting the run.

The liquid metering pump (MILTON ROY, LMI J051-191) used during Phase III for fuel delivery was replaced by two more precise metering pumps from Eldex, one for fuel, and the other for water when testing steam reforming. Their model numbers are A-120-S and A-30-S respectively.

3.2 New Gas Chromatography Analysis

In order to get the complete picture of the products of catalytic cracking and steam reforming, we set up a second Gas Chromatograph, a Hewlett Packard 5890 Series II, and put it in use side by side with the first GC, a Varian 3300. The HP 5890 was specially customized to separate heavy hydrocarbons up to C_{36}, but still retained the ability to handle gas phase samples such as C_1 to C_4. The Varian 3300 was optimized to separate hydrogen and gaseous or light hydrocarbons up to C_7. The combination of these two GCs, along with a newly installed liquid phase sampling port in the effluent line, gave us, for the first time, the ability to analyze the instantaneous composition of both gas and liquid phase while the system was running. This ability allowed us to monitor the changes inside the catalyst bed much more closely.

4. TEST RESULTS AND DISCUSSIONS

4.1 New Types of Catalyst for Diesel Cracking

During Phase IV, in order to promote the conversion efficiency of liquid to gaseous fuel, a number of new catalysts and combinations of catalysts were tested for diesel cracking. Catalysts studied included both commercially available ones and those designed and synthesized at Aspen Systems.

4.1.1 LZY-84 Catalyst

LZY-84 is a Y-type zeolite manufactured by UOP, it has a Si/Al ratio of 2.95. It is basically the same zeolite as USY from United Catalyst. Because United Catalyst has no plan to produce any more USY in the near future, LZY-84 was brought in as the substitute. Previous results indicated that, for diesel cracking, HZSM-5 was a better catalyst than USY; but for cracking the remaining liquid of diesel cracking, USY performed better. This suggested that a combined catalyst bed consisting of both types of zeolite should be further studied.

Two tests involving LZY-84 were carried out, both at 500°C wall temperature, 100 psig reactor pressure and a low fuel flow rate of 0.8 cc/min. In one test, LZY-84 with Nickel gave a low conversion efficiency of 15% for diesel cracking, which is not surprising given the performance of USY on diesel. In the other test, the catalytic reactor was split into two sections to contain two catalyst beds in series. HZSM-5 was used upstream, and LZY-84 downstream. The ratio of HZSM-5 to LZY-84 was 60/40 both in terms of weight and volume. This combined catalyst bed gave a conversion efficiency of 45% on diesel.

Several other types of catalyst were tested at the same temperature, pressure and fuel flow rate, including, Nickel/ HZSM-5, Nickel/ LZY-84, Nickel/Molybdenum/HZSM-5 and HZSM-5. For all these types of catalyst, the catalyst temperature, which was monitored by a thermocouple probe allocated at the geometric center of the catalyst bed, was above 430°C. For the combined catalyst, the catalyst temperature was only 406°C, while the conversion efficiency was the second highest (see Figure-2).

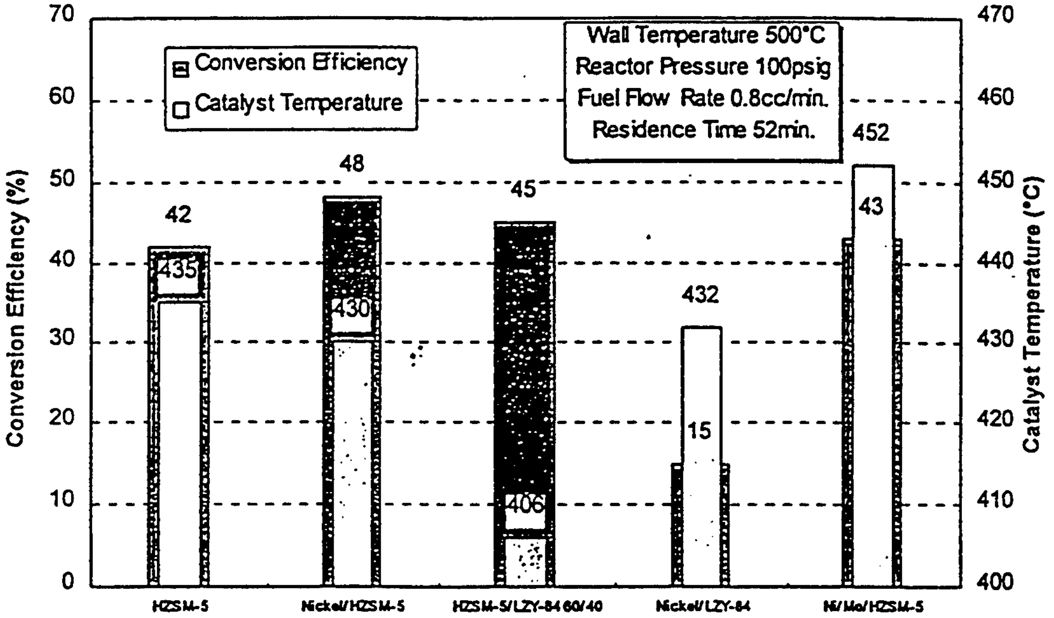


Figure- 2: **Comparison of the Performance of Different Types of Catalyst at 500°C and 100 psig.**

When diesel was cracked by HZSM-5 into smaller molecules, larger hydrocarbon molecules, like aromatics, branch paraffins and olefins, were also generated. These high-boiling-point large components along with the carbon residue were the cause of cocking, which resulted in the deactivation of the catalyst and clogging. Because of the similarity between the USY and the LZY-84, it was reasonable to expect LZY-84 to promote cracking of large-molecule hydrocarbons as well. This removal of heavy components would depress cocking inside the catalyst bed. Like the cracking diesel, cracking of large-molecule hydrocarbons is endothermic as well, explaining the lower catalyst temperature of the combined catalyst. In earlier test results, a lower catalyst temperature usually led to a longer catalyst lifetime, but it was achieved by raising fuel flow rate at the price of lower conversion efficiency. Together with HZSM-5, LZY-84 showed the potential of extending the catalyst life time without compromising the conversion efficiency.

4.1.2 Nickel-Treated HZSM-5 Catalyst

As indicated by previous test results, hydrogen is one of the byproducts of the catalytic cracking of diesel. This is specially the case at high reactor temperature. But in terms of generating gaseous fuel via cracking diesel, the presence of hydrogen gas in the product has a negative effect on the overall conversion efficiency. In the process of catalytic cracking, H-C and C-C bonds in the hydrocarbon molecules are first broken. These large chain-like molecules are turned into smaller piece called radicals. These unstable radicals are either shorter carbon chains or free hydrogen atoms that need to recombine with each other to form stable molecules. The desired end products are C_1 to C_4 paraffins and olefins, which are in the vapor phase at room temperature. To form the desired products, free hydrogen atoms have to combine with unsaturated shorter carbon chains. If they combine with each other to form hydrogen gas, unsaturated carbon chains have to bond with other carbon atoms, resulting in large-molecule hydrocarbons and even carbon residue. Given the complicated random process of catalytic cracking, generation of hydrogen gas is not completely avoidable, so in order to promote the yield of gaseous fuel, it is important to make use of the generated hydrogen. This is done through a process called hydrogenation, in which hydrogen atoms are attached to hydrocarbon radicals to stabilized them, thereby improving the overall conversion efficiency. A hydrogenation catalyst is needed in this process to force free hydrogen atoms to combine with unsaturated carbon chains instead of combining with each other.

Nickel has been proven in the industry to be an effective hydrogenation catalyst. A procedure of implanting nickel on zeolite by liquid ion-exchange was developed at Aspen Systems. 100 g of HZSM-5 or LZY-84 zeolite was immersed in 200 cc of 10w% nickel nitrate solution for 5 hours under stirring. Then the catalyst was dried at 125°C and calcinated at 400°C. Finally the catalyst was activated by hydrogen gas at 400°C before use. The nickel content in the catalyst treated this way was between 4 to 6w%.

Batches of nickel treated catalyst were tested at 100 psig and 500 psig and temperatures ranging from 500°C to 650°C. Two fresh batches of nickel treated HZSM-5 were tested at 500°C under 100 psig, as shown in Figure-3, their average conversion efficiency was 48%, comparing with that of untreated HZSM-5 which was 42%,. At 600°C and 500 psig, the improvement of nickel treatment was more pronounced: the conversion efficiency rose from 46% to 64%. (Figure-3)

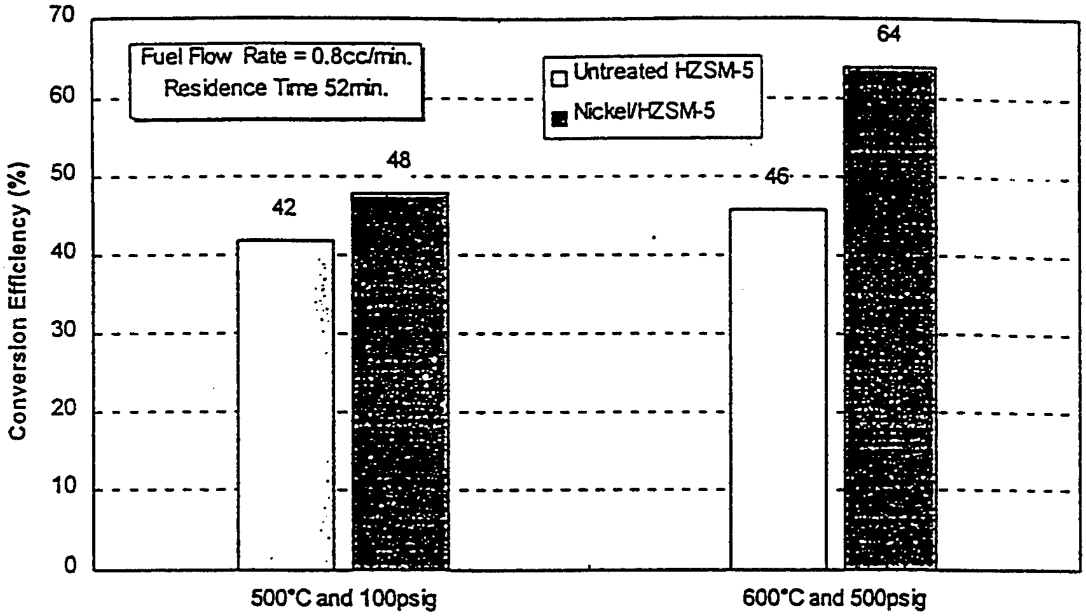


Figure- 3: Improvement of the Performance of HZSM-5 by Nickel.

Another notable difference in the case of nickel treated HZSM-5 was the delay for the first drop of remaining liquid to show up in the collecting bottle. In the experimental setup, effluent stream out of the reactor was controlled by a three-way valve leading to either the by-pass or collecting bottles (Figure 1). For every test, only after all the operating parameters (like temperatures, pressure and fuel flow rate) became stable, was the effluent stream switched from by-pass to collecting bottles. The first collecting bottle was located 30 in. downstream of the three-way valve, so it took some time for the remaining liquid to pass through this distance and show up in the first collecting bottle. This time delay was 2 to 5 minutes for all the previous tests, but for the test of nickel treated HZSM-5 it was 20 to 34 minutes.

The long time delay for the remaining liquid only occurred when the catalyst was used for the first time. One batch of the Nickel/HZSM-5 was tested on February 12, 1997, the first drop of remaining liquid did not show up until 20.5 minutes after the three-way valve was switched and 19 ml of fuel had been pumped into the reactor. The whole test lasted for 4.3 hours and the conversion efficiency was 44%. The same batch of catalyst was tested again the next day, this time the first drop showed up in 5 minutes and the conversion efficiency dropped to 27%. When the conversion efficiency for Nickel/HZSM-5 was plotted against running time, a similar (dropping) curve was obtained regardless of the operating parameters. The conversion efficiency started very high at the beginning, theoretically 100% for the first 20 to 34 min., until the first drop of remaining liquid showed up, then dropped sharply and gradually flattened in 2 to 4 hours. Figure-4 is an example of these curves.

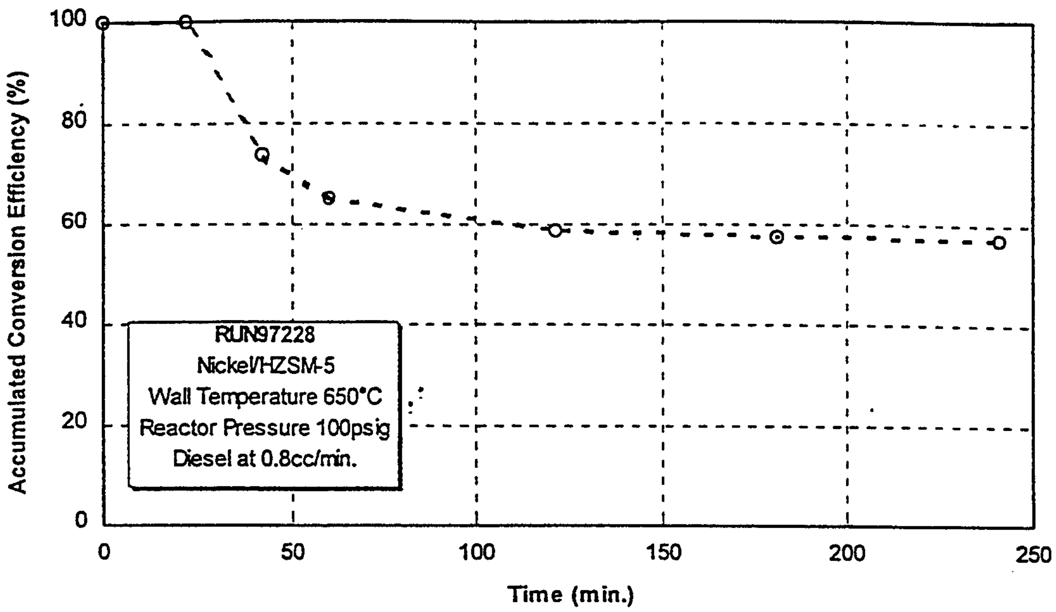


Figure- 4: Accumulated Conversion Efficiency vs. Running Time for Nickel/HZSM-5.

This "dropping" curve of conversion efficiency against running time suggested that the catalyst was deactivated in 1 to 2 hours. It was presumed that the presence of nickel was the reason for the increased performance, and the instability of the nickel was the cause of the degradation.

In order to stabilize nickel ions in zeolite, one batch of Nickel/HZSM-5 was modified further by molybdenum hexacarbonyl vapor. This HZSM-5 with both nickel and molybdenum ions was tested at 500°C and 100 psig, but the conversion efficiency turned out to be 43%, compared with those of 42% and 48% for untreated HZSM-5 and Nickel/HZSM-5. As molybdenum was not effective in stabilizing nickel, other hydrogenation promoting metals or other methods of stabilizing nickel needed to be explored.

4.1.3 Platinum-Treated HZSM-5 Catalyst

As with nickel, platinum is also known in the petroleum industry to promote hydrogenation, only with higher activity and stronger resistance to poisoning. A liquid immersion process was developed during this reporting period to implant platinum onto the surface of HZSM-5 and other types of zeolite. A certain amount of platinum solution was poured into zeolite, just enough to fill all the pore volume. Then this wet zeolite was dried in an oven. The platinum content of Pt/HZSM-5 synthesized by Aspen Systems was 0.1% by weight. At 500°C and 100 psi, it gave a conversion efficiency of 49%, compared with 48% for Ni/HZSM-5 and 42% for plain HZSM-5 (see Figure-5).

4.1.4 HZSM-5 with HYC-652 Catalyst

A common known practice in the petroleum industry is to utilize molybdenum to stabilize nickel. Aspen Systems treated some HZSM-5 with both nickel and molybdenum, but the results were not satisfactory. Additionally, the process of implanting molybdenum through vapor deposition is highly toxic and hard to control. Hence, a better method has to be found to combine nickel and molybdenum with zeolite.

HYC-652 is manufactured by Acreon Catalysts. It is a zeolite based catalyst in the form of extrudates containing nickel and molybdenum oxides. According to its MSDS, it has a nickel oxide content of 1-6Wt.%. and molybdenum trioxide content of 4-25Wt.%. It was mixed with plain HZSM-5 with a weight ratio of 1:1, then tested at 500°C and 100 psi. The resulting conversion efficiency was 50% at the end of a 4-hour run, compared to 48%, 43% and 42% for Ni/HZSM-5, Ni/Mo/HZSM-5 and plain HZSM-5, respectively (see Figure-5). Although the 1:1 weight ratio used in the test was not necessarily optimum, the mixed catalyst performed as well as Ni/HZSM-5, and better than Ni/Mo/HZSM-5. So instead of implanting nickel and molybdenum directly onto zeolite, we can just simply mix HYC-652 with HZSM-5. This reduces the cost and complexity of preparing the catalyst, since the implanting process is lengthy for nickel and highly toxic for molybdenum.

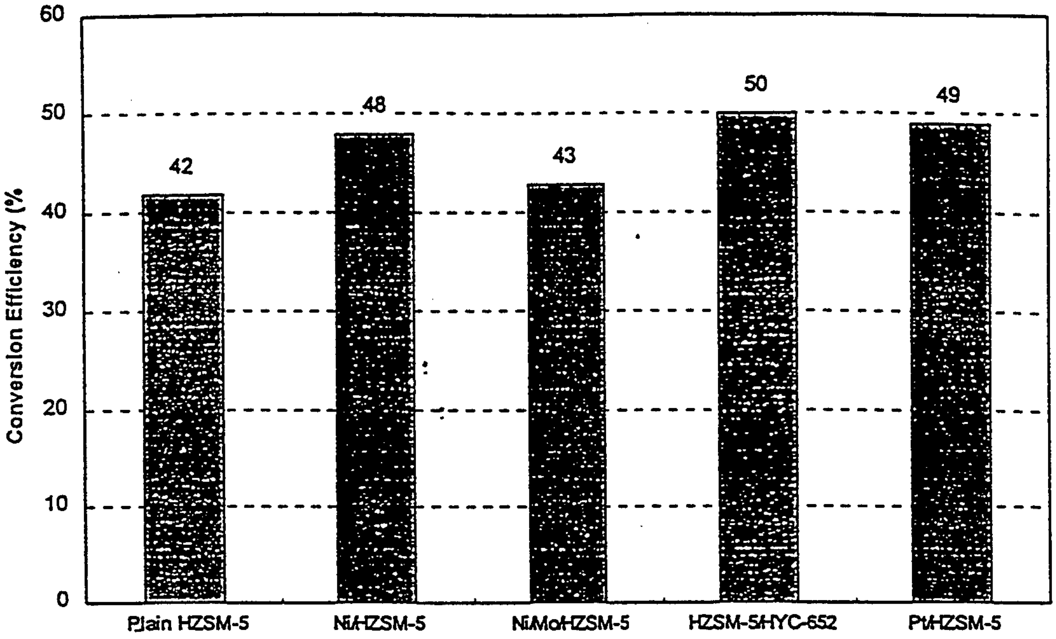


Figure- 5: Conversion Efficiency of Different Types of Catalyst at 500°C and 100 psig with 52 min. Residence Time.

4.1.5 Maximization of the Conversion Efficiency at Low Temperature

Diesel is known to coke at approximately 800°F (427°C) and above. If a centralized fuel processing unit can function well with a catalytic cracker operated below this temperature, preventing coke formation will become an easy task, simplifying the design, manufacturing and operating procedures. By modifying different types of catalyst, we investigated a method to maximize the conversion efficiency of diesel to gaseous fuel at temperature below 800°F. Catalysts tested includes: HZSM-5, USY, Beta, 8%Ni/HZSM-5, HZSM-5/USY with 1:1 weight ratio and HZSM-5/ICI 46-1 with 1:1 weight ratio.

In the tests of low temperature cracking, we investigated a new type of zeolite, Beta from PQ Corporation. Two types of zeolites had been studied extensively in the previous phases of this project, HZSM-5 and USY. Compared with USY, HZSM-5 has higher Si/Al ratio, and higher hydrocarbon cracking activity, but its smaller pore size is not suitable for cracking the branched paraffins found in diesel. Beta is in between HZSM-5 and USY in terms of these properties. But it was reported to have higher resistance to deactivation than the other two zeolites [17].

Another type of nickel-bearing catalyst, 46-1 from ICI Katalco, was tested after it was mixed with HZSM-5. This is a commercially available steam reforming catalyst with

26% of nickel oxide on ceramic support. With a 1:1 weight ratio used in this experiment, the mixture of HZSM-5 and ICI 46-1 had a nickel content of 9wt%.

Diesel cracking tests of different kinds of catalysts were carried out at 450°C wall temperature, 300 psi reactor pressure and 104 min. residence time. The temperature at the center of the catalyst bed was different for each kind of catalyst, with the lowest of 390°C for USY, the highest of 432°C for HZSM-5/46-1, and
the rest between 412°C and 428°C.

Figure-6 is a plot of conversion efficiencies of the different catalysts versus reaction time. As illustrated in Figure-6, the activity of all six catalysts decreased as reaction time increased. As expected, HZSM-5/USY gave the highest initial conversion efficiency, followed by Ni/HZSM-5 and plain HZSM-5. But HZSM-5/USY deactivated very fast and ended up in the fourth place after 18 hours. USY gave the lowest initial activity and fastest deactivation. Beta only showed moderate activity and resistance to deactivation.

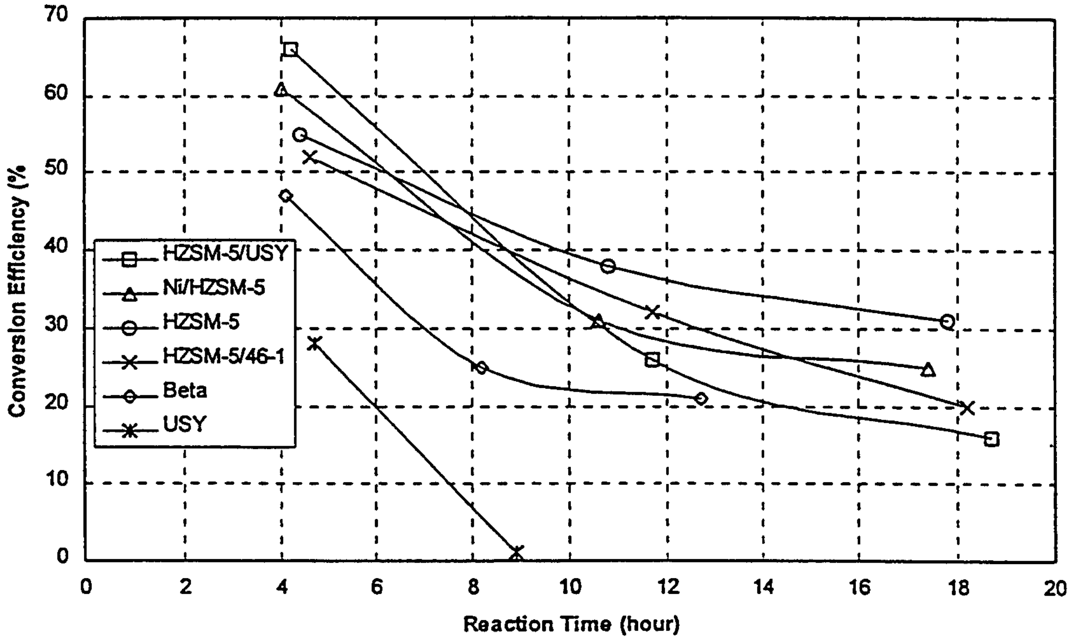


Figure- 6: Conversion Efficiency of Different Types of Catalyst at 450°C and 500 psig with 140 min. Residence Time.

Plain HZSM-5 exhibited the best resistance to deactivation among all six catalysts, including Ni/HZSM-5 and HZSM-5/46-1. The nickel content in Ni/HZSM-5 and HZSM-5/46-1 was introduced to promote hydrogenation of heavy hydrocarbons to prevent coking. The reason why the inclusion of nickel was not effective could be due to one or both of the following: the temperature was too low to generate significant amount of hydrogen, or the nickel was not active enough at this low temperature.

4.2 Effects of Pressurization and Improved Heat Transfer

4.2.1 Pressure Effects

The effect of pressure on the catalytic cracking of diesel was studied using HZSM-5 and Nickel/HZSM-5 catalysts. The pressures tested were 0, 30, 100 and 500 psig. Test results showed that increased pressure had a small positive effect in terms of conversion efficiency. For fresh HZSM-5, at 500°C, conversion efficiency rose from 40% to 42% when pressure increased from 0 to 100 psig; while at 600°C, the improvement was from 43% to 46% for the same pressure change (see Figure-7). Nickel treated HZSM-5 benefited more from pressurization than the untreated batch. As shown in Figure-8, at 500°C and 100 psig, the average conversion efficiency for fresh Nickel/HZSM-5 was 48%, while at 600°C and 500 psig, the conversion efficiency rose to 64%, but with the same pressure of 100 psig, even at 650°C, the conversion efficiency was only 57%.

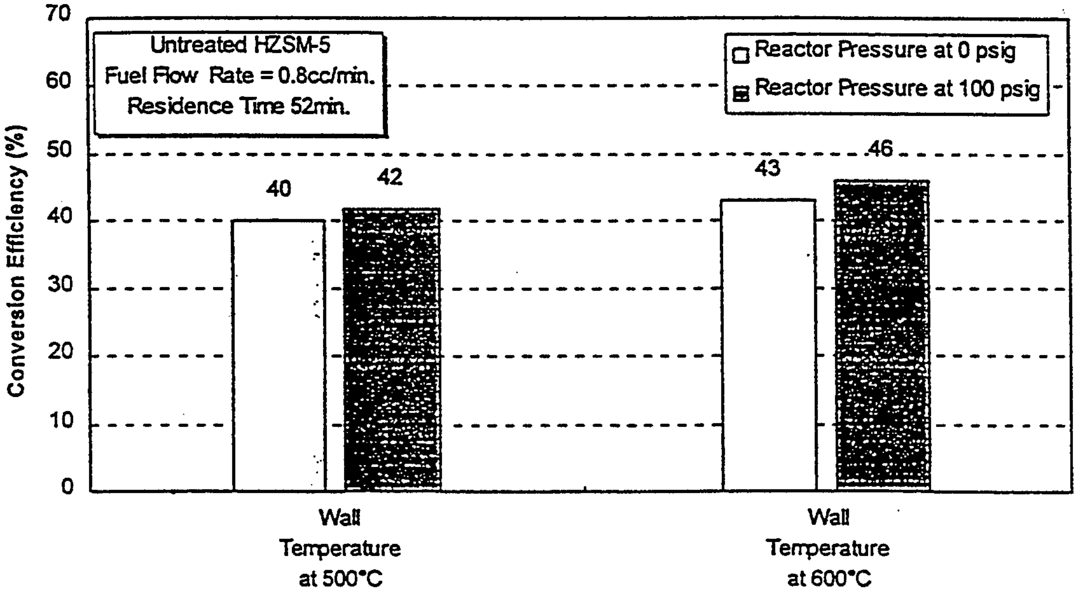


Figure- 7: Pressure Effect on Performance of HZSM-5 at 500°C and 600°C.

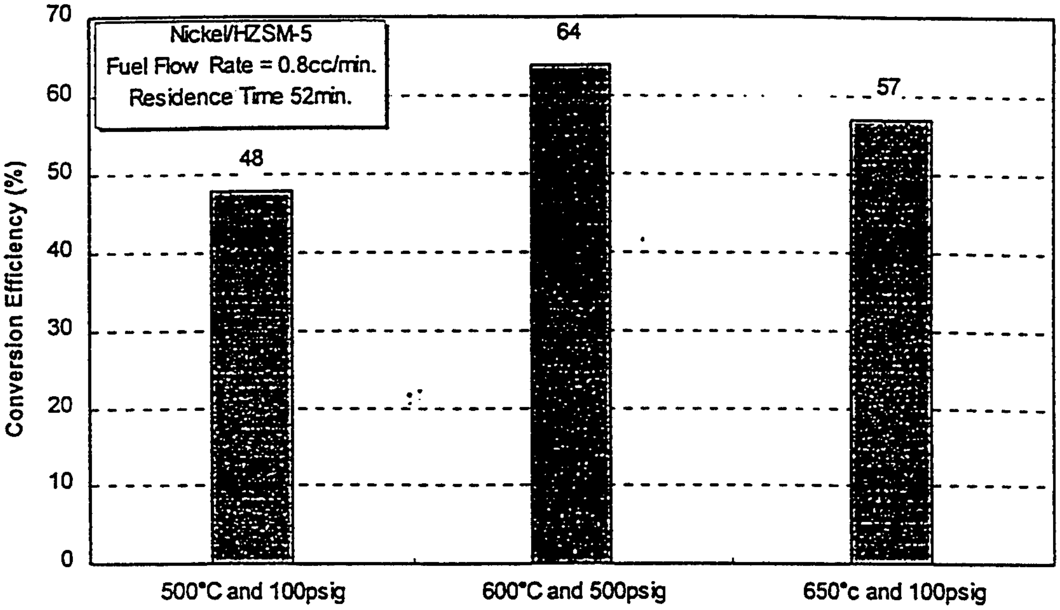


Figure- 8: **Pressure Effect on Performance of Nickel/HZSM-5.**

Two batches of HZSM-5 were tested under alternating pressure, at high and low fuel flow rates respectively. The alternating pressure test was carried out at a fixed temperature, starting with one run at a high pressure, then two or three runs at a lowered pressure, and finally another run at the original high pressure. Both batches showed that the catalyst degraded faster under alternating pressure than constant pressure, i.e., the conversion efficiency dropped faster from run to run (shown in Figure-9). This may suggest that special attention needs to be paid to the start-up and shut-down processes of a pressurized cracking system.

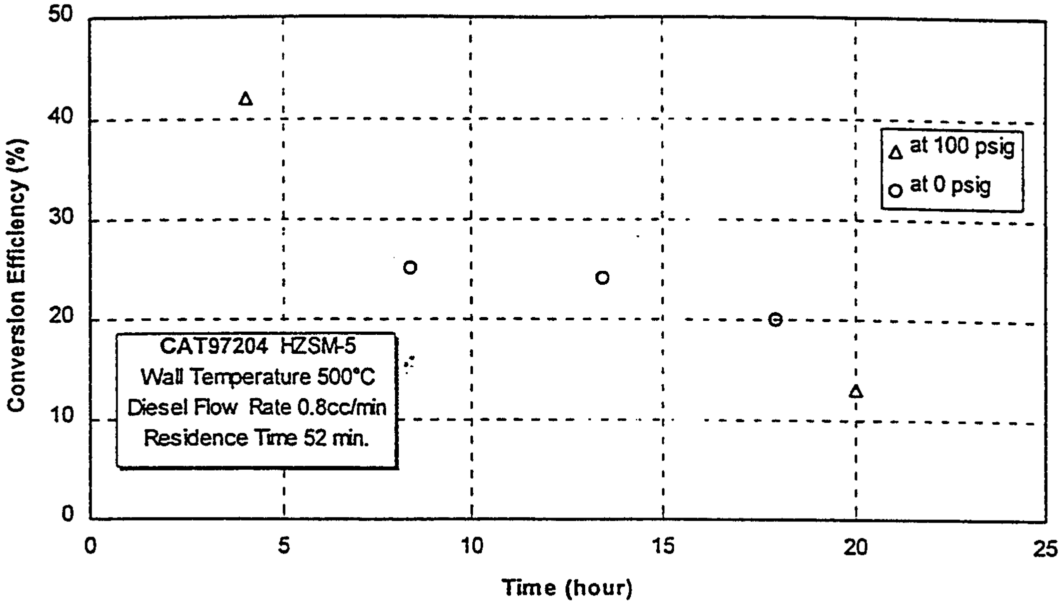


Figure- 9: **Performance of HZSM-5 under Alternating Pressure.**

We observed that at very high pressure, 500 psig, catalyst lifetime was severely curtailed. Both the HZSM-5 and Nickel/HZSM-5 reached their end of life in a little bit more than two hours, compared with more than 20 hours at lower pressure.

4.2.2 Small-Diameter Reactor

We ran a test to determine the effect of lowering the residence time (high flow rate) on the lifetime of the catalyst. However, in previous tests with low residence time, we had observed a substantial temperature gradient from the wall to the center of the reactor. This caused us to be uncertain as to what different portions of the catalyst were doing.

To avoid this problem, we decided to use a smaller diameter reactor. The new reactor had an outer diameter of 3/8", compared to the 3/4" for the previous ones. Because of the smaller volume and radius, it offered a higher space velocity and smaller temperature gradient from the wall to the center, thus resulting in more uniform catalyst temperature.

Ni/HZSM-5 catalyst was used since previous tests showed that with nickel-treated HZSM-5, the improvements caused by pressure were more pronounced than with plain HZSM-5. One test, conducted at 600°C and 500 psi and a residence time of 17 min., resulted in a conversion efficiency of 37%, but the catalyst bed clogged in 2.2 hours. Up to this point, all the tests conducted at 500 psi (at 600°C and 650°C), clogged rapidly regardless of the type of catalyst (plain HZSM-5, Ni/HZSM-5 and Pt/HZSM-5) or residence time of 52 min. or 17 min. It was concluded that 500 psi is too high a pressure for catalytic cracking of diesel. This is probably because, at such a high pressure, polymerization of olefins created by the cracking reaction becomes significant. The polymerization of these olefins results in high-boiling-point substances which will accumulate inside the catalyst bed and coke. Another test was carried out with the same conditions but at 300 psi. The result was a conversion efficiency of 35%, slightly lower than the previous one, but the catalyst showed no sign of clogging at the end of a four-hour test. The test was stopped because the conversion efficiency was still not satisfactory. The fact that the small-diameter reactor did not result in a higher conversion efficiency indicates that the cause of lower conversion efficiency, in high-space-velocity case, is not only because of the lower temperature at the core of the reactor, but also because of lower catalyst to feedstock ratio.

4.3 Diesel Cracking with Steam Reforming

4.3.1 HZSM-5 and Nickel-Treated HZSM-5

Previous tests had indicated that a higher reactor temperature resulted in a higher conversion efficiency of diesel to gaseous fuel. But severe carbon formation (coking) is also associated with high temperatures, leading to catalyst deactivation and the plugging of the reactor by carbon deposition. Steam reforming has been practiced industrially for decades. It utilizes water to convert carbon and hydrocarbons to hydrogen and carbon monoxide. Since both hydrogen and carbon monoxide are gaseous fuels, with the proper catalyst and diesel/steam ratio, steam reforming is a promising method to prevent coking and improving the efficiency of the cracking system at the same time.

Two batches of fresh catalyst were tested to the end of their lifetime to examine the effect of steam reforming. One was plain HZSM-5, with only diesel as input. The other was 8%Ni/HZSM-5, the input was diesel plus 10v% to 20v% of water. Nickel content on HZSM-5 was expected to catalyze steam reforming and encourage hydrogenation. Both batches of catalyst were tested at 700°C wall temperature, 0 psi reactor pressure and 104 min. residence time, the catalyst temperature for both batches was stabilized between 687°C and 693°C. Droplets of water were found in the collection bottle of the diesel/water run. The volume of water consumed in the reaction was 8vl% of the diesel.

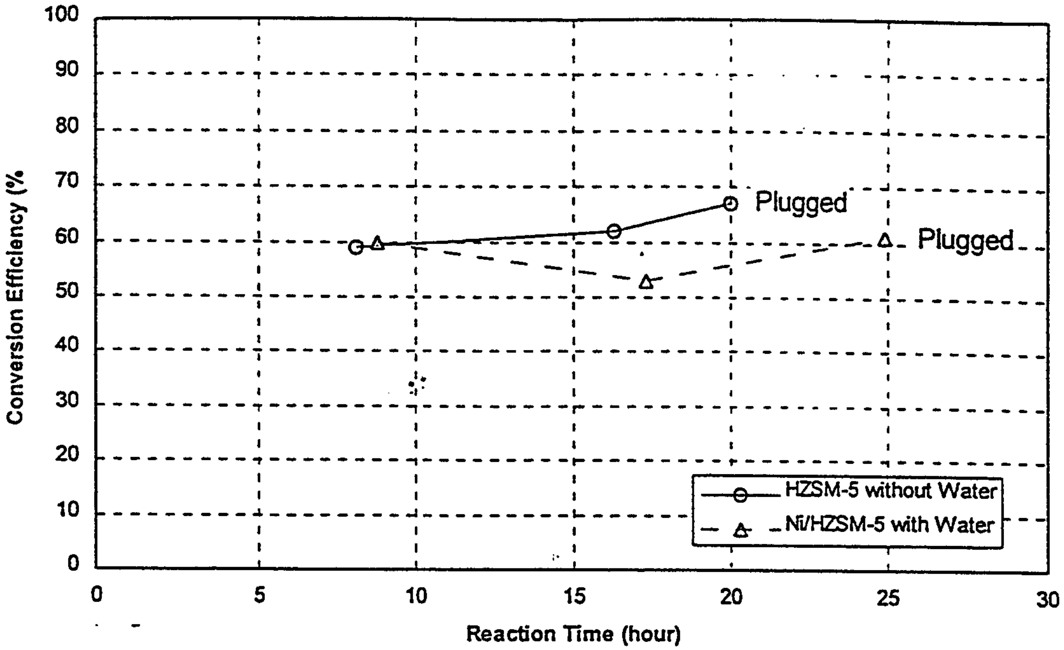
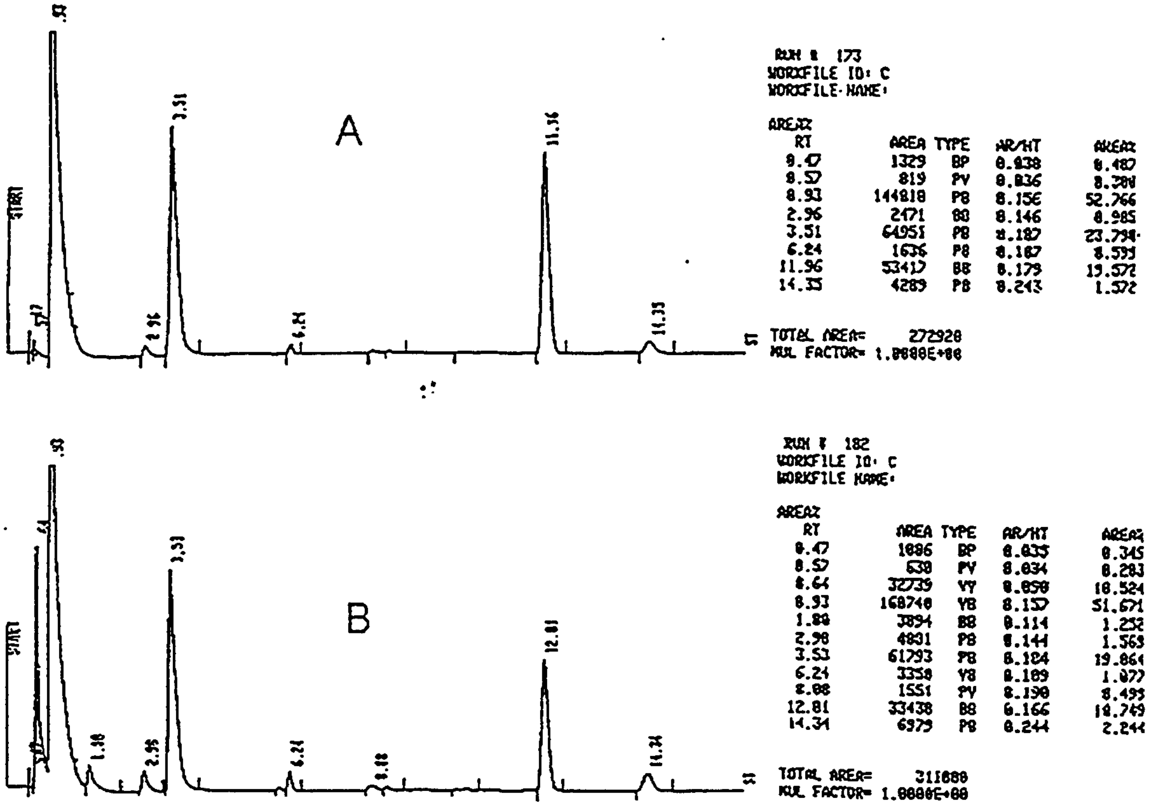


Figure- 10: **Conversion Efficiency at 700°C and 0 psig and 140 min. Residence Time, with and without Water.**

Figure-10 is a comparison of the performance of the catalyst with and without water. It shows that the conversion efficiency was lowered slightly by the presence of water, but the lifetime of the catalyst was extended from 20 hours to 25 hours (not a significant amount).

Figure-11 is the GC analysis of the gas phase samples of the two batches of catalyst. These samples were taken when the catalysts were still fresh. So the major component of both samples was methane, which has a peak at retention time (RT) of 0.93 min. in the GC analysis. The GC of the cracking/steam reforming test showed two additional peaks, one at RT=0.64 and the other at RT=1.88, which correspond to CO and CO_2 respectively. The presence of CO in the effluent is a clear evidence of steam reforming reaction. The small amount of CO_2 was a product of CO disproportionation, which should be avoided because the other product of this disproportionation is carbon. Hydrogen showed up in both GCs at RT=0.47. Less hydrogen was found in the cracking/steam reforming test. This is an indication that the nickel used in that test was promoting hydrogenation of hydrocarbons.

In the GCs of the cracking/steaming reforming test, the CO peak grew smaller with time, and finally disappeared at 16 h while the reactor got plugged at 25 h. One possible explanation is that the sulfur contents in diesel deactivated the nickel catalyst and stopped the steam reforming. A steam reforming catalyst with stronger resistance to sulfur poisoning is needed for this application.



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WORKFILE NAME:

AREA%
  RT        AREA TYPE   AR/HT      AREA%
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  0.57       819   PV   0.036      0.300
  0.93    144018   PB   0.156     52.766
  2.96      2471   BB   0.146      0.905
  3.51     64951   PB   0.187     23.798
  6.24      1636   PB   0.187      0.599
 11.96     53417   BB   0.179     19.572
 14.35      4289   PB   0.243      1.572

TOTAL AREA=    272928
MUL FACTOR= 1.0000E+00
```

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RUN # 182
WORKFILE ID: C
WORKFILE NAME:

AREA%
  RT        AREA TYPE   AR/HT      AREA%
  0.47      1086   BP   0.035      0.345
  0.57       638   PV   0.034      0.203
  0.64     32739   VV   0.050     10.524
  0.93    160740   VB   0.157     51.671
  1.00      3894   BB   0.114      1.252
  2.98      4831   PB   0.144      1.553
  3.53     61793   PB   0.124     19.864
  6.24      3350   VB   0.109      1.077
  8.08      1551   PV   0.130      0.499
 12.81     33438   BB   0.166     10.749
 14.34      6979   PB   0.244      2.244

TOTAL AREA=    311080
MUL FACTOR= 1.0000E+00
```

Figure- 11: Gas Chromatography of Cracking Test at 700°C and 0 psig and 140 min. residence time, A) without Steam Reforming, B) with Steam Reforming.

4.3.2 Molybdenum Carbide as Cracking/Steam Reforming Catalyst

Nickel catalysts are used industrially for steam reforming because of their fast turnover rates, long term stability and low cost. However they are also subjective to deactivation by coking and sulfur poisoning. Noble metal catalysts have stronger resistance to deactivation, but their high cost and limited availability have limited their application. In the last 20 years, group VI transition metal carbides have been found to be active catalysts, comparable to platinum group metal catalysts for a number of reactions.

In a parallel DOE sponsored project, Aspen Systems tested molybdenum carbide to identify coke-resistant catalysts for partial oxidation of gasoline. The research performed during this effort indicated that this catalyst might also be effective for steam reforming. As a result, we conducted a small in-house effort to verity our hypothesis. Molybdenum carbide supported by alumina (Mo_2C/ Al_2O_3) was tested for diesel cracking/steam reforming at 700°C wall temperature, 150 psi reactor pressure and 104 min. residence time. The pressure of 150 psi was chosen because Mo_2C was reported to oxidize to MoO_2

at atmospheric pressure. The catalyst temperature was 650°C. The water to diesel volume ratio was 1:1. Four percent of the water input was consumed by the reaction.

Figure-12 illustrates the performance of molybdenum carbide as a catalyst for diesel cracking/steam reforming. The conversion efficiency was above 70% for 6 hours after starting, which was never achieved by any of the catalysts tested before. Figure-13 is a GC of a gas phase sample taken at 2 hours after the beginning of the experiment. Compared to the GCs of cracking/steam reforming tests with Ni/HZSM-5 as catalyst, the CO peak (at RT=0.60) was much larger at the same reaction time, indicating more intensive steam reforming reaction. The test lasted only 6 hours because the reactor coked. However, in this instance alone, the coking occurred only in the portion of the reactor tube downstream of the catalyst bed, not inside the catalyst (in tests with other catalysts the catalyst pellets themselves would coke). This indicated that the molybdenum carbide catalyst was hydrogenating the carbon atoms successfully and that with proper design, there was a possibility of eliminating the coking.

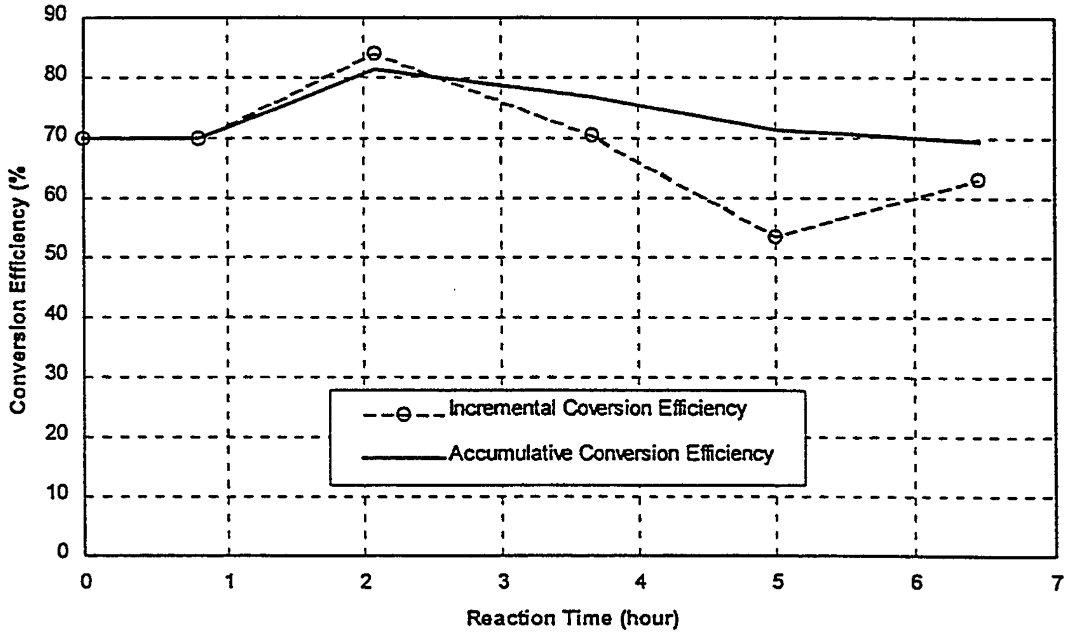
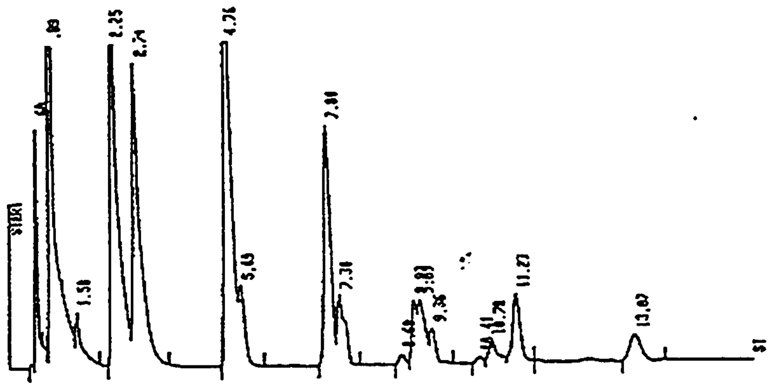


Figure- 12: Conversion Efficiency of Diesel Cracking/Steam Reforming with Molybdenum Carbide as Catalyst, at 700°C and 150 psig and 104 min. Residence Time.

Compared with the cracking/steam reforming tests using Ni/HZSM-5, the water input in molybdenum carbide test was 4 to 9 times more, resulting in a 40°C lower catalyst temperature, but the actual water consumption in the reaction was only half, 4v% versus 8v% of the input diesel, indicating the water input may be cut down more without compromising the conversion efficiency of liquid to gaseous phase fuel.



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RUN #  244
WORKFILE ID: C
WORKFILE NAME:

AREA%
   RT          AREA TYPE    AR/HT        AREA%
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  0.89        82469   PB    0.084       14.039
  1.50          924   BB    0.024        0.157
  2.25       108260   PV    0.163       18.431
  2.74        84685   VB    0.108       14.417
  4.76       115090   PV    0.171       19.592
  5.09        19785   VB    0.165        3.368
  7.00        60163   PV    0.169       10.242
  7.30        20929   VB    0.204        3.563
  8.69         2136   PV    0.143        0.364
  8.97        10346   VV    0.110        1.761
  9.09        17629   VV    0.106        3.001
  9.36         8416   VB    0.160        1.433
 10.41         1202   PV    0.147        0.205
 10.70         6366   VV    0.209        1.084
 11.23        19622   VB    0.199        3.340
 13.87        10985   PB    0.202        1.870

TOTAL AREA=      587420
MUL FACTOR= 1.0000E+00
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Figure- 13: Gas Chromatograph of Diesel Cracking/Steam Reforming with Molybdenum Carbides as Catalyst, at 700°C and 150 psig and 140 min. Residence Time.

Though these results were encouraging, we did not pursue them any further due to lack of funding.

5. SUMMARY AND CONCLUSIONS

During Phase IV, Aspen Systems, Inc. studied the yield of the gaseous fuel generated by the catalytic cracking/reforming of diesel. The accomplishments and conclusions are summarized as follows:

- Nickel ions implanted in zeolite, as well as nickel mixed with zeolite, can promote hydrogenation in catalytic cracking, therefore increase the overall conversion efficiency, especially in a pressurized reactor. But nickel has to be stabilized to make it less vulnerable to the sulfur contents in diesel;

- Improved heat transfer inside the reactor did not result in a high conversion efficiency of diesel to gaseous fuel;

- Pressure has a small positive effect on the conversion efficiency of diesel to gaseous fuel. However, a high pressure of 500 psig promoted coking dramatically, therefore severely shortening catalyst lifetime;

- Molybdenum carbide showed potential as an efficient and durable catalyst for cracking and steaming reforming of diesel. It gave a conversion efficiency of 70% for 6 hours with no sign of degradation at 700°C and 150 psig;

- The centralized fuel processing unit was conceptually designed to be a combination of catalytic cracking and steam reforming reactor.

In summary, the best results achieved during this project came at the very end with the testing of molybdenum carbide. However, since the coking problem was not resolved during this effort, The Natick Labs Program Manager, Mr. Don Pickard, felt that there were other more promising developments, such as the reformers developed by ADL for gasoline conversion, that overshadowed the promise of Aspen Systems' progress. Therefore no further research and development of this technology was authorized.

This document reports research undertaken at the
U.S. Army Soldier and Biological Chemical Command,
Soldier Systems Center, Natick, MA, and has been
assigned No. NATICK/TR-00/006 in a series of reports
approved for publication.

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