SECTION 1: REPORT COVER PAGE

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Project Title: Advanced Catalytic Hydrogenation Retrofit Reactor

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2: EXECUTIVE SUMMARY

Industrial hydrogenation is often performed using a slurry catalyst in large stirred-tank reactors. These systems are inherently problematic in a number of areas, including industrial hygiene, process safety, environmental contamination, waste production, process operability and productivity. This program proposed the development of a practical replacement for the slurry catalysts using a novel fixed-bed monolith catalyst reactor, which could be retrofitted onto an existing stirred-tank reactor and would mitigate many of the limitations and problems associated with slurry catalysts. The full retrofit monolith system, consisting of a recirculation pump, gas/liquid ejector and monolith catalyst, is described as a monolith loop reactor or MLR. The MLR technology can reduce waste and increase raw material efficiency, which reduces the overall energy required to produce specialty and fine chemicals.

The key objective of this program is to develop and demonstrate a practical MLR pilot system using realistic reaction chemistry and to confirm that high reaction rates, long catalyst life and high selectivity can be achieved with a suitable monolith catalyst. The pilot plant is designed to be a platform from which candidate chemistries can be evaluated and their suitability for MLR technology can be determined. The pilot plant design is flexible enough to allow testing of a variety of specialty hydrogenation chemistries, and at the same time it is highly instrumented to allow commercial scaleup design information to be obtained from customer trials.

The development program was divided into two work activity elements, with the goal of developing and demonstrating the MLR technology using the hydrogenation of nitrobenzene to aniline as a benchmark chemistry. The hydrogenation of nitrobenzene is a standard reaction chemistry used in the fine and specialty chemical industry to characterize catalyst performance and is employed as a working model in this development program. The first stage of development focused on the characterization and elucidation of the fundamental elements that compose the technology: chemistry/catalysis and process engineering. In this stage of work, two monolith catalysts were identified that had the activity, selectivity and life that met the program goals. In addition, fundamental engineering process information such as pressure drop, mass transfer, and ejector performance in the MLR were characterized. During the second stage of work activities, the information from the fundamental process and catalyst technology was used to design, fabricate, install and operate a pilot-scale MLR system at Air Products and Chemicals' corporate pilot plant facilities in Pace, Florida.

Between October 2001 and January 2002, the MLR pilot plant was successfully demonstrated. The pilot plant performed as expected, yielding normalized hydrogenation reaction rates and aniline selectivity that were equivalent to the lab system. The lab consists of a two-liter reactor system with a two-inch long monolith, while the MLR pilot plant operates with a fifteen-gallon tank fitted with a three-foot long monolith. This virtual one-to-one scaleup from the lab to the pilot plant is unique in three-phase catalytic systems and demonstrates the potential utility of the MLR in streamlining the development of new hydrogenation process chemistries. The inorganic wash-coated monolith catalyst supplied by COMPANY 1 out-performed the polymer-coated monolith formulation, meeting activity, selectivity and life goals.

The original MLR concept is covered by a patent application that predates the DOE OIT funding; however, three patent applications were filed on inventions stemming directly from the DOE OIT-funded part of this program. The first patent application, "Hydrogenation with Monolith Reactor under Conditions of Immiscible Liquid Phases," has been allowed, but not issued. This patent describes the unique ability of the MLR to operate with two immiscible liquid phases, a mode of operation that normally is not practical with slurry catalysts and that allows novel hydrogenation synthesis pathways. This was demonstrated in both the lab and the pilot plant with two-phase nitrobenzene hydrogenation. The second patent, "Polymer Network/Carbon Layer on Monolith Support and Monolith Catalytic Reactor," describes a novel low surface area polymer coating, which can be used as a support for precious metal catalysts to effect hydrogenation. The third patent is a continuation in part of the second. There is no U.S. patent office action on the last two patent applications at the writing of this report.

All major milestones in this program were successfully completed. A few time delays and unexpected problems were encountered during both phases of the project; however, the total project was completed on time and less than 5% over budget. The first setback occurred with the failure to identify a suitable carbon-based monolith structure. An intensive program was undertaken to develop a novel alternative catalyst based on a polymer coating of the monolith. The initial scaleup of the polymer synthesis yielded inconsistent polymer quality, making catalyst fabrication impractical. A polymer synthesis program produced a scaleable polymerization process, which was used to make monolith catalysts for the pilot plant. During the second phase of the program, the pilot plant construction contractor encountered difficulty in the fabrication of the recirculation pump. A new pump manufacturer was identified, and a suitable pump was installed. After installation it was discovered that a number of welds failed to meet ASTM standards. Once the poor welds were identified and repaired, start-up of the pilot plant was uneventful.

The MLR technology and business review team at Air Products has approved the program for commercialization, and commercialization activities are proceeding. Two lab test studies have been completed for the manufacture of a specialty chemical intermediate and a pharmaceutical intermediate. In both cases the MLR study gave mixed results. We are currently assessing the next steps for those customers and lining up a number of new test studies. Market analysis of the fine, specialty and pharmaceutical industry has yielded an amenable market of 1.0 billion lb/yr of hydrogenated products. An active marketing program is underway, and we are beginning to line up customers for testing over the next year. Our goal is have a commercial MLR system in place by the end of calendar year 2003.

Estimates of energy and environmental impact were revised from the original project estimates using the OIT web tool. These changes reflect a better understanding of customer hydrogenation processes from market studies. The energy savings was reduced from 10 to 2%, and the waste reduction was increased from 2 lb/1000 lb product to 43 lb/1000 lb product.

3: INTRODUCTION

Major Industry Issues and Drivers

Industrial hydrogenation is often performed by using slurry catalyst reaction systems in large stirred-tank reactors. These systems are inherently problematic in a number of areas, including industrial hygiene, safety, environmental, waste production, operability and productivity.

Slurry hydrogenation catalysts are finely divided powder catalysts that are handled manually during a typical hydrogenation operation in a stirred-tank reactor. These powdered catalysts are often pyrophoric, creating safety concerns. They are also often made with noble and heavy metals such as platinum, palladium, ruthenium, cobalt, and nickel. Special precautions must be taken to so that these manually handled powders do not pose a respiratory hygiene problem for workers.

Filtration is necessary to remove these slurry catalysts after the completion of the reaction process. The filtered material must then be disposed of as hazardous solid waste. Often yield reductions occur as valuable product permanently wets the waste catalyst. Even if partially recycled, the catalyst contaminates washing solvents, leading to higher volumes of hazardous waste. Spills and releases from opening vessels, especially filtration vessels, often occur, leading to environmental discharges and contamination. This is especially true when filtration equipment failures occur.

Increases in the catalyst charge to a reactor may decrease the reaction time to improve productivity, but the extra catalyst increases the filtration time, reducing the desired productivity. This stalemate often occurs, and decreases the options of a plant to increase productivity.

Slurry processes suffer from the problem that during start-up and shutdown of a process, the catalyst is in constant contact with the reaction contents. This contact occurs during heat-up, cool-down, pressurization, and venting of the stirred tank and leads to by-product formation and catalyst fouling or deactivation.

Program Goals and Objective

The key objective of this program was to develop and demonstrate a practical MLR pilot system using realistic reaction chemistry and to confirm that high reaction rates, long catalyst life and high selectivity can be achieved with a suitable monolith catalyst. The pilot plant is designed to be a platform from which candidate chemistries can be evaluated and their suitability for MLR technology can be determined. The pilot plant design is flexible enough to allow testing of a variety of specialty hydrogenation chemistries and at the same time is highly instrumented to allow commercial scaleup design information to be obtained from customer trials.

Key to the successful commercial implementation of the MLR technology is cost-effective development of customized catalyst formulations for individual specialty chemical processes. This will be done during the commercialization phases of this program. It was not the intention of this program to develop a better process to manufacture aniline *per se*, and as a direct comparison with processes to produce aniline, the MLR is not an obvious competitive choice with existing optimized commercial processes. Chemical selectivity greater than 98% for the

nitrobenzene test chemistry was considered adequate to demonstrate the application of MLR technology.

System Description

The MLR is an integrated reaction system designed for retrofit onto an existing commercial reactor. The MLR replaces the fine slurry catalysts used during hydrogenation in a stirred-tank reactor with an integrated system of three basic engineering components: a pumped recirculation loop, a gas ejector, and a monolithic reactor. A monolith is a honeycomb structure that is usually ceramic-based and serves as a support for a metal catalyst. A photograph of a catalytic monolith is shown in Figure 3.1. Monoliths have been used in the automotive industry (as catalytic converters) for decades. The innovation in this program is to apply the monolith concept to chemical hydrogenation that involves two-phase flow with a simple method to recycle the hydrogen.

Figure 3.1: Cross-Sectional Photograph of Catalyst-Coated Monolith with a Density of 400 Cells/Square Inch

The envisioned MLR system is illustrated in Figure 3.2. The low-pressure drop of the monolithic reactor allows for rapid recirculation of the contents of a stirred-tank reactor over the monolithic reactor. This yields a process with operational characteristics similar to a well-mixed slurry reactor, but with the benefits of a fixed-bed reactor.

The pump forces the contents of the reactor into the gas/liquid ejector, where the liquid flow compresses and mixes with the hydrogen from the head of the reactor and passes the two-phase mixture over the monolithic reactor. This forced flow can be theoretically adjusted to meet the

demands of a variety of hydrogenation processes. The ejector eliminates the need for a separate recirculation gas compressor or any other gas/liquid distribution device.

Figure 3.2: The Monolith Loop Reactor, MLR, Integrated Reactor System

A major benefit of this reactor design is its ability to precisely start and stop a batch hydrogenation reaction by initiating or terminating circulation of the reactor contents through the monolithic reactor. Slurry processes suffer from the problem that, during start-up and shutdown of a process, the catalyst is in constant contact with the reaction contents, as described above. The MLR will offer a much greater degree of process control, thus aiding in the reduction and elimination of many by-products. This benefit was not fully realized with the nitrobenzene test chemistry used in this study due to the high intrinsic yield of the reaction under process conditions.

Literature

Monolithic catalysts, best known for their application in automotive catalytic converters, feature a honeycomb channel structure to which a catalytic material is applied. Their application in gas-liquid reactions (especially hydrogenations) has been the subject of much research since the 1980s, when the first production-scale process (the hydrogenation step in the manufacture of hydrogen peroxide) was commercialized. Recently, both scientific literature [1, 2] and patent literature [3, 4] have proposed many new potential monolith applications. Until now, most proposed applications have been in medium- to large-scale, continuous chemical processes, but developments such as the general monolith loop reactor concept described by Heiszwolf *et al.* [5] indicate that monolith catalysis is ready to make an impact on smaller scale batch hydrogenation processes. The scientific literature has focused on simple “shower-head” liquid-gas distribution

to the monolith catalysts, with the reactor performance dependent on gravity as a driving force for mixing, mass transfer and distribution. A more robust system, which improves distribution, recycles the unreacted hydrogen and provides sufficient pressure to overcome the limitations of gravity, is necessary to make this technology more generally applicable.

Summary of Advantages of the Monolith Loop Reactor

1. Elimination of slurry catalysts to minimize handling, environmental, waste and safety problems associated with slurry catalyst processes.
2. An easily retrofittable technology designed as a replacement for existing slurry hydrogenation technology. This ease of retrofit maximizes the potential adoption by the U.S. chemical industry.
3. Unique gas/liquid distribution and gas recirculation system to allow for operation that can be tailored to a variety of hydrogenation chemical processes.
4. Precise control of hydrogenation reaction to eliminate by-products by control of the recirculation loop.
5. Reduced energy consumption due to higher productivity and improved yields.

Technical Program Summary

The proposed work sought to develop a new integrated catalyst reactor system, the monolith loop reactor (MLR), which can be retrofitted onto existing commercial slurry-catalyst, stirred tank reactors, and can mitigate the problems associated with using slurry catalysts. The development program was divided into two work activity elements, with the goal of developing and demonstrating the MLR technology using the hydrogenation of nitrobenzene to aniline as a benchmark chemistry. The hydrogenation of nitrobenzene is a standard reaction chemistry used in the fine and specialty chemical industry to characterize catalyst performance and is used as a working model in this development program. The first stage of development focused on the characterization and elucidation of the fundamental elements that compose the technology: chemistry/catalysis and process engineering. In this stage of work, two monolith catalysts were identified that had the activity, selectivity and life that met the program goals. In addition, fundamental engineering process information such as pressure drop, mass transfer, and ejector performance in the MLR were characterized. During the second stage of work activities, the information from the fundamental process and catalyst technology was used to design, fabricate, install and operate a pilot-scale MLR system at Air Products' corporate pilot plant facilities in Pace, Florida.

Test Chemistry

Test chemistry was selected to demonstrate the suitability of the MLR technology and to provide marketing technical information and realistic benchmarking data for comparison with commercial fine and specialty hydrogenation processes. Originally in the OIT proposal, the hydrogenation of aniline to cyclohexylamine was selected as the test chemistry. Later in the program, the test chemistry was changed to the hydrogenation of nitrobenzene to aniline. This was done after market surveys of specialty and fine chemical producers identified nitrobenzene hydrogenation as a standard used across the industry to benchmark catalyst performance and activity. It was not the intention of this program to develop a better process to manufacture

aniline *per se*, and as a direct comparison with processes to produce aniline, the MLR is not an obvious competitive choice with existing optimized commercial processes. Chemical selectivity greater than 98% for the nitrobenzene test chemistry was considered adequate to demonstrate the application of MLR technology.

Catalyst Development and Optimization

Catalyst development was done within Air Products' Corporate Science and Technology Center. Customized catalysts were also fabricated from cordierite and carbon monolith support. In addition, a novel polymer-based wash coat was developed and applied to a cordierite monolith support, which gave a catalyst with high rates and selectivity. COMPANY 1 provided commercial-type catalysts for evaluation in both lab and pilot studies.

In order to define the catalyst and operating conditions on a laboratory scale, a 2-liter batch reactor, a novel in-house catalyst testing basket system with a specialized agitator, was adapted to fit into the reactor to simulate MLR operation. This allowed the use of existing laboratory infrastructure to be applied to the testing program. Benchmarking studies verified the performance of this approach.

Laboratory work was performed to develop suitable catalysts with the activity, life and selectivity to successfully hydrogenate nitrobenzene, the test chemistry. After more than ten catalysts were tested, two catalysts were selected that yielded high rates, long life and satisfactory selectivity. The first catalyst was based on a novel polymer-coated monolith developed by Air Products, and the second catalyst was supplied by COMPANY 1 and was prepared using a commercial inorganic wash coat formulation. Both catalysts were tested in the MLR pilot plant.

The catalyst-testing program also yielded some exciting and unexpected results. It was found that the monolith catalyst could operate unexpectedly well with two liquid phases present, and additionally a low surface area catalyst could yield high rates and selectivity. The first observation was made during the neat hydrogenation of nitrobenzene, which yielded a high reaction rate and high selectivity, even with the formation of both an aqueous and an organic phase. With slurry hydrogenation catalysts, the formation of two phases is often problematic, as the slurry catalyst preferentially partitions into one of the liquid phases, stalling the reaction rate and impacting selectivity. These results provided the basis of three patent applications.

Monolith Reactor Options

Originally in the OIT proposal, it was suggested that the monolith catalyst component of the MLR follow two parallel paths: the development of a catalyst-coated monolith and the development of a monolith channel bed reactor (monolith substrate with catalyst particles stacked in the monolith channels). It was recognized early that the pressure drops associated with the channel bed concept were too high to be practical, and this approach was abandoned. In addition, success in developing both a polymer and inorganic wash-coated monolith catalyst eliminated the need to pursue the channel bed concept.

Engineering Development

A 25-gallon Plexiglas® hydraulic prototype of the MLR was constructed and tested to characterize the performance of the gas-liquid ejector in combination with 2-in. diameter blank monolith catalysts in an air/water system. Pressure drops across monolith beds between 2 and 3 feet long with multiphase flows were characterized, and practical operating windows were established for the combined system. Mass transfer was characterized using standard air oxidation of sulfite solutions. The system was found to be robust and able to operate under realistic and commercially viable conditions with commercial process components: pump, ejector and monolith catalyst.

Pilot Plant Design, Construction and Installation

The pilot plant was designed based on the data generated during the hydrodynamic and mass transfer studies from the hydraulic testing unit. The pilot plant was constructed at COMPANY 4 and installed at Air Products' pilot facility in Pace, Florida. Delays in delivery were encountered due to unexpected pump failure and the failure of some pipe welds to meet ASME X-ray code requirements. These deficiencies were identified and corrected during the safety review and equipment testing phases of start-up. The full operational start-up proceeded without incident on 15 October 2001.

Pilot Plant Studies

Between October 2001 and January 2002, the MLR pilot plant was successfully demonstrated. The pilot plant performed as expected, yielding normalized hydrogenation reaction rates and aniline selectivity that were equivalent to the lab system. The lab consists of a 2-liter reactor system with a 2-inch long monolith, while the MLR pilot plant operates with a 15-gallon tank fitted with a 3-foot long monolith. This virtual one-to-one scaleup from the lab to the pilot plant is unique in three-phase catalytic systems and demonstrates the potential utility of the MLR in streamlining the development of new hydrogenation process chemistries. The inorganic wash-coated monolith catalyst supplied by COMPANY 1 out-performed the polymer-coated monolith formulation, meeting activity, selectivity and life goals. This catalyst has been selected as a starting point formulation for new commercial testing activities.

Intellectual Property

Two patent applications were filed based on pre-agreement developments: the original MLR concept patent with the pump, ejector and monolith catalyst (application serial number 09/573,726), which has been allowed, and the laboratory catalyst testing basket used in the autoclave (application serial number 10/076,813), which is pending.

Three patent applications under the DOE-OIT agreement were developed:

Application 09/839,699, "**Hydrogenation With Monolith Reactor Under Conditions of Immiscible Liquid Phases,**" was filed in April 2001. The application has been allowed; it describes and claims an improved process for the hydrogenation of organic compounds in the presence of water or another immiscible liquid. The two-phase system can result from water generated in the process or from water added to the reaction mix. The improvement due to using

a monolith for this system was demonstrated for nitrobenzene hydrogenation. The advantages are that: (1) no co-solvent is required to maintain a single phase; (2) because solvent is not used, a high reactant throughput may be obtained; (3) as we demonstrated, a more consistent rate may be obtained; and (4) separation of catalyst from liquid products may be simplified.

Application 09/867,959, “**Polymer Network/Carbon Layer on Monolith Support and Monolith Reactor**,” was filed in May 2001 as a continuation-in-part, CIP, on 09/839699. Its status is pending and is awaiting the first U.S. Patent Office action. The CIP below encompasses claims in 09/867,959.

Application 10/002,250 “**Coated Monolith Substrate and Monolith Catalysts**,” was filed in October 2001 as a continuation-in-part of application 09/867,959 (cited above). The status is pending. CIP 10/002,250 describes and claims a low surface area monolith without restriction on its application. The application claims a monolith support having BET surface area from 0.1 to 25 m²/g. In addition to the coatings based on polyfurfuryl alcohol and other carbon layer precursors, inorganic wash coats are claimed.

Comparative Analysis of Alternative Approaches

The alternative approach to our proposed technology can be summarized as traditional enhancements of slurry-catalyst, stirred-tank hydrogenation systems. This included the addition of catalyst filtration capacity, enhancements in mass transfer with new agitation equipment, and increasing catalyst charges to the reactor system. These solutions still do not reduce the inherent problems of slurry catalysts that are avoided by the MLR technology. A possible competing technology is to use a packed-bed catalyst reactor rather than a monolith catalyst, but the large pressure drops of the packed bed preclude this option as a simple retrofit to an existing reactor.

In particular, when a chemical producer using a slurry phase hydrogenation process is capacity limited or seeks to improve yields, technical options are often limited. The processor may consider increasing the catalyst charges to the slurry phase process to increase reaction rates. While this is known to increase rates and decrease reaction processing time, it also creates two additional problems. First, increasing the catalyst charge to the stirred-tank reactor will force the processor to increase filtration capacity or accept a longer filtration time, which ultimately decreases the benefit from faster reaction rates. This may be expensive if capital is needed to increase filtration capacity and only exacerbates the environmental, safety, waste and handling issues associated with slurry catalysts. In addition, the increase in the reaction rate may force the slurry hydrogenation process to become mass-transfer limited or starved for hydrogen. Operation under mass-transfer control often reduces selectivity and the productivity benefits originally sought. To operate with higher slurry catalyst loading, the processor may have to enhance mixing in the stirred-tank reactor to mitigate the selectivity problem encountered by operation at higher rates. In summary, simply adding more catalyst often creates the need to invest in both filtration and mixing technology. The MLR is a creative and unique solution to this problem. Since filtration is no longer needed, filtration times for a batch process are eliminated, slurry catalyst handling problems are eliminated, and the unique monolithic reactor, in combination with the gas eductor, simultaneously improves the gas/liquid mass transfer along

with the catalytic reaction. Additionally the high mass transfer can improve the selectivity of the process.

Results of OIT Energy Web Tool

Estimates of energy and environmental impact using the OIT web tool are listed in Tables 3.1 and 3.2. The energy savings was reduced from 10 to 2%, and the waste reduction was increased from 2-lb/1000 lb product to 43-lb/1000 lb product. This was done to better reflect results of market analysis and laboratory studies compared to the original savings estimated in the DOE-OIT proposal.

Table 3.1: Original Estimate of Energy and Waste Savings in DOE-OIT Proposal

User Inputs					
Chain:	SPECIALTY	% Energy Savings			
		Feedstocks:	0.00%		
Derivative:	HYDROGENATED	% Energy Savings			
		Heat/Steam:	0.00%		
% of Market Impacted:	50.00%	% Energy Savings			
		Electricity:	10.00%		
Annual Growth Rate:	7.00%	Solid or Liquid	2 lbs per 1000 lbs of		
		Wastes:	product		
		Non-Combustion	0 lbs per 1000 lbs of		
Year of Introduction:	2003	Air Pollutants:	product		
Market Penetration Curve:	20 Year Market Saturation				

Energy Impacts for SPECIALTY: HYDROGENATED					
(Based on the input provided above, this technology will have the following impacts:)					
	2005	2010	2015	2020	
MARKET PENETRATION	6.70%	17.70%	39.20%	65.90%	
MARKET (Million lbs)	47	174	541	1,275	
ENERGY SAVINGS					
Feedstock Energy Savings (trillion Btu)	0	0	0	0	
Heat/Steam Energy Savings	0	0	0	0	
Electricity Savings (trillion Btu)	0.006	0.021	0.065	0.153	
POLLUTANT REDUCTIONS (lbs)					
Carbon (MMTCE/yr)	0.0001	0.00038	0.00117	0.00275	
Nitrogen Oxides (NOX)	1,579	5,850	18,170	42,842	
Sulfur Oxides (SOX)	1,872	6,936	21,544	50,798	
Carbon Monoxide (CO)	271	1,003	3,115	7,344	
Volatile Organic Compounds	34	125	389	918	
Particulates	34	125	389	918	
Other (million lbs)	0	0	1	3	

Table 3.2: Updated Estimate of Energy and Waste Savings Based on Market Analysis

User Inputs			
Chain:	SPECIALTY	% Energy Savings	
		Feedstocks:	0.00%
		% Energy Savings	
Derivative:	HYDROGENATED	Heat/Steam:	0.00%
		% Energy Savings	
% of Market Impacted:	50.00%	Electricity:	2.00%
		Solid or Liquid	43 lbs per 1000 lbs
Annual Growth Rate:	7.00%	Wastes:	of product
		Non-Combustion	0 lbs per 1000 lbs of
Year of Introduction:	2003	Air Pollutants:	product
Market Penetration Curve:	20 Year Market Saturation		

Energy Impacts for SPECIALTY: HYDROGENATED					
(Based on the input provided above, this technology will have the following impacts:)					
	2005	2010	2015	2020	
MARKET PENETRATION		6.70%	17.70%	39.20%	65.90%
MARKET (Million lbs)		47	174	541	1,275
ENERGY SAVINGS					
Feedstock Energy Savings					
(trillion Btu)		0	0	0	0
Heat/Steam Energy Savings		0	0	0	0
Electricity Savings (trillion Btu)		0.001	0.004	0.013	0.031
POLLUTANT REDUCTIONS (lbs)					
Carbon (MMTCE/yr)		0.00002	0.00008	0.00023	0.00055
Nitrogen Oxides (NOX)		316	1,170	3,634	8,568
Sulfur Oxides (SOX)		374	1,387	4,309	10,160
Carbon Monoxide (CO)		54	201	623	1,469
Volatile Organic Compounds		7	25	78	184
Particulates		7	25	78	184
Other (million lbs)		2	7	23	55

4: CUMULATIVE PROJECT MILESTONE INFORMATION

All project milestones were met and are summarized in Table 4.1. A few notable problems were encountered during the program, which led to delays. These included the development of a novel catalyst with a polymer wash coat and rework of pilot plant equipment failures.

The development of a polymer-coated monolith catalyst was not anticipated in the original scope of work. Early setbacks and exploratory catalyst fabrication studies led to this novel idea. Resources were added to the program to quickly develop a stable, workable polymer that could be applied to the monolith cordierite substrates. Within four months, the polymer was optimized and synthesized, and coating techniques were developed to coat enough monolith supports for the pilot plant studies.

The pilot plant was constructed at COMPANY 4 and installed at Air Products' pilot facility in Pace, Florida. Delays in delivery were encountered due to unexpected pump failure and the failure of some pipe welds to meet ASME X-ray code requirements. These deficiencies were identified and corrected during the safety review and equipment testing phases of start-up. The full operational start-up proceeded without incident on 15 October 2001.

Table 4.1: Summary of Project Milestones

Task	Description	Original Deadline	Completion Date
1.1 1.2	Lab Catalysis and Catalyst Optimization	1 January 2000	1 April 2001
1.3	Process Definition	1 July 2000	1 July 2000
1.4	Catalyst Life Studies	1 October 2001	1 April 2001
1.5 1.6	Gas-Liquid Mass Transfer and Hydraulic Analysis	1 October 2000	1 July 2000
1.7	Solid-Liquid Mass Transfer and Hydraulic Analysis	1 January 2001	1 April 2001
1.8	Hydraulic Stability Characterization	1 August 2000	1 September 2001
2.1 2.2	Pilot Plant Definition and Engineering	1 October 2000	1 July 2000
2.3	Pilot Plant Construction	1 July 2001	1 July 2001
2.4 2.5	Pilot Plant Start-Up and Process Studies	1 August 2001	1 January 2002

5: BUDGET

5.1 Hours and Cost Breakdown By Task

The MLR project finished slightly over budget, with all tasks completed (see Table 5.1). The proposed total project budget was \$3,163,260, and cost share was 33% DOE and 67% Air Products (\$1,043,875 and \$2,119,385, respectively). Actual spending through 30 May 2002 is \$3,301,240, indicating that the project went over budget by \$137,980 (this accounts for less than 5% of the total project budget).

The shifting of man-hours from Task 1.4 to Task 1.1 occurred in the early phases of the project. This additional effort was needed to develop a working knowledge of potential MLR catalysts and how these catalysts were affected by this new procedure. Task 1.4 will need to be revisited at a later time and will focus on specific customer chemistries. The other large variance, which occurred in Tasks 2.3 and 2.4, was partially due to the difficulties with the pilot plant construction company (COMPANY 4), obtaining and installing a functioning pump, and correcting mistakes made by COMPANY 4.

Table 5.1 Cost Breakdown by Task and Hours Breakdown by Sub-Task for the Entire Project. (Actual numbers through May 2002 were used for calculations.)

	Proposed Hours	Actual Hours	Variance	Proposed Cost	Actual Cost	Variance
Task 1.1 Lab Catalyst Studies	3038	6257	(3,219)			
Task 1.2 Catalyst Optimization	488	201	287			
Task 1.3 Process Definition	338	17	321			
Task 1.4 Catalyst Life Studies	3750	169	3,581			
Task 1.5 Hydraulic Studies Bench Reactor	975	132	843			
Task 1.6 Gas-Liquid Mass Transfer Studies	383	1220	(837)			
Task 1.7 Catalyst-Liquid Mass Transfer Studies	383	262	121			
Task 1.8 Hydraulic Stability	1088	1500	(412)			
Task 1 Totals	10443	9758	685	\$1,464,951	\$1,610,011	\$145,060
Task 2.1 Scope and Definition of Pilot Plant	638	551	87			
Task 2.2 Pilot Plant Engineering P&ID	900	368	532			
Task 2.3 Pilot Plant Construction	300	4064	(3,764)			
Task 2.4 Pilot Plant Start-Up	450	3256	(2,806)			
Task 2.5 Pilot Plant Studies	900	74	826			
Task 2 Totals	3188	8313	(5,125)	\$1,565,567	\$1,508,229	\$57,338
Task 3.0 Management and Reporting	900	1583	(683)	\$132,742	\$183,000	\$50,258
	14531	19654	(5,123)	\$3,163,260	\$3,301,240	\$137,980

5.2 Allocation of Time to PI and Key Personnel

As seen in Table 5.2, the only time variation occurred with the Research Associate. This variation was due to the difficulties with the pilot plant construction and pilot plant start-up.

Table 5.2: Allocation of Time to PI and Key Personnel

	Proposed Man Months	Actual Man Months	Variance
Principal Investigator (Dr. Reinaldo Machado)	10	10	0
Sr. Research Associate (Dr. Francis Waller)	5	4	1
Research Associate (Dr. Robert Broekhuis)	7	13	6

5.3 Spending By Fiscal Year

Table 5.3 illustrates spending by fiscal year. The spending was low during the kick-off phase of the project in fiscal year 2000. Difficulties in the building and start-up of the pilot plant pushed fiscal 2001's budget over by \$371,873. Delays in the pilot plant start-up during fiscal year 2001 caused additional project costs to be pushed into fiscal year 2002.

Low estimates on the costs of the pilot plant equipment and lab materials accounted for some of the project overrun. Included in the original proposal were \$502,572 for the pilot plant equipment and \$86,850 for laboratory materials. Both estimates were low, with actual spending for pilot plant equipment at \$645,793 and actual spending for laboratory materials at \$198,000.

Table 5.3 Spending by Fiscal Year

	Proposed Spending	Actual Spending	Variance
Fiscal Year 2000	\$1,742,353	\$1,143,048	\$599,295
Fiscal Year 2001	\$1,420,907	\$1,792,780	\$(371,873)
Fiscal Year 2002	\$0	\$365,412	\$(365,412)
Total	\$3,163,260	\$3,301,240	\$137,980

SECTION 6: TECHNICAL

6.1 Chemistry and Catalyst Development

Traditional monolith catalyst technology developments and applications have focused on gas-phase chemical processes. This is natural since the original application of monolith catalysts have been for exhaust gas treatment in the automotive industry. A variety of commercial formulations for gas phase applications are available, and they typically use inorganic wash coatings to form the support for the metal catalyst. On the other hand, slurry-based catalysts that are used for the manufacture of specialty chemicals employ primarily carbon-based materials as supports for the catalytic metals. This section of the development program focused on evaluating traditional commercial-type, inorganic, wash-coated catalysts that were provided by COMPANY 1 in addition to novel monoliths, which more closely resemble carbon-based supports.

Customized carbon-type catalysts were fabricated from cordierite and carbon monolith supports. Catalytic metals were applied directly to the carbon monoliths. A novel polymer-based wash coat was developed and applied to a cordierite monolith support to give it carbon-like properties. Of the carbon-based supports, the polymer-coated cordierite gave a catalyst with highest activity and selectivity using the nitrobenzene hydrogenation test chemistry operated in a lab autoclave test unit.

COMPANY 1 provided commercial-type, inorganic-based catalysts for evaluation in both lab and pilot studies, and applied catalytic metals to polymer-coated cordierite supports fabricated at Air Products.

Catalyst Optimization (Task 1.2)

Lab-Scale Monolith Testing Unit

To expedite the catalyst development program, a simple and effective laboratory reactor tool was necessary to conduct the hydrogenation process chemistry. A 2-liter batch autoclave reactor was fitted with a custom gas-induction impeller and catalyst holder that provided optimal gas dispersion and high liquid flow through the monolith catalyst. This test unit and catalyst holder is the subject of U.S. Patent Application 10/076,813 and allowed existing lab-testing infrastructure to be used in testing monolith catalysts. In a typical hydrogenation experiment one liter of the reaction solution and a 2-inch diameter by 2-inch length monolith catalyst fixed in the holder were charged to the autoclave. Figure 6.1.1 illustrates the features of the testing unit.

Figure 6.1.1: Lab-Scale Monolith Testing Unit

Test Reaction

The hydrogenation of nitrobenzene to aniline was selected as the model reaction. Market studies confirmed that this reaction is recognized as a standard in the fine and specialty chemicals industry to characterize and rank catalyst performance. In addition, the test reaction builds on Air Products' interest in nitroaromatic hydrogenation. The experimental data for this reaction is general and universally recognized, allowing it to be presented to external customers without proprietary concerns.

Both GC and HPLC methods were developed to analyze for all the expected products and potential co-product chemistry. Figure 6.1.2 summarizes all of the reaction chemistry anticipated for the hydrogenation of nitrobenzene to aniline. Molar selectivity is based on internal standard methods, with the moles of nitrobenzene as the basis of comparison.

The performance of the lab-scale monolith-testing unit was compared to a published hydrogenation rate. Under similar reaction conditions and catalyst loading ($\sim 5\%$ Pd), the lab-scale monolith-testing unit gave a hydrogenation rate approximately twice ($23.6 \text{ moles H}_2/\text{m}^3 \text{ catalyst/sec}$) that of the published rate by Hatziantoniou, et al [7], ($15.4 \text{ moles H}_2/\text{m}^3 \text{ catalyst/sec}$).

Figure 6.1.2: Nitrobenzene Test Chemistry

Low Surface Area Monolith Wash Coats

Traditionally in the development of gas-phase heterogeneous catalysts, high surface area is associated with high catalyst activity. After many monolith catalysts were tested, it was recognized that monolith catalysts having improved catalytic hydrogenation activity could be achieved by preparing them with a low surface area compared to conventional monolith catalysts. For example, monolith catalysts with a surface of 25 m²/gram (or less) yielded excellent hydrogenation activity. This is illustrated in Table 6.1.2.

The polymer-coated catalysts were created by first preparing a viscous liquid polymer solution that would serve as a wash coat. The polymer was synthesized using an acid-catalyzed polymerization of furfuryl alcohol (PFA), pyrrole and polyethyleneglycol-methylether (PEG 750). The polymer was dip-coated onto a cordierite monolith having a square channel structure with between 100-800 cells per square inch. The coated monolith was dried at 80°C in N₂, then heat-treated at 280°C in N₂, followed by 280°C in 5% O₂ in N₂ to produce the polymer-coated monolith. The catalytic metal was then deposited by an incipient wetness technique. The

monolith catalysts were then heat treated as above: 80°C in N₂ and 280°C in N₂. The surface area of the monolith catalysts was measured by adsorption of N₂ or Kr using the BET method.

Characterization of the Preferred Carbon-Coated Monolith Catalyst

TGA/IR

Using a TGA/IR (Thermal Gravimetric Analysis and Infrared Spectroscopy) technique, a temperature ramp was applied to samples of the polymer-coated monolith to characterize the polymer curing/activation profile. During the temperature ramp, weight is lost due to the release of volatile compounds, which are then chemically identified using infrared spectroscopy. Using this technique, it was verified that at 300°C, significant weight loss occurs that corresponds to a “glycol like” material believed to be decomposition products from the breakdown of polyethyleneglycol-methylether. This method tends to yield materials with high surface areas, which are undesirable. To avoid the high surface area, a final curing thermal profile was used to activate the polymer at 280°C in N₂, followed by a short treatment in 5% O₂ at the same temperature. The first step was used to partially decompose the polymer without weight loss, and the second was employed to activate the surface and develop limited surface area.

Infrared spectroscopy (IR) can also be used to understand the surface character of the cured and activated polymer. The spectra of the polymer surface were taken with an IR microscope (Figure 6.1.3). Note that after heating the sample to 300°C, we observed a significant drop in the intensity of the peaks around 3300, 2876, 1300 and 1100 cm⁻¹. The two primary bands that diminish at 2876 and 1100 cm⁻¹ are associated with a glycol type species. This result is consistent with the loss of polyethyleneglycol-methylether from the polymer.

Figure 6.1.3: IR Spectra of PFA-Coated Monolith, Before and After Heating to 300°C

SEM Photomicrograph

Scanning Electron Microscopy, SEM, photomicrographs were taken of the surface of the monolith to help understand surface texture. As shown in Figure 6.1.4, at 5,000x, the surface of cordierite displays large particles fused together, which is consistent with the high-temperature firing used to manufacture this material. By contrast, the coated cordierite has a much smoother surface, similar to one that was coated with a polymer. Note also that the coated cordierite does show some holes or cracks that would form when the polyethyleneglycol-methylether decomposes and forces its way out of the polymer. Figure 6.1.4 shows the same sample at 20,000x. The coated sample displays a smoother surface, with small Pd crystallites.

Figure 6.1.4: SEM Images of Three Stages of Fabrication of the Cordierite Monolithic Catalyst: 1) 5,000x Magnification of Cordierite Substrate Surface, 2) 5,000x Magnification of Cordierite Substrate Coated with Polymer and Treated, 3) 20,000x Magnification of Coated Cordierite Showing Dispersed Pd Particles

X-Ray Diffraction

X-Ray Diffraction, XRD, patterns were generated from several PFA-coated monoliths, but typically the only crystalline material identified was the cordierite substrate. Due to the complex pattern and high intensity of the peaks, it was impossible to differentiate Pd or PdO from cordierite, and as a result Pd or PdO crystallite sizes could not be measured.

Surface Area

Initially, the catalyst surface area was measured using N₂ BET. However, since the catalysts with the best activity have surface areas <10 m²/g, the probe gas was switched from N₂ to Kr to increase measurement sensitivity. In most gas-phase reactions, high activity is associated with high catalyst surface area. However, in liquid-phase reactions, the opposite trend appears to dominate this reaction. For example, Table 6.1.1 summarizes surface area and nitrobenzene hydrogenation rate. In general, the low surface area samples yield the highest reaction rate. This is consistent with mass transfer control and is key to the high rate in this reaction. This suggests that all the metal is accessible in the low surface area wash coat.

Table 6.1.1: Pd/Carbon Monolith Catalysts

					BET	Micro PV	Meso PV	Median PD
Sample	Prep.	Comments	NB-1 Rate	NB-8 Rate	m ² /g	cc/g	cc/g	Å
17659-17-26	APCI	PFA	100	100	<1			
17790-14-19	APCI	PFA	96	97	0.43			
17790-17-15	APCI	HSA, PFA	65	78	3.48			
17790-16-23	APCI	Cordierite	36	17	0.21			
17759-19-36	APCI/COMPAN Y 2		21	12	466	0.21	0.01	30
EP-5995	COMPANY 1/COMPANY 4	2% Pd	82	7	<1			
EP-5994	COMPANY 1/COMPANY 4	1% Pd	25	17	<1			
17790-24-32	APCI/COMPAN Y 3	WV-779	29	13	348		0.14	35
17790-22-30	APCI/COMPAN Y 3	WV-780HP	39	25	372		0.22	40
17790-28-47	APCI	Phenolic Resin	87	52	<1			

Notes: APCI=Air Products
HSA= High Surface Area
NB-1= Nitrobenzene hydrogenation rate use 1
NB-8= Nitrobenzene hydrogenation rate use 8
PV= Pore Volume, cc/g
PD= Pore Diameter in Angstroms

Testing of Monolith Catalysts

The lab-scale monolith-testing unit was used to characterize the performance of a series of catalysts made from monolith substrates from various suppliers. These suppliers included COMPANY 1, COMPANY 2 and COMPANY 3. The catalytic metal was added either by COMPANY 1 or Air Products. During the hydrogenation reaction, hydrogen uptake vs. reaction time data was measured, and a hydrogenation rate vs. conversion plot was obtained. The hydrogen pressure data was corrected for compressibility. The reported rate of hydrogenation in the tables was measured at 50% conversion, and selectivity was measured at 100% conversion. In Table 6.1.2, the hydrogenation rate of several monolith catalysts is compared. The furfuryl alcohol polymer wash coat, calcined at 280°C, yielded a monolith catalyst with a surface area ≤ 12 m²/gram. These catalysts have a higher hydrogenation rate than does a monolith catalyst with no wash-coat layer or monolith catalysts with high surface areas.

Table 6.1.2: Hydrogenation of 40-wt% Nitrobenzene in Isopropanol¹

Monolith	Layer/L	Surface Area ³	Rate ²		Sel. ⁶
			Init. ⁴	Final ⁵	
2% Pd/cordierite ⁷	none	<1	33	16	98
1.5% Pd/L/cordierite ⁷	polymer	<1	92	91	97
3.1% Pd/L/cordierite ⁷	polymer	12	61	74	97
1.7% Pd on carbon composite ⁸	carbon composite	466	20	13	98
4.6% Pd on carbon composite ⁹	carbon composite	372	36	23	93

1. 120°C, 200 psig, 1500 rpm in lab-scale monolith autoclave testing unit

2. moles H₂/m³ catalyst/second

3. m² per gram

4. second experimental run

5. eighth experimental run

6. aniline(mol %)

7. 400 cpi

8. 200 cpi; COMPANY 2

9. 250 cpi; COMPANY 3

In Table 6.1.3, the hydrogenation rate of nitrobenzene is compared for two low-surface-area monolith catalysts where only nitrobenzene (no solvent) is charged to the reactor. In these two reactions, the reaction mass starts as one liquid phase, but becomes two liquid phases as water, a co-product in the reaction, accumulates. In both of these reactions, the hydrogenation reaction rate is only reduced by ~50 to 30% compared to a one-phase (co-solvent) reaction. Also in these two experiments when the hydrogen uptake curve is re-plotted as hydrogenation rate vs. time, the hydrogenation rate is nearly constant until the end of the reaction. The nearly constant hydrogenation rate was not expected, since the co-product water formed during the reaction formed two immiscible phases. As the concentration of the water increased, one would expect the hydrogenation rate to decrease.

Table 6.1.3: Hydrogenation of Nitrobenzene¹

Monolith	Layer/L	Surface Area ²	Rate Init. ^{3,4}	Sel. ⁵
1.5% Pd/L/cordierite ⁶	polymer	<1	42	99
3.1% Pd/L/cordierite ⁶	polymer	12	44	99

1. 120°C, 200 psig, 1500 rpm in lab-scale monolith autoclave testing unit
2. m² per gram
3. moles H₂/m³ catalyst/second
4. second experimental run
5. aniline (mol%)
6. 400 cpi

Catalyst Life Studies (Task 1.4)

PFA Wash-Coat Monolith Catalyst

A series of autoclave batch experiments was run in sequence with 40% nitrobenzene in isopropanol at 120°C, 200 psig and 1500 rpm. Figure 6.1.5 shows aniline selectivity vs. run number. Within experimental error, the selectivity was nearly constant. Typical molar selectivity at >99.98% nitrobenzene conversion was: 98.5% aniline, 0.5% cyclohexanone, 0.02% cyclohexylamine and 0.98% coupling products and unknowns.

Figure 6.1.5: Extended Testing of PFA Monolith Catalyst – Selectivity

In Figure 6.1.6, the rate of hydrogenation at 60°C (i.e., under kinetic conditions obtained during initial temperature ramp) was plotted vs. run number from the same set of experiments. The decrease in activity was not due to Pd loss, but to activity decline through another mechanism.

Figure 6.1.6: Extended Testing of PFA Monolith Catalyst – Rate of Hydrogenation

Extended Testing of CAT-XXX Wash-Coated Monolith Catalyst

A similar series of autoclave batch experiments was run in sequence with 40% nitrobenzene in isopropanol under the same reaction conditions as the polymer-coated monolith. Figures 6.1.7 and 6.1.8 show that both the selectivity and rate of hydrogenation were nearly constant. Typical molar selectivity at >99.98% nitrobenzene conversion was 98.1% aniline, 0.5% cyclohexanone, 0.03% cyclohexylamine and 1.4% coupling products and unknowns.

Figure 6.1.7: Extended Testing of COMPANY 1 CAT-XXX Monolith Catalyst - Selectivity

Figure 6.1.8: Extended Testing of COMPANY 1 CAT-XXX Monolith Catalyst – Rate of Hydrogenation

For the test depicted in Figure 6.1.8, a different lab-scale monolith-testing unit was introduced during run numbers 10-16. The performance of the monolith catalyst recovered when the experiments were returned to the original lab-scale monolith-testing unit.

Palladium Metal Loss Studies

Two studies were conducted to determine palladium loss from the cordierite monolith catalysts used for nitrobenzene hydrogenation. A 2% Pd/PFA polymer monolith catalyst and a 0.5% Pd/CAT-XXX monolith catalyst were each tested in five sequential runs at 60°C and 200 psig.

In testing the 2% Pd/PFA polymer monolith catalyst, the Pd concentration in all five reaction products was <0.1 ppm, or ~0.1 mg per run. With 1000 mg Pd on the fresh catalyst, this was considered an insignificant loss. The spent catalyst was not analyzed for Pd because, due to variable Pd deposition in preparation, more than 500 runs would be required to detect the indicated level of Pd loss shown in Figure 6.1.4. This will be explored in future customer trials.

In testing the 0.5% Pd/CAT-XXX monolith catalyst, the Pd concentration was 0.6 ppm in the first run and <0.1 ppm thereafter. Again, metal loss was insignificant. With 250 mg Pd in fresh catalyst, more than 100 runs would be required to detect metal loss by spent catalyst analysis. This high retention of Pd is consistent with sustained CAT-XXX hydrogenation activity seen in Figure 6.8. After a conditioning run, the CAT-XXX monolith catalysts showed no significant activity loss over 22 runs – even at 120°C.

Recommendation for Pilot Plant

Based on the extended testing of the PFA wash-coated monolith, the CAT-XXX monolith catalyst and the Pd loss studies, both catalysts were deemed suitable for testing in the pilot plant at Pace, Florida.

Intellectual Property and Patents

Three patent applications were derived from the catalyst development effort.

Application 09/839699, “**Hydrogenation With Monolith Reactor Under Conditions of Immiscible Liquid Phases**,” was filed in April 2001. The application has been allowed by the U.S. Patent Office. The application describes and claims an improved process for the hydrogenation of organic compounds in the presence of water or another immiscible liquid. The two-phase system can result from water generated in the process or from water added to the reaction mix. The improvement due to using a monolith for this system was demonstrated for nitrobenzene hydrogenation. The advantages are that: (1) no co-solvent is required to maintain a single phase; (2) because solvent is not used, a high reactant throughput may be obtained; (3) as we demonstrated, a more consistent rate may be obtained; and (4) separation of catalyst from liquid products may be simplified.

The general claims include any monolithic catalysts for use in the process, while specifically polyfurfuryl alcohol polymer / network carbon-coated monoliths are claimed. Claims include a wide range of reactions, monolith characteristics, and reaction conditions.

Relative to a slurry reactor, the monolith system is particularly well suited for two-phase operation because the problems of separating a powder from two phases are eliminated.

Application 09/867,959, “**Polymer Network/Carbon Layer on Monolith Support and Monolith Reactor**,” was filed in May 2001 as a continuation-in-part of 09/839699. Its status is pending and awaiting first USPTO action. The CIP below encompasses claims in 09/867,959.

Application 10/002,250, “**Coated Monolith Substrate and Monolith Catalysts**,” was filed in October 2001 as a continuation-in-part of application 09/867,959 (cited above). The status is pending. CIP 10/002,250 describes and claims a low surface area monolith without restriction on its application. The application claims a monolith support having BET surface area from 0.1 to 25 m²/g. In addition to the coatings based on polyfurfuryl alcohol and other carbon layer precursors, inorganic wash-coats are claimed.

The novel feature of this material, the low surface area of the carbon, is a beneficial property in liquid-phase systems in which high surface area aggravates mass transfer limitations. Because most monoliths are applied to gas phase systems, this benefit is generally not appreciated.

6.2 Engineering Development

This phase of the MLR development program focused on generating fundamental engineering data that would be used to design a working pilot scale MLR system. The key outcome of this activity is demonstrating the lab test chemistry at a pilot scale using the catalyst developed in the catalyst development phase. The catalyst and process performance between the lab and pilot scale are compared to confirm the suitability of the MLR for scaleup.

Process Definition (Task 1.3)

From a review of literature studies and preliminary observations in the Monolith Loop Hydrodynamic Test Unit, suitable ranges for flow rates of gas and liquid reaction components, expressed in terms of superficial phase velocities, were determined to be 0.15-0.40 m/s for each phase, with the limitation that the ejector imposes an upper threshold on the gas holdup of about 60%. No inherent limitations on process temperature and pressure have been identified; with appropriate engineering, any set of operating conditions practically encountered in gas-liquid reactions can be employed within the MLR system. Practical ranges are from sub-ambient to 250°C for temperature, and from 15 to 1500 psig for pressure.

Mathematical models of monolith reactors and MLR processes have been constructed, and will be used for purposes of data interpretation, as well as process design and scaleup.

Hydraulic Studies (Task 1.5)

Monolith Loop Hydrodynamic Test Unit

Hydraulic studies were carried out to characterize ejector performance, monolith reactor pressure drop and overall flow patterns in a scaled-down MLR system. Experiments were performed in the Monolith Loop Hydrodynamic Test Unit (MLHTU), shown in Figure 6.2.1. The MLHTU was constructed from clear plastic to enable visual observation of flow patterns. It consists of a hold tank, a centrifugal pump, a gas-liquid ejector and a reactor tube, along with instrumentation for pressure, temperature and flow measurement. Aqueous liquid is pumped from the hold tank

to the ejector, which draws in either ambient air or nitrogen. The two-phase mixture passes through the monolith stack back to the hold tank.

The monolith stacks used for these studies consisted of a number of monolith segments stacked lengthwise, each 2 inches in diameter. A 2-foot stack was constructed from eight 3-inch-long elements; a 4-foot stack was constructed from eight 6-inch-long elements. No effort was made to align the channels of adjacent monoliths, nor were the monoliths deliberately spaced.

The MLR concept gives the best performance at high superficial velocities of both gas and liquid. At these conditions, the rate of mass transfer in the monolith channels is high. Additionally, the velocity with which the two-phase flow exits the ejector is high, leading to a turbulent frothy/bubbly flow pattern in the mixing zone between the ejector and the monolith. For this reason, minimum superficial gas and liquid velocities of about 0.1 m/s were maintained. The maximum superficial velocities were determined by the circulation pump capacity and the suction capacity of the ejector. For the configurations tested, the practical superficial velocity limits were 0.32 m/s for liquid and 0.42 m/s for gas.

Figure 6.2.1: Schematic of the Monolith Loop Hydrodynamics Test Unit (MLHTU)

Ejector Operating Envelope

The specific configuration of the ejector within the MLHTU (pump, ejector and monolith stack) gives rise to an operating envelope that encloses the possible gas and liquid flows for a particular configuration. The envelopes are typically plotted on a superficial velocity map, with liquid velocity (equivalent to liquid flow rate) on the horizontal axis and gas velocity (equivalent to gas flow rate) on the vertical axis. These plots all follow the same general trends, described below; an example is shown in Figure 6.2.2. All superficial velocities will be related to a stack of 2-in.-diameter, 400-cpsi monolith elements, which reflects an open flow area of 15.0 cm². The liquid velocity is determined almost entirely by the pressure at which liquid is presented to the ejector, which in turn is determined by the position of the liquid valve at the pump discharge. The liquid flow rate is also somewhat affected by the pressure in the ejector chamber, and therefore by the position of the gas throttling valve, but this is a second-order effect. The superficial gas velocity is determined by both the gas and the liquid pressures feeding the ejector. The lower the liquid pressure (and therefore, the liquid flow rate), the lower the gas flow rate. At a given liquid flow rate, the gas flow rate may be manipulated using the gas-throttling valve.

Figure 6.2.2: Example of the Operating Envelope on a Superficial Velocity Map

The two paragraphs above imply that a given combination of gas and liquid superficial velocities can be achieved by only one position of the gas and liquid feed valves, when the second-order effect of gas feed pressure on liquid flow rate is ignored. All operating points lie within a roughly triangular operating area on the superficial velocity map. For any particular

configuration, the maximum superficial gas velocity is achieved at the condition with both gas and liquid valves fully open. We refer to this as the unrestricted flow condition. The operating area of the map is confined by two curves extending from the unrestricted superficial velocities. One curve is followed when the liquid valve is throttled while the gas valve remains fully open; along this curve, both gas and liquid superficial velocities decrease. The other curve is generated by throttling the gas valve while leaving the liquid valve open; while the superficial gas velocity decreases along this curve, the superficial liquid velocity increases slightly, due to the decreasing pressure in the ejector chamber.

The shape and position of the operating area depend, among other things, on the ejector (nozzle) installed in the MLHTU, the monolith bed configuration, and the temperature and composition of the liquid. The operation of the MLR is summarized by Broekhuis et al. [6].

Two-Phase Flow Patterns

Gas and liquid exit the ejector as a pseudo-homogeneous mixture, with gas bubbles as the discrete phase and liquid as the continuous phase. No attempt was made to characterize this dispersion (e.g., in terms of bubble size distribution), but visual observation and inferences from other measurements cast some light on the dispersion properties.

When deionized water is used as the motive liquid, large bubbles are observed in the mixing section between ejector and monolith, most likely due to coalescence both in the diverging section of the ejector and in the mixing leg itself. When electrolyte solutions are used, the bubbles in the mixing section are much smaller (due to the non-coalescing nature of such solutions), and the flow pattern in this section appears to be more chaotic, with better distribution of the dispersion to the monolith. A more in-depth approach to characterizing gas-liquid flow uniformity will be presented in Task 1.8.

Monolith Pressure Drop

The ability of the ejector to draw gas into the circulating liquid stream decreases as the backpressure at the ejector outlet increases. In an MLR system, this backpressure is due to frictional pressure drop through the monolith reactor. Although several approaches to modeling the pressure drop for gas-liquid flow through monoliths have been published, no one model has emerged as universally appropriate. This is likely due to the dependence of pressure drop on the state of the incoming flow (bubble size and distribution), which means that pressure drops must be measured for the combined ejector/monolith system.

In this report, pressure drops are analyzed according to the customary friction factor formulation for flow:

$$\Delta P_{\text{fric}} = 4f \cdot \frac{1}{2} \rho_L v^2 \cdot \frac{L}{d_c}, \text{ with } v = u_L + u_G \quad (6.2.1)$$

Monolith channel diameters are small, which means that practical flows through monoliths take place in the laminar regime. In this regime, the friction factor is inversely proportional to the Reynolds number. For example, for single-phase flow through a round or square channel:

$$f_L = 16/Re_L, \text{ or } (f Re)_L = 16 \quad (6.2.2)$$

where, $Re_L = \{\rho_L (u_L + u_G) d_C\} / \mu_L$

ρ_L = liquid phase density,

$u_L + u_G$ = liquid and gas phase velocities respectively,

d_C = monolith channel width,

μ_L = liquid phase viscosity.

Subscripts L and G refer to the liquid and gas phase, respectively.

Following this formalism, pressure drop results measured in the MLHTU will be reported in terms of the product of friction factor and Reynolds number, $f_{LG} Re_L$ for gas-liquid flow. The pressure drop for liquid-only flow, for both deionized water and electrolyte solutions, was found to conform to equation 6.2.2 over the entire range of liquid flows. This is evidence that the electrolyte concentration does not affect the pressure drop for liquid-only flow.

Most pressure-drop measurements were taken for gas-liquid flow. The manipulated variables for these studies were: gas and liquid flow rates (according to the superficial velocity map described above), monolith channel density and stack height, and liquid composition (deionized water, 0.05M Na_2SO_4 , 0.10M Na_2SO_4).

Figure 6.2.3 shows results from several sets of measurements using a 4-foot-high, 600-cpsi monolith stack. Black symbols represent liquid-only results, while the other colors represent gas-liquid results at various flow conditions (gas-to-liquid ratios). It is evident that the introduction of gas raises the friction factor, the only exception being deionized water at low flow rates. Another obvious trend is the increase in friction factor with electrolyte concentration. This is almost certainly due to the decreasing coalescence tendency, which leads to smaller bubbles being fed to the monolith, giving rise to shorter gas and liquid slugs moving through the channels. Literature models have suggested that friction factors increase with decreasing slug length; this parameter is difficult to measure directly, but the trend is supported by the current data. We have not identified a literature model capable of predicting or correlating our experimental pressure-drop results.

At likely process operating flows ($u_L = u_G = 0.3$ m/s) and non-coalescing conditions, the friction factor f_{LG} is more than twice f_L , the friction factor for liquid flowing at the same velocity. This must be taken into account in the design of the commercial ejector/reactor combination.

Figure 6.2.3: Gas-Liquid Friction Factor vs. Total Superficial Velocity for Measurements using the 4-ft x 600-cpsi Monolith Stack

Gas-Liquid Mass Transfer (Task 1.6)

For successful implementation of MLR technology, mass transfer from hydrogen bubbles to the catalytic surface must be fast. To successfully scale up the system components, the mass transfer rate must be predictable, preferably through the use of a predictive model describing the effects of various system properties and parameters on the rate of mass transfer. The overall mass transfer rate can be broken down into several component processes, in which hydrogen is transferred from gas to liquid, from liquid to solid, and/or directly from gas to solid. Each of these mass transfer paths must be understood, so that the MLR technology can be confidently scaled up to both pilot-plant and commercial scale. This task focused on characterizing gas-liquid mass transfer, which is typically expressed as the liquid-side mass transfer parameter k_{La} . Gas-liquid mass transfer is commonly studied by observing the transfer of oxygen from air to water. The literature describes numerous methods for determining gas-liquid mass transfer coefficients in such systems. In preparation for this task, we reviewed dynamic, steady-state and batch methods, and concluded that the batch method was most suitable for use in the MLHTU. In the batch method, an aqueous sodium sulfite solution is oxidized by ambient air. The time required to consume all sulfite is measured by monitoring the dissolved oxygen concentration in the liquid. Assuming that the rate of mass transfer is constant throughout the experiment, k_{La} follows by mass balance. Advantages of the batch method are that it is simple and it does not rely on the accuracy of DO probes or titrations.

The batch method as described in the literature was adapted for use in the MLHTU. To achieve the most accurate results, a two-point measurement method was developed. The equations governing the calculation of oxygen transfer rate and k_La were derived for this system, which has the distinction of having a blend of back-mixed and plug-flow characteristics. A typical oxygen breakthrough curve for mass transfer measurements in the MLHTU is shown in Figure 6.2.4.

In preliminary experiments we found that gas-liquid mass transfer is strongly affected by electrolyte concentration. Therefore, experiments must be carried out at a constant electrolyte concentration to attain reproducible, meaningful results. All further experiments were carried out at $[\text{Na}_2\text{SO}_4] = 0.1 \text{ mol/l}$.

Figure 6.2.4: Typical Oxygen Breakthrough Curve Generated In The MLHTU

Representative results gathered using a 4-foot-long, 600-cpsi monolith stack are given in Figure 6.2.5. The results are presented on a superficial velocity map. Clearly, gas-liquid mass transfer becomes faster as both gas and liquid superficial velocities increase. Similar results were obtained for different monolith configurations (stack heights and channel densities).

Although the original intent of this task was to develop models describing gas-liquid mass transfer, analysis of the results showed that the information required for successful design of a commercial MLR system could only be gained from experiments conducted in a reaction system with a catalytically active monolith. Therefore, the results from this MLHTU study were used as a guide to select suitable operating conditions for experiments in the MLR pilot plant. Pilot plant trials are described in Task 2.5 below.

Figure 6.2.5: Mass Transfer Results for 4-foot 600-cpsi Monolith Stack. The Ejector Operating Envelope is Indicated in Blue; K_{ja} Values (S^{-1}) for Each Measurement Point are Given in the Figure.

Catalyst-Liquid Mass Transfer (Task 1.7)

For measuring mass transfer between the liquid phase and the catalyst surface, we intended to use a method based on hydrogen peroxide decomposition described in the literature. On further investigation, we learned that this method would not be successful in MLHTU studies. Instead, our overall model development has drawn from various approaches to liquid-solid mass transfer modeling described in the literature.

Hydraulic Stability (Task 1.8)

It was identified early in the MLR development program that uniform distribution of gas and liquid across the monolith inlet is crucial to successful operation. This task aimed to characterize the quality of the distribution by using a tomographic visualization technique.

Electrical Resistance Tomography (ERT) was used to characterize phase distribution in the MLHTU. Electrodes arranged in a circle around a planar gap between two monolith elements measure the conductivity of the fluid flowing through the monolith. Rapid successive measurements result in a two-dimensional conductivity map, from which the gas holdup can be determined. Gas-liquid flow patterns through the monolith were successfully visualized and analyzed. The degree of homogeneity was evaluated for various experimental setups. Individual tomograms for various feed gas holdups are shown in Figure 6.2.6. The colors in the tomograms

vary from red (all liquid) to blue (all gas). Besides analysis by visual inspection of the tomograms, the tomographic information may be subjected to statistical analysis, which leads to a quantitative measure of homogeneity.

Figure 6.2.6: Tomography Images for Experiment for Increasing Air Flow Rates. The Gas Volume Fraction ϵ_G is given for Each Tomograph.

Using artificial obstructions, we demonstrated that this tomographic technique was capable of discerning flow inhomogeneity. However, with the MLHTU equipment operating normally, no significant inhomogeneity was observed. At least at the 2-inch scale, the ejector distributes gas and liquid uniformly across the monolith reactor. We are currently evaluating the use of ERT at a larger scale for a full-scale hydrodynamic demonstration unit.

6.3 Pilot Plant Design, Construction, Start-Up and Hydrogenation Studies (Tasks 2.1-2.5)

After the initial phases of both the catalyst and hydrodynamic programs were completed, the next step was demonstration of both the catalytic reaction and hydrodynamics aspects of MLR technology at an intermediate scale. A pilot plant was designed to prove the process concept, to conduct further R&D at the larger scale as necessary, and to serve as a business development tool for use in customer trials and demonstrations. The process flow diagram is illustrated in Figure 6.3.1.

Figure 6.3.1: Process Flow Diagram For MLR Pilot Plant. The Primary Process Components are a 20-Gallon Hold Tank, a Magnetically Driven Centrifugal Pump, a Gas-Liquid Ejector and a Four-Foot-Long, 2-Inch-Diameter Monolith Reactor. Auxiliary Components Include a Gas Feed and Vent System, a Sampling Loop, and a Heating Oil System.

To meet these varying needs, the construction and instrumentation of the pilot plant were engineered with an emphasis on maximum flexibility and ease of data analysis: the pilot plant operating window extends from 0 to 1500 psig and ambient to 400°F, and the Hastelloy metallurgy can accommodate the great majority of envisioned customer applications. The apparatus is extensively instrumented (temperature, pressure, flow and level measurements) to allow a wealth of data to be collected for use in process scaleup. The pilot plant accommodates a stack of 2-inch-diameter monoliths, up to 4 feet in height, with a maximum liquid batch size of 20 gallons.

The pilot plant was constructed at COMPANY 4., and installed at Air Products' Pace, Florida pilot facility (Figure 6.3.2). Start-up occurred on 15 October 2001. The initial pilot campaign was designed to prove the MLR concept and the catalyst performance in the hydrogenation of nitrobenzene to aniline, which is the test chemistry demonstrated at the lab scale.

Figure 6.3.2: MLR Pilot Plant after Installation at Air Products' Pace, Florida Pilot Facility. Side View Showing Hold Tank at Mid-Level and Ejector at Top Level, with the Monolith Reactor Extending Between These Levels.

Equipment Performance

Performance testing, completed at COMPANY 4's facility, uncovered several issues that required resolution to meet design criteria and address various concerns. After these items were corrected, the equipment functioned satisfactorily upon start-up.

The main process pump had been a primary concern in pre-start-up. The pump that was ultimately selected and installed runs smoothly and delivers the desired head/flow rate characteristic. Its variable frequency drive is an effective means for moderating head pressure, if necessary.

The ejector meets our requirements, drawing a sufficiently high hydrogen suction flow to sustain high rates of reaction. The experiments reported here were conducted using the larger nozzle, which resulted in higher liquid and gas superficial velocities than were attained in the Monolith Loop Hydrodynamic Test Unit.

An oil skid provides heating/cooling to the MLR skid via a process heat exchanger. It has demonstrated sufficient capacity for our early trials, but its ultimate capacity is below our expectations, and has limited to some extent the choice of operating conditions. Tying in to a facility chiller system has subsequently increased its capacity.

Gauge and differential pressure transmitters yield accurate and consistent results with minimal drift. Similarly, temperature measurement has been problem-free, with consistent temperature readings across measurement points.

The hydrogen gas flow meter, a thermal-type mass flow meter, may be reading low. This is suspected because the hydrogen mass balance for batch hydrogenation runs is consistently off by at least 10%. The offset appears to be more pronounced during runs with slow hydrogen uptake, which suggests that the accuracy of the flow meter deteriorates near the bottom of its scale. We will address this issue by calibrating and possibly re-ranging the instrument.

The motive liquid flow meter, a MicroMotion coriolis-type mass flow meter, measures and reports the flow and density of the liquid upstream of the ejector and the liquid flow control valve. The measured flow is consistent with the expected pressure-flow characteristic of the ejector, and the measured density is in good agreement with thermodynamic property predictions. At some conditions, the liquid flow signal becomes erratic, with rapid variations, the cause of which is not clear. We will discuss and attempt to resolve the stability issue with MicroMotion technical support.

The suction gas flow meter, which is also a MicroMotion coriolis-type mass flow meter, reported erratic and apparently high flow rates during the initial phase of nitrobenzene testing. Condensation of vapors in the suction line was identified as a likely cause for this behavior. This hypothesis was supported by the fact that the temperature measured inside the flow meter was consistently well below (as much as 50°F) the temperature of the liquid in the hold tank. Heat-tracing this line and installation of a custom steam-traced jacket around the flow meter helped improve performance. A test at process conditions must still be conducted. The heat tracing was

applied toward the end of the nitrobenzene trials; therefore, the gas flow results for most experiments are unreliable. Follow-up experiments will focus on the effects of varying gas and liquid flow rates.

The process is operated from a PC running RSView HMI software, which interfaces with an Allen Bradley PLC at the skid. Ladder logic and HMI functionality had been thoroughly tested and debugged during performance testing, so that very few problems were encountered after start-up. Data acquisition has been reliable and effective, which has ensured that a wealth of information has been collected from the experiments conducted so far.

Initial Nitrobenzene Hydrogenation Results

Nitrobenzene hydrogenations were conducted with batches of 10 or 15 gallons of 40% nitrobenzene in isopropanol as solvent. Standard operating conditions were chosen to be 250°F (121°C) and 200 psig, with fully open gas and liquid valves (resulting in a liquid flow of 9.5 gpm). Most experiments were carried out with COMPANY 1CAT-XXX catalyst. First a single 6-inch active element (surrounded by blank cordierite elements) was loaded into the reactor; subsequently, the number of elements was increased to two, four and finally six. During this time, two experiments were conducted using neat nitrobenzene instead of the 40% solution. Some variations were made in temperature, pressure, and flow rates. Finally, a few experiments were conducted using PFA catalyst elements. For both the CAT-XXX and the PFA monoliths, the palladium metal loading was chosen to be 100 g Pd/ft³ monolith. The pilot-plant performance data is summarized in Table 6.3.1.

To prove basic operability and safety, the first several runs were conducted with a single 6-inch-long CAT-XXX monolith element in the MLR reactor at standard operating conditions. The primary purpose of these runs was to demonstrate that the equipment could be safely run, and to collect reaction rate data to compare with laboratory data.

The reaction rate results were encouraging. Control loops were tuned so that temperature and pressure during the reaction phase were fairly steady, and rates matched those expected from laboratory trials. In subsequent trials, the number of 6-inch catalyst elements in the MLR pilot reactor was gradually increased: one → two → four → six. The reaction rate profiles for representative runs at the standard operating conditions (200 psig, 250°F) are shown in Figure 6.3.3. Even though the data for two elements is scattered due to imperfect tuning, it is clear that performance does not decrease with an increasing amount of catalyst: the rate profiles, expressed per unit of catalyst volume, remain remarkably similar. They also continue to compare well to laboratory results, with the pilot plant exhibiting slightly higher rates at the four- and six-element loadings.

Table 6.3.1: Overview of Pilot Plant Runs. For each Run, the Catalyst Type and Amount, the Liquid Volume and Nitrobenzene Concentration, and the Operating Temperature and Pressure are given, as well as the Average Rate Measured between 40% and 60% Conversion.

Run date	Run #	catalyst	# of elements	Volume gal	CNBZ	temp. °F	pressure psig	rate mol/m ³ s
10/15/01	1	CAT-XXX	1	9.1	20%	217	200	84
10/16/01	2	CAT-XXX	1	9.8	40%	258	202	89
10/17/01	3	CAT-XXX	1	9.8	40%	253	200	79
10/18/01	4	CAT-XXX	1	9.8	40%	254	200	65
10/22/01	5	CAT-XXX	2	9.8	40%	263	200	72
10/24/01	6	CAT-XXX	2	9.8	40%	253	200	71
10/25/01	7	CAT-XXX	2	14.7	40%	242	200	67
11/5/01	8	CAT-XXX	4	14.7	40%	257	200	93
11/6/01	9	CAT-XXX	4	14.7	40%	251	200	89
11/7/01	10	CAT-XXX	4	14.7	40%	ramp	200	70
11/12/01	11	CAT-XXX	6	14.7	40%	263	200	91
11/13/01	12	CAT-XXX	6	14.7	40%	258	200	87
11/14/01	13	CAT-XXX	6	14.7	40%	248	200	82
11/15/01	14	CAT-XXX	6	14.7	40%	240	150	50
11/19/01	15	CAT-XXX	6	14.7	40%	248	150	49
11/20/01	16	CAT-XXX	6	14.7	40%	248	150	43
11/28/01	17	CAT-XXX	6	10.0	100%	250	200	23

12/3/01	18	CAT-XXX	6	10.0	100%	249	400	62
12/5/01	19	CAT-XXX	6	14.7	40%	250	150	45
12/6/01	20	CAT-XXX	6	9.8	40%	176	150	23
12/10/01	21	CAT-XXX	2	14.7	40%	250	200	68
12/11/01	22	CAT-XXX	2	14.7	40%	256	400	197
12/12/01	23	CAT-XXX	2	14.7	40%	ramp	200	71
12/14/01	24	CAT-XXX	2	14.7	40%	ramp	300	144
12/18/01	25	CAT-XXX	2	14.7	40%	250	200	66
12/19/01	26	CAT-XXX	2	14.7	40%	250	200	65
12/20/01	27	CAT-XXX	2	14.7	40%	180	steps	83
1/7/02	28	PFA	3	14.7	40%	252	200-400	57
1/8/02	29	PFA	3	14.7	40%	250	400	44
1/9/02	30	PFA	3	14.7	40%	274	400	52

Figure 6.3.3: Comparison of Reaction Rate Profiles (Rate vs. Conversion) for Runs with Different Amounts of Catalyst, at Nominally the Standard Operating Conditions (200 psig, 250°F). Note that Units of Rate are given as $[\text{mol H}_2/(\text{m}^3_{\text{monolith s}})]$.

Temperature Ramp Experiment

In laboratory R&D trials, a wealth of information was deduced from autoclave reaction experiments in which the temperature was slowly increased over the duration of the reaction. This generated rate vs. temperature data, which can be used to investigate the reaction kinetics, the hydrogen mass transfer rates, and the transition between kinetically limited and mass-transfer-limited regimes.

An analogous experiment was carried out in the pilot plant, using two CAT-XXX catalyst elements at 200 psig and temperatures ranging from 80 to 320°F. Rates and temperatures were measured as a function of time, and the results were fit using a mixed mass-transfer/kinetic model developed with laboratory results. The fit was excellent, as shown in Figure 6.3.4. The parameters in the kinetic expression were the same order of magnitude as for equivalent lab experiments, which suggests that the catalyst preparation was successfully scaled up, yielding an equivalent catalyst. The mass transfer parameter that resulted from the model fit was in the same range as for laboratory autoclave runs – about 3 s^{-1} . Apparently, the overall mass transfer characteristics of the laboratory and pilot equipment are similar.

Effect of Hydrodynamic Operating Conditions

The standard hydrodynamic operating conditions maintained during nearly all pilot runs were: pump rotation speed 55Hz, motive liquid and suction gas control valves 100% open. At standard process conditions, these hydrodynamic settings result in a pump head of 67-70 psi (measured at ejector inlet) and a liquid flow rate of 9.5 gpm. The gas flow rate is not well defined at this time, since the suction gas flow meter did not yield accurate results. Experiments after initial heat tracing was installed indicated a gas flow rate of about 20 gpm (2.7 acfm), which is somewhat higher than seen during subsequent hydrodynamic testing at near-ambient temperature (after improved heat tracing was installed). The gas holdup corresponding to 20 gpm is 68%, which raises questions about the nature of the two-phase flow downstream of the ejector. Additional information will be collected during follow-up testing at process conditions when the heat-traced gas flow meter is fully functional.

For certain episodes of some experiments, the gas or liquid flow rates were partially restricted. During these episodes, reaction rates consistently decreased. This is consistent with our knowledge that at process conditions, the overall rate of reaction is predominantly limited by mass transfer from the gas bubbles to the monolith channel walls. The overall mass transfer rate increases with the channel velocity. Because of the uncertainty in the gas flow rate measurement, quantitative conclusions about the effect of flow conditions on overall performance cannot be drawn yet.

Figure 6.3.4: Rate vs. Time Data for the Temperature-Ramp-Experiment. Also shown is the Kinetic and Mass Transfer Model Fit to the Data.

Hydrogenation of Neat Nitrobenzene

Laboratory trials showed that a monolith catalyst can effectively carry out the hydrogenation of nitrobenzene in the presence of a second (aqueous) phase. This allows neat (undiluted) nitrobenzene to be converted, which is not practical in a slurry hydrogenation reactor. Several pilot runs using neat nitrobenzene were conducted to compare lab and pilot plant performance. Nitrobenzene was hydrogenated using six CAT-XXX catalyst elements at 250°F. One run was conducted at 200 psig, and the other at 400 psig. The rates measured at the lower pressure were lower than those in the lab (25 vs. 40 mol H₂/m³s). At the higher pressure, the rates more than doubled (to >65 mol H₂/m³s), bringing them closer to the ones expected based on our laboratory work. A lower kinetic rate on the catalyst surface is the most likely cause of the slower overall rate; further catalyst optimization would be required to achieve higher rates.

Stability of CAT-XXX Catalyst

The first two catalyst elements inserted into the reactor were present for the entire set of CAT-XXX runs, allowing the activity of these elements to be compared at various stages of the pilot trials. It should be noted that for some reason the runs with the first two elements consistently showed lower normalized reaction rates than the runs with four and six elements, as can be seen in Figure 6.3.3.

Five runs were conducted using the two original elements at standard conditions; rate results are summarized in Table 6.3.2.

Table 6.3.2: Pilot Plant Run Summary

Date	10/24/01	10/25/01	12/10/01	12/18/01	12/19/01
Run#	6	7	21	25	26
Rate (mol H ₂ /m ³ s)	70.5	67.9	68.0	65.7	64.8

An overall downward trend in activity is apparent, but is minor compared to the rate variation from experiment to experiment. For example, the rate difference between adjacent runs 6 and 7 is much larger than the difference between distant runs 7 and 21 (the intervening runs included temperature ramp testing and neat nitrobenzene runs).

Any activity decline might be attributed to intrinsic deactivation of the catalytic activity, or to complete or partial blockage of some of the monolith channels. There is a small upward trend in measured pressure drop across the reactor (from 29 to 33 kPa), which may indicate that flow through some channels was restricted in the later runs.

Note, however, that rate data at standard process conditions is rather insensitive to decreases in the intrinsic catalyst activity, since the overall rate is determined to such a large extent by mass transfer at those conditions. Lower-temperature testing would be required in a true-life study, which was not carried out as part of these initial trials.

Several end-of-run product samples were analyzed for palladium using ICP/AES. In each of the samples, the palladium concentration was above the detection limit (1 ppm), but below the limit

of quantitation (3 ppm). The low concentrations are consistent with earlier findings from the lab trials; a palladium mass balance shows that less than 2% of the palladium contained on the monolith is lost per run.

PFA-Coated Catalyst Testing

A batch of PFA-based carbon-coated monolith catalyst was prepared for use in the pilot plant. Previous preparations at Air Products had shown performance similar to that of the CAT-XXX catalyst when tested at standard process conditions (at lower temperature, the PFA catalysts showed lower rates). To prepare catalyst for the pilot trials, the carbon-coating procedure was scaled up and carried out in our laboratory, with palladium deposition by COMPANY 1. The palladium metal loading (100 g Pd/ft³ monolith) corresponds to about 0.7 wt % (based on the total monolith weight), compared to 2 wt % used in earlier lab trials.

Laboratory testing of the pilot catalyst lot indicated it had a lower activity than previous preparations, most likely because of the lower palladium loading. This lower activity translated to the pilot results. Reaction rates at standard conditions were considerably lower than with the CAT-XXX catalyst: about 33 mol/m³s, compared to 80-100 mol/m³s for CAT-XXX. As expected, elevating temperature and pressure increased the rates, but the intrinsic activity of this lot was clearly low. The pilot plant reaction rate was even lower than the one measured in the lab, which may mean that this catalyst loses activity when exposed to air for extended lengths of time. Considerable optimization of this catalyst formulation would be required to achieve a commercially viable catalyst for implementation in MLR systems.

Conclusions

Hydrogenation of nitrobenzene using Monolith Loop Reactor technology was successfully demonstrated at the scale of the MLR Pilot Plant: 15-gallon batch volume, reactor of 2-in. diameter and up to 3-ft length of active catalyst. Thirty batch runs were conducted between October 2001 and January 2002, at standard operating conditions (250°F, 200 psig) and variations thereof, while varying parameters such as amount of catalyst and nitrobenzene feed concentration.

Pilot plant operability has been excellent. Temperature and pressure control is adequate after initial heuristic tuning, and can probably be further improved by rigorous tuning and perhaps including a feed-forward algorithm. The instrumentation and data acquisition have allowed detailed analysis of the pilot results. A few minor instrumentation problems require further resolution.

Both catalyst candidates identified from laboratory trials were tested in the pilot plant. COMPANY 1's CAT-XXX catalyst performed according to expectations, matching results from laboratory runs at similar conditions. A modified formulation of Air Products' PFA-based catalyst did not perform nearly as well.

Hydrogenation of neat nitrobenzene proved to be slower at the pilot plant than in the laboratory, for reasons that remain unexplored. Attaining favorable rates required operation at higher temperature and pressure, compared to standard conditions.

7: COMMERCIALIZATION SUMMARY

7.1 Status of the Follow-On Funding Commitments

Air Products and Chemicals, Inc. has committed an additional \$2,000,000 in funding for fiscal year 2002 (Oct. 1 2001- Sept. 30, 2002) and will continue the program through the end of fiscal year 2003, provided that certain technical and commercial milestones are met. This support funding is summarized below:

- i. Date: October 1, 2001- September 30, 2002
- ii. Amount: \$1,200,000
- iii. Source: Air Products and Chemicals Inc.

- i. Date: October 1, 2002- September 30, 2003
- ii. Amount: \$850,000
- iii. Source: Air Products and Chemicals Inc.

In addition, a commercial partner, a major supplier of catalysts to the chemical industry, has committed additional resources to the overall program. As of July 2002, no leveraged follow-on research funding has been secured for this project.

In March 2002, a project pre-proposal was prepared and submitted to the Department of Energy's NICE³ commercial demonstration program. This pre-proposal was developed jointly with the prospective customer of the technology and the New York Energy Research and Development Authority (NYSERDA). This agency was also committed to providing financial support for the proposed project. The proposal received favorable review and a full proposal was encouraged.

During the course of the laboratory evaluation phase of this particular customer project, it was found that the catalyst activity and selectivity were limited at the desired process conditions. This is not seen as a general failure of the MLR technology, but a limit based on the available selection of suitable catalysts at this point in time. Therefore we were unable to meet the technical objectives for this project. In light of this finding, a decision was made in June 2002 not to proceed with submission of a full proposal.

As we continue to engage other specialty chemical producers in the marketplace, we will continue to assess the value of leveraged funding as a mechanism to mitigate the risk associated with the implementation of this technology at the commercial scale.

7.2 Commercialization Activities Related to Follow-On Funding Commitment

The team has developed a detailed assessment of the market for this technology. The fine and specialty chemicals industry is still viewed as the principal host for the technology. In particular, those processes that currently utilize powdered precious metal catalysts such as platinum and palladium constitute the most amenable segment of the chemical industry. This segmentation is consistent with that used in the initial market assessment included in the original submission to the DOE OIT program for consideration.

Based on the benefits of the MLR technology defined in Table 7.2.1, an economic model quantifying the value associated with those benefits has been developed.

Table 7.2.1: A List of Features of the Monolith Loop Reactor Technology and the Corresponding Benefits That a Specialty Chemical Manufacturer Can Expect With Implementation of this Technology

FEATURE	EXPECTED BENEFIT
•Higher gas/liquid mass transfer	–Lowers capital cost (results from improved reaction rates for mass transfer limited reactions)
•Increased catalyst productivity	–Lowers catalyst inventory per unit of product –Lowers cost through lower metal inventory
•Elimination of filtration & catalyst handling	–Reduces catalyst losses –Improves safety –Reduces worker exposure –Decreases environmental effects (less catalyst in the wastewater system)
•Separation of reactants and catalyst during reactor heat-up and cooldown	–Minimizes by-products –Improves yield
•Retrofit to batch reactor	–Provides a low capital option for incremental capacity (utilizes existing infrastructure) –Provides a shorter lead time for new chemistries (less scaleup, simpler catalyst “system”)
•Potential for on-site catalyst regeneration	–Offers higher productivity, lower cost –Reduces catalyst handling (lower attrition, improved worker safety and health)
•Small size / modular	–Offers possibility of economical new multi-step chemistries –Offers possible small-scale manufacturing plants –Offers greater batch plant flexibility
•Potential to handle “problem chemistries”	–Eliminates filtration prior to product separation –Minimizes ancillary equipment

7.2.1 New Products and Processes

Two new catalysts for the conversion of industrially important chemicals have been developed during the course of this program. The first is a carbon-based monolith catalyst and the process for the small-scale manufacture of this material. It has been demonstrated as a viable material for the conversion of nitrobenzene to aniline. This catalyst has been demonstrated at the pilot scale. A viable commercial manufacturing process has not been developed as of the date of this report.

A second monolith catalyst for which a viable commercial-scale production process has been developed was also identified during the course of this program. The catalyst has been demonstrated at the pilot plant scale. Evaluation of this material for a range of other hydrogenations at the laboratory scale has shown it to be a viable commercial catalyst. It appears that these catalysts, with chemistry-specific modifications, will form the basis of the early commercial monolith catalysts for hydrogenation processes.

In addition to the development of these catalyst products, the program has supported the development of a unique monolith-catalyst-based hydrogenation reactor system. This patented technology is being actively marketed to the specialty chemical industry as a bolt-on retrofit technology for operators of existing slurry catalyst-based, stirred tank-reactor systems. Air Products is also assessing the viability of this technology as a stand-alone method for the production of chemicals that require hydrogenation during their manufacture.

The technology package is currently being marketed to a sub-segment of the fine chemicals industry that uses precious metal catalysts. It has been found that one of the economically important benefits of the technology is the decrease in precious metal losses. In some cases, prospective users of the technology may be able to realize cost reduction benefits on the order of \$1.5-2.0 million per year through reduced metal losses alone. To date, it has been difficult to demonstrate in a general way consistent yield advantages with this process at the laboratory scale; nevertheless, yield improvements are anticipated once the catalyst bed is separated from the reaction mass during heat-up and cool-down steps of the reaction (see Section 6). Such an improvement in yield has been observed for the nitrobenzene conversion at the pilot-plant scale.

Several prospective customers are currently assessing the benefits of this technology for a range of chemical hydrogenations. The pilot plant will be used as a final demonstration of the total benefits that should be anticipated when commercial processes are converted to monolith-based technology.

In addition to marketing these products and processes, the program has led to a development services-based business to market the know-how and capabilities of the development team. The process development business has resulted in ~\$75,000 in revenue to date. This unique offering combines Air Products' unequaled experimentation capability developed under this program with the MLR pilot plant to offer a novel process development service to the chemical industry. It ensures that potential customers interested in the MLR technology can quickly and cost-effectively assess the suitability of their chemistry to the unique features of the MLR technology.

7.2.2 Patents

A total of three patent applications related to the MLR technology developed during the course of this program have been filed by Air Products with the United States Patent Office. In addition, two other patent applications supporting MRL technology were developed before the DOE-OIT contract. These are summarized in Table 7.2.2.1.

Table 7.2.2.1: Monolith Loop Reactor (MLR) Technology Patents and Applications

Application Serial Number	Title and Status
09/573,726	Retrofit Reactor Including Ejector and Monolith Catalyst. Filed with USPTO. Patent Allowed
09/839,699	Hydrogenation with monolith reactor under conditions of immiscible phases. Filed with USPTO. Patent Allowed.
09/867,959	Polymer network/carbon layer on monolith support and monolith catalytic reactor. Filed with USPTO. Patent Pending
10/002,250	Coated Monolith Substrate and Monolith Catalysts. Filed with USPTO. Patent Pending
10/076/813	Catalyst Holder and Agitation system for Converting Stirred Tank Reactor to Fixed Bed Reactor. Filed with USPTO. Patent Pending

7.2.3 Publications and Presentations

Table 7.2.3.1 provides a list of the publications and presentations describing various aspects of the technology that have been published during the course of the research program.

Table 7.2.3.1. Publications and Presentations describing Monolith Loop Reactor (MLR) Technology

#	Titles and details
1	The Ejector-Driven Monolith Loop Reactor—Experiments and Modeling. R.R. Broekhuis, R.M. Machado, and A.F. Nordquist. <i>Catalysis Today</i> (69) p 87. October 2001
2	The Monolith Loop Reactor, MLR™: Practical Hydrogenation Process Intensification for the Specialty and Fine Chemical Industry. R.M. Machado, F.J. Waller, R.R. Broekhuis, F.C. Wilhelm, B.P. Roy, A.F. Nordquist and K.R. Heier. <i>Proc. Mettler-Toledo Reaction Eng. Conf., Lucerne, Switzerland, 2001.</i>
3	Immobilizing Homogeneous Catalyst for Organic Reactions. F.J. Waller. <i>ORCS Conf Proc.</i> (June 2002), San Antonio, Texas.
4	Advanced Catalytic Hydrogenation of Fine Chemicals. F.J. Waller, R.R. Broekhuis, A.F. Nordquist, F.C. Wilhelm, and R.M. Machado. <i>Nor. Am. Cat. Soc. Mtg. Proc. Toronto, Canada. June 2001.</i>

7.3 Promotional Media

A series of suitable brochures, presentations and datasheets has been developed, and these are being distributed in the marketplace to promote the advantages of this technology for the manufacture of several specialty chemical classes.

In September or October 2002, we will issue a press release to announce the formation of a joint marketing alliance with a major catalyst manufacturer. This should greatly accelerate the pace of adoption of this technology by companies who use precious metal catalysts in hydrogenation processes.

7.4 Revenues

Significant resources were committed to the commercialization of the MLR technology in May 2001. Efforts to sell the technology in the marketplace were initiated following the start-up of the pilot plant facility in October 2001. To date the total revenues that are associated with this project are from three commercial evaluations of the technology at the laboratory scale (Table 7.4.1). No projects have moved to the commercial scale as of July 2002.

Table 7.4.1: Revenue from MLR Technology

Project	Scope	Revenue	Outcome	Follow-on Evaluation
Customer A	Catalyst Screen	\$25,000	Viable catalyst not identified	No
Customer B	Catalyst Screen	\$12,000	Viable catalyst not identified	To be Determined
Customer C	Catalyst Screen	\$35,000	In process on 07/02	To be determined
Total		\$72,000		

7.5 Commercialization

As stated in Section 7.4, Air Products has committed significant resources to assure the successful commercialization of the MLR technology developed under this program. This includes a total of four fulltime staff members and the supporting infrastructure. The technology and business resources have been organized into a focused work team supported through Air Products' Chemical Process Industries Division. In addition, a global marketing alliance with a large catalyst producer has been secured to supply the commercial quantities of monolith catalysts needed by the prospective customers.

To manage the risk associated with the adoption of new technology, smaller scale processes were viewed as the most amenable for the rapid incorporation of this technology within the chemical industry. While this segment does not represent the largest opportunity for the technology, it balances the competing needs of rapid adoption and scale of the commercial opportunity. Therefore, the segment of the industry that operates catalytic batch reactor-based processes was identified as the segment that would be most attractive from the perspective of rapid commercialization of MLR. Selecting hydrogenation reactions was based principally upon the technical experience of the team supporting the initiative. Furthermore, hydrogenations represent 10-20% of all reactions conducted by participants in the fine and specialty chemicals segment¹.

Through the use of a market segmentation analysis, we determined that the high price of precious metals such as platinum and palladium constitutes the most important improvement to the overall economics of many catalytic hydrogenation processes. Therefore this sub-segment has been identified as the initial target market to pursue within the fine and specialty chemicals industry. An analysis of the global market suggests that the potential value of these markets is

on the order of \$0.5 billion. Adding reaction classes will significantly increase the size of this opportunity. This market segment comprises a wide range of company types, from companies with \$10-30 billion in annual sales with hundreds of products to operations with revenues on the order of \$70 million and only one or two products. On a global scale, we have determined that there are a total of 200-300 reactors potentially amenable to the MLR technology.

The market need for reaction technology is rather fragmented, with a diverse range of hydrogenations utilized by participants in the target segment. This has meant that an efficient means to screen numerous chemistries to determine their suitability to the MLR process has been necessary. The high throughput capability in the customer evaluation and process development stages is intended to address this characteristic of the chosen market segment.

A significant barrier to the rapid adoption of the MLR technology is the existing slurry catalyst-based process. While there are considerable advantages to a fixed-bed catalyst technology such as MLR, in most cases, companies are using slurry catalysts successfully to produce a wide range of commercial products. The required equipment for processing catalysts is already installed at most facilities. Furthermore, slurry catalysts have the advantage that they can be quickly changed within a reactor to adapt to new chemistries or production conditions.

Nonetheless, the current downturn in the economy coupled with the inexorable downward pressure on prices in the specialty chemicals segment has many companies looking for processes that can substantially reduce costs of production. MLR offers the potential of achieving this goal, and this has stimulated interest in pursuing the technology, even for some manufacturers whose existing businesses are economically marginal.

Another obstacle to entering this market is the *highly fragmented* nature of the segment and the need to meet the specific requirements of individual customers. Within certain categories of processes, principally those companies who produce pharmaceutical intermediates, it is essential that MLR-based technology be specified early in the development of new compounds, since certifying new processes in the Drug Master File (DMF) of materials that are used in drugs is particularly onerous.

In addition to the segmentation analysis that was completed based upon the technical characterization of the technology, Air Products conducted extensive interviews with potential users of the technology to gauge interest in its features and benefits. The feedback from this process has helped to guide the development of the MLR offering.

MLR technology will be sold as license grants to practice the technology coupled with the sale of enabling equipment and the catalysts necessary for successful implementation. This technology can be readily retrofitted to the existing infrastructure within the majority of batch reactor-based facilities. With DOE/OIT and the appropriate state agency support, a full-scale MLR retrofit to the existing batch reactor infrastructure at a fine chemical or pharmaceutical manufacturer's production facility is the next logical step for this technology. However, MLR technology has not yet been commercially validated. Therefore, first-time implementation carries considerable commercial and technical risk coupled with stringent regulations and costs imposed by the introduction of any new technology in an FDA-regulated production

environment in which many of the prospective users of this technology operate. Demonstration of the MLR technology will provide commercial validation of an energy-efficient solution for a priority area defined in the “Chemicals Roadmap” and will pave the way for additional retrofitting across the chemicals industry.

7.6 Comparison to Original Market Projections

The initial projections for adoption of the technology assumed that the identification and development of suitable catalysts could be based on the knowledge developed for the slurry catalyst industry. During the development of the MLR technology, it has become apparent that broad selections of suitable monolith catalysts with properties comparable to those in common use in the slurry catalyst industry are not commercially available. This issue is being addressed by developing functionally equivalent catalysts with compositions suitable for formulation on monolith substrates for each potential user of the MLR technology. This additional goal has significantly increased the complexity of identifying suitable materials for specific hydrogenation reactions.

These limitations related to the identification of suitable monolith-based catalysts for the in-kind replacement of existing carbon-based slurry catalysts is a significant barrier to the proliferation of the technology. The commercial team recognized this as a bottleneck in early 2001, and a high throughput screening capability was therefore identified as an essential resource for the commercialization of this technology. The technical team has developed a system suited to screening of large numbers of potentially useful catalytic materials. It is anticipated that this capability will come on-stream in October 2002, and it will enable the processing of a range of potential catalysts for each reaction in a parallel fashion to allow the team to quickly move towards a catalyst solution.

Current operating rates within the specialty chemicals segment that includes most of the targeted customers for this technology are below installed capacity. This limitation has diminished the value of productivity increases. The overall size of this opportunity and the potential benefits that this technology can deliver to specific customers is unchanged. Segmentation analysis has focused commercialization efforts where the MLR can deliver the greatest economic benefits.

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