High Throughput Program for the Discovery of NOx Reduction Catalysts

Discovery of New NOx Reduction Catalysts for CIDI Engines Using Combinatorial Techniques (DE-FC26-02NT41218)

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GOAL

To develop new catalytic materials for NOx reduction lean exhaust conditions (diesel and GDI) using fast throughput techniques

Outline for the Review

- **Program overview**
- Discovery Approach and Results
- GM Reactor Studies and Validation
- Informatics
  - Instrumental Data Import
  - Database
  - Trend Analysis
- Summary and Future

Combinatorial Catalyst Methods

What are we trying to do?

- Discover entire "families" of new NOx reduction catalysts for lean to stoichiometric exhaust conditions using high throughput (combinatorial) techniques

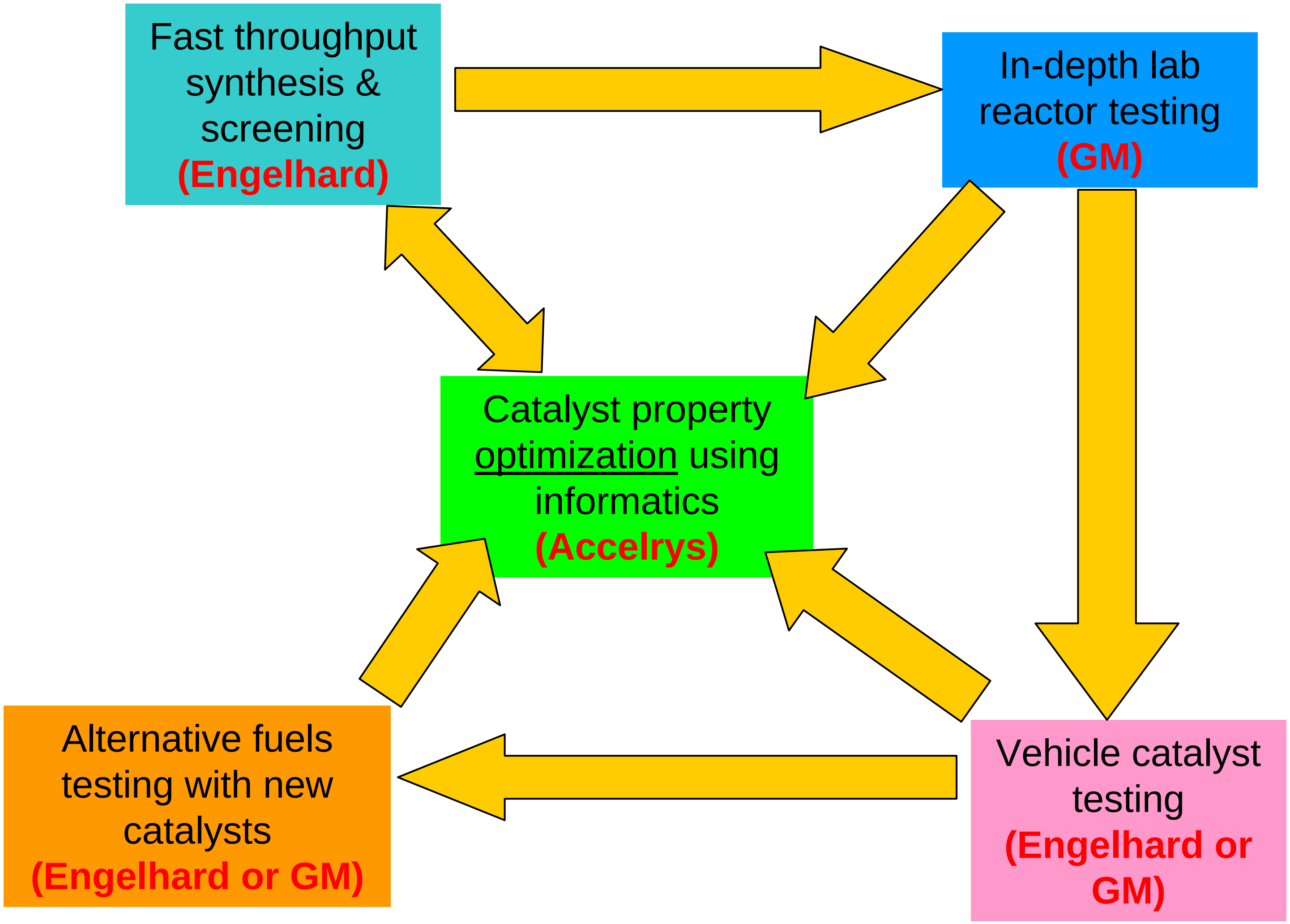
How is it done today? What are the limitations of current practice?

- Single material analysis at a time: 2-4 weeks,high cost per material, insufficient materials for "data mining".

What is this approach?

- Fast throughput (combinatorial approach) uses parallel synthesis, multiple sample reactor, detailed single sample reactor and informatics to speed up the sample evaluation into the hundreds per month

Program Tasks and Process Flow



Possible Reactions for Catalytic Material Discovery

- **NOx Reduction**

  $$2NO + HC + 4O_2 = N_2 + 3CO_2 + 4H_2O$$

  (best solution; on board reductant)

  $$2NO + 2NO_2 + 4NH_3 = 4N_2 + 6H_2O$$

  (infra-structure issues)

- **NOx Decomposition**

  $$2NO = N_2 + O_2$$

  (typically too slow)

Status

- GM project initiated 2002 (with 65% cost share by DOE)
- Focus is on Selective Catalytic Reduction (SCR) with reductants from the fuel (e.g.; n-octane, iso-octane, etc.)
- No restriction on Engelhard sales of catalyst products developed under this program
- Over 2000 new materials have been evaluated and approximately 10% are promising leads on new catalytic materials
- Informatics software has been written and is being used to refine the compositions of the hits into possible viable lean SCR catalysts

Catalytic Activities/Properties Needed from New Materials

- If it were sufficiently active, fuel reduced SCR would be the preferred aftertreatment technology for lean burn engines
- Multi-mode diesel combustion (using HCCI) will lower the engine out NOx and PM emissions for low load conditions
- Low temperature conversion (150-200 ^{o}C) for cold starts will continue to be needed
- Conversions from 40-80% over a European cycle or FTP using diesel fuel as a reductant will probably be a viable catalyst
- 60% conversion for a gasoline fueled future engine technologies may be sufficient

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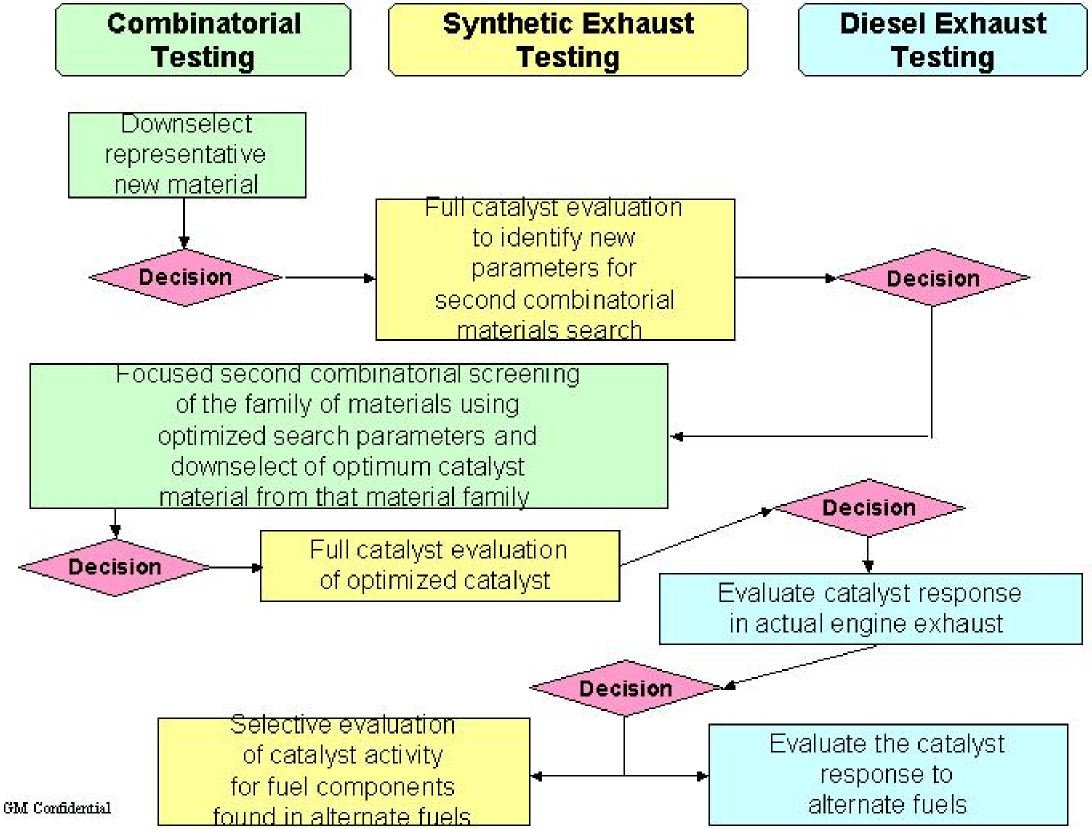
Discovery Flow Chart



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Discovery Testing Conditions

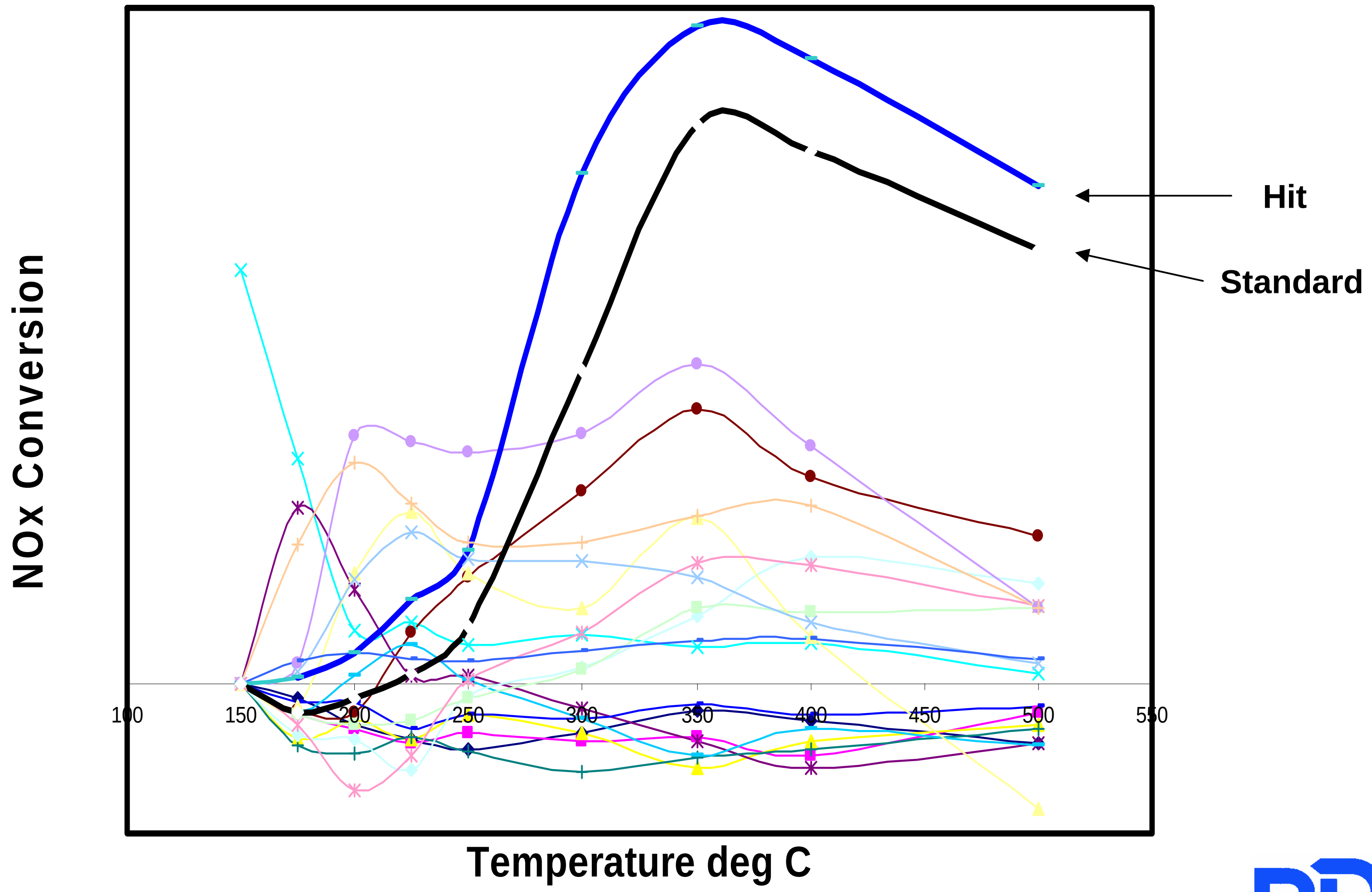
	Diesel	Stoichiometric (Gasoline)	Decomposition
NOx ppm	400	900	400
O_2 %	10	0.6	10
CO_2 %	5	10	5
HC (C1) ppm	4000	720	0
C1/N	10	0.8	0
CO ppm	745	0.8 %	745
H_2 ppm	245	0.27 %	245
He	balance	balance	balance
H_2O %	5	10	5

Temperatures: 150, 175, 200, 225, 250, 300, 350, 400, 500°C; H_2O as % of dry flow

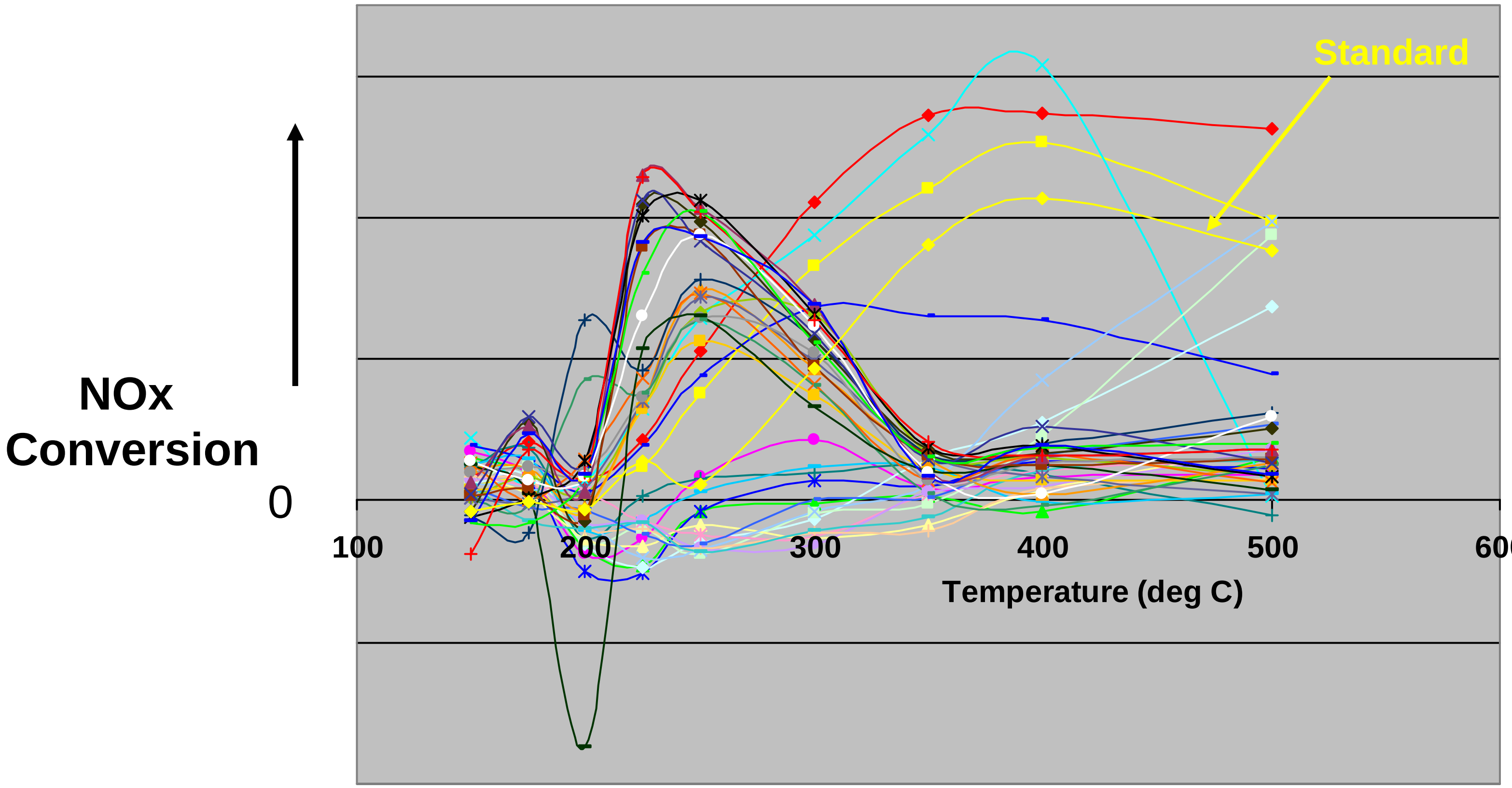
Catalyst Candidate Selection

- **Criteria for Selection**
  - **Max NOx conversion $\geq$ 70-80% of standard at either test condition. or**
  - **Wider temperature window than standard, with at least moderate activity. or**
  - **Unexpected positive performance.**
- **Possible Deselection Criteria in Phase II**
  - **by product formation: N_2O, HCN, NH_3 etc**
  - **adsorption**
  - **poisoning sensitivity: e.g., S, etc.**
  - **Narrow temperature window**
  - **Poor activity for full range fuel**
  - **Material toxicity**
  - low activity
  - cost

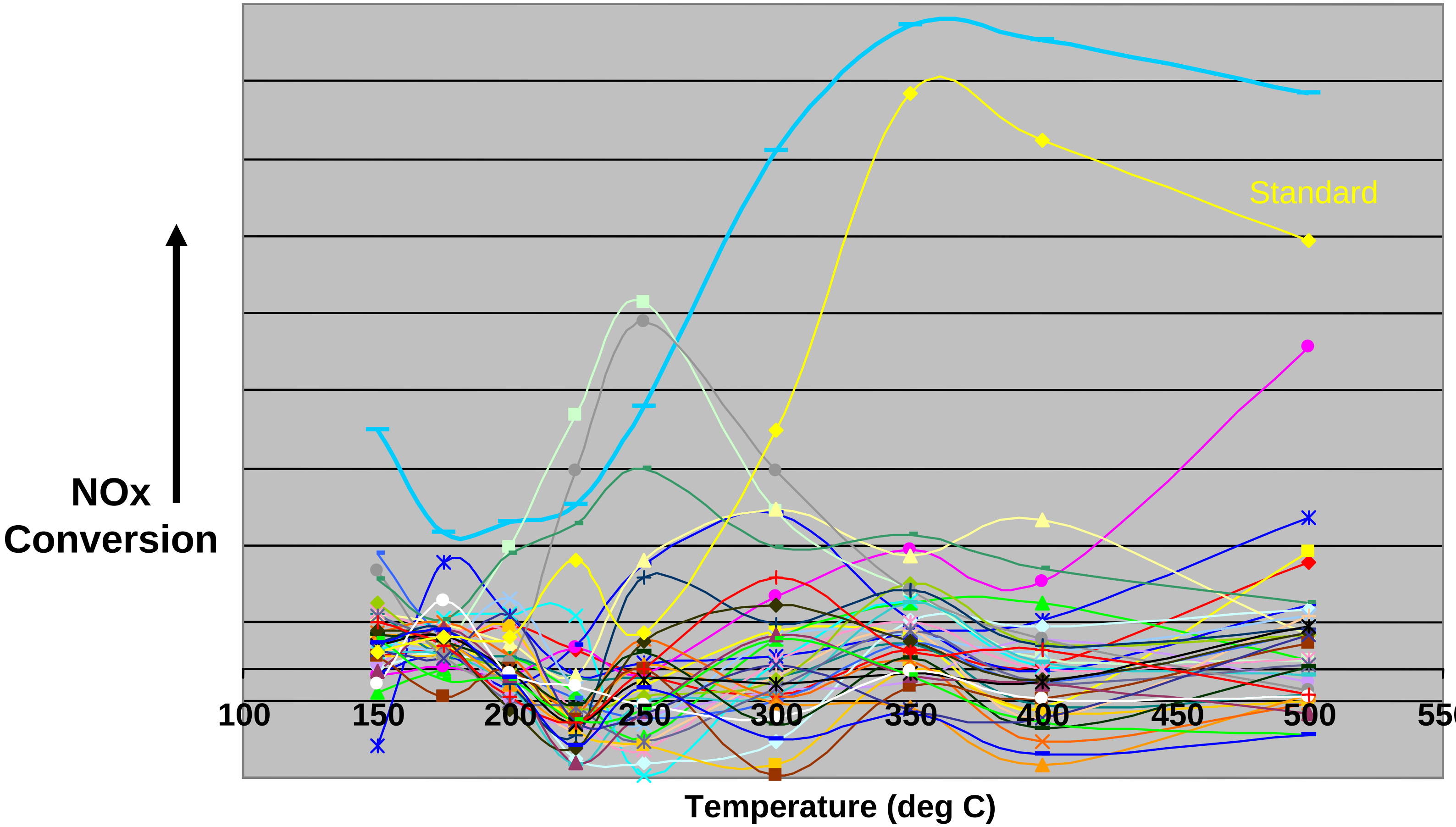
Typical Fast Discovery Run with a "Hit"



Some Results Exceed Standard



Certain Samples Stand Out



"Hit"

- Materials tested for NOx catalytic activity
- Optimum operating conditions not yet determined
- Composition will need to be refined to optimize activity, durability and operating range
- Chances for elimination as a catalyst include N2O production, low activity, unacceptable reductant, cost, and sensitivity to poisoning.
- Optimized catalytic material will undergo a feasibility analysis for application to GM engines

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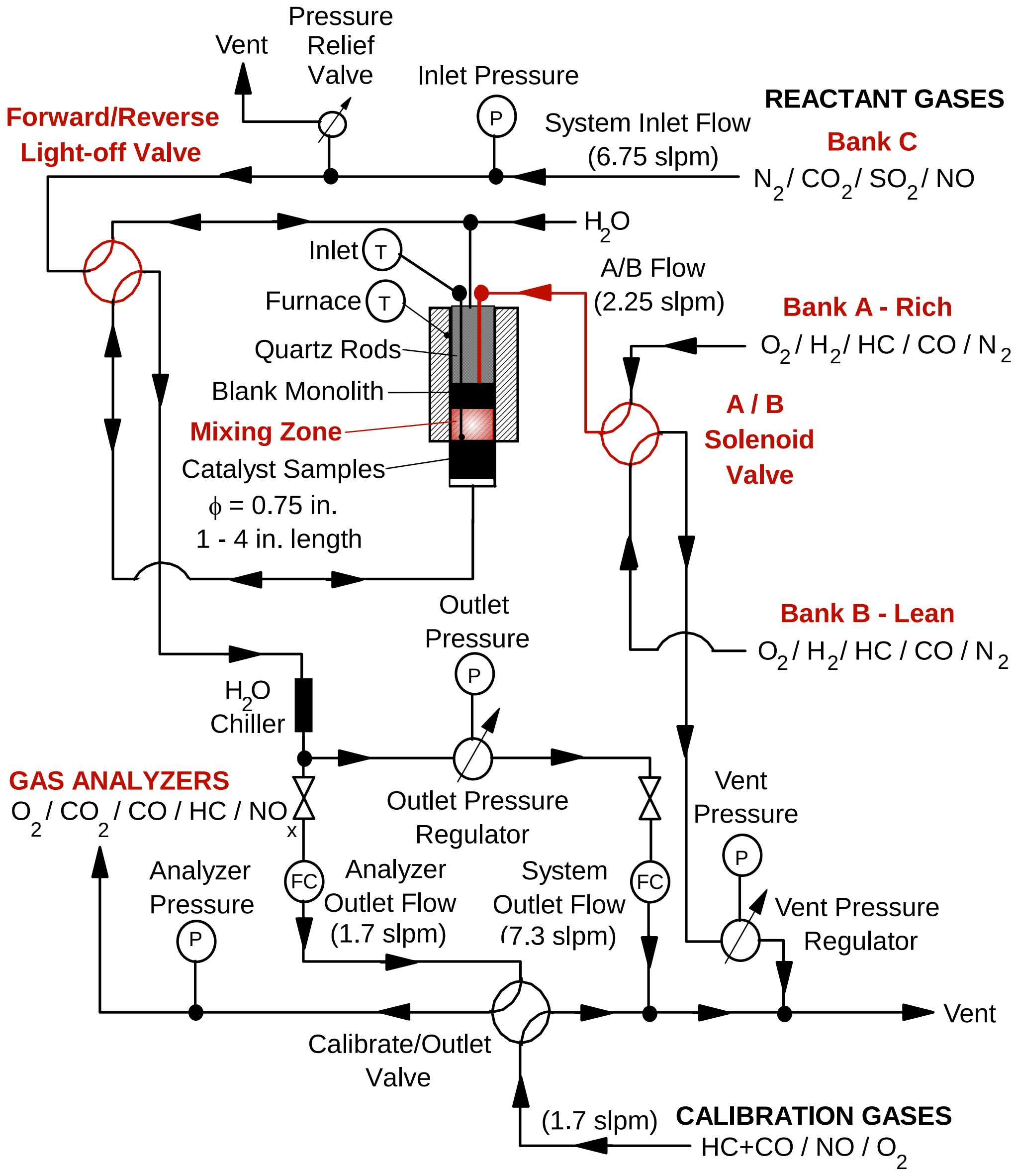
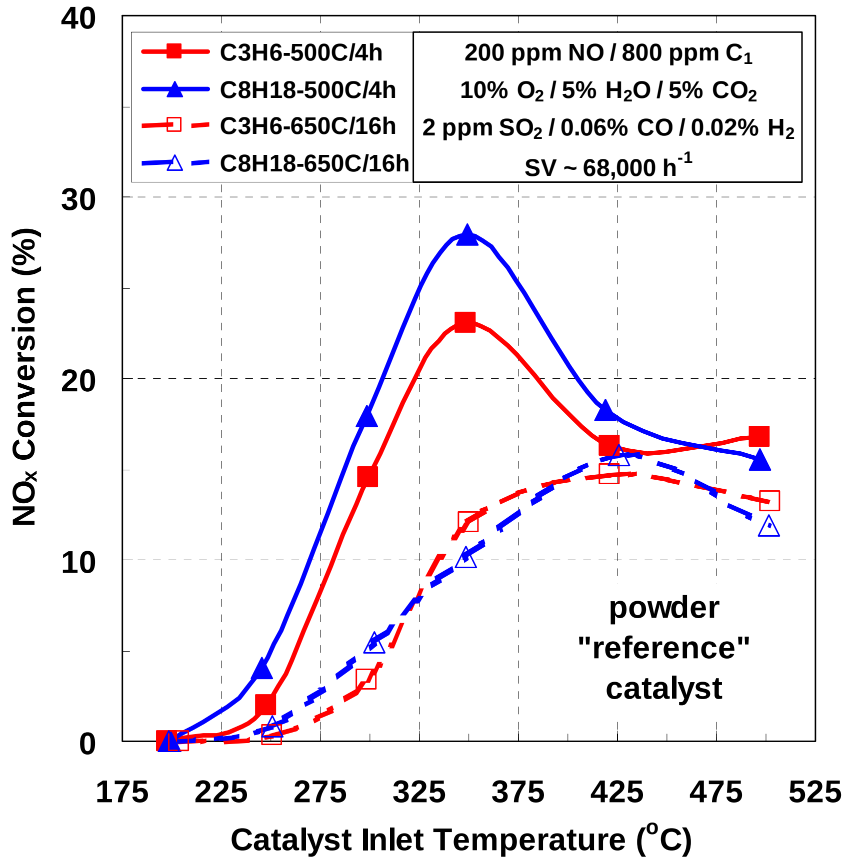
GM Powder Reactor

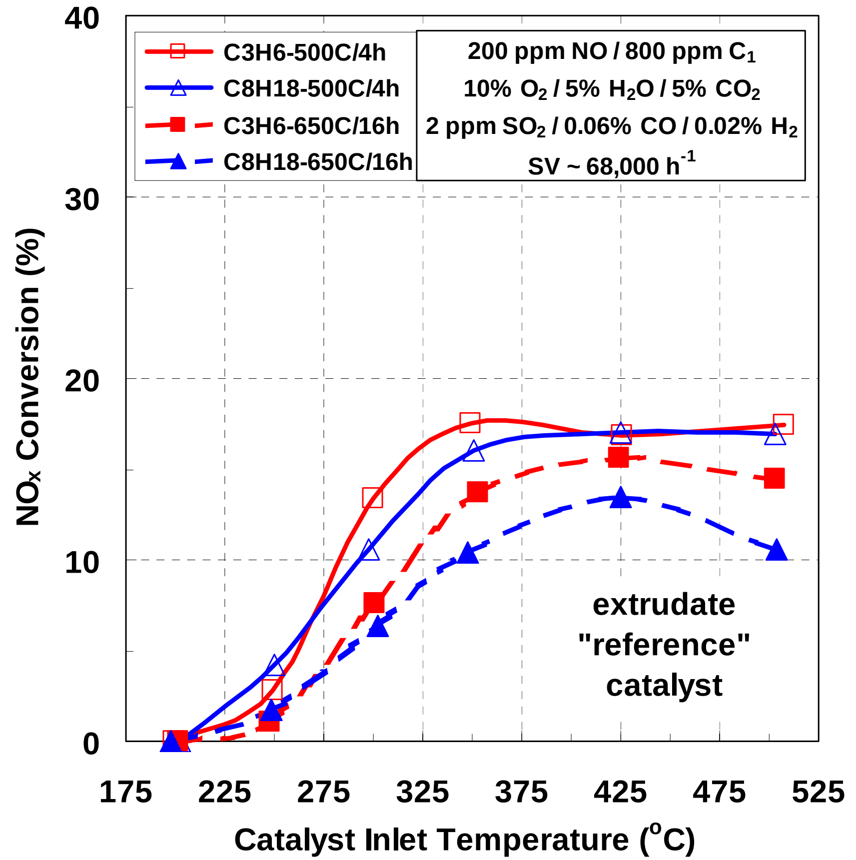


GM Reactor Test Matrix ("aged" samples):

1) Temperature sweep
   - 200-600°C, standard conditions
     - **EC:** 400 ppm NO, 500 ppm n-C_8H_{18} (HC: $C_1/N = 10$), 10% O_2, 5% H_2O, 5% CO_2, 745 ppm CO, 245 ppm H_2, balance N_2 at ~50,000 h^{-1}
     - **GM:** 200 ppm NO, 100 ppm n-C_8H_{18} (HC: $C_1/N = 4$), 10% O_2, 5% H_2O, 5% CO_2, 600 ppm CO, 200 ppm H_2, 2 ppm SO_2, balance N_2 at ~68,000 h^{-1}
2) NO_x ratio sweep at temperature from peak activity in # 1
   - NO/NO_2 = 250/0, 175/75, 125/125, 75/175, 0/250
3) Reductant sweep at peak activity from # 2 (HC: C_1/N = 4, 8, & 10)
   - n-octane, iso-octane, m-xylene, propene, ethanol / acetaldehyde
4) Oxygen sweep at peak activity from # 3
   - 0%, 0.5%, 4%, 10%
5) Temperature sweep with optimum conditions from # 2 → # 4
6) Aging with 20 ppm SO_2 (16h at 650°C, AIR+10% H_2O) and repeat temperature sweep under same conditions as # 5
7) Input all data files in Combimat 2.0 database

"Aged-severe" Engelhard Standard Catalyst:





- "Peaked" NO_x conversion behavior disappears upon severe aging
- Higher $T_{50\%}$ and lower NO_x conversion after severe aging, as expected
- C_3H_6 and C_8H_{18} ~same over "aged" powder **and** extrudate samples

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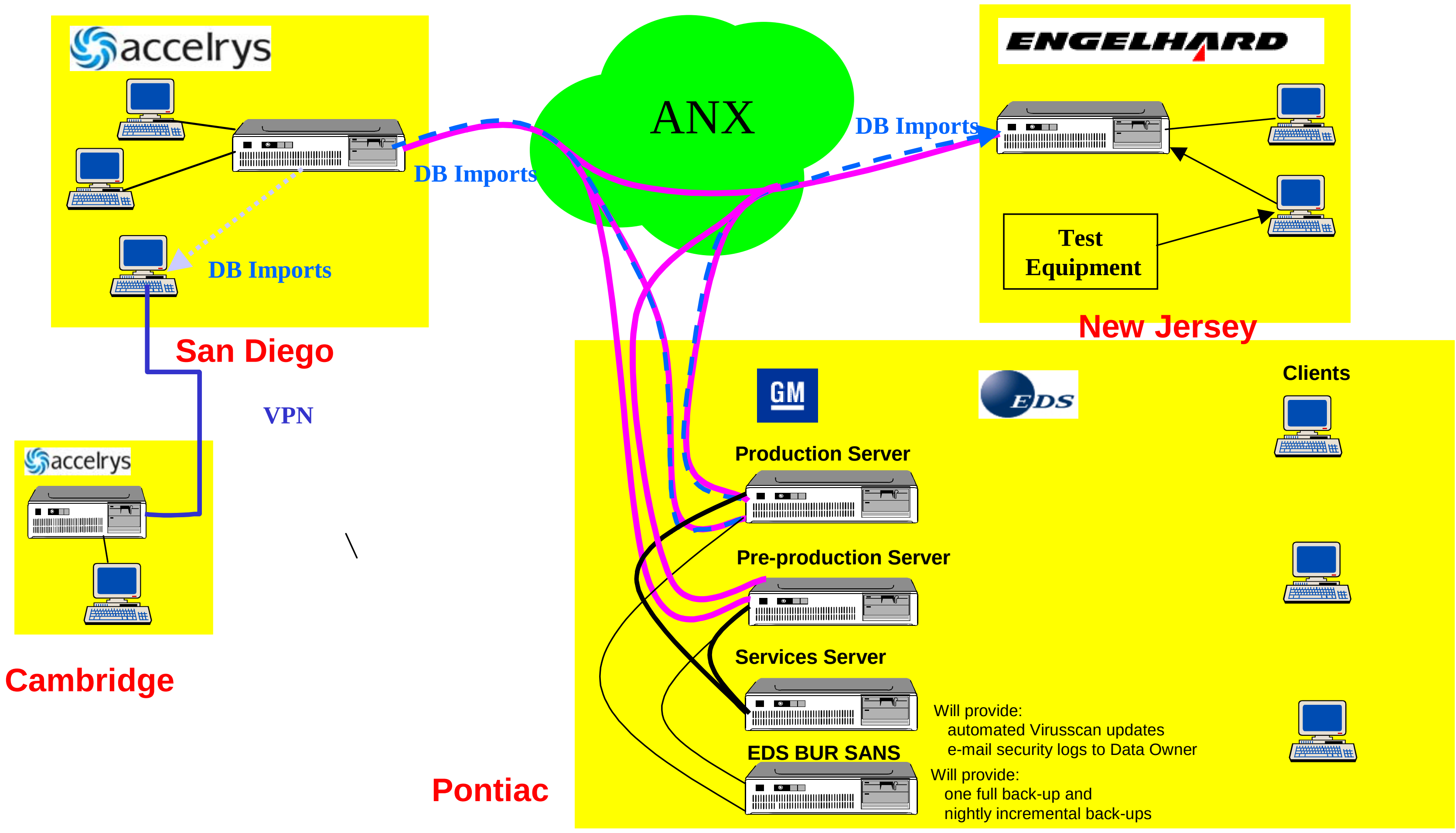
Informatics From Accelrys

- Informatics will be used to optimize the compositions of the “hits”.
  - Database is newly developed for this project (CombiMat 2.0)
    - Material compositions, catalytic activity and structure analysis are included in the database
    - GM has the master database
  - To facilitate the project, GM/Accelrys/Engelhard are interconnected with secure ANX lines for software development, database replication and trend analysis
  - Trend analysis will be used to do design of experiment for optimizing catalyst composition from a “hit”

Informatics Interconnectivity



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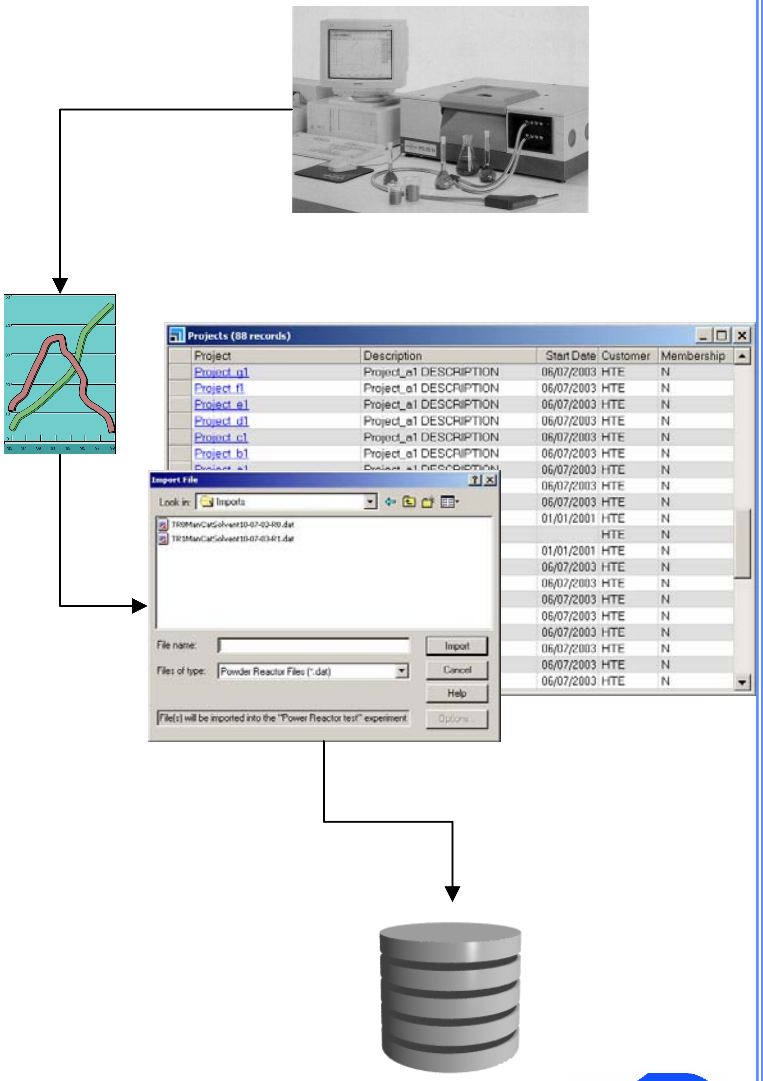
Data Import

- Instruments write data in their native formats
  - Data import tool recognizes 5 different formats, is extensible
  - Additional formats will be delivered in FY 2004
- Easy file selection via Common File Dialog
  - User chooses file(s)
  - File(s) transferred to database server and loaded
- Data may subsequently be viewed, filtered, sorted, searched on



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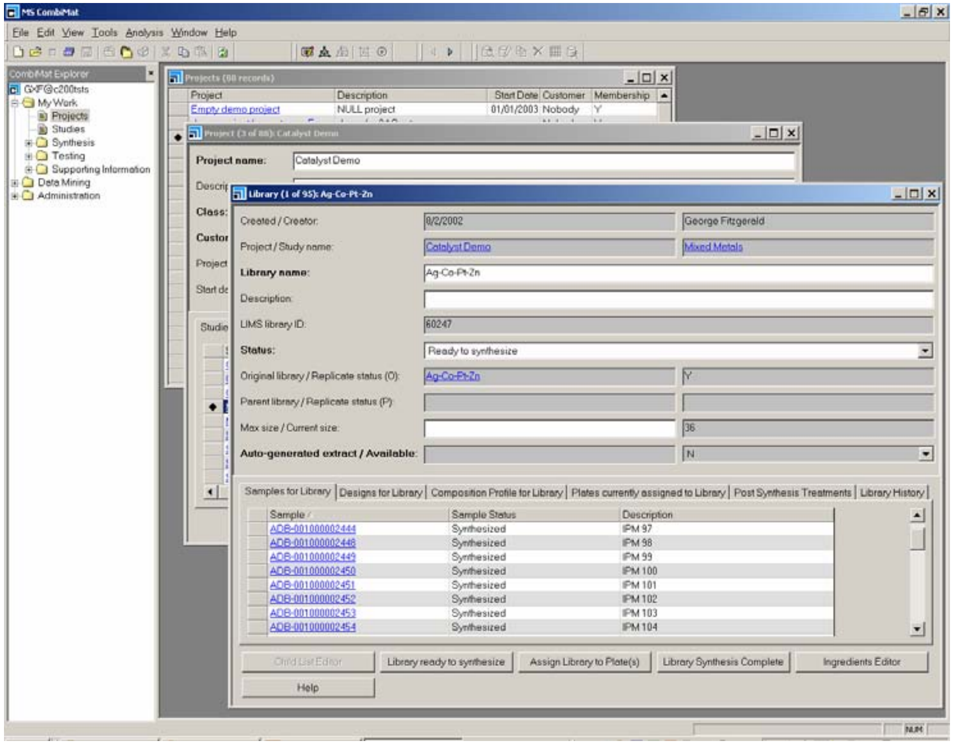
CombiMat 2.0

- Delivers the tools needed to store, query, and retrieve all data relating to the project
- Installed on our test server
- Used for the first set of trend analyses
- Accelrys is tuning and customizing as needed



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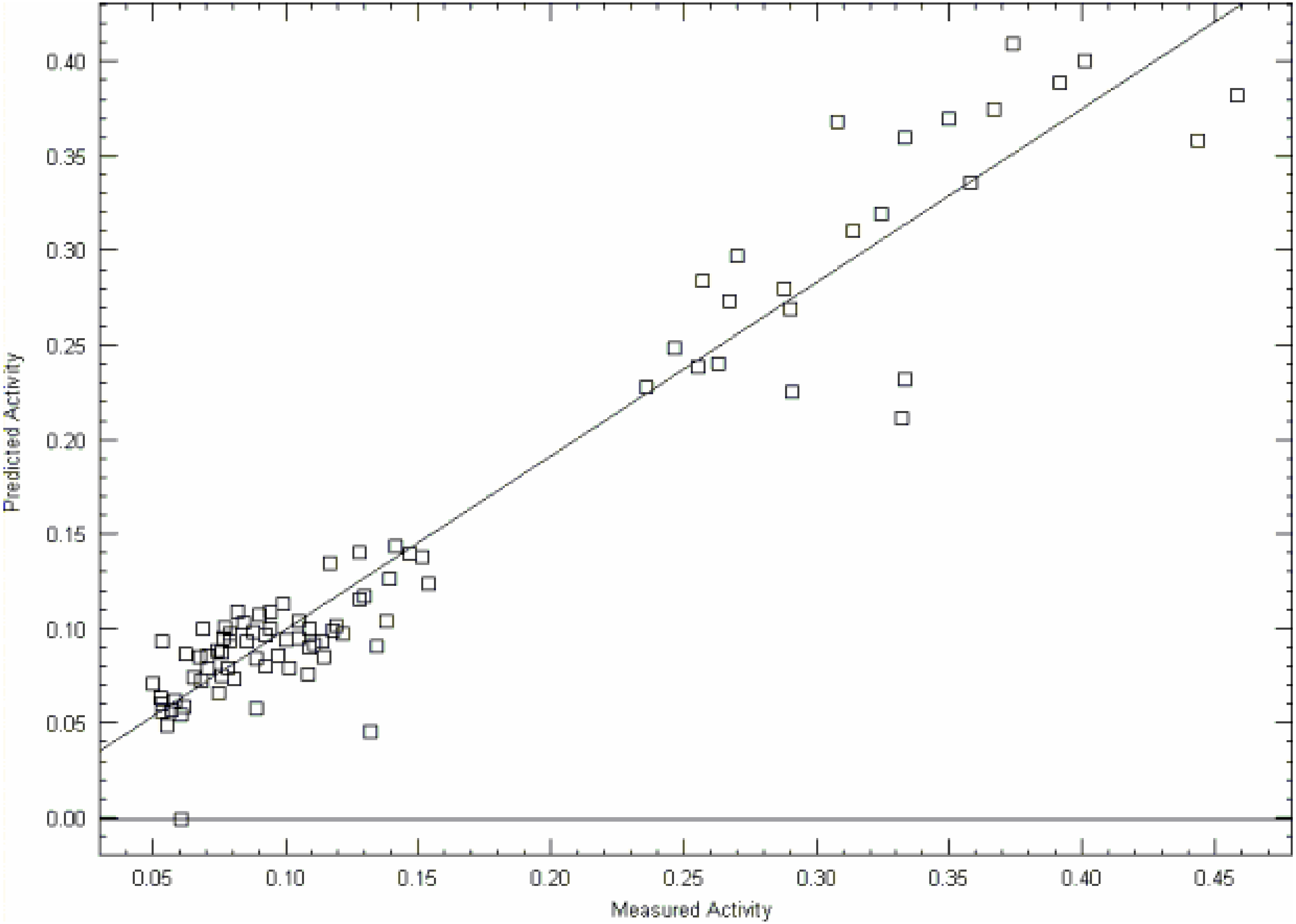
Quality of Fit for Activities



Genetic Function Algorithm (GFA) effective for fits of activity versus composition

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Summary

- All the instruments are operational and have been validated up through engine scale
- Database has been developed and is operational
- Tools for transfer of data from the instruments to the database have developed and are in use
- Data taking has begun and we have evaluated over 2000 new materials since spring which are entered into the database
- We are getting approximately 10% “hits” which is very encouraging.
- GM reactor has been modified and we are testing extrudates
- Trend analysis has been started and is beginning to show results