Spatial Atomic Layer Deposition to Scale Manufacturing of Robust Catalysts for Biomass Conversion Applications

Cooperative Research and Development Final Report

CRADA Number: CRD-17-715

NREL Technical Contact: Derek Vardon

NREL is a national laboratory of the U.S. Department of Energy
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Contract No. DE-AC36-08GO28308

Technical Report
NREL/TP-5100-73532
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Cooperative Research and Development Final Report

Report Date: November 30, 2018

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the final CRADA report, including a list of subject inventions, to be forwarded to the DOE Office of Science and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: Forge Nano

CRADA number: CRD-17-715

CRADA Title: Spatial Atomic Layer Deposition to Scale Manufacturing of Robust Catalysts for Biomass Conversion Applications

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1	$150,000.00
TOTALS	$150,000.00

Abstract of CRADA Work:

This CRADA will facilitate technology maturation for NREL-developed ALD-coated catalyst materials that are tailored for durability during harsh biomass conversion chemistries. This project will address optimizing process parameters for scale-up of Al_2O_3 ALD-coated catalysts, demonstrating ALD-coated catalyst performance for muconic acid hydrogenation, and validating economic models that project significant cost benefits for ALD-enhanced catalytic processes. This work will strengthen private-public partnerships in the area of advanced catalyst manufacturing for energy-related technology. Critical information will be collected to elevate the Technology Readiness Level and increase our competitiveness for cooperative R&D agreements and licensing. Success of this work will be crosscutting as it can facilitate advanced catalyst development for both renewable and conventional processes.

Summary of Research Results:

Task 1: Synthesize and characterize scaled Al_2O_3 ALD-coated Pd catalysts at the kilogram scale.

ALD catalyst coating formulations developed by NREL at the 100-mg scale were scaled by Forge nano by three-orders of magnitude to the 100-g scale. Initially, 1 kilogram of 1.0 wt% Pd on Al_2O_3 catalyst powder and 1 kilogram of commercial TiO_2 catalyst support pellets were obtained from Alfa Aesar. The commercial TiO_2 supports were not available with Pd, which required in-house loading of Pd at NREL to produce 100 grams of 0.5 wt% Pd/TiO_2 powder catalyst. Multiple batches of each catalyst were coated with low-cycle Al_2O_3 ALD with trimethyl aluminum (TMA) and water precursors by Forge Nano, with samples ranging from the 10-gramto 100-gram scale. Replicate ALD coatings runs were performed to allow for measuring coating reproducibility. The uncoated and ALD-coated catalyst materials were characterized to determine their morphology via surface area, pore volume, and pore diameter measurements, as well as and Pd accessibility via CO chemisorption measurements, as shown in **Table 1**. Batch reactor screening tests were used to evaluate catalyst muconic acid hydrogenation activity and Pd leaching stability (**Scheme 1, Table 1**). Screening results showed a 2-fold to 5-fold reduction in Pd leaching with ALD coating, with significantly greater activity retained on the Al_2O_3 ALD-coated Pd/TiO_2 catalyst. Therefore, this material was down-selected for further testing. For the down-selected Forge Nano Al_2O_3 ALD Pd/TiO_2 catalyst, ALD coating uniformity was evaluated by scanning electron microscopy with energy disperse x-ray spectroscopy (SEM-EDS). SEM-EDS imaging confirmed highly uniform Al_2O_3 ALD on the TiO_2 catalyst support, as shown in **Figure 1** below.

Scheme 1. Reaction network for the hydrogenation of muconic acid to adipic acid via hexenedioic acid as the intermediate.

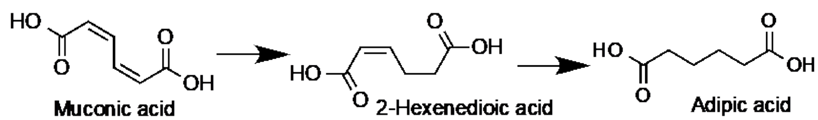

Table 1. Summary of catalyst material properties for the uncoated and ALD-coated catalysts produced by Forge Nano. Catalysts were screened for their hydrogenation activity and Pd leaching stability using 15-min single time point batch reactions. Reaction conditions: 15 mg catalyst, 24 °C, 24 bar H_2, 25 mL 1 wt% muconic acid in ethanol, stirring 1600 rpm. The Al_2O_3 ALD-coated Pd/TiO_2 catalyst showed superior hydrogenation activity with complete conversion of muconic acid during the screening tests. Therefore, adipic acid yields were reported for this catalyst.

Catalyst	Surface Area (m^2/g)	Pore Vol. (cm^3/g)	Avg. Pore Radius (nm)	CO Uptake (umol/g)	Muconic Acid Conv. (%)	Pd leaching (ppm)
Pd/Al_2O_3	148	0.47	6.4	23	97	5.79
FN 10g Pd/Al_2O_3	145	0.43	6.0	1	61	1.02
FN 100g Pd/Al_2O_3	144	0.44	6.1	2	59	0.34

Catalyst	Al Loading (wt%)	Surface Area (m^2/g)	Pore Vol. (cm^3/g)	Avg. Pore Radius (nm)	CO Uptake (umol/g)	Adipic Acid Yield (%)	Pd leaching (ppm)
Pd/TiO_2	-	137	0.51	7.5	25	100	6.04
FN 10g Pd/TiO_2	2.8	119	0.44	7.4	23	47	3.23
FN 10g Pd/TiO_2	2.4	122	0.44	7.3	15	51	3.05

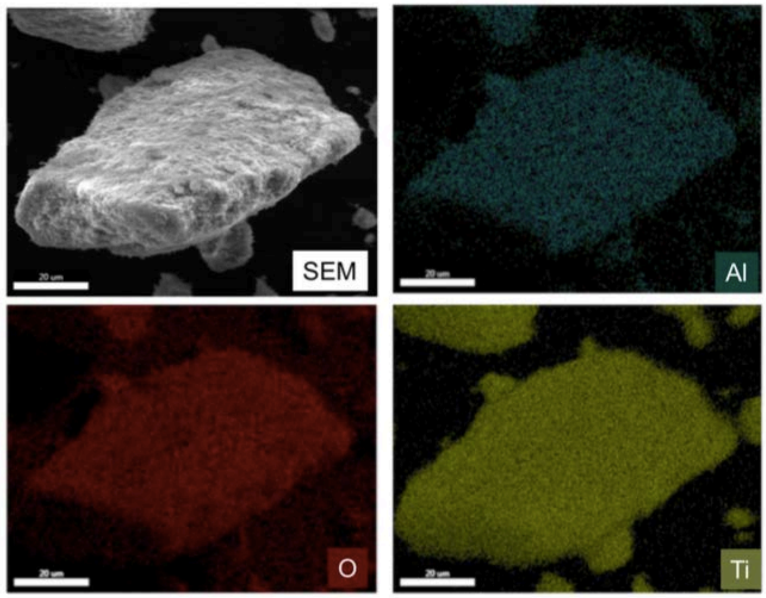

Figure 1. SEM-EDS imaging of the Forge Nano Al_2O_3 ALD coating on the Pd/TiO_2 catalyst, showing uniformity of Al throughout the catalyst particle surface.

Task 2: Demonstrate superior ALD-coated catalyst performance for bio-adipic acid production.

Time series batch reactor testing was then performed to confirm the activity and selectivity for adipic acid production. The Forge Nano ALD-coated catalyst showed rapid hydrogenation activity, similar to the uncoated catalyst, and near quantitative selectivity to adipic acid (**Figure 2**) and Pd leaching reduced by ~2-fold (**Table 1**). Based on these results, the catalyst was then subjected to time-on-stream under both partial and complete conversion conditions in a continuous flow trickle bed reactor (**Figure 3**). The ALD-coated catalyst showed ~15-fold reduction in Pd leaching under partial conversion conditions, while still retaining comparable activity to the uncoated catalyst for muconic acid conversion. Complete conversion to adipic acid was also demonstrated with the Forge Nano ALD catalyst for 100 hours of time-on-stream when using a weight hourly space velocity of 1.0 h^{-1}. The ALD coating showed ~5-fold reduction in Pd leaching (**Table 2**), demonstrating the productivity and stability of the Forge Nano ALD-coated catalyst under these conditions.

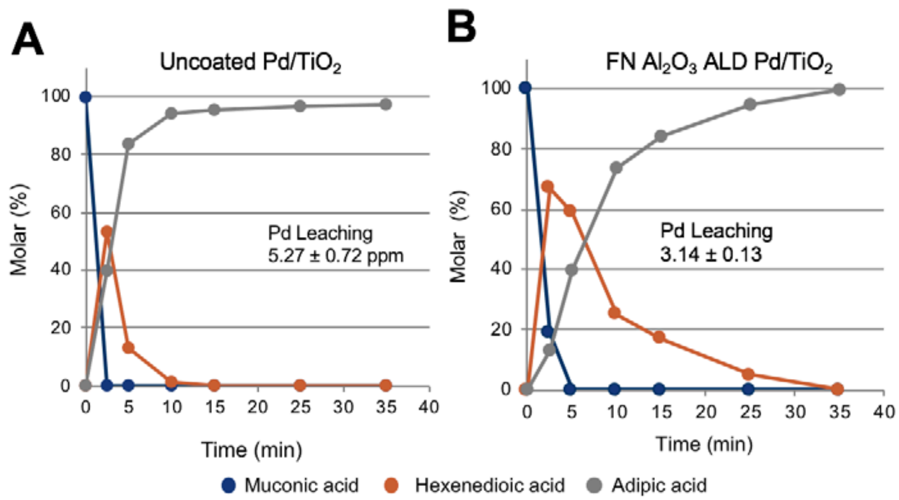

Figure 2. Batch reactor catalyst time series using the uncoated Pd/TiO_2 catalyst (A) and the Forge Nano ALD-coated Pd/TiO_2 catalyst (B). Reaction conditions: 15 mg catalyst, 24 °C, 24 bar H_2, 25 mL 1 wt% muconic acid in ethanol, stirring 1600 rpm.

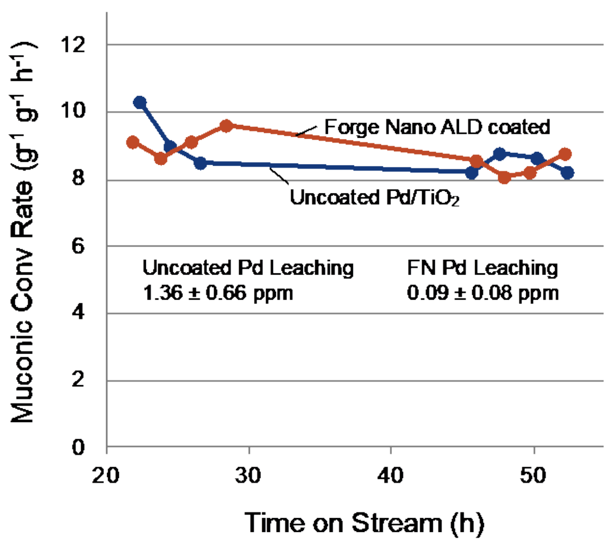

Figure 3. Continuous reactor performance of the uncoated and Forge Nano ALD-coated Pd/TiO_2 catalyst, showing reductions in Pd leaching with retained muconic acid hydrogenation activity within the variability of the uncoated catalyst. Reaction conditions: 6 mg catalyst, 24°C, 34.5 bar, 100 sccm H_2, 0.25 ml/min 1 wt% muconic acid in ethanol.

Table 2. Summary of the Forge Nano ALD-coated Pd/TiO_2 catalyst performance and leaching stability under complete conversion conditions to adipic acid. Reaction conditions for FN catalyst: 300 mg catalyst, 70°C, 34.5 bar, 100 sccm H_2, 0.63 ml/min 1 wt% muconic acid in ethanol.

Catalyst	Pd Leaching (ppm)	Adipic Acid Yield (%)
Pd/TiO_2	0.45	>99%
FN 10g Pd/TiO_2	0.09	>99%

Task 3: Develop business plan and licensing strategy for ALD catalysts.

ALD coating manufacturing costs were then estimated for the Pd/TiO_2 based on consultation with Forge Nano (**Table 3**). For the uncoated catalyst, the uncoated catalyst price was estimated to be $130/kg, with the majority of the cost due to Pd metal loading despite the 0.5 wt% loading. For the ALD coating, the TMA precursor was the major cost contributor. A conservative precursor utilization rate of 50% was assumed, although utilization rates of >80% are projected through tuning the ALD process window with capture and recycle technologies. TMA has been widely the studied for Al_2O_3 ALD due to its ease of application. Evaluation of lab-scale prices show that TMA is not the cheapest precursor available (**Figure 4A**); however, the production of ALD coatings at the kilotonne scale for commodity chemical production has potential to significantly drive down precursor costs (**Figure 4B**). Similar to PGM catalyst manufacturing, economic incentives exist for vertically integrating ALD precursor production with the ALD coating process. Likewise, the application of low-cycle ALD on catalysts with higher Pd content may further increase the value provided, as PGM content is still the dominant material cost driver. Industrial catalysts can easily contain up 5% Pd content, which would equate to <3% incremental cost with ALD coating due to the high price of the uncoated catalyst ($1300 kg^{-1}).

Table 3. Summary of cost contributions during ALD catalyst coating manufacturing.

Uncoated catalyst	0.5% Pd/TiO_2
Pd metal 5-year average price	$23 g^{-1}
TiO_2 support unit price	$10 kg^{-1}
Uncoated catalyst surface area	130 $m^2 g^{-1}$
Uncoated catalyst price	$130 kg^{-1}
ALD catalyst coating Al content	3.5 wt%
ALD mass of Al_2O_3 added per kg catalyst	0.066 kg
ALD precursor utilization rate	50%
ALD coating manufacturing cost per kg catalyst	$5 kg^{-1}
TMA precursor unit price, log-log regression	$0.14 g^{-1}
TMA precursor Al content	37.4%
ALD precursor cost per kg of catalyst	$31 kg^{-1}
ALD coating with 30% margin per kg catalyst	$41 kg^{-1}
Final ALD-coated catalyst cost	$160
ALD-coated catalyst price increase	23%
TMA precursor unit price, lab-scale	$1.46-3.22 g^{-1}
Triisobutylaluminum precursor unit price, lab-scale	$1.07-1.36 g^{-1}
Aluminum trichloride precursor unit price, lab-scale	$0.05-0.08 g^{-1}
Titanium tetrachloride precursor unit price, lab-scale	$0.15-0.33 g^{-1}
Tetrakis(dimethylamido)zirconium unit price, lab-scale	$25-62 g^{-1}

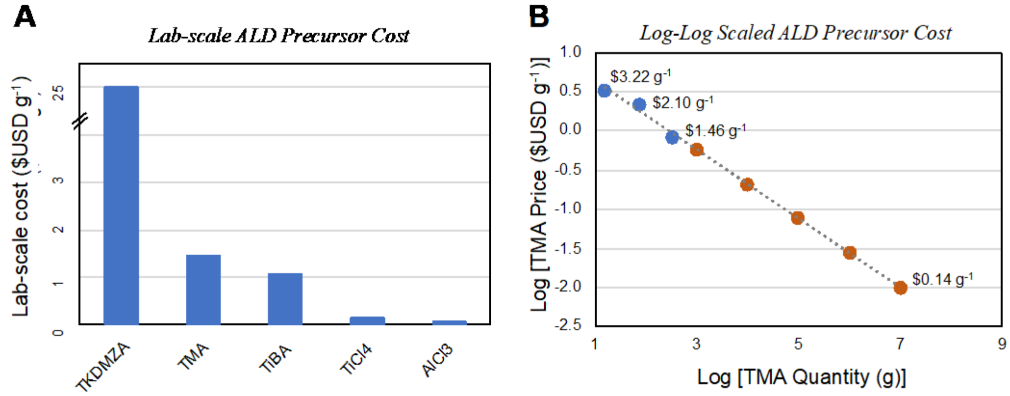

Figure 4. Lab-scale costs for a variety of ALD precursors, showing the potential for ALD coating cost reductions through precursor selection (A). Projected cost reductions when scaling the TMA Al_2O_3 precursor used in this project to the scale of usage for commodity chemical catalyst production (B).

To illustrate the potential of low-cycle ALD coatings to reduce the minimum selling price (MSP) of biobased adipic acid, techno-economic analysis (TEA) was performed for an n^{th}-generation biorefinery producing 70 kilotonnes of adipic acid per year. In this hybrid process, microorganisms are used to convert biomass-derived sugars into muconic acid, which is crystallized and catalytically hydrogenated to adipic acid (**Figure 5A**). A baseline scenario was modeled with the following parameters: WHSV of 1.0 h^{-1} muconic acid in ethanol over 0.5% Pd/TiO_2 packed in a trickle bed reactor, bio-adipic yield of 99%, and catalyst cost of \$130 kg^{-1} based on the spot price of Pd, bulk TiO_2, and material preparation costs. The catalyst lifetime was assumed to be 0.5 years, representative of harsh process conditions. Under these conditions with a glucose feedstock, the adipic acid minimum selling price (MSP) was \$2.47 kg^{-1}, which is near the upper limit of the 10-year petrochemical price range projections.

The impact of the catalyst lifetime on the hydrogenation process cost was modeled for lifetimes up to 5 years, as catalyst lifetime is difficult to estimate from bench-scale data. Since catalyst lifetime impacts both capital and operational costs, a nonlinear cost dependence was observed (**Figure 5B**). For a lifetime of 0.5 years, the costs due to the hydrogenation unit operation equate to \$0.32 kg^{-1} of adipic acid, which is 12.9% of the MSP. For commodity petrochemicals, catalytic unit operation costs are typically <10% of the MSP. If the catalyst lifetime is extended to one year, the hydrogenation unit operation contribution drops to \$0.22 kg^{-1} of adipic acid, which is 9.2% of the MSP (\$2.35 kg^{-1}). The impact of Pd leaching on the MSP was dramatic, even at ppm levels, as shown in **Figure 5B.** Sensitivity analysis was then used to evaluate the impact of adipic acid selectivity (90.0-99.9%), WHSV (0.25-4.0 h^{-1}), catalyst cost (\$33-260 kg^{-1}), and reactor capital (0.25-4.0x) for the one-year lifetime scenario. As shown in **Figure 5D,** selectivity is increasingly impactful at low values due to the strong dependence of MSP on product yield. WHSV is also a key driver until a WHSV of 2 h^{-1}, with further gains providing diminishing MSP improvements. Varying catalyst costs and reactor capital had a lesser impact due to the high baseline WHSV of 1.0 h^{-1} and 30-year chemical plant amortization.

Lastly, the impact of ALD-coated catalyst price (\$163–780 kg^{-1}) was compared to the harsh 0.5-year lifetime scenario for an uncoated catalyst to determine the necessary improvements in catalyst stability and retained activity, as highlighted in **Table 4**. A modest 25% increase in catalyst cost can readily be justified through lifetime extension to one year, so long as 75% of the initial catalyst activity is retained. However, even a 50% increase in catalyst cost can be justified through a catalyst lifetime extension to 2 years with 50% activity retention. Although projected cost estimates for ALD coating at the scale of catalyst manufacturing can greatly vary based on the type of ALD precursor, scale of precursor production, and estimated precursor utilization efficiency, this analysis highlights that ALD catalyst coatings for harsh environments have the potential to favorably impact process economics for biobased adipic acid if sufficient lifetimes improvements and retained activity can be achieved for supported Pd catalysts.

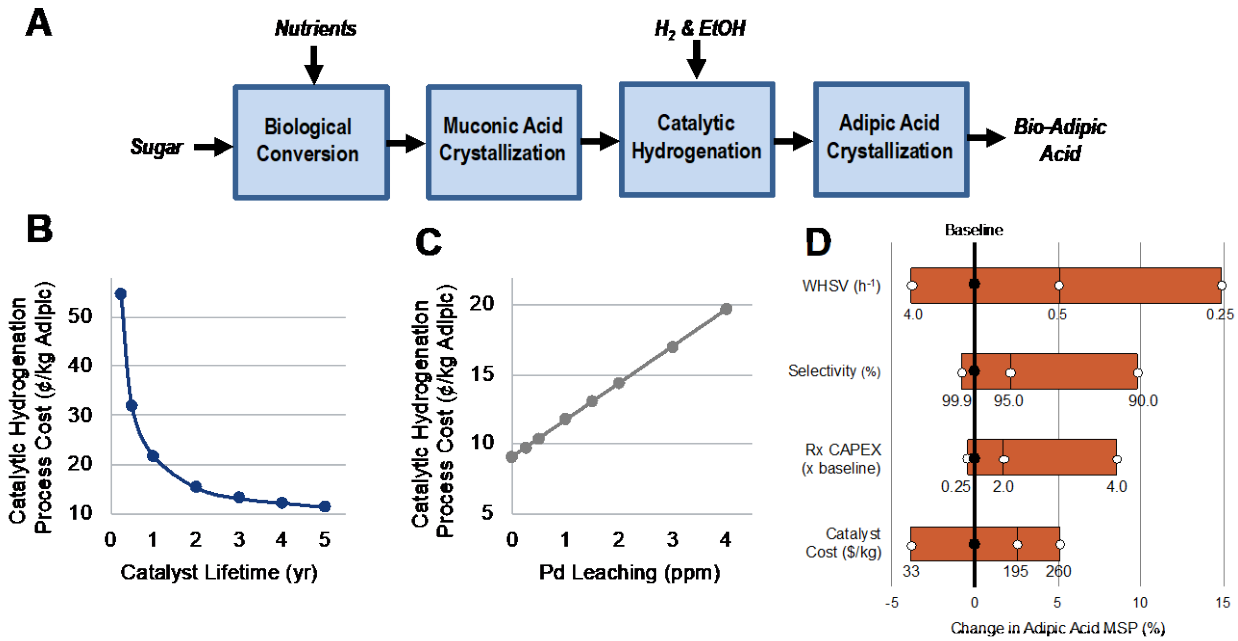

Figure 5. Techno-economic analysis of the biobased adipic acid production process (A), showing the cost impact of catalyst lifetime (B), Pd leaching (C), and catalyst unit operation cost sensitivities (D).

For the near-term path to market, companies that can vertically integrate ALD precursor manufacturing with the ALD coating stand to benefit most from early adoption of this technology. ALD catalyst coatings for commodity chemical production will require significant volumes of ALD precursors, and companies that produce their own precursor stand to benefit from lower ALD precursor costs. A similar strategy is applied in the platinum group metal catalyst market, where the most competitive companies control the supply chains for platinum group metal production. To reduce the timeline for commercialization with ALD-coated catalysts, “steel in the ground” process chemistries should also be targeted, as further efforts are needed to develop the supply chain and infrastructure for biobased chemical production. Both conventional and renewable process chemistries stand to benefit from the enhanced stability offered through ALD coatings, providing a two-pronged path for future catalyst development.

Table 4. Impact on the minimum selling price (MSP) of biobased adipic acid production when varying ALD coating costs, catalyst lifetime, and performance for various scenarios.

Scenario	Catalyst Cost ($ kg^{-1})	Lifetime (yr)	WHSV (h^{-1})	Catalytic Hyd. Process Cost ($ kg^{-1} Adipic)	Adipic Acid MSP ($ kg^{-1})	% MSP Catalyti
Baseline: Moderate Severity	130	1	1.0	0.22	2.35	9.2
Baseline: Increased Severity	130	0.5	1.0	0.32	2.47	12.8
ALD 1	163			0.74	2.82	26.4
ALD 2	195			0.88	2.93	29.8
ALD 3	260	1	0.25	1.14	3.16	35.9
ALD 4	390			1.67	3.63	45.8
ALD 5	780			3.25	5.03	64.5
ALD 6	163			0.41	2.52	16.4
ALD 7	195			0.48	2.58	18.6
ALD 8	260	1	0.50	0.61	2.70	22.6
ALD 9	390			0.88	2.93	29.8
ALD 10	780			1.67	3.63	45.8
ALD 11[B]	163			0.30	2.43	12.5
ALD 12	195			0.35	2.47	14.1
ALD 13	260	1	0.75	0.44	2.54	17.1
ALD 14	390			0.61	2.70	22.6
ALD 15	780			1.14	3.16	35.9
ALD 16	163			0.42	2.54	16.4
ALD 17	195			0.48	2.60	18.5
ALD 18	260	2	0.25	0.62	2.72	22.6
ALD 19	390			0.88	2.97	29.6
ALD 20	780			1.68	3.72	45.1
ALD 21[B]	163			0.25	2.39	10.5
ALD 22[B]	195			0.28	2.42	11.7
ALD 23	260	2	0.50	0.35	2.48	14.1
ALD 24	390			0.48	2.60	18.5
ALD 25	780			0.88	2.97	29.6
ALD 26[A]	163			0.20	2.33	8.3
ALD 27[B]	195			0.22	2.36	9.2
ALD 28[B]	260	2	0.75	0.26	2.40	10.9
ALD 29	390			0.35	2.48	14.1
ALD 30	780			0.62	2.72	22.6
ALD 31[B]	163			0.31	2.45	12.5
ALD 32	195			0.35	2.49	14.1
ALD 33	260	3	0.25	0.44	2.58	17.1
ALD 34	390			0.62	2.75	22.5
ALD 35	780			1.16	3.28	35.2
ALD 36[A]	163			0.20	2.34	8.4
ALD 37[B]	195			0.22	2.36	9.2
ALD 38[B]	260	3	0.50	0.26	2.41	10.9
ALD 39	390			0.35	2.49	14.1
ALD 40	780			0.62	2.75	22.5
ALD 41[A]	163			0.16	2.30	6.9
ALD 42[A]	195			0.17	2.32	7.5
ALD 43[A]	260	3	0.75	0.20	2.35	8.6
ALD 44[B]	390			0.26	2.41	10.9
ALD 45	780			0.44	2.58	17.1

Subject Inventions Listing:

None

ROI #:

None

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