

Accelerated Deployment of Nanostructured Hydrotreating Catalysts – Final Report

Energy Systems Division

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Hydrotreating Catalysts
Final Report**

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Abstract

Nanomanufacturing offers an opportunity to create domestic jobs and facilitate economic growth. In response to this need, U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy issued a Research Call to develop nanomanufacturing capabilities at the National Laboratories.

High performance catalysts represent a unique opportunity to deploy nanomanufacturing technologies. Re-refining of used lube oil offers an opportunity to create manufacturing jobs and decrease dependence on imported petroleum. Improved catalysts are required to produce a better quality product, decrease environmental impact, extend catalyst life, and improve overall economics of lube oil re-refining.

Argonne National Laboratory (Argonne) in cooperation with Universal Lubricants, Inc. (ULI) and Chemical Engineering Partners (CEP) have carried out a Cooperative Research and Development Agreement (CRADA) to prepare nanostructured hydrotreating catalysts using atomic layer deposition (ALD) to exhibit superior performance for the re-refining of used lube oil.

We investigated the upgrading of recycled lube oil by hydrogenation using commercial, synthetically-modified commercial catalysts, and synthesized catalysts. A down-flow (trickle bed) catalytic unit was used for the hydrogenation experiments. In addition to carrying out elemental analyses of the various feed and product fractions, characterization was undertaken using H^1 and C^{13} NMR.

Initially commercial were evaluated. Second these commercial catalysts were promoted with precious metals using atomic layer deposition (ALD). Performance improvements were observed that declined with catalyst aging. An alternate approach was undertaken to deeply upgrade ULI product oils. Using a synthesized catalyst, much lower hydrogenation temperatures were required than commercial catalysts. Other performance improvements were also observed. The resulting lube oil fractions were of high purity even at low reaction severity. The products recovered from both the ALD and other processes were water-white (even those from the low temperature, low residence time (high space velocity), low conversion runs). These results indicate that highly upgraded recycle lube oils can be produced using ALD-deposited active metal catalysts. The use of H^1 and C^{13} NMR for the characterization of the treated lube oils has been shown to be effective.

Table of Contents

Abstract	1
Introduction	3
Experimental	6
Results and Discussion	8
Summary and Conclusions	10
Acknowledgements	10
References	10
Figures	12
Appendix: Background Information	13

Introduction

Nanomanufacturing offers an opportunity to create domestic jobs and facilitate economic growth. In response to this need, U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy issued a Research Call to develop nanomanufacturing capabilities at the National Laboratories.

As of 2008, the U.S. Government has invested \$8.3 billion in nanotechnology and made great strides in gaining fundamental knowledge at the nanometer-scale. Nanotechnology has the potential for major improvements in energy applications. To capture the potential benefits of nanotechnology to a greater extent, applied research needs to be augmented to accelerate the convergence of nanoscience towards nanomanufacturing. To enable this transition will require a pioneer project to demonstration that Laboratory nanotechnology R&D (Stage-Gate 1-2) can rapidly reach a Stage 5 and impact commercial development. This pioneer demonstration requires both an R&D organization with expertise in the nanotechnology platform and a committed industrial partner with an immediate technology need in a commercial deployment. Timing is critical in high energy use/large carbon footprint industries because tight (and variable) margins preclude investments in long-term R&D programs.

High performance catalysts represent a unique opportunity to deploy nanomanufacturing technologies. Hydrotreating, or re-refining, of used lube oil offers an opportunity to create manufacturing jobs and decrease dependence on imported petroleum. Improved hydrotreating catalysts are required to produce a better quality product, decrease environmental impact, extend catalyst life, and improve overall economics of lube oil re-refining. Currently >85 % of the >7 billion pounds of used oil is simply burned as fuel, while only ~14 % is recycled. Hydrotreating is a major operation in petroleum processing, so the full market opportunity is significantly larger.

Argonne National Laboratory (Argonne) in cooperation with Universal Lubricants, Inc. (ULI) and Chemical Engineering Partners (CEP) were awarded funded in response to the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy Research Call “NANOMANUFACTURING FOR ENERGY EFFICIENCY 2008

Original CRADA Goals:

Argonne, ULI and CEP entered into a Cooperative Research and Development Agreement (CRADA) to prepare nanostructured hydrotreating catalysts using atomic layer deposition (ALD) to produce superior performance for the re-refining of used oil. Argonne invented methods for preparing nanostructured catalysts that exhibit superior performance in bench-scale testing. In this project, Argonne’s goal will demonstrate that a new nanomanufacturing technique, ALD, enables us to rapidly develop, evaluate, and deploy catalysts for industrial utilization. As a test of this capability, Argonne will design, screen, and manufacture hydrotreating catalysts for the re-refining of used oil. Argonne will make these catalysts available for the partner to develop these catalysts and integrate them into their re-refining facility. In addition to the energy, environmental, and economic benefits associated with oil recycling, the successful completion of this project will demonstrate the capability of this nanomanufacturing technology to rapidly impact industrial catalysts in a broad range of energy intensive, large carbon footprint applications.

Recent work at Argonne has advanced the state-of-the-art for preparing nanostructured catalysts using ALD. These catalysts exhibit superior performance in bench-scale testing. ALD can manufacture catalysts with exceptional dispersion, uniformity and controlled loading. ALD catalysts have the potential to improve the efficiency of any reaction where high-performance catalysts are required for high activity and selectivity. In addition, ALD makes very efficient use of deposited metals or their oxides, thereby lowering the catalyst manufacturing cost.

Prior to this project, Argonne and ULI have never worked together. ULI became familiar with Argonne's expertise due from Argonne's prior reports on oil re-refining. The goal of this project was to work closely together to design, screen, and develop novel nanostructured hydrotreating catalysts in time for deployment in ULI's second facility. If successful, this project would serve as the bench case for rapid public/private deployment of nanotechnologies in industrial time scales. This would open the market for rapid acceleration of nanotechnology R&D and deployment of nanomanufacturing in high energy use/carbon footprint industrial processes.

Potential Impact Catalyst improvements in existing processes

A recent study of the potential energy savings from the implementation of improved catalyst selectivity in the entire US chemical industries estimate energy savings of 280-600 TBtu/yr assuming that the remaining theoretical margin for catalyst improvement is cut in half. These projections are based on the replacement of catalysts in existing processes. In order to realize some of this potential using ALD catalyst requires broad adoption in industry of the development function.

Oil re-refining

Re-refining is potentially a multi-billion pound market. By competing with crude oil at current prices above \$100 / barrel, re-refining offers the potential for substantial economic returns. With superior processing technology based on the new hydrotreating nanocatalysts, we expect to be able to out-compete other waste recyclers for access to materials.

Hydrotreating

In a typical hydrotreating process the oil mixes with hydrogen and is heated to reaction temperature and passes through the first of several catalyst beds. The reacting mixture is reheated between catalyst beds. The first catalyst bed is sacrificial, accumulating catalyst poisons such as heavy metals and sodium. The reaction product enters a high pressure separator with the vapor recycling through a compressor to mix with the incoming oil and the liquid flashing into a low pressure separator. High purity makeup hydrogen is added to the recycle gas to replace hydrogen consumed by chemical reaction and solution losses. In the low pressure separator, the vapor is purged from the process and the liquid flows to a stripping column to remove hydrogen sulfide, ammonia, and water.

Catalyst life is three to five years. As the catalyst ages, the reaction temperatures must be increased. The end of run is determined by the temperature above which the catalyst would be damaged. Another contributing factor to catalyst aging is coke formation on the catalyst surface.

Samples and Information from the Partners:

In the initial concept Argonne planned to evaluate commercial hydrotreating catalysts as references for the hydrotreating of representative recycle oil. Subsequently, these and other catalysts would be treated using ALD for the deposition of controlled amounts of additional

active metals. Two catalysts were provided by ULI/CEP. The catalyst specifications and promoters are proprietary.

A series of oil samples were also provided. Several gallons of a typical hydrotreating feed oil isolated after pretreatment. The oil pretreatment included caustic scrubbing (removal of organic chlorides, acidic sulfur, and heavy metals), flash evaporation (removal of water and naphtha) and wiped film evaporation/distillation (removal of asphaltic residue). A reference sample of plant hydrotreated oil was also provided. Several other oil samples were also evaluated.

Selected Operating Conditions Based upon Information from the Partners:

Plant operating conditions were provided to design experimental operating conditions. A summary of the commercial recycle lube oil facility, denoted as the “Evergreen Process” is available at: <http://www.docstoc.com/docs/84568245/Economics-of-Used-Oil-Recycling-Still-Slippery>. Specific plant operating conditions are proprietary. Experiments were designed to minimize low severity and to produce intermediate oil conversion level. This enabled us to differentiate catalyst activity levels.

Literature

Lube Oil Properties:

The properties of lubricating oil that are currently available on the open market are described by Lillard, Jones, and Anderson¹, Wang and Zhang² and Duan et al³ as a starting point for the basestocks. In general, lubricating oils contain paraffins (both normal and iso) and naphthenes with additional hydrocarbons. Typically, each supplier uses “additive packages” to modify oil such as viscosity index, lubricity and anti-wear properties, corrosion inhibitors, antioxidants, pour point depressants, anti-foaming agents, sludge suspending/dispersing agents and the likes. For the most part, these additives remain in the recycle oil after use. Many are subsequently removed during the initial steps of spent oil recovery.

The properties of recycled oil vary greatly depending upon the location, climate, type and duty of vehicles in use, etc. There is no universal reference standard. One example is summarized in the technical report “Chemical Analysis of Lubricating Oil Samples from a Study to Characterize Exhaust Emissions from Light-Duty Gasoline Vehicles in the Kansas City Metropolitan Area”.⁴ Observations regarding the compositions include:

- Zn, P, Ca, and S were the predominant elements in lubricating oils. The abundances of these four elements were similar in used and unused oils in terms of both concentration and percentages to sums of the elements.
- Concentrations of total hopanes and total steranes in used oils were similar to unused oils for lower PM emitters, but were enriched in used oils for higher emitters by up to a factor of 20 for hopanes and a factor of 10 for steranes. Loss of more volatile components of the oil is one possible explanation for this enrichment. The magnitude of the enrichment suggests that there may be other contributing factors. The composition of hopanes, in percentage of individual hopanes relative to the sum of total hopanes, was similar among all oils.
- Concentrations of alkanes were higher in used oils by about a factor of 2-3 compared to unused oils. Enrichment of light alkanes (e.g., C₁₂ and C₁₃) is likely due to absorption of blow-by exhaust containing unburned gasoline. We speculate that

thermal cracking of heavier alkanes in the combustion process might be the source of enrichment of the midrange ($C_{16} - C_{28}$) alkanes.

- Polyaromatic hydrocarbons (PAHs) were generally undetectable in unused oil. PAHs were found in all used lubricating oil with no apparent relationship to exhaust PM emission rate. Insufficient information was available to determine the relationships between PAH concentrations in lubrication oil and mileage accumulation (Hypothesis 3). However, the absence of PAHs in unused lubricating oil indicates that their presence in used oil is due to absorption of blow-by exhaust containing fuel-combustion associated PAHs.

The ULI recycle oil originated from the same general area summarized in the report.

2D C^{13}/H^1 Characterization of Lube Oils:

Two-dimensional C^{13}/H^1 characterization of liquid samples is an established analytic procedure.^{5,6} This characterization is particularly useful for observing and differentiating PAHs in the oil samples.

Hydrotreating:

Hydrotreating as well as hydroprocessing and hydrofining typically refers to the catalytic hydrogenation of refinery streams for the improvement of properties without significant cracking to generate lower molecular weight fractions. As noted by Satterfield⁷ “hydrotreating may be used as a finishing process in the manufacture of lubricants and special oils. The catalyst is typically $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$, which is sulfided before use.” Rana, et al⁸ reviewed commercial processes for the upgrading of heavy oils and residua using hydroconversion. Additional information is available in the patent literature^{9,10} and a special issue of Applied Catalysis¹¹.

Hydrotreating of waste, spent or recycled lube oils is generating interest. Pasadakis, et al,¹² described an evaluation of Ni/Mo , Co/Mo , Ni/W , and Co/W on a variety of supports for the hydrotreating of refinery spent lube oil. They focused on sulfur reduction (HDS), the reduction of aromatics content while minimizing hydrogen consumption. Catalysts containing Ni/Mo on $\gamma-Al_2O_3$ exhibited the highest hydrogenation and hydrodesulphurization ability. Co/Mo on $\gamma-Al_2O_3$ was also an effective catalyst. While the Co/Mo and Ni/Mo catalysts were active for HDS and aromatics reduction, they also were required significant hydrogen consumption. Catalysts supported by ZrO_2 were also effective for efficiently removing sulfur and ensuring adequate hydrogenation with low hydrogen consumption.

Experimental

Reactor System:

A continuous-flow catalytic-bed unit was used for reactions. A flow schematic for operation with a fixed bed of particulate catalyst is presented in Figure 1. The liquid oil feed was provided by an ISCO high pressure syringe pump. The gaseous feeds were provided from cylinders using Brooks mass flow controllers. The feed oil and gases passed down (i.e. trickle-flow) through a preheater/reactor that consisted of a 1/2-in.-O.D. (3/8-in.-I.D.) tube of 36 in. length. The reactor section consisted of the following zones:

1. An empty (quartz wool) zone to serve as a preheater (length = 18 in. (46 cm))
2. Inert packing consisting of low-surface α -Al₂O₃ to ensure radial flow dispersion (4 in(10 cm))
3. Supported catalyst that was mixed with inert filler (2-3 in. (5-8 cm))
4. Additional α -Al₂O₃ packing

The preheater/reactor had a total of six internal and two external thermocouples. The reactor temperature was controlled using the thermocouple at the center of the active catalyst bed.

The hydrotreating experiments were carried out at 210°C - 290°C (410°F - 550°F), ~54 MPa (790 psia), 100% H₂ feed gas ~4.0 L/hr, and oil feed rates of 5 - 15 mL/hr. The charge of active catalyst was either 1.0 or 2.0 grams.

The reactor effluent was cooled in one of two parallel a wet-ice-cooled traps. Samples were periodically recovered for weighing and sampling. The pressure of the off-gas was controlled, and it was subsequently metered and sampled.

Gas composition was determined using an HP 6890 Series gas chromatograph (GC) that had been modified by LINC Quantum Analytics of Foster City, CA. It had three columns: (1) a molecular sieve column (7 ft x 1/16 in. 13X 45/60) for light gas retention and separation, (2) a capillary column (50 m x 0.53 mm KCl modified Al₂O₃ PLOT) for hydrocarbon analysis by a flame ionization detector (FID), and (3) a packed column (7 ft x 1/16 in. Hayesep A 60/80) for CO₂ separation and analysis using a thermal conductivity detector (TCD).

Elemental analyses of selected oil samples were conducted by Galbraith Laboratories, Inc., Knoxville, TN. The kinematic analyses and viscosity indices were determined by Texas OilTech Laboratories, Houston, TX.

All NMR experiments were performed at Argonne using a Bruker Avance III 500 MHz NMR spectrometer (11.7 T). With the use of the nitrogen pre-cooler, heater coil, and the variable temperature controller, the temperature was stable at 294.3 ± 0.1° K. The ¹H spectra were recorded with a two channel 5 mm direct detection, single axis gradient, variable temperature probe with ²H lock at 76.773 MHz. 1000 acquisitions, 4 s recycle delay, 4 μs pulse width (70°) and 6 kHz sweep width.

Catalyst Synthesis, Preparation, and Properties

Catalyst synthesis, preparation, and characterization are proprietary and/or CRADA protected.

ALD Reactant Exposure Time Determination: Reactant gas contact times must be determine the required time to fully saturate the inner surface of the catalyst particles with ALD. Contact time requirements were evaluated using the very well behaved ZnO ALD system. Diethyl zinc and water were used to deposit ZnO, which is easily imaged with EDAX mapping and can also be easily visualized using secondary electron imaging in standard SEM. In a viscous flow ALD reactor, the most important factors determining the required contact time are the partial pressure of the gaseous reactant, carrier gas flow rate and utilization factor. In general for supports with very high surface area such as the substrates in this study, the delivery rate of the ALD reactant gas is the main determining factor. Therefore, lower vapor pressure reactants require more time to deliver a saturating quantity of the reactant.

Metal oxides were deposited on catalysts using a viscous flow ALD reactor¹³ at 1 Torr pressure using ultrahigh purity nitrogen carrier gas at a mass flow rate of 20 sccm and a temperature of

125°C. The catalyst was first heated to 250°C for one hour to remove physisorbed water and then weighed dry prior to loading into the ALD reactor. Approximately 1 g of catalyst was contained in a fixed-bed powder fixture. The time of the metal exposure was varied to provide a saturation time trend. The degree of saturation was also evaluated by measuring the mass change of the sample and comparing this mass change to the expected mass gain calculated from known ALD growth rates on flat surfaces and the measured BET surface area of the catalyst support.

Sample specific ALD conditions are CRADA-protected.

Results and Discussion

Reference Data and Experiments:

The level of aromaticity of the two reference samples are compared using H^1 -NMR spectral results. H^1 spectra are of higher precision than C^{13} -NMR spectra due to available instrumentation and operating time. The level of aromatics was significantly reduced and the levels of alkenes were essentially removed as a result of the hydrotreating steps.

Reference experiments were conducted with a reactor filled with α -alumina (inert) particulates without active catalyst. Some hydrogenation occurred, but there was little desulfurization and reduction of alkenes. No aromatics reduction was observed.

Commercial Catalyst Evaluation Experiments:

The extent of hydrogenation of the lube oils was strongly dependent on the choice of catalyst. Catalytic reduction of aromatics and alkenes was evaluated with H^1 -NMR spectra. There was an initial level of catalytic aromatic reduction, but this decreased significantly during subsequent reaction periods. The trends exhibited in aromatics reduction were similar to those in alkene reduction. ALD-modified commercial catalysts performed similar to commercial catalysts.

ALD-Synthesized Catalyst Evaluation Experiments:

Catalysts prepared by ALD was superior to incipient wetness impregnation (IWI), even with composition was very similar. In both cases, much lower hydrogenation temperatures were needed in comparison to commercial catalysts. Alternatively, less ALD catalyst would be required for equivalent aromatics removal. This would likely enhance catalyst life. There are two significant results. First, all products, from both the ALD and IWI were water-white (even those from the low temperature, low conversion runs.) Second, selected samples of the ALD product samples were submitted for viscosity Index (VI) determination. The VI results indicate that the product VI was unchanged from the feed V-301 oil suggesting that VI is independent of aromatics and heteroatoms concentration.

Discussion of the NMR Spectra:

NMR spectroscopy was used to quantitatively measure the trends from the reductive catalysis of used lube oil. H NMR spectra were monitored to observe the change in the levels of aromatic and aliphatic hydrogen atoms. Integrated signal intensity from three distinct regions (0.0 - 3.0 ppm, 3.0 - 6.8 ppm, and 6.8 - 9.0 ppm) enables evaluation of catalyst performance.

The first region is identified with aliphatic hydrogen; hydrogen atoms bonded to sp^3 hybridized carbon atoms methine (CH), methylene (CH_2), and methyl (CH_3).

The second region can include some methine and methylene hydrogen on the high-field region but also hydrogen atoms bonded to non-aromatic sp² hybridized carbon and hydrogen atoms bonded to oxygen, nitrogen, and sulfur. Although at low concentration, some of these resonances are very narrow and can be assigned to specific chemical moieties.

The third region is identified with hydrogen bonded to sp² hybridized aromatic carbon atoms. The absolute concentration of hydrogen in this region can be used to determine the amount of aromaticity assuming the ratio of non-protonated carbon atoms, from fused rings and substitution, remains similar for reactant and product. Quantitative C¹³ NMR spectroscopy is a superior tool but is impractical for screening a large number of samples. Increased hydrogen to carbon ratios corresponds to increased fraction of aliphatic hydrogen in the proton NMR spectra. In this regard, a 15-minute NMR spectrum is a cost effective method for quickly screening large number of samples.

The spectra show very broad resonances in the most intense regions. The broad resonances occur from the superposition of a large number of chemical variants with subtly varying chemical shifts and from long correlation times of larger molecular species. The presence of some very narrow line-width species indicates that the line-broadening is homogeneous. Also, line-broadening from paramagnetic species is probably negligible.

Other than changes to relative concentration, difference spectra reveal little in the regions between 0.0- 3.0 ppm and 6.8 - 9.0 ppm. No specific chemical functional groups can be discerned from the one-dimensional H¹ NMR spectra. Within the center region of the spectra, significant differences in narrow resonances occur with catalytic reduction. Nearly complete elimination of these resonances occurs for the most successful catalysts.

These spectra reveal dramatic changes and the chemical composition at low concentration in the middle region of the spectra. In particular the hydrogen bonded to non-aromatic sp² hybridized carbon and hydrogen bonded to heteronuclei are eliminated in effective catalytic reduction. These results are consistent with known reactions of pure starting materials with the investigated catalysts.

The two-dimensional HSQC C¹³ /H¹ NMR spectra were recorded for a subset of samples. From these spectra, one can readily determine the hydrogen bonded to heteronuclei (by difference) and the methylene to methine and methyl ratio (by DEPT sub-spectra). Moreover, the intense aromatic and aliphatic regions now display changes in two-dimensions that were not apparent in the one-dimensional analysis. Specifically, the aromatic resonances appear to be selectively reduced in the low-field hydrogen/ high-field carbon region. The methyl region appears unchanged in either analysis. This also is consistent with the facts; the only possible source of new methyl resonances would be from reduction of terminal alkenes (a minor component) or from fragmenting larger molecules (unlikely with the studied catalysts).

The detected chemical moieties were consistent with the C¹³ and H¹ chemical shift values and are likely targets of the catalytic reduction. This chemical specificity is possible because of the very narrow resonances and distinct chemical shifts of these species. Controlled studies of model compounds could be conducted to investigate whether the catalysts are effective in the absence of complex chemical environment of lube oil.

Summary and Conclusions

The project goal was to prepare nanostructured hydrotreating catalysts using atomic layer deposition (ALD) to that superior performance for the re-refining of used oil. Three sets of catalysts were evaluated for upgrading recycled lube oil by hydrogenation (commercial catalysts, ALD-modified commercial catalysts, and ALD (or IWI)-synthesized catalysts.

We conclude that it is possible to prepare highly upgraded recycle lube oils using ALD-deposited active metal catalysts after the initial hydrotreating of the recycle oils. The ALD catalyst could potentially be used as a finishing catalyst in the existing plant process allowing a lower temperature to be used with existing commercial catalyst beds thus extending useful life of the catalyst bed. This conclusion is based on the plant operator's criteria that the high temperature of the catalyst is required to reduce the aromatics content and achieve low color of the finished product. Both of these are achieved at a much lower temperature using the ALD synthesized catalyst. Commercialization will require methods to reduce precious metal loading in these catalysts. An economic analysis is not possible at this stage.

The use of H^1 and C^{13} NMR and two dimensional C^{13}/H^1 NMR for the characterization of the treated lube oils has been shown to be effective.

Acknowledgements

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References

1. Lillard, J. G.; Jopnes, W. C.; Anderson, J. A. J., *Ind. Eng. Chem* 1952, *44* (11), 2623-2631.
2. Wang, F. C.-Y.; Zhang, L., Chemical composition of group II lubricant oil studied by high-resolution gas chromatography and comprehensive two-dimensional gas chromatography. *Energy & Fuels* 2007, *21* (6), 3477-3483.
3. Duan, P.; Qian, K.; Habicht, S. C.; Pinkston, D. S.; Fu, M.; Kenttamaa, H. I., Analysis of base oil fractions by $ClMn(H_2O)(+)$ chemical ionization combined with laser-induced acoustic desorption/Fourier transform ion cyclotron resonance mass spectrometry. *Analytical Chemistry* 2008, *80* (6), 1847-1853.
4. Fujita, E. M.; Campbell, D. E.; Zielinska, B.; Arnott, W. P.; Chow, J. C., Concentrations of air toxics in motor vehicle-dominated environments. *Research report (Health Effects Institute)* 2011, (156), 3-77.
5. Berger, S.; Braun, S., *200 and more NMR experiments : a practical course*. 3rd rev. and expanded ed.; Wiley-VCH: Weinheim, 2004; p xv, 838 p.
6. Pochapsky, T. C.; Pochapsky, S. S., *NMR for physical and biological scientists*. Taylor & Francis: New York, 2007; p xxii, 372 p.
7. Satterfield, C. N., *Heterogeneous catalysis in industrial practice*. 2nd ed.; Krieger Pub.: Malabar, Fla., 1996; p xvi, 554 p.

8. Rana, M. S.; Samano, V.; Ancheyta, J.; Diaz, J. A. I., A review of recent advances on process technologies for upgrading of heavy oils and residua. *Fuel* 2007, 86 (9), 1216-1231.
9. Mears, D. E. F., (CA), Hunter, Michael G. (Downey, CA) Hydroprocessing for producing lubricating oil base stocks. 1994.
10. Cody, I. A. B. R., (LA, US), Murphy, William J. (Baton Rouge, LA, US), Hantzer, Sylvain (Praireville, LA, US), Larkin, David W. (Baton Rouge, LA, US), Gallagher Jr., John E. (Fairfax Station, VA, US), Kim, Jeenok T. (Fairfax, VA, US) Process for preparing basestocks having high VI. 2007.
11. Geantet, C.; Vrinat, M., Active Phases for Hydrotreating Catalysis - Preface. *Appl. Catal. A-Gen.* 2007, 322, 1-2.
12. Pasadakis, N.; Yiokari, C.; Varotsis, N.; Vayenas, C., Characterization of hydrotreating catalysts using the principal component analysis. *Appl. Catal. A-Gen.* 2001, 207 (1-2), 333-341.
13. Elam, J. W.; Groner, M. D.; George, S. M., Viscous flow reactor with quartz crystal microbalance for thin film growth by atomic layer deposition. *Rev Sci Instrum* 2002, 73 (8), 2981-2987..

Figures

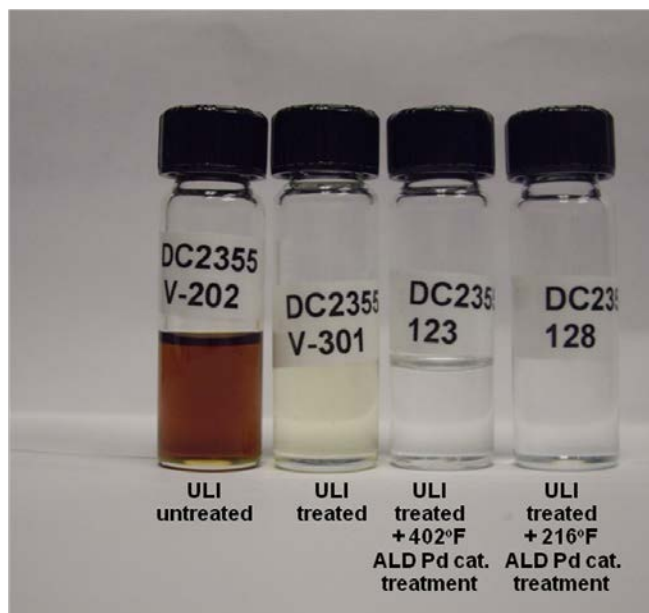
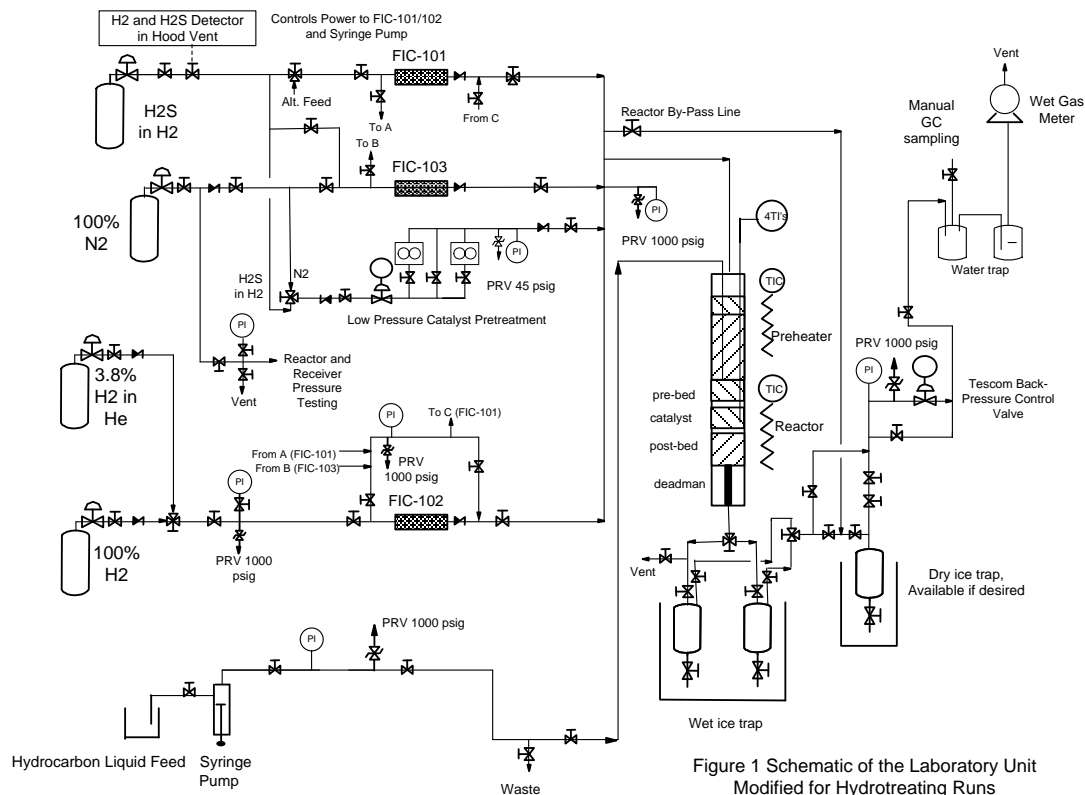


Figure 14 - Color of Treating Used Oil showing deep level of aromatics removal by the Pd on silica catalyst. All other tested catalysts produced a color intermediate between the ULI untreated and ULI treated samples shown here (due to intermediate conversion).

Appendix: Background Information

Funding Profile:

Federal Funding: \$800,000

Estimated Cost Share funding: \$250,000

Publications and Presentations

Seth W. Snyder, Joseph Libera, Jeffrey Elam, William Ragland, Joseph Franceschi, Alan Libshutz, James Condela **“Accelerated Deployment of, Nanostructured Hydrotreating Catalysts”**, presented at the AIChE National Meeting, Nashville TN, November 10, 2009



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