

**IMPROVED CATALYSTS FOR HEAVY OIL UPGRADING BASED ON ZEOLITE Y  
NANOPARTICLES ENCAPSULATED STABLE NANOPOROUS HOST**

**NINTH SEMI-ANNUAL TECHNICAL PROGRESS REPORT**

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## I. ABSTRACT

The addition of hydrothermally-aged zeolite Y precursor to an SBA-15 synthesis mixture under a mildly acidic condition resulted in the formation of a mesoporous aluminosilicate catalyst, Al-SBA-15. The Al-SBA-15 mesoporous catalyst contains strong Brönsted acid sites and aluminum (Al) stabilized in a totally tetrahedral coordination. The physicochemical characteristics of the catalyst varied as a function of the synthesis conditions. The catalyst possessed surface areas ranging between 690 and 850 m<sup>2</sup>/g, pore sizes ranging from 5.6 to 7.5 nm, and pore volumes up to 1.03 cm<sup>3</sup>, which were comparable to the parent SBA-15 synthesized under similar conditions. Two wt % Al was present in the catalyst that was obtained from the reaction mixture that contained the highest Al content. The Al remained stable in totally tetrahedral coordination after calcination at a temperature of 550°C. The Al-SBA-15 mesoporous catalyst showed significant catalytic activity for cumene dealkylation, and the activity increased as the amount of zeolite precursor added to the SBA-15 mixture was increased. In preparation for the final phase of the project, the catalyst was embedded into a pseudoboemite alumina (catapal B) matrix and then formed into pellets. In the final phase of the project, the pelletized catalyst is being evaluated for the conversion of a heavy petroleum feedstock to naphtha and middle distillates. This phase was significantly delayed during the past six months due to a serious malfunction of the fume hoods in the Clark Atlanta University's Research Center for Science and Technology, where the project is being conducted. The fume hood system was repaired and the catalyst evaluation is now underway.

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## **II       DISCLAIMER**

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### III LIST OF ABBREVIATIONS

Al	Aluminum
SBA-15	University of California-Santa Barbara Mesoporous Material No 15
Al-SBA-15	Aluminum-containing SBA-15
MPa	Mega pascal
GC/FID	Gas chromatograph with Flame Ionization Detector
g	grams
nm	nanometers

#### IV EXECUTIVE SUMMARY

The objective of this project is to synthesize nanocrystals of highly acidic zeolite Y nanocrystals, encapsulate them within the channels of mesoporous (nanoporous) silicates or nanoporous organosilicates, and evaluate the “zeolite Y/Nanoporous host” composites as catalysts for the upgrading of heavy petroleum feedstocks. In comparison to conventionally-used zeolite Y catalysts of micron size particles, the nanocrystals (< 100 nm particle size) which will contain shorter path lengths, will allow faster diffusion of large hydrocarbon substrates through the channels and cages (<1 nm size) of the zeolite. This is expected to significantly reduce deactivation of the catalyst and prolong the life of catalyst. Encapsulating zeolite Y nanocrystals within the nanoporous materials will protect its external surfaces and pore entrances from being blocked by large hydrocarbon substrates, since these substrates will initially be converted to small molecules by the nanoporous host (a catalyst in its own right). The project consists of four major tasks as follows: 1) synthesis of the nanoparticles of zeolite Y (of various chemical compositions) using various techniques such as the addition of organic additives to conventional zeolite Y synthesis mixtures to suppress zeolite Y crystal growth; 2) synthesis of nanoporous silicate host materials of up to 30 nm pore diameter, using poly (alkylene oxide) copolymers which when removed will yield a mesoporous material; 3) synthesis of zeolite Y/Nanoporous Host composite materials as potential catalysts; and (4) evaluation of the catalysts for the upgrading of heavy petroleum feedstocks.

This report highlights the progress during the final phase of the project. In the prior report, it was highlighted that several samples of Al-SBA-15 mesoporous catalysts were fabricated into pellets (extrudates) as follows. The preparation of the catalyst pellets involved two successive steps. First alumina paste suitable for extrusion was prepared from pseudoboemite catapal B by kneading the pseudoboemite powder with a 5 % acetic acid (peptizing) solution. The paste was then mixed with SBA-15 /Zeolite-Y composite catalyst with kneading until it formed a “plastic-feeling” paste. In a typical experiment, 8.0g of the pseudoboemite powder, 2.0g of SBA-15/Zeelote-Y composite, 6.5g water, and the appropriate quantities of peptizing agent was used in each batch. The peptizing agent was added slowly over a 20-minute period with continuous mixing and kneading. The paste was extruded through a garlic press, and then dried in a

thermolyne tube furnace at a temperature of 250°C for 1 hour. The dried extrudates were then calcined at a temperature of 250°C for 1 hour and then at a temperature of 500°C for 2 hours in the presence of flowing dry air. The pellets were then impregnated with 15 wt % ammonium heptamolybdate solution, dried for 12 hours at a temperature of 100°C in an air oven, and calcined for 2 hours at a temperature of 500°C under dry air circulation. Nickel was then introduced by a second impregnation with a 16 wt % nickel nitrate solution, followed by drying at a temperature of 100°C in an air oven and final calcinations for 1 hour at a temperature of 500°C.

In the final phase, the samples are being evaluated for the conversion of heavy petroleum feedstocks. This phase was significantly delayed during the past six months due to a serious malfunction of the fume hoods in the Clark Atlanta University's Research Center for Science and Technology, where the project is being conducted. The fume hood system was repaired and catalyst evaluation is now underway.

## **V INTRODUCTION**

The objective of this project is to synthesize nanocrystals of highly acidic zeolite Y, encapsulate them within the channels of mesoporous (nanoporous) silicates or nanoporous organosilicates and evaluate the “zeolite Y/Nanoporous host” composites as catalysts for the upgrading of heavy petroleum feedstocks. In comparison to conventionally-used zeolite Y catalysts of micron size particles, the nanocrystals (< 100 nm particle size) which contain shorter path lengths, will allow faster diffusion of large hydrocarbon substrates through the channels and cages (<1 nm size) of the zeolite. This is expected to significantly reduce catalyst deactivation and prolong the life of the catalyst. Encapsulating zeolite Y nanocrystals within the nanoporous materials will protect its external surfaces and pore entrances from being blocked by large hydrocarbon substrates, since these substrates will initially be converted to smaller molecules by the nanoporous host (a catalyst in its own right). The project consists of four major tasks as follows: 1) synthesis of the nanoparticles of zeolite Y (of various chemical compositions) using various techniques such as the addition of organic additives to conventional zeolite Y synthesis mixtures to suppress zeolite Y crystal growth; 2) synthesis of nanoporous silicate host materials of up to 30 nm pore diameter, using poly (alkylene oxide) copolymers which when removed will yield a mesoporous material; 3) synthesis of zeolite Y/Nanoporous Host composite materials as potential catalysts; and 4) evaluation of the catalyst for the upgrading of heavy petroleum feedstocks.

### **V-1 BACKGROUND**

In previous reports, the synthesis and characterization of Al-SBA-15 mesoporous catalysts was highlighted. The details were also published in the December 2006 issue of Journal of Porous Materials. In summary, the catalysts with strong Brönsted acid sites and Al stabilized in a totally tetrahedral coordination were synthesized from the addition of hydrothermally aged zeolite Y precursor to SBA-15 synthesis mixtures under a mildly acidic condition of pH 5.5. The materials possessed surface areas between 690 and 850 m<sup>2</sup>/g, pore sizes ranging from 5.6 to 7.5 nm, and pore volumes up to 1.03 cm<sup>3</sup>. These properties are comparable to parent SBA-15 synthesized under similar conditions. Two wt % Al was present in the catalyst that was obtained from the reaction mixture that contained the highest Al content. The Al remained stable in

totally tetrahedral coordination after calcination at a temperature of 550°C. It was also highlighted in a previous report that the Al-SBA-15 mesoporous catalyst showed significant catalytic activity for cumene dealkylation, and that the activity increased as the amount of zeolite precursor added to the SBA-15 mixture was increased. The activity of the catalyst was not affected by the aging time of the precursor for up to the 24-hour aging period. This method of introducing Al and maintaining it in a total tetrahedral coordination is very effective, in comparison to other direct and post synthesis aluminations reported. In the final phase of the project the fabrication of the catalysts into extrudates was accomplished and mild hydro-cracking reactions are being conducted in the laboratory to evaluate the catalysts for petroleum conversion.

## VI EXPERIMENTAL DETAILS

### *Fabrication of Pellets*

The preparation of the catalyst pellets involved two successive steps. First alumina paste suitable for extrusion was prepared from pseudoboehmite catapal B by kneading the pseudoboehmite powder with a 5 % acetic acid (peptizing) solution. The paste was then mixed with SBA-15 /Zeolite-Y composite catalyst with kneading until it formed a “plastic-feeling” paste. In a typical experiment, 8.0g of the pseudoboehmite powder, 2.0g of SBA-15/Zeolite-Y composite, 6.5g water, and appropriate quantities of peptizing agent was used in each batch. The peptizing agent was added slowly over a 20-minute period with continuous mixing and kneading. The paste was extruded through a garlic press, and then dried in a thermolyne tube furnace at a temperature of 250°C for an hour. The dried extrudates were then calcined at a temperature of 250°C for one hour and at a temperature of 500°C for 2 hours in the presence of flowing dry air. The pellets were then impregnated with a 15 wt % ammonium heptamolybdate solution, dried for 12 hours at a temperature of 100°C in an air oven, and calcined for 2 hours at a temperature of 500°C under dry air circulation. Nickel was then introduced by a second impregnation with a 16 wt % nickel nitrate solution, followed by drying at a temperature of 100°C in an air oven and final calcinations for one hour at a temperature of 500°C (Figure 1). The pellets will be further analyzed for final surface area, and the nickel and molybdenum loadings through chemical analysis with a Perkin Elmer Elan 9000 Inductively Coupled Plasma/Mass spectrometer.

### *Gas Oil Conversion*

In this, the final phase of the project, the Al-SBA-15 catalysts samples are to be evaluated for the conversion of heavy petroleum feedstocks. However, this phase was delayed during the past six months due to a serious malfunction of the fume hoods in the Clark Atlanta University's Research Center for Science and Technology, where the project is being conducted. The fume hood system was repaired. (see Appendix 1 for email). Evaluation of the catalyst is now underway. In addition the analytical method for the analysis of reaction products was established. This involved calibration of the Hewlett Packard Series II Gas Chromatograph which was fitted with a Flame Ionization Detector (GC/FID). The calibration was performed using ASTM D2887 simulated distillation method with an n-alkanes calibration standard mixture. An unconverted crude oil sample was also analyzed for its hydrocarbon distribution under the same ASTM analytical conditions.

For evaluation of the catalysts, a preliminary experiment on the mild hydrocracking of the gas oil was conducted in a 500-ml batch high-temperature, high-pressure Parr autoclave (Figure 1). A 4 gm sample of Al-SBA-15 catalyst pellets was added to the reactor. The catalyst was first sulfided with 5% hydrogen sulfide ( $H_2S$ ) in nitrogen at a temperature of 400°C for 2 hours. The gas oil feedstock employed was a metal-free, low-sulfur gas oil containing 79 wt % heavy fraction (Figure 2). A 60g aliquot of gas oil was added to the reactor. The reaction was conducted at a temperature of 400-500°C and a hydrogen pressure of 5.5 MPa for 2 hours. The liquid reaction product was collected and is awaiting analysis by GC/FID under the ASTM D2887 simulated distillation method.



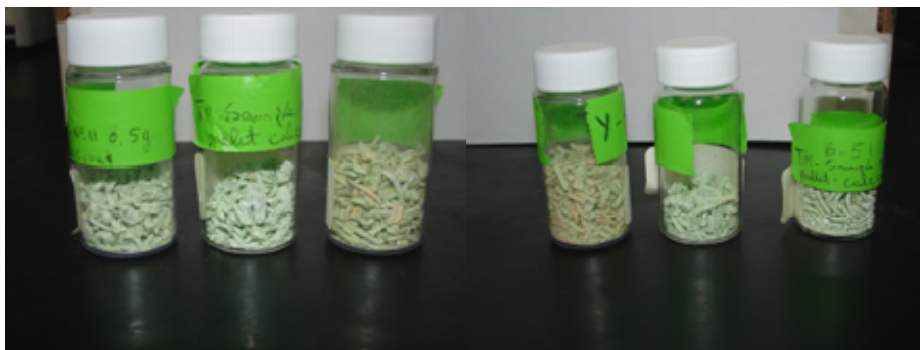
**Figure 1.** High temperature-high pressure reactor used in heavy oil conversion.



**Figure 2.** Heavy-oil feedstock used in catalyst evaluation.

## VII RESULTS AND DISCUSSION

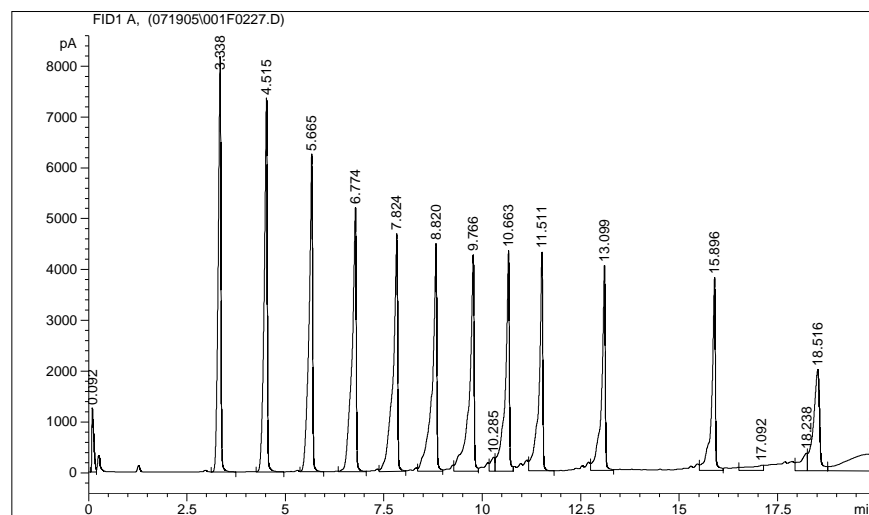
### *Pellets Preparation*



**Figure 3.** Catalyst pellets loaded with nickel and molybdenum.

Figure 3 shows various samples of catalysts pellet loaded with nickel and molybdenum. The samples are currently being evaluated for the conversion of gas oil to naptha and middle distillates under mild-hydrocracking reaction conditions.

### *GC Analysis of n-Alkanes Calibration Standard Mixture and Heavy Oil*



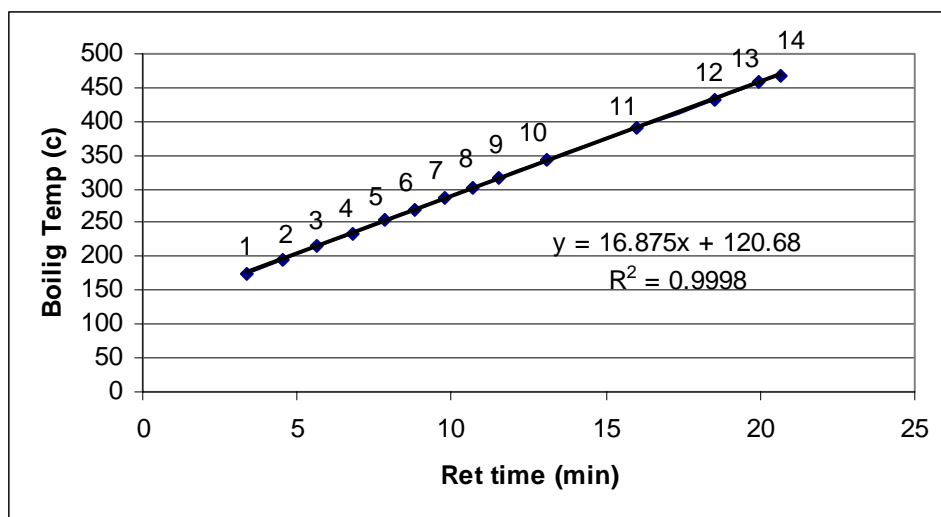
**Figure 4.** Gas chromatogram showing retention time profile of n-alkanes calibration standard mixture under ASTM D2887 method.

Figure 4 shows the gas chromatographic retention time profile of n-alkanes calibration standard mixture under ASTM D2887 method and the boiling point-retention time correlation graph is presented in Figure 5. The identity of each peak in Figure 4 is presented in Table 1. The straight line correlation that was obtained is consistent with that expected from ASTM D2887 method.

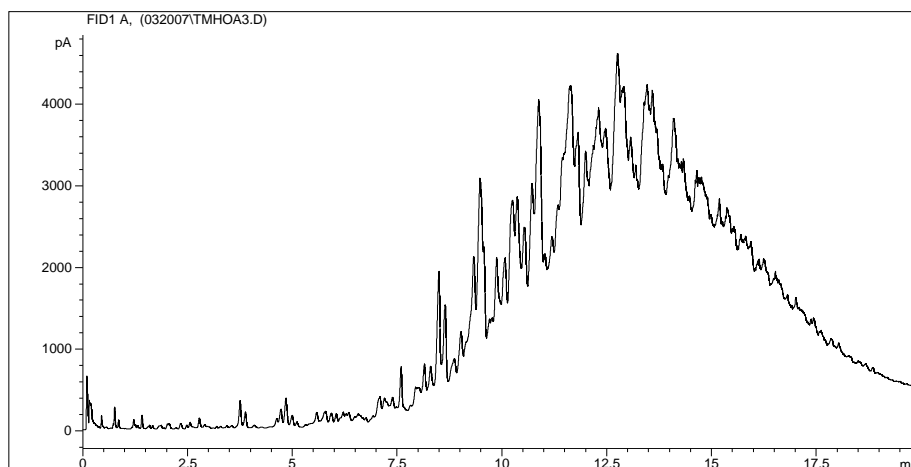
**Table 1.** n-Alkanes Retention Times and Boiling Points

Peak No.	Compound name	RT	BP (°C)
1	n-decane	3.3	174
2	n-un decane	4.5	196
3	n-dodecane	5.7	216
4	n-tridecane	6.8	235
5	n-tetradecane	7.8	253
6	n-pentadecane	8.8	270
7	n-hexadecane	9.8	287
8	n-heptadecane	10.7	302
9	n-octa decane	11.5	317
10	n-eicosane	13.1	343
11	n-tetra cosane	16.0	391
12	n-octcosine	18.5	432
13	n-dotriacontane	20.0	458
14	n-hexatriacontane	20.7	467

(See Figures 4 and 5)



**Figure 5.** ASTM D887 simulated distillation curve showing correlation of boiling points of n-alkanes with their retention times from Figure 4.



**Figure 6.** Gas chromatogram showing retention time profile of gas oil feedstock before catalytic conversion.

Figure 6 shows the gas chromatographic profile of the gas oil feedstock under ASTM 2887 simulated distillation method. Analysis of the profile is not yet completed in time for this report. However, preliminary assessment shows a very high percentage of the hydrocarbon constituents in the naphtha and heavy oil ranges.

## VIII CONCLUSIONS

Composite catalysts of mesoporous materials were successfully formed into pellets for further evaluation for the mild-hydrocracking of heavy petroleum feedstocks to naphtha and middle distillates. The results from the preliminary reactions on the conversion of heavy gas oil are not yet available due to significant project delay during the past six months. The delay was the result of a serious malfunction of the fume hoods in the Clark Atlanta University's Research Center for Science and Technology, where the project is being conducted. The fume hood system was repaired and catalyst evaluation is now underway.

## IX FUTURE WORK

Future work will be focused on completing the evaluation of catalysts for the conversion of heavy gas oil to naphtha and middle distillates.

## X TECHNOLOGY/INFORMATION TRANSFER

### Students:

The following are students who have worked on the project at various stages since inception:

Tesfamariam Mehreteab	M.S. graduate student (Chemistry)
Yohannes Ghirmazion	M.S. graduate student (Chemistry)
Fengling Ding	M.S. graduate student (Chemistry)
Ifedapo Adeniyi	Sophomore undergraduate (Chemistry & Engineering)
Taurean Hodges	M.S. graduate student (Chemistry)
Selassi Blavo	B.S. (Chemistry and Chemical Engineering)

### Presentations and Publications:

- 1) *Mesoporous Aluminosilicate Catalysts from FAU Precursor under Mild Acidic Conditions and with Al in Totally Tetrahedral Coordination*, Conrad W. Ingram, Yohannes Ghirmazion and Tesfa Mehreteab. Published in *Journal of Porous Materials*, December 2006.
- 2) "On the Incorporation of Tetrahedral Aluminum in SBA-15 from Zeolitic Seeds" Conrad W. Ingram, Yohannes Ghirmazion and Tesfamariam Mehreteab presented at the XXIX Annual British Zeolite Association Conference to be held in Ambleside, UK from 30th July to 4th August.
- 3) *Development of potential gas oil cracking catalysts by incorporating tetrahedral aluminum in SBA-15* submitted for presentation to Division of Petroleum Chemistry for the 232nd ACS National Meeting, San Francisco, CA, September 10-14, 2006 in San Francisco (from 09-10-2006 to 09-14-2006).
- 4) *Improved Catalysts for the Heavy Oil Upgrading Based on Zeolite Y Nanoparticles Encapsulated in Stable Nanoporous Host*, Yohannes Ghirmazion and Conrad Ingram, to presented at the University Coal Research/HBCU/MIs Contractors' Review Conference, June 7-8 2005, Pittsburgh, Pennsylvania.
- 5) *Mesoporous Composites from the Sequential Combination of Hydrothermally Treated Colloidal Zeolitic Silicate Precursors*: Yohannes Ghirmazion and Conrad Ingram: presented

at Division of Colloid and Surface Chemistry for the 230th ACS National Meeting, in Washington, DC, Aug 28-Sept 1, 2005 in Washington (from 08-28-2005 to 09-01-2005).

- 6) *Synthesis of Mesoporous Solids Containing Zeolitic Phase from Hydrothermal Treatment of Colloidal Zeolite Y Precursors* " Yohannes Ghirmazion and Conrad Ingram; presented at Pacifichem 2005, Hawaii, December 2005.
- 7) *Synthesis and Catalytic Properties of Hierarchical Mesoporous Aluminosilicate Assembled from Zeolite Y Precursors*, Conrad W. Ingram, Yohannes Ghirmazion, and Ifedapo Adeniyi, presented at the Singapore International Chemical Conference 4, December 8-10, 2005, Singapore.
- 8) *Enhancing the Catalytic Properties of Ordered Nanoporous Silicate Using Hydrothermally Treatment Zeolitic Precursors*, Conrad W. Ingram, Yohannes Ghirmazion, and Ifedapo Adeniyi; Nanomaterials and Composites: Synthesis, Properties and Applications II57th Southeast / 61st Southwest, Joint Regional Meeting of the American Chemical Society, November 1 - 4, 2005, Memphis, Tennessee.
- 9) *Preparation of Nanosized micro/mesoporous composites via sequential synthesis of zeolite Y/SBA-15 phases*; Yohannes Ghirmazion and Conrad W. Ingram, to be presented at the ACS National Meeting, Washington DC, August, 2005 .
- 10) *On the Synthesis of Zeolite Y Nanocrystals in the Presence of Tetramethylammonium Bromide*, Yohannes Ghirmazion\* and Conrad W. Ingram, presented at the 227 ACS National Meeting, Anaheim, California, March 28 - April 1, 2004 .
- 11) *Non Ionic Surfactant Mediated Templated Synthesis of Phenylene-Bridged Organosilicate*, Yohannes Ghirmazion\*, Conrad Ingram, presented at the 55th Southeast Regional Meeting (SERMACS), Atlanta, GA, November 16-19, 2003.
- 12) *A Comparison of Synthesis Strategies for Aryl Functionalized Ordered Nanoporous Organosilicates using Nonionic and Cationic Surfactants*, Yohannes Ghirmazion\*, Conrad Ingram presented at the 55th Southeast Regional Meeting (SERMACS), Atlanta, GA, November 16-19, 2003.
- 13) *Phenylene-Bridged Mesoporous Organosilicate from Nonionic Surfactant Templated Synthesis*, Conrad Ingram\* and Yohannes Ghirmazion, presented at the 4th International Mesosstructured Material Symposium, May 1-4, 2004, Cape Tow, South Africa.
- 14) *Synthesis of Aromatic Bridged Ordered Mesoporous Organosilicate with Cetyltrimethylammonium Cation as Templating Agent* was presented at the 4th International Mesosstructured Material Symposium, May 1 -4, 2004, Cape Tow, South Africa.

## XI REFERENCES

None in this report.

### APPENDIX 1. Fume Hood malfunction e-mail communication.

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**From:** Williams-Kirksey, Shirley

**Sent:** Monday, February 05, 2007 3:36 PM

**To:** Abrahams, Paul; Bu, James; Ingram, Conrad; McGeady, Paul; Mitchell, Mark; Parker, Cass; Reed, James L.; Thedford, Roosevelt; Ananaba, Godwin; Chaudhary, Jaideep; Cook, Deborah; Finkelstein, Isabella; Harris, Winfred; Jideama, Nathan; Jaideep Chaudhary Lab; Khan, Shafiq; Klueva, Natalya; Logan, David; Musey, Paul; Odero-Marah, Valerie; Seffens, William; Webb, Melvin; Hylton, Donald

**Subject:** Fume Hoods are Working

Dear Colleagues,

On February 5, 2007 I spoke to Mr. Larry Jennings, Director of Facilities, about the status of the fume hoods. ARS has advised Mr. Jennings that all fume hoods are operable and can be used by faculty and students.

NOTE: The process of fine tuning continues, and a hood may be offline for a *short* period of time. However, the major work has been completed.

If you have questions, please contact me at x6770 or [skirksey@cau.edu](mailto:skirksey@cau.edu)

We thank you for your patience and understanding.

Thank you.  
S. Williams-Kirksey, Ph.D.  
Interim Dean