Collaborative Research and Development (CRD) Grants Progress Report

Due Date: **July 1, 2007**
Covers the Period: **July 1, 2006 to July 1, 2007**

Is your personal information below correct? (please enter an "x" in the appropriate box)

__X__ **Yes**
_____ **No** (please make the necessary corrections)

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Is the project information below correct?

__X__ **Yes**
_____ **No** (please make the necessary corrections)

Project title: Catalytic combustion for the elimination of methane, BTEX and other VOC

File Number: CRDPJ 325997 - 05

Co-investigators(s):

S.E. Wanke, Chemical and Materials Engineering, Alberta

Collaborator(s):

Supporting Organization(s):

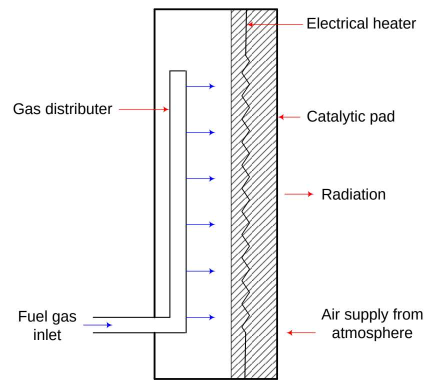
E. Dupuis, Husky Oil Operations Ltd
T. Such, Petroleum Technology Alliance Canada
B. Peachey, New Paradigm Engineering Ltd
P. Howie, Scott-Can Industries Ltd

Note: The project began in March 2005, at which time the money from CAPP (ERAC programme, administered by PTAC) was awarded. The NSERC CRD portion was awarded in October of 2005, and the NSERC start date was October 1. Therefore the industrial and NSERC payments are out of phase. The third and final instalment of the industrial contribution has been received by the University.

1. Progress Towards Objectives/Milestones

1. Introduction and scope

This project is part of an initiative to address methane and VOC vent emissions in upstream oil and gas operations that are currently considered to be uneconomic and technically difficult or impossible to reduce by other means. The overall objective is to develop and prove concepts for reactor technologies to enable economical mitigation of these emissions from various sources, including small isolated and fugitive sources.



This research deals with solutions of concentrated methane that contain higher hydrocarbons, both BTEX (benzene, toluene, ethylbenzene and xylene) and non-BTEX organic compounds. Typical sources include glycol dehydrators and tank vents. For these vent streams, catalytic combustion is a viable mitigation option, where a suitable catalytic reactor is used to destroy the hydrocarbons. For this application we consider the counter flow diffusive radiant heater as a viable choice.

2. The counter diffusive catalytic reactor

In the diffusive radiant heater, the catalyst is supported on a porous fibre "pad". A concentrated fuel stream is fed to the back of the pad, while the combustion air diffuses from the front in counter flow. The intent is to have a very simple converter unit for concentrated vent hydrocarbon streams at an extremely low cost. Although the prime directive is the destruction of hydrocarbons, including BTEX, these reactors could also supply supplemental heat for process streams, building heat, power generation, cooling or other applications, which would significantly enhance the economics of the units.

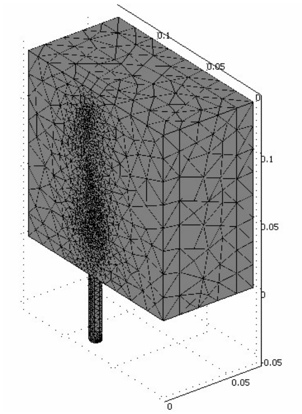
3. Goals set for this reporting period

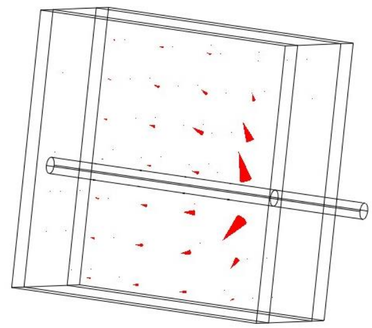
(1) Build a three dimensional computer model for the system and use it for a parameter study.
(2) Study fuel slippage issues with BTEX in the real heater.
(3) Use the micro-reactor to collect data for the kinetic model.
(4) Continue with catalyst characterization.

4. Goals achieved in this reporting period

Goal 1: Three dimensional model

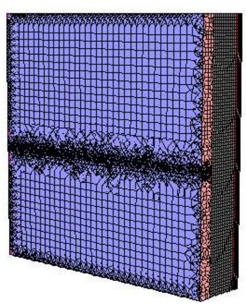
Many design and operational scenarios can be investigated using a computer model. The model is based on the solution of the governing conservation equations. Generalities of the equations and solution methodology will only be given here; details are available on request. Essentially the species balances, energy balance and momentum balance equations are solved with the appropriate boundary conditions. For flow in the porous catalyst pad, we use the volume average Navier-Stokes equation. The finite element software package COMSOL Multiphysics was initially used to solve the equations.
In the first instance we built a two dimensional model of the heater, that was discussed in the last report. Preliminary work on the three dimensional model was also performed using the commercial finite element modelling package COMSOL Multiphysics. We started by building a one quarter size model of the system. The mesh is shown below, left.

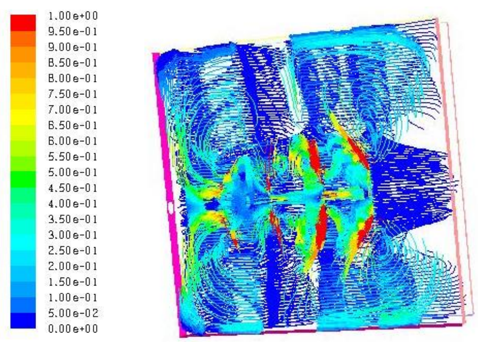




We ran first the velocity only (momentum balance equation). Recall that the feed pipe at the back of the heater contains a regularly spaced series of holes for the feed gas to be distributed. The simulations showed that in fact most of the feed came out of the first set of holes, as shown by the velocity vectors in the figure above right. Overall, the conclusion at this point is that the fuel distributor can be replaced by a simple open ended pipe. This proposal has been tested experimentally and shown not to make a noticeable difference in performance.

During the execution of the problem it became apparent that the COMSOL software package was not the best solution for the modelling software, because it consumes too much execution time. We have switched to Fluent (a finite volume CFD package) and rebuilt the model. Fluent poses its own, and different, set of challenges for implementation, however we are well on the way to resolving them. The full size unit has been coded and modelled for the flow distribution, and the result is shown below. On the right is the mesh, and on the left is the velocity flow pattern. The trend is the same as for the quarter size unit modelled using COMSOL.

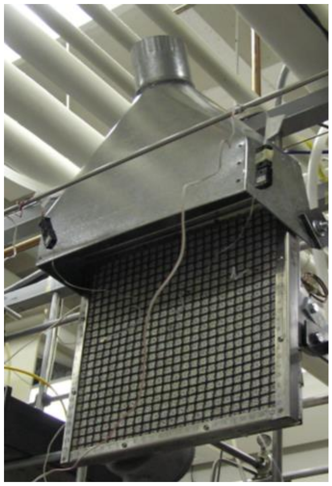


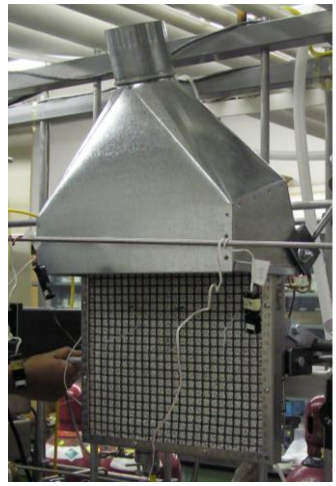


The next step, which is underway, is to implement the full reaction and temperature balance model. We must then validate the model with experiments.

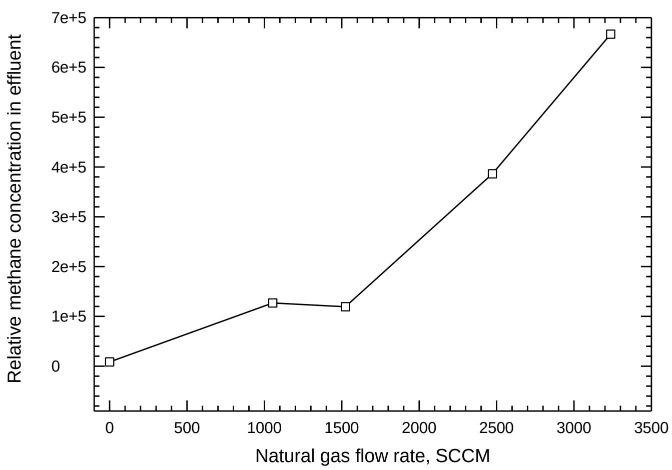
Goal 2: Fuel slippage

In this part of the study, we wanted to quantify the fuel slippage issues and also to examine further the causes of the uneven temperature distribution in the pad observed and discussed in the last report. We have set-up a 1 ft square commercial unit in the laboratory and instrumented it to explore the variation of temperature and concentration. The unit was modified to operate on the domestic natural gas supply, and adjusted so that a variable flowrate could be imposed. This year a collection hood was added to the unit, so that the exhaust gas was funnelled through a single pipe, from which a gas sample could be taken for analysis. Pictures of the unit thus modified are shown below.



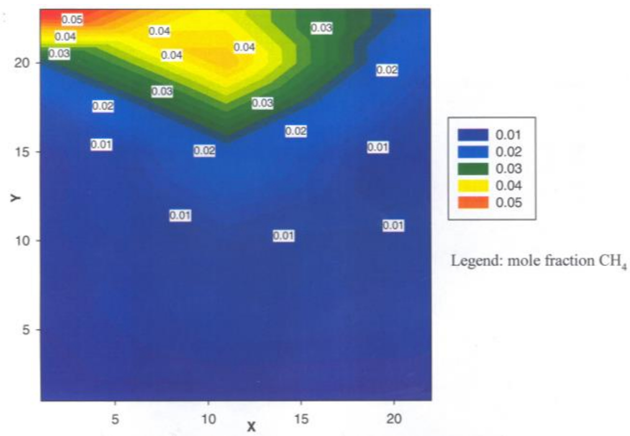


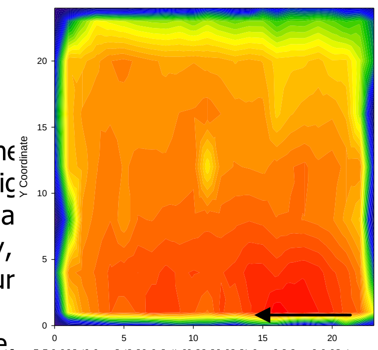
We had previously detected slippage at the front by "sniffing" the effluent. Now we performed a series of experiments where the flowrate of methane was increased slowly and the concentration of methane in the effluent was recorded. The methane will be diluted by the surrounding air that flows up the front of the unit as a result of natural convection. However, a higher concentration will be indicative of more slippage. A graph of slippage plotted against methane inlet flowrate is given below.



The above graph shows the trend in the slippage. Following modification of the analysis system to allow measurement of both methane and carbon dioxide, a more quantitative estimate of the fuel slippage and fraction conversion was made. The most useful measure of the slippage is the fractional methane conversion. Knowing this value allows the total flux of methane to be calculated. We have computed that the fractional conversion of methane is 77 %, 60 % and 55 % at methane flowrates of 1, 2.5 and 3 litres per minute respectively. These conversions are fairly low. However, we have seen that when toluene is injected at a mole percent of around 4, we cannot detect any toluene in the effluent. The maximum temperature in the pad moves closer to the pad surface, and the methane conversion is reduced. However, these results indicate that BTEX conversion will be essentially complete under standard operating conditions. We suspect that the limiting step is the diffusion of oxygen from the surrounding air, which is in turn controlled by the boundary layer development.

The following picture shows the concentration of methane in the gas located about 1 cm in front of the heater. It is clear that the methane concentration is higher near the top of the heater, which is consistent with the temperature being lower there. Also, there will be an accumulation effect near the heater top.





Previously, we reported on the non-uniform temperature distribution in the figure on the right. This fig report. It was observed tha near the system boundary, the atmosphere occur the pad had a hot spot corner on the above figure, location of the feed pipe. The arrow shows the location of the feed pipe. We had speculated that this hot spot was the result of feed mal-distribution. To investigate this idea, we changed slightly the location of the feed distributor in the back, and then measured the temperature profile at different heater orientations. The heater was successively rotated so that the feed was from each side, the top and the bottom, as denoted by the arrows in the figures below. In each case, the heater was observed to be hotter at the bottom of the pad. This observation rules out feed distribution as the cause. It is speculated now that the effect may be caused by the natural convection boundary layer at the front of the pad, through which the oxygen must diffuse.

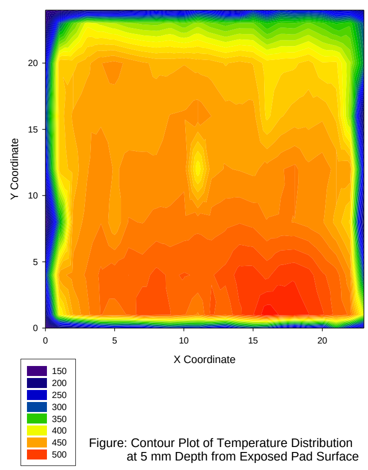
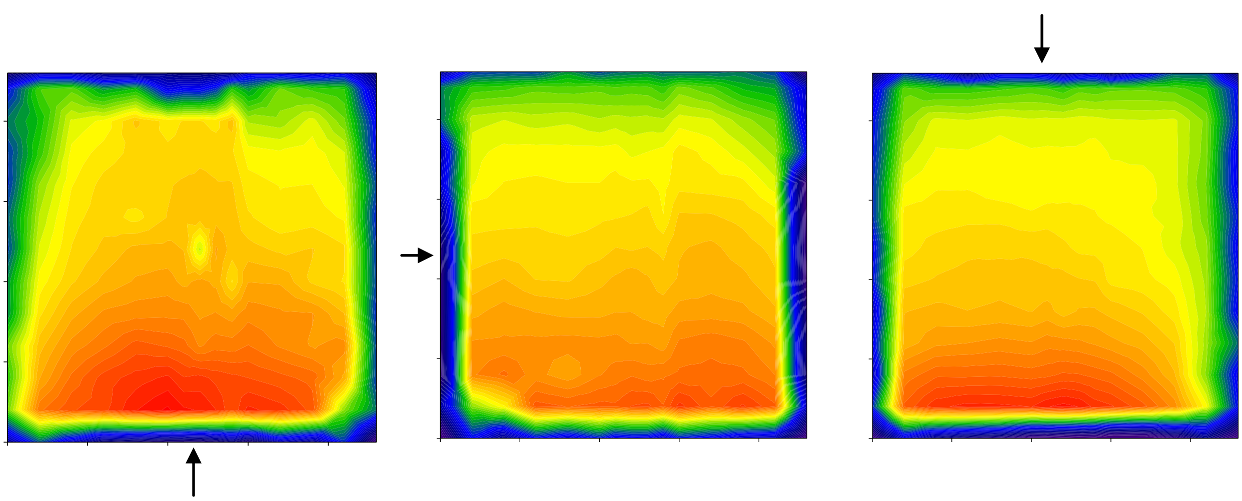


Figure: Contour Plot of Temperature Distribution at 5 mm Depth from Exposed Pad Surface

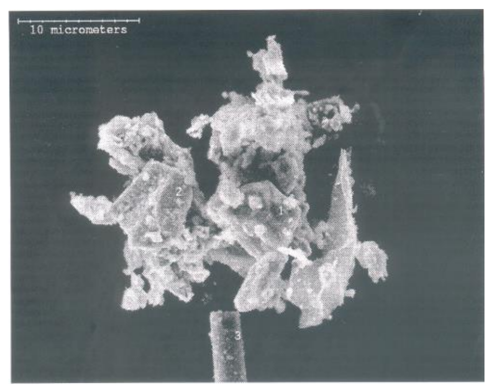


Goal 3: Collection of data in the micro reactor

In the last report we discussed the construction of a micro reactor in which we planned to take measurements to be used for kinetic modelling. This work will commence shortly. We have used a different reactor system to test some commercial palladium catalysts for activity in methane combustion and to investigate the effects of such things as water in the feed. The data are in the process of being analysed, and will be used to plan the new experiments.

Goal 4: Catalyst characterisation

In the first year we started some catalyst characterization work, although these results were not included in the first report. This work continued through this year. We have examined several commercial pads from different suppliers using a variety of techniques, including BET surface area analysis, SEM (Scanning Electron Microscopy), XRD (X-ray diffraction) and neutron activation analysis. In the current year we plan to use hydrogen adsorption to characterize the metal dispersion. We have observed that there is a fairly large variation of properties among the different pads. For example, the fibre support can be either crystalline or amorphous. In some cases, the catalyst is placed on the fibre network as small particles, whereas in other cases the catalyst is impregnated directly into the fibres. The effective catalytic surface area also has considerable variation, as does the precious metal loading. These properties will be related to the relative activities during this year. The following pictures show two representative electron micrographs of a sample catalyst. The picture on the left shows the fibre network and the figure on the left shows a catalyst particle.



5. Goals to be achieved in the next year

Funding was approved by ERAC for year three of the project. The goals for this year are basically extensions of the goals for year 2. Also, it should be noted that although this is the final year of the project from an ERAC funding perspective, the work will continue until it is complete. The NSERC portion of the funding expires in September 2008.

(1) Use the three dimensional computer model for more parameter studies.
(2) Continue with the fuel slippage study with BTEX in the real heater.
(3) Use the micro-reactor to collect data for the kinetic model.
(4) Catalyst development and characterisation.

2. Research Team

Please provide an overview of the participation in, and scientific contributions to, the project for each member of the research team (principal investigator, co-investigators, collaborators, company and government scientists, research associates, postdocs, students, etc.).

The following list describes the research team that has worked on the project since it started.

Principal and co-investigators:
R.E. Hayes and S. E. Wanke

The two co-investigators oversee the project and jointly supervise the personnel. REH has expertise in modelling and catalytic combustion, whilst SEW has expertise in catalysis.

Research Associates:
Joseph Mmbaga and Benlin Liu

Both Dr. Liu and Dr. Mmbaga have contributed mainly to the computational aspects of the project, including code development and tuning. Dr. Liu left in October 2005 to pursue a career in industry. At that time, Dr. Mmbaga joined the project. His primary role is to assist in the modelling endeavors.

Postdoctoral Fellows
Hassan Hammawa (2005) and Tariq Mannan (2006 on).

Both of these PDF worked on experimental aspects of the project. Initially HH was the primary PDF. After his departure TM assumed responsibility for this aspect. He primarily works on the experimental aspects of the project.

Graduate Students
Attreeye Basu, Naeimeh Jodeiri, Rajab Litto, PhD students, Hemant More, MSc student,

Attreyee Basu worked on modelling and experimental aspects until August 2005, when she departed. Naeimeh joined the project in January 2006. She has taken three courses and started work on 3D modelling. Her work was briefly interrupted by a period of maternity leave in 2006. Once the 3D model is running to satisfactory levels, she will commence work on data collection with the micro reactor apparatus. In addition to these two students whose primary project relates to the heaters, two other students were involved. Rajab Litto (PhD student) did a study of kinetics on palladium based catalysts to develop activity data for comparison purposes. Hemant More (MSc student, completed) did a study on three dimensional modelling with COMSOL as part of project to compare the 3D solvers in COMSOL. In September, Guangyu Huang, from Zhejiang University, China is scheduled to join the group as an MSc candidate. He will work on catalyst development. As an undergraduate, Guangyu has experience in the development of oxidation catalysts.

Undergraduate Student

Pierre Lauthier worked for four months on the project investigating the use and limitations of using the Volume Averaged Navier Stokes equation (VANS) for combined porous media and regular flows, with emphasis on the interface boundary conditions.

3. Training

Please list **each** trainee (Undergraduate Students, Master's Students, Doctoral Students, Postdoctoral Fellows, Research Associates, Technicians …) on a separate line in the table below providing: a) the number of years they have been on the project, b) the percentage (%) of time each type of trainee spent on this project, and c) the percentage (%) of funding from this CRD grant. If a trainee is fully paid from other sources, enter "0" in the "% of funding from this grant" column. Insert additional rows if necessary. (DO NOT INCLUDE FAMILY NAMES.)

Specify type of trainee (e.g. M.Sc., Ph.D. etc) **(one trainee per line)**	**(a)** **Number of calendar years on the project**	**(b)** **% of research time spent on this project**	**(c)** **% of funding from this grant**
Undergraduate student	0.33	100 %	100 %
Masters student	0.33	25 %	25 %
Doctoral student	1.5	100 %	75 %
Doctoral student	0.5	100 %	50 %
Doctoral student		25 %	25 %
Postdoctoral fellow	1.5	100 %	100 %
Postdoctoral fellow	1	100 %	100 %
Research Associate	1.8	80 %	80 %
Research Associate	0.5	50 %	20 %

4. Dissemination of Research Results and Knowledge and/or Technology Transfer

4.1 Please provide the number of publications, conference presentations, and workshops to date arising from the research project supported by the grant in the table below.

Publications, Conference Presentations, etc.

______ None to date

- OR -

	Number of publications, presentations…		
Status	**Refereed Journal Articles**	**Conference Presentations/ Poster**	**Other (including Technical Reports, Non-Refereed Articles, etc.)**
Accepted/Published		5	2
Submitted		1	

4.2 Please provide the bibliographical reference data for the above publications, conference presentations and workshops under the corresponding headings. For publications, specify whether submitted, accepted or published.

Refereed Journal Articles:

Conference Presentations/Poster:

R.E. Hayes, N. Jodeiri, T. Mannan, J. Mmbaga and S.E. Wanke, Designing Catalytic Radiant Heaters for Fugitive Methane and BTEX Combustion, *1st International Congress on Green Process Engineering*, Toulouse, France, April 24 (poster with refereed proceedings)
J. Mmbaga, T.M. Mannan, N. Jodeiri, S.E. Wanke and R.E. Hayes, Modelling of catalytic radiant heaters*, COMSOL Users Conference 2006*, Las Vegas October 2006. (poster with extended abstract)
R.E. Hayes and S.E. Wanke, Catalytic combustion for the elimination of methane, BTEX and other VOC, *Air Issues Forum and Poster Session for the Upstream Oil and Gas Industry*, Calgary November 23, 2006. (oral)
H. Hammawa, T. Mannan, J. Mmbaga, B. Liu, S.E. Wanke and R.E. Hayes, Using counter-diffusive catalytic radiant heaters for fugitive methane and BTEX combustion, *19th Canadian Symposium on Catalysis,* Saskatoon, May 2006. (poster)
R.E. Hayes and S.E. Wanke, Catalytic combustion for the elimination of methane, BTEX and other VOC, *Air Issues Forum and Poster Session for the Upstream Oil and Gas Industry*, Calgary September 28, 2005. (oral)

Other (Including Technical Reports, Non-Refereed Articles, etc.):

Two End of year reports prepared for CAPP/PTAC/ERAC and distributed to partners. Further, a number of progress reports have been made to the partners and the ERAC committee. These primarily consist of emailed updates and teleconferences.

4.3 **Patents and Licences**

Please provide in the table below the **number** of patents (filed and issued) and licences to date arising from the research project supported by the grant in the table below. (Provide details in 4.4.)

__X__ Not applicable

- OR -

_____ None Yet Filed/Issued

	Number of Patents				
Description	**CANADA**	**U.S.**	**EP**	**OTHER**	**TOTALS**
# of Patent Applications Filed					
# of Patents Issued					

# of Licences [ ] **(Provide details in 4.4.)**

4.4 Please provide details (titles, patent application number, patent number…) about the above listed patent applications, patents, and licences under the corresponding headings.

Patent Applications Filed:

Patents Issued:

Licences: (licencees, exclusive/non-exclusive…)

4.5 Describe how the results achieved to date are being transferred to the user sector and the prospects for their commercial/industrial exploitation.

Prospects for the Transfer of the Results to the User Sector

The results are currently being transferred to the user sector via reports and presentations. Based on the results to date, we expect that there will be the potential for a field trial.

5. Problems Encountered

Identify the main problems encountered during this instalment of the grant from the list below (select all that apply):

_X___ Technical or scientific problems
______ Problems with direction of research or findings
______ Equipment and facilities
_X___ Staffing issues (including students)
______ Funding problems
______ Partner withdrew from project
______ Partner interaction issues
______ Other (specify) ____

- OR -

______ No problems occurred during this instalment of the grant

Briefly describe the main problems identified above and the steps taken to resolve each one.

Some problems with gas analysis that proplonged obtaining reproducable results for the slippage studies. There was also some delay because one PhD student took a maternity leave. An MSc student who was supposed to join the project in January was unable to obtain a study permit. A new student has been identified who is expected to join in September for an MSc.

6. Collaboration with Supporting Organizations

6.1 Who initiated this CRD project?

__X__ The university researcher
_____ The industry partner
_____ Shared initiation (university/industry)
_____ Other (specify) ____________________

6.2 In what way were the partners directly involved in the project (select all that apply)?

_____ Partners were not involved in the project apart from their financial
__X__ Partners were available for consultation
__X__ Partners provided facilities
_____ Partners participated in the training
_____ Partners received training from university personnel
__X__ Partners discussed the project regularly with the university team
Number of meetings during the period covered by this report: __4__
_____ Partners were involved in the research

6.3 Describe the partner's involvement and comment on the collaboration.

All of the supporters have been involved in the collaboration. The primary role of PTAC is to administer the funding. They organised the *Air Issues Forum and Poster Session for the Upstream Oil and Gas Industry* where preliminary results were presented. Scott-Can has provided technical support and materials. New Paradigm has provided industry perspectives and provided field test data. Husky Energy has provided technical information and advice. As noted, meetings to exchange information have been held with all parties.

6.4 Was the total amount of cash committed by the partner during the period covered by this report received?

__X__ Yes
_____ No

6.5 Was any in-kind received from the partner during the period covered by this report?

__X__ Yes
_____ No

6.6 For cash and in-kind received, please enter the amounts below, along with the amount of cash and in-kind committed in the original proposal. If no in-kind was received, please enter "0". Where in-kind was not committed enter "n/a".

	Amount Committed	**Total Amount Received to Date**
Cash	70 725	70 725
In-Kind		1 000

6.7 Describe the in-kind received and explain variations between commitment and actual cash and in-kind contribution if applicable.

Scott-Can provided some new heater pads and some instrumentation. They also provided information.

7. Financial Information

Budget Item	Budget for this instalment (as outlined in original proposal)	Actual expenditures for currect instalment, up to Report due date	Projected expenditures from Report due date do end of this instalment	Planned expenditures for the next instalment
Salaries and Benefits				
Students	35 000	20 856	12 000	35 000
Postdoctoral fellows	33 000	24 219	9145	33 000
Technical/professional assistants	33 000	34 172	9815	35 000
Other (specify)				
Equipment and Facilities				
Purchase or rental	9000	1589		
Operation and maintenance costs				
User fees				
Materials and Supplies				
Materials and supplies	8000	2010	600	3610
Travel				
Conferences	2500	8115		1000
Project related travel	2500	1000		1000
Collaboration/consultation				
Dissemination Costs				
Publication costs				
Other (specify)				
Other (specify)				
Totals	123 000	91 961	30 960	108610

Please provide detailed explanations for any deviation in the current period and in the budget for the coming year. (Note that deviations from the budget of greater than 20 per cent require pre-approval from NSERC.)

Note 1: Because the payments are out of phase, this report covers the reporting period, but parts of two instalments of the industrial contributrion.

There were no significant deviations in the budget. In the total HQP budget, the expences for the RA were a bit higher than budgeted, although this will fall in the final year. The travel budget was also higher than expected owing to increased costs in the travel sector. On the othre hand, we spent a bit less than expected on equipment and supplies by using existing equipment that became available.

Note 2: The planned expenditures for the final year of the project reflect the out of phase funding cycle and the expected actual balance that will be available to the project as of Oct. 1, 2007. This amount is tentatively calculated to be $108 610. All of this amount is budgeted to be expended by Sep. 30, 2008 in accordance with the agreement.

Note 3: The third and final industrial installment has been paid already.