COLLABORATIVE RESEARCH AND DEVELOPMENT (CRD) GRANTS

Progress Report Due Date: July 1, 2006
Covers the Period: October 1, 2005 to July 1, 2006

Please verify your personal and project information below and make the necessary corrections.

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

File No: CRDPJ 325997 - 05

Co-applicant(s):
S.E. Wanke, Chemical and Materials Engineering, Alberta

Supporting Organization(s):
B. McKeage, Husky Oil Operations Ltd (now Elisabeth Dupuis, note change)
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. Thus, this the work done that this report covers work was completed from March 1, 2005 to June 30, 2006.

1. PROGRESS TOWARDS OBJECTIVES/MILESTONES

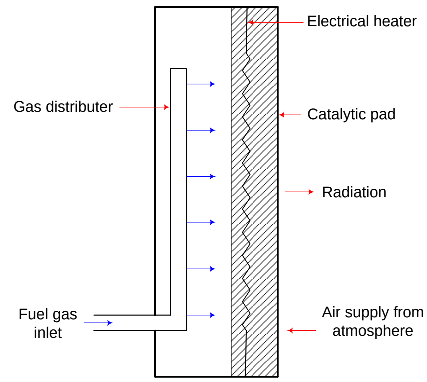
1. Introduction and scope

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 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 "pad" made from a suitable fibre. 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.



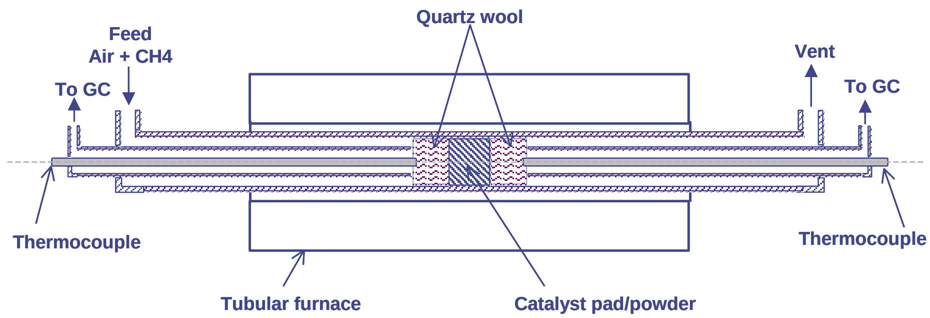
3. Goals set for this reporting period

(1) Research, design and construction of a micro-reactor apparatus suitable for testing catalyst activity and comparing relative reactivity of different hydrocarbons.
(2) To install a small commercial reactor in the laboratory with full instrumentation to study effects such as temperature and flow mal-distribution, and to study fuel slippage.
(3) Development of a computer model for the system. The models for both the commercial unit and the micro-reactor are required.
(4) Evaluation of current catalyst performance, including determination of the reaction kinetics.

4. Goals achieved in this reporting period

Micro-reactor (goals 1 and 4)

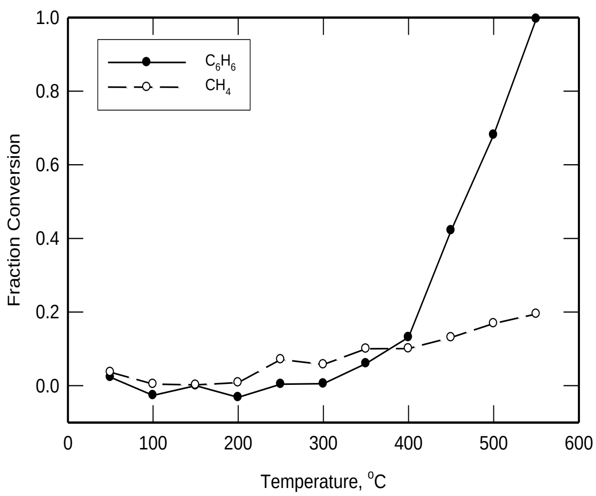
The objective of this phase of the experimental part was to research, design, construct, and test a micro-reactor apparatus that would be used to obtain accurate experimental data needed for kinetic studies and catalyst evaluation. The constructed micro-reactor consists of a 316 SS tube (⅜″ dia. × 20″ long) concentrically connected at both ends with ¼″ diameter tubes. The later are connected concentrically to ⅛″ diameter thermocouples. The ¼″ tubes and the thermocouples on both ends of the ⅜″ tube extend by ~9¼″ into it (see figure below). The annular spaces between the ⅜″ and the ¼″ tubes, and between the ¼″ tubes and the thermocouples are used for fuel/air, and GC sample flow respectively.

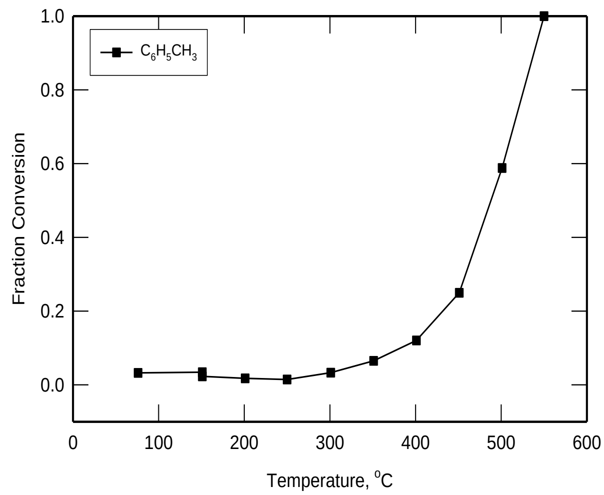


The reactor can be operated in ordinary mode with pre-mixed feed (as shown in the diagram) or it can be operated in counter diffusive mode, where the air and methane are admitted from opposite ends of the reactor. The reactor is heated by a tubular furnace (1¼″ dia. × 12″ heated length). Four pieces of ceramic half-cylinders suspend the reactor concentric to the furnace. The reactor is connected to gas supply and liquids evaporation system. The reactor design allows for co-feeding premixed fuel/air stream or the two streams can separately be fed from opposite ends of the reactor similar to radiant heaters. The reactor system was tested successfully for a combined on stream time of 50 h. All experimental data are logged on a PC, and the reactor is controlled using a Labview module.

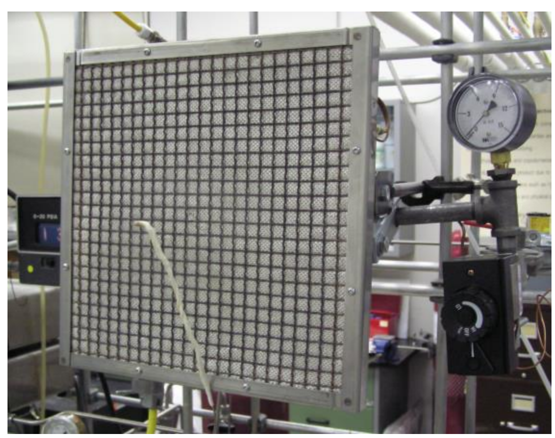
One of the first tasks to perform once the reactor was debugged and calibrated was to examine the relative reactivity of several commercial catalysts and to compare the rates of destruction of methane and BTEX. In these sets of experiments we are only interested in comparative activity, because we know that in the commercial heater we can achieve excellent conversion of methane.

A number of commercial catalysts, including both platinum and palladium were tested. Methane, air and BTEX were injected into the reactor. The conversion of each was monitored. In all cases the trends in conversion were the same. We show two typical results here; the conversion over a commercial Pt catalyst for a given set of reaction conditions. The first graph compares the activity of methane and benzene, and the second graph shows the activity of toluene. We conclude from these results that benzene and toluene are more reactive than methane, which demonstrates that catalytic combustion using the radiant heater type reactor is promising.





Installation of commercial reactor (goal 2)



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 gas supply, and adjusted so that a variable flowrate could be imposed.

Operational concerns include uniformity of temperature, flow mal-distribution and fuel slippage. Fuel slippage occurs when not all of the fuel reacts, and thus passes unburned through the system. Although this may not be a major issue with methane, it will be for the BTEX compounds. By sampling from the front of the system we are able qualitatively to monitor the fuel slippage issue. Not surprisingly, we have found that at low flow rates there is no detectable slippage, but at a critical flow rate slippage is detected. At the moment we do not have a method to quantify precisely the amount of slippage, and we are still thinking about the best design for a system to do this. We have also modified the system to inject precise amount of BTEX into the system using high precision metering pump.

The temperature distribution in the catalyst pad was measured at two depths of pad. The distribution at 5 mm depth is shown in the figure on the left.

It is observed that the temperature is lowest near the system boundary, where convection losses to the atmosphere occur. It was also observed that the pad had a hot spot near the lower right hand corner on the above figure, which corresponds to the location of the feed pipe. If we overlay the temperature distribution on a picture of the heater with the pad removed, (not shown) it is be seen that the hot spot corresponds to the section below the feed pipe. Because the feed pipe diameter is close to the clearance space behind the pad, it is suggested that this blocks the methane flow, causing feed mal-distribution. We are currently considering methods to improve fuel distribution at the heater back. For larger heaters, the arrangement of the feed pipes changes, so the flow mal-distribution should be different in those heaters.

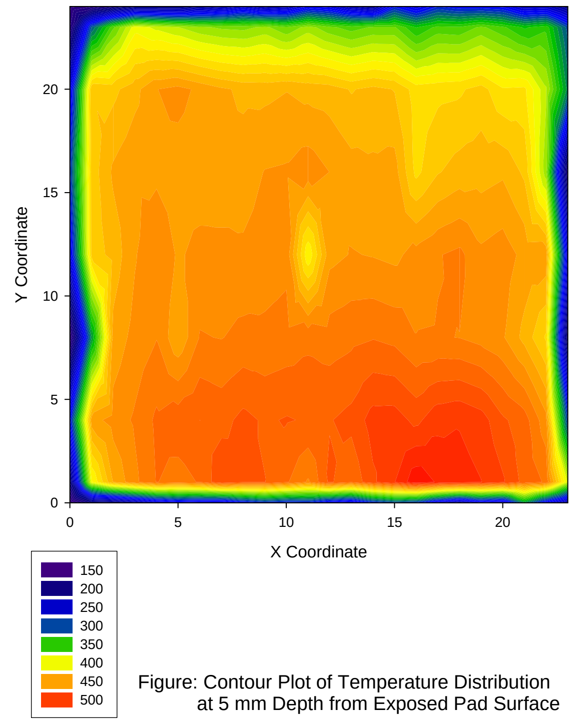


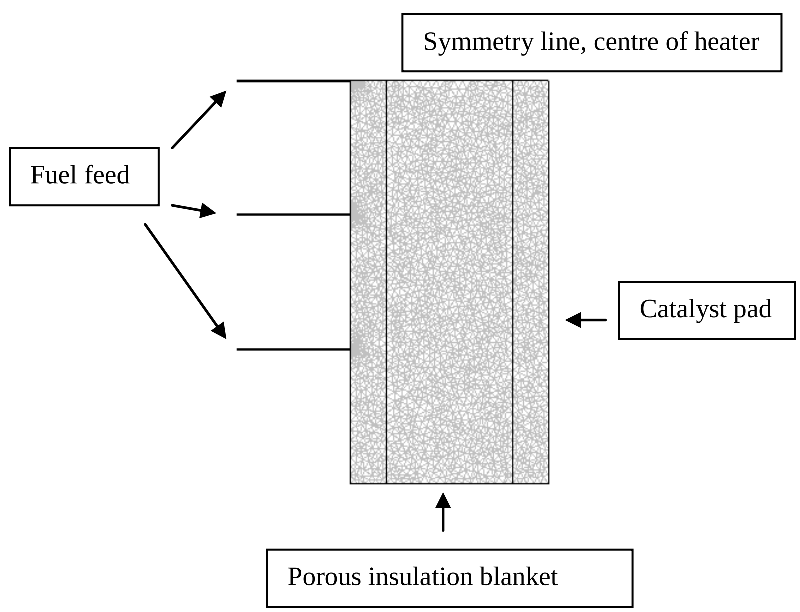
Figure: Contour Plot of Temperature Distribution at 5 mm Depth from Exposed Pad Surface

We should shortly be able to measure fuel slippage and reactivity issues with BTEX in the actual heater, and suggest methods for improved feeding.

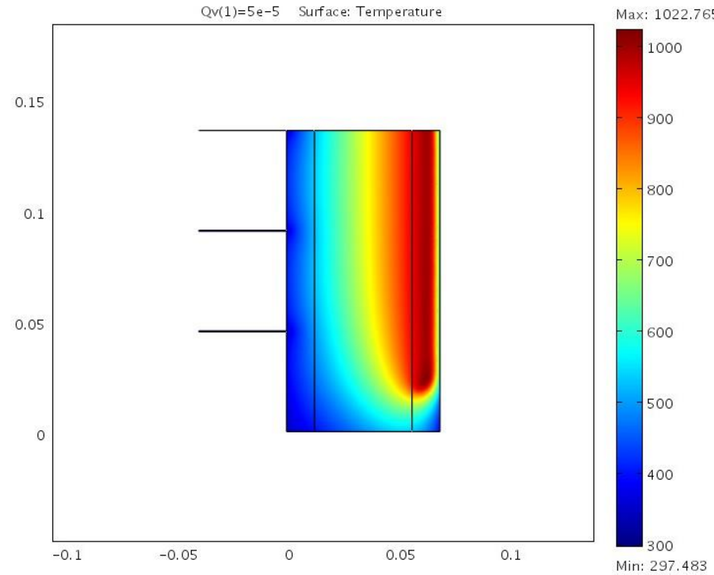
Computer model for the system (goal 3)

Many design and operational scenarios can be investigated using a properly validated computer model. The model is based on the solution of the governing conservation equations. These equations are solved using the finite element method. 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 is used to solve the equations.

In the first instance we have built a two dimensional model of the heater. The model domain represents a cross sectional slice taken through the centre of the system. Further, we have assumed symmetry about the mid-plane, thus we consider only a half height of the system. Fuel is fed at the back through long narrow slots. This method is required to impose correctly the boundary conditions on the 2D system. A picture of the model domain is shown on the right, with the finite element mesh.

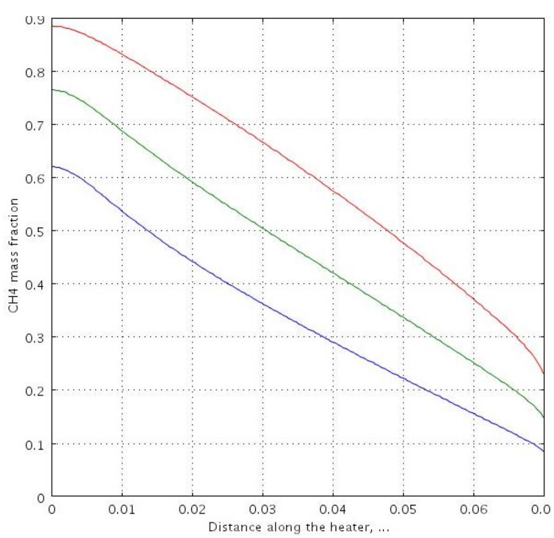


We are currently using the model as an aid in understanding the performance of the heater. The work has yet to be validated against the actual apparatus, however, the trends are the same. We show in the following some typical modelling results. The next step will be to continue with a parameter study and then to build a real three dimensional model.

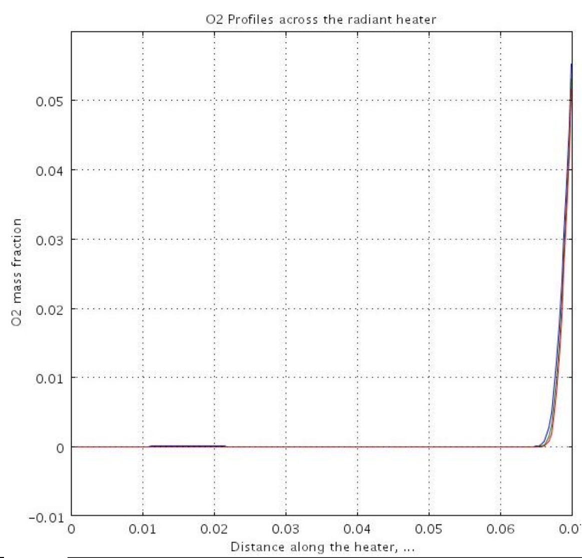


The figure on the right shows a typical temperature distribution in the unit. The maximum temperature occurs near the interface of the catalyst pad and the insulating blanket.

The concentration profiles are the most difficult to determine analytically. The figures following show the mass fraction of methane and oxygen as a function of distance from the back of the heater to the front. The profiles are shown along the centreline. Three curves are presented. These represent the profiles at different volumetric flow rates of fuel. It is clearly noticeable how quickly the oxygen is depleted. The limiting parameter in the operation of these units is the rate of oxygen diffusion from the air into the pad. As the fuel flowrate increases, the oxygen is depleted more rapidly, and the concentration of methane at the exterior surface of the pad rise. Any value of methane concentration above zero implies slippage.



Mass fraction of methane along the centreline from the back to the front at three flowrates.



Mass fraction of oxygen along the centreline from the back to the front at three flowrates.

5. Goals to be achieved in the next year

(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.

2. RESEARCH TEAM

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

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 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.

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.

Graduate Students
Attreeye Basu and Naeimeh Jodeiri, PhD students

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.

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.

3. Training

Please provide the number of each type of trainee working on the project and also provide the percentage (%) of time spent by each type of trainee on this project (e.g., *If there were four doctoral (PhD) students working on the project and two of them spent half their time working on another project then 75 per cent of the four doctoral students' time was spent on this project.)*

Type of trainee	Number	% time spent on project
Undergraduate students	1	100 %
Master's students		
Doctoral students	2	100 %
Postdoctoral Fellows	2	100 %
Research Associates	2	100 %
Technicians		
Other (specify)		

4. Dissemination of Research Results and Knowledge or Technology Transfer

4.1 Publications/ Conference Presentations etc.:

Please list all publications (specify if submitted or accepted/published) arising from the research supported by the grant, conference presentations, other reports and/or workshops in the table below. Please provide full reference for each.

☐ None to date

– OR –

Full Citation (Title/reference)
Refereed Journal Articles (Published/accepted)
Conference Presentation/Poster (specify)
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: technical reports, non-refereed articles etc. (specify)
End of year one report prepared for CAPP/PTAC/ERAC and distributed to partners.

4.2 Patents and Licenses
Please list all of the patents, licenses or options issued or executed in Canada, the United States, or elsewhere as a direct result of the research project.

☐ Not Appropriate -OR- ☒ None yet Filed/Granted

-OR-

DESCRIPTION	CANADA	U.S.	OTHER	OWNER OWNED
PATENT APPLICATIONS FILED:				
PATENTS ISSUED:				
LICENSES OR OPTIONS:				**NA**
				NA
TOTALS:				**NA**

4.3 Have any results to date been transferred to the partner? ☒**Yes** ☐ **No**

NO. OF REPORTS PREPARED FOR THE PARTNER: 1 .

IF YES, DESCRIBE:

An end of first year report was prepared for the partners. Various meetings have also been held.

5. MAIN PROBLEMS ENCOUNTERED

5.1 Identify the main problems encountered during this instalment of the grant from the list below (select all that apply):
☒ No problems occurred during this instalment of the grant
OR
☐ Technical or scientific problems
☐ Problems with direction of research or findings
☐ Communication issues
☐ Insufficient Equipment and/or facilities
☐ Staffing issues (including students)
☐ Funding problems
☐ Partner issues
☐ Other (specify):

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

There were no serious problems. The first student, Attreyee Basu left the University of Alberta in August 2005 to persue studies at the University of Saskatchewan. A new PhD student was recruited. Dr. Hassan Hammawa left the group to accept a position at the University of Calgary. He was replaced by Dr. Mannan. Dr. Liu left in October 2005 for a job in industry and was replaced by Dr. Mmbaga.

6. Collaboration with The Partners

6.1 Who initiated this CRD project?

☒ University researcher
☐ Industry partner
☐ *Shared initiation (university/industry)*
☐ Other (specify): _______________.

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

☐ Partners were not involved in project apart from their financial contribution.
OR
☒ Partners were available for consultation.
☒ Partners provided facilities.
☐ Partners provided on-site training of students.
☐ Partners received training from university personnel.
☒ Partners discussed the project regularly with the university team.
(No. of meetings held per year __4__).
☐ Partners carried out research activities integral to the project were involved in research activities of project.

6.3 Describe their 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 Cash received from the company during the period covered by this report:

☒ **Yes** ☐ **No**

Amount? $ 141 450 (two payments of $70 725, recall that the NSERC and CAPP payments are out of synch)

6.5 In-kind received from the company during the period covered by this report:

☒ **Yes** ☐ **No**

Estimated value? $ 8000/yr .
Describe the in-kind received:

Scott-Can provided two commercial heaters plus a variety of catalytic pads for analysis. New Paradigm provided some field test data on methane combustion tests. Husky provided technical information. Scott-Can, New Paradigm and Husky have also given in-kind salary support.

7. Financial Information

7.1 An up-to date Grants in Aid of Research, Statement of Account (Form 300) must be provided for both the NSERC contribution and the company contribution to this CRD. Please forward the Forms 300 with your report, or ask your finance department to forward them directly to the attention of the Account or Portfolio Manager named in the attached letter.

7.2 Using the form provided below, and combining the NSERC and industry contributions, please report your budget for this instalment, your actual expenditures to date, as well as your projected expenditures for the remainder of this instalment and the planned expenditures for next year.

Budget Item	Budget for this instalment (as outlined in original proposal)	Actual expenditures for current instalment, up to Report due date	Projected expenditures from Report due date to end of this instalment	Planned expenditures for period of next instalment
Salaries and Benefits				
a) Students	35000	21458	10000	35000
b) Post-doctoral Fellows	33000	16053	7691	33000
c) Technical/ Professional Assistants	33000	26007	12978	40000
d) Other (specify)				
Equipment or Facility				
a) Purchase or rental	9000	1052	8000	9000
b) Operation and maintenance costs				
c) User fees				
Materials and Supplies				
a) Materials and Supplies	8000	4488	2000	8000
Travel				
a) Conferences	2500	1257		2500
b) Field work				
c) Collaboration/ consultation	2500	650	1000	2500
Dissemination Costs				
a) Publication costs				
b) Other (specify)				
Other (specify)				
a)				
b)				
Totals:	123000	70965	41669	130000

7.3 Budget Justification
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, per line item, require pre-approval from NSERC).

Note that because the NSERC and CAPP payments are out of phase, the above expenditure is for the first full year of CAPP (March 1, 2005 to Feb 28, 2006) and the NSERC grant for the first nine months. Overall, there is a small surplus over a full budget year; this is expected to disappear in the second year owing to higher RA salary. Overall, over 80 % of the budget will be for the support of HQP.