Appendix 7.1

Final Report of Networks – Catalysis

UK-Brazil Collaborative Research Networks Programme

CATALYSIS NETWORK

Contract CON/800/29/2255010/LIV

Final Report

Period to February 2003

1. BACKGROUND AND THEMES OF THE COLLABORATION

Within the frame of the UK-Brazil Collaborative Research Networks Programme, a UK Catalysis network has been established, comprising expertise in chemistry and chemical engineering. Its objectives are to create, operate, and maintain an international collaboration with the corresponding Brazilian catalysis network. This international collaborative network provides opportunities for the development of research projects exploring themes of interest to both countries, with potential industrial applications, and firms up collaborations between four UK (Liverpool, Bradford, Cardiff, Bath) laboratories.

The two themes for the UK-Brazil collaboration are:

- The upgrading of light alkanes (natural gas: C_1-C_4 alkanes) to olefins, oxygenates, chlorine- and bromine-containing compounds, and fuel blending components.
- The hydrocracking of heavy oil fractions to produce fuel range hydrocarbons.

Both themes aim at maximising the utilisation and at adding value to the lower and higher ends of the world's hydrocarbon resources, i.e., light alkanes and heavy oil fractions. The optimal use of these natural resources also has several environmental advantages, i.e., the production of cleaner fuels with higher performance, the minimisation of refinery heavy hydrocarbon by-products, and the use of chlorine and bromine to produce valuable chemicals.

Both themes comprise basic and applied research, and are targeted to objectives recognised as being of paramount importance by national and international panels.

Six actions were planned originally (see Report #1). Three of them are progressing, a fourth one is still being considered, and the last two are put on hold pending adequate financial support as well as further discussions with the Brazilian groups to focus their objectives.

2. THE UK-HEFCE CATALYSIS NETWORK

The UK laboratories (institutions) involved in this project were selected according to their ability to develop research projects matching the interests of the Brazilian research teams as well as their common research interests and desire to collaborate at the UK level.

Coordinators

Professor Eric Derouane has been the network coordinator until the end of December 2002. Professor Derouane moved to a new position at the University of Algarve in Portugal from the beginning of January 2003 and Dr Stuart Taylor is acting coordinator of the final stages of the network activities and funding.

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Note: Dr J. Quartararo replaces Dr. S B Abd Hamid who has returned to Malaysia. Dr N Winterton has now also joined the network. Professor J.C. Vedrine and Dr J. Quartararo left the University of Liverpool at the end of December 2002 to take up positions in France.

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The UK network comprises two Departments of Chemistry (University of Liverpool and University of Wales at Cardiff) and two Departments of Chemical Engineering (University of Bath and University of Bradford). The members of the network have complementary expertise. The synergy between the UK teams to undertake collaborative research projects with their Brazilian colleagues are shown in Table 1.

Table 1. Synergy between the UK teams for the selected research projects

Project	Chemistry		Chemical Engineering	
	Liverpool	Cardiff	Bath	Bradford
Methane upgrading	v	v	v	
Methane oxyhalogenation	v	v	v	
C_2-C_4 alkane oxidations	v	v	v	
Hydrocracking	v	v		v

The general and complementary areas of expertise of the UK teams are:

- Liverpool: Development and characterisation of catalysts, mechanistic and kinetic studies.
- Cardiff: Development and characterisation of catalysts, mechanistic studies.
- Bath: Novel catalytic reactors development, catalytic reaction modelling, process evaluation.
- Bradford: Novel reactors development, reaction/reactor modelling.

3. COLLABORATION WITH THE BRAZILIAN NETWORK

3.1. General principles and methods

Funding provided by HEFCE is entirely devoted to foster and strengthen the networking between the UK teams and to ensure that the interactions between the Brazil and UK network are constructive and benefit to all members. Collaborations between the UK teams on the basis of research projects financed by EPSRC are encouraged.

Collaboration of the UK and Brazil networks is fostered and maintained through a variety of actions and methods:

- Regular communications between the UK and Brazil teams involved in the selected research projects, including pro-active exchange of information, and meetings (general or specific) of members of the UK network.

- Reciprocal visits: four members of the UK network visited their counterparts in Brazil in late 2000. No joint meeting was organised in 2001 as funding had to be secured on the Brazilian side. The coordinator of the Brazilian network, accompanied by Dr Fabio Passos visited the UK in February 2002. A programme of visits was planned and accomplished so that the members of the Brazilian network visited all the UK participants. Detailed discussions were carried out at these meetings to develop strategies for future cooperation. The visit of the Brazilian network representatives culminated in their attendance at the annual review workshop at HEFCE on 19 February 2002. Time and budget permitting a further visit of UK participants to Brazil is planned in 2003.
- Possibilities to exchange postgraduate students and of joint degrees are being investigated. The problem of UK fees has not yet been resolved.
- Origination of a workshop to review the research activities of the UK network and its collaboration with the Brazilian network. The original plan was to invite Brazilian collaborators, a representative of HEFCE, Prof B Clarkson, and delegates of UK companies which have manifested their interest for the network, to attend a workshop held simultaneously with the RSC Catalyst Life Cycle conference held at The University of Bath in September 2002. unfortunately, it was not possible to hold such a workshop due to prior commitments of many participants. However, a number of UK participants did attend and a meeting of the UK part of the network was held.
- Preferential exchange of educational and research information between the UK and Brazil networks members. A web-site (http://www.catalysisnetwork.com, operated by the University of Bath) has been set up to promote communication between the UK and the Brazil teams with a public domain advertising the network and its achievements. A secured domain is used for the exchange of research information between the network members.
- The UK and Brazil network coordinators monitor activities on a regular basis and the progress of the research is disseminated on the network web site.

3.2 The Brazil network (Rio de Janeiro)

The following Brazilian teams are involved in this programme.

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4. PROGRESS IN THE YEAR 2002

The objectives were:

- To maintain the UK network.
- To continue the initial links established with the Brazilian network.
- To agree on collaborative research projects (UK and Brazil).
- To define methods for an efficient collaboration between the UK and the Brazilian networks.

All four objectives were reached. The UK network has maintained close contacts between its members to define and focus the research areas for its collaboration with the Brazilian teams. Although both parties have genuine common research interests, it appears that setting up efficient collaborations is still hindered by financial issues, i.e., registration fees for Brazilian exchange students in the UK and support from EPSRC to the UK teams for projects of common interest. Does EPSRC have or plan to have a department fostering international applied research projects such as those initiated by this network?

Ways to achieve a successful collaboration were identified. Originally six collaborative research projects were considered and discussion between the networks, and internally, resulted in the following research programmes. Three (1,2,4) of them are proceeding. Another one (6) is still being considered. The other two projects (3,5) remain on hold. See below for details.

Project 1: Methane upgrading (METUP) *(Project proceeding)*
UK coordinator: E G Derouane
Brazilian coordinator: J L Monteiro

Methane to:	aromatics and hydrogen (zeolite catalysts)	UK and Brazil
	alkylaromatics and hydrogen (zeolite catalysts)	UK
	non-aromatic hydrocarbons (zeolite catalysts)	Brazil
	ethylene (mixed oxide catalysts)	Brazil
	higher hydrocarbons from ethylene (zeolite catalysts)	UK and Brazil

Objective: Search for more diverse and useful products than only benzene and naphthalene.
UK groups: Liverpool, Bath, Bradford.
Brazilian groups: COPPE, IME, CENPES, INT, UFF.

This research project is proceeding in the UK, currently with in-house LCIC funding. Directions for future work are conditions for operating at lower reaction temperature to yield alkyl aromatics and branched aliphatics. A one-year Mexican PDRA (José Luis Rico, financed by LCIC and public Mexican funds) worked on this project at LCIC during 2001 and 2002. A proposal to EPSRC describing the potential use of a membrane reactor is in preparation led by Chemical Engineering at Bath. This project, from the Brazilian side, is supported by Faperj and Petrobras. Discussions are still ongoing between the UK and Brazilian networks to continue work in this area and secure the funding required.

Project 2: Selective oxidation of propane (SOPOR) (*Project proceeding)*
UK coordinators: SH Tayloe and JC Védrine
Brazilian coordinator: M Schmal

Propane to:	propene (mixed oxide catalysts)	Brazil
	acrolein (miscellaneous catalysts)	UK
	acetic acid (miscellaneous catalysts)	UK
	propan-1-ol and propan-2-ol (mixed oxide catalysts)	UK
	acrylic acid (miscellaneous catalysts)	UK
	acrylonitrile (zeolite catalysts)	UK

Objective: Identify and control the factors affecting selectivity in the oxidative functionalisation of propane. Potential catalysts are modified zeolites, mixed oxides, heteropolyacids/salts, supported metals.
UK groups: Liverpool, Bath, Cardiff.

Brazilian groups: COPPE, IQ/UFRJ, INT.

This research project is proceeding in the UK, currently with in-house LCIC funding, with respect to the oxidation of propane to acrolein, acrylonitrile, and acrylic acid. This project currently involves three PDRA 's at the LCIC. Two of them have submitted their Ph.D. theses. This project is now supported by Faperj from the Brazilian side, the objective being the oxy-dehydrogenation of propane to propene using mixed oxides. In the UK, research proceeds on the oxy-dehydrogenation of propene using heteropolyacids (HPA) and their salts (LCIC) and on the selective oxidation of propane to formaldehyde and acrolein using mixed oxides and novel BN supported oxide catalysts 2 students at Cardiff). An EPSRC proposal involving the teams in Cardiff and Liverpool was submitted to the EPSRC (responsive mode) to secure funding to continue these studies in the UK. Despite being highly rated the proposal did not receive funding. Conference presentations on this work were delivered at the ACS National Spring meeting (Orlando, April 2002) by Dr S Taylor, Mr A Pollard and Professor JC Vedrine. Papers disseminating this work have also been accepted for publication in the internationally refereed journal Catalysis Today. There continues to be interest in this work from the Brazilian side and further roods need to be explored so that continued funding can be obtained.

Project 3: Oxyhalogenation and upgrading of methane (OXYM) *(on hold for the time being)*
UK coordinator: I Kozhevnikov
Brazilian coordinator: E Fallabella

Methane + X_2 to CH_3X + HX (mixed oxide, zeolite, and HPA catalysts)	UK and Brazil
HX + O_2 to H_2O and X_2	UK
CH_3X to ethylene and ethylene to higher HC's (zeolite catalysts)	UK and Brazil
Ethylene + X_2 to halogenated compounds ($C_2H_{4-x}X_x$) (? as catalyst)	Brazil
CH_3X to halogenated compounds ($C_2H_{4-x}X_x$) (? as catalyst)	UK and Brazil

Objective: Identify and control the factors affecting selectivity. Primary interest is the production of ethylene and higher HC's using X_2 to selectively activate methane. Additional interest on the production of C_2H_{4-x} X_x and other halogenated compounds,
UK groups: Liverpool, Bath, Cardiff
Brazilian groups: IQ/UFRJ, CENPES

To date no funding is available in the UK but this type of catalysis is well funded in Brazil (Faberg, Finep/Petrobras). The interest of both parties appear to be very different (Brazil groups are mostly interested in bromination rather than chlorination, and the UK groups lack expertise in chlorination). I Kozhevnikov who was the coordinator of this project joined the team for Project 2 in view of his expertise in catalysis by HPAs.

Project 4: RF-assisted hydrocracking of gas-oil (RAFT) (Proceeding)
UK coordinator: R Walls
Brazilian coordinator: M.Sugaya, Petrobras/CENPES

Objective: Examine the possibility to have a pilot plant installed at CENPES to use the technology developed in Bradford.
UK group: Bradford
Brazilian group: PETROBRAS/CENPES

This project proceeds well and reciprocal visit have taken place. Dr Sugaya visited Bradford in September 2001. Evaluation of the results obtained in Bradford using the technology developed by Prof Walls group is now taking place at Petrobras. Both parties have started cooperative work. It will be funded by Petrobras in Brazil but funding, so far, is not yet available in the UK. Further development of this theme will depend on the future of Chemical Engineering at the University of Bradford.

Project 5: Ethanol to acetic acid and other oxygenated compounds (ACE) (on hold for the time being)
UK coordinator: A Lapkin
Brazilian coordinator: L G Appel

Proposed catalysts:
Gas phase oxidation: SmO_2/MoO_3
Liquid phase oxidation: Bi/Pt-C
Objectives: Sustainable production of acetic acid, other uses of ethanol (in case ethanol cannot be used as fuel additive), new liquid phase reactors, membrane separation of alcohols.
UK groups: Bath, Cardiff
Brazilian groups: UFRJ, INT

This project needs more thinking both in terms of chemistry and economic evaluation. UK and Brazil interests may also diverge. Ethanol is not a readily available feedstock in the UK whilst it is used widely in Brazil..

Project 6: Partial oxidation of methane (METRO) (being considered)
UK coordinator: R Walls
Brazilian coordinator: F B Passos

Catalysts: Pt/ZrO_2 and Pt/CeO_2
Objective: Production of hydrogen by partial oxidation of CH_4. Design and optimisation of a membrane reactor to produce pure O_2 needed for partial oxidation.
UK groups: Bath, Bradford
Brazilian groups: UFF, INT

Although there is interest in Brazil and funding is available (Faperj, Finep/Petrobras), the UK team has not yet been able to identify objectives that might trigger interest from the UK industry. If funding can be obtained the group in Bath will look into the potential use of perovskite catalysts and membrane technology to enhance hydrogen production.

5. PLANS FOR THE FUTURE, POSSIBLE OBSTACLES AND SUSTAINABILITY

The Network has been functioning for a considerable time period and the broad plans for the future can be sumarised:

- The UK network is functioning well and since its establishment communication and collaboration between the different groups has been enhance. It is the aim to continue this collaboration between the groups. Professors Derouane and Vedrine have now left the UK, however the links developed still remain and future collaboration is likely. In addition, Bath and Cardiff universities have recently submitted a collaborative proposal, building on the relationship established through the UK as part of the network.

- The link between the UK and Brazilian networks has also proved valuable and it is envisaged that these links will be maintained in the future.

Against this background, the benefits of the network are clear. In order to maintain the established links and continue the function of the network once HEFCE funding has ceased the following are identified as key requirements:

- To raise additional support from public and industrial sources support for the research projects.
- Develop further the appeal and impact web site for the UK-Brazil network.
- Plan and organise UK-Brazil workshop.
- Plan and accomplish a second visit of UK delegates (3-4) to Brazil to present and disseminate more widely research which has been completed to date and investigate the potential for .
- Confirm agreements for students exchange/joint projects.

Obstacles appear currently to be on the UK side:

- Funding remains the major obstacle to achieve future plans. The funding for the network has aided the establishment of the networks, however, funding for the research projects remains problematic. Many applications and have been made for EPSRC funding that success has been limited. In particular research at Liverpool and Cardiff has been supported to a large extent by internal university funding.
- *Sandwich studentships* for the exchange of students: (i) can the tuition fees for Brazilian students in the UK be levied or paid for by HEFCE (no tuition fees are charged in Brazil, neither for Brazilian nor foreign students), (ii) what are the UK regulations for joint UK-Brazil degrees?

Discussions amongst the network indicate that there is a willingness to continue the work and collaboration established by the network. Without the aid of external funding it is not expected that the network will function to the same extent as it has with the HEFCE funding. For example, funds to aid travel and subsistence for meetings with in the UK and in Brazil will have to be obtained elsewhere. The departures of professors Derouane and Vedrine to Portugal and France respectively also means that if the network is to function with the same participants it must be extended outside the UK. However, the participants are keen to continue their collaboration with each other and it is envisaged that this and the collaboration with Brazil will be sustained but on a more informal basis.

6. TANGIBLE OUPUTS, DISSEMINATION AND ACHIEVEMENTS

Most of the research projects are already progressing and networking in the UK will result in larger research groups interacting horizontally, combining chemical and chemical engineering expertise. By the end of the year 2003, it is expected that the UK-Brazil collaborative network will be fully operational, that joined research projects will be in place, and that a mechanism will have been defined to actively disseminate the results within the two networks. It is anticipated that visits of Brazilian students will take place in the future, and although they will be outside the timescale of the network funding they will, nevertheless, be a direct consequence of the network.

Three research projects of common interests to the UK and Brazilian teams have been selected and are now progressing, a possible fourth one has also been identified. Meetings between representatives of the Brazilian and UK teams have taken place at international conferences (Montpellier, Limerick) and regular contacts have been maintained between the network coordinators. Funding for the Brazilian network, from Faperj and Finep/Petronas has been confirmed in late September 2001. A website has been set up (www.catalysisnetwork.com) and is now operational at the University of Bath.

At the end of the project the UK network has:

- Demonstrated the importance of horizontal collaborations combining complementary expertises and skills, at the UK and international levels,
- Established a firm and long-lasting collaboration with the Brazilian network,
- Demonstrated that the HEFCE pilot programme of research network is an efficient way to create, promote, and support new and synergistic collaborations,
- Created links between UK and Brazil groups which may benefit to the UK chemical industry.

The results of the research projects will initially be disseminated within the two networks. The website comprising both public and secured domains will enable to maintain continuous communication between the UK and Brazil teams, and publicise the activities of the network. Patents will be applied for as necessary, IPR issues being handled as described in section 7. currently there are no patterns arising directly from the UK/Brazilian network. However, the multi-disciplinary nature of the teams has resulted in cross-fertilisation of ideas and thinking and it is apparent that considerable *know how* has been generated from these collaborations.

Joint publications in journals of international standing as well as joint communications at major international meetings will also publicise the output of the research. Although joint publications have not yet resulted de Cross collaboration of the work means that they will be likely in the future. Research from the network has already been published in international journals, and for example Dr Taylor and Professor Vedrine presented related work in the same session on propane oxidation at an international conference in 2002.

The achievements and outcomes of the network are broadly those that were expected. It is considered a major achievement to establish and integrate a diverse group of researchers from different institutions and to interface this group with a similar group in Brazil. The process of identifying a key areas of interest that matched the expertise of the network participants was also a major achievement and took significantly longer than was originally expected. However, the areas identified clearly encompass the expertise of the teams and are of direct relevance to UK and Brazilian industries. It was expected that within the framework provided by the network it would be possible to secure outside funding. Although some funding has been secured indirectly it has proven more difficult than expected to obtain funding from the EPSRC to directly support network projects.

7. IPR ISSUES

Market sensitivity and intellectual property rights (IPR) issues will be addressed on a case by case basis. IPR will be shared proportionally to the contribution of each partner/collaborator to the invention. Clarification of the industrial access rights is still needed. It is likely to depend on the amount of industrial support, the number and origin of the teams supported, etc. It is envisaged that IPR issues might be resolved by adopting a scheme similar to that practiced by the NATO Science for Peace Programme which appears to resolve international, academic, and industrial sensitivities.

8. INDUSTRIAL AND COMMERCIAL PARTNERSHIPS

From the UK side, contacts were made with ICI/Synetix, BP Amoco Chemicals, Shell Chemicals, and Johnson-Matthey. BP Amoco Chemicals and Johnson Matthey have manifested verbally their interest. ICI/Synetix has confirmed in written its interest. No tangible manifestation of these interests however took place. From the Brazilian side, there is a confirmed interest of Finep/Petrobras and Faperj. Several other UK companies support to the current publicly (EPSRC) funded projects which are part of the collaborative network.

Although no direct funding has been awarded from industry to support projects in the UK for the UK-Brazilian network, it is clear that they are aware of the network's existence and the areas of research in which it is investigating. It is not immediately apparent why none of the industrial companies have not contributed funding directly to the UK-Brazilian network projects. It may have been due to concerns relating to IPR and confidentiality although mechanisms are in place to deal with both issues. The projects selected are all of industrial significance to both chemical manufacturers and catalyst manufacturers. Although direct funding has not been forthcoming it must be noted that all the UK research groups receive funding from one or more of the industrial companies approached. Thus, indirectly the research groups are supported by industry and some of this support filters through to provide services, chemicals, and infrastructure that impact on the research carried out within the UK Brazilian network.

9. SPIN OFFS

No spin offs have as yet been identified.

10. USE OF HEFCE FUNDS

To be supplied by Liverpool University

11. LESSONS LEARNT

The following lessons have been learnt from establishing and running the UK Brazilian catalysis network:

- The initial meetings of the UK participants of the network were particularly important to establish the key areas of Catalysis for investigation. These areas focused on the expertise of members of the team and on areas of particular industrial interest.
- The initial visit of four members from the UK network to Brazil early in the project helped to clearly define the research projects and establish initial contact with Brazilian collaborators.
- The visit of members of the Brazilian network to the UK and their subsequent visits to all the UK universities provided an opportunity to discuss project details in more depth and reinforce collaboration.
- The establishment of a website with Secure and public domain areas provided an excellent platform for dissemination of information to all network members and other interested parties.
- When the opportunity arose it was beneficial to meet in small groups to briefly discuss network research progress, and often these small group meetings replaced larger and more formal meetings.
- The successful establishment of the network did not necessarily guarantee funding from the EPSRC and Industry to support the research project areas, and securing a funding proved more difficult than initially estimated.