

Energy, Mines and Resources Canada

# CANMET

Canada Centre for Mineral and Energy Technology

Centre canadien de la technologie des minéraux et de l'énergie

Énergie, Mines et

**Ressources** Canada

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ACTIVITIES REPORT - 1987

HYDROCARBON CONVERSION SECTION

Staff - Hydrocarbon Conversion Section

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#### HYDROCARBON CONVERSION SECTION

#### Summary

Researchers in the Hydrocarbon Conversion Section perform mission oriented research studies in two areas, Natural Gas Conversion and Upgrading Heavy Oils and Residuals. The section is one of seven sections within the Synthetic Fuels Research Laboratory. The experimental facilities are located at the west end of Ottawa within the Energy Research Laboratories, a division of CANMET (Canada centre for mineral and energy technology). Enquires should be addressed to:

> The Director Energy Research Laboratories CANMET 555 Booth Street Ottawa, Ontario KlA 0Gl, Canada

Sommaire

Les chercheurs dans la section de valorisation des hydrocarbures sont charges d'entreprendre des études sur la conversion du gaz naturel et sur la valorisation des huiles lourdes et des braies. Cette section fait partie du laboratoire de recherche sur les combustibles synthétiques qui en comprend sept au total. La section possède des laboratoires situés dans l'ouest d'Ottawa parmi ceux des Laboratories de recherche sur l'énergie, une division de CANMET (Centre canadien de la technologie des minéraux et de l'énergie). Pour de plus amples renseignements, communiquer a l'adresse suivante:

> Le Directeur Laboratories de recherche sur l'energie CANMET 555 rue Booth Ottawa, Ontario KIA 0Gl, Canada



#### HYDROCARBON CONVERSION SECTION

#### HUMAN RESOURCES

The distribution of human resources (for fiscal year 1987/88) is:

	Person Years
Natural Gas Conversion	4
Upgrading Heavy Oils	l
TOTAL	5

# Research Scientists

Marten Ternan, B.A.Sc.(British Columbia), Ph.D.(McGill), P.Eng. -Section Head (Hydrocarbon Conversion)

Gilles Jean, B.Sc.(Rimouski) Ph.D.(Western Ontario) -Technology Leader (Natural Gas Conversion)

Jan Galuszka, B.Sc., M.Sc., Ph.D. (Jagiellonian, Cracow, Poland)

Vincenza Allenger, B.Eng.(McGill), M.A.Sc.(Ottawa)

# Engineering and Scientific Support

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The above resources are supplemented by additional resources in the analytical laboratories and in some cases by collaboration with colleagues in other groups of CANMET.

Lists of publications (P), contract reports (CR) and contracts awarded (CA), which are related to various aspects of the above two topics are provided at the end of this document.

# NATURAL GAS CONVERSION

The primary use for natural gas is as a stationary fuel in domestic and industrial heating. It is also used in manufacturing chemicals (hydrogen and methanol). A more recent development is the use of compressed natural gas as a vehicle fuel. Although Canada exports a significant quantity of natural gas to the United States, there are currently large quantities available for other uses. One alternative would be to convert natural gas to higher molecular weight hydrocarbon liquids which would be used in transportation.

It has been predicted that the supply of conventional petroleum crude oil from Canadian sources will decline substantially over the next 10 years. One possibility would be to manufacture a synthetic crude oil from natural gas. Synthetic crude oil from natural gas would have to compete with synthetic crude manufactured from oil sands. Another possibility would be to convert natural gas to premium quality fuel products such as high octane gasoline or high cetane number diesel. For example a high cetane product might command a premium price as a blending component when added to the low cetane diesel fuels currently manufactured from oil sands.

There are several different reactions for the conversion of natural gas (Pl). For the purpose of this discussion direct reactions will be defined as those in which methane reacts directly to form a product (usually an intermediate product). Indirect reactions will be those in which an intermediate product reacts further to form a final product. Direct reactions can be classified into five different types.

- 1. Methane pyrolysis/dehydrogenation
- 2. Methane-steam reforming
- 3. Methane partial oxidation
- 4. Methane oxidative coupling
- 5. Methane-olefin reactions

The intermediate products from these reactions may be used in a multitude of subsequent indirect reactions. The following examples are only a partial listing.

- 6. Polymerization
- 7. Fischer Tropsch
- 8. Methanol to Gasoline
- 9. Dehydrogenation/Cracking

To date research activities within our laboratories have considered three of the above topics (items 4,6 and 7). The contracted out research has covered a broader range of topics (items 1,3,4,5,7 and 8).

# Acetylene Polymerization

Principal Researcher: Vincenza Allenger (613) 995-6392

Pilot plant experiments and engineering studies (CRll, CRl2) on the conversion of natural gas to acetylene were among the contracted-out research investigations. These studies are being complimented by an in-house investigation focussed on the polymerization of acetylene to high octane fuels. The variables being investigated include processing conditions and catalyst composition. Liquid products were identified (P2) using capillary chromatography with a flame ionization detector and a mass spectrometer detector. The goal of the work was to identify reaction conditions which maximized acetylene conversion (P3, P4) and the yields of desirable products (eg. BTX). An important aspect in the reaction appears to be the formation of a carbonaceous deposit on the catalyst surface. At high conversions this deposit is considered to be converted to desirable reaction products. Since substantial catalyst deactivation occurs, considerable attention is being given to identifying processing conditions (P5) at which it is minimized.

# Fischer-Tropsch Synthesis

Principal Researcher: Jan Galuszka (613) 995-6414

Synthesis gas (CO and  $H_2$ ) can be produced by steam reforming natural gas. Fischer-Tropsch synthesis has been used for many years in South Africa to produce a product which contains a wide spectrum of components, from gases to waxes. The goal of this research is to produce a product having a much narrower distribution of components and having a high cetane number (P6).

To perform this work a new catalyst must be formulated and tested. A fully computerized and automated reaction system has been designed and constructed for testing purposes. This system has several unique features such as, on line qualitative analysis of liquid and gaseous products, heating and cooling action for exothermic processes using a multizone furnace, and on line quantitative yield measurement of liquid phase products.

Experiments (P7, P8) have shown that synthesis gas reactions also form a carbonaceous deposit on the catalyst surface. The finding that the catalyst composition influences the character of the deposit is of particular interest.

# Investigation of Chemisorbed Intermediates

Principal Researcher: Jan Galuszka (613) 995-6414

A specialized experimental system has been constructed for these studies. It has a unique combination of Fourier Transform Infrared Spectroscopy (FTIR), Mass Spectrometry (MS) and a capability for both Temperature Programmed Reaction and Desorption. This will permit studies on the identification of catalytic sites, catalyst poisoning, surface reactions, and the direct examination of adsorbed species

Since the carbonaceous deposit on the catalyst is known to have an important effect on the product distribution, studies on its characterization have been initiated. One characterization technique involves the adsorption of acetylene on the catalyst surface with simultaneous monitoring of the catalyst surface by FTIR spectroscopy. Another technique involves hydrogenation of the catalyst surface deposit and using mass spectrometry to measure the type of gaseous products formed. These and other examinations are in progress using catalysts of different composition. This should result in a knowledge of both the relationship between the catalyst composition and the adsorbed intermediate, as well as the relationship between the intermediate and the product distribution.

# Oxidative Coupling

Principal Researcher: Gilles Jean (613) 995-4473

Preliminary studies on oxidative coupling are being initiated. In oxidative coupling methane reacts directly with oxygen to form water and a hydrocarbon (usually ethylene or ethane).

2 CH4 + 02 ---> 2 C2H4 + 2 H20 not balanced

Subsequently ethylene will have to be polymerized to form the final fuel product.

Oxidative coupling has the advantage of being exothermic, in contrast to the formation of acetylene and the formation of synthesis gas, which are both endothermic. Therefore, oxidative coupling does not have the large energy requirements of the other two reactions. Unfortunately it also has disadvantages. For example, the excess hydrogen in the original methane is converted to water. It would be preferable to produce hydrogen, as a gas, since it is a desirable by-product which adds value to a process.

#### Technology Review

One of the current objectives is to have all of the scientists in the section contribute to a review. Known technologies for natural gas conversion (P9, P10, P11) will be compared. Relevant scientific studies will also be included. Hopefully the potential benefits from various research options can be rated and the results used in choosing future research directions.

# UPGRADING HEAVY OILS AND RESIDUALS

This technology has a large mandate and a corresponding amount of resources (30 person years). Only those projects to be performed by the staff of the Hydrocarbon Conversion section (1 person year) will be described here.

Commmercial plants for medium severity hydrocracking of Lloydminster heavy oil (COOP - Regina) and Athabasca bitumen (Syncrude - Fort McMurray) are currently being constructed. A high severity hydrocracking demonstration plant (PetroCanada - Montreal) began operating in 1985. The hydrocracking processes are superior to the older coking processes in that they produce higher yields of liquid distillates and no undesirable coke. However they do produce some unreacted +525 C pitch. Commercial plants will process the pitch in coking units. The higher the severity of the hydrocracking process, the smaller the yield of pitch, but the greater the yield of coke from that pitch when it is processed in coking units. Although the use of hydrocracking instead of coking for primary upgrading causes a tremendous decrease in the net coke yield, it would still be desirable to produce something useful from the pitch instead of additional coke.

This work is divided into two parts; the development of better catalysts for primary upgrading by medium and high severity hydrocracking, and research on a process for the utilization of the unreacted +525 C pitch, which would be a desirable alternative to coking process9

#### New Hydrocracking Catalysts

Principal Researcher: Marten Ternan (613) 996-4570 ext 165

A series of studies on residual oil hydrocracking catalysts have been performed within our laboratory. Large pore catalysts have been developed which allow the large carbonaceous molecules to diffuse at greater rates (Pl2, Pl3, Pl4). It has been shown (Pl5, Pl6) that improved results can be obtained by modifying the chemical composition of the catalysts. In the present work attempts will be made to combine several of these effects into a single catalyst.

#### Combined Catalytic Cracking and Gasification

Principal Researcher: Marten Ternan (613) 996-4570 ext 165

The unconverted residuum by-product from a heavy oil hydrocracker will be the feedstock for an upgrading process which combines catalytic cracking and catalytic gasification (P17). The catalytic cracking step will produce distillate liquids which can be used in fuel products. The catalytic gasification step will produce hydrogen which can be used in hydrocracking processes (P18, P19).

Experiments are being performed in a microbalance reactor. Work is directed at the identification of a catalyst which is bifunctional, that is a catalyst which is useful for both cracking and gasification reactions.

#### EXPERIMENTAL EQUIPMENT

The Energy Research Laboratories have a variety of experimental facilities. The following list includes apparatus normally used by members of the Hydrocarbon Conversion section, as well as a vast amount of apparatus that is normally used by members of other sections.

- High Pressure Vapour Phase Continuous Flow Reactor reactor volume 900 mL design pressure 10 MPa design temperature 525 C
- High Pressure Liquid Phase Continuous Flow Reactor fixed bed holding 150 g of catalyst design pressure = 65 MPa normal operating pressure = 15 MPa Maximum temperature 600 C Normal operating temperature 450 C
- Atmospheric Pressure Vapour Phase Continuous Flow Reactor fixed bed holding 5 g of catalyst operating temperature 600 C
- Pulse Reaction and Adsorption System model compound studies surface acidity by ammonia adsorption chemisorption studies
- Microbalance Atmospheric Pressure Batch Reactor maximum catalyst sample = 25 g maximum temperature = 1000 C
- Catalyst Manufacturing Facilities catalyst extrudates catalyst pellets
- Catalyst Geometrical Properties surface area (nitrogen BET) pore size distribution (Hg porosimetry) pycnometry

Surface Analysis XPS Auger scanning electron microscopy EDAX

Analytical Facilities ASTM procedures for analyzing gases, liquids and solids proton nmr carbon 13 nmr GCMS GC-FTIR atomic absorption X-ray fluorescence

#### CONTRACTING-OUT PROCEDURES

There are three mechanisms for contracting out research.

Research proposals prepared by government scientists are sent to several contractors who submit bids. Potential bidders are identified from a computerized source list (SPIN), which is maintained by Supply and Services, Canada.

The 50/50 Energy Conversion Program considers proposals which originate from organizations or groups of organizations. In this program the federal government shares the cost of the research (maximum = 50 %) with industry (which pays the other 50 %). The industrial partner has the right to use and to sublicense any patents resulting from the work. The final report can be kept confidential for a short time (usually 6 months).

The Unsolicited Proposals Program allows organizations to submit proposals on their own initiative. To be accepted these proposals must relate to one of the government research programs, must have scientific merit and technical feasibility, and must describe a unique feature. The federal government pays 100 % of the cost and owns all patents resulting from the work.

Additional information on contracting out can be obtained

from:

Director Science Programs Branch Science and Professional Services Directorate Supply and Services Canada 12C1, Phase III Place du Portage Hull, Quebec K1A 0S5 (819) 997-7428

You should expand to discuss - Completed Contrat Reports

#### REFERENCES

Publications in Scientific Periodicals and Conference Proceedings

- Pl. G. Jean, V. Allenger and M. Ternan, "Natural Gas: Alternative source of liquid fuels," Proc. 37th Can. Chem. Eng. Conf., The Chemical Institute of Canada, Ottawa, 1987, pp. 409-411.
- P2. V.M. Allenger, D.D. McLean and M. Ternan, "Direct condensable vapour analysis by capillary gas chromatography," J. Chrom. Sci. 24, 95-98 (1986).
- J. Chrom. Sci. 24, 95-98 (1986). P3. V.M. Allenger, D.D. McLean and M. Ternan, "The influence of infra-red radiation on acetylene conversion," Fuel 66, 435-436 (1987).
- P4a. V. Allenger, C. Fairbridge, D.D. McLean and M. Ternan, "Reaction of acetylene over fluorinated alumina catalysts," J. Catal. 105 71-80 (1987).
- J. Catal. 105 71-80 (1987). P4b. V. Allenger, D.D. McLean and M. Ternan, "Conversion of acetylene to liquid fuels," Proc. 34th Can. Chem. Eng. Conf., The Chemical Institute of Canada, 1984, pp. 135-137.

P5. V.M. Allenger, J.R. Brown, D.D. McLean and M. Ternan, "Deactivation of fluorinated alumina catalysts in acetylene polymerization," Proc. 37th Can. Chem. Eng. Conf., The Chemical Institute of Canada, Ottawa, 1987 pp. 1-3.

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- P6. R.L. Varma, N.N. Bakhshi, J.F. Mathews and S.H. Ng, "Performance of combined cobalt nickel zirconia and HZSM-5 catalyst systems for carbon monoxide hydrogenation," Can. J. Chem. Eng. 63, 612 (1985).
- P7. J. Galuszka and Y. Amenomiya, "Infrared study of coadsorption of CO and H<sub>2</sub> on alumina supported nickel catalysts," in Catalysis on the Energy Scene (eds. S. Kaliaguine and A. Mahay), Elsevier, Amsterdam, 1984, pp.63-75.
- P8. J. Galuszka and M.H. Backk, "Iron surface morphology factor in the growth of filamentous carbon,"Carbon 22, 141 (1984). P9a. R.L. Varma, K. Jothimurugesan, N.N. Bakhshi, J.F. Mathews and
- P9a. R.L. Varma, K. Jothimurugesan, N.N. Bakhshi, J.F. Mathews and S.H. Ng, "Direct conversion of synthesis gas to aromatic hydrocarbons:product distibution with time on stream," Can. J. Chem. Eng. 64, 141-148 (1986).
  - PlOa. R.L. Varma, N.N. Bakhshi, J.F. Mathews and S.H. Ng, "Induction Periods for conversion of synthesis gas to aromatics containing hydrocarbons using a dual reactor system," Applied Catalysis (1987).
  - PlOb. R.L. Varma, N.N. Bakhshi, J.F. Mathews and S.H. Ng, "Performance of Dual-Reactor System for Conversion of Syngas to Aromatic-Containing Hydrocarbons," Ind. Eng. Chem. 26 183-188 (1987).
  - Plla. H.D. Gesser, N.R. Hunter and C.B. Prakash, "The direct conversion of methane to methanol by controlled oxidation," Chem. Rev. 85 (4), 235-244 (1985).
  - Pllb. N.R. Hunter, H.D. Gesser, L.A. Norton and D.P.C. Fung, "The direct conversion of natural gas to methanol by controlled oxidation at high pressure," Proc. 35th Can. Chem. Eng. Conf., The Chemical Institute of Canada, Ottawa, 1985, pp. 480-485.

Pllc. P. Meubus, "Methane polymerization in a hollow cathode discharge," Proc. 35th Can. Chem. Eng. Conf., The Chemical Institute of Canada, Ottawa, 1985.

/ Pl2. M. Ternan, R.H. Packwood, R.M. Buchanan and B.I. Parsons, "Preparation of High Porosity Catalysts," Can. J. Chem. Eng. 60 , 33-39 (1985).

- P13. P.J. Champagne, E. Manolakis and M. Ternan, "Molecular weight distribution of Athabasca bitumen," Fuel 64, 423-425 (1985).
- Pl4. M. Ternan, "Diffusion of liquids in pores," Can. J. Chem. Eng. 65 244-249 (1987). Pl5. M. Ternan, "Catalysis, Molecular Weight Change and Fossil Fuels," Can. J. Chem.Eng. <u>61</u>, 133-147 (1983).
- Pl6. P.M. Boorman, J.F. Kriz, J.R. Brown and M. Ternan "Hydrocracking bitumen derived from oils sands with sulphided MoO<sub>2</sub>-CoO catalysts having supports of varying composition," Proc. 8th Intern. Congr. Catal. 2 Verlag-Chemie, Weinheim, FRG, 1984, pp. 281-291.
  - P17. M. Ternan and M.V.C. Sekhar, "Catalytic Conversion of Heavy Hydrocarbon Materials, " Canadian Patent 1,123,774 issued May 18, 1982.
  - Pl8. M.V.C. Sekhar and M. Ternan, "Catalytic gasification of char from hydrocracked pitch," Fuel Proc. Technol. 6 61-73 (1982).
  - Ternan and M.V.C. Sekhar, "The catalytic steam gasification P19. M. of chars from various sources by K2CO2," Fuel Proc. Technol. 10 77-89 (1985).

Completed Contract Reports

- \*CR1. B.W. Wojciechowski, The construction and activation of a multireactor synthesis catalyst testing apparatus, Contract Serial No. 1SU82-00155, MON 86-2917, December 1983.
- \*CR2. M.H. Back, Carbon deposit morphology on metal surfaces during hydrocarbon synthesis, Contract Serial No. 1ST83-00197, MON 5-5950, May 1985.
- \*CR3. B.G. Keefer, Thermally coupled pressure swing adsorption for natural gas conversion to liquid fuels, Contract Serial No. 0SQ85-00131, MON 87-0605, July 1986.
- \*CR4. N.N. Bakhshi, Direct production of aromatic hydrocarbons / gasoline from synthesis gas, Contract Serial No. 1SU.82-00308, MON 85-5951, May 1985.
- \*CR5. N.N. Bakhshi, Direct production of gasoline range hydrocarbons from Syngas in a dual bed reactor system, Contract Serial No. 0ST84-00321, MON 86-5106, May 1986.
- \*CR6. K. Leen, Direct conversion of synthesis gas to high octane gasoline over HZKQ-1B zeolite, Contract Serial No. 0SQ84-00081, July 1986.
- \*CR7. K. Leen, Mise au point et essais de performance d'un nouveau catalyseur pour la conversion des alcools simples en essences synthetiques, Contract Serial No. 1SQ82-00179, MON 86-2910, September 1985.

- \*CR8. H. Gesser, The production of methanol by controlled oxidation of methane at high pressures, Contract Serial No. 0SU82-00258, May 1984.
- \*CR9. H. Gesser, Study of the direct oxidation of methane to methanol, Contract Serial No. 0ST83-00404, May 1985.
- \*CR10. H. Gesser, Product optimization of the direct conversion process of natural gas to methanol, Contract Serial No. 0ST85-00032, September 1986.
- \*CR11. N.Cooke, Conceptual design and techno-economic assessment of three electricity-based reactor processes for the production of liquid fuels and/or hydrocarbons from natural gas, Contract Serial No. 0SQ83-00070, MON 86-5133, March 1985.
- \*CR12. N. Cooke, Technical and economic assessment of producing liquid fuels from natural gas via an electricity based acetylene process, Contract Serial No. 0SQ84-00209, March 1986.
- \*CR13. P. Meubus, Conversion du methane en essence par reaction en cathode creuse, Contract Serial No. 1ST84-00189, MON 86-6106, Fevrier 1986.

\*The government reports with a MON (micromedia order number) can be purchased from Micromedia Ltd, 165 Hotel de Ville, Hull, Quebec, J8X 3X2, (819)770-9928. Inquires concerning the government reports without a MON number can be addressed to Technical Information Division, CANMET, 555 Booth St. Ottawa, Ontario, KIA 0G1, (613)995-4059.

# Contracts Awarded

V

- Petro Canada (W. Lewis) The conversion of methane over selected solid catalysts
- Petro Canada (R. Lennox) Investigation of the Process Conditions for the Synthesis of Liquid Distillates from Light Olefins
- Universite du Quebec a Chicoutimi (P. Meubus) Methane Conversion Using a Hollow Cathode
- Centre de Recherche Industrielle du Quebec (K. Leen) Conversion of Synthesis Gas into Diesel using the Novel ZKQ Catalyst
- Centre de Recherche Industrielle du Quebec (K. Leen) The Conversion of Synthesis Gas into Diesel using the Novel Catalyst CL-18
- Guelph Chemical Laboratories (R. Pandey) Natural Gas Conversion to Liquid Fuels over Superacids
- Guelph Chemical Laboratories (R. Pandey) Carbon Molecular Sieves Based Synthesis

Guelph Chemical Laboratories (R. Pandey) Development and Evaluation of Catalysts for the Hydrogenation of Raw Cold Lake Pitch

Universite de Laval (S. Kaliaguine) Preparation and Pretreatment of Trifunctional Deoxygenation Catalysts

University of Western Ontario (H. DeLasa) Application of the Pseudoadiabatic Catalytic Reactor