

NOVEL CATALYTIC CO-PROCESSING OF BIOWASTES WITH FOSSIL FUELS

c. Identification and Significance of the Problem

Liquids from biowaste -- particularly paper and other plant derived wastes -- if converted to hydrocarbon liquids could only supply a few percent of this country's transportation fuel need. While not inconsequential, this contribution could be powerfully leveraged using the excess hydrogen transfer potential of biomass in the water critical region (WCR) to convert coal and natural bitumen (tars or black oils) to liquid fuels. Emerging WCR technology converts toxic waste to benign products with hydrogen donating properties. Combined with the early results of the reactivity of organic materials in this environment, the WCR appears a more promising route than the more conventional co-liquefaction of biomass with synfuels. Biomass chemistry in the WCR detoxifies hazardous metal and halogen contaminants and homogenous catalytic processing of synfuels in this medium reduces sulfur and metal contamination of the products. The approach therefore addresses both improved liquid fuels production and reduction of ecologic concerns associated with liquid fuels and with waste disposal. Our proposal is rests in use of homogeneously catalyzed WCR reactivity of the wastes to co-process synfuels and biowaste more effectively.

d. Background, Technical Approach and Potential Uses

d1. Background and Technical Approach

This brief review firstly recognizes direct liquefaction of plant biomass by thermolytic or hydrogenolytic processing and co-processing which have been examined particularly in the last 20 years with some modest success. However, because of the high reactivity particularly of cellulosic biomass in WSC and because homogeneously catalyzed redox reactions are possible in this environment, the nature of WCR chemistry relevant to more effective conversion of biomass and co-conversion of biomass and hydrogen deficient syncrude sources are set forth here.

Liquefaction of biomass from many origins has been examined as a potential hydrocarbon fuel source^{1,2} since the oil crises of the '70's. The venerable pyrolytic approach, produces gas, liquids, and much char^{3,4}. A short contact time pyrolysis process developed by Occidental produces about 25% liquids⁵. Elliot has reviewed heterogeneous catalytic conversion with hydrogen or carbon monoxide/steam⁶. By this method, liquid yields up to 40%⁷ have been obtained. Generally, process energy costs were high because of harvesting and/or collection charges, and to the dilute hydrocarbon content resulting from the high oxygen and water components in most sources⁸.

Co-processing low H/C feeds--resids, natural bitumens, and coal and shale kerogens--with higher H/C oil seeking to ameliorate the substantial and expensive hydrogen requirement in their conversion to useful liquid fuels⁹ has been an active research area¹⁰. From recognition of hydrogen transfer processes, donor solvents were devised and used to bridge some of the difficulties¹¹. Co-processing resids with coals appears most effective with low rank coals, lignites and

sub-bituminous coals^{12 13}. More current studies are directed toward interactive pathways between the feed types^{14 15 16}. Coal catalytic co-processing with wastes, for example, plastics^{17 18} and tires¹⁹ gave improved oil yields and quality,

Biopolymers such as cellulose have a strong free energy potential to dismutate to hydrogen and CO₂. If hydrogen or better, donor intermediates, were coupled effectively with hydrocracking, deoxygenation, and saturation of syn-fuel sources, this would be a useful addition to liquid syn-fuel and even conventional fuel production. Co-processing studies of biomass²⁰ with low and mid-rank coals have been reported which show a small synergistic yield effect. Wender and co-workers²¹ recently reported an incremental yield increase in co-processing paper with coal in a tetralin donor system while in CO/H₂O, paper co-processing gave little yield increase but the liquid quality was significantly higher.

Coal and shale kerogen conversion in CO/H₂O as an *in situ* hydrogen source via the water gas shift (WGS) reaction, as suggested by the Wender reference above, has received much attention. With type I (Green River) shale, this is hardly more effective than SC H₂O alone²². Coal systems show improved conversions with and without hydrogenation catalysts such as cobalt molybdena. Again conversions were greater for low ranked coals and decreased to higher ranks^{23 24 25}. Sulfur compounds appear to enhance conversion^{26 27}. To promote WGS, homogeneous catalysis with caustic²⁸ and Fe(CO)₅²⁹ have been used. In these complex systems, interactions among reactants with catalysts as well as with each other occur, often adverse. For example, using compounds modeling coal functionalities, Takemura et al found that without CO, both Mo and W catalysts promoted C-C bond cleavage, but with CO, only W was effective for cracking³⁰. Many of these studies were directed toward reaction paths and intermediates³¹ and showed that H₂ and CO were not the only reductants, rather, other intermediates such as formate ion were also present.

Liquefaction of woody biomass in aqueous medium occurs fairly rapidly between 200 and 300°C. particularly in acidic or basic conditions. Anderson and Wiser have reviewed pioneering work on pyrolysis and hydrogenative (including CO/H₂O) conversion of waste biomass³² Ligno-cellulosic reactions (plant derived matter) are compactly summarized by Chum and Baiszer³³. Antal has found that pyrolysis of biomass in steam at atmospheric pressure produces hydrocarbon rich synthesis gas and much char³⁴. Cellulose in water at 270°C in basic conditions gives 34% conversion based on carbon³⁵. Addition of CO enhances the liquid yield. One literature report indicates CO/H₂O liquefaction of cellulosic pulp in the presence of Ru₃(CO)₁₂ and base produces a high quality oil in 98-99% yield³⁶, and bagasse (sugarcane waste) was reduced by formate (which can arise from CO/H₂O) at 350°C in water³⁷. Other waste materials, especially lignin containing and glycosidic wastes, are also reactive under these conditions³⁸ and are feasible candidates for coal and kerogen co-processing feeds in aqueous systems. These processes generally leave some residual carbonaceous char as one reaction product.

Although these hydroxylic materials will normally char in pyrolysis, Modell has shown that in H₂O (SC) these materials cleanly decompose^{39 40}. This approach is being explored actively at Sandia, at Texaco and at U. of Texas Austin, among other

places. Not only does the WCR eliminate char, it also converts (detoxifies) hazardous matter as halogenated organics to produce water soluble salts. A recent patent claims the use of a biomass carbon source such as a carbohydrate to promote base catalyzed decomposition of organics, both halogenated and non-halogenated, in aqueous media above 200°C⁴¹.

Organic Reactivity in the Water Critical region (WCR) has not been extensively explored. Although strictly, the water critical region lies above the water critical point, $T_c = 374^\circ\text{C}$, $P_c = 218\text{ atm.}$, $\rho_c = 0.31\text{ g/ml}$, solubilities depend upon density of the fluid phase as well as temperature and the chemical nature of the fluid. Consequently, the aqueous liquid phase below T_c similarly shows enhanced solubility of both ionic solids and hydrocarbon substrates. Similarly, the aqueous non-condensable fluid appreciably above T_c retains its solvency of inorganics, solvates them, and even ionizes them provided the water density (partial pressure) remains liquid-like, say 0.3 g/ml. Further, solutes, both polar and non-polar, alter the phase structure so that the "critical region is band about the pure substance T_c ". For these reasons, the concept of a water critical region is more realistic than "supercritical water".

For aqueous SC fluids, the temperature range of the WCR is one in which many organics thermally transform or decompose, conversion in aqueous media began to stimulate interest in '60s. In that period, the relatively high solubilities of both organic and inorganic materials in the WCR (300-450°C) were systematically examined^{42 43 44}. Interest in applications supercritical extraction⁴⁵ with water as well as other fluids arose from this work.

At Amoco Oil Co., conversion to and extraction of liquids in WCR was examined for coals (about 30% ash free basis at 400°C⁴⁶), shales (90% a.f. above 375°C⁴⁷) and tar sands. With coal, liquid production in the aqueous system was about the same as that in toluene or other non-donor solvent. However, with shale, coal and tars, the normal gaseous products of dry pyrolysis -- light olefinic gases, H_2S , COS -- were largely absent in the aqueous system indicating that some non-pyrolytic chemistry was occurring in the WCR. An additional benefit was that residual coal and shale mineral solids were relatively easily separated from the heavy oils very likely because of modification of the asphaltenic content of the products. These results pointed to a reductive environment although no added hydrogen was present. Subsequent work^{48 49}
^{50 51} on low and mid-rank coals has extended Amoco Oil results and generally demonstrated higher coal liquid yields with or without hydrogen although the conversions were too low to compete with donor systems.

Winters, Lewan and others applied these results to evaluation of source rocks and showed that water in the range 300-350°C effectively extracted oils from shales still without formation of olefinic material characteristic of dry pyrolysis⁵². This methodology, termed hydrous pyrolysis, has become widely used by geochemists to simulate petroleum generation potential and quality.

Reaction paths and reactivities in aqueous systems in the critical region have been

reported in recent years for pure compounds modeling coal and shale kerogen functional group types. Klein has reported pyrolyses of benzyl ethers at 350-400°C in dense water noting that the products and product yields differ somewhat from those of non-aqueous pyrolysis⁵³. Several groups^{54 55 56} have determined reactivities of several organics in super-critical water which have suggested that multiple pathways in addition to simple homolytic are operating. Recently, Siskin, Katritsky, and co-workers produced an exhaustive survey the aquo-chemistries of acyclic, carbocyclic, and carbocyclic heterocyclic compounds in the range 250 to 350°C^{57 58 59}. The latter workers report high conversions, for example, of olefins, alcohols, aldehydes and aliphatic ethers in water at 250°C with product patterns characteristic of ionic reactions. Above 350°C, they find free radical derived thermolytic products approaching par with those from ionic paths and suggest that water would have less effect on product slates at higher temperature. However, they do not report pressure effects and in the (poorly delineated) critical region of a complex water hydrocarbon mixture, the relative stabilization of ionic intermediates would depend strongly upon the density, and therefore pressure, of the system. This is an area which deserves further attention.

At Amoco Oil Company in the early '70s an investigation of the reactivity of resids and bitumens in supercritical water revealed that the quality of heavy oil products was improved in the presence of group eight metal salts⁶⁰. For example, treatment at 400°C in an aqueous fluid (fluid density ca. 0.3 g/ml) containing ruthenium chloride, increased the H/C atom ratio of a Texas vacuum resid (1.43 to 1.52) and of a topped Athabasca bitumen (1.46 to 1.48). These results pointed to a reductive environment although no added hydrogen was present. With a high sulfur resids and tar sands oils, 50-80% metals removal (Ni, V) and 70-80% desulfurization could be achieved. From an IL#6 coal, 55% overall desulfurization was realized in liquids and recovered solids.⁶¹,

In this work, olefins were found to react facilely in the WCR. Thus, hex-1-ene, in addition to isomerizing rapidly to its internal isomers, gave hexane, pentane and CO₂ (very small amounts of hexan-2-one and hexan-3-one also formed). In the presence of dissolved ruthenium or rhodium salts, the hexenes were converted almost quantitatively n-hexane and n-pentane in a 2/1 mol ratio with CO₂ accounting for the missing carbon. Hexan-1-ol and hexaldehyde gave the same paraffinic products indicating that the olefin reacts by hydration, dehydrogenation, decarbonylation, and the shift reaction to give pentane and two mols of hydrogen (actual or virtual) which appears as hexane. The activity of dissolved salts in this process, shown as hexane yield in a 2 hr experiment at 350°C in the figure to the right, peaks sharply for ruthenium and is small

for 3rd row salts. Addition of base remarkably enhances the activity. The rather simple product slate contrasts with the observations of Siskin *et al*^{41 42} which would suggest a more complex product mixture. The strong dependence of conversion on the catalyst type points to a metal-organic pathway which would provide another alternative to simple ionic or radical products. From XPS results, ruthenium was recovered as an hydrous oxide mainly in the III state and other salts presumably follow a similar course in SC water. The reaction course appears consistent with dehydrogenation of alcohol to aldehyde and hydrogenation of olefin to paraffin as slow steps in the sequence. This would further be consistent with soluble metal alkoxides being key intermediates in the process. Although speciation in the WCR are not known, alcohol dehydrogenation via alkoxide is has been recorded⁶². The activity enhancement at high pH would accord with such intermediates. Coal solubilization using metal alkoxides reported by Stock⁶³ supports this view. Reports of coal⁶⁴ and shale⁶⁵ liquefaction in methanol and methanol-water might similarly involve alkoxides. Ross and Blessing have discussed hydride transfer as a reducing path in alcohol systems⁶⁶.

Other oxides as MnO₂ or TiO₂ were poor catalysts but had a promotional effect with the group eight metals. The graph shows that for hexene to hexane sequence, the activity of metal oxide promoted ruthenium catalysis relative to neat Ru ion (k_{prom}/k_{neat}) is quite substantial MnO₂. Very likely, these oxides are also dissolved in the WCR, but their function is not known. Probing experiments showed that toluene and benzaldehyde with Ru in SC water gave benzene and CO₂ analogously to the olefin process. These unsaturate reactions thus might be a source for the reducing environment in the aqueous SC region which

could be used syn-fuel conversions.

High reductive capacity of glucosidic biopolymers based on the alcohol and aldehyde chemistries with metal catalysts in the aqueous critical region might therefore be anticipated. Recently, stilbene was found to be reduced by glucose in an aqueous solution of RuCl₃ at 350-375°C (McCollum, unpublished observation).

From these background considerations, use of ligno-cellulosic bio-waste as a reductive material with coal appears to have industrial potential. Some attractive aspects include:

1. It is a relatively high value application of the waste.

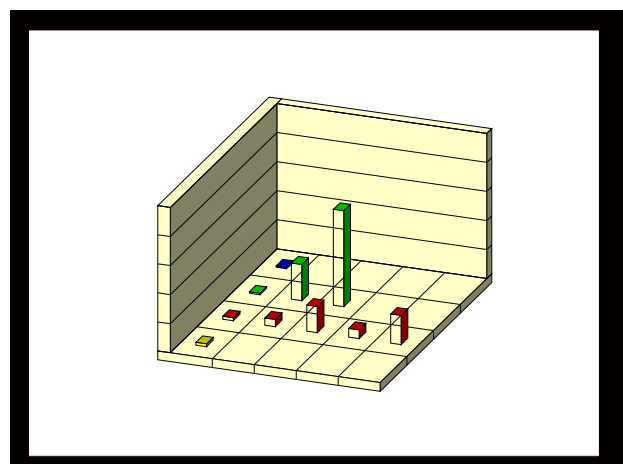
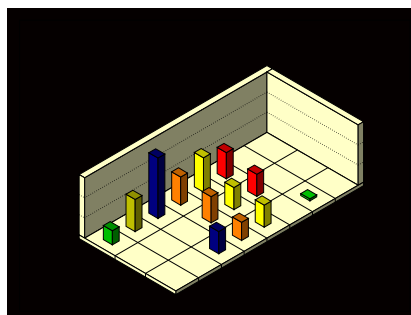


Figure 1 Catalyst Activity based on Hexene Conversion to Hexane



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Figure 2 Metal Oxide Promoters

2. It's reductive potential is thermodynamically high if suitable reaction paths are found.
3. The waste material has already been collected for other processing or more likely, disposal purposes.
4. The waste is a renewable resource, i.e., it is CO₂ neutral to the environment.
5. The approach can probably convert most non-reused wastes to assets.
6. Sufficient ligno-cellulosic biowaste is generated in the U.S. to co-process a significant fraction of the annual coal production.
7. Reactions in the WCR will detoxify contaminants introduced with both the waste biomass and the hydrocarbon co-feed.

There are also areas of concern including:

1. A successful process will probably require high pressure vessels, but compression would be either autogenous (batch system) or hydrostatic (flow system) eliminating the need for gas compression.
2. Catalyst retention, either by fixed bed or by recycling of active sludge would be required, if expensive catalysts prove necessary.
3. To minimize transportation costs, syn-fuels processing plants and biowaste collection points should be reasonably close.

The technical proposal drawn from these results embraces aqueous co-processing ligno-cellulosic wastes together with bitumens, refinery resids, and low H/C coal or shale kerogens (particularly "Type II" kerogens) Key features are the need for a liquid-like fluid density in the aqueous critical region and use of group eight metal catalysts in a high pH environment to direct decomposition of the biopolymers.

d2. Anticipated Results

Processes optimized for liquefying and/or upgrading variously coal synfuels, shale concentrates, and very likely, tar sands bitumens and refinery vacuum resids should ultimately emerge from this project. The processes should operate at milder temperature/time severities compared with conventional processing but will employ higher (hydrostatically generated) pressures.

Conversion of wastes to useful and environmentally benign products will provide a valuable alternative to waste management planners and firms. Although the processes will pull in the time frame for shale and particularly coal liquefaction costs reach parity with petroleum, probably they will be of immediate interest to oil refiners for treating

resids. They will also provide a valuable outlet for waste material otherwise causing disposal problems and thus be attractive to waste management firms. Sugar cane or corn product manufacturers could also use the approach as an outlet for using their wastes. Fuel applications for municipal waste are already being examined and use here would be a prominent candidate as an alternative route. Because catalysts compatible with WCR conditions will be unconventional, catalyst manufacturers will have to supply a new market built around WCR processing. A number of small companies and University projects dealing with SC fluid processes (e.g., Modek Corp., Phasex Inc., U. Texas-Austin) would have an interest in promoting this work.

d3. Significance of Phase I Effort

Since relatively little work has been reported on reactivity and reaction paths of bio-matter under these conditions, and this chemistry will necessarily need to be emphasized in phase I, but "proof of concept" experiments with representative synfuels and cellulosic reductants will be done. These and a preliminary economic scoping will would form the basis for a phase II proposal.

In phase II, a catalyst development program would be initiated to determine activity, sensitivity to inhibitors, catalyst robustness and life or recovery and recyclability. We would also explore reactor configurations (batch, stirred tank, slurry flow) and feed systems and carry out bench scale demonstrations. Investigation of the chemistry of the conversion reactions would be continued through this period to guide catalyst development. Economic projections based on bench scale data would be done.

e. Phase I Technical Objectives

Phase I will emphasize the chemistry of ligno-cellulosic matter in the WCR in the presence of group 8 metal ions, particularly that related to hydrogen transfer to hydrogen deficient materials. Both model compounds and representative coal and shale kerogens will be used as hydrogen acceptors.

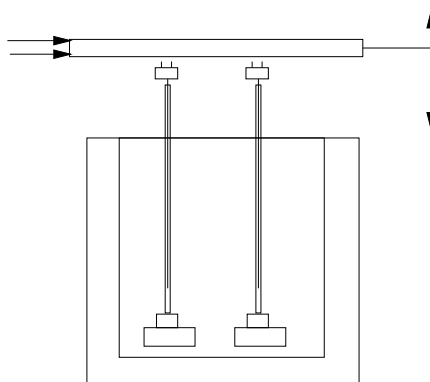
Questions we need to address include:

1. Establishing the nature of H-transfer from simple and polymeric glucosides to acceptor models for hydrogenation and for hydrocracking unsaturates and polyhydroxy aromatic materials.
2. Conducting a variables study (T, time, [reactants]/water ratio, [catalyst]).
3. Screening catalysts (does order found for olefins hold?).
4. Testing effectiveness of different bio-mass types.
5. Examining interactive effects with sulfur and nitrogen (not strong in olefin and resid work).
6. Doing "proof-of-concept" tests with coal and shale kerogens with cellulosic materials.

7. Economic scoping to identify cost sensitive aspects needing attention in further concept development.

f. Work Plan- Phase I

We propose to examine the experimental questions using small-scale tubing (Neavel type) reactor batch experiments. Several experiments at once can be carried out using a sand bath heater. Model compounds will be used to define reactions involved in cellulosic decomposition and interaction with hydrogen acceptors. Coals (Utah HVba), type I shale (Green River), and Athabasca bitumen will be used in the proof of concept experiments. Mono and disaccharides, cellulose, and pulped paper will be used as "donor" sources. Water will generally be used in 3/1 weight excess; the water charge will be designed to nearly fill the system at reaction temperature. The system will be de-aerated prior to heating. We will measure gas (weight loss, GC), liquid (weight, GC, IR, Oil-Resin-Asphaltene for synfuel feeds), and solids (weight, extractables, ash, elemental analyses as warranted) to determine conversions and products.



Specifically, we propose to examine:

Figure 3 Micro-Reactor System

1. Reaction of glucose, a reducing and a non-reducing disaccharide, and cellulose, anisole and guaiacol (models to assess ether cleavage and de-oxygenation in lignin like models) in water at two temperatures (e.g. 275 and 350°C, two reaction times, neat and with Ru, at autogenous and basic pH.
2. Reaction of cyclo-octene (to reduce side reactions which in acyclic olefins compete with saturation) to establish the hydrogenation-dehydrogenation equilibrium with glucose under the above conditions.
3. Screening group 8 metal salts with cyclo-octene under a condition set selected from step 2.
4. Examine reactions of *n*-nonylbenzene (for side-chain cracking) and 2-*n*-hexyltetralin (for aromatic dehydrogenation-cracking) with Ru and glucose at a condition set selected from step 2.
5. Examine reactants of step 4 and of cyclo-octene with Ru and glucose with Mo, W and Mn oxides to determine promotional effect on cracking and hydrogen-transfer.
6. Examine conversion of pulped paper as a ligno-cellulose at conditions selected

from model compound runs.

7. Proof-of-concept runs of pulped paper with above syncrude types..

Some areas which should be examined in any continuing work include total pressure effects, a two-phase solvent system such as water/toluene, and other biowastes potential reductants.

Based upon the proof-of-concept experiments, a scoping economic evaluation will be done to determine order of magnitude cost and more importantly at this stage, to identify the most cost sensitive areas which require attention in any further work.

g. Project Description - Phase I

1. Project Objective

The applicant shall study the chemistry of catalysed decomposition of ligno-cellulosic and derivative matter in the water critical region (WCR) and its interaction with hydrogen deficient substrates, first model compounds and then synfuels. These results will initiate design of a process for utilising biowaste as an effective hydrogen donor for liquefying and upgrading coal and shale kerogens.

2. Project Description

The work to be performed consists of the following tasks:

1. Assembly of mini-reactor system for small scale batch work.
2. Study of behavior of ligno-cellulosic materials with Ru salts in the WCR and of hydrogen transfer from these systems to model olefin and aromatic acceptors.
3. Multi level process variable study of the glucoside donor-unsaturated acceptor processes.
4. Screen group 8 metal salts for hydrogen transfer activity and screen group 5, 6, and 7 metal oxides as promoters of hydrogen and transfer.
5. Conduct proof-of-concept co-conversions of coals and shale kerogens with biomass and biomass waste (e.g. paper) in the WCR.
6. Conduct a scoping economic study of a conceptual process cost and to identify the most cost sensitive aspects of it.
7. Prepare Final Report.

3. Performance Schedule

Task 2.1 will be completed within one month after start of work.

Task 2.2 will be completed within two months after start of work.
Task 2.3 will be completed by three months after start of work.
Task 2.4 will be completed by four months after start of work.
Task 2.5 and 2.6 will be completed by five months after start of work.
Task 2.7 will be completed by six months after start of work.

h. Related Research

Dr. John D. McCollum, principal investigator of the proposed project, has worked on several aspects of the three synfuel sources, coals, shales and tar sands since 1973. Initially, the work focused on conversions in water in its critical region; ten patents were generated from this effort. For several years, he was concerned with a chemical approach to concentration of hale kerogen, work from which two patents issued. Most recently, he has been concerned with approaches to moderate severity liquefaction of coal and shale kerogens based upon the nature of the crosslinks of the macromolecules. A patent application based upon this work is pending. Earlier in his career at Amoco, Dr. McCollum was active in mass spectrometry, a field which has proven valuable as GC-MS evolved to a potent analytical tool for synfuels.

Dr. Ken Robinson, key team member of the proposed project, has been deeply involved in numerous coal liquefaction and other synfuel projects for the last 16 years. He has been successful in obtaining a patent for the Amocat family of liquefaction catalysts used in some of the H-Coal program at Catlettsurgh, KY.

Dr Rodney Mieville, the other key team member, has been intimately involved in the science of adsorption, since the start of his technical career. He has studied adsorption on reforming catalysts, molecular sieves and more recently was involved in a unique adsorbent system emission control of automobiles during cold-start. He is well qualified to participate on the research team on this project and is currently involved on developing drinking water carbons under an SBIR grant from the EPA.

i. Key Personnel

Dr. John D. McCollum (Principal Investigator)

Ph.D. Organic Chemistry, 1957, Harvard University
A.M. Organic Chemistry, 1951, Harvard University
B.S. Chemistry, 1949, University of Illinois

Experience-

1990-present: Consultant Synfuels

Consultant in synfuel chemistry.

1988-1989: Amoco Oil Company

Research Associate

Exploratory research on resid and bitumen thermal chemistry. Project leader,

biomimetic methane oxidation.

1986-1988: Amoco Corporation

Research Associate

Kerogen structural features and reactivity; organic geochemistry.

1982-1985: Amoco Oil Company

Research Associate

Oil shale beneficiation, liquefaction. Organic-mineral bonding in and mineral separation from coals, shales, and tar sands.

1966-1981: Amoco Oil Company

Project Manager

Cool plasma and aqueous super-critical hydrocarbon chemistry. Shale, coal, biomass liquefaction, microbiological desulfurization and denitrogenation.

1960-1965: Amoco Oil Company

Senior Project Chemist

U.S. Government contract research in radiation chemistry (Air Force) and fluorine oxidizer chemistry (ARPA).

1953-1959: Standard Oil Company (Indiana)

Project Chemist

Platinum catalytic reforming. Organic mechanistic mass spectrometry.

Fellow, American Institute of Chemists; member, American Chemical Society, Chicago Catalysis Society.

19 Patents, 10 publications, a book chapter.

Publications:

E.R. Alexander, M.R. Kinter, J.D. McCollum, "*Mechanism of Formation of Dibenzoylfurazane Oxide from Phenylmethylcarbinol*", J. Am. Chem. Soc. **1950**, 72, 801.

E.R. Alexander, J.D. McCollum, D.E. Paul, "*Synthesis of Ethyl t-Alkyl Cyanoacetates*", J. Am. Chem. Soc. **1950**, 72, 4791.

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S. Meyerson, J.D. McCollum, "*Organic Ions in the Gas Phase. X. Decomposition of Benzaldehyde under Electron Impact*", J. Am. Chem. Soc. **1963**, 85, 1739.

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J.D. McCollum, W.F. Wolff, "*Chemical Beneficiation of Oil Shale*", Energy Fuels **1990**, 4, 11.

Patents:

J.R. Coley, B.L. Evering, J.D. McCollum, "*Hydroforming Light Naphtha*", US 2,861,964.

P. Fotis, J.D. McCollum, "*Hydrogenation Method*", US 3,324,018.

J.F. Connolly, R.F. Flannery, J.D. McCollum, "*Electroreduction of Aromatic Compounds to their 1,4-dihydro Derivatives*", US 3,699,020.

J.D. McCollum, L.M. Quick, "*Process for Recovering and Upgrading Hydrocarbons from Oil Shale and Tar Sands*", US 3,948,754; US 3,958,755.

J.D. McCollum, L.M. Quick, "*Process for Upgrading a Hydrocarbon Fraction*", US 3,960,706; US 3,960,708; US 3,989,618.

J.D. McCollum, L.M. Quick, "*Process for Recovering Upgraded Products from Coal*", US 3,983,027; US 3,983,028; US 3,988,238.

J.D. McCollum, L.M. Quick, "*Process for Recovering and Upgrading Hydrocarbons from Tar Sands*", US 4,005,005.

J.D. McCollum, L.M. Quick, "*Process for Recovering and Upgrading Hydrocarbons from Oil Shale*", US 4,151,068.

J.D. McCollum, "*Method for Detecting Underground Conditions*", US 4,199,026; US 4,266,608.

I. Ginsburgh, J.D. McCollum, "*Method for Detecting an Underground Flame Front Using Resistance Probes*", US 4,210,868.

I. Ginsburgh, J.D. McCollum, "*Induction Coil Method for Detecting an Underground Flame Front*", US 4,210,867.

W.F. Wolff, J.D. McCollum, "*Method for Treating Shale*", US 4,584,088; US 4,668,380.

Dr. Ken Robinson (Team member)

D.Sc. Ch.E. 1970, Washington University-St. Louis

M.S. Ch.E. 1964, University of Michigan

B.S. Ch.E. 1963, University of Michigan

Experience-

11/89 to 4/92: Amoco Corporation

Manager, Technical University Relations

Technical liaison with major universities in the United States. Technology transfer and coordination of external research.

11/84-01/89: Amoco Oil Company, Research and Development

Research Associate

Exploratory process research on heavy oil conversion, asphaltene solubility-solids formulation, and coal-resid coprocessing.

01/80-11/84: Standard Oil (Indiana)

Director, Coal Utilization

01/73-01/80: Amoco Oil Company, Research and Development

Project Manager

Petroleum Refining Research and Synfuels

1/65-1/73: Monsanto Company

Senior Development Engineer

Member of AIChE, ACS, Chicago Catalysis Society

Professional Engineer in Illinois

5 Patents, 14 Publications

Publications:

1. K. K. Robinson, and D. E. Briggs, "*Isothermal Pressure Drop Across Banks of Finned Tubes*," Heat Transfer-Los Angeles, Chemical Engineering Progress Symposium Series, Vol. 62, No. 64, 177 (1966).
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Ph.D. Physical Chemistry, 1964, University of Western Ontario, Canada, Thesis:
Photo-Addition of Methyl Mercaptan to Olefins
ARIC Chemistry, 1953, Northern Polytechnic London University, England

Experience:

1964-1992: Amoco Oil Research and Development
Associate Research Scientist

Worked on a variety of projects including combustion kinetics, oil additives and catalysis, petroleum processes, adsorption, and inorganic membranes. The catalytic work involved all aspects of catalysis including reaction kinetics, coke and poisoning deactivation, synthesis and characterization and assessment of adsorbent and catalytic materials.

1954-1961: British Petroleum Research and Development
Research Chemist

Member of the ACS, RSC (Royal Society of Chemistry), NATAS (Thermal Society), and the Catalysis Society of North America. Chairman of Surface Acidity Task Group of D.32 Committee ASTM
6 Patents, 25 Publications

Publications:

1. D. M. Graham, R. L. Mieville, R. H. Pallen, and C. Sivertz, "*Photo-Initiated Reactions of Thiols and Olefins, I. The Thiyl Radical Catalyzed Isomerization of Butene-2 and 1,2-Ethylene-d₂*," CANADIAN JOURNAL OF CHEMISTRY, Volume 42 (1964).
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18. R. L. Mieville, presentation at the Symposium on Multimetallic Catalysts Presented before the Division of Petroleum Chemistry, Inc., American Chemical Society in Seattle on March 20-25, 1983, entitled "*Platinum-Rhenium Interaction: A Temperature-Programmed Reduction Study*."
19. R. L. Mieville, presentation at the Symposium on Zeolite and Shape Selective Catalysis Presented at the AIChE Annual Meeting in Houston on March 29-April 2,

1987, entitled "*Interacrystalline Zeolite Diffusion.*"

20. R. L. Mieville and M. G. Reichmann, presentation at the Symposium on Preparation and Characterization of Catalysts Presented Before the Division of Petroleum Chemistry, Inc., American Chemical Society, Los Angeles Meeting on September 25-30, 1988, entitled "*Temperature-Programmed Desorption Study of CO on Pt Reforming Catalysts.*"
21. R. L. Mieville, D. M. Trauth, and K. K. Robinson, General Papers (Poster Session) Presented Before the Division of Petroleum Chemistry, Inc., American Chemical Society in Miami Beach on September 10-15, 1989, entitled "*Asphaltene Characterization and Diffusion Measurements.*"
22. R. L. Mieville, D. M. Trauth, and K. K. Robinson, presentation at the Symposium on Convection and Diffusion in Porous Catalysts at the AIChE Annual Meeting in San Francisco on November 5-10, 1989, entitled "*Asphaltene Characterization and Diffusion Measurements.*"
23. B. L. Meyers and R. L. Mieville, "A Comparative Study of TGA and TPR on Ni-W Hydroprocessing Catalysts," (Paper # 111, ACS Meeting).
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Patents:

1. R. L. Mieville, "*Improvements in or Relating to the Production of Oxygenated Organic Compounds,*" US 882,863.
2. R. L. Mieville, "*Middle Distillate Fuel Oil Compositions Having Improved Pumpability,*" US 3,807,975.
3. R. L. Mieville, "*Middle Distillate Fuel Oil Compositions Having Improved Pumpability,*" US 3,807,990.
4. R. L. Mieville, "*Catalyst for Selective Hydrocracking of Alkylbenzenes,*" US 4,171,290.
5. R. L. Mieville, "*Reforming with a Catalyst Comprising Iridium, Zirconia, and Alumina,*" US 4,297,205.
6. R. L. Mieville, "*Methods to be Used in Reforming Processes Employing Multi-Metallic Catalysts,*" US 4,048,058.

j. Facilities/Equipment

Mega-Carbon has their laboratory and corporate offices in St. Charles, IL. The research facilities provide a full service organization in which all resources are under one roof: chemical engineering, computer technology, process assembly, and maintenance. Additionally Mega-Carbon has a full complement of chemical research equipment including UV spectrometers gas chromatographs, analytical balances, temperature controllers, furnaces, and test rigs. Mega-Carbon recently completed research on an improved drinking water carbon for the Environmental Protection Agency through a Phase I SBIR grant. Additionally Mega-Carbon is located near Northwestern University, in Evanston IL, where it is possible to have analyses run on the adsorbents to determine surface area, examine its microstructure via scanning microscopy, and measure its adsorption capacity.

k. Consultants

Formal consultancies will not be used in Phase I.

l. Similar Grant Applications, Proposals, or Awards

No prior, current, or pending support for proposed work.

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Mega-Carbon Proposal

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