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**The Extraction of Bitumen from
Western Tar Sands**

**Annual Report
July 1990 - July 1991**

**Alex G. Oblad
James W. Bunker
Milind D. Deo
Francis V. Hanson
Jam D. Miller
J. D. Seader**

Work Performed Under Contract No.: DE-FC21-89MC26268

**For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880**

**By
University of Utah
Departments of Fuels Engineering, Metallurgical Engineering,
and Chemical Engineering
1471 Federal Way
Salt Lake City, Utah 84102**

April 1992

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EXECUTIVE SUMMARY

Principal Investigator

Alex G. Oblad

Two Whiterocks bitumen fractions (cut points: 617 and 728 K) were evaluated for potential asphalt applications. The results indicated that the 617 K plus bitumen fraction had excellent physical properties and passes the specifications for an AC-10 viscosity graded asphalt. The 728 K plus bitumen fraction failed to meet the current asphalt cement specifications.

Since naphthenic hydrocarbons were the major constituents of the low boiling range fraction (477-617 K), it can be considered as an excellent candidate for the production of high density aviation turbine fuels.

The major constituents of the low molecular weight portion (477-728 K) of Whiterocks bitumen are naphthenic hydrocarbons containing 1 to 5 rings. These include alkylcyclohexanes, alkyldecalins, tricyclic terpanes, steranes, tetracyclic terpanes, and pentacyclic terpanes. Lesser amounts of aromatic hydrocarbons are also present in this fraction. These aromatic hydrocarbons can be classified as alkylbenzenes, benzomonocycloparaffins, phenyl (cyclohexyl) alkanes, alkyl-naphthalenes, benzodicycloparaffins, benzotricycloparaffins, alkylacenaphthenes, and naphthalene monocycloparaffins. Only trace amounts of paraffins, C_{19} - C_{21} , were detected in this study and were identified as isoprenoid hydrocarbons. Several tricyclic carboxylic acids (dehydroabiatic acids) and pentacyclic terpenoid carboxylic acid (hopanoid acid) were also detected. Most of the compounds identified in this study are similar to the biological markers found in Green River oil shale.

The intensity of signals in the range of 0.5-1.0 ppm of PMR spectra of bitumen fractions suggests that the bitumen consists largely of methyl groups attached to alkyl chains, naphthenic rings, and naphtheno-aromatic rings. Solution phase ^{13}C NMR indicates that the native Whiterocks bitumen consists of long alkyl chains (normal and isoprenoid chain) bound to polycyclic naphthenic, naphtheno-aromatic and aromatic cores. The results from GC-MS, Py-MS, FTIR, PMR and ^{13}C NMR confirmed this finding.

The Oil Sand Research and Development Group at the University of Utah has managed to acquire sufficient mineral ore samples from the Asphalt Ridge oil sand deposit to characterize three potential mining/surface recovery sites on the deposit. The crushed ore will be used in all process research and development aspects of the program.

A study of a diverse group of oil sand bitumens from the oil sand deposits of Canada and the United States was undertaken to verify the relationship between the bitumen viscosity and its

carboxylic acid content. Viscosity of each of the bitumens was determined in the temperature range (60-90° C) and all of them were found to deviate slightly from Newtonian behavior.

The bitumens were fractionated using a modified SARA (saturates, aromatics, resin and asphaltenes) type analysis. The separated fractions were examined by transmission and specular reflectance FTIR spectroscopy. The FTIR analysis indicated that the carboxylic acids in the bitumen accumulated in the polar fractions and particularly in the resin fraction. Although it was apparent from analyses that in general a bitumen with higher viscosity contained a larger amount of carboxylic acids, a precise relationship could not be established. The fractional compositions of the bitumens indicated that the viscosity of a given bitumen cannot be correlated with its asphaltene content alone.

The data from this study clearly indicated that the bitumen viscosity was related to the amount of carboxylic acids distributed among its polar fractions. Earlier studies had indicated that asphaltenes played an important role in determining the viscosity of bitumen. It is suggested that both asphaltenes and carboxylic acids present in the resin fraction interact in a synergistic manner to determine the viscosity of bitumen.

The release of surface active compounds to the aqueous phase during hot water processing of oil sand distinctly effects bitumen recovery. The role of surfactant in the hot water process was investigated almost exclusively for the Athabasca oil sands. Our study of surfactant interactions was initiated with isolation of the natural surfactant present in the aqueous phase from hot water processing of Asphalt Ridge and Whiterocks oil sands from Utah. Many structural similarities for the isolated surfactant were observed, however, the amount of sublated substances from each oil sand bitumen differed by almost threefold, which correlates well with the tendency of stable froth formation during flotation.

Another surface chemistry investigation was aimed at improving bitumen recovery during the hot water process. Up till now, the solid phase interaction with bitumen and with the aqueous phase was of primary concern. In this regard, we have accepted that filming of air bubbles with oil is advantageous for effective gravity separation and flotation of bitumen from digested oil sand slurry. The probability of filming increases, the more the air-water interfacial tension prevails over the sum of the oil-water and the air-oil interfacial tensions. It has been found using model systems that optimum filming conditions exist for certain free surfactant concentration. The research on the influence of surfactant released from oil sand on filming of air bubbles will be continued and further evidence for the importance of this phenomenon is expected.

The efficiency of water-based separation of oil from sand

particles is dependent on the nature of the oil-sand association and a preliminary examination of this bonding has been completed. The degree of hydration of the sand surface at the time of contact with oil was related to the subsequent efficiency of the oil-sand separation process. Oil-coated sand particles which had intrinsic water left on their surface during sample preparation were easily processed in hot water separation experiments, and 64 to 90% of the oil was removed. On the other hand, only 1 to 23% separation and oil recovery was possible when a calcinated sand-oil mixture was used.

Important aspects of kerosene penetration into oil sand have been investigated. The natural oil sand porosity was measured and used to analyze the performance of the hot water process. The natural oil sand porosity accessible by diluent has a crucial impact on the reduction of bitumen viscosity, and influences the penetration time required for successful bitumen separation from oil sand by hot water processing. Thus the oil sand porosity is an important variable which determines appropriate operating conditions. Experimental results indicate that diluent penetration into the Asphalt Ridge oil sand (high porosity) is almost complete after 30 minutes, whereas for the Whiterocks oil sand (low porosity) the penetration process is much slower, and still not complete after 15 hours regardless of the ambient temperature.

For the first time an air-sparged hydrocyclone was used for scavenger flotation of the digested oil sand slurry, directly following primary recovery in the gravity cell. High investment and operating costs can be expected, due to huge amounts of oil sand slurry needed to be processed to recover the bitumen if conventional flotation machines are installed. In this regard, the high specific capacity air-sparged hydrocyclone (ASH), at least 100 times greater than conventional flotation equipment, offers some advantages for residual bitumen recovery from rougher tailings. In a preliminary investigation the 2-inch ASH system (throughput of 60-70 Lpm of diluted digested oil sand slurry) was evaluated in laboratory separation tests. Larger units would be used in pilot or plant scale testing. Approximately 55 to 65 percent of the process water was recovered in the overflow product for recycle. A high separation efficiency was achieved with respect to small, free bitumen droplets, while bitumen-sand aggregates reported to the underflow product.

The final task involved Whiterocks Utah bitumen concentrate clean-up. The separation efficiency of gravity sedimentation and centrifugation were compared. Final removal of residual water (<6 wt%) was also attempted in an electrostatic cell with a pulsating DC electric field. The lowest concentration of dispersed water attained was below 4 wt% while that of the fine minerals did not exceed 0.5 wt%.

The operability and reliability of the data obtained with the

coupled fluidized-bed reactor system for processing of Utah's oil sands have been significantly improved. Modifications of the laboratory unit have included installation of an up-to-date Hewlett-Packard computer system for process control and data acquisition, installation of an improved oil-sand feeder system, and upgrading of the reactors to provide better operation and control. Shakedown tests of the rebuilt reactor system using clean sand has shown encouraging results of the system itself and its control.

The erosion potential of the heat pipes has been investigated. Results of these studies have shown that the heat pipes will have a useful life exceeding that expected of the reactors and other critical equipment likely to be used in a commercial operation.

A novel approach to improving the efficiency of the combustion of the coked sand in a two-stage reactor arrangement has been evaluated via development of a mathematical model of this system. The results appear promising in that combustion in the two sequential reactors requires a smaller overall volume than that required in a single combustor reactor. Evaluation of the cost of this dual reactor system and its operation indicates that it will be a minor factor in the overall cost of the process.

Studies of fluidization efficiency in the laboratory apparatus has been carried out. A review of the available literature showed a great disparity in the prediction of the regimes of slugging and bubbling which can occur in our apparatus using our feed materials. An experimental program was carried out to provide critical data of these two regimes in our apparatus. The presence of the heat pipes in the reactors extends the desired bubbling zone while inhibiting the slugging pattern. A statistical analysis of the available data of the fluctuations of the pressure drop across the fluidized bed can be used to indicate the nature of the fluidization occurring in an operating reactor.

The Acrison feeder has been tested and shown to be a suitable device for feeding undiluted oil sands to a fluidized bed reactor. In the course of testing, several important feeding variables were identified and a set of preferred conditions for feeding was determined. The conditions for successful feeding of oil sands include the following; low auger speeds (<20 RPM); a water jacketed auger cylinder to maintain approximately 15°C feed temperature; and oil sand feed moisture content of <1 wt% on an air dry basis.

Ambient temperature testing of the 6 inch I D reactor confirmed the suitability of a modified L-valve for solids withdrawal. This solves a long-standing mechanical problem with fluidized bed reactors. Fluidization tests confirmed the U_{mf} predictive methodology previously reported and the existence of a U_{mf} and temperature relationship.

The rotary kiln process was evaluated as a possible option for the thermal processing of mined Utah oil sands, and a series of continuous-flow pyrolysis experiments were successfully conducted in a rotary-kiln reactor. The process variables investigated included the pyrolysis reactor temperature, the solids retention time in the pyrolysis zone, the sweep gas flow rate, and the bitumen content of the feed sand. The experimental results indicated that the pyrolysis temperature, and the solids retention time in the pyrolysis zone were the two most important variables affecting the hydrocarbon liquid and gas yields in the rotary kiln. The liquid product (C_5) yield generally decreased with increasing reactor temperature. Concomitant with this decline in the liquid yield, there was an increase in the light gas (C_1-C_4) yield. The liquid product yield increased with decreasing the solids retention time while the light gas yield decreased. No significant effect of the sweep gas flow rate on the product distribution and yields was observed. The quality of the bitumen-derived liquids was significantly better than that of the bitumen.

The process variable data obtained in this exploratory investigation indicated that a rotary kiln pyrolysis process could be a feasible alternative to a fluidized-bed thermal process for the production of an upgraded bitumen-derived hydrocarbon liquid from Utah oil sands. The pyrolysis temperature and the solids retention time in the pyrolysis zone were the two most important variables affecting the produced hydrocarbon liquid from gas yields in rotary kiln pyrolysis. The maximum C_5 plus hydrocarbon liquid yield, 68.7 wt%, was obtained at a reactor temperature of 798 K and a solids retention time of 10 minutes with the Whiterocks west-south oil sand sample. The liquid product (C_5 plus) yield generally decreased with increasing reactor temperature at a fixed solids retention time while the light gas ($C_1 - C_4$) yield increased and the coke yield decreased slightly. The quality of the liquid product generally declined as reactor temperature increased. The liquid product (C_5 plus) yield increased with decreased solids retention time at constant temperature while the light gas ($C_1 - C_4$) yield decreased. The coke yield was relatively insensitive to the solids retention time. The product distribution and yields and total liquid properties were independent of the sweep gas flow rate. The bitumen-derived hydrocarbon liquid produced in the rotary kiln reactor was significantly upgraded relative to the native bitumen. It would be an excellent hydrogen refinery feedstock. The lumped kinetic model used in the preliminary mathematical modelling study predicted the product distribution trends observed experimentally in the rotary kiln reactor with respect to both temperature and solids retention time.

The pyrolysis of bitumen-impregnated sandstone produces three primary product streams: C_1-C_4 hydrocarbon gases, a C_5^+ total liquid product, and a carbonaceous residue on the spent sand. The bitumen-derived hydrocarbon liquid was significantly upgraded relative to the native bitumen: it had a higher API gravity, lower

Conradson carbon residue, asphaltene content, pour point and viscosity and a reduced distillation endpoint relative to the native bitumen. The elemental composition was little different from that of the native bitumen except for the hydrogen content which was lower. Thus, integration of the bitumen-derived liquid into a refinery feedstock slate would require that it be hydrotreated to reduce the nitrogen and sulfur heteroatom concentrations and to raise the atomic hydrogen-to-carbon ratio.

The bitumen-derived liquid produced in a 4-inch diameter fluidized-bed reactor from the Whiterocks oil sand deposit has been hydrotreated in a fixed-bed reactor to determine the extent of upgrading as a function of process operating variables. The process variables investigated included total reactor pressure (11.0-17.2 MPa (1600-2500 psig)); reactor temperature (617-680 K (650-765°F)) and liquid hourly space velocity (0.18-0.77 LHSV). The hydrogen/oil ratio was fixed in all experiments at 890 m³/m³ (5000 SCF H₂/bbl). A sulfided Ni-Mo on alumina hydrodenitrogenation catalyst was used in these studies.

The extent of denitrogenation and desulfurization of the bitumen-derived liquid was used to monitor catalyst activity as a function of process operating variables and to estimate the extent of catalyst deactivation as a function of time on-stream. The apparent kinetics for the nitrogen and sulfur removal reactions were determined. Product distribution and yield data were also obtained.

The processing sequence, oil sand pyrolysis followed by hydrotreating, appeared to be a viable concept by which the Whiterocks oil sand resource could be exploited.

The 477-617 K (400-650°F) boiling range fraction of the hydrotreated bitumen-derived liquid would be an excellent candidate for high-density aviation turbine fuels. Catalyst activity during the hydrotreating of Whiterocks bitumen-derived liquid remained stable during 800 hours of operation and should remain reasonably stable for longer periods. The catalyst deactivation rate was 0.14°C/day (0.25°F/day). The reactivity of the bitumen-derived liquid was similar to the reactivity of shale oil.

The apparent reaction orders were 1.55 and 1.5 for nitrogen and sulfur removal, respectively. These fractional orders suggested the occurrence of many parallel first order reactions, each with a different first order rate constant. The activation energy for denitrogenation was 75.3 kJ/mol (18 kcal/mol) at lower conversions and temperatures where less refractory nitrogen-containing species reacted. At higher temperatures and conversions where the more refractory species reacted the activation energy was 184.1 kJ/mol (44 kcal/mol). The activation energy for desulfurization was 92.1 kJ/mol (22 kcal/mol) over the range of temperatures studied.

The conceptual methodology has been developed by which commercial scale ebulliated bed reactors can be scaled down to laboratory size for process development studies.

Supercritical fluid extraction of complex hydrocarbon mixtures is important in separation processes, petroleum upgrading and enhanced oil recovery. Extractions of a crude oil, a bitumen-derived liquid and bitumen were conducted at several temperatures and pressures with carbon dioxide and propane in order to assess the effect of the size and type of compounds that comprise the feedstocks on the extraction process.

It was observed that the pure solvent density at the extraction conditions was not the only variable governing extraction and that the proximity of the extraction conditions to the pure solvent critical temperature affected the extraction yields and the compositions of the extract phases. In fact, higher oil yields were obtained at lower solvent reduced densities when the extraction temperatures were in the vicinity of the pure solvent critical temperature.

In the crude oil and native bitumen extractions, it was observed that as the extraction time and/or the extraction pressure increased, heavier compounds were found in the extract phases. This preferential extraction was not observed with the bitumen-derived liquid. The nondiscriminatory extraction behavior of the bitumen-derived liquid was attributed to its thermal history and to the presence of olefins and significant amounts of aromatics.

Phase behavior calculations using the Peng-Robinson equation of state and component lumping procedures provided reasonable agreement between calculated and experimental results for the crude oil and bitumen extractions, but failed in the prediction of the bitumen-derived liquid extractions.

**Characterization of the Native Bitumen
from the Whiterocks Oil Sand Deposit**

Principal Investigator:	F. V. Hanson
Co-Principal Investigator:	M. D. Deo
Postgraduate Fellow:	C. H. Tsai

The characterization of the native Whiterocks bitumen and distilled boiling range fractions of the Whiterocks bitumen continued during the 1990-1991 contract period. The boiling range fractions were evaluated for various transportation fuel and asphalt applications. A bibliography specific to the Whiterocks oil sand deposit is presented in Appendix A.

SYNOPSIS

The native Whiterocks (Utah) oil sand bitumen was separated into several boiling range fractions for detailed analysis and characterization. The lighter fraction (477-617 K) was evaluated for use as a transportation fuel and the residues (>617 K and >728 K) were evaluated for use as road asphalts. The 617 K plus residue from the Whiterocks bitumen can be classified as a viscosity grade AC-10 asphalt whereas the 728 K plus residue failed to meet asphalt specifications. Apart from the asphalt specification tests, several sophisticated techniques were used to characterize these fractions. The detailed structure of the low molecular weight portions of Whiterocks bitumen (477-617 K and 617-728 K) was determined by combined gas chromatography and mass spectrometry (GC-MS). Several physical properties were also measured to evaluate the potential of the 477-617 K fraction as a high density-energy aviation turbine fuel. This lower molecular weight fraction

of the bitumen contained predominantly naphthenic hydrocarbons and lesser concentrations of aromatic hydrocarbons. This was confirmed by the FTIR spectra and by the GC-MS analyses. As a result, the 477-617 K fraction appeared to be an excellent candidate as a feedstock for the production of high density, aviation turbine fuels following mild hydrotreating. The heat of combustion, 135,500 BTU/gal., exceeded the specification for the high density/energy JP-11 aviation turbine fuel. The naphthenic hydrocarbons included alkylcyclohexanes, alkyldecalins, tricyclic terpanes, steranes, tetracyclic terpanes, and pentacyclic terpanes. The aromatic constituents were determined to be alkylbenzenes, benzomonocycloparaffins, phenyl(cyclohexyl)alkanes, alkylacenaphthenes, and naphthalene monocycloparaffins. These compounds were similar in nature to those found in the Green River shale oil.

The proton and carbon-13 nuclear magnetic resonance characteristics of the native Whiterocks bitumen were determined by comparing the spectra of the samples to literature assignments. The tentative structural assignments of pyrolysis products were also obtained from the spectra of Curie-point low voltage mass spectrometric analysis. The results obtained from proton magnetic resonance and carbon-13 nuclear magnetic resonance and pyrolysis mass spectrometry analysis suggested that the native bitumen consists mostly of short- and long-chain (i.e., normal and isoprenoid chains) alkylsubstituents attached to polycyclic naphthenic and naphtheno-aromatic moieties.

INTRODUCTION

A knowledge of the structural types present in the various boiling range fractions of the native bitumens from the oil sand deposits of Utah is important for the development of novel bitumen upgrading process concepts and/or for the modification of existing petroleum crude upgrading processes to accommodate bitumen feedstocks. In the past two decades, the chemical compositions of coal derived liquids and shale oils have been extensively investigated by various spectroscopic techniques ¹⁻⁴. On the other hand, the characterization of United States oil sand bitumens have received less attention ⁵⁻⁷.

Utah oil sand bitumens have specific gravities which range from 0.98 to 1.03, and H/C atomic ratios which range from 1.67 to 1.43.^{8,9} These properties are similar to those of reduced petroleum crude. The similarities in geochemical origins of oil sand bitumen and conventional petroleum suggest that refined products derived from the bitumen will be interchangeable with petroleum-derived products of the same boiling range. Therefore, it is expected that petroleum residuum conversion processes can be utilized for oil sand bitumen upgrading and refining. These include conventional delayed coking, hydroprocessing and delayed coking, hydrotreating and hydrocracking, hydroprocessing and catalytic cracking, and solvent deasphalting.¹⁰ It has been shown that hydroprocessing followed by delayed coking or catalytic cracking has a slight advantage over conventional delayed coking or solvent deasphalting.¹¹ Unfortunately, considerable amounts of less

valuable and poorer quality by-products cannot be avoided from most of these processes. The development of process concepts for the production of high density aviation turbine fuels led to proposals involving the mild hydrogenation of the appropriate boiling range fractions of oil sand bitumens.¹² The naphthenic nature of the Uinta Basin bitumens^{8,9} and of high-density aviation turbine fuels¹² led to the speculation that the 477-617 K boiling range fraction from the Uinta Basin bitumens or bitumen-derived hydrocarbon liquids might be excellent candidates for high-density aviation turbine fuels after mild hydrogen treatment to reduce organic nitrogen, sulfur and oxygen heteroatoms and to saturate aromatic species. This speculation was based primarily upon the analysis of a high density aviation turbine fuel which was determined to have an average empirical formula¹² given by: $(CH)_{3.48} (CH_2)_{8.72} (CH_3)_{3.93}$. On the other hand, the potential of Uinta Basin bitumens for asphalt production has also been recognized. An Asphalt Ridge bitumen that was subjected to a rolling thin film oven treatment (RTFO) met the established physical and chemical specifications for a viscosity grade AC-20 asphalt.^{9,10}

Detailed compositional information on petroleum liquids has been obtained by separating the compounds on a gas chromatographic column and identifying them by mass spectrometry. Most of the work in this area has been performed by geochemists, who have tried to establish a connection between the compounds identified in the samples and their biological origins.¹³ Apart from this application, the information can be used to evaluate various

enhanced oil recover (EOR) production schemes and processing strategies for the produced liquids.

There has been only one detailed study of the different types of compounds present in a Uinta Basin oil sand bitumen. The study was conducted by Reed¹⁴, who investigated two outcrop samples and three core-hole samples from the P.R. Spring oil sand deposit. Reed¹⁴ reported a distribution of tricyclic alkylated diterpanes, and pentacyclic triterpanes. There have been numerous studies on related materials, such as Green River oil shale.¹⁵⁻¹⁹ The similarity in the compounds identified in these investigations and those reported by Reed¹⁴, suggest a similar origin for the different types of hydrocarbon materials in the Uinta Basin.

The Utah oil sand bitumens contain about 40-70% nondistillable high molecular weight species (>811 K). Thus detailed structural information for these bitumens is somewhat difficult to develop; however, some structural information can be deduced from the various spectroscopic techniques.

Proton and ¹³C nuclear magnetic resonance (NMR) are particularly useful to delineate the main hydrogen and carbon types in a sample. These methods have been used to successfully characterize coal derived liquids, shale oils, crude oils, and Athabasca oil sand bitumen and bitumen-derived hydrocarbon liquids^{1,2,20-30}. Curie-point low voltage mass spectrometric analysis is a useful technique for determining the chemical structures of distillable components and of pyrolysis products produced from the nondistillable fractions. Therefore, tentative structural

assignments for complex mixtures can be made from the spectra obtained by pyrolysis-mass spectrometric (Py-MS) analyses.

The purpose of this study was to evaluate the potential of the Whiterocks oil sand bitumen for the production of asphalt by removal of the lower boiling components and for the production of high-density aviation turbine fuels from the 477-617 K fraction. The fractions were first separated by careful vacuum distillation. Asphalt specification tests were performed on each of the heavier fractions (617 K plus and 728 K plus). The lighter fraction (477-617 K) was evaluated as a potential source of high density-aviation turbine fuel. In addition, we have examined the composition of Whiterocks oil sand bitumen (Utah) using nuclear magnetic resonance and pyrolysis-mass spectrometry analyses. This work was undertaken in order to expand our knowledge of the composition of Utah's oil sand bitumens and to provide information for the evaluation and development of upgrading process concepts for these bitumens.

EXPERIMENTAL METHODS AND PROCEDURES

Raw Materials

The oil sand used in this study was a fresh, deep-mined sample of the ore from the open-pit mine on the west flank of the Whiterocks oil sand deposit. The bitumen was obtained by conventional Dean-Stark extraction of the mined oil sand ore from the Whiterocks deposit with toluene. The toluene was removed by careful rotary evaporation (Büchi Rotavapor RE 120) at 358 K at 20 mm Hg for 5 hours. Previous studies of laboratory scale extraction

with a variety of Utah oil sands--Whiterocks, P.R. Spring, Oil Sand Triangle, etc.--indicated that toluene was the superior solvent for the separation and recovery of the native bitumen.

Elemental analyses and physical properties were also determined to complete the characterization of these fractions. Detailed compositional analysis was accomplished by GC-MS and FTIR. These data were used to clarify the chemical nature of the fractions.

Vacuum Distillation/Fractionation

A modified vacuum distillation assembly was used for removing light ends from the Whiterocks bitumen.³¹ Instead of Claisen-type distillation column, a Vigreux Claisen type distillation column, packed with 5x5 mm Rasching rings was used for better separation. Two lower boiling range fractions, 477-617 K and 617-728 K of the bitumen were distilled overhead and collected for subsequent analysis.

Asphalt Specification Tests

Physical properties of the asphalt samples were measured at the State of Utah Department of Transportation Materials and Testing Laboratory. Procedures used were recognized standard specification tests for asphalt cement properties.³²

Elemental Analyses and Physical Properties Determination

The elemental analyses-carbon, hydrogen and nitrogen- of the native bitumen and the bitumen boiling range fractions were quantitatively determined using a Leco Carbon-Hydrogen-Nitrogen

Determinator, Model CHN-600. Sulfur contents were determined using a Leco Sulfur Determinator Model SC 132. A pycnometer (Mettler/Paar DMA 40 - Digital Density Meter) was used to measure the specific gravities of the bitumen fractions and a bomb calorimeter (Paar 1241 Automatic Adiabatic Bomb Calorimeter) was used to determine the heat of combustion of the bitumen and the overhead fractions. The specific gravities of the bitumen residues and the native bitumen were determined following the procedure outlined in the standard ASTM D70 test.

Simulated Distillation

The boiling point distributions of the native bitumen and the boiling range fractions were determined by simulated distillation. Before analysis, the samples were dissolved in dichloromethane. The analyses were performed on a programmed Hewlett-Packard Model 5730A gas chromatograph: the oven temperature was programmed from 243 to 623 K at 11°C/min and held at 623 K for 5 min; the injector temperature was 623 K; and the FID detector temperature was 673 K. The GC column consisted of a U-shaped 18" x 1/4" O.D. stainless steel tube packed with 3% Dexsil 300 on Anakrom Q. Boiling point temperatures were calibrated with a standard mixture of normal paraffins (C_3 - C_{44}).

Fourier Transform Infrared Spectroscopic Analysis

The Fourier transform infrared (FTIR) spectra were obtained with a Perkin Elmer 1600 instrument in the absorbance mode. Absorbance spectra of the native bitumen and the bitumen residue

were obtained by directly smearing the samples on KBr windows. Absorbances for the lower boiling range fractions of the bitumen were determined in a liquid cell with a pathlength of 0.015 mm.

Gas Chromatography - Mass Spectrometry

The bitumen boiling range fractions were analyzed by gas chromatography/mass spectrometry. The gas chromatographic analyses were performed on a Hewlett-Packard Model 5890A instrument equipped with a capillary injector and a linear temperature programmer. The standard operating conditions were as follows: the column was a 15m x 0.25mm open tubular column coated with SE-54 (DB-5, J&W Scientific); the helium carrier gas flow rate was 4 ml/min; the oven temperature was programmed from 323 to 523 K at 2°C/min and held at 523 K for 5 min or from 323 to 573 K at 5°C/min and held at 573 for 5 min; and the injector temperature was 563 K. The mass spectrometer used had an ion trap detector (ITD - Finnegan MAT 700) operated with a scan range of 40 to 450 amu at 2 scan/sec. Mass spectra were determined at an ionizing voltage of 70 ev, and a source temperature of 503 K.

Curie-Point Low Voltage Mass Spectroscopic Analysis

Curie-point low voltage mass spectroscopic (LV-MS) experiments were carried out using an Extranuclear Model 5000-1 Curie-point pyrolysis mass spectrometry (PY-MS) system. Twenty-five microgram quantities of the native bitumen were coated on ferromagnetic wires from dichloromethane suspensions. The wires were inserted into borosilicate glass reaction tubes and placed in the vacuum system

of the mass spectrometer. The ferromagnetic wires were inductively heated at approximately 100°C/sec to an equilibrium temperature of 883 K. The total analysis time was 15 seconds, LV-MS conditions were as follows: the inlet temperature was held at 339 K, the electron ionization voltage was 12 ev (set value), the scanning rate was 1000 amu/s, the total scanning time was 24 seconds, and the mass range scanned was m/z 40-340.

Carbon-13 and Proton Nuclear Magnetic Resonance Spectra

Samples for the measurement of ^{13}C -NMR spectra were prepared by dissolving approximately 200 to 250 mg of the sample in two milliliters of deuterated dichloromethane. The ^1H and ^{13}C -NMR spectra were obtained with a Varian XL-300 FT spectrometer. The ^{13}C spectra were obtained using a sweep width of 23.98 MHz, a data acquisition time of 0.62 seconds, a 90° pulse of 25 microseconds and a pulse delay of five seconds after each transient. Tetramethysilane (TMS) was used as an internal standard to calibrate the chemical shifts.

RESULTS AND DISCUSSION

The analytical data for the native bitumen and the boiling range fractions; elemental composition, atomic H/C ratio, specific gravity, heat of combustion, and simulated distillation, are summarized in Table 1. The sulfur content appeared to be almost uniformly distributed throughout the bitumen boiling range. On the other hand, the high contents of nitrogen and oxygen in the bitumen residue suggest that these heteroatom compounds exist predominantly

Table 1. Properties of the Native Bitumen and Bitumen Fractions from the Whiterocks Tar Sand (Utah) Deposit

Fraction	Native Bitumen	477-617 K Bitumen Fraction	617-728 K Bitumen Fraction	>728 K Bitumen Fraction
wt%	100	6.1	14.6	78.2 ^a
Property				
Elemental analysis				
C, wt%	85.80	86.49	86.23	85.43
H, wt%	11.55	12.27	11.75	10.84
N, wt%	1.10	0.21	0.55	1.52
S, wt%	0.40	0.37	0.42	0.36
O, wt%	1.15	0.66	1.05	1.85
Atomic H/C ratio	1.62	1.70	1.64	1.52
Specific gravity (289 K/289 K)	0.985	0.8989	0.9409	1.003
Gravity, °API	12.2	25.9	19.0	9.9
Heat of combustion,				
Btu/lb (Gross)	18,600	19,120	18,780	--
Btu/lb (Net)	17,700	18,070	17,820	--
Btu/gal (Net)	145,500	135,500	139,900	--
Simulated distillation ^c				
IBP, K	511	--	--	--
Volatility				
(<1000°F), wt%	44.1	--	--	--
IBP-477 K, wt%	0.0	--	--	--
477-617 K, wt%	6.2	--	--	--
617-811 K, wt%	37.9	--	--	--
>811 K residue, wt%	55.9	--	--	--

^a 1.1 wt% of bitumen was lost during the fractionation

^b Determined by difference.

^c 5 wt% - 595 K; 10 wt% - 654 K; 15 wt% - 697 K; 20 wt% - 729 K; 25 wt% - 746 K; 30 wt% - 759 K; 40 wt% - 795 K.

in the high molecular weight portion of the bitumen. Therefore, hydrotreating the whole bitumen to remove heteroatom compounds might prove difficult and would be accompanied by the consumption of considerable amounts of hydrogen to eliminate the nitrogen compounds.

Aviation Turbine Fuel Potential

A comparison of the physical properties of the 477-617 K fraction of the Whiterocks bitumen with those of a thermally-stable high density aviation turbine fuel and with the tentative specifications for high-density, high-energy jet fuel is presented in Table 2. The physical properties of 477-617 K fraction indicate the potential for use as a high-density advanced jet fuel. Although the heat of combustion per unit mass in this fraction is slightly lower, it can be improved by hydrotreating at mild hydrogenation conditions. Hydrotreating would also increase the hydrogen content and the atomic H/C ratio. The net heat of combustion per unit volume exceeds the values reported for the JP-11 specifications and for a thermally-stable high density aviation turbine fuel. The specific gravity versus the heat of combustion curve is plotted in Figure 1 for a range of aviation turbine and Ram-jet fuels. It is interesting to note that the 477-617 K fraction of the Whiterocks bitumen falls on the curve prior to mild hydrotreatment.

Table 2. Comparison of the Properties of the 477-617 K Fraction of the Whiterocks Bitumen, a Thermally-Stable High Density Jet Fuel and the Tentative Specifications for High Density, High Energy Jet Fuels

Property	477-617 K Fraction of Whiterocks Bitumen	Thermally Stable High Density Jet Fuel ^a JP-8	Density Aviation Turbine Fuels Specifications	
			JP-11	
Specific Gravity (289 K / 289 K)	0.8989	0.843	>0.840	>0.900
API Gravity, °API	25.9	36.3	<37.0	<25.7
Atomic H/C Ratio	1.70	1.89	--	--
Hydrogen content, wt%	12.3	13.7	13.0	12.0
Heat of combustion,				
Btu/lb (Gross)	19,120	19,500	--	--
Btu/lb (Net)	18,070	18,340	--	--
Btu/gal (Net)	135,500	129,000	>130,000	>135,000
Freeze Point, K _(max)	<206	198	227	227

^a This fuel sample was provided by the Wright Aeronautical Laboratories at Wright-Patterson Air Force Base.

Asphalt Potential

The results of the asphalt specification tests for the bitumen residues (>617 K and >728 K) are presented in Table 3. The viscosity, 1,100 poise, classifies the >617 K bitumen fraction as an AC-10 viscosity-graded asphalt. The tests indicated that the kinematic viscosity and penetration meet the established specifications. A ductility of >100 cm for a 1,100 poise viscosity material is considerably higher than the 75 cm minimum specification. The second bitumen residue fraction (>728 K) did not meet required specifications for any viscosity-graded asphalt; however, this bitumen fraction could be blended with a suitable

Figure 1 Aviation Turbine and Ram Jet Fuel Density versus Net Heating Value

Table 3. Results of Asphalt Specification Tests for Bitumen Residual Fractions

Property	>617 K Bitumen	>728 K Bitumen	AC-10 Specification
Viscosity			
333 K (poise)	1,100	7,005	1,000 $\pm$ 200
408 K (centistokes)	260	640	250 (minimum)
Ductility 277 K, cm	100*	broken	75 (minimum)
Penetration @ 298 K			
100 g, 5 sec (1/10 mm)	110	29	80 (minimum)
Test on Residue from Rolling Thin-Oven Test			
Viscosity @ 333 K (poise)	1,857	11,010	4,000 (maximum)
% loss on heat	0.90	0.11	0.50 (maximum)

aromatic flux oil to produce commercial penetration-grade asphalts. The light fractions (477-728 K) of the bitumen could also be used as an FCC or hydrocracker feedstock for the production of transportation fuels.

Fourier Transform Infrared Spectra Analysis

The approximate positions of the bands observed in FTIR spectra and their probable assignments are presented in Table 4. The principal chemical constituents of the Whiterocks bitumen are most likely naphthenic hydrocarbons as indicated by the observation of strong- and medium-intensity bands due to C-H stretching, C-H bending, and skeletal vibrations and relatively weak intensity

Table 4. Probable Assignments of Infrared Absorption Bands in Whiterocks Native Bitumen and Boiling Range Fractions

Absorption band, cm^{-1}	Assignment
3480	N-H stretching in pyrolytic type compound
3400 - 3200 (broad)	O-H and N-H stretching in multiple H-bonded compound
2960 $\pm$ 10	C-H stretching (asymmetrical) in $-\text{CH}_3$
2920 $\pm$ 10	C-H stretching (asymmetrical) in $-\text{CH}_2$
2870 $\pm$ 10	C-H stretching (symmetrical) in $-\text{CH}_3$
2850 $\pm$ 10	C-H stretching (symmetrical) in $-\text{CH}_2$
2727	C-H stretching vibration at the bridgehead carbon
1700 - 1710	Carbonyl C=O vibration
1600	C=C stretching vibration (conjugated) and skeletal ring vibration
1450 $\pm$ 20	C-H asymmetric bending ($\text{C}-\text{CH}_3$ group)
1380-1370	C-H symmetric bending ($\text{C}-\text{CH}_3$ group)
1385 - 1375 and 1370 - 1365	C-H bending ($-\text{C}(\text{CH}_3)_2$ group)
1170 - 1140	$\text{C}-(\text{CH}_3)_2$ skeletal vibration
875 - 865	
814	
767	Aromatic C-H bending (out-of-plane)
743	
698	

bands near 1600 cm^{-1} . This speculation is confirmed by the relatively high H/C atomic ratio, 1.62, which is characteristic of naphthenic crudes. Evidence for the presence of gem-dialkyl substituents in the naphthenic rings is found in the doublet of skeletal vibration bands near 1366 and 1376 cm^{-1} (approximately equal intensity) observed in the FTIR spectra of the 477-617 K and 617-728 K fractions.

Gas Chromatography - Mass Spectroscopy Analysis

The chromatograms of the 477-617 K and 617-728 K fractions of the Whiterocks bitumen are presented in Figures 2 and 3, respectively. The mass spectrum of the peaks marked (1 through 18) on the chromatograms are presented in Figures 4 through 8. Identification of individual compounds are based on the comparison to known spectra from the literature.^{13-19, 33-40} The normal alkane carbon number range investigated was C_{11} to C_{20} for the former fraction and C_{20} to C_{35} for the latter. It should be noted that the fractions were separated based on their boiling points and contained all the chemical types in that particular boiling range. This makes it difficult to separate all the compounds on a GC column. Many compounds co-elute and resolution is not very good, which makes it difficult to identify each individual compound. However, a great deal can still be learned about the basic skeletal features of these compounds by comparison of their fragmentation patterns with the ionization schemes of known compounds and, more importantly, by comparison with the types of compounds known to be present in these types of materials.

Figure 2 Reconstituted Ion Chromatogram of the 477-617 K Fraction from the Whiterocks Bitumen

Figure 3 Reconstituted Ion Chromatogram of the 617-728 K Fraction of the Whiterocks Bitumen

Figure 4. Mass Spectra of Bicyclic Sesquiterpenoids in the Whiterocks Bitumen

Figure 4. Mass Spectra of Bicyclic Sesquiterpenoids in the Whiterocks Bitumen (cont.)

Figure 5. Mass Spectra of Tricyclic Terpanes in the Whiterocks Bitumen

Figure 6. Mass Spectra of Steranes in the Whiterocks Bitumen

Figure 7. Mass Spectra of Tetracyclic Terpanes in the Whiterocks Bitumen

Figure 8. Mass Spectra of Pentacyclic Terpanes in the Whiterocks Bitumen

The results of these analyses indicated that the 477-617 K and 617-728 K bitumen fractions contain mostly naphthenic hydrocarbons (1- to 5-rings) and small amounts of naphtheno-aromatic hydrocarbons. In this work, several peaks were identified as C_{19} , C_{20} , and C_{21} isoparaffins. This finding is consistent with the discovery of researchers working with related hydrocarbon materials such as Green River shale. Anders and Robinson¹⁷ found predominantly naphthenic compounds and some isoprenoids in the saturate fraction of the Green River shale bitumen. Normal alkanes were absent or present in very small concentrations.

Saturated Cyclic Hydrocarbons

C_nH_{2n} Series: The molecular ions for the compounds in the series C_nH_{2n} (1-ring) occurred at m/e's of 210, 224, and 280. These are single-ringed naphthenic compounds of carbon number C_{15} , C_{16} and C_{20} . In the cycloalkane constituents from Green River shale bitumen, carbon numbers C_{17} and C_{18} were absent or present in very low concentrations. The major fragmentation ions (m/e's) are 69, 83, 97, 111, and 125. This suggests that these compounds are polyalkyl-substituted cyclohexanes with a strong likelihood of being tetraalkyl-substituted cycloalkanes. As has been pointed out by Anders and Robinson¹⁷, it is speculated that numerous carotenoids existing in nature lead to tetraalkyl-substituted cyclohexanes. These polyalkyl-substituted cyclohexanes are minor constituents in the lighter fraction of Whiterocks bitumen.

C_nH_{2n-2} Series: Parent molecular ions identified in the C_nH_{2n-2} series (2 rings) were at m/e's of 152, 166, 180, 194, 208, 222,

278, and 292. These correspond to bicyclic naphthenes in the carbon number range C_{11} - C_{21} . It is difficult to identify these compounds as alkyl hexahydroindanes or alkyl-substituted decalins. The major fragmentation ions are 67, 81, 95, 109, and 123 (Figure 4). These compounds show marked similarity to that of bicycloalkanes detected in the saturated fraction from Green River oil shale.¹⁷

C_nH_{2n-4} Series: The components of the series C_nH_{2n-4} (3-rings) exhibit nearly identical mass fragmentation patterns and have a prominent m/e of 191 in their mass spectra. The molecular ions corresponding to these components have m/e's of 234, 262, 276, 290, 304, and 318. These tricyclic terpanes were observed in the 650-850°F fraction. The compounds correspond to carbon numbers in the range C_{18} - C_{31} . These tricyclic terpanes resembled mass spectra similar to those reported for compounds found in coal and plant resins, crude oil, Green River oil shale, and Athabasca oil sands.^{13,17,35} The mass spectra of several of these components are presented in Figure 5. These tricyclic terpanes are believed to have pentacyclic triterpanes as their parent compounds.

C_nH_{2n-6} Series: The molecular ions (m/e's 274, 316, 330, 372, 386, and 400) of compounds in the C_nH_{2n-6} (4-rings) series were determined. These tetracyclic naphthenes are in the carbon number range C_{20} - C_{29} . Three mass spectra which suggest that these compounds are C_{27} (cholestane), C_{28} (ergostane), and C_{29} (stigmastane) steranes are presented in Figure 7. The first mass spectrum presented in Figure 7 has an (M-H)⁺ ion at 273 and its fragmentation pattern is

different from α -phyllocladane.¹³ This compound is probably an isomer of kaurane or iosene. Two tetracyclic terpanes ($C_{26}H_{42}$ and $C_{27}H_{44}$) were identified as 17, 21-secohopanes that have been confirmed to be present in the hydrocarbon resource found in sedimentary rocks.³⁶ These compounds are thought to be derived from the pentacyclic hopanoids by cleavage of the C-17(21) bond during diagenesis or maturation.³⁶ A tetracyclic terpane ($C_{23}H_{40}$) had the molecular ion at m/e 316 and gave strong intensities of fragmentation peaks at m/e of 55, 67, 81, 95, 109, and 177 (Figure 7). The low intensity of the $(M-15)^+$ peak suggested that this compound probably had a structure similar to 17, 21-secohopanes except that there is no gem-dimethyl substituent in C-4. Instead, this compound only has one methyl substituent in the C-4 position (I).

C_nH_{2n-8} Series: The molecular ions (m/e 's of 384, 398, 412, 426, and 440) of compounds in the C_nH_{2n-8} (5-rings) series are characterized as pentacyclic triterpenoids (Figure 8). These are

in the carbon number range C_{28} - C_{32} . Gammacerane ($C_{30}H_{52}$) is the most often reported compound in this class. The C_{28} , C_{29} , C_{31} and C_{32} hopanes have also been observed in different petroleum materials.

Aromatic Hydrocarbons

The parent molecular ions identified as aromatic hydrocarbons are tabulated in Table 5. The types of aromatic compounds can be classified as follows: C_nH_{2n-6} series (alkylbenzenes); C_nH_{2n-8} series (benzomonocycloparaffins and phenyl (cyclohexyl) alkanes); C_nH_{2n-10} series (alkylnaphthalenes and benzodicycloparaffins); C_nH_{2n-12} series (benzotricycloparaffins); and C_nH_{2n-14} series (alkylacenaphthenes or naphthalene monocycloparaffins). The proposed structures of these aromatic hydrocarbons are shown in II to X.

Table 5. "Parent" Molecular Ions of the Aromatic Hydrocarbons in the Light Ends (477-728 K) of Whiterocks Bitumen

Compound Classification	Molecular Ion	Empirical Formula	Probable Structure Assignment
$C_n H_{2n-6}$	190	$C_{14} H_{22}$	Alkylbenzene (II)
	218	$C_{16} H_{26}$	"
$C_n H_{2n-8}$	146	$C_{11} H_{14}$	Benzomonocycloparaffins (III)
	160	$C_{12} H_{16}$	or phenyl (cyclohexyl) alkanes (IV)
	174	$C_{13} H_{18}$	"
	188	$C_{14} H_{20}$	"
	202	$C_{15} H_{22}$	"
	216	$C_{16} H_{24}$	"
	230	$C_{17} H_{26}$	"
	244	$C_{18} H_{28}$	"
	258	$C_{19} H_{30}$	"
	272	$C_{20} H_{32}$	"
$C_n H_{2n-10}$	242	$C_{18} H_{26}$	Benzodicycloparaffins (VI,VII)
	256	$C_{19} H_{28}$	"
	298	$C_{22} H_{34}$	"
	340	$C_{25} H_{40}$	"
	382	$C_{28} H_{46}$	"
$C_n H_{2n-12}$	170	$C_{13} H_{14}$	Alkyl naphthalenes (V)
	184	$C_{14} H_{16}$	"
	324	$C_{24} H_{36}$	Benzotricycloparaffin (VIII)
$C_n H_{2n-14}$	196	$C_{15} H_{16}$	Alkylacenaphthenes or naphthalene
	224	$C_{17} H_{20}$	monocycloparaffin
s (IX or X)	252	$C_{19} H_{24}$	"
	280	$C_{21} H_{28}$	"
	322	$C_{24} H_{34}$	"

In general, the most likely progenitors of these phenyl (cyclohexyl) alkanes compounds are thought to be derived from tricyclic and pentacyclic terpenoids or even steroids by aromatization of one-ring and cleavage of the center or B-ring bond during maturation.³⁹ The alkylbenzenes could be of mono-, di-, tri- or tetraalkyl variety and isoprenoid compounds or degraded caretenoids are believed to be their source compounds. The C_nH_{2n-8} series aromatics are more likely to be tetralin homologs than other possible structural types possible.¹⁹ For the C_nH_{2n-10} series, 3-ring cycloalkano aromatic compounds are a stronger possibility than other structural types. At higher molecular weights, it is difficult to distinguish between numerous combinations of rings and double bonds possible. Hence, for these compounds, only the structural possibilities have been pointed out.

Oxygenated Compounds

A large number of tricyclic and pentacyclic carboxylic acids have been detected in heavy oils and oil sand bitumens (Athabasca)⁴⁰. In the present study, several carboxylic acids have also been detected. These include benzodicycloparaffinic carboxylic acids ($C_{16}H_{20}O_2$, $C_{17}H_{22}O_2$, and $C_{20}H_{28}O_2$) and pentacyclic carboxylic acid ($C_{28}H_{46}O_2$). The compound having the empirical formula $C_{20}H_{46}O_2$ is a probable isomer of dehydroabietic acid which can be found in coal and plant resins and in the geosphere.

Proton Nuclear Magnetic Resonance

The 1H spectra of the native Whiterocks bitumen and the 477-

617 K fraction of the bitumen are presented in Figures 9 and 10. The distribution of hydrogen into various types is summarized in Table 6. Olefinic hydrogens in the native Whiterocks bitumen amounted to 1.2%. No olefinic protons were found in the 477-617 K fraction of the bitumen. This observation agreed with the results from gas chromatography-mass spectrometry (GC-MS) analysis of this fraction ⁴¹. This suggests that the olefinic bonds in the native Whiterocks bitumen occur in the high molecular weight portion of bitumen. This is consistent with the results of Thiel and Gray ²⁶ who reported that olefinic bonds could be present in the resin fraction of oil sand bitumen.

The range of the methyl hydrogens shift was from 0.5 to 1.0 ppm. The chemical shifts for the methyl hydrogens depend upon the length of carbon chain to which the methyl group is attached and the number of adjacent hydrogens ^{42,43}. The data in Table 6 suggests that a considerable number of methyl groups are present in these samples. The presence of polymethylated cyclic hydrocarbons was inferred from the results of the GC/MS analyses of the lighter fractions (477-617 K and 477-728 K) of the native Whiterocks bitumen ⁴¹.

The chemical shifts in the range from 1.0 to 1.9 were due to methylene hydrogens in long-chain or branched hydrocarbons, cyclic methylene hydrogens, and methide hydrogens. The broadened resonance signals in this range (Figures 9 and 10) suggest that there are high concentrations of naphthenic species in the Whiterocks bitumen fractions. The sharp resonance signal at 1.26

Figure 9. Proton NMR Spectrum of the Native Whiterocks bitumen

Figure 10 Proton NMR Spectrum of the 477-617 K Fraction of the Whiterocks Bitumen

Table 6. Distribution of Hydrogens in the Whiterocks Oil Sand Bitumen and the 477 - 617 K Fraction of the Whiterocks Bitumen

Hydrogen Type	Chemical Shift Region (ppm ^a)	Whiterocks Native Bitumen (%)	417-617 K Fraction of Whiterocks Bitumen (%)
<u>Aliphatic Hydrogens</u> (total)	0.5 - 4.0	90.0	94.4
Alpha Hydrogens (total)	1.9 - 4.0	8.8	13.5
Methylene Hydrogens Alpha to Aromatic Rings	2.3 - 4.0	5.4	7.9
Methyl Hydrogens Alpha to Aromatic Rings	1.9 - 2.3	3.4	5.6
Methyl Hydrogens to Aromatic Rings	0.5 - 1.9	81.2	80.9
Beta + Gamma Hydrogens (total)			
Naphthenic Hydrogens Beta to Aromatic Rings, β -CH ₂ - and β -CH ₃ to Aromatic Rings and Alkane Methylene Hydrogens	1.0 - 1.9	46.2	34.5
γ , γ '-CH ₃ to Aromatic Rings and Alkane Methyl Hydrogens	0.5 - 1.0	35.0	46.4
<u>Olefinic Hydrogens</u> (total)	4.0 - 6.0	1.2	0.0
<u>Aromatic Hydrogens</u> (total)	6.0 - 9.0	8.8	5.6
1-ring	6.0 - 7.3	4.6	3.3
2-ring	7.3 - 7.8	2.3	1.3
3-ring	7.8 - 9.0	1.9	1.0

^aRelative to TMS

ppm in Figure 9 can be assigned to acyclic methylene. Although the signal intensity is strong, the width of the signal is not narrow enough to suggest the domination of long normal alkane groups. Because methyl branching in alkanes tends to broaden the methylene resonance signal, the higher the degree of branching, the greater the width of the methylene signal ⁴³. The evidence of both long chain normal and branched paraffinic groups in the Whiterocks bitumen is supported by ¹³C NMR. This observation will be discussed in the next section.

The low aromatic hydrogen content suggests a high degree of aromatic substitution of aliphatic chains and naphthenic rings.

Carbon-13 Nuclear Magnetic Resonance

The ¹³C NMR spectra of the native Whiterocks bitumen and the 477-617 K fraction of the Whiterocks bitumen are presented in Figures 11 and 12, respectively. The carbon aromaticities, f_a , (includes olefinic carbons) of these samples are 23.3% and 16.7%, respectively. The carbon aromaticity of the native Whiterocks bitumen is slightly lower than that reported for shale oils² [24.4%]. The resonances in the range between 0 and 70 ppm are due to linear and branched alkanes, cycloalkanes, and alkyl substituents associated with aromatic or hydroaromatic rings ⁴⁴⁻⁵³. The detailed assignments for these resonances are presented in Table 7. The carbon types indicated by the spectra in Figure 11 and 12 were compared with model compound results reported ¹. Many of the peaks are presumed to be due to steranes, and tricyclic, tetracyclic, and pentacyclic triterpanes, which were previously

Figure 11. Carbon-13 NMR Spectrum of the Native Whiterocks Bitumens.

Figure 12. Carbon-13 NMR Spectrum of the 477-617 K Fraction of the Whiterocks Bitumen

Table 7. Aliphatic Carbon Types Identified by ^{13}C NMR from Whiterocks Bitumen Fractions.^a

Peak Number	Chemical Shift (ppm) ^b	Assignment ^c
1	11.6	CH_3^d and (ethyl branch)
	12.2 - 12.6	
	14.3	
	14.6	
	16.5	
2	19.2	
3	19.8	
	20.1	
4	22.7	
5	22.9	
6	24.8	
7	25.2	
	27.4	
	27.8	
8	28.3	
9	29.8	
10	30.05	

Table 7. Aliphatic Carbon Types Identified by ^{13}C NMR from Whiterocks Bitumen Fractions.^a (cont)

Peak Number	Chemical Shift (ppm) ^b	Assignment ^c
11	32.2
12	33.1
	33.5	$\text{Ar}-\overset{*}{\text{CH}_2}-$
13	34.9
14	37.1	(isolated methyl branch)
15	37.7
	39.3
16	39.8
	42.5	C or CH_2

^aReferences 1, 25-27

^bRelative to internal, standard tetramethylsilane (TMS)

^cAsterisk indicates carbon position.

^dMethyl groups in bridgehead position of steranes, e.g., C_{18} , C_{19} in 5- α Cholestane and 5- α Ergostane⁴⁵

determined to be present in the Whiterocks bitumen by GC/MS analyses ⁴¹.

The signals at 14.3, 22.9, 32.2, 29.8, and 30.05 ppm belong to α , β , γ , δ , and ϵ -carbons of aliphatic hydrocarbons with chain length $n_c \geq 10$, respectively ^{49, 51}. The ratio of normal methyl (peak 1) to long chain methylene (peak 10 or peak 9 and 10) can be used to determine the average normal chain length L . The average normal chain length is given by

$$L = 6 + 2(A_9 + A_{10})/A_1. \quad (1)$$

where A_n is the area under peak n ¹. The average normal chain length was calculated to be 26 after substituting peak areas into the Equation (1). This value is higher than for that calculated for the Athabasca oil sand bitumens ⁵⁴ [10] and lower than that calculated for the Green River oil shale bitumen ²⁷ [32]. It should be noted that cyclic groups connected by a long alkyl chain would contribute to peak 10 without contributing to peak 1. Therefore, the average normal chain length of 26 could be slightly higher than the true value.

In addition to long normal paraffin chains, a significant amount of long isoprenoid chains were also detected as evidenced by the series of peaks listed in Table 7 (e.g., peaks 2, 3, 4, 6, 7, 8, 12, 13, 14, 15, and 16). Only traces of paraffinic species were detected in the study of the 477-617 K and 477-728 K fractions of the Whiterocks bitumen by GC-MS analyses ⁴¹. Therefore, these alkyl chains appear to be attached to aromatic, naphtheno-aromatic and

naphthenic cores. These compounds have boiling points above 728 K.

The ratio of any of the four polyisoprene peaks (peaks 3, 6, 12, and 15) to the long-chain methylene (peak 10) can be used to determine the relative abundance of long-chain isoprenoid and normal chains in the sample ²⁷. This value is 0.58 for the native Whiterocks bitumen. This value is higher than the value for oil shale bitumen [0.47] and for shale oils ²⁷ [0.28].

In the aliphatic carbons chemical shift range, the peaks in the 15-20 ppm range are due to rings, or branched alkanes and/or naphthenes. The broad resonance in the chemical shifts between 20 and 55 ppm is due to cyclic alkanes and alkylaromatics. These signals are most likely associated with carbons of fused-ring/naphthenic cycloalkanes ^{44,45,47,48,50,52,53}. The cycloalkanes would be present as a variety of isomers and stereoisomers that cause additional changes in the chemical shifts. The resulting complexity of the 20-55 ppm band makes any structural details difficult to interpret.

The lack of a sharp peak at a chemical shift of 30.05 ppm in the 477-617 K fraction of the Whiterocks bitumen suggests that there are no alkyl chain substituents or long chain alkanes in this sample. This observation was verified by GC-MS analysis of this sample ⁴¹.

The presence of a variety of aromatic carbons is indicated in the 110-165 ppm region. The resonances in this range are due to unsubstituted aromatic and polycyclic aromatic, heterocyclic and phenol type species.

Pyrolysis-Mass Spectrometry Analysis

The result of Curie-point low voltage MS analysis of Whiterocks bitumen is given in Figure 13. The tentative structure assignments for the pyrolysis products from the Whiterocks bitumen are as follows:

alkenes: (m/z : 42, 56, 70, 84, 98, 112, 126, 140, 154, 168, 182),
condensed naphthenes: (m/z : 81, 95(96), 109(110), 123(124),
137(138), 151(152), 165(166), 179(180), 193(194), 207(208),
221(222), 236, 250), 2 rings/molecule; m/z : 149, 163, 177, 191,
205, 219, 233, 3-5 rings/molecule; m/z : 189, 202, 217, 4
rings/molecule); alkylbenzenes (m/z : 106, 120, 134); alkyl-naphth-
alenes (m/z : 156, 170, 184, 198); phenols (m/z : 122, 136, 150);
alkylphenanthrenes (m/z : 178, 192, 206, 220, 234); alkylchrysenes
(m/z : 228, 242, 270); alkylpyrene/alkylfluoranthenes (m/z : 202,
216, 230, 244, 258, 272, 286, 300), alkylpicenes (m/z : 278, 292);
alkyltetrahydrophenanthrenes (m/z : 182, 196, 210, 224, 238, 252,
280); alkyltetralins/alkylindole (m/z : 131, 145, 159, 173, 187),
alkyloctahydrophenanthrenes, trinaphthenebenzenes (m/z : 141, 155,
169, 183, 197); alkylhydroxytetralins (m/z : 148, 162, 176);
alkylquinoline (m/z : 157, 171, 185, 199, 213, 227, 241); alkylcarbazole
(m/z : 167, 181, 195, 209, 223); and alkylacridine/alkylbenzoquinoline
(m/z : 179, 193, 207, 221, 235). The probable structure for the ion peaks, m/z , 208, 222, 236, 250 is shown by structure (XI).

Figure 13 Curie-Point Desorption Mass Spectrum of the Native White rocks Bitumen

The predominant species in the Whiterocks bitumen were condensed (fused ring) naphthenes. The majority of the cyclic units (alicyclic, naphthenics, aromatics) in the Whiterocks bitumen contain 1 to 5 rings. It should be noted that the native Whiterocks bitumen consists of about 30% saturated hydrocarbons which are predominantly naphthenes. The strong intensity of condensed naphthenic hydrocarbons (Figure 13) suggests that a portion of the naphthenic hydrocarbons could be derived from the resin and asphaltene fractions. The identified polynuclear aromatics in this study are similar to the polynuclear aromatics found in the volatile products from the thermal decomposition of Athabasca oil sand bitumen and Green river oil shale.^{3,55} The Py-MS result does not detect sulfur species because of the low concentration of sulfur originally present in the native Whiterocks bitumen.

The information obtained from the GC-MS analyses of the 477-617 K fractions of the Whiterocks bitumen, coupled with the PMR, ¹³C NMR, FTIR, and Py-MS analyses of native Whiterocks bitumen suggests that the native Whiterocks bitumen consists mostly of short- and long-chain (normal and isoprenoid) alkylsubstituents attached to polycyclic naphthenic, naphtheno-aromatic and aromatic moieties.

CONCLUSIONS

Two Whiterocks bitumen fractions (cut points: 617 and 728 K) were evaluated for potential asphalt applications. The results indicated that the 617 K plus bitumen fraction had excellent physical properties and passes the specifications for an AC-10

viscosity graded asphalt. The 728 K plus bitumen fraction failed to meet the current asphalt cement specifications.

Since naphthenic hydrocarbons were the major constituents of the low boiling range fraction (477-617 K) of the Whiterocks bitumen, it can be considered as an excellent candidate for the production of high density aviation turbine fuels.

The major constituents of the low molecular weight portion (477-728 K) of Whiterocks bitumen are naphthenic hydrocarbons containing 1 to 5 rings. These include alkylcyclohexanes, alkyldecalins, tricyclic terpanes, steranes, tetracyclic terpanes, and pentacyclic terpanes. Lesser amounts of aromatic hydrocarbons are also present in this fraction. These aromatic hydrocarbons can be classified as alkylbenzenes, benzom monocycloparaffins, phenyl (cyclohexyl) alkanes, alkyl naphthalenes, benzodicycloparaffins, benzotricycloparaffins, alkylacenaphthenes, and naphthalene monocycloparaffins. Only trace amounts of paraffins, C_{19} - C_{21} , were detected in this study and were identified as isoprenoid hydrocarbons. Several carboxylic acids were also detected. They are tricyclic carboxylic acids (dehydroabietic acids) and pentacyclic terpenoid carboxylic acid (hopanoid acid). Most of the compounds identified in this study are similar to some of the biological markers in fossil energy resources such as Green River oil shale.

The significant intensity of signals in the range of 0.5-1.0 ppm of PMR spectra of bitumen fractions suggests that the bitumen consists largely of methyl groups attached to alkyl chain,

naphthenic rings, and naphtheno-aromatic rings. Solution phase ^{13}C NMR indicates that the native Whiterocks bitumen consists of long alkyl chains (normal and isoprenoid chain) bound to polycyclic naphthenic, naphtheno-aromatic and aromatic cores. The results obtained from various spectroscopic techniques (i.e., GC-MS, Py-MS, FTIR, PMR and ^{13}C NMR) confirm this finding.

FUTURE ACTIVITIES

The Whiterocks bitumen will be distilled into an 811 K overhead fraction and an 811 K plus residual fraction. The 811 K overhead fraction will be analyzed by high resolution gas chromatography mass spectrometry analysis. This analysis will then provide a basis with which to initiate a detailed evaluation of the following processing sequences:

**Acquisition of the Bitumen Impregnated
Sandstone from the Asphalt Ridge Oil Sand Deposit**

Principal Investigator: F. V. Hanson

INTRODUCTION

The second phase of the oil sand acquisition program was completed during the 1990-1991 contract period. The funding for this sample acquisition trip was provided by the University of Utah, Center of Excellence Oil Sand Project. A deposit reconnaissance was made on September 5, 1990 by F. V. Hanson. K. M. Clem and J. E. Faussett accompanied Hanson in the selection of the sites which were to be mined in the subsequent visit. Three sites identified during the reconnaissance trip were identified as the Northern Pit, the County Pit, and the Southern Pit. The actual mining operation was conducted on September 19, 1990, with equipment and operators provided Mr. John E. Fausett.

This segment of the final report contains a geologic summary of the Asphalt Ridge oil sand deposit and a description of the three sites selected for mined ore sample acquisition. The report is based upon information derived from the reconnaissance trip, published geologic and technical reports, and unpublished geologic file reports and field notes. A bibliography specific to the Asphalt Ridge oil sand deposit is presented in Appendix B.

DESCRIPTION OF THE ASPHALT RIDGE OIL SAND DEPOSIT

Location

The Asphalt Ridge deposit is located in the north-central portion of Uintah County, Utah, being approximately 5 miles west of the town of Vernal, Utah. The central (County) site of the deposit

is accessible from U.S. Highway 40, the northern site from State Highway 121, and the southern pit site from the Naples-Bonanza Road. Several dirt roads provide access to various other outcroppings and subsurface areas. The Asphalt Ridge deposit lies along the ridge by the same name and trends in a southeast direction.

Geology

The deposit is located on the northeastern flank of the Uinta Basin. The exposed strata consists of the Cretaceous Mesaverde Group and the Eocene-Oligocene Duchesne River Formation. The Mesaverde Group in this area is divided into two formations: the Asphalt Ridge Sandstone and the overlying Rim Rock Sandstone. These formations are separated by a thin tongue of Mancos Shale. The Asphalt Ridge and the Rim Rock members are composed of marine sandstones. The thickness of the Rim Rock formation varies from less than 100 to over 300 feet, due to variable truncation of the unit prior to deposition of the younger strata.

The designation of tertiary strata in the area has been the subject of considerable discussion. The Uinta formation overlies the Green River Formation which overlies the Wasatch Formation at Raven Ridge to the south; however, the Green River Formation and the Wasatch Formation have not been identified at Asphalt Ridge. The Uinta Formation - Duchesne River Formation contact is also unclear at Asphalt Ridge. Since these two formations are similar lithologically and their contact gradational, this report will combine the two units. The Duchesne River Formation lies

unconformable on the Rim Rock Sandstone and consists of interbedded fluvial sandstones with associated shales and conglomerates.

The dip of the Rim Rock beds ranges from 8 to 30 degrees, while the Duchesne River beds dip 9 to 20 degrees to the south and southwest. This angular unconformity pinches out several thousand feet of the Wasatch, Green River and Uinta formations. Asphalt Ridge is part of a northwest-southwest trending set of hogback ridges, extending south to Raven Ridge. This hogback is the result of regional subsurface thrust faulting from the Uinta Mountains to the north. Numerous minor faults and joints occur along the length of the ridge and trend from north 50 west degrees to north 70 west degrees.

Lithology - Character of Reservoir

Oil impregnation occurs along the strike of the Asphalt Ridge, within the Rim Rock sandstone and the Duchesne River Formation. The Rim Rock sandstone is fairly uniform in lithology, being a well sorted, high chert (60%) content sand. The chert grains are sub-angular while the quartz grains are sub-rounded. The clastic beds of the Duchesne River Formation commonly contain saturation. These beds range from thin seams to almost 100 foot thick zones; however, the saturated beds can not be traced continuously from one end of the deposit to the other. Although they commonly contain rich zones, they are variable in size and distribution.

Various authors [56,57] have suggested that the oil probably originated from the Green River Formation and migrated updip along the Tertiary - Cretaceous unconformity. Sulfur isotope studies

support this theory [58].

Resource Estimate

Numerous resource estimates have been reported for the Asphalt Ridge deposit [56,57,59-63]. Spieker [61] calculated proven reserves at 900 million barrels with 400 million in the Rim Rock formation and 500 million in the Duchense River formation and estimated a total resource of nearly 2 billion cubic yards in the outcrop. The estimate was based on the assumption that the deposit extended 1.5 miles into the subsurface. Kayser [56] estimated nearly 700 million barrels in the Rim Rock formation for a 5,250 acre parcel on the deposit. The Utah Geological and Mineral Survey [60] classified the deposit as a giant deposit with 1,048 million barrels of gross bitumen-in-place, of which 435 million barrels were classified as measured, 435 million barrels were classified as indicated, and the remainder were classified as inferred.

Relation to Other Deposits

The Asphalt Ridge deposit is separated from the Northwest Asphalt Ridge deposit by a northeast-trending fault. Both deposits are essentially continuous; however, the Asphalt Ridge sandstone is saturated in the Northwest Asphalt Ridge deposit whereas it is not saturated in the Asphalt Ridge deposit.

The strata to the south and west of the Asphalt Ridge deposit are truncated by upper Tertiary sediments. Thus, the petroleum bearing strata occur entirely in the subsurface. Core drilling has encountered saturated zones at depths of 2,000 feet [57].

Description of Sampling Sites

A reconnaissance field trip led by Francis V. Hanson was conducted on 5 September 1990, for the purpose of identifying suitable locations which to obtain sizeable quantities of oil sand ore for research and development studies at the University of Utah and to determine the potential for on-site test facilities. Three sites were visited on the Asphalt Ridge deposit and were identified as 1) the Northern Pit, 2) the Central (County) Pit, and 3) the Southern Pit. The approximate locations of the three sites are indicated on Figure 14.

Northern Pit

The Northern Pit is located in the NE/4 of the NE/4 of section 25, Township 4 South, Range 20 East and in the NW/4 of the NW/4 of section 30, Township 4 South, Range 21 East. Samples of saturated sandstone were taken by the University of Utah Oil Sand Research and Development Group. The sample site was located in the NW/4 of the NW/4 section 30, Township 4 South, Range 21 East (Figure 14). The elevation of the outcroppings was between 6,100 and 6,200 feet. Several openings and one 150 feet long drift into the saturated sandstone in the vicinity were reported in 1926 [65].

The saturated outcrop zone is located within the uppermost part of the Mesaverde Group, within the Rim Rock Sandstone. A published [56] measured section indicates a continuous saturated zone of 123 feet. A fault at the north end of the ridge in section 25, Township 4 South, Range 20 East trends north and drops in the Rim Rock Sandstone to the west. This fault intersects and off sets

Figure 14 Sample Site Locations on the Asphalt Ridge Deposit

another fault trending north-northeast with the down thrown side to the northwest. This fault separates the Northwest Asphalt Ridge deposit from the Asphalt Ridge deposit [62].

Bitumen extracted from various Asphalt Ridge samples has been analyzed by fractional distillation methods [64] and for sulfur isotopes [58]; however, exhaustive chemical, physical and spectroscopic characterization of the native Asphalt Ridge bitumen has not been reported.

Elemental analyses and gravities for several Asphalt Ridge samples [19,58,64] obtained from the outcrops in the Northern Pit region are presented in Table 8. The 69-9E sample [64] from the Rim Rock formation was obtained from a quarry at the north end of the Asphalt Ridge where the deposit terminates against a cross-cutting fault. The site was located in the NW/4 of NW/4 section 30, Township 4 South, Range 21 East [64]. The PC-65-5 [19] sample was from the Rim Rock Sandstone from the County Pit located in the SE/4 of the SE/4 of section 30, Township 4 South, Range 21 East [19]. The 1836 sample is from the Rim Rock sandstone, located in the SE/4 of the SE/4 section 30, Township 4 South, Range 21 East [58]. The analyses for the PC-65-5 sample are typical of the Uinta basin bitumens whereas the atomic H/C ratio for the 69-19E sample is high, relative to the other Asphalt Ridge and Uinta Basin bitumens.

Table 8

Analyses of Selected Asphalt Ridge Samples
from the Northern Pit Area

Sample Identification Number	69-19E ⁽⁶⁴⁾	PC-65-5 ⁽¹⁹⁾	1836 ⁽²⁰⁾
Saturation, wt.	17.0	--	--
Elemental Analysis			
C, wt. %	71.0	85.3	--
H, wt. %	10.3	11.2	--
N, wt. %	0.9	1.0	--
S, wt. %	0.19	0.28	0.3
Specific Gravity	0.990	0.986	
--			
API Gravity, °API	12.9	12.0	--
Sulfur Isotope, SS ³⁴	--	--	+21.0

Central (County) Pit

The County Pit is located in the S/2 of the SE/4 of section 30 and in the N/2 of the NE/4 of section 31, Township 4 South, Range 21 East. Samples of saturated sandstone were taken by the University of Utah Oil Sand Research and Development Group. The location of the site was in the S/2 of the S/2 of the SE/4 of section 30, Township 4 South, Range 21 East. The elevation of the outcroppings was approximately 5,900 feet.

Development of the County Pit dates back to the late 1800's with sidewalks and streets in Vernal being constructed with the oil sand ore [65]. A number of unsuccessful shallow wells were drilled

down dip of the outcrops between 1910 and 1950 in the hope of locating fluid petroleum below the asphaltic seal [57]. During the 1930's a oil sand extraction plant was built by a "Doc Rehme". The plant utilized a hot water separation process [66].

In the early 1950's the Knickerbocker Investment Company and W.M. Barnes Engineering Company acquired a large block of patented and unpatented oil placer mining claims and began the first comprehensive drilling, mapping, and evaluation program on Asphalt Ridge [66]. Bituminous sand was shipped to California where Barnes had built an extraction pilot plant for process development studies.

The County Pit is owned by the W.M. Barnes Engineering Company, and is presently under contract to the Uintah County Highway Department. The point of contact with the Highway Department is Mr. Paul Felch (The County Shop is located at 392 East 200 South, Vernal; ((801) 789-1070). Pit location contract is Mr. Dennis Slaw. Mined road asphalt is restricted only to county highway usage. Mr. Slaw indicated that 3,000 tons per week of prepared road asphalt was being produced at the site.

Operations at the pit include several (3) earth-moving tractors and a separator. The primary earth-moving tractor is a track-driven bulldozer which has a front-end loader on one side and a set of five claws on the back. The tractor is used to rip and loosen a level bench of saturated rock. Then a cover of barren, unsorted alluvium (gravel and dirt) is spread over the ripped saturated rock. The tractor then repeatedly runs over the bench,

using the claws to mix the saturated rock with the alluvium. Once the rock is thoroughly mixed, the front-end loader on the tractor is used to push the mixture eastward and off the bench onto a loading pile. Another tractor located at this eastward, lower-lying area transfers the mixture from the loading pile onto a vibrating sorter which sorts the mixture according to aggregate size. Aggregate suitable for road-base asphalt is then loaded for paving material. Aggregate not suitable is returned to the process for ripping and re-mixing with alluvium.

The saturated outcrop is located in the uppermost part of the Mesaverde Group, within the Rim Rock Sandstone. During the field trip, a saturated zone of greater than 70 feet thick was estimated to be exposed. A published measured section [56] indicated a continuous saturated zone of 190 feet. A prominent fault trends North 24 West degrees as the County Pit in sections 30 and 31, Township 4 South, Range 21 East. The fault surface is nearly vertical and the displacement is 150 feet down on the west side. This fault marks the eastern limit of saturation in the area, with the saturated Rim Rock Sandstone against the Asphalt Ridge Sandstone.

Bitumen samples extracted from selected outcrops have been analyzed by fractional distillation [64] and for sulfur isotopes [58]. The RK-I-3 sample [58] is from the lowerpart of the Rim Rock formation located in the section NW/4 of section 30, Township 4 South, Range 21 East. The RK-I-4 sample [58] was from the upperpart of the Rim Rock located in the NW/4 section 30, Township 4 South,

Range 21 East.

Table 9

Analyses of Selected Asphalt Ridge Samples
from the Central Pit Area

Sample Number	Sulfur Wt %	Sulfur Isotope
RK-I-3 ⁽⁵⁸⁾	1.0	+19.8
RK-I-4 ⁽⁵⁸⁾	1.0	+21.6

Southern Pit

The Southern pit was located in the NE/4 of the SW/4 of section 31, Township 5 South, Range 22 East. The elevation was approximately 5,100 feet. Samples of saturated sandstone were taken by the University of Utah Oil Sand Research and Development group. The location was in the S/2 of the NE/4 of the SW/4 section 31, Township 5 South, Range 22 East. Access is 1,500 feet east of the eastern edge of the pit.

During the early 1970's Major Oil Company [66] and later the Arizona Fuels Corporation and Fairbrim Company [67] obtained a working agreement with Sohio Natural Resources Company on a tract on the southend of the ridge (Section 36, Township 5 South, Range 21 East; Section 31, Township 5 South, Range 22 East) to strip mine the oil sands and to build an extraction plant. The material was crushed and conveyed to flotation cells where a hot water/solvent process was used to strip the bitumen from the sand. The bitumen was shipped to the refinery located in Roosevelt, Utah. The

following data concerning the "Sohio Mine" was derived from updated field notes prepared by Campbell [68], petroleum geologist formerly of the Utah Geological and Mineral Survey.

- 190 acres to be mined.
- 1,400 cubic yards bituminous sand per day to be mined, with a possible ultimate capacity of 10,000 cubic yards oil sand ore per day and 3,000 cubic yards overburden per day.
- 1,000 barrels bitumen per day recovery, with a ultimate recovery of 5,000 barrels per day.
- Ore thickness averaging 65 feet, with 57% average oil saturation and 28.2% average porosity.

The outcrop saturated zone was located in the uppermost part of the Mesaverde Group within the Rim Rock Sandstone. During the field trip, a saturated zone of greater than 60 feet thick was estimated to be exposed. A published measured section indicated a continuous saturated zone of over 150 feet [56]. Oil extracted from the deposit has been analyzed by fractional distillation [64] and for sulfur isotopes [58].

The PC-65-6 sample is from the Duchesne River Formation from the South Pit, located in the NE/4 of SW/4 of section 31, Township 5 South, Range 22 East [56]. The RK-V-4 sample is from the Uinta Formation, located in the NW/4 of section 31, Township 5 South, Range 22 East [58]. The RK-V-5 sample is from the uppermost saturated zone with the Uinta Formation; located in the NE/4 of section 36, Township 5 South, Range 21 East [58]. The 1835 sample

is from the Uinta Formation, located in the NE/4 of the SW/4 of section 31, Township 5 South, Range 22 East.

SUMMARY AND CONCLUSIONS

The Oil Sand Research and Development Group at the University of Utah has managed to acquire sufficient mineral ore samples from the Asphalt Ridge oil sand deposit to characterize three potential mining/surface recovery sites on the deposit.

FUTURE ACTIVITIES

The drum quantity samples from specific locations will be mixed so that representative samples can be obtained for analyses. Detailed physical, chemical and stereoscopic analyses will be conducted to characterize the native bitumen from the Asphalt Ridge oil sand deposit.

Table 10

Analyses of Selected Asphalt Ridge Samples
from the Southern Pit Area

Sample Identification Number	PC-65-6 ⁽⁵⁸⁾	RK-V-4 ⁽⁵⁸⁾	RK-V-5 ⁽⁵⁸⁾	1835 ⁽⁵⁸⁾
Elemental Analysis				
C, wt%	83.6	--	--	--
H, wt%	11.0	--	--	--
N, wt%	0.96	--	--	--
S, wt%	0.62	--	--	--
Specific Gravity	1.013	--	--	--
API Gravity, °API	8.2	--	--	--
Sulfur Isotope, δS^{34} (per mil)	--	+15.6	+7.0	+20.1

THE INFLUENCE OF CARBOXYLIC ACID CONTENT ON BITUMEN VISCOSITY

Principal Investigator
Co-Principal Investigator
Post Doctoral Fellow

J.D. Miller
F.V. Hanson
K. Bukka

INTRODUCTION

The viscosity differences among the bitumens from the Athabasca and Cold Lake oil sand deposits were small^[69]. This is in contrast to the bitumens from different Utah oil sand deposits. In the latter case the viscosities varied by almost two orders of magnitude for the bitumens from the Whiterocks and Sunnyside deposits. Bitumen viscosity has been shown to be a significant parameter in the separation of bitumen from oil sand, particularly in the modified hot water process^[70,71]. Thus, it is essential that the relationship between bitumen viscosity and its chemical composition be established. Several attempts have been made to relate the bitumen viscosity to its chemical composition. These studies attempted to develop correlations between viscosity and chemical properties such as molecular weight^[72], asphaltene content^[73] and sulfur content^[74] of the bitumen. Since native bitumens are complex hydrocarbon mixtures, the relationship between viscosity and chemical composition is unlikely to be revealed by the determination of macroscopic chemical properties. It was recently reported^[75] that viscosity was related to the spin-spin relaxation rates, which were determined from the ¹³C NMR spectroscopic analysis of the bitumen samples.

It is likely that viscosity may depend on several factors,

rather than any single chemical feature. Christensen, et al.^[74] proposed that the viscosity of bitumens could be correlated with the asphaltene content of the bitumen; that is, the greater the asphaltene content of the bitumen the higher the viscosity. The Christensen correlation^[74] was an extension of the structural model of asphalt proposed by Nellensteyn^[76]. This model visualized bitumen as a suspension of asphaltenes in a mixture of naphthenes and paraffins. The suspension was stabilized by the constituent aromatics and resins which were presumed to be concentrated at the interface thereby acting as surfactants. However, the inadequacy of the Christensen correlation^[74] became apparent when the viscosities and asphaltene contents of the Athabasca, Asphalt Ridge, and Whiterocks bitumens were compared.

In view of the reported discrepancy between the viscosities of some bitumens and their asphaltene contents, the Whiterocks and Sunnyside bitumens were fractionated due to the significant differences in their viscosities. The fractions were spectroscopically analyzed to establish a qualitative relationship between viscosity and chemical properties^[77]. It was observed that the viscosity was related to the carboxylic acid content of the bitumen, and that these carboxylic acids were concentrated in the resin fractions.

It was suggested that the carboxylic acids increased the viscosity through interactive hydrogen bonding with asphaltene moieties. These observations supported the Nellensteyn model^[76] and identified the type of interactions between asphaltene and resins

(possibly aromatics) as described in the model. The conclusions were based on FTIR spectroscopic analysis of the separated fractions of the bitumens.

In the current study, the data base used to establish the relationship between the carboxylic acid content of a bitumen and its viscosity was expanded to include several other bitumens. The bitumens were from the oil sand deposits of Utah, Oklahoma, Alabama, and Athabasca (Canada). All the bitumens were fractionated and the fractions were examined by FTIR spectroscopy. Since it had been shown earlier⁽⁷⁾ that acids in the bitumen concentrate in the resin fractions, quantitative estimations of the acid components present in the resin fractions were made by potentiometric titrations.

EXPERIMENTAL

Six bitumen samples were chosen for fractionation and subsequent characterization. Five of the samples were U.S. oil sands and the sixth was from the Athabasca (Alberta, Canada) deposit. Three of the five U.S. samples were from Utah deposits: Asphalt Ridge, Sunnyside, and Whiterocks and the other two were from Spring Creek, Alabama, and Oklahoma. The bitumens were separated from the mineral matter by Dean-Stark toluene extraction. The bitumens were recovered from the bitumen-toluene solutions in a rotary vacuum evaporator. The residual toluene in the bitumens was determined by gas chromatography and found to be less than 0.1% by weight.

Viscosity

The viscosity of the Whiterocks bitumen was measured on a Brookfield viscometer with a cone and plate assembly. A 3" cone was used and the viscosity measurements were made at a single shear rate in the temperature range 30-90°C. Viscosity measurements of the other bitumen samples were made on a Rheometrics System IV viscometer using a parallel plate geometry. The instrument was equipped with heating controls, and the viscosity measurements were made at several shear rates and temperatures for each bitumen sample.

Elemental Analyses and Molecular Weight Determinations

Elemental analyses of the bitumens were performed on LECO-600 and LECO SC-132 analyzers. Oxygen contents were calculated by difference. The molecular weight data were determined by vapor phase osmometry (Galbraith Laboratories, Inc., Knoxville, Tennessee).

Fractionation of Bitumens

The bitumen samples were fractionated according to the scheme presented in Figure 15. The experimental details of the fractionation procedure have been reported elsewhere [77,78]. The aromatic fractions for the Asphalt Ridge and Sunnyside bitumens were not sub-fractionated as shown in Figure 15.

FTIR Transmission and Specular Reflectance Spectroscopy

Two different FTIR techniques were used to analyze the bitumens and their SARA fractions. The transmission technique was

Figure 15. SARA Bitumen fractionation scheme.

employed for the less viscous (saturate and aromatic) fractions. The specular reflectance (SR) technique was used for the bitumens and the more viscous fractions. The details of the SR accessory and the method were described in an earlier communication from this laboratory ⁽⁷⁸⁾. All spectra were obtained on a Digilab FTS-40 spectrometer equipped with a Model 3240-SPC data processing system. The instrument was fitted with a liquid nitrogen cooled MCT (Hg-Cd-Te) detector. Software capability of the instrument included baseline correction, spectral subtraction, deconvolution and band fitting. Transmission spectra were obtained by smearing the samples on KBr windows (25x4 mm). Sample application was adjusted in a predetermined manner which depended upon the sharpness of the major absorbance bands in the spectrum of the sands. Primary spectra of the samples were obtained in the mid-IR region (4000-700 cm^{-1}) with a nominal resolution of 4 cm^{-1} .

Since each bitumen fraction consisted of a number of compounds, the bands observed in the infrared spectrum were complex. Characteristic absorbance bands were deconvoluted using the instrument software 'Bandfit' to estimate the carboxylic acids present in the resin and asphaltene fractions. Deconvolution was accomplished by approximating the band position, band width and its percent Gaussian character. The areas under the carboxylic acid peaks were estimated. It was assumed that the concentration of the components which gave rise to the predominant aliphatic C-H bands in the 3000-2800 cm^{-1} region were equal for the resin fractions of the different bitumens. The band areas for the

carboxylic acids, estimated by the 'Bandfit' software, were ratioed to the aliphatic C-H band areas. These ratios were used to provide an estimate of the carboxylic acids content of the different resin fractions.

Potentiometric Titrations of the Resin Fractions

An earlier study^[77] indicated that the carboxylic acids present in the bitumen accumulated in the resin fraction. The resin fractions were subjected to potentiometric titrations to estimate the amount of acids present. Since resins are only partially soluble in polar solvents and the potentiometric titrations require a conducting medium, a mixture of solvents was used to dissolve the resin fraction^[78]. The solvent mixture consisted of tetrahydrofuran and methanol mixed in the ratio of 60:40 (by volume), respectively. Resin solutions in the mixed solvent were titrated against a standard sodium hydroxide solution. In all titrations the ratio of resin-to-solvent was arbitrarily maintained at 1g per 120 ml. Since methanol reacts with sodium hydroxide, a background titration was performed on the solvent mixture and appropriate corrections were made to the resin titration. Titrations were carried out on a Fisher Accumet pH meter (Model #805MP). The acid contents were expressed as milliequivalents per gram of the resin fraction.

Sequential Hydrolysis of the Resin Fractions

It was apparent from the infrared profiles of the resin fractions that the absorbance bands for carbonyl groups were related to several oxygen functionalities such as acids, esters,

carboxylates, acid anhydrides, and carbonyls. In order to verify the presence of these functional groups in the resins, a sequential hydrolysis was performed on selected resin fractions. The experimental methodology adopted for the hydrolysis was similar to that proposed by Speight and Moschopedis ^[79]. The hydrolysis scheme is reproduced in Figure 16. The product obtained at the end of each step in the resin hydrolysis was examined using SR-FTIR spectroscopy.

RESULTS AND DISCUSSION

Viscosity

The viscosities were measured at several shear rates at each temperature and the value at zero shear rate was obtained by extrapolation of the plot of viscosity versus shear rate. Ward and Clark^[81] reported that the viscosity of the Athabasca bitumens was independent of shear rate. In this investigation shear thinning was observed for all the bitumens studied except Whiterocks, the viscosity of which was measured at a single shear rate. However, the variation was not significant and it was concluded that the deviations from Newtonian behavior were small (Figure 17). A similar deviation from Newtonian behavior was reported for the Athabasca bitumen^[56]. Viscosity data for the Alabama and Oklahoma bitumens were recently reported ^[82]. The plot of log (viscosity) versus $1/T$ was linear for each of the six bitumens. A typical plot is presented in Figure 18. The slopes and the intercepts from these plots are presented in Table 11.

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Figure 16. Sequential hydrolysis scheme of the bitumen resin fraction.

Figure 17. Variation of bitumen viscosity with shear rate ($T=333K$)

Figure 18. Variation of Alabama bitumen viscosity with temperature.

Table 11. Viscosity data for the tar sand bitumens.

Bitumen Source	Viscosity @50°C. Pa.S.	Slope	Intercept	r ²
Athabasca	3	7035	-18.46	0.935
Whiterocks	33	12910	-36.47	1.000
Asphalt Ridge	43	9692	-23.95	0.988
Sunnyside	1260	13825	-33.36	0.975
Oklahoma	2195	13265	-33.37	0.967
Alabama	2500	16638	-43.40	0.998

The magnitude of the slope for each bitumen, which represents the flow activation energy was found to increase in the order:

Athabasca < Asphalt Ridge < Whiterocks
< Sunnyside < Oklahoma < Alabama.

The measured viscosities of the bitumens varied by more than three orders of magnitude, and the experimental technique prevented the measurement of the viscosity of all bitumens at single temperature with reasonable accuracy. Viscosities at 50°C were obtained for each of the bitumens from the plots and are listed in Table 11. The results indicated that the bitumen viscosity increased in the order:

Athabasca < Asphalt Ridge < Whiterocks
< Sunnyside < Oklahoma < Alabama.

This order was maintained in all subsequent tables in an attempt to relate the viscosity to other reported properties.

Elemental Analysis and Molecular Weight

The elemental analyses of the bitumens together with their number averaged molecular weights and empirical formulae are presented in Table 12. The data were examined in an attempt to correlate the bitumen viscosities to the sulfur contents and molecular weights of the bitumens^[72, 74]. It is evident from Table 12 that the bitumen sulfur contents viscosities increased with increasing molecular weight; however, this relationship was too general to provide insight regarding bitumen viscosity.

Fractionation

The compositions of the bitumens, as determined by the SARA fractionation scheme (Figure 15), are presented in Table 13. The recoveries obtained in the fractionation procedure are also reported. The losses were attributed to strongly adsorbed components which could not be eluted with the most polar solvent. The fractional compositions for the Alabama and Oklahoma bitumens were recently reported by Misra, et al.^[82].

The establishment of empirical relationships between the viscosity of the bitumen and its chemical composition will likely require several parameters. Among these are the saturates and asphaltene contents of the bitumen. It was presumed that compositional (SARA) analyses of the bitumens combined with FTIR analysis of the various fractions would lead to the identification

Table 12. Elemental analysis of the bitumen samples under study.

Bitumen Source	Wt. %					Atomic Ratio				Molecular Weight	Empirical Formula
	C	H	N	S	O	H/C	N/C	S/C	O/C		
Athabasca	83.19	10.12	0.47	4.72	1.50	1.460	0.0048	0.0213	0.0135	407	$C_{28}H_{41}N_{0.14}S_{0.60}O_{0.38}$
Whiterocks	86.40	11.50	1.10	0.40	0.50	1.597	0.0109	0.0017	0.0043	500	$C_{36}H_{58}N_{0.39}S_{0.06}O_{0.16}$
Asphalt Ridge	84.47	11.00	1.06	0.44	3.03	1.563	0.0108	0.0020	0.0269	490	$C_{34}H_{54}N_{0.37}S_{0.07}O_{0.93}$
Sunnyside	84.92	10.28	0.90	0.50	3.40	1.453	0.0091	0.0022	0.0300	588	$C_{42}H_{60}N_{0.38}S_{0.09}O_{1.25}$
Oklahoma	82.56	9.55	0.94	2.64	4.31	1.388	0.0098	0.0120	0.0392	772	$C_{53}H_{73}N_{0.52}S_{0.64}O_{2.08}$
Alabama	84.89	9.61	0.90	1.90	2.70	1.358	0.0091	0.0084	0.0239	578	$C_{41}H_{56}N_{0.37}S_{0.34}O_{0.98}$

Table 13. Fractional composition of bitumens under study.

Bitumen Fraction	Weight Percent					
	Athabasca	Whiterocks	Asphalt Ridge	Sunnyside	Oklahoma	Alabama
Saturates	34.6	30.2	32.4	24.9	18.9	25.6
Aromatics-I MAH	21.9	14.6	22.4	18.1	8.4	23.3
Aromatics-II DAH	3.1	6.8			1.5	
Aromatics-III PAH	1.7	3.4		0.5	0.6	0.8
Resin-I	24.7	38.8	37.6	30.0	21.0	21.4
Resin-II	0.7	1.3		0.6	0.8	0.6
Asphaltenes	15	3.6	7.3	23.7	41.8	26.7
% Recovery	100	98.8	99.7	97.8	93.0	98.9

of those classes of compounds and/or functional groups that impact the viscosity. The results presented in Table 13 indicated a significant variation in the amount of each fraction for the bitumens. However, there were no apparent trends that would account for the variations in bitumen viscosity. For example, the Oklahoma bitumen had a high viscosity and a relatively small amount of saturates; whereas the Whiterocks bitumen had a high saturates content but a low viscosity. On the other hand, comparison of bitumens based on asphaltene contents indicated that the viscosity appeared to increase with an increase in the concentration of asphaltenes. The Athabasca bitumen which contained 15 wt% asphaltenes and had a viscosity of 3 PaS whereas the Whiterocks and Asphalt Ridge bitumens which contained 3.6 and 7.3 wt% asphaltenes, respectively, had viscosities of 33 and 44 cps, respectively. Thus, the apparent relationship between asphaltene content and viscosity is tenuous at best. An attempt to correlate the bitumen viscosity with the resins-I and composite aromatics [monoaromatics (MA), dinuclear aromatics (DA), and polynuclear aromatics (PA)] fractions led to the same conclusion. Thus, the comparison of bitumens, based on their fractional compositions, clearly indicates that there are no reliable compound-type features which can be correlated satisfactorily with the bitumen viscosity.

FTIR Characterization of Bitumen Fractions

In a recent study⁽⁷⁾ it was shown by FTIR analysis that a relatively large proportion of the carboxylic acids present in the Asphalt Ridge and Sunnyside bitumens, were concentrated in the

resin-I fraction. The carboxylic acids correlated qualitatively with the bitumen viscosity; that is, a bitumen with higher viscosity also contained larger amounts of carboxylic acids. However, due to the complex nature of the bitumens no quantitative relationship could be established between the acid content and the viscosity.

The resin-I fractions of the bitumens used in this study were analyzed by FTIR in an attempt to verify the relationship between the carboxylic acid content and the viscosity. The resin-I fraction will be referred to as the resin fraction in the remainder of the text since the resin-II fraction was quantitatively too small to permit a detailed analysis. The FTIR spectra of the resin fractions are presented in the Figure 19. The relevant region of the spectra are presented to accentuate the differences among the resin fractions. The presence of carboxylic acids in the resin fractions were indicated by the characteristic absorbance band at 1702 cm^{-1} [80]. An examination of the spectra revealed several interesting differences among the resin fractions. These differences were observed in the $700\text{--}1000\text{ cm}^{-1}$, $1000\text{--}1300\text{ cm}^{-1}$ and $1800\text{--}1600\text{ cm}^{-1}$ regions of the spectra. The $700\text{--}1000\text{ cm}^{-1}$ region was considered unimportant to this discussion since it has been attributed to aromatic substitution in the constituent molecules. The distinctive features of the $1000\text{--}1300\text{ cm}^{-1}$ region were the bands at 1032 cm^{-1} and 1298 cm^{-1} . The band at 1032 cm^{-1} has been attributed to C-O and C-S stretching vibrations [83] however, it was not possible to make a definitive assignment since the bands for

Figure 19. SR-FTIR spectra of bitumen resin fractions.

the standard organic compounds containing C-O and C-S bonds occur at the same position. The band at 1032 cm^{-1} was relatively intense for the Athabasca and Oklahoma bitumens (Figure 19). Since the sulfur contents of these bitumens were higher than the other bitumens, it was presumed that the band at 1032 cm^{-1} was due to compounds containing C-S groups. The bands at 1298 cm^{-1} and 1180 cm^{-1} for Athabasca and Oklahoma resin fractions were also similar. It was thought that these two bands were also related to compounds containing sulfur functional groups.

The region from 1690 cm^{-1} to 1800 cm^{-1} appeared to be the most characteristic signature region for the resin fractions. The Whiterocks, Asphalt Ridge, Sunnyside and Alabama resin exhibited similar bands at 1702 cm^{-1} (variation in the band maxima for the resin fractions was less than 6 wave numbers); however, each had a different intensity. This region was relatively complex for the Athabasca resin fraction; that is, there were two distinct bands at 1726 cm^{-1} and 1775 cm^{-1} and a shoulder at 1702 cm^{-1} . The band at 1726 cm^{-1} was the most prominent. The spectrum appeared less complex for the Oklahoma resin fraction with two distinct bands at 1726 cm^{-1} and 1702 cm^{-1} .

The bands at 1775 cm^{-1} and 1726 cm^{-1} have been attributed to the carbonyl groups present in acid anhydride and esters, respectively^[80,84]. The band at 1702 cm^{-1} has been attributed to the carbonyl group of a carboxylic acid. Based on these assignments, the Athabasca bitumen was presumed to contain significant amounts of esters and anhydrides and a small amount of carboxylic acids.

The intensities of the 1726 cm^{-1} and 1702 cm^{-1} bands for the Oklahoma resin fraction were approximately equal which may indicate that the bitumen contained equal amounts of esters and acids (assuming that their characteristic bands have the same absorption coefficients). The resin fractions from the other bitumens appeared to contain only carboxylic acids. These differences in the compositions of resin fractions were interpreted to have important implications in terms of the physical properties of the bitumens, particularly their viscosities.

Christensen, et al.^[73], successfully correlated the viscosity with the asphaltene content of the bitumen. Thus, an attempt to relate compositional differences to viscosity was made in terms of the structural model of bitumen^[76,85]. The model envisions that the bitumen was a suspension of solid asphaltenes in paraffinic and naphthenic oils and that the suspension was stabilized by the resin and, to some extent, aromatic fractions. The stability of the suspension required that the compounds present in the resin and aromatic fractions were positioned at the interface between the suspended asphaltenes and the saturates. The stabilization was explained by charge neutralization (on the asphaltenes) and/or dipole-dipole interactions. Although the nature of these interactions were not well defined, hydrogen bonding may have played a role. This model led to the presumption that the viscosity depended upon several factors: the amount of asphaltenes, saturates, and resins (and possibly aromatics) in the bitumen and upon the strength of the interactions between the asphaltenes and

resins.

Although the asphaltene content plays an important role in determining bitumen viscosity, the viscosity is not solely dependent on the asphaltene content. The Athabasca, Asphalt Ridge and Whiterocks bitumens had relatively low asphaltene contents; however, they had high viscosities. Thus, factors other than asphaltene content influence the viscosity of heavy oils and bitumens. In a recent study of two Uinta basin bitumens, it was shown that a bitumen with high viscosity also contained a high concentration of carboxylic acids^[77]. The carboxylic acids, which were concentrated in the resin fraction, were presumed to stabilize the asphaltene suspension through hydrogen bonding between the resins and asphaltenes. Hydrogen bonding interactions have been reported earlier^[80,86], the relationship between the viscosity and such interactions has not been explored.

In this study the bitumen samples viscosities could not be correlated by the asphaltene contents. Thus, it was believed that SARA fractionation and characterization of individual fractions could identify specific classes of compounds such as carboxylic acids which correlate with viscosity. A comparison of the FTIR spectra of the resin fractions, Figure 19, indicated that the band at 1702 cm^{-1} was significant in that the viscosities of the Whiterocks, Asphalt Ridge, Sunnyside, Alabama, and Oklahoma correlated with the band intensities. The Athabasca bitumen had the lowest viscosity and a low intensity band at 1702 cm^{-1} , a moderately intense band at 1775 cm^{-1} , and a strong band at 1726 cm^{-1} .

This implies that carboxylic acids (1702 cm^{-1}) effectively contribute to hydrogen bond formation, whereas the esters (1726 cm^{-1}) and anhydrides (1775 cm^{-1}) contribute little to an increase in viscosity. The importance of carboxylic acids as a correlating parameter for viscosity was inferred from the data for the Athabasca bitumen; a high asphaltene content did not lead to high viscosity. This was attributed to the low concentration of carboxylic acids which was deemed inadequate to suspend and stabilize the relatively large amount of asphaltenes (compared to Whiterocks and Asphalt Ridge samples). Similarly, the Oklahoma bitumen, which has the highest asphaltene content (41 wt%), did not exhibit the highest viscosity due to a low concentration of carboxylic acids, thus the asphaltenes were not stabilized. The presence of esters in the Oklahoma resin fraction, Figure 19, did not appear to stabilize the asphaltenes but it had a high viscosity. The high viscosity observed for the Alabama sample may have been due to the high asphaltene content (27%) and adequate amounts of carboxylic acids for stabilization.

In all these cases, comparisons of the carboxylic acids among the various resin fractions were made on the basis of band intensities. Such a comparison implicitly assumed that all carboxylic acids had similar absorption coefficients and that their hydrogen bonding potentials were the same. Quantitative comparisons of these acids in a complex mixture without an internal standard was difficult. Quantification of the infrared absorbance bands using the instrument software ('Bandfit') was made and the

results are presented in Table 14.

Table 14. Quantitative comparison of the carboxylic acids present in the resin fractions of bitumens as determined from the FTIR absorbance bands.

Bitumen Source	Area ¹ Under The Carboxylic Acid Band @ 1700 cm ⁻¹	Area ¹ Under The Aliphatic C-H Stretching bands	Relative Carboxylic Acid Content ²
Athabasca	3.83	66.27	0.058
Whiterocks	3.18	72.96	0.044
Asphalt Ridge	5.05	66.89	0.044
Sunnyside	8.69	95.14	0.091
Oklahoma	19.30	123.85	0.156
Alabama	3.17	51.10	0.062

1. Area under the overwhelming C-H stretching band stretching from 3111 cm⁻¹ to 2661 cm⁻¹ (units are arbitrary).

2. These are normalized values obtained from the ratio: [Area under 1700 band] / [Area under the aliphatic C-H bands].

However, comparison of the computed areas in Table 14 must be interpreted with caution. The 'Bandfit' software deconvoluted each band into several peaks with different band widths and percent gaussian character. These difference influence the determination of the areas under the carboxylic acid bands. As described in the experimental section, the carboxylic acid band areas used to compare different resin fractions were ratioed to aliphatic C-H band areas. Although there are certain limitations in such comparisons, nevertheless distinct trends were observed.

Potentiometric Titrations of the Resin Carboxylic Acids

Potentiometric titrations were carried out in a non-aqueous solvent to quantify the carboxylic acids present in the resin fractions. Even this method of acid quantification is not without its limitations. The potentiometric method assumed that the amount of basic compounds present in all resin fractions were the same. The titration of the acid compounds against a standard base resulted in the precipitation of the salts. These precipitates were observed to have deposited on the electrodes and as a result, may have interfered with the titration measurements. Nevertheless, such titrations have been used to identify and estimate the acid and base components of bitumen^[79]. A typical titration plot is presented in Figure 20. The titration data for the resin fractions are presented in Table 15. A gradual increase in the acid content

Table 15. Quantitative comparison of the carboxylic acids present in the resin fraction of bitumens as determined by the potentiometric titration method.

Bitumen Source	Milliequivalents of acid/g resin
Athabasca	0.343
Whiterocks	0.111
Asphalt Ridge	0.198
Sunnyside	0.338
Oklahoma	0.310
Alabama	0.290

of the bitumen with bitumen viscosity (see Table 11) was observed. The Athabasca bitumen appeared to be an exception once again. The acid content of the Athabasca bitumen, as determined by the

Figure 20. Potentiometric titration of the Alabama resin fraction.

potentiometric titration, was high when compared with the other bitumens based on the intensity of the resin fraction absorption band at 1702 cm^{-1} . Even the titration profile of the Athabasca resin fraction, which is presented in Figure 21, appeared to be different; there were two end points. The anomalous behavior of the Athabasca resin can be explained by ester hydrolysis during the titration. Esters undergo hydrolysis in weak alkaline solutions at room temperature. Thus, the titration of the Athabasca resin fraction indicated a high value for the acids content which may have been misleading. Such behavior for Athabasca bitumen had been noted earlier^[80]. Then the esters present in the bitumen were susceptible to hydrolysis. As a result, the acid content of the bitumen is difficult to determine in the presence of esters. In the case of the Whiterocks, Asphalt Ridge and Sunnyside bitumens, the viscosity increased with increased content acid. The Alabama and Oklahoma bitumens exhibited relatively high acid contents. However, esters were also present in the Oklahoma resin fraction; thus the acid content of the Oklahoma bitumen may have been overestimated. It was clear that although bitumens with higher viscosity invariably contained higher concentrations of carboxylic acids, the establishment of a precise quantitative relationship between the two was not possible. This was due in part to the difficulty in estimating the acid contents of bitumens.

Sequential Hydrolysis of the Athabasca Resin Fraction

Since the carboxylic esters were presumed to interfere with the analysis for carboxylic acids, it was important to establish

Figure 21. Potentiometric titration of the Athabasca resin fraction.

their presence in the bitumen without ambiguity. The presence of carboxylic acids and esters were established from the FTIR profiles; however, due to the proximity of their absorbance bands (20 wave numbers apart) in such a complex mixture, their presence in the resin fraction was verified by hydrolysis product analysis.

Since the Athabasca bitumen was shown to contain a greater proportion of esters and anhydrides, its resin fraction was subjected to sequential hydrolysis. The method used was similar to that reported by Speight and Moschopedis^[80], and the hydrolysis scheme is presented in Figure 16. The product obtained at the end of each step was examined by SR-FTIR. The spectrum of the untreated resin fraction and its hydrolysis products are presented in Figure 22. The spectrum of the product obtained after treatment of the resin fraction with potassium bicarbonate (Figure 22b) indicated that anhydrides were the first to hydrolyze yielding free carboxylic acids. This was inferred from the near disappearance of the absorbance band at 1775 cm^{-1} and a corresponding increase in the band at 1702 cm^{-1} . At this stage the band intensities of the ester and acid carbonyls at 1726 cm^{-1} and 1702 cm^{-1} , respectively, appeared to be nearly identical. In the second step, a mild hydrolysis of the product from step 1 with sodium hydroxide solution, caused the ester to hydrolyze to an acid (Figure 22c). This was accompanied by an increase in the intensity of the band at 1702 cm^{-1} while the band at 1726 cm^{-1} diminished significantly. The residual absorbance band at 1726 cm^{-1} (Figure 22c) indicated that a small portion of the ester remained unhydrolyzed. In step 3, the product from step 2

Figure 22. SR-FTIR spectra of the Athabasca resin hydrolysis products.

was refluxed with sodium hydroxide. The spectrum of the product from step 3 exhibited a single absorbance band at 1702 cm^{-1} which indicated that a majority of the esters had been hydrolyzed (Figure 22d). The carboxylate salts that formed during the hydrolysis of anhydrides and esters remain in the organic phase or pass into the aqueous phase depending upon their solubilities. In the final step these carboxylates were converted to carboxylic acids by treatment with a hydrochloric acid solution (step 4).

Thus, the infrared spectra of the products produced during the sequential hydrolysis of the Athabasca resin fraction indicated that the band observed at 1726 cm^{-1} was due to esters. Since esters are not as capable as carboxylic acids in hydrogen bond formation, it is interpreted that bitumens with esters would not be as visous as the carboxylic acids would render them to be. Since the presence of esters was overwhelming as compared to the carboxylic acids in the Athabasca bitumen (Figure 19), the viscosity is explained to be very low in comparison to other bitumens. In addition to Athabasca bitumen, Oklahoma bitumen also shows significant amounts of esters (Figure 19). In spite of such large amount of asphaltenes (41%) present in the Oklahoma bitumen, its viscosity was found to be less than that of Alabama bitumen which has only 27% asphaltenes (Table 13). This can probably be explained by an insufficient amount of carboxylic acids in the bitumen (Table 15) to stabilize the relatively large amount of asphaltenes.

SR-FTIR Spectra of Asphaltenes

The proposed structural model for bitumen viscosity required interaction between the asphaltenes and the carboxylic acids in the resin fraction to produce a stable suspension of asphaltene particles. Since the chemical composition of the resin fraction was shown to play an important role in this interaction, it is anticipated that the composition of asphaltenes also plays an equally vital role. SR-FTIR examination of the asphaltene fractions from the six bitumens indicated that there were significant differences between them. The spectra of the asphaltene fractions are presented in Figure 23. It is evident from the spectra that the Oklahoma and Sunnyside asphaltene fractions had the highest concentrations of carboxylic acids. The differences among all others were small in comparison. A quantitative comparison of the acids present in the asphaltene fractions by the potentiometric titration method was difficult as these fractions were not adequately soluble in all the attempted solvents. Furthermore, precipitation was extensive during the titration and the precipitates adhered to the electrode rendering the titration readings unreliable. However, a semi-quantitative comparison was made of the area under the carboxylic acid band for each asphaltene fraction by deconvolution of the absorbance band using the 'Bandfit' software. As described earlier, the values for these areas were normalized assuming that the aliphatic C-H contents of all bitumens were equal. comparison of the areas for the asphaltene fractions from the six bitumens are presented in

Figure 23. SR-FTIR spectra of bitumen asphaltene fractions.

Table 16. The relatively high acid content of the Oklahoma

Table 16. Quantitative comparison of the carboxylic acids present in the asphaltene fractions of bitumens as determined from the FTIR absorbance bands.

Bitumen Source	Area ¹ Under The Carboxylic Acid Band @ 1700 cm ⁻¹	Area ¹ Under The Aliphatic C-H Stretching bands	Relative Carboxylic Acid Content ²
Athabasca	2.99	68.54	0.044
Whiterocks	1.96	58.73	0.033
Asphalt Ridge	3.49	80.22	0.044
Sunnyside	3.50	53.46	0.065
Oklahoma	9.50	54.76	0.173
Alabama	2.51	57.78	0.043
<p>1. Area under the overwhelming C-H stretching band stretching from 3111 cm⁻¹ to 2661 cm⁻¹ (units are arbitrary).</p> <p>2. These are normalized values obtained from the ratio: [Area under 1700 band] / [Area under the aliphatic C-H bands].</p>			

asphaltene fraction may explain its high viscosity in spite of its relatively low acid content in the resin fraction (compared to the Sunnyside resin fraction).

From the fractional analyses of bitumens and their characterizations, it becomes evident that bitumen viscosity, being a complex variable, cannot be related to any single chemical property. In addition to the demonstrated dependence of bitumen viscosity on asphaltenes^[73] the results from this study identify another variable, namely, the carboxylic acids content. In a broad sense, the results demonstrate that a bitumen with high viscosity

invariably contains a large amount of carboxylic acids. The dependence of bitumen viscosity on carboxylic acids was clearly demonstrated where asphaltenes content fails to explain the viscosity variation among bitumens. However, the role of these two variables may be complementary in accounting for the viscosity of the bitumen. The viscosity of bitumen is mainly attributed to the suspended asphaltenes. The asphaltene suspension in bitumen is stabilized by the carboxylic acids through a hydrogen bonding mechanism. Such a stabilization can also be brought about more or less by other functional groups such as aldehydes, ketones, esters, amines, amides and sulfoxides. Not only that the carboxylic acids are relatively more abundant in the bitumen, but also, the energy of hydrogen bonding involving these acids is higher than those involving the above-mentioned groups.

A notable exception to the proposed interpretation is the Alabama bitumen. The viscosity value for this bitumen was the highest of all the bitumens reported, but the acid content of both the resin and asphaltene fraction does not show a particularly high value. Further, it must be pointed out that in bitumens of high viscosity, viz., Alabama and Oklahoma the percentage of the resin fraction itself in the bitumen is small (Table 12). In addition, there is no evidence to believe that the carboxylic acids present in all the resin fractions are the same. On the contrary, the small differences in the carboxylic band maximum (1669 to 1708 cm^{-1}) observed for different resin fractions may indicate that there are some differences among them. It is reasonable to assume that

different carboxylic acids have different hydrogen bonding potentials. Finally, the role of the saturates and aromatic fractions in the bitumen should not be underestimated.

SUMMARY AND CONCLUSIONS

In order to verify the recently reported relationship between the viscosity of bitumen and its carboxylic acid content^[77], a study of a diverse group of oil sand bitumens was undertaken. A total of six bitumens derived from the oil sand deposits of Canada and the United States was chosen. Viscosity of each of the bitumens was determined in the temperature range (60-90° C) and all of them were found to be non-Newtonian in character. However, the departure from the ideal Newtonian behavior was relatively small.

All bitumen samples were fractionated using a modified SARA (saturates, aromatics, resin and asphaltenes) type analysis. The separated fractions were examined by transmission and specular reflectance FTIR spectroscopy. The FTIR analysis indicated that the carboxylic acids in the bitumen accumulated in the polar fractions and particularly in the resin fraction. These carboxylic acids were semi-quantitatively estimated from their characteristic FTIR absorbance bands by a band fitting method. These estimations were shown to be limited by the complexity of the material and the instrument software. The carboxylic acids in the resin fraction were also estimated by potentiometric titration using a mixed solvent. Although it was apparent from both these analyses that in general a bitumen with higher viscosity was shown to contain a larger amount of carboxylic acids, a precise relationship could not

be established.

The fractional compositions of the bitumens indicated that the viscosity of a given bitumen cannot be correlated with its asphaltene content alone. Athabasca bitumen was shown to be least viscous of all the bitumens though it contains a moderate amount of asphaltenes. The FTIR spectra indicated that its resin fraction contained predominantly esters which did not stabilize the asphaltenes as effectively as carboxylic acids, hence the low viscosity for Athabasca bitumen. The presence of esters in the Athabasca resin fraction was confirmed by the hydrolysis of the resin fraction and analysis of the hydrolysis products by FTIR.

The data from this study clearly indicated that the bitumen viscosity was related to the amount of carboxylic acids distributed among its polar fractions. A quantitative estimate of these acids was limited by the complexity of the sample and by the uncertainties of the analytical methods. Earlier studies had indicated that asphaltenes played an important role in determining the viscosity of bitumen. It is suggested that both asphaltenes and carboxylic acids present in the resin fraction interact in a synergistic manner to determine the viscosity of bitumen. These conclusions provide an extension and a validation of the bitumen viscosity model developed by Nellensteyn^[76].

FUTURE ACTIVITIES

The attempt to correlate bitumen viscosities with key chemical properties will be continued using the PR Spring bitumen.

WATER BASED OIL SAND SEPARATION TECHNOLOGY

Principal Investigator:	J. D. Miller
Co-Principal Investigator:	J. Hupka
Graduate Students:	Y. Yang
	J. Drelich
	D. Lelinski

INTRODUCTION

The 1990/91 research program for the water-based separation technology includes oil sand characterization, digestion and pretreatment with diluent, bitumen recovery from digested oil sand slurry, and bitumen concentrate clean-up. The report is organized in several chapters in which the major research activities of the past year are presented and discussed. The two initial sections are devoted to characterization of oil sand and oil sand processing products, whereas the remaining four sections pertain to processing technology.

The release of surface active compounds to the aqueous phase during the hot water processing of oil sand distinctly effects bitumen recovery, and depends on temperature and alkalinity. It has been widely accepted that naphthenic acids present in the crude oil or bitumen interact with alkali to form a surface active soap. The significance of other anionic surfactants, namely sulfate and sulfonate compounds, with respect to oil recovery efficiency has also been shown. The role of surfactants in the hot water process was investigated mainly for the Athabasca oil sands. Our study of surfactant interactions was initiated with isolation of the natural surfactants present in the aqueous phase from hot water processing of Asphalt Ridge and Whiterocks oil sands. A sublation technique

was used to isolate the free surfactants and accompanying species from the aqueous phase. Many structural similarities for the isolated surfactants were observed, however, the amount of sublated substances from each oil sand bitumen differed by almost threefold.

Filming of air bubbles is understood as advantageous for effective gravity separation and flotation of bitumen from digested oil sand slurry. The probability of filming increases, the more the air-water interfacial tension prevails over the sum of the oil-water and the air-oil interfacial tensions. The filming process was examined experimentally using the Questar 100 long distance microscope coupled with a video camera. Oil droplets and air bubbles were generated by means of automated syringes in an aqueous phase containing varying amounts of sodium dodecyl sulfate. The experiments have shown that the time which elapsed from attachment to the initiation of filming increased exponentially with increasing molecular weight of the oily phase. The shortest filming time was achieved, as expected, for the maximum in the spreading coefficient.

The efficiency of water-based separation of oil from sand particles is dependent on the nature of the oil-sand association and a preliminary examination of this bonding has been completed. The degree of hydration of the sand surface at the time of contact with oil was related to the subsequent efficiency of the oil-sand separation process. Variables which influence hot water separation were correlated by multiple linear regression, and a second order experimental model was obtained. The processing temperature

appeared to be the most significant variable, followed by digestion time and pH. Oil-coated sand particles which had intrinsic water left on their surface during sample preparation were easily processed in hot water separation experiments, and 64 to 90% of the oil was removed. On the other hand, only 1 to 23% separation and oil recovery was possible when a calcinated sand-oil mixture was used.

Some aspects of kerosene penetration into oil sand have been investigated. The natural oil sand porosity was measured and used to analyze the performance of the hot water process. Subsequently, pretreatment experiments, using 20 kg oil sand samples (Asphalt Ridge and Whiterocks, Utah), and kerosene as a diluent were carried out at the expected summer temperature (26°C) and the expected winter temperature (-14°C). The natural oil sand porosity accessible by diluent has a crucial impact on the reduction of bitumen viscosity, and influences the penetration time required for successful bitumen separation from oil sand by hot water processing. Thus the oil sand porosity is an important variable which determines appropriate operating conditions. Experimental results indicate that diluent penetration into the Asphalt Ridge oil sand (high porosity) is almost complete after 30 minutes, whereas for the Whiterocks oil sand (low porosity) the penetration process is much slower, and still not complete after 15 hours regardless of the ambient temperature.

The grade of bitumen concentrate produced in the hot water separation process depends primarily on the degree of oil

liberation from sand during digestion. However, bitumen recovery to the concentrate is also influenced by the separation technique used for bitumen recovery. Scavenger flotation of the digested oil sand slurry, directly following primary recovery by flotation or gravity separation, can reduce bitumen content in the tailings even below 0.4 weight percent. Nevertheless, high investment and operating costs can be expected, due to huge amount of oil sand slurry needed to be processed to recover the bitumen if conventional flotation machines are installed. In this regard, the high specific capacity air-sparged hydrocyclone (ASH), at least 100 times greater than conventional flotation equipment, offers some advantages for residual bitumen recovery from rougher tailings.

In a preliminary investigation the 2-inch ASH system (throughput of 60-70 Lpm of diluted digested oil sand slurry) was evaluated in laboratory separation tests; of course, larger units would be used in pilot or plant scale testing. Approximately 55 to 65 percent of the process water was recovered in the overflow product for recycle. A high separation efficiency was achieved with respect to small, free bitumen droplets, while bitumen-sand aggregates reported to the underflow product.

Experimental data of Whiterocks Utah bitumen concentrate clean-up are presented and discussed. Sedimentation and centrifugation were used to remove mineral particles and water droplets. Final removal of residual water (<6 wt%) was also attempted in an electrostatic cell with a pulsating DC electric field. The lowest concentration of dispersed water attained was

below 4 wt% while that of the fine minerals did not exceed 0.5 wt%.

ISOLATION OF SURFACTANTS FROM OIL SAND PROCESS WATER

INTRODUCTION

The carboxylate surfactant released to the aqueous phase in the hot water separation process appears to play a critical role in determining the maximum bitumen recovery^[87-89]. The concentration of surfactants in equilibrium with oil sand is expected to determine their adsorption density at various interfaces. It is reported that a single such equilibrium concentration will establish the condition for maximum recovery^[88]. This relationship appears to hold for all feed grades of oil sand irrespective of contamination or aging.

The surfactants are occasionally available from the oil sand as mined prior to processing but more generally are produced during the hot water process by reaction of the added sodium hydroxide or carbonate with certain acids naturally occurring in the bitumen. The reactions in which sodium hydroxide participates are more numerous than just those which generate surfactant. It is evident that clay minerals react with natural surfactants. The observation that the hot water process is critically dependent upon surfactant interactions provided the possibility for additional understanding of the fundamental aspects of the process. It may be possible to improve the efficiency of the hot water process by maintaining the surfactants concentration at the desired level.

More efforts to study the role of surfactants in the hot water process were made for the Athabasca oil sands than for the U.S. oil

sands. In our approach to the problem it was decided that due to the low content of swelling clays in the U.S. oil sand deposits the study of surfactant interactions should first be directed to sand grains, and later to clays. As a first step in this area of research, efforts were made to isolate the natural surfactants present in the aqueous phase from the hot water processing of two Utah oil sands.

EXPERIMENTAL

Batch experiments were carried out in a 5 gal double bladed stirred tank reactor (steam heated) at the following conditions: kerosene pretreatment with 2 hours penetration time, digestion at 55-65°C for 10 minutes, with 1 g Na_2CO_3 and 0.5 g of $\text{Na}_5\text{P}_3\text{O}_{10}$ per kg of oil sand. In each experiment 20 kg of oil sand and 7 L of tap water were used. Sodium tripolyphosphate was added to eliminate the destructive impact of polyvalent cations on the concentration of the carboxylic surfactants. After digestion the oil sand pulp was discharged into a container with 10 L of hot water, and stirred gently. The bitumen which floated to the surface was skimmed-off, and the turbid aqueous phase was placed in 4L glass bottles. After several hours of sedimentation the remaining turbidity was eliminated by centrifugation.

A sublation technique was used to isolate the free surfactants and accompanying species from the aqueous phase^[9]. In this regard 100 g/L of NaCl and 5g/L of NaHCO_3 were dissolved in the aqueous phase prior to purging the solution with nitrogen at a rate of 0.25 L/min for 20 minutes. For collection, 100 mL of ethyl acetate was

used as the receiving phase in the sublation apparatus. Each 900 mL sample of the aqueous phase was subltated twice. The surfactant-rich ethyl acetate was drained to a separatory funnel after each run (to separate residual aqueous phase), collected in a glass bottle, and submitted to rotary evaporation (50°C, 5 kPa).

RESULTS AND DISCUSSION

For each sample the rotoevaporation of the ethyl acetate solution resulted in two products. When the volume of the solution was reduced by evaporation from the original 3L to about 100 mL gradually a white precipitate formed. The precipate was filtered, washed with ethyl acetate, and dried. Distillation of the remaining 100 mL of the solution resulted in an oily residue. Brief, descriptive characteristics of both products is provided in Table 17. The substances differed totally with respect to solubility in water and in propanol. The precipitate after solvent removal resembled granulated powder, and was suspected to be a mixture of inorganic salts. The oily phase was assumed to be the residue containing surfactants. FTIR spectroscopy was used to examine the composition of these two products. The analysis was done by the diffuse reflectance spectroscopy in a KBr matrix (0.5% oil residue, and 2% precipitate by weight).

The FTIR spectra are presented in Figures 24 through 27. For both oil sands investigated it is clear that the oily residue is an organic phase rich in carboxylic groups, see Figure 24 and 26. Not

Table 17. Preliminary Characterization of Substances Isolated from Ethyl Acetate Solution

SUBSTANCE	SOLUBILITY IN		VISCOSITY AT 20°C	SMELL	COLOR
	WATER	PROPANOL			
AR-S ¹	Soluble	Not Soluble	Powder	None	Yellowish
AR-O ²	Not Soluble	Soluble	Very Viscous	Very Intense	Dark Brown
WR-S ³	Soluble	Not Soluble	Powder	None	Yellowish
WR-O ⁴	Not Soluble	Soluble	Less Viscous than AR-O	Less Intense than AR-O	Less Dark

¹precipitate obtained from Asphalt Ridge oil sand

²oily residue obtained from Asphalt Ridge oil sand

³precipitate obtained from Whiterocks oil sand

⁴oil residue obtained from Whiterocks oil sand

Figure 24. FTIR Spectrum of Oil Residue Separated by Sublation from Tailings Water from Hot Water Processing of the Asphalt Ridge Oil Sand.

Figure 25. FTIR Spectrum of Sediment Separated by Sublation from Tailings Water from Hot Water Processing of the Asphalt Ridge Oil Sand.

Figure 26. FTIR Spectrum of Oil Residue Separated by Sublation from Tailings Water from Hot Water Processing of the Whiterocks Oil Sand.

Figure 27. FTIR Spectrum of Sediment Separated by Sublation from Tailings Water from Hot Water Processing of the Whiterocks Oil Sand.

many structural differences between the Asphalt Ridge and the Whiterocks oil sand can be noticed. The characteristic peak around 1720-1730 cm^{-1} which is attributed to C=O stretching frequency indicates the acidic form of the surfactant. Interestingly, this peak is absent in the organic phase remaining in the precipitate, however, another band (1564 and 1583 cm^{-1}) which can be attributed to both (symmetric and asymmetric) stretching vibrations of the

group, indicates that only the deprotonated molecules were found adsorbed on the precipitate. Judging the absorbance level in the C-H stretching frequencies, there is a comparable number of CH_2 and CH_3 groups which means that the aliphatic chains are short. Additionally, there are a lot of C-H bonds associated with aromatic rings, which is characteristic for naphthenic acids. There is not clear evidence that HSO_3^- groups ($\sim 1100 \text{ cm}^{-1}$) are present.

The precipitate appears to be inorganic in nature with a prevailing content of phosphates (compare very strong band at 1115-1130 cm^{-1} characteristic of phosphorus-oxygen bonds, Figures 25 and 27). The inorganic salts originating from processing both oil sands are contaminated with organic substances, mostly surfactants.

The spectra in Figures 25 and 27 indicate that the sediment which precipitated from the ethyl acetate solution still contained distinct amounts of organic matter despite thorough washing with solvent. The Whiterocks precipitate retained significantly more organic phase than the Asphalt Ridge precipitate which correlates well with the more intense yellow color of the Whiterocks precipitate. The precipitate from both oil sands contained more water than the oily phase, which again speaks for the inorganic nature of the sediment.

The amounts of surfactants isolated (at the same sublation conditions for each run) from the aqueous phase originating from the hot water process of 20 kg oil sand are given in Table 18.

The data in Table 18 indicate that more inorganic salts were carried to the ethyl acetate for the Whiterocks oil sand process water than for the Asphalt Ridge oil sand process water despite the same sublation conditions and the same volume of ethyl acetate employed. The higher surfactants concentration in the Whiterocks process water might facilitate formation of smaller nitrogen bubbles and thus enhance the intake of the salt from the aqueous phase. Despite higher bitumen grade, the Asphalt Ridge oil sand yielded 815 mg of surfactants, compared to 1320 mg for the Whiterocks oil sand, which is almost three times less surfactants per unit weight of bitumen for the Asphalt Ridge than for the Whiterocks oil sand. The difference can be correlated with the oxygen and nitrogen content in the bitumen, as given in the lower part of Table 18. Apparently more oxygen is present in the

Table 18. Amount of Surfactants Released from 20 kg Samples of Asphalt Ridge and Whiterocks Oil Sands

Conditions	Asphalt Ridge	Whiterocks
Volume of sublated water, L	14	14
Total volume of aqueous phase		
- in digester, L	7	7
- in gravity cell, L	20	20
Released surfactants*, mg	815	1320
Concentration of surfactants during digestion, mg/L	116	189
Surfactants released per kg of bitumen, mg/kg	340	917
Inorganic salts entrapped in solvent, mg	450	1060
Concentration of inorganic salts in solvent before evaporation, mg/L	150	353
Elemental Analysis of Bitumen ⁽⁹¹⁾		
C, wt. %	85.2	85.0
H, wt. %	11.7	11.4
N, wt. %	1.0	1.3
S, wt. %	0.6	0.4
O, wt. %	1.1	1.6

*corrected for aqueous phase left in tailings and bitumen concentrate

Whiterocks oil sand bitumen in the form of carboxylic groups (naphthenic acids). Later, the correlations between sulfate/sulfonate surfactants and the sulphur content of bitumen will be examined. Much lower concentrations of these surfactants can be expected as follows from the IR spectroscopy.

The amount of free surfactants present during oil sand digestion, see Table 18, remains in good agreement with our observations of the flotation process used for residual bitumen separation from the digested oil sand slurry. Unlike Asphalt Ridge oil sand, the Whiterocks oil sand showed a strong tendency to produce a voluminous froth during flotation. In our 5 and 20 kg batch experiments foaming was particularly intense and almost out of control for the North-West part of the deposit. Additionally, the high concentration of surfactants, as is the case for the Whiterocks oil sand may exert a detrimental effect on the air bubble filming by bitumen. First, air bubble entrapment in the displaced bitumen during digestion will be diminished, therefore bitumen recovery to the gravity concentrate will be impaired. Second, by the bitumen concentrate flotation can also be affected, particularly when the process water is recycled. This leads to surfactant concentrations during flotation which are comparable to those during digestion.

The data in Table 18 indicate that more inorganic salts were carried to the ethyl acetate for the Whiterocks oil sand process water than for the Asphalt Ridge oil sand process water despite the same sublation conditions and the same volume of ethyl acetate

employed. The higher surfactant concentration in the Whiterocks process water might facilitate formation of smaller nitrogen bubbles and thus enhance the intake of the salt from the aqueous phase⁽⁹¹⁾.

SUMMARY AND CONCLUSIONS

Many structural similarities for the isolated surfactant were observed, however, the amount of surfactants released from each oil sand bitumen differed by almost threefold. Sodium tripolyphosphate added to the digestion step sequestered cations which could form insoluble soaps with free surfactants, thus making the quantitative results more reliable. Our findings support experimental data for the Athabasca oil sands that different surfactants concentrations can be expected in the hot water process as the effect of the feed source. Recovery of bitumen from the oil sands is dependent on several factors such as the bitumen viscosity and fines content which are the most crucial for the success of the process. The concentration of surfactants is also among these factors determining the hot water process efficiency for the domestic oil sands.

FUTURE ACTIVITIES

Surface chemistry research on wetting phenomena will be continued in order to better understand process variables controlling the separation process. An important step in this research is the identification of surfactants released from the bitumen during processing and the influence of these surfactants on

filming of air bubbles by digested bitumen. An improved bitumen recovery during separation in a gravity cell is expected when filming is spontaneous and takes place in a very short time.

AIR BUBBLE FILMING BY BITUMEN

INTRODUCTION

The gas phase plays an important role in the hot water processing of oil sands. First, air bubbles are entrapped in bitumen during digestion enabling separation of the bitumen concentrate by gravity. Second, air is used for the flotation of fine bitumen droplets and bitumen-sand aggregates from liberated sand particles in tailings. In order to avoid disturbances in process water recycle, and keep the processing cost as low as possible, frothers are, generally, not used because surfactants are released from the bitumen during digestion.

Bitumen droplets in successfully digested oil sand slurry (75 wt.% solids, which is typical for the University of Utah water-based separation process) exist as a broad size distribution with droplets from a few micrometers to 1 mm in size. The large bitumen droplets can be rapidly separated in a gravity cell assuming that they contain a sufficient amount of entrapped air. Fine bitumen droplets and bitumen-sand aggregates caught in the fast settling tailings, or fine droplets present in the middlings layer, require flotation for fast and complete recovery. Flotation of negatively charged mineral particles competes with the flotation of negatively charged bitumen droplets resulting in an inferior flotation concentrate quality, when compared to gravity separation^[92]. In this regard efficient separation of small bitumen droplets is

expected to be strongly influenced by the sand particles size distribution.

With respect to the flotation step, it has been established that large bitumen drops report to the concentrate due to an air bubble entrapment mechanism^[93]. Bubble entrapment can take place only in bitumen droplets considerably larger than air bubbles. The encapsulation of air bubbles in bitumen droplets of 0.5 mm and below (i.e., smaller than the air bubbles generated in the flotation machine) still occur by attachment and filming. Of course, the necessary surface conditions for spreading at the air-water interface must be satisfied^[94]:

$$\gamma_{a/w} > \gamma_{o/w} + \gamma_{a/o} \quad (2)$$

where: γ -interfacial tension, mN/m, at air (saturated with water vapor, particularly at elevated processing temperature) -water (a/w), oil-water (o/w) and air-oil (a/o) interfaces.

For all the systems investigated during our experiments the interfacial tension parameter β , identical with the spreading coefficient,

$$\beta = \gamma_{a/w} - (\gamma_{o/w} + \gamma_{a/o}) \quad (3)$$

was evaluated. It is understood here that a positive spreading coefficient will result in an enhanced separation of bitumen droplets from the digested oil sand slurry. The first part of the investigation was devoted to model systems in which both

reagent grade and commercial hydrocarbons were used as the oil phase, while sodium dodecyl sulphate dissolved in deionized water was the surfactant solution.

EXPERIMENTAL

In order to find the most favorable conditions for air bubble filming by oil, the three interfacial tensions indicated above were determined at different sodium dodecyl sulphate concentrations, ranging from 10^{-6} to 10^{-2} M. Several pure hydrocarbons (n-heptane, n-decane, n-dodecane, n-tetradecane, and n-hexadecane) and a bitumen-kerosene blend with different bitumen/kerosene weight ratios) were used in these experiments. The measurements were carried out using the du Noüy ring method, with Krüss semiautomatic tensiometer type K10T. The du Noüy ring method is suitable for the surface tension measurements of pure liquids but has not been recommended for solutions of surfactant^[95, 96]. The adsorption of surfactant from solution may alter the required complete wettability of the platinum ring leading to low results. For example, surface tension of up to 10 mN/m lower can be obtained for sodium laureate solutions at pH=1 after an extended period of time^[97]. Nevertheless, the platinum ring technique is acceptable for applied research^[98] bearing in mind the possible systematic error. Based on statistical analysis the relative error in our measurements was $\pm 5\%$.

The bubble filming conditions were estimated and verified experimentally using Questar 100 long distance microscope

coupled with a video camera. Oil droplets and air bubbles were generated in water (containing varying amounts of sodium dodecyl sulfate) by means of automatic microsyringes and the drainage time needed for the oil droplet to film the bubble measured. Another, more simple technique for the examination of bubble filming by oil involved generation of oil droplets in sodium dodecyl sulfate solution with a syringe, and determination of the drainage time of the oil droplet residing under the surface of the surfactant solution. All interfacial tension and filming measurements were carried out at 20°C.

RESULTS AND DISCUSSION

Oil, Bitumen and Water Surface Tension

Adsorption of surfactants on the du Noüy ring alters the results of the aqueous phase surface tension and the oil-water (O/W) interfacial tension. Additionally, it is known that the equilibrium surface (or interface) tension depends upon the surfactant concentration. The time effect extends for more than 10 hours and is most pronounced for dilute solutions (below 10^{-2} M) and diminishes markedly for larger concentrations⁽⁹⁶⁾; the effect reflects the tendency of the interface to reach equilibrium. All the surface and interfacial tension measurements were taken after 30 minutes of contact between phases with the platinum ring submerged in the aqueous phase from the beginning of the experiment to ensure reproducibility.

The surface tensions of all liquid phases used in our investigation are presented in Table 19. The experimental data

Table 19 Surface Tension of Pure Hydrocarbons, Bitumen Solution in Kerosene, and Sodium Dodecyl Sulfate Solution in Water

Liquid	Surface Tension, at 20°C mN/m Measured; Literature	Ref.
n-heptane	20.9	20.14 [99]
n-decane	24.5	-
n-dodecane	26.0	- [100]
n-tetradecane	27.4	- [100]
n-hexadecane	28.8	-
kerosene	27.5	-
Bitumen Solution in Kerosene		
- 20 wt% bitumen	25.3	-
- 40 wt% bitumen	25.6	-
C ₁₂ H ₂₄ SO ₃ Na solution in water		
- 0	72.1	72.94 [99]
- 10 ⁻⁶ M	72.1	-
- 10 ⁻⁵ M	71.4	-
- 5.10 ⁻⁵ M	67.8	-
- 10 ⁻⁴ M	56.1	-
- 5.10 ⁻³ M	36.9	-
- 10 ⁻² M	24.9	-

determined with the platinum ring technique corresponds well with the surface tensions available in literature.

Oil (Bitumen)-Water Interfacial Tension

Two different approaches were used to find out the O/W interface tension variation with time. In the first series of measurements the surfactant solution was equilibrated for a given time with hexadecane and put into the tensiometer cell. Next, the ring was submerged in the aqueous phase, the oil was

poured on top, and the measurement completed after 30 minute time interval. See curve (1) Figure 28. The other approach involved equilibration of the oil and surfactant solution in the tensiometer cell. As can be seen in Figure 28, the interfacial tension for the $5 \cdot 10^{-5}$ M sodium sulfate solution/hexadecane system decreased steadily with time for both oil/water equilibration techniques. Nevertheless, equilibration done outside the cell (the procedure involved frequent shaking of the separatory funnel containing both liquids) resulted in a 5 mN/m higher interface tension. Lower interface tension indicated by curve (2) most probably resulted from more extensive surfactant adsorption on the platinum ring. Based on these results, the experimental technique represented by curve (1) was adopted.

The oil-water interfacial tensions for pure hydrocarbons (hexane, decane, dodecane and hexadecane) are compared to literature in Figures 29 to 32. Our results can almost be superimposed on the data of Gillap et al.^[101, 102], who employed the Wilhemy plate method but the aqueous phase contained 0.1 M NaCl. However, a significant difference can be noticed with results of Davis & Smith^[103] (Wilhelmy plate) and Rehfeld^[104] (drop-volume method) who used water, oil and surfactant of a high purity. The interfacial tension curves for pure hydrocarbons are collected in Figure 33. All hydrocarbons exhibit similar interfacial tension change with increasing concentration of the surfactant.

The interfacial tensions for kerosene and for kerosene-tar

Figure 28. Aqueous sodium dodecyl sulfate solution surface tension variation with time for two oil-water equilibration techniques. 1- surfactant solution equilibrated for a given time with hexadecane outside tensiometer cell; 2- equilibration of hexadecane and surfactant solution in the cell with platinum ring immersed in the aqueous phase.

Figure 29. n-hexane - water interface tension versus sodium dodecyl sulfate concentration.

Figure 30. n-decane - water interface tension versus sodium dodecyl sulfate concentration.

Figure 31. n-dodecane - water interface tension versus sodium dodecyl sulfate concentration.

Figure 32. n-hexadecane - water interface tension versus sodium dodecyl sulfate concentration.

Figure 33. Pure hydrocarbons-water interface tension versus sodium dodecyl sulfate concentrate.

sand bitumen blend are shown in Figure 34. The kerosene interfacial tension curve is different from those curves for pure hydrocarbons, and it is distinctly different from the kerosene bitumen curve. Above a surfactant concentration of 10^{-4} M all interfacial tension curves are superimposed.

The parameter β calculated from Equation (3) versus surfactant concentration is presented in Figures 35 and 36. For pure hydrocarbons and kerosene a distinct maximum at $5 \cdot 10^{-5}$ M occurs. The largest maximum is for kerosene: 28 mN/m. Hexadecane can be distinguished from the other oils because β is negative in a wide range of the surfactant concentration. When aliphatic hydrocarbons are considered, the parameter β becomes decreasingly smaller with an increase in the molecular weight of the hydrocarbon (Figure 35). Judging from the three interface tensions, the tendency of the kerosene-bitumen blends to spread at the water surface is more pronounced. The β parameter remains strongly positive (26 mN/m) and constant for surfactant concentrations from 0 to 10^{-5} M, then β rapidly decreases reaching a slightly negative value at 10^{-2} M.

Impact on the Hot Water Process

As is evident from other studies, the concentration of surfactant plays a significant role in the bubble filming process^[94]. Consequently the release of surface active agents to the aqueous phase ("free" surfactant) during hot water processing of oil sand should be expected to effect bitumen recovery depending on temperature and alkalinity^[88, 92]. It has

Figure 34. Kerosene and kerosene-tar sand bitumen blend interface tension versus sodium dodecyl sulfate concentration.

Figure 35. Parameter β calculated from Equation (40) versus surfactant concentration for pure hydrocarbons.

Figure 36. Parameter β calculated from equations (40) vs. surfactant concentration for kerosene and kerosene-tar sand bitumen blend.

been widely accepted that naphthenic acids present in the crude oil or bitumen interact with alkali to form a surface active soap. The significance of compounds, with respect to other anionic surfactants, namely sulfate and sulfonate oil recovery efficiency has also been shown^[88]. An excessive addition of NaOH or Na₂CO₃ during digestion is avoided in the hot water process due to the increased release of surfactants to the aqueous phase. Surfactants exceeding a critical concentration reduce the bitumen zeta potential and diminish the disjoining pressure at the bitumen/mineral interface. Thus, surfactants inhibit bitumen disengagement from sand particles. Additionally, with the surfactants content approaching the critical micelle concentration (CMC) the filming phenomenon is less likely to occur (Figure 35) and bitumen separation from the digested oil sand slurry may be thwarted. Excessive concentration of surfactants during flotation can impair the quality of separation due to retardation of the filming process. Further, such high concentration of surfactants can lead to excessive foaming, which results in an extremely voluminous bitumen concentrate. The concentration of surfactants in the aqueous phase during flotation can be controlled by water recycle ratio, and the percent solids in the flotation cell.

Air Bubble Filming

Air bubble filming experiments have shown that the time which elapsed from the moment of oil droplet attachment to the initiation of filming increases exponentially with an increase

of molecular weight of the oil phase. The shortest filming time was found, as expected, for a maximum value of the β parameter. These data are presented in Figure 37 (each experimental point represents the mean value for 20 drops) and indicate that the drainage time remains in excellent correlation with the β parameter. With respect to pure hydrocarbons and kerosene the effect is insignificant (represented by factor of 2). However, preliminary measurements revealed that addition of bitumen to kerosene lowers dramatically the coalescence time, at least for the surfactant concentration below 10^{-5} M.

SUMMARY AND CONCLUSIONS

The spreading coefficient, or the parameter β , had a maximum of 5 mN/m at 10^{-5} to 10^{-4} M surfactant concentration, with negative values at 10^{-5} to 10^{-4} M. Maxima were observed only for pure hydrocarbons and kerosene (for kerosene the coefficient was equal almost 30 mN/m). For the bitumen-kerosene blend the β parameter was positive at all low concentrations, but rapidly decreased beginning from a concentration of 10^{-5} M, and reached negative values at 10^{-3} M.

The smallest filming time was found for the maximum value of the β parameter for both techniques used to measure the drainage time.

The numerical value of the interfacial tension parameter at the maximum was largest for n-heptane (17 mN/m), and clearly decreased when the molecular weight of the oil phase increased.

In order to evaluate the impact of platinum ring

Figure 37. Time of oil droplet coalescence at air/water interface.

wettability by the surfactant solution on the surface tension contact angle measurements have been initiated.

The effect of temperature change should be comparable for all surface (interface) tensions therefore the dependence of the β parameter on the surfactant concentration should also hold for higher temperatures. In the case of hot water processing of oil sands the air bubbles are saturated with water vapor which would tend to increase the oil surface tension and unfavorably influence the air bubble filming by bitumen.

FUTURE ACTIVITIES

Surface chemistry research on wetting phenomena will be continued in the next year to provide better understanding of process variables and to enhance separation of phases throughout the bitumen recovery process. This will include contact angle measurements in bitumen-quartz and bitumen-clay systems, gas bubble filming by oil, coalescence of dispersed water droplets stabilized in the bitumen concentrate, and coalescence of oil droplets at solid surfaces. FTIR Spectroscopy and electrophoretic mobility measurements will be applied. Further evidence for the importance of the wetting phenomena will be demonstrated from surface/interfacial tension measurements for model systems.

PRELIMINARY EXAMINATION OF OIL BONDING AT SAND SURFACES AND ITS INFLUENCE ON HOT WATER SEPARATION

INTRODUCTION

The importance of oil-sand interactions has been recognized for a long time in petroleum recovery^[105] and in mineral processing where the organic phase serves as collector or modifier during flotation^[106]. In this particular paper other processes requiring oil-sand separation are being considered, namely:

- oil sand processing, specifically hot water separation,
- removal of oil spills from beaches
- oil-contaminated soil remediation
- oily sludge processing.

All these processing situations are aimed at recovery of the oil phase. The oil can be used as a primary (oil sands) or a secondary (contaminated ground or sludge) source of liquid fuel. Environmental concerns may sometimes provide the greatest incentive for processing. The amount of the organic phase in these materials ranges from a few percent to as much as fifty percent. However, the solid phase usually constitutes the major component of the material. Attempts have been made to recover the oil phase by hot water digestion technology (followed by separation of phases) from all the oil-containing materials listed above^[107-109].

The mineral matter, which is mostly composed of silica-based minerals (with the exception of oily sludge from tank bottom^[108]), can be classified into two groups which differ significantly regarding the stability of the system:

- fine solid particles which form clusters or tend to accumulate

at the interface, and thus stabilize oil-in-water or water-in-oil emulsions, and

- coarse mineral particles which constitute a framework the pores of which are filled with gas, organic, and aqueous phases.

The importance of fine solids accumulation at the interface, and their role as stabilizers in multiphase systems has been clearly indicated in the literature^[110,111]. However, it is the separation efficiency of the oil phase from the coarse mineral particles which determines the oil recovery in the concentrate, and the concentrate grade. The significance of oil bonding to sand is of particular importance in the hot water processing of oil sands^[112]. The nature of the bitumen-solid bond as well as the phenomena accompanying oil sand bitumen displacement were reviewed by Sepulveda^[113].

It has been recognized that the initial conditions of the oil-sand contact have a strong impact on the success of oil sand processing for bitumen recovery. Similarly, the separation of the components of oily soil may also depend on the surface chemistry of the original oil-soil contact conditions, including the degree of hydration of the solids surface, or the presence of ionic species and surfactants. This is not only the case with oil spills and alluvial oil sludge but also includes the interactions of the overburden material with the oily phase during oil sand processing.

FUNDAMENTAL CONSIDERATIONS

The presence of water molecules between a sand grain and the oil phase forming a film around the grain certainly will alter the

change in the surface free energy (ΔG) for the detachment of oil from sand in an aqueous environment. ΔG must be negative for spontaneous roll-up of the organic film.

$$\Delta G = \gamma_{ow} + \gamma_{sw} - \gamma_{os} \leq 0 \quad (4)$$

where: γ - is interfacial tension at oil-water (ow), solid-water (sw), and oil-solid (os) interface.

The lack of water, meaning direct bonding of oil to the sand, should result in smaller γ_{os} because, simplifying, dispersion forces almost entirely account for the attractive forces at the silica-saturated hydrocarbons interface^[114-116]. Additionally, due to the weakly acidic nature of silica, basic constituents of the oil will firmly bond to the surface unless stronger base from the aqueous phase is available. In practice, complex crude oil (or oil sand-derived bitumen) should form a much stronger bond at a dehydrated silica surface than should a simple saturated hydrocarbon compound. On the other hand, a multimolecular water layer would significantly attenuate oil-sand interactions therefore the term γ_{os} in Equation (4) would accept its largest value. Detailed analysis of oil sand bitumen film retardation from hydrated silica surface was given by Takamura and Chow^[116]. For a sufficiently thick water film the oil can be treated as already separated from the sand surface. The equilibrium condition to which Equation (4) pertains may not be attainable in actual hot water processing of oily material.

Thus the question arises about the possible degree of hydration of the surface of quartz grains at the moment of contact with oil. Takamura^[111] assumed that the Athabasca oil sand was

formed by the immiscible displacement of a wetting phase (water) by a non-wetting phase (oil) in a porous medium. By calculating the disjoining pressure he came to a conclusion that the thickness of the aqueous film on silica does not exceed 15 nm. A corresponding thickness of water layer can be expected from the heat of adsorption of water on silica from the gas phase, as discussed by Nutting^[117]. Depending on water molecule orientation the thickness of a strongly bound water layer, amounting 73 molecular diameters, is found between $73 \times 0.135 \text{ nm} = 9.9 \text{ nm}$ and $73 \times 0.196 \text{ nm} = 14.3 \text{ nm}$. Numerous later publications pertain predominately to characterizations of water adsorbed onto silica gel. When quartz is preheated above 300°C its hydrophilic surface silanol groups -Si(OH)-Si(OH)- give off water, leaving behind hydrophobic siloxane groups -Si-O-Si-^[100]. The lower is the temperature at which the oil-sand contact occurred the more water molecules separating oil from the sand surface can be expected which should facilitate the oil-sand digestion in an alkaline aqueous environment.

The objective of this investigation was to provide experimental evidence for the dependence of the efficiency of oil separation from sand during hot water processing on the degree of silica hydration. In this regard model oil-sand blends were prepared such that for some samples the oil could directly react with the sand surface, while for other samples a thin film of water was present between the two phases.

EXPERIMENTAL

Model blends of commercial "LUX 10" engine oil (oil without

additives; saturated hydrocarbons of density 890 kg/m³ and viscosity 340 mPa·s at 20°C), and intentionally weathered Russian crude oil (884 kg/m³, 24 mPa·s at 20°C after weathering) were prepared with a beach sand and then subjected to hot water separation experiments. As evidenced by gas chromatographic simulated distillation data, the volatility of oil at 449°C (C₃₀) was 21% while the volatility of the crude oil was 66%. The viscosity of the oils used allowed the oil phase to retract from the sand surface at any processing temperature^[117]. The oils, used in the research, were also sufficiently fluid to be uniformly mixed with sand in the desired weight proportion.

The sand was sampled from a beach on the Baltic sea near Gdańsk, Poland thoroughly rinsed with deionized water and submitted for size analysis. See Table 20. More than 85% of the sand was in

Table 20. Particle size distribution of beach sand used for preparation of model oil-sand blends

Size Fraction μm	Weight Percent
800-630	0.4
630-430	2.1
430-320	9.7
320-250	15.4
250-200	23.0
200-150	23.7
150-120	25.4
<120	0.3

the 150-320 μm size range with almost no fines below 120 μm. The sand was composed of over 90 % transparent, rounded α-SiO₂

crystals. Other minerals were: feldspars and quartzite including sparsely distributed dark grains of magnetite, garnet and biotite - as revealed by microscopic and x-ray diffraction analyses.

The model oil-sand blends (5 to 25 wt% oil) were prepared from sand dried at 60°C for 4 hours, and then mixed with oil at ambient temperature. The air relative humidity was 65% at 20°C (which allows to assess the thickness of water film on quartz^[100]). Some experiments required preliminary sand calcination at 550°C for 8 hours bearing in mind that at 573°C α -quartz (hexagonal) is transformed into β -quartz (trigonal). Eventual formation of microcracks caused by quartz transformation could result in stronger oil bonding at the sand surface. Sand calcinated at 550°C was cooled-down in a desiccator, and then combined with oil (heated and dehydrated) at about 200°C. All oil-sand blends were left at least 24 hours for equilibration prior submitting to separation.

The oil-sand separation strategy was essentially carried out according to the hot water processing procedure for the treatment of oil sands^[113]. The Box and Wilson algorithm was used to settle the optimum experimental conditions for the separation of oil from sand and to identify the main processing variables which determine the efficiency of separation. A detailed description of the optimization procedure and results can be found elsewhere^[118]. A 3.5 L Denver-type flotation cell was used for both digestion and flotation. After a specified time of digestion the air suction valve was opened and the bitumen concentrates were collected for a 1+2+3+4 minute time sequence in order to evaluate the flotation

kinetics. The concentration of the oily sand throughout the process was 20 wt%. Sodium carbonate was used to control the pH. The desired amount of sodium carbonate was determined by titration of the sand slurry at the temperature of processing. Analysis of the concentrate and tailings was carried out in a Dean-Stark apparatus. The residual emulsified oil in the aqueous phase was determined by CCl_4 extraction followed by UV analysis.

RESULTS AND DISCUSSION

Optimization of the Oil-Sand Separation Process

The impact of operating variables such as percent solids in the digester, and intensity of agitation has already been established for oil sands^[70,119]. Similarly, those conditions most favorable for the flotation of Asphalt Ridge oil sand have been identified^[120]. In this regard, the following variables were selected as the main factors which were expected to influence the coefficient of separation (CS) for the combined digestion-flotation processing of the model oil-sand blends: temperature (x_1), oil weight percent in the feed (x_2), digestion time (x_3), and pH - controlled by Na_2CO_3 addition (x_4). All other digestion and flotation conditions were maintained constant. To test the effect of these four variables, a two level, four variable factorial design with center point replication was used. The coefficient of separation is a one-parameter description of the efficiency of separation for a binary system, and physically represents the fraction of the feed material that undergoes perfect separation.

The range of variables used in these experiments is given in Table 21.

Table 21. Variable ranges for factorial design (2^4) experiments

Variable	Symbol	Units	Coded Values		
			-1	0	+1
Temperature	x_1	K	323	333	343
Oil Content	x_2	wt%	5	15	25
Digestion Time	x_3	s	60	180	300
pH	x_4	-	7.8	8.7	9.6

The results from 25 processing tests were correlated by multiple linear regression to obtain a second order experimental model, in the following final form^[118].

$$\begin{aligned}
 CS = & 0.6831 + 2.01 \cdot 10^{-2} x_1 + 1.90 \cdot 10^{-2} x_3 + 1.82 \cdot 10^{-2} x_4 + \\
 & 1.81 \cdot 10^{-2} x_1 x_4 + 1.33 \cdot 10^{-2} x_2 x_3 + 0.93 \cdot 10^{-2} x_3 x_4 + \\
 & 1.74 \cdot 10^{-2} x_1^2 - 2.33 \cdot 10^{-2} x_2^2 + 6.19 \cdot 10^{-2} x_3^2 + \\
 & 3.36 \cdot 10^{-2} x_4^2
 \end{aligned} \tag{5}$$

The regression coefficients corresponding to x_2 , $x_1 x_2$, $x_1 x_3$ and $x_2 x_4$ were not statistically significant therefore these terms were eliminated from Equation (5). As indicated by Equation (5), temperature appeared to be the most significant variable, followed by digestion time and then pH. The quality of the data described by the model is illustrated in Figures 38 and 39 where fitted and experimental values are compared by isoefficiency graphs in the

Fig. 38. Isoefficiency graph for $X_2 = 25$ wt% and $X_3 = 1$ min. The cross symbol pertains to experimental data; encircled numbers indicate the value of coefficient of separation in percents.

Fig. 39. Isoefficiency graph for $X_2 = 5$ wt% and $X_1 = 5$ min. The cross symbol pertains to experimental data; encircled numbers indicate the value of coefficient of separation in percents.

temperature-pH coordinate system for two digestion times and two compositions of the oil-sand blend. The data shows good agreement between experimental and fitted values of the coefficient of separation.

Further analysis of the objective function (CS) revealed⁽¹¹⁸⁾ that a maximum should be present for the x_2 parameter (oil content in the sand) while the remaining three parameters x_1 (temperature), x_3 (digestion time), and x_4 (pH) show a minimum for the CS. However, due to the interaction effects only the region of greatest processing efficiency can be determined. The dependence of the coefficient of separation vs. temperature and pH for selected processing conditions is presented in Figures 40 and 41. On both graphs there is a minimum in the separation efficiency. The minimum can result from the superposition of two effects: the extent of oil displacement from sand, and the degree of oil dispersion in the aqueous phase. The dispersion of oil liberated from sand increases in more alkaline solutions, which is intensified at more elevated temperatures, thus the flotation efficiency decreases. However, on the other hand, higher alkalinity results in an increased ability of the aqueous phase to wet the sand surface and to displace oil. Thus it might be expected that the separation efficiency would go through a minimum with respect to these process variables. Comparison of curve 3 and 4 in Figure 40 shows the importance of prolonged mixing during digestion, which indicates, that the system was still approaching equilibrium.

Fig. 40. Processing efficiency vs. temperature; X_2 - oil content, X_3 - digestion time, X_4 - pH

Fig. 41. Processing efficiency vs. pH; X_1 - temperature, X_2 - oil content, X_3 - digestion time

First order flotation kinetics were observed for 21 of the 25 processing tests with a rate constant from $2.5 \cdot 10^{-3}$ to $4.2 \cdot 10^{-3} \text{ s}^{-1}$. The aqueous phase after flotation contained 0.2 to 1.2 % of emulsified oil with an oil droplet size (Sauter diameter) of a few micrometers. The amount of residual emulsified oil in the process water was 2 to 4 times higher when the alkalinity was increased from pH=7.8 to pH=9.6. The oil which reported to the flotation concentrate contained several percent of emulsified water. Microscopic analysis revealed that minerals accompanying quartz in the beach sand (particularly magnetite) were enriched in the oil concentrate.

Impact of Silica Dehydration

After completion of the optimization experiments which confirmed amenability of the hot water process for oil separation from model oil/sand mixtures (5 to 25 wt% of the oil), the separation tests were repeated with crude oil-sand blends, and with engine oil-sand blends prepared with roasted, hot sand. The IR spectra revealed that both oils were predominantly paraffinic with rather long aliphatic chains. The presence of oxygen was evident for the crude oil by the hydroxyl, carbonyl and carboxylic groups while oxygen was absent in the engine oil.

The separation efficiency data for both oils mixed with both as received and roasted sand are presented in Table 22. The impact of the feed source and the degree of silica hydration is evident.

Table 22 Oil-sand separation efficiency for hydrated and dehydrated sand

Processing Conditions:

Temperature	70°C
pH during processing	8.7
Oil content	15 wt%
Digestion time	5 min
Flotation time	10 min

Hot Water Separation Product	Component Hydrated Sand	Grade, wt% - Dry Basis Dehydrated Sand	
ENGINE OIL			
Concentrate	Oil	98.7	92.6
	Sand	1.3	7.4
Tailings	Oil	<0.1	7.0
	Sand	99.9	93.0
Coefficient of Separation*		0.895	0.230
WEATHERED CRUDE OIL			
Concentrate	Oil	96.5	16.5
	Sand	3.5	83.5
Tailings	Oil	1.2	13.4
	Sand	98.8	86.6
Coefficient of Separation*		0.635	0.011

* CS - The coefficient of separation is the separation efficiency and represents the fraction of feed which undergoes perfect separation to oil and sand; CS is calculated as the difference between the recovery of oil and the recovery of sand in the oil concentrate⁽¹¹³⁾.

In comparison to the engine oil, notably lower separation efficiency was obtained for hydrated sand mixed with crude oil; the CS dropped from 0.895 to 0.635. The residual crude oil content in tailings was 1.2% compared to less than 0.1% for the engine oil.

The quality of the oil concentrate did not change yet. The most pronounced drop in the CS occurred for the dehydrated sand-oil blends. With respect to the engine oil the CS decreased four times compared to the hydrated sand while for the crude oil the CS reached hardly 0.011, and practically no liberated oil reported to the concentrate. The oil grade of the concentrate corresponded to that of the feed.

The results obtained demonstrate that the presence of even a thin water layer at the silica surface can significantly attenuate oil bonding to sand while considerable surface forces are established under direct silica-oil contact. These strong forces result predominantly from the interaction between oxygen and nitrogen containing functional groups present in the oil phase. As expected, the engine oil which contained almost exclusively aliphatic hydrocarbons was less firmly bound at the sand surface as compared to the crude oil case.

Separation Efficiency

The concentration of the oily sand feed in the suspension was maintained at 20 wt% throughout the entire experiment. Previous data for the hot water processing of oil sands indicate that the optimal value is about 75 wt% solids^[113, 119]. The CS diminished 6% when the slurry contained 50% oil sand instead 75% oil sand. Therefore it is expected that the separation efficiency obtained in this research can be significantly improved. The concentrated slurry is expected to behave like a non-Newtonian liquid, most probably pseudoplastic. The viscosity of the suspension plays a

major role in the establishment of stress field during digestion:

$$\tau = \mu_a (du/dx) \quad (6)$$

where: τ - shear stress, Pa

du/dx - shear rate, s^{-1}

μ_a - apparent viscosity, Pa·s

and can be estimated from several empirical equations^[121, 122]. Based on these equations, the suspension viscosity can increase by more than one order of magnitude when the solids content increases from 20 to 75 wt%. The low shear stress available during digestion accounted for the strong impact of the digestion time on the coefficient of separation, compare curves 3 and 4 in Figure 40.

SUMMARY AND CONCLUSIONS

Model oil-sand blends were prepared from beach sand which contained different amount of adsorbed water. An effective separation of oil from the sand was accomplished by digestion and flotation in an alkaline environment, with sodium carbonate being the only additive in the process. The Box and Wilson optimization technique used to determine the optimum operating conditions demonstrated shallow minimum (50-55°C and pH 8.0-8.5) in the coefficient of separation (CS) for the examined range of process variables. The quality of separation (being characterized by the CS) was found to be independent of the oil content of the oil-sand blend whereas the processing temperature had the strongest influence on the separation yield. The tendency of oil to form

emulsion appeared to limit the flotation efficiency, and was suspected for the minimum in the CS. In this regard, processing should be carried out above 60°C and at pH>8.5, or at 50°C and pH close to 10. It was also found that the sand with indigenous water left on its surface (dried at 60°C for 4 hours) could be easily separated from oil in the hot water experiments, while practically no separation occurred when the calcinated sand-crude oil mixture was used. Water molecules adsorbed at a silica surface can significantly attenuate oil bonding to sand while, considerable surface forces are established under direct silica-oil contact.

FUTURE ACTIVITIES

A similar procedure to that described in Chapter ?? will be employed to repeat the experiments with bitumen recovered from oil sand. The bitumen will be diluted with toluene in order to mix it uniformly with sand. Later the toluene will be evaporated under vacuum to provide the model oil sand. Beside beach sand (i.e. almost pure quartz sand) selected tailings size fractions from the hot water process will also be used. The research should provide important information on the role of the indigenous water in oil sands processing.

OIL SAND PRETREATMENT WITH DILUENT

INTRODUCTION

As is true in most process engineering situations, operation of a hot water processing plant (for the recovery of bitumen from oil sand) will strongly depend on the uniformity of the feed material. This becomes even more critical when diluent is used prior to digestion in order to reduce bitumen viscosity^[70, 123]. The critical bitumen viscosity below which a rapid increase in separation efficiency is observed was found to be 1.5 Pa·s (15 cP). The amount of diluent (such as kerosene or naphtha) required to lower the digestion-separation temperature to 50-55°C for most Utah oil sands is from 10 to 35 wt% with respect to bitumen content, and can be predicted from the bitumen viscosity curves^[70, 123]. Some organic solvents may exhibit greater dissolution power with respect to bitumen than kerosene or naphtha, however, due to the cost and/or volatility their commercial value is limited^[71].

An industrial operation involving diluent spraying of crushed oil sand will require tight measures to prevent health and fire hazards, and to avoid air pollution. Because of the diluent vapor pressure the system must be maintained below 40 to 50°C in order to prevent ignition risk of hydrocarbon vapors. A rotating drum, which can easily be designed to provide sealed-off space for diluent spraying, has been selected for oil sand mixing in our experiments. The importance of diluent pretreatment is discussed with respect to certain oil sand properties which impact the separation efficiency in hot water processing.

FUNDAMENTAL CONSIDERATIONS

Two phenomena control diluent mixing into the bitumen phase during pretreatment of oil sand, namely capillary action and diffusion. Depending on origin and properties, the oil sand feed generally exists as particle aggregates from 1/2 inch to two inches in size (larger feed fragments are expected for less consolidated oil sand, such as Asphalt Ridge). Diluent is sprayed on the surface of these feed particle aggregates and the capillary action enables the diluent to penetrate and wet the bitumen contained therein. With respect to diluent pretreatment the actual oil sand porosity, i.e., the pore volume of the bitumen impregnated sandstone which is filled with gaseous hydrocarbons, air or water, is of critical importance for diluent mixing due to the capillary transport. The unoccupied-by-oil part of the pore volume will be termed here the natural porosity of oil sand. After penetration and wetting, diffusion finally leads to a uniform mixture of bitumen and diluent. The lower the oil sand porosity and the higher the bitumen viscosity, the longer the penetration time required for complete and uniform bitumen dilution. The wetting ability of the diluent is of pronounced importance, particularly when capillaries are filled with water. Diluent penetration will also depend on the ambient temperature (water may freeze in oil sand pores in the winter season.).

The diluent imbibition of the oil sand can be modelled as an adsorption process in a bundle of capillary tubes. Some oil sands may be partially saturated with water. In such cases, the diluent

will have to displace capillary water. Assuming that the porosity is of an open type, a mathematical approach used to describe oil migration into a porous material^[124] can be adopted for diluent penetration. The capillaries in the oil sand are considered to be sufficiently small that the influence of gravity can be neglected compared to the capillary pressure. The time (t, in seconds) required to fill the capillary can thus be derived from the Poiseuille and the Young-Laplace equations:

$$t = 8\mu_d L^2 / d \Delta\sigma \quad (7)$$

$$\Delta\sigma = \sigma_{ws} - \sigma_{ds} - \sigma_{dw} \cos\beta \quad (8)$$

where:

μ_d	-	dynamic viscosity of diluent, Pa.s
L	-	capillary length, m
d	-	capillary diameter, m
σ_{ws}	-	water-solid (capillary wall material) interface tension; or gas solid interface tension when no water is present, N/m
σ_{ds}	-	diluent-solid (capillary wall material) interface tension N/m
σ_{dw}	-	diluent-water interface tension; or diluent-gas interface tension when no water is present, N/m
β	-	contact angle of the interface with the capillary wall measured through the most dense phase, deg.

It follows from Equation 7 that the transport of the diluent can be completed in a few minutes when the dimension of the oil sand aggregate is substituted for L. This is true even if the diluent is not sprayed uniformly, provided that the diluent

preferably wets the oil sand ($\Delta\sigma > 0$), and μ_d does not increase due to bitumen dissolution. In reality, however, the "diameter" of the pores change, and the pore length L may exceed the dimensions of the oil sand aggregate. Additionally, the diluent viscosity can increase significantly if the native bitumen viscosity is low. Also it should be recognized that some oil sand capillaries are open on one side only which can contribute to an extended diluent penetratic time. Of course, in order to maintain a large $\Delta\sigma$ the diluent should not be added during the oil sand digestion step (because σ_{dw} drops in the alkaline environment) but in the pre-treatment step prior to digestion. Finally, very limited driving force for diluent penetration is available in those aggregates of oil sand where sand gains are not completely covered with bitumen. In view of the foregoing Equation 8 probably represents the best case situation.

NATURAL POROSITY OF OIL SAND

Much faster diluent penetration into the bitumen can be expected if the volume of diluent contained within the oil sand (equal to the natural pore volume) is not smaller than the required amount of diluent estimated from viscosity curves. Otherwise, diluent penetration would be slow and additional reduction in the size of oil sand aggregates would be required for effective diluent diffusion. Based on the literature, the porosity (including all fluid phases) of the oil sand host rock ranges from 15 to 40%^[125], see Table 23. These values can be related to the original,

Table 23. Tar Sand Reservoir Characteristics^[105]

Location	Grade % oil	Porosity %	Oil Saturation %	Overburden ft	Thickness ft
Utah	4-10	15	23-72	0-500	10-60
Texas	----	30	35-55	1500	15-330
Kentucky	6-10	15	20-70	0-200	10-50
California	≤30	30-40	50-75	0-3200	50-400
Alabama	1.5	6-24	4-56	0-1000	10-300

almost unconsolidated sand and soft sandstone, ranging in texture from a fine silt to a coarse grit. Oil saturation usually represents 50% of the porosity.

Consolidated oil sands (i.e., oil sand in which sand grains are firmly bound by carbonates and/or silicates; e.g., from the Sunnyside and Whiterocks deposits) require feed size reduction down to a few millimeters, unless a powerful shear force field is provided during digestion which facilitates disintegration of the oil sand aggregates down to the elemental sand grains. An extensive size reduction of the consolidated oil sand automatically leads to better bitumen exposure to the diluent. However, the feed size reduction (in addition to that obtained during the ore excavation) is usually not necessary for unconsolidated oil sands, such as the oil sands from the Asphalt Ridge and P.R. Spring deposits. In any case the lack of sufficient pore volume available for diluent accommodation may seriously hinder the dilution rate, resulting in an extended penetration time or incomplete bitumen

displacement from sand.

The natural pore volume V_p can be calculated by subtraction of the volume of bitumen and sand from the total volume V_T of the oil sand:

$$V_T - V_p = m_b / \rho_b + m_s / \rho_s \quad (9)$$

where m_b , m_s - mass of bitumen and sand

ρ_b , ρ_s - density of bitumen and sand.

By definition, natural porosity ϵ is equal to: $\epsilon = V_p / V_T$; and the weight fraction of bitumen in the oil sand X_b is equal to: $X_b = m_b / (m_b + m_s)$, which allows us to eliminate V_T and m_s from Equation (9):

$$V_p = m_b [1 / \rho_b + (1 - X_b) / \rho_s X_b] \epsilon / (1 - \epsilon) \quad (10)$$

Assuming complete filling of the natural pore volume by diluent (density, ρ_d), the diluent mass m_d is equal to: $m_d = \rho_d V_p$, thus the weight percent of diluent in bitumen that can be accommodated by the oil sand pores (α):

$$\alpha = m_d / m_b$$

$$\alpha = [1 / \rho_b + (1 - X_b) / \rho_s X_b] [\epsilon \rho_d / (1 - \epsilon)] 100\% \quad (11)$$

It is assumed that only the weight percent of diluent represented by the parameter α is readily available for bitumen dilution in the oil sand.

In order to estimate how amenable a particular oil sand may be

to diluent pretreatment the oil sand natural porosity was measured, the parameter α calculated from Equation (11), and the data compared with the required amount of diluent estimated from the viscosity curves^[70, 123].

POROSITY MEASUREMENTS

The pore volume available for diluent was determined by submersion of oil sand samples in two liquids of differing ability to wet, and thus penetrate, the capillaries. These liquids were water and methyl alcohol. Generally, water does not migrate to any great extent into the capillaries of most oil sands while methanol does. The difference in volume for the same oil sand sample immersed in water, and later in methanol allows for the determination of the natural porosity. Methanol mixes well with water and does not dissolve the bitumen to any appreciable extent (thus the oil sand structure and bitumen distribution within the pores remains unaltered) which is crucial for the measurement. Volumetric measurements were supplemented by weighing each oil sand sample: prior to and after submersion in water, prior to and after submersion in alcohol, and after alcohol removal under vacuum at 25°C for 24 hours. Oil sand samples of 20 to 100 g were placed in water for a few minutes only, while soaking in methanol required at least 24 hours and frequent shaking in order to facilitate gas phase release from the pores. Each value of the natural porosity for a given oil sand sample was obtained from at least five independent samples. As described, the technique allowed the determination of the natural porosity with $\pm 20\%$ accuracy. The data

obtained also allowed for the calculation of the apparent density which includes water present in oil sand samples.

POROSITY RESULTS AND DISCUSSION

The original porosity of the host sandstone and the degree of saturation with bitumen determine the natural porosity. Higher natural porosity may also mean greater sensitivity of the mined oil sand to oxidation, which can alter processing efficiency. The range in experimental porosity was found to depend upon the location of the oil sand deposit, as reported in Table 24. With respect to hot water processing at 50°C, the data from Table 24 indicate that only for certain oil sands is the pore volume sufficient to contain all the kerosene necessary for bitumen dilution. In the case of the Hill Creek, Asphalt Ridge and Athabasca oil sands complete digestion and release of bitumen from sand is possible. For the other oil sands undigested particles are frequently found in the digested oil sand slurry. These undigested particles will report to the concentrate or will be found in the tailings, depending on the residual bitumen content, the degree of bitumen dilution, and the bitumen surface characteristics^[126].

By limiting the amount of diluent available to the bitumen, the natural oil sand porosity can be a decisive factor in determining the lower limit of the processing temperature. For example, the porosity of the P.R. Spring oil sand is 5.5% which allows for only 18.3% diluent (with respect to bitumen) while 20% diluent is required at 50°C to secure bitumen viscosity below 1.5 Pa.s. The extra diluent will not be able to fill the capillaries

Table 24. Natural Porosity and Diluent Availability during Pretreatment for several Utah Oil Sands and for a Sample of the Athabasca Oil Sand

Tar Sand Deposit	Nature ¹⁾	Bitumen	Bitumen Viscosity	Tar Sand Apparent	Natural Porosity ²⁾		Amount of Diluent	
		Content wt%	at 50°C Pa.s	Density kg/m ³⁾	Range %	Mean Value %	Required ³⁾ wt%	Available wt%
Athabasca	N	14.4	5	1910-2060	10.5-15.2	12.0	5	36.8
Asphalt Ridge	N	12.5	80	1980-2050	3.2-5.7	5.0	14	16.0
Hill Creek	C	3.4	--	1890-1960	15.0-15.5	15.2	-	177.3
P.R. Spring	N	12.0	280	2030-2290	2.7-6.2	5.5	20	18.3
Sunnyside	C	9.5	1500	2030-2240	1.0-1.6	1.2	24	4.7
Whiterocks	C	7.5	110	2230-2240	1.9-2.2	2.0	17	9.7

1) C - consolidated; N - not consolidated

2) Pore volume in oil sand occupied by gas, air or water, and open for diluent penetration

3) Based on viscosity curve for processing at 50°C, see reference^[123]

Assuming complete filling of pore volumes with diluent

and hence will not effectively penetrate the oil sand in the few hours of pretreatment time that would be available in a commercial operation. In this case a diminished bitumen recovery would be expected.

The impact of the natural porosity can be better illustrated with the Sunnyside and the Whiterocks oil sand. The hot water processing of Sunnyside yields a bitumen concentrate of inferior quality, compared to the bitumen concentrate from the Asphalt Ridge oil sand despite proper dilution of the oil sand^[70, 71, 92, 128]. The poor separation was attributed to compositional and, eventually, chemical heterogeneity. Our porosity data provides new evidence that the lower separation efficiency for bitumen recovery from these oil sands can also be related to porosity and inadequate viscosity control during pretreatment.

The apparent density, which is given in the fifth column in Table 24, does not always correlate with the measured oil sand porosity because some pores are closed to diluent penetration. It was observed, that porosity determined from several small pieces of oil sand was greater than the porosity determined from one larger oil sand fragment, which may support the existence of the inaccessible void space within the oil sand.

TAR SAND PRETREATMENT WITH DILUENT

The bitumen from almost all U.S. deposits is more viscous than that from the Athabasca oil sands, therefore, a moderate processing temperature for the U.S. oil sands requires significant bitumen dilution with an organic solvent during the oil sand pretreatment

step⁽⁷⁰⁾. The pretreatment step involves diluent spraying on the "dry" oil sand feed prior digestion. Considering the bitumen concentrate clean-up, which is one of the final operations for the hot water process, the more diluted the bitumen prior to digestion the more favorable are the subsequent dissolution kinetics of the bitumen concentrate in the organic solvent (kerosene)⁽¹²⁷⁾.

EXPERIMENTAL PROCEDURE

In order to select proper pretreatment conditions and to provide design information for pretreatment, diluent penetration experiments have been completed. Two oil sand samples of comparable bitumen viscosity, namely samples from the Asphalt Ridge and the Whiterocks deposits, were selected. Generally, the Asphalt Ridge oil sand does not require additional size reduction beside that which occurred during the mining operation, therefore, despite screening, large size feed material (greater than several inches) should be expected due to the sticky nature of the oil sand and the high content of bitumen. On the other hand, the Whiterocks oil sand had to be crushed and screened. The resulting product of up to 3/4" in size is easy to handle because it is less vulnerable to secondary consolidation.

The experiments and procedure involved both a short time for mixing and a longer time for penetration after diluent addition. The experiments were carried out in a cement mixer (33 rpm, max. load 50 kg, max. internal dia. 60 cm) using 20 kg feed samples. The oil sand was placed in the rotating cement mixer, and then sprayed with kerosene (13 wt.% with respect to bitumen) for 40

seconds. The drum was then allowed to rotate for an additional 2 or 5 minutes (mixing time). When mixing was complete the oil sand was discharged to a polyethylene tray and a layer of approximately 42x38x8 cm was formed. Six of 50 to 60 g cylindrical samples of the oil sand from different locations throughout the entire layer were taken after a certain penetration time (usually after 3 minutes, 10 minutes, 20 min, 1 h, 3 h, and 16 h) and were then analyzed in the Dean-Star apparatus. Diluent spraying was done at both summer (26°C) and winter (-14°C) temperatures. Frozen oil sand samples were procured with the application of a sharp-edge metal sampler which was forced through the layer with a hammer. The experimental conditions are given in detail in the upper part of the Table 25. An important point is revealed in the lower part of Table 25, which contains the average bitumen content based on six samples related to a given penetration time. The average bitumen content of the oil sand remains relatively constant throughout the entire experiment, which demonstrates the reliability of the experimental technique, whereas, the standard deviation of bitumen content changes significantly with the penetration time, as discussed in the next paragraph.

PRETREATMENT RESULTS AND DISCUSSION

The effectiveness of diluent migration into the oil sand was evaluated by simple statistical analysis of the data pertaining to the organic phase (bitumen + diluent) content. The standard deviation(s) for each set of the six oil sand samples was calculated:

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$$s = \pm [\sum (f_1^2 + \dots + f_N^2) / (N-1)]^{1/2} \quad (12)$$

where: F - deviation of particular measurement from the mean ($\bar{x}$)

N - number of measurements; N = 6

In order to better compare oil sands of different bitumen content, the relative standard deviation (RSD), also known as the coefficient of variation, or the relative error, was used:

$$RSD = S/\bar{x} \cdot 100\% \quad (13)$$

and plotted versus time which had elapsed after diluent addition to the oil sand. See Figures 42 to 45. It was anticipated that the kerosene distribution would become increasingly more uniform due to the capillary action. Additionally, because of the dissolution in the diluent, the bitumen should be also more evenly distributed throughout the oil sand. Therefore, after a certain time, the RSD should reach a plateau, which would indicate the end of the capillary transport of the diluent, and would simultaneously determine the minimal penetration time necessary for the oil sand pretreatment step.

The experimental results for the Asphalt Ridge oil sand sample at 26°C ambient temperature are present in Figure 42. Each curve in this pilot represents one of three different experimental conditions: 5 min oil sand mixing after diluent spraying, 2 min oil sand mixing after diluent spraying and a blank experiment in which

Fig. 42. Relative standard deviation of bitumen + kerosene content for Asphalt Ridge oil sand after pretreatment in rotating drum and storage in 8 cm thick layer at 26°C; 13 wt% kerosene with respect of bitumen.

Fig. 43. Relative standard deviation of bitumen + kerosene content for Whiterocks oil sand after pretreatment in rotating drum, and storage in 8 cm thick layer at 26°C; 13 wt% kerosene with respect to bitumen.

Fig. 44. Relative standard deviation of bitumen + kerosene content for Asphalt Ridge oil sand after pretreatment in rotating drum, and storage in 8 cm thick layer at -14°C; 13 wt% kerosene with respect to bitumen.

Fig. 45. Relative standard deviation of bitumen + kerosene content for Whiterocks oil sand after pretreatment in rotating drum, and storage in 8 cm thick layer at -14°C ; 13 wt% kerosene with respect to bitumen.

no diluent was used (the oil sand was formed into a layer after 3 minutes of preliminary mixing, see experimental procedure). The RSD diminishes rapidly for the first 10-20 minutes and seems to approach a plateau after 60-80 minutes of diluent penetration. The RSD of the bitumen content, when diluent was not used, remained unchanged and relatively high, (approximately 2.7%) indicating local compositional heterogeneity of the 20 kg oil sand sample being examined. Prolonged mixing time had little effect of the diluent penetration rate at 26°C.

The RSD change for the Whiterocks oil sand (at the expected summer temperature) followed the same trend as that obtained for the Asphalt Ridge oil sand. Nevertheless, the scatter of the organic phase content, as given by the magnitude of the RSD, was slightly smaller than that for the Asphalt Ridge oil sand, which can be attributed to the more uniform saturation of the oil sand with bitumen. This feature may also have resulted from smaller size and narrower size distribution of the feed material. The migration of the diluent was slower, with the RSD reaching a plateau after 15 hours. The prolonged diluent-bitumen contact resulted in mutual dissolution of both organic phases which resulted in extended penetration time. In the case of the Whiterocks oil sand the diluent penetration could also be enhanced from macro-pores formed by the well-crushed feed material. However, these void spaces are of much greater size when compared to natural capillaries and under these circumstances diluent transport may no longer be dependent on capillary forces.

Table 25. Tar Sand Pretreatment with Diluent. Processing Conditions:

Weight of oil sand sample: 20kg

Diluent: kerosene

Amount of diluent added (with respect to the bitumen content in oil sand): 13%

Mixing device: rotating drum with lifters, 33 rpm (42" dia. cement mixer)

Description	1	2	3	4	5	6	7	Experiment 8	9	10
Tar Sand Deposit*	W.R.	W.R.	W.R.**	W.R.	W.R.	A.R.	A.R.	A.R.**	A.R.	A.R.
Bitumen Content	7.2	7.2	7.2	7.2	7.2	12.5	12.5	12.5	12.5	12.5
Temperature, °C	-14	-14	24	26	25	-13	-14	26	23	23
Mixing Time, min.	2	5	-	2	5	2	5	-	2	5
Maximum Oil Sand Feed size, cm	<2.5	<2.5	<1.5	<1.5	<1.5	15	10	<8	<5	<5
Penetration Time***, min	Average Bitumen Content Based on Six Samples, wt. %									
3	7.26	7.23	7.22	7.23	7.20	12.57	12.51	12.56	12.68	12.61
10	7.30	7.20	7.27	7.31	7.25	12.59	12.51	12.49	12.71	12.65
20	7.22	7.29	7.22	7.26	7.28	12.73	12.70	12.53	12.70	12.54
60	7.28	7.26	7.20	7.26	7.25	12.64	12.76	12.50	12.57	12.54
180	7.23	7.28	7.30	7.24	7.33	12.66	12.89	12.47	12.54	12.50
960	7.25	7.23	-	7.27	7.30	12.62	12.65	-	12.40	12.49

* W.R. - Whiterocks (South-West); A.R. - Asphalt Ridge ** no kerosene was used in these experiments *** Penetration Time which elapsed when samples were taken varied slightly from one experiment to the next; exact values were used in Figure 42 to 47.

Another set of experiments was carried out during the winter season, when the outside temperature dropped to minus 14°C. The results are presented in Figures 42 and 43. For both cases, the penetration rate did not change when compared to the summer temperature (26°C). The lack of significant difference in the penetration rate for the summer and winter temperatures is somewhat surprising. According to Equation (7) the time for penetration should be dependent on the temperature sensitive viscosity term. Hence, a lower temperature should lead to higher diluent viscosity and a longer penetrating time. Such is not the case, and it seems that other factors must be taken into consideration. For example the viscosity of the diluent in the summer may be higher than expected due to bitumen dissolution into the diluent. Also it can be imagined that the higher summer temperatures may seal off pores and thus make penetration more difficult. Some beneficial effect of the extended mixing can however, be noticed. Frozen Asphalt Ridge feed fragments did not break so easily during the preliminary penetration of oil sand prior to diluent addition. In this case a less uniform kerosene distribution is obtained; higher and more varied RSD values were observed.

In addition to bitumen content, the water content was also determined. Only the summer ambient temperature results are presented in Figure 46 and 47. During winter experiments (performed in the open air) a slight precipitation of snow at the time of sampling distorted the water balance. Considering water content change in the oil sand, there is clear evidence, comparing

Fig. 46. Average water content for Asphalt Ridge oil sand after pretreatment in rotating drum, and storage in 8 cm thick layer at 26°C; 13 wt% kerosene used with respect to bitumen.

Fig. 47. Average water content for Whiterocks oil sand after pretreatment in rotating drum, and storage in 8 cm thick layer at 26°C; 13 wt% kerosene with respect to bitumen.

water loss from the oil sand to which kerosene was not added, that the diluent stimulates evaporation due to water displacement from the capillaries. This effect is more pronounced for the Asphalt Ridge oil sand (which contains large pore volume and apparently wide capillaries), and does not depend on the mixing time after diluent addition.

SUMMARY AND CONCLUSIONS

The natural porosity of oil sand accessible by diluent has a crucial impact on the reduction of bitumen viscosity, and influences the penetration time required for successful bitumen separation from oil sand. Thus the oil sand porosity can control the lowest processing temperature applicable, unless crushing to almost elemental grains is provided prior to diluent pretreatment.

The change of the relative standard deviation of the oil sand grade indicates that diluent penetration into the Asphalt Ridge oil sand was almost complete in about 30 minutes whereas for the Whiterocks oil sand the penetration process was slower, and still not complete after 15 hours regardless of the ambient temperature.

After diluent pretreatment the bitumen is more uniformly distributed within the oil sand. Diluted oil sand does not undergo secondary consolidation and is easier to handle when compared to the as received feed. Diluent application in the pretreatment step is recommended only when the feed has a proper size as established by the natural porosity of the oil sand.

A rotating drum seems to be adequate for oil sand pretreatment. Since mixing time after diluent spraying had little

impact on the penetration kinetics the drum used for pretreatment should have only two sections: the inlet section serving for preliminary size reduction of oil sand lumps (this section is necessary only for nonconsolidated oil sands), and the diluent spraying section.

FUTURE ACTIVITIES

In the future work effort will be continued to correlate diluent penetration time in the oil sand pretreatment step with the extent of bitumen disengagement from sand, with the overall separation yield, with the oil sand microstructure, and with the extent of oil sand size reduction.

BITUMEN SEPARATION FROM DIGESTED OIL SAND SLURRY

INTRODUCTION

Bitumen recovery from oil sands by water-based surface processing is accomplished in two main stages: digestion and phase separation^[119, 129, 130]. While digestion requires only 25-30 wt% of the aqueous phase, the separation stage is carried out in a diluted oil sand suspension in order to enhance the efficiency of bitumen recovery. Thus, with a reduced amount of solids (e.g. 20 wt%), the volume of the oil sand slurry increases several times with respect to that during digestion which in turn increases the equipment and processing cost accordingly. Two approaches have been adopted for bitumen separation from digested oil sand slurry:

1. bitumen concentrate separation in a gravity cell followed by flotation of middlings and rejection of coarse sand to the tailings pond, as practiced at both commercial plants in Alberta, Canada. This processing strategy allows for a significant reduction of material to be floated right after gravity separation.
2. bitumen concentrate separation in a gravity cell followed by flotation of the entire oil sand slurry, as proposed for the processing of Utah oil sands, in order to maximize bitumen recovery to the concentrate and minimize bitumen (and diluent, if used) loss with the spent sand.

In order to have a successful gravity separation the bitumen must be displaced from sand, form relatively large droplets, and have a density sufficiently lower than that of the aqueous phase (due to

air entrapment or diluent addition). Laboratory experimental results for U.S. oil sands^[130], Canadian oil sands^[131] show that tailings from the gravity cell usually contain more than 1% bitumen. If this bitumen is disposed with the spent sand, the bitumen recovery to the concentrate can exceed 90% for a high grade feed (above 10% bitumen), but will remain well below 90% for a lean oil sand (less than 8% bitumen). Further, water-based processing of oil sands at a moderate temperature (50°C) requires diluent addition prior digestion^[70]. This diluent present in the bitumen from 5 to 30 wt% will also be lost proportionately with the tailings.

Flotation of the digested oil sand slurry, directly following digestion or after gravity separation, can reduce bitumen content in the tailings even to 0.2 %^[70, 122]. However, higher investment and operating costs can be expected, due to the greater amount of material being processed for bitumen recovery, particularly if conventional flotation machines are installed. In this regard, the use of air-sparged hydrocyclone (ASH) flotation is of interest because of its high specific capacity. The ASH offers high specific capacity at least 100 times greater than the capacity of conventional flotation equipment and its utility has been recognized in a number of applications. Aeration under turbulent shearing conditions, as is developed in the ASH, should benefit the separation process by disrupting mineral-bitumen interactions, according to the model and experimental data of Hall and Tollefson^[111, 133]. Processing oil sands with high fines content

(residing at the bitumen-water interface) should therefore be less demanding.

Appreciable research effort has been directed toward the processing of Athabasca oil sand tailings in order to recover residual bitumen^[133]. In another research project, foam separation and air flotation were investigated to solve the environmental problems associated with the treatment of wastewater generated by in situ bitumen recovery^[134]. ASH flotation may provide another useful approach for the treatment of these process streams.

THE PRINCIPLE OF OPERATION OF THE AIR-SPARGED HYDROCYCLONE

Two aspects of conventional flotation technology - limited fine particle recovery and relatively slow flotation rates - led to the concept of air-sparged hydrocyclone flotation^[135, 136]. The design was envisioned to establish a controlled high force field by swirl flow in order to increase the inertia of fine particles and to produce a high density of fine air bubbles with a directed motion to improve collision efficiency. The net result is effective fine particle flotation with retention times approaching intrinsic bubble attachment times. This corresponds to a capacity on the order of 100-600 tpd/ft³ of cyclone volume, at least 100-300 times the capacity of a conventional mechanical or column flotation cell.

In air-sparged hydrocyclone flotation, the slurry is fed tangentially through a conventional cyclone header into a porous tube to develop a swirl flow of a certain thickness in the radial direction (called the swirl-layer thickness). The flow is then

discharged through the annular opening created between the tube wall and a froth pedestal which is located on the cylindrical axis at the bottom of the ASH. Air is sparged through the jacketed porous tube wall and is sheared into numerous small bubbles by the high-velocity swirl flow of the slurry. Hydrophobic particles in the slurry collide with these bubbles, and, after attachment, are significantly reduced in their tangential velocity and transported radially into a froth phase which forms on the cylindrical axis. The froth phase is supported and constrained by the froth pedestal and thus moves towards the vortex finder of the cyclone header, being discharged as an overflow product. Hydrophilic particles generally remain in the slurry phase and are discharged as an underflow product through the annulus between the porous tube wall and the froth pedestal. This preferred design is a result of more than a decade of both fundamental and applied research at the University of Utah.

The high processing capacity of the ASH is due to the extremely short retention time, less than one second in a 2-inch system. In this way, optimal control of all the design and operating variables is essential for effective flotation. When compared to conventional flotation, ASH flotation requires a greater degree of control and the flotation performance of the ASH system drops significantly if the levels of the process variables are displaced from optimum conditions. It is advised that only minus 100 mesh fines should be used for the 2-inch ASH flotation testing due to the strong centrifugal force developed in the 2-inch

ASH system. This top size limit can be increased to about 28 mesh when a 6-inch ASH system is utilized. With a 15-inch ASH system, it is anticipated that even coarser feed material can be processed.

EXPERIMENTAL

Bitumen separation by ASH flotation was preceded by oil sand digestion (after pretreatment with diluent - 15 wt% kerosene with respect to bitumen) using the experimental procedure described previously^[70, 137]. Processing parameters are provided in Table 26 and 27. Sodium carbonate was used to control pH, and sodium tripolyphosphate was used as chelating and dispersing agent. A five gallon, double blade stirred tank reactor (800 rpm, 20 kg oil sand per test), and a small cement mixer (40 kg oil sand per test, 33 rpm) were used for digestion. After digestion, the slurry was discharged to a gravity separator, diluted with warm water to 55 wt% sand content, and the bitumen concentrate was skimmed from the surface. Next, the slurry was transferred to a 150 gal agitated tank and diluted with warm water to 6 wt% solids. See the schematic of the experimental set-up shown in Figure 48. The oil sand suspension was continuously agitated to maintain the sand in suspension (with limited success, however). The suspension was subsequently discharged to a 50 gal tank from which a submerged centrifugal pump fed the ASH-2C. All undigested oil sand particles larger than 10 mesh (2 mm) were screened between the 150 gal tank and the 50 gal tank and removed from the suspension. The 2" diameter ASH system consisted of two sections 34+17 cm (total length 51μm). The slurry flow rate was maintained constant at 70

Fig. 48. Simplified flowsheet for hot water processing of oil sand employing ASH for final bitumen separation; 1. digester, 2. gravity cell, 3. 150 gal tank, 4. 10 mesh screen, 5. 50 gal tank, 6. slurry pump, 7. air-sparged hydrocyclone (ASH), 8. 80 gal receiving tanks.

Table 26. Constant Processing Parameters

Digestion	
- Amount of Solids [wt%]	75
- Time [min]	5
Gravity Separation	
- Amount of Solids [wt%]	~55
- Temperature [°C]	50+60
ASH Flotation	
- Temperature [°C]	~50
- Slurry Flow Rate [dm ³ /min]	70
- Air Flow Rate [dm ³ /min]	90

Table 27. Process Variables

Characteristics	Processing Parameters			
	Whiterocks #1	Whiterocks #2	Asphalt Ridge #1	Asphalt Ridge #2
Digestion				
- Reactor type	rotating drum	stirred tank	stirred tank	rotating drum
- Temperature [°C]	56	40	50	55
- pH	-	9.3	-	8.7
- Na ₂ CO ₃ [g/kg of oil sand]	1	1	1	1.5
- Na ₃ P ₃ O ₁₀ [g/kg of oil sand]	0.5	0.5	0.5	0.5
ASH Flotation				
- Amount of Solids [wt%]	0.9	-	0.7	0.6
- Ration OF/UF	1:1.1	-	3.2:1	2.3:1

L/min, and the air flow rate was 90 L/min (60 + 30 L/min). The Whiterocks (North-West location, 6 wt% bitumen) and the Asphalt Ridge (County open-pit mine, 13 wt% bitumen) oil sands were used.

In each run the suspension contained in the 150 gal tank was continuously fed to the ASH system until the contents of the tank were exhausted. The overflow and the underflow streams were collected in 80 gal containers, and the bitumen content in the overflow froth product and in the underflow tailings product was analyzed.

RESULTS AND DISCUSSION

Addition of frothers, beside native surfactants released to the aqueous phase during digestion, is not practiced in the hot water process. In fact, excessive foaming was encountered during conventional flotation (38 L, Denver type cell) of oil sand samples from certain locations of the Whiterocks deposit. It was expected that ASH flotation or column flotation may benefit from such a substantial presence of natural frothers. Eventually, the froth may be washed to increase the grade of the bitumen concentrate. It was also expected that the ASH flotation would be influenced by the extent of bitumen displacement from sand and by the ability of bitumen to encapsulate air bubbles.

Primary Separation by Gravity

The degree of bitumen liberation from sand depends directly on the processing conditions used during digestion. Compare, for example, the efficiency of gravity separation reported in Table 28. Mechanical energy dissipation in the slurry seems to be of pronounced importance. Each of the conditioning devices which were used for oil sand digestion provided a different level of

mechanical energy which resulted in differences in the shear force field. It was estimated that stronger shear forces (by a factor of 2 or 3) were acting on oil sand particles in the stirred tank reactor than in the rotating drum. Consequently, the primary separation efficiency associated with gravity separation of the bitumen concentrate was larger for the stirred tank reactor. Stirred tank digestion of the Asphalt Ridge oil sand yielded 92.8 % recovery, and 89.0 wt% grade of the bitumen concentrate (dry basis, diluent subtracted). However, only 19.4 % primary recovery

Table 28. Bitumen distribution between concentrates and tailings in the hot-water process employing ASH for final bitumen separation.

Characteristics	Processing Results							
	Whiterocks # 1		Whiterocks # 2		Asphalt Ridge # 1		Asphalt Ridge # 2	
	Recovery	Grade	Recovery	Grade	Recovery	Grade	Recovery	Grade
Gravity Concentrate	26.9	62.0	49.0	63.0	92.8	87.6	19.4	79.3
Sedimented Sand in 150 gal and 50 gal Tanks	16.2	1.0	-	-	3.9	0.9	15.4	2.6
Screened-off Undigested Aggregates > 2 mm	20.3	3.8	-	-	0.1	0.9	18.0	15.5
ASH Underflow								
- Froth	10.3	53.7	-	-	0.0	-	4.5	67.7
- Sediment	5.2	1.0	3.4*	1.8*	0.9	2.0	16.3	24.0
ASH Overflow								
- Froth	10.5	68.5	29.6**	85.9**	0.3	17.6	12.8	79.1
- Sediment	10.6	25.0	-	-	2.0	7.0	13.6	60.2

* tailings quality for column flotation
** froth quality for column flotation

and 79.0 wt% grade were obtained after digestion in the rotating

drum reactor. In addition to the lower level of agittation, the low processing temperature (40°C) would lead to inadequate reduction in bitumen viscosity and too is responsible for the poor digestion efficiency. With respect to the Whiterocks oil sand the recovery was 26.9 % and the concentrate grade 62.0 wt% for the rotating drum. However, for almost the same experimental conditions digestion efficiency was greater in the stirred tank reactor: 49 % bitumen recovery and 63 wt% grade, as revealed in Table 28.

It has to be emphasized that some digestion parameters (temperature, alkalinity) were intentionally adjusted at such levels that oil sand tailings of different residual bitumen content (after gravity separation) were available for the ASH flotation. Nevertheless, most of the undigested particles were separated on a 10 mesh screen before entering the 50 gal tank. With respect to the Asphalt Ridge oil sand digested in the stirred tank reactor, bitumen recovery to the screened-off particles was only 0.1 %. The bitumen content of these particles was 0.9 wt%. Digestion in the rotating drum resulted in 18.0 % bitumen recovery to the overscreen particles (15.5 wt% bitumen grade). Digestion of the Whiterocks oil sand in the #1 experiment resulted in 10 mesh overscreen particles which contained 3.8 wt% bitumen, which accounted for 20.3 % recovery. Tailings from the Whiterocks oil sand #2 experiment were used in flotation column batch tests (discussed below), therefore screening of the entire tailings stream was not required.

Air Bubble Encapsulation by Bitumen

Air plays an important role in the hot water processing of oil

sands. First, air bubbles are entrapped in bitumen during digestion enabling separation of the bitumen concentrate by gravity. Second, air is used for flotation of fine bitumen droplets and bitumen-sand aggregates from tailings.

Bitumen droplets in successfully digested oil sand slurry exist as a broad size distribution with droplets from a few micrometers to 1 mm. The large bitumen droplets can be rapidly separated in a gravity cell assuming that they contain a sufficient amount of entrapped air. Bitumen droplets and bitumen-sand aggregates which are entrapped in fast settling tailings, or form a middlings layer require flotation for fast and complete recovery.

It has been suggested that encapsulation of air bubbles in bitumen occurs by air bubble entrapment mechanism^[120] or by attachment and filming^[138]. The encapsulation of air bubbles by bitumen provides exceptional adherence of air bubbles to bitumen drops and bitumen-sand aggregates which should prevent detachment in a highly turbulent flow in the ASH. Our own data indicate^[126] that the necessary surface conditions for oil spreading at the air-water interface can be satisfied for the oil sand processing strategy developed at the University of Utah. The coalescence of bitumen droplets and the bitumen-air attachment steps are considered "fast"^[139] which spoke for the flotation tests in the ASH.

Performance of the ASH

It was already mentioned that the size of particles floated in the 2 inch ASH should not exceed 150 μm , however 85 % of the sand

grains in the Asphalt Ridge oil sand, and 70 % of the sand grains in the Whiterocks oil sand are larger than 150 μm . The particle size limit can be increased to about 650 μm for the 6 inch ASH. Unfortunately, employment of the 6 inch ASH requires handling of large flow rates of the oil sand suspension which is not possible under laboratory conditions. Our 2" diameter ASH flotation tests were carried out with the above constraints in mind.

The immediate consequence of the presence of the large size mineral particles was their rapid sedimentation in the 150 gal storage tank, and in the 50 gal distribution tank - despite vigorous stirring. About 85 to 90 % of mineral matter in the oil sand was screed-off or settled out, and did not enter the ASH. Thus the suspension fed to the ASH contained only 1 % solids compared to the expected 6 % solids. Due to a considerable dilution of the tailings the concentration of natural frothers was low and did not result in dense froth. In an actual oil sand processing plant the process water will be recycled and therefore should contain a considerable amount of surfactants sufficient to form a stable froth.

In both streams collected from the ASH a froth layer and a sediment were formed. Solids (aggregated with bitumen) which reported to the overflow apparently were no longer supported by air bubbles (when the original froth collapsed) and formed the sediment. The froth layer in the underflow collecting tank was formed from sand-bitumen aggregates which were dragged to the underflow due to strong centrifugal forces acting in the

hydrocyclone. As expected, most of the free (i.e. not associated with sand grains) bitumen droplets reported to the overflow. The bitumen-sand aggregates reported either to the overflow or to the underflow depending on the bitumen/sand weight ratio and the amount of air entrapped in the bitumen, compare the microscopic photograph presented in Figure 49. That is why a mean bitumen recovery to the overflow was only twice that in the underflow for the Asphalt Ridge #1 experiment and even less for the two other experiments. See Table 27. Almost no bitumen was recovered to the overflow for the Asphalt Ridge #1 experiment when complete digestion was accomplished. Free bitumen droplets were present in the suspension, and very little residual bitumen was attached to the sand, therefore all the bitumen-sand aggregates reported to the underflow.

Column Flotation

Preliminary batch column flotation tests were also carried out in order to compare the separation efficiency with that obtained by ASH flotation. A glass column 100 cm long and 6.0 cm dia, similar to that used by Schultz and Mehta^[140], served for flotation. An easily replaceable porous glass frit (15 μ m and 50 μ m) served as a sparger. Digested Whiterocks oil sand slurry after bitumen gravity separation (see Table 28) was diluted to 8 wt% solids, screened by 10 mesh screen and floated in the column. Similar to the results obtained with the ASH flotation only 10 % of the bitumen originally contained in the feed was floated in the column. Ten minute runs resulted in 80 % reduction of bitumen content in

Fig. 49. Aerated bitumen-sand aggregates present in ASH overflow froth.

the slurry. A high air flow rate had to be used to diminish coarse sand settling, nevertheless, residual bitumen associated with coarse sand grains did not report to the concentrate. The air concentration in the column varied from 2.3 to 3.9 % by volume. Analogous to the ASH froth, microscopic observations revealed that the froth collected in the column contained air bubbles filmed with bitumen thus strongly adhering to the sand particles.

COMMENTS AND CONCLUSIONS

Bitumen-sand agglomerates were almost evenly distributed to the underflow and the overflow of the ASH. Free bitumen droplets reported to the overflow.

Natural hydrophobicity of oil sand bitumen and density difference between the bitumen and the tailings sand should enhance flotation in the ASH. However, the separation results become unpredictable when bitumen firmly adheres to sand grains, such as in the insufficiently digested oil sand slurry.

A thorough testing in a pilot plant utilizing recycled process water is indispensable for the correct evaluation of the ASH flotation technology in the oil sand processing. In order to float oil-sand aggregates a larger-diameter ASH (eg. 6" diameter) is recommended in which smaller centrifugal forces counteract the bubble buoyancy forces.

FUTURE ACTIVITIES

Future research on this topic will be aimed at improving bitumen recovery by gravity separation as well as scavenging the

tailings stream for recovery of residual bitumen. A new cell design - combining gravity separation and flotation - for bitumen recovery from digested tar sand slurry will be proposed and the principles of operation discussed. However, the cell construction and the amenability tests will require operation of a 50 bpd pilot plant. With respect to the residual bitumen in tailings, the air-sparged hydrocyclone (ASH) flotation technology will be utilized and the performance characteristics of the ASH will be carried out by large scale laboratory testing.

SAND AND WATER SEPARATION FROM BITUMEN CONCENTRATE

INTRODUCTION

The bitumen concentrate from hot water processing of oil sands requires removal of solid particles and dispersed water before an upgrade or utilization. In both commercial plants in Alberta, Canada, the bitumen concentrate is first diluted with naphtha to lower the bitumen viscosity, and to increase the difference in density between the organic phase and the aqueous phase and then submitted to centrifugation. After centrifugation the bitumen-naphtha blend still contains 4 to 7 wt.% water and up to 0.5 wt.% solids^[141].

Laboratory clean-up experiments employing Utah oil sand bitumen concentrates resulted in residual 0.5 wt% mineral matter and about 10 wt% water after centrifugation^[137]. In this regard, water dispersion in the bitumen concentrate seems to be particularly well stabilized. The presence of fine solids was regarded to significantly increase the stability of water-in-oil (W/O) emulsions, as discussed in details in several review articles^[142-144].

Available literature pertains to dissolution of solvent extracted bitumen or to solvent extraction of oil sand but not to dissolution of bitumen concentrate. Bitumen concentrate dissolution rate would depend heavily on concentrate composition and the design of the contactor. However, it is difficult to use the results from one contactor to predict the performance of another because of the complex mass transfer phenomena involved. The rotating disk

method^[145] can ease interpretation of the dissolution data, but it is not amenable to the bitumen concentrate.

Our laboratory experiments included sedimentation and centrifugation for the removal of fine particles and dispersed water from the bitumen concentrate. Also, the impact of the direct current (DC) electric field on the coalescence of water droplets suspended in the bitumen phase was investigated. The bitumen concentrate used in the clean-up tests originated from water-based bitumen recovery experiments described previously^[146]. The oil sand was sampled from two locations at the Whiterocks deposit (West-Central and North-West sites). Bitumen concentrates from gravity cell and following one minute flotation were mixed together, and stored for several days in a tight container prior to the clean-up experiments. Depending on the experimental conditions, the Dean-Stark analysis of the combined concentrates showed 25 to 52 wt% bitumen, 19 to 58 wt% solids, and 2 to 30 wt% water. Subsequently, the concentrate was mixed with kerosene in different proportions shortly before each clean-up test.

DISSOLUTION OF BITUMEN CONCENTRATE IN KEROSENE

Solubility Experiments

A laboratory helical stirrer (type IKA-RW 15 Janke&Kunkel, Germany) was used in the setup for the examination of bitumen concentrate dissolution kinetics in kerosene, and for preparation of the bitumen-kerosene blends used in the clean-up experiments. The helical impeller was 75 mm in diameter (d), 100 mm in length (L), and had 22.5 mm worm lead (S). Two mixing vessels, 160 mm and

114 mm diameter (D), were used. The distance between the impeller and the bottom of each vessel was maintained at approximately 4 mm (the impeller was submerged into the bitumen concentrate). The liquid level in the mixer was kept 3 to 6 mm above the impeller. All experiments were carried out at 300 rpm constant rotational speed. The stirring vessel was partially submerged in a water bath to provide isothermal conditions during the experiment. Prior to the dissolution tests the bitumen concentrate and the solvent were heated to the desired temperature. When the preparatory activities were complete, the required volume of kerosene was poured into the stirred tank on the top of the bitumen concentrate, and the stirrer was turned on. Samples of 10 mL were withdrawn with a pipette (1 cm below the liquid surface) at specified times. Each sample was centrifuged, and analysed, after dilution, in a UV-VIS spectrometer at 400 nm and 500 nm. The calibration curve for bitumen in kerosene is presented in Figure 50. Due to extensive dilution of the samples a rather high experimental error ($\pm 15\%$) was found.

RESULTS AND DISCUSSION

The bitumen concentrate recovered in the hot water process exhibited similar consistency to the toluene extracted bitumen, i.e. greater than 1 Pa.s at 50°C^[146]. For an efficient clean-up to take place the viscosity was reduced to less than 100 mPa.s. The results of three dissolution experiments are presented in Figure 51. Process parameters such as the mixer size, the temperature, and the ratio of bitumen concentrate to kerosene by volume were

Fig. 50. Calibration curve for bitumen concentration in kerosene

Fig. 51. Kinetics of bitumen dissolution in kerosene
 1- weight ratio of bitumen concentrate to kerosene
 $c/k=1.0$, temperature $T=46^{\circ}\text{C}$, $d/D=0.469$
 2- $c/k=3.0$, $T=50^{\circ}\text{C}$, $d/D=0.656$
 3- $c/k=2.5$, $T=60^{\circ}$, $d/D=0.656$

selected arbitrarily with no systematic examination of these process variables. Each experiment was repeated twice, and the mean value is presented.

The dissolution process was slower when the larger mixer ($d/D=0.469$) was used. The helical stirrer did not provide sufficient circulation near to the bottom where the bitumen remained undissolved. Penetration of kerosene into this layer was limited due to a high concentration of solid particles, and required a much longer mixing time. The kinetics of bitumen dissolution in kerosene improved significantly for the mixer of smaller diameter ($d/D=0.656$), compare curve 2 and 3 in Figure 51. Practically no undissolved residue was observed for this experimental set-up after 90 min of stirring. The bitumen concentrate was suspended (and the bitumen was dissolved) in less than 5 minutes. There was no essential difference between the dissolution kinetics for both runs (curve 2 and 3), except the very beginning of the process when the stirrer revolutions were out of control due to the high viscosity of the bitumen concentrate.

SEPARATION OF SOLIDS AND WATER IN GRAVITY AND CENTRIFUGAL FORCE FIELDS

Sedimentation Tests

The diluted bitumen concentrate was subjected to gravitational separation in 250 mL graduated cylinders at 22°C. After two hours of sedimentation 35 to 40 mL samples of the supernatant were syphoned 5 to 10 mm below the liquid surface, and analysed for fine solids and water by the Dean-Stark method. In some runs the

kinetics of sedimentation was monitored and the sediment composition was analysed.

Two kinds of bitumen concentrates, one freshly separated from the oil sand, and a second which had been stored from 3 to 5 days in open container, were used in the sedimentation tests. Different bitumen concentrate/kerosene ratios were used in these experiments. The residual concentrations of water and the mineral particles in the supernatant after two hours of sedimentation are given in Table 29. The concentration of solids in the supernatant from the as received bitumen concentrate did not exceed 2.5 wt% after 2 h of sedimentation while the concentration of the dispersed water remained below 5 wt%. As expected, the settling efficiency decreased for higher concentrations of bitumen due to the corresponding viscosity increase. The concentration of the fine mineral particles in the supernatant was greater for the stored bitumen concentrate, however, no difference in water content was observed. It is evident that water droplets promote sedimentation of the fine solid particles.

The sedimentation kinetics of the mineral particles and the water droplets are presented as semilog plots in Figures 52 and 53. The concentration of solids in the supernatant dropped almost linearly with time in that plot at the initial stage (see Fig. 52). After two to three hours only the finest particles of water or solids were present, therefore, most of the sediment layer was formed at that time (Fig. 53). The sedimentation process was

Fig. 52. Sedimentation kinetics of solids and water droplets (weight ratio of bitumen concentrate to kerosene: 3.0, temperate: 20°C)

Fig. 53. Formation of sediment (weight ratio of bitumen concentrate to kerosene: 1.1, temperature: 20°C, H -hight of sediment level, H_0 -total level of suspension)

Table 29. Clean-up results for the Whiterocks oil sand bitumen concentrate by sedimentation (2h, 20°C) and centrifugation (2600 rpm, 3 min, 20°C). Original water content in the as received bitumen concentrate 12-20 wt%, and in the stored bitumen 8-14 wt%

Concentrate/Kerosene		Residual Concentration		
Weight Ratio	Sediment.	Solids [wt%]	Water [wt%]	
		Centrifug.	Sediment.	Centrifug.
1.0	0.2	<.1	4.8	4.7
1.4	0.2	<.1	0.8	1.5
1.6	1.4	<.1	2.1	1.8
1.7	0.2	<.1	1.1	1.0
1.9	0.2	<.1	1.2	0.9
2.0	2.3	<.1	3.8	3.1
2.2	1.9	<.1	3.0	2.2
2.3	2.2	<.1	3.1	1.9
2.3	0.2	<.1	1.3	1.0
3.0	0.7	0.5	4.6	4.8
3.6	1.4	0.5	4.9	4.8
Stored Bitumen Concentrate				
1.0	0.9	<.1	1.7	1.0
1.5	1.1	<.1	2.7	0.8
2.1	5.6	1.2	1.0	1.0
2.3	7.1	0.8	0.9	1.5
2.8	2.9	2.3	1.2	2.0
3.3	5.7	2.5	4.0	4.2
3.8	8.4	3.1	4.7	3.6

continued for the next 3 days, however, no further compression of the sediment was noticed. The sediment contained from 54 to 60 wt% solids, and from 9 to 15 wt% water in all the three samples that were examined.

Centrifugation

A laboratory centrifuge, type GT-2 (VWR Scientific, 2600 rpm, 3 min runs, 40 mL samples), was used in the bitumen concentrate-kerosene mixture clean-up tests conducted at 22°C. The content of solids and water in the supernatant and in the hydrated sediment were determined as previously. Similar to the gravity separation, newly received and stored (therefore exposed to the air for several days) concentrates were used for the centrifugation experiments.

The residual concentrations of solids and water in the supernatant after 3 min centrifugation at 2600 rpm are presented in Table 29. The centrifugation at the above conditions proved not to be efficient for water removal. The concentration of the mineral particles, however, did not exceed 0.5 wt% for bitumen concentrate/kerosene weight ratios from 1:1 to 1:3.6, and even dropped below 0.1 wt% for more diluted concentrates. Similar to gravity sedimentation, a decrease in the efficiency of solids separation was observed when the stored bitumen concentrate was subjected to centrifugation. As could be expected, centrifugation resulted in a better separation of solids than by sedimentation. Simultaneously, the sediment was better compressed and contained 68-73 wt% solids and 12-16 wt% water. Centrifugation did not reduced the water content below the level obtained for 2 h sedimentation (Table 29). Excessively small droplet size, and the association of water droplets with mineral particles seem to account for the low separation efficiency.

Microscopic observations revealed that all water droplets which

remained suspended in the centrifuged bitumen-kerosene mixture were below 2 μm . These results correlate well with the mathematical estimation for the maximum droplet size under the conditions of centrifugation. The feed contained numerous small water droplets of 5 μm and below with sparse larger drops (sometimes even 500 μm). Some water droplets investigated under the microscope were surrounded by fine particles. Such small particles were also noticed in the sediment, which supports the assumption about their positive role in stimulating faster sedimentation of the solid particle-water droplet agglomerates. The microscope was not an adequate instrument to determine the water droplet size distribution. Water droplets below 2 μm were often difficult to distinguish from the fine mineral particles.

DISPERSED WATER REMOVAL IN ELECTROSTATIC COALESCER

Experimental Procedure

The coalescence of water drops in an electric field may be considered another advanced separation technique for cleaning of diluted bitumen concentrates^[147]. The attractive forces resulting from the electric field facilitate contact of water droplets which leads to enhanced coalescence. A small electrostatic cell (150x100x70 mm), described elsewhere^[148], was used for the separation of the dispersed water. Samples of diluted bitumen concentrates were used in these experiments. Each sample was first subjected to one hour sedimentation resulting in 3 to 8 wt% suspended mineral particles concentration. The electric field intensity was controlled by voltage adjustment and by changing the

distance between the electrodes. Additional water was dispersed in some samples prior feeding into the cell in order to enhance coalescence. In some experiments a glass wool was placed between the electrodes to promote the coalescence of water droplets at the filaments. The Dean-Stark toluene extraction was still satisfactory for the analysis of the residual water content.

Water Separation Results

The results of several experiments with the DC electrostatic cell are presented in Table 30. The effectiveness of the dispersed water separation obtained for each sample was rather poor. The performance of the cell did not improve after addition of dispersed water to the emulsion, and even with the glass wool (packing density 50 kg/m³) placed between the electrodes. The three possible reasons for the limited separation efficiency are discussed below.

A. The Size of Water Droplets

The attractive force between adjacent droplets, polarized in the electric field, is defined by the following expression^[147, 148].

$$F = K\epsilon E^2 r^6 / d^4 \quad (14)$$

where: K is a constant; ϵ is the emulsion permittivity; E is the electric field intensity; r is the radius of the droplet, and d is the distance between two droplet centers. Despite the wide range of the water drop size distribution observed, the major mass of water was found to be present in droplets smaller than 2 μ m. The attractive force between these fine droplets should be very small.

(See also equation 15.) It has been reported in the literature for the AC electric field^[150, 151] that the coalescence rate increases with an increase in the water droplet diameter and a similar tendency can be expected for systems with the DC polarization. According to Hano et al.^[150], the coalescence rate is proportional to the third power of the Sauter drop diameter (d_{32}), see equation 16. Goto and others^[151] suggested that there is a certain droplet size limit below which emulsion breaking in the electric field is not effective. Even additional dispersed water (3 to 20 μm droplet size) introduced into the bitumen concentrate-kerosene blend did not improve the efficiency of separation, compare Table 30. The attractive forces should be enhanced as a result of the decrease in the interdroplet distance and the increase in the droplet diameter.

B. Effect of Oil Viscosity.

The mobility of a water droplet has a direct impact on the separation efficiency and it depends on the viscosity of the organic phase (μ). For the laminar region of movement the drag force is controlled by the Stokes' law:

$$F = 6\pi r\mu u \quad (15)$$

where: u is the water droplet velocity, and r is the radius of a spherical particle.

The viscosity of oil strongly affects the coalescence rate of the water-in-oil emulsion. Based on the literature^[150], the rate constant (k) for water separation in an electrostatic cell with the AC polarization is given by^[143]:

$$k = CE^{0.5}d_{32}^3\mu^{-3.2} \quad (16)$$

Table 30. Dispersed water removal in electrostatic cell

Concentrate/Kerosene Weight Ratio	Temperature [°C]	Electric Field Strength [kV/m]	Time [min]	Settling Time [h]	Water Content		
					Initial [wt%]	Final [wt%]	Reduction [%]
1.0	20	420	5	2	3.7	3.3	10.8
2.5	20	550	3	2	4.3	3.6	16.3
3.0	20	430	5	1.5	2.9	2.5	13.8
1.1	20	846	5	20	2.6	1.1	57.7
1.1	20	400	3	2	2.6	1.7	34.6
1.1	55	846	5	0.5	2.6	2.4	7.7
1.1	40	846	5	0.5	2.6	2.5	3.8
4.5	20	233	3	0.25	9.8	8.8	10.2
0.9 ^{TV}	20	400	8	2	15	10	33
2.0 ^{AV}	20	800	3	0.25	8.0	5.7	28.8
2.1 ^{GV}	20	570	5	0.25	5.8	3.2	44.8

^{TV} - bitumen concentrate was mixed with tap water-in-kerosene emulsion;

^{AV} - bitumen concentrate was mixed with sulfuric acid ($4 \cdot 10^{-3}$ M)-in-kerosene emulsion;

^{GV} - glass wool was placed between electrodes;

where: C is a constant depending on the cell construction and the emulsion properties. The viscosity of the organic phase in our W/O emulsion remained within 40 to 100 mPa·s which is an order of magnitude larger compared to 1.5-12 mPa·s used by Hano et al.^[150]. Viscosity reduction due to the elevated clean-up temperature (50°C) did not improve the separation efficiency, see Table 30.

C. The Presence of Fine Particles.

The resistance of water droplets to coalescence can result from the accumulation of fine solid particles at the interface, and the formation of a tough interfacial film. The bitumen concentrate used in our experiments contained originally 19 to 58 wt% solids. After dilution with kerosene, and preliminary sedimentation the solids content decreased to below 8 wt%. Only such an emulsion was treated in the electrostatic cell.

The effect of fine solid particles on the stability of a model water-in-kerosene emulsion was examined. The fine particles were recovered from the bitumen concentrate-kerosene mixture by extraction with toluene in the Dean-Stark apparatus, and added to the model emulsion. The difference in the susceptibility to separation of the uncontaminated emulsion and of the emulsion with added solid particles was determined, and the results are presented in Table 31. The separation efficiency of water dropped drastically from 89% to 39% when fine particles were suspended in the model emulsion. It was also observed that the water which accumulated at the bottom of the cell formed large drops stabilized by fine particles.

Table 31. Results of dispersed water (pH = 9.0) separation from model water-in -kerosene emulsion in the electrostatic cell - the effect of mineral particles (E = 800 kV/m, T = 20°C, t = 1 min, t₂ = 5 min)

Initial Concentration of Solids [wt%]	Water [wt%]	Final Concentration of Water [wt%]	Percent Reduction
0	8.1	0.9	88.9
1.5	7.9	4.8	39.2

DROPLET COALESCENCE TIME

The coalescence time of water drops settling at the oil/water interface was measured. Water drops, 2-3 mm in diameter, were generated in oil from a microsyringe and allowed to settle at the oil-water interface. A diluted bitumen concentrate (50 wt% kerosene) was used as the oil phase. Solid particles and most of dispersed water were removed by 30 min centrifugation. The coalescence time was defined as the time which elapsed from the moment of collision of drop with the interface to the moment of the drop disappearance (coalescence) in the bulk liquid. The coalescence time was calculated as a mean value from 50 to 60 measurements.

The experiments with water separation in the electrical cell discussed above provided clear evidence that fine mineral particles stabilize the water-in-bitumen concentrate emulsion. Additionally, colloidal particles such as asphaltenes can further induce resistance of the system to phase separation. The accumulation of fine particles (brown in color) at the water/oil interface, after some "aging" of the system, was observed for the bitumen-kerosene

mixtures from which solid particles were thoroughly removed by centrifugation. The coalescence of water drops at the "aged" interface was much slower, see Figure 54. The presence of a tough interfacial film was reported in the literature for similar systems^[152]. The water droplets surrounded by such a film could not coalesce in some cases^[153]. Similarly, precipitated waxes in crude oil were reported to effectively stabilize water-in-oil emulsions^[154].

SUMMARY AND CONCLUSIONS

The bitumen concentrate originating from the hot water separation of the Whiterocks oil sand was treated to remove dispersed water and fine mineral particles. It was found that the bitumen concentrate could be completely dispersed in kerosene in 5 min at 50°C, using a cylindrical mixer (of diameter D) equipped with a helical stirrer (of diameter d) at 300 rpm, when the d/D ratio was 0.656.

Centrifugation tests revealed that the residual contamination of the bitumen solution in kerosene did not exceed 0.1 wt% solids when the weight ratio of the bitumen concentrate to kerosene was smaller than 3.0. The solids content in the supernatant increased for larger organic phase viscosities (due to a greater bitumen content) and for the bitumen concentrate which was stored and exposed to the air for a few days. The water content after centrifugation remained between 1 and 5 wt% which is comparable to the efficiency in the commercial plants in Alberta, Canada^[141].

The clean-up results of 2 hour sedimentation are comparable to

Fig. 54. Coalescence time of water drops at oil/water interface
oil phase: 50 wt% kerosene and 50 wt% bitumen concentrate
Aqueous phase:
1- pH=5.8 - 30 min. equilibration time
2- pH=5.8 - 24 hours equilibration time (stored in dark vessel)
3- pH=7.1 - 30 min equilibration time
4- [J=7/1 - 24 hours equilibration time (exposed to fluorescent light)

3 min centrifugation, and again were better for the fresh concentrate. The sedimentation efficiency showed a maximum for 1 to 1:9 bitumen concentrate/kerosene weight ratio. The concentration of solids did not exceed 0.1 wt%, and the content of water remained well below 5 wt%. A significant amount of water was lost due to evaporation when the bitumen concentrate was stored and exposed to the air which influenced the separation efficiency of mineral particles.

Residual water removal in the electrostatic cell supplied with the DC pulsating polarity did not result in better separation efficiency than 2 h sedimentation. It was later demonstrated that the stabilizing impact of fine particles accumulated at the water/oil interface hindered the drop-drop coalescence, and the efficiency of the entire clean-up process.

FUTURE ACTIVITIES

Dissolution of the bitumen concentrate derived from Utah oil sand by hot water separation will be studied in a stirred tank reactor. The dissolution constitutes an important step in the bitumen concentrate clean-up process. A dimensional analysis will be performed for the system which will be utilized to construct a number of bitumen concentrate dissolution maps from the experimental data. Studies on bitumen concentrate clean-up aimed at characterization and utilization/recycle of oily sludge produced in the cleaning process will be carried out.

**EXTRACTION OF BITUMEN FROM WESTERN OIL SANDS
BY AN ENERGY-EFFICIENT THERMAL METHOD**

**Principal Investigator
Graduate Student**

**J.D. Seader
C.J. Coronella**

INTRODUCTION

During the year ending July 1991, significant work was accomplished in the recovery of bitumen from oil sands by an energy-efficient thermal method. A previously constructed coupled fluidized-bed reactor system was modified to take advantage of modern technology for the purposes of ease of processing oil sands and of more efficient process control. The effect of conducting the coke combustion in two fluidized beds in series was investigated by an efficient and complete mathematical model. In order to allay fears that the heat pipes used in this system might easily deteriorate, a study of erosion effects was undertaken. Finally, a comprehensive study was undertaken to determine the regime of fluidization for different operating conditions.

The reactor system includes two thermally coupled fluidized-bed reactors. In the first reactor, bitumen is pyrolyzed at 450-550°C using nitrogen as the fluidizing gas. The vaporized products are mostly condensed to yield a synthetic crude oil. Coke, formed as a by-product in the pyrolysis reactor, and left behind on the sand, flows into the second reactor and is combusted with air at 550-650°C. Excess energy generated by the combustion reaction is then transferred by three liquid-potassium-containing heat pipes to the first reactor, providing the energy required by the pyrolysis

reaction and the preheat for bringing the feed to operating temperature. Previous studies indicate that the oil yield is strongly affected by the temperature and the solids retention time in the pyrolysis reactor. The temperature in the pyrolysis reactor is mainly determined by the energy transferred by the heat pipes, which is a function of the temperature difference between the two reactors. The solid retention time is controlled by regulating the sand hold-up by a solids control valve at the base of the bed. A computer control system is used to precisely regulate these key operating variables, thus providing an efficient method for process study.

REBUILDING THE LABORATORY COUPLED-BED REACTOR SYSTEM

During the fiscal year 1990-1991, a two-stage fluidized-bed reactor for thermal recovery of bitumen from Utah oil sands, previously constructed by Smart⁽¹⁵⁵⁾ was redesigned and reconstructed. The rebuilt system that will be used for optimization studies to investigate an optimal reactor configuration and set of operating conditions is now undergoing shakedown tests. Details of the modifications made to the system are given in the following subsections.

Computer control system

Since the Hewlett-Packard HP-1000 minicomputer with HP-2250 measurements system that was previously used for data logging and control is out-dated and no longer operable, a new computer control system, consisting of a microcomputer and a data acquisition unit,

was installed to replace the old control system. An HP Vectra personal computer with a 20 MHz 80386 CPU, 80387 math co-processor, 4 Mbytes of RAM, and 42 Mbyte hard disk drive is employed as the process controller. The data acquisition unit is an HP-E1301A unit featuring several different-sized slots. This unit can be easily configured with a variety of plug-in cards to meet data acquisition needs. It also handles communications of control signals and data between the computer and the process via an HP-IB (Hewlett-Packard Interface Bus) interface. The unit contains programs in ROM that allow it to accept streams of commands and data from the computer, compile the commands, and then execute the commands in the real-time environment of the external system. The commands received from the computer are written with SCPI (Standard Commands for Programmable Instruments). The following plug-in cards are installed in the data acquisition unit:

1. A 16-bit digital multimeter (HP E1326B): This multimeter can measure various electrical signals such as DCV, ACV, and resistance with excellent precision, to 1 microvolt, with its sensitive DC voltmeter. Its combination with a programmable gain amplifier and two multiplexers results in a multichannel scanning multimeter with the ability to process a wide variety of analog input signals.

2. Two 16-channel thermocouple relay multiplexers (HP E1347A) provide the basic analog-to-digital conversion capability for data logging. Each multiplexer has a built-in thermistor reference junction so that 16-channel thermocouple measurements can be made.

Thus, one of the multiplexers is used to measure temperatures, i.e., the voltage signals from 16 K-type thermocouples. Another multiplexer is used to read the output signals of four pressure transmitters which monitor the pressure drops across the fluidized beds and the maximum pressures below the gas distributors.

3. A 4-channel D/A converter (HP E1328A), provides four independent, isolated channels of digital-to-analog output capability (voltage or current). In this research, two output channels send variable voltage signals to the two pressure transducers, which control the solid flow valves for level control of the pyrolysis and combustion reactors. Thus, the solid retention times in both reactors can be accurately controlled. The other two output channels are used to control temperatures in the two reactors by sending 0 to 10 volt signals to the single-phase, phase-angle-fired (SCR) power controllers. Then, the SCR power controllers regulate power into the heating wires wrapped around the reactors.

4. One 16-channel form C switch (HP E1364A). This module consists of 16 independent single-pole, double-throw relays, allowing a wide variety of devices and signals to be switched. These relays are used for an emergency situation, in which case, the data acquisition/control system will detect the problem and energize appropriate relays to turn off the power supply or perform other procedures.

A computer code written in Microsoft's Quick Basic language has been developed for data acquisition and execution of control

algorithms. The velocity form of the digital PID control algorithm was first implemented and tested. Even though satisfactory control results can be achieved by the PID algorithm, other possibly better control algorithms are under investigation. Typical procedures for process control include: the acquisition of on-line data, noise rejection of collected data, comparison of process variables and set points, calculation of appropriate control signals, and transfer of control signals to the process.

Reactor System

Based on previous experience^[155] it was concluded that the major operation difficulties include occasional bridging of the oil sand in the feed hopper, a gradual build up of pressure in the upper reactor due to cake formation on the sintered-steel filter, and mechanical problems associated with the upper solids control valve. To overcome the difficulties, the reactor system has been updated to incorporate the latest and best improvements in technology.

1. Feeding system. A volumetric feeder (Model BDF-1) purchased from Acrison Inc., was installed to replace the previous screw feeder. This feeder features two specifically designed large augers and an independent metering auger located in the feed chamber (i.e., hopper). The two large augers generate bi-directional internal forces to avoid the above-mentioned bridging problem and the metering auger is able to control the feed rate with a high degree of precision and reliability. Copper tubing is coiled around the discharge cylinder of the feeding system for the

purpose of keeping the oil sand cool to preclude stickiness. The discharge cylinder can be flushed with nitrogen gas to prevent vaporized products from flowing back to the feeding system, resulting in high temperature and plugging problems.

2. Fluidized-bed reactors. Many of the mechanical parts of the existing reactor system, such as gas distributors, solids control valves, and flow meters, have been replaced. The gas distributors used in this study consist of a sand retainer and a perforated plate to support the sand bed and to evenly distribute the fluidizing gases, respectively. The perforated plate is placed directly below the sand retainer to allow for a large pressure drop so as to distribute the gas flow evenly across the cross sectional area of the bed. Several broken holes were found on the previous sand retainers, which are believed to be caused by either erosion due to high gas velocity, corrosion due to high operating temperature, or stress resulting from thermal expansion. The old sand retainers were replaced by new ones made by sandwiching a layer of 100 Tyler mesh stainless-steel screen between two disks fabricated from 1/16-inch stainless-steel plate. The discs were arc-welded along the edges to secure the screen and prevent gas leakage. As a rule of thumb in distributor design, the pressure drop across the distributor should be at least 10% of the pressure drop across the bed. Preliminary tests of the distributors indicate that fluidization and gas flow are relatively uniform in the combustion reactor. However, nonuniform fluidization was visually observed in the pyrolysis reactor, due primarily to the

small pressure drop across the perforated plate. It was decided to construct a perforated plate with 1-mm diameter holes and center-to-center hole spacing of 15 mm made from 1/16-inch stainless-steel plate so as to generate approximately 30% of the bed pressure drop. It is believed that uniform fluidization can be achieved by using the new gas distributor, but it remains to be tested.

3. Heating System. Previous studies have shown that the thermal process, based on the use of heat pipes, can supply its own energy for operation, provided that the oil sand used has a minimum bitumen content of 8 weight percent. For oil sands with a bitumen content lower than 8 wt%, energy released by the exothermic coke oxidation reaction may not be sufficient to preheat the oil sand feed and to supply heat for the pyrolysis reaction. Thus, additional energy provided by electric heaters in the combustion bed is necessary. In the previous design, all of the energy required in the pyrolysis reactor was supplied entirely from the combustion reactor via three heat pipes; no external additional energy was used in the pyrolysis bed. It is obvious that the amount of energy transferred by the heat pipes, which depends on external energy into the combustion reactor, has to be controlled in order to control the pyrolysis reactor temperature. Thus, the additional energy into the combustion reactor was considered then to be the manipulated variable for temperature control in the pyrolysis reactor. Because this design makes the reactor system highly thermally coupled, the temperature of each reactor is not easily controlled. For instance, a very large time constant was

found in the temperature control system of the pyrolysis reactor, which indicates sluggish temperature control. To improve the temperature controllability, both reactors are now equipped with independent electrical heaters to allow for separate temperature control for each reactor. The electric heater, assembled by inserting a 16-gauge nichrome heating wire into a high temperature insulation hose made of silica fiber, has been tested and operated over 3 months with no signs of deterioration. In addition to the computer control system, two microprocessor-based temperature controllers (Athena Model 7000) and six variable transformers were installed to provide better temperature control. All insulation and heating elements of the system were replaced by new units having better insulation properties and higher reliability.

4. New adiabatic reactor. One of the important aspects of this research is to construct an optimum reactor system and then conduct demonstration runs with different Utah oil sands. A mathematical model^[156] suggests the possibility of greatly reducing the combustion reactor size by switching to a two-stage configuration, i.e., a series of fluidized combustion and adiabatic reactors, which is described elsewhere in this report. Accordingly, in addition to the existing two fluidized beds (pyrolysis and combustion reactors), a third fluidized-bed reactor was made of stainless steel with a diameter of 4.25 inch and a height of 55 inches. The gas distributor is a perforated steel plate, 1/16-inch thick with 1 mm-diameter hole and center-to-center hole spacing of 10 mm. This reactor is currently being used as an erosion test

unit, discussed below, and will be eventually modified and placed directly below the existing combustion reactor. With the incorporation of the new reactor, it is anticipated that the residual coke can be nearly completely burned in a smaller reactor system.

Shakedown Tests

The modification and rebuilding of the existing reactor system is essentially completed. Several shakedown tests of the rebuilt reactor system using clean silica sand have been conducted. Based on these test runs, the reactor system showed promise of smooth operation for long periods of time. The only anticipated problem not yet addressed is that of the gradual build up of pressure in the pyrolysis reactor, as a result of caked fines on the sintered steel filter. All tests runs experienced adequate control to allow the study of process variables.

To illustrate the performance of the control system, data obtained from a test run are shown in Figures 55 and 56. In this test run, a sand feed rate of 8 lb/hour and a fluidizing gas flow rate of 60 SCFH (standard cubic feet per hour) were employed. As shown in Figure 55, with PI control, pressure drop across each reactor (or bed level) is adequately maintained constant, with sand hold-up of 8 lb and 16 lb for the control set points for pyrolysis and combustion reactors, respectively. Because the amount of sand in the combustion reactor is disturbed by a non-constant solid flow-rate from the pyrolysis reactor through the upper solids control valve, larger pressure fluctuations are observed in the

Figure 55.

Experimental pressure drop response using PI control algorithm with new reactor.

Figure 56. Temperature responses to setpoint changes using PID control algorithm with new reactor.

combustion reactor than in the pyrolysis reactor. However, the maximum fluctuation is only 7%. Temperatures in the pyrolysis (T_p) and combustion (T_c) reactors were controlled according to the following sequence over a 5-hour period: $T_p=450^\circ\text{C}$, $T_c=500^\circ\text{C}$ --> $T_p=450^\circ\text{C}$, $T_c=550^\circ\text{C}$ --> $T_p=500^\circ\text{C}$, $T_c=550^\circ\text{C}$ --> $T_p=550^\circ\text{C}$, $T_c=600^\circ\text{C}$. As shown in Figure 56, with PID control, the temperature of each reactor can be controlled independently. However, an oscillatory temperature profile is clearly observed in the pyrolysis reactor while the temperature profile of the combustion reactor is relatively stable. In the rebuilt system, the temperature of the pyrolysis reactor is affected by two energy sources: external energy provided by an electric heater and energy transferred from the combustion reactor. Since the latter energy source is not a controlled variable and can be regarded as a load disturbance, accurate control of the pyrolysis bed temperature is not easily achieved.

In order to compare the new system with the previous temperature-control design, temperature data obtained from the previous control system are shown in Figure 57, where a smooth, but very slow, temperature change in the pyrolysis reactor is obtained after a step change in the combustion-bed temperature is made. In previous runs, it was observed that the heat transfer rate in the heat pipes increased rapidly after the operating temperature in the combustion bed climbed above 450°C . This is because the liquid potassium in the heat pipes only starts to vaporize at fairly high temperatures. Thus, in this particular run, the step change of

Figure 57. Typical reactor temperature history for old reactor.

temperature was controlled in the near-optimal region to illustrate the characteristic of the heat pipes.

There are two major disadvantages to the previous temperature-control design: slow response and high dependence of the pyrolysis bed temperature on the combustion-bed temperature. Thus, the temperature of each reactor can not be arbitrarily controlled. Because of the nature of the thermally coupled-bed reactor system, good temperature control is not easily realized by the PID controller. Thus, research on developing a model-based control algorithm, e.g., internal model control (IMC), is being investigated. Such a control system will result in reduced temperature oscillations, such as those seen in Figure 56.

EROSION TEST OF HEAT PIPES

The extent of metal loss caused by erosion and/or corrosion of the heat pipes that thermally couple the fluidized-bed reactor is an important consideration because severe wear by would limit the life of the reactor system. To design a fluidized bed with minimum wear by particles, it is important to know how the wear rate depends on the variables associated with the operating conditions. The objectives of this study are to investigate the influences of tube configuration and operating parameters on metal loss, especially in fluidized beds operated in the bubbling and slugging regimes expected for commercial operation.

Wear experiments were performed in the fluidized-bed test unit as described in the preceding section. The gas distributor is a perforated steel plate, 1/16-inch thick, with 1 mm-diameter holes

and center-to-center hole spacing of 10 mm. The fluidizing gas was air with a superficial velocity of 0.09-0.42 m/s. A differential pressure gauge was used to monitor bed level, which was maintained constant by adding suitable amounts of sand during a run in the case of severe entrainment of the sand. Solid metal rods of 1/4-inch diameter stainless steel 316 were used to simulate the heat pipes. The rods could be mounted in either vertical or horizontal configuration with lengths of 7 and 3 inches, respectively. In most cases, metal rods were located approximately 2 inches above the distributor, fully immersed in a bed of silica sand 14 inches deep. The experiments were conducted at 500°C, with 10 lb of silica sand in the bed. The sand has a narrow size distribution, with an average particle size of 180 μm . Four different excess gas flow rates were tested: 0.0665, 0.133, 0.266, and 0.399 m/s.

Most wear rates were determined based on the weight loss during an approximately 336-hour continuous operation. As many as three successive runs of this time duration were made with the same rods, for a total of about 1000 hours of operation. Following each test run, the weight loss of individual rods was measured with a Denver Instruments scale accurate to 0.1 mg and its wear rate was then determined based on the average weight loss of the six metal rods.

The experimental results of two 1000-hour-total erosion tests using six SS316 rods as specimens are given in Figure 58 for gas superficial velocities of 0.133 and 0.266 m/s, an operating temperature of 500°C, and clean silica sand with an average

Figure 58. Cumulative weight loss over a long period operation.

particle diameter of 180 μm . The metal rods were mounted in a vertical configuration to simulate the orientation of heat pipes in our laboratory reactor system. As shown in Figure 58, the cumulative weight loss increases with operation time and a higher superficial gas velocity causes a larger weight loss.

The wear rate can be calculated based on the weight loss per period of time, i.e., the slopes of the cumulative-weight-loss curves. Figure 58 shows that the wear rate (or slope) decreases with time and then seems to be tending towards a constant value after about 400 hours of operation. Thus, it is concluded that a steady wear rate is achieved after about two weeks of operation. Initial wear rate is herein defined as wear rate calculated on the basis of weight loss in the first two-week period. The calculated initial wear rates were 1.134 and 1.948 nm of rod depth per hour for gas superficial velocities of 0.133 and 0.266 m/s, respectively, while the corresponding steady wear rates were 0.731 and 1.165 nm/hr, respectively. Based on the steady wear rate, a heat pipe with an 0.065-inch wall thickness would require more than 150 years to wear through for all gas flow rates studied thus far.

For commercial applications, steady wear rate is of more concern than initial wear rate. However, it is very time-consuming to obtain a steady-state wear-rate datum (i.e., 45 days). Instead, the initial 14-day wear rate was used to investigate the influence of process variables on erosion. Even though these two wear rates are not the same, the ratios of initial wear rate to steady wear rate were found to be approximately the same, based on the data

shown in Figure 58. Thus, it is hoped that conclusions drawn based on the initial wear rate are indicative of the steady-state wear rate.

By varying gas superficial velocity, the effect of excess gas velocity ($u-u_m$) on initial wear rate was obtained, as shown in Figure 59. It is clearly seen that wear rate is proportional to excess gas velocity but is less sensitive at relatively high velocities, which is not in agreement with the literature^[157, 158]. This discrepancy could be due to rod configuration, since most results reported in the literature are for the erosion of a bank of horizontal tubes, whereas this study involves vertical rods. Additionally, most data reported in the literature were taken from experiments in circulating beds, whereas our experiments were conducted in either the bubbling or slugging regimes. However, more data taken under different operating conditions are necessary to reach a conclusive result.

MODELLING AND OPTIMIZATION

It has previously been suggested to conduct the coke combustion in two fluidized beds in series, thereby reducing the total residence time required to burn off nearly all of the coke, with slight loss in energy to the pyrolysis bed. A detailed mathematical model of the effects of this change follows.

The equations that were used to model the combustion beds were derived according to the procedure outlined by Grace^[159]. Briefly, the primary features of Grace's two-phase bubbling-bed model are as follows: 1. The fluidized bed is said to have two phases, a bubble

Figure 59. The influence of excess gas velocity on wear rate.

phase with low solids concentration, and a dense phase. 2. The dense phase has a constant void fraction of ϵ_{mf} , that at minimum fluidization. 3. Essentially all of the gas flow passes through the bed in bubbles, i.e., there is no net flow of gas in the dense phase. 4. Gas is exchanged continuously between the two phases through the axial direction of the bed. 5. The solids are perfectly mixed throughout the bed. 6. The bubbles pass through in plug flow while exchanging mass with the dense phase. 7. The bed operates isothermally.

With the assumptions detailed above, a mass balance for chemical species i in the bubble phase gives

$$\frac{-d(uC_{i,b})}{dz} + k_{g,i}a_b e_b (C_{i,d} - C_{i,b}) + r_{i,b} e_b = 0 \quad (17)$$

and in the dense phase

$$k_{g,i}a_b e_b (C_{i,b} - C_{i,d}) + r_{i,d}(1 - e_b) = 0 \quad (18)$$

In equation 17, the first term represents convection, the second term represents mass transfer between the dense and bubble phases, and the last term is due to chemical reaction.

Upon solution of these equations (details of which are given by Coronella^[156], one may study the influence of operating conditions on reaction conversions. For the case of single-stage coke-combustion, the effect of mean particle residence time, $\bar{t}$ upon the overall coke conversion, $\bar{x}$, was studied by varying $\bar{t}$ only while holding all input variables constant, with the result shown

in Figure 60. Note that an incremental improvement in $\bar{x}$ requires greater increases in $\bar{t}$ (i. e., hold up) at higher conversions. The conversion increases from 94.2% to 97% with an increase in $\bar{t}$ from 1200 seconds to 2400 seconds, but only increases further to 98.1% with an increase in residence time to 3600 seconds.

It is expected that increasing residence time should result in increased coke conversion at a diminishing rate, since the coked sand particles are assumed to be well mixed throughout the bed, and are modelled by a CSTR mixing model according to Kunii and Levenspiel^[160]. Thus, complete conversion can never be obtained, even when the mean residence time is increased dramatically.

To model the effects of adding a second fluidized-bed stage to the combustion zone, the previously described simulation^[156] was modified to model the two linked fluidized beds. The fundamental governing equations are identical in both beds. However, the expression for coke conversion had to be rewritten, since particles entering the second stage have had most or all of the coke burned off in the first stage.

In order to predict the total amount of coke combusting in the combustion bed, it is necessary to know ξ , the fraction of the particles residing in the bed that still have coke remaining on the particle surface. All of the coke will burn off of a single particle of size d_i in the time τ_i . Thus, if the particles passed through the fluidized bed in plug flow, a residence time of only τ_i would be required; however, the particles in a bubbling fluidized are well mixed^[156] and so are subject to a residence time

Figure 60.

Effect of particle residence time on coke conversion for single stage coke combustion.

distribution (RDT).

$$E(t) = \frac{1}{\bar{t}} \exp \frac{(-t)}{\bar{t}} \quad (19)$$

Particles that reside in the bed for time greater than τ_i will be clean (no coke) and particles staying in the bed less than τ_i will still be reacting. Hence,

$$\xi_i = \int_0^{\tau_i} E(t) dt = 1 - \exp \frac{(-\tau_i)}{(\bar{t})} \quad (20)$$

Now, in the second-stage combustion bed, this is not quite true. ξ_i is substantially smaller than this, since most particles entering the bed are already clean. Let T_{ij} denote the residence time in the second-stage combustor required for completion of the coke oxidation reaction on a particle of diameter d_i that stayed in the first bed for time t_j . Then

$$T_{ij} = (1 - x_{ij}) \tau_{A1} \quad (21)$$

where

$$x_{ij} = \min(1, (1 - \frac{t_j}{\tau_{c1}})) \quad (22)$$

Here x_{ij} is the fraction of the coke that was burned in the first bed, τ_{c1} is the residence time in the first-stage combustion bed required for complete combustion of the coke on a particle of size d_i , and τ_{A1} is the residence time in the second bed (at temperature T_A) that would be required for complete combustion of all the coke on a particle if the particle entered the second

combustion bed directly from the pyrolysis bed. Then the fraction of particles still reacting in the second combustion reactor is

$$\xi_{A1j} = \int_0^{\tau_{1j}} E(t) dt = 1 - \exp\left(-\frac{\tau_{1j}}{\tau_A}\right) \quad (23)$$

To find the average ξ_{A1} , we take the mean over the value of t_j . For a continuous distribution of t_j , this becomes

$$\xi_{A1} = \int_0^{\infty} E(t_j) \xi_{A1}(t_j) dt_j = \int_0^{\infty} \frac{1}{\tau_c} \exp\left(-\frac{t}{\tau_c}\right) \left(1 - \exp\left(-\frac{\tau_{1j}}{\tau_A}\right)\right) dt \quad (24)$$

Note that $\xi_{A1j} = 0$ for all $t_j > \tau_{c1}$. After a bit of calculus and algebra, this becomes

$$\xi_{A1} = 1 - K_1 \exp\left(-\frac{\tau_{c1}}{\tau_c}\right) + (K_1 - 1) \exp\left(-\frac{\tau_{A1}}{\tau_A}\right) \quad (25)$$

where

$$K_1 = \frac{\tau_c \tau_{A1}}{\tau_c \tau_{A1} - \tau_A \tau_{c1}} \quad (26)$$

The expression for the conversion on a particle in the first stage combustion bed x_{1j} is given above, and the weighted average $\bar{x}_1$ is

$$1 - \bar{x}_{c1} = \int_0^{\tau_{c1}} E(t) (1 - x_{1j}) dt = 1 - \xi_{11} \tau_c / \tau_{c1} \quad (27)$$

In the second bed, the conversions are added:

$$x_{1j}(t) = \min\left(1, \frac{t_j}{\tau_{c1}} + \frac{t}{\tau_{A1}}\right) \quad (28)$$

Then, $\bar{x}_{A1}$ the average conversion of particles of diameter d_1 leaving

the bed is

$$\overline{x_{A1}} = \int_0^{\tau_{A1}} E_c(t_j) \left(\int_0^{\tau_{1j}} E(t) (1-x_{1j}(t)) dt \right) dt_j \quad (29)$$

Thus, conversion is averaged over the RTD of both reactors. The final expression is

$$\overline{x_{A1}} = \frac{\overline{\tau_A}}{\tau_{A1}} + \frac{\overline{\tau_c}}{\tau_{c1}} + \frac{\overline{\tau_A}}{\tau_{A1}} (K_1 - 1) \exp\left(-\frac{\overline{\tau_{A1}}}{\tau_A}\right) - \frac{\overline{\tau_c}}{\tau_{c1}} K_1 \exp\left(-\frac{\overline{\tau_{c1}}}{\tau_c}\right) \quad (30)$$

The weighted average over particle size of coke conversion $\overline{x}$, is the same in both beds, and is given by Coronella^[156]:

$$1 - \overline{x} = \frac{\sum_i C_{o,i} w_i / d_{p,i}^3 (1 - \overline{x}_i)}{\sum_i C_{o,i} w_i / d_{p,i}^3} \quad (31)$$

In addition, an energy balance around the second-stage coke combustion reactor was written to solve for the steady-state temperature in the bed. The sand enters the bed quite hot, and is heated further by the release of energy in the exothermic coke oxidation reaction. However, the incoming gas must be heated from T_1 , the temperature achieved in the preheating section, to T_A , the operating temperature of the bed.

A detailed energy balance around the second-stage combustion bed is presented here:

$$\frac{M_G}{A_{DA}} (1 - f_{cc}) \int_{T_A}^{T_o} C_{sand} dT + u_A(O) \frac{(1 - y_{O2,A}(O))}{y_{O2,A}(O)} C_{O2,b}^A(O) \int_{T_A}^{T_1} C_{p,K_2} dT$$

$$+ u_A(O) (1-x_{O_2,A}) C_{O_2,b}^A(O) \int_{T_A}^{T_1} C_{p,O_2} dT + u_A(O) x_{O_2,A} C_{O_2,b}^A(O) \int_{T_0}^{T_1} C_{p,O_2} dt$$

$$+ \frac{I_A^T}{A_{bA}} \left(\int_{T_0}^{T_e} C_{coke} dT + (-\Delta h^\circ) \right) + \frac{I_A^T}{A_{bA}} \frac{m_H}{2M_H} \int_{T_A}^{T_0} C_{p,H_2O} dT$$

$$+ u_A(L) C_{CO_2,b}^A(L) \int_{T_A}^{T_0} C_{p,CO_2} dT + u_A(L) C_{CO,b}^A(L) \int_{T_A}^{T_0} C_{p,CO} dT = 0 \quad (32)$$

The first term represents the change in enthalpy of the sand itself. Assuming that the air fed to the beds is composed of solely nitrogen and oxygen, the second term is due to heating the air feed from T_1 to T_A . It is assumed that the air will be preheated by the spent sand to $T_1 = (T_A - 15^\circ\text{C})$. The next two terms account for heating/cooling the unreacted and reacted oxygen to T_A and T_0 , respectively. T_0 is the standard temperature of reaction of the coke oxidation reaction, 298 K. If we assume that essentially all of the coke leaving the first stage combustion bed is burned, the fifth term accounts for the exothermic heat of reaction and for cooling the coke down to T_0 . The final three terms account for heating the products of reaction, H_2O , CO_2 , and CO , from the standard temperature to the reactor temperature.

Here, sand is considered to be pure SiO_2 , which undergoes a phase change at 847 ± 1.5 K, from α -quartz state to β -quartz state^[161]. So two different heat capacities were used, depending on temperature, and the heat of phase change was accounted for also. In order to achieve convergence when solving equation (32) for T_A ,

the heat of phase change was distributed across the temperature range 847 - 848 K. Thus, a one-to-one correspondence between the temperature and the balance was achieved.

Figure 61 presents fractional coke conversion, $\bar{x}$, in the second-stage combustion reactor as a function of cumulative residence time in both reactors for base-case operating conditions. As seen in Figure 60, a mean residence time of 6300 s is required for 99% coke conversion in a single fluidized bed. However, with two reactors in series, the same conversion can be achieved with a residence time in the first reactor of $\bar{t}_c = 1500$ s and in the second reactor, $\bar{t}_A = 100$ s, for a cumulative residence time of only 1600 s. Despite the reduced mean residence time, coke conversion in the first-stage reactor remains high at 95%, ensuring an adequate supply of heat for the pyrolysis reactor. As in the first reactor, $\bar{x}$ increases quickly with $\bar{t}$ at low residence times, slows down, and then asymptotically approaches 100%.

The temperature inside the second-stage combustion bed, T_A , is found by solving the energy balance. In Figure 62, T_A is shown as a function of $\bar{t}_A$ where the first-stage combustion bed particle residence time $\bar{t}_c$ and bed temperature, T_c , are constant at 1500 s and 848 K, respectively. The temperature rapidly approaches a constant value, reflecting the extent of the exothermic coke oxidation reaction. The temperature shown at $\bar{t}_A = 0$ is hypothetical, since it implies that there is no bed, but the low temperature is the equilibrium temperature of the hot sand (848 K) and the incoming air at $T_A = 15^\circ\text{C}$.

Figure 61. Effect of particle residence time on coke conversion for two-stage coke combustion.

Figure 62. Effect of residence time on bed temperature in second-stage combustion reactor.

REGIME CLASSIFICATION STUDY

In order to properly scale-up an existing fluidized-bed reactor, it is necessary to apply a comprehensive model of the hydrodynamics, reaction kinetics, heat transfer, and the interaction of these phenomena. A prerequisite of this work is to identify the regime of operation. Certainly, all hope of successful scale-up must be abandoned if no attempt is made to operate both large and small reactors in the same regimes. A summary of the possible regimes of operation in a fluidized bed is given by Coronella⁽¹⁵⁶⁾. Under the operating conditions of the 4-inch reactor in this study, only the bubbling and slugging regimes need to be considered.

The bubbling regime is characterized by the passage of small bubbles, continually growing by coalescence, throughout the height of the bed. The particles in a bubbling bed are well mixed by the jostling of the bubbles. The bubble size is larger at the top of the bed, and is most accurately described by a distribution, rather than by a single size.

In a slugging bed, the bubble size has grown to its maximum, the bed diameter. The rate at which the bubbles pass through the bed is significantly reduced, compared to that in a bubbling bed. Consequently, particle mixing is slower in a slugging bed. Since the bubbles (slugs) have grown to a maximum and uniform size, they pass through at a single frequency.

There have been several studies presented in the

literature^[162-165] aimed at predicting the gas-flow rate demarcating

the bubbling and slugging regimes. Figure 63 shows several curves predicting Q_m , the volumetric flow rate at the onset of slugging, as a function of bed holdup for a 4-inch bed of sand. Note that for deep beds, the onset of slugging is constant, or nearly so, with respect to bed hold-up, for each of the correlations given. The explanation given by Baeyens and Geldart^[165] seems most reasonable. They claim that a minimum bed height must be considered in conjunction with a minimum gas-flow rate. Thus, at a single gas-flow rate, a shallow bed will bubble, a deep bed will slug, and in the middle, a bed is in a state of transition known as developing slugging. The curve in Figure 64 credited to Baeyens and Geldart^[165] is that for fully developed slugging, and is given by

$$u_{ms} = u_{mf} + 0.07 \sqrt{g D_b} + 0.0016 (60 D_b^{0.175} - L_{mf})^2 \quad (33)$$

where all quantities are given in cgs units. The third term is included only for shallow beds, where $L_{mf} < 60 D_b^{0.175}$

Each of the other curves in Figure 63 is derived from a semi-empirical correlation for bubble growth given by Darton et al.^[166] and modified by Stubington et al.^[167]:

$$d_b(z) = 0.43 (u - u_{mf})^{0.4} (z + 4 \sqrt{A_0})^{0.8} g^{-0.2} \quad (34)$$

Figure 63. Comparison of slugging correlations for 4-inch reactor.

Deo et al.^[167] maintain that a bed is slugging when d_b ($0.4 L_{mf}$) $> D_r/3$, where equation 34 is used to find d_b . Darton et al.^[166] used two separate criteria, one based on equation 35 and the other based on a criterion of Stewart and Davidson^[162] to establish u_m . The curve attributed to bubble growth is one proposed here, and sets the criterion for minimum slugging as $d_b(L) > 0.6 D_r$. Thus, a bed is slugging when the bubble size at the top of the bed is greater than six-tenths of the bed diameter. Referring to the description of Baeyens and Geldart^[165], this criterion establishes the onset of slugging, but not fully developed slugging.

Because of the wide disagreement of the correlations in Figure 63, an experimental program has been undertaken to identify the best correlation for the advanced thermal oil sand processing reactor with vertical heat pipes by studying the statistical properties of the bed pressure-drop data, as described by Svoboda et al.^[164]. This method is based on the fact that bubbles erupting on the surface of a fluidized bed cause the pressure drop across the bed to fluctuate rapidly. These pressure fluctuations can be recorded and subsequently studied using statistical analyses and correlated to the regime of fluidization.

Method

The studies were conducted with silica sand fluidized in a 4-inch glass bed. The sand has a narrow size distribution, and the mean, given by is $\bar{d}_p = 170 \mu m$.

$$\overline{d_p} = \frac{1}{\sum_i \frac{w_i}{d_i}} \quad (35)$$

These studies were conducted using a 4-inch ID cylindrical glass reactor, 60 inches tall. The distributor is made of 1/8-inch-thick sintered steel. Since it is suspected that the presence of heat pipes in the reactor will have some influence on the fluidization regime, for some tests the bed was fitted with a unit made up of three 0.75-inch diameter vertical rods, constructed of aluminum, to simulate the presence of the heat pipes. The rods are on a triangular pitch and extend from 0.5 inch above the distributor to the top of the reactor.

Pressure drop data were transmitted by a differential pressure gauge installed by Smart^[155]. The pressure taps were installed below the distributor and at the gas exit line. The data were recorded by a recently installed HP data acquisition unit, described elsewhere in this report. Using this system, data were recorded at a frequency of 19 Hz.

The procedure used for different amounts of sand in the bed, either with or without the vertical-rod insert, was quite simple. The weighed sand was dropped into the reactor from the top, and subsequently, the bed was fluidized at a gas rate high enough to ensure active bubbling. Then the air flow was slowly reduced, over the period of about a minute, to zero, after which the bed height was measured. This was done to ensure consistency in the height measurement. Then the data acquisition program was started. For

each of several gas flow rates, starting with the largest, finishing with the smallest, the program recorded the pressure drop 500 times, (at a frequency of 19 Hz,) the gas flow rate was recorded, and visual observations of the bed were recorded, as described below. This procedure was repeated several times with varying amounts of sand in the bed.

Results and Discussion

For each gas flow rate, the apparent regime, as determined by visual inspection, was recorded. If only very small bubbles erupted on the surface of the bed, or if there were no bubbles at all, then it was said to be in an unfluidized state. If bubbles were visible along the length of the column, and the diameter of bubbles erupting on the surface was obviously less than the bed diameter, and the height of the bed was relatively constant, then the bed was said to be in the bubbling regime. The bed was said to be in the slugging regime when bubbles were visible along the entire length of the column, and when at some point along the column bubbles seem to span the width of the column or when the level of the bed fluctuated widely.

Since the transition from slugging to bubbling was never sharp, a range of values of Q_{ms} was identified for each experiments. These results are presented in Figures 64 and 65. The results are widely scattered as a result of the difficulty in objectively interpreting such subjective data (visual observations). Note that the data for Q_{ms} in the baffled bed (i.e., the bed containing the three vertical rods), is multiplied by the ratio of free cross

Figure 64.

Effect of three vertical rods on minimum slugging.

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*For the data taken with vertical rods, the flow rates have been corrected to account for open area only.

Figure 65.

Effect of three vertical rods on minimum slugging.

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sectional area in the open bed to free cross sectional area in the baffled bed, in order to make the comparison at equal superficial velocities, rather than volumetric flow rate.

Apparently, the presence of vertical rods inhibits the onset of slugging somewhat. This is most noticeable when comparing at equal static bed height, rather than equal bed weight. The reason for the apparent inconsistency is simple. For two beds containing an equal weight of sand, the bed with the vertical rods is taller, since the rods occupy approximately 10% of the cross sectional area. Since bubbles grow with height, it is natural that a higher bed should slug at a lower gas flow rate. There are several vague references in the literature to the effect of vertical tubes suppressing the onset of the slugging regime^[169-172].

Figure 66 compares the observed values of Q_{ms} with those predicted in Figure 63. Based on these experimental curves alone, it would be difficult to identify a correlation which best predicts the transition to the slugging regime. It is, however, rewarding to note that the curves follow qualitatively the same trend with bed holdup.

Typical pressure-fluctuation data for bubbling and slugging are shown in Figure 67. There is an obvious quantitative difference in the fluctuations between the two cases. Pronounced fluctuations occur in the slugging regime, while the fluctuations in the bubbling regime are hardly noticeable. For each flow rate, the mean, maximum, minimum, and standard deviation of the fluctuations were calculated, such as that shown in Figure 68. This

Figure 66. Comparison of slugging correlations with observations.

Figure 67. Pressure-drop fluctuations across a fluidized bed.

Figure 68.

Statistical analysis of pressure fluctuations.

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is similar to data presented in the literature^[173]. Obviously, the standard deviation of the fluctuations for slugging is much larger than that for bubbling.

Leva et al.^[174], claim that pressure fluctuations are 5 - 10% of the mean pressure drop for slugging, so an attempt was made to identify the regime of operation on this basis. Thus, for each flow rate, several variables were defined:

$$\delta^+ = \frac{\Delta P_{\max} - \bar{\Delta P}}{\bar{\Delta P}} \quad \delta^- = \frac{\bar{\Delta P} - \Delta P_{\min}}{\bar{\Delta P}} \quad \delta = \frac{\sigma}{\bar{\Delta P}}$$

Subsequently, δ^+ , δ^- and δ were plotted as a function of gas flow rate, as shown in Figure 69. Generally, δ was nearly linear with flow rate, while δ^+ and δ^- were less predictable. For each experiment (weight of sand in the bed), these three curves, δ^+ , δ^- and δ were interpolated to 5 and 10%. Finally, these interpolated values were plotted against the weight of the sand in the bed to determine whether any of these parameters could be used to predict the onset of slugging. The results for the unbaffled bed, along with the observed values, are shown in Figure 70. The curves representing the fractional pressure-drop fluctuations are relatively constant for all bed sizes. This is disappointing, since it was predicted in Figure 63 and visually observed that shallow beds require a greater fluidizing gas velocity for slugging. This leads us to believe that Leva's claim is useful as a general guideline, but not as a quantitative measure for determining the onset of fluidization.

Recently, several researchers^[164, 175-177] have taken another

Figure 69. Pressure fluctuations over mean as a function of gas flow rate.

Note: These data were calculated with a single value of ΔP_{mean}

Figure 70.

Minimum slugging in 4-inch bed; no vertical rods.

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statistical approach to studying the pressure-drop fluctuation data for the purpose of regime classification. This method uses the power spectrum of the data to identify the critical frequency. Theoretically, a slugging bed should have an easily identifiable frequency, since the slugs are of a uniform size and rise through the bed at a uniform rate. Similarly, a bubbling bed should have a wider distribution of frequencies, since bubbles erupting at the surface of the bed are not of a single size, and hence rise through the bed at different rates. Preliminary results of this method appear promising; however, more work is needed to verify its applicability.

SUMMARY AND CONCLUSIONS

The coupled fluidized-bed reactor system for the thermal extraction of bitumen from oil sands has been extensively revamped. Modifications include the installation of a modern Hewlett-Packard system for data acquisition and control, the installation of an Acrison volumetric feeder, the replacement of most parts of the reactors, including distributors, insulation, etc., and the installation of a heating system in the pyrolysis bed. The reactor was tested successfully for capability of processing clean sands. An efficient control system has been implemented to control the bed temperatures and bed inventories.

The phenomenon of heat-pipe erosion has been investigated. Preliminary conclusions imply that concern regarding heat pipe erosion is unwarranted.

A mathematical model and subsequent computer simulation of the

two-stage coke-combustion zone has been performed. Conducting the coke combustion in two beds in series requires a smaller total volume than that required for the same extent of coke combustion in one bed. Additionally, the cost in terms of lost energy for transfer to the pyrolysis bed is quite small.

An investigation into the regime of operation of the fluidized beds in the reactor system under consideration has been undertaken. A literature review resulted in a great disparity in predicting the boundary between the bubbling and slugging regimes. No quantitative data are available to predict the effect of the heat pipes on the fluidization regime. Hence, an experimental program was undertaken. Apparently, the presence of vertical tubes in a fluidized bed extends the bubbling regime and inhibits the onset of the slugging regime. A statistical analysis of the fluctuations in pressure drop across the bed can be used to assess the regime of operation.

FUTURE ACTIVITIES

Control algorithms that might improve control performance are being investigated. Due to the thermal coupling of the system, attention will be paid to temperature dynamics and de-coupling methods for optimum control. Thermal processing of Whiterocks oil sand in the revamped fluidized-bed reactor system will be initiated. Since an optimal reactor configuration and set of optimum operating conditions can be predicted by our mathematical model, one of the major purposes of this work is to demonstrate these conditions. Several extended runs of more than two days

duration with Utah oil sands will be conducted. The collected liquid products will be hydrotreated to determine the attractiveness of the treated products as synthetic fuels. Finally, the two-stage coke-combustion concept will be assembled and tested.

A model and simulation of the two-stage combustion zone is complete. Subject to the availability of an accurate model of pyrolysis reaction kinetics, little additional work will be required to complete a model of the pyrolysis bed. Subsequently, the thermal link between the two reaction zones will be modelled by solving simultaneous energy balances of the primary combustion bed and the pyrolysis bed, including heat transfer to and from the heat pipes. Finally, appropriate mathematical optimization techniques will be applied to completed simulation with the goal of optimizing both reactor configuration and reactor operation.

To quantify the degree of heat-pipe erosion and corrosion during bed operation that might be experienced commercially, a systematic erosion study of heat pipes (or metal rods) in the fluidized bed at high temperature and for bubbling/slugging regimes will be continued. Based on the results of this study, the practical constraints, including installation, life expectancy, replacement, etc., on the use of heat pipes in a commercially configure plant will be determined.

An extensive program is underway to map fluidization regimes from operating conditions. The spectral analysis method will be fully investigated for its usefulness in identifying the regime of operation for the glass beds operated at ambient conditions.

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Subsequently, the thrust of the research will be directed at mapping the fluidized beds in the thermal oil-sands processing reactor. Pressure-fluctuation data will be recorded in the two beds, analyzed, and then the regime of operation will be identified. The conclusions, in conjunction with correlations available in the literature, will be directly applicable to scale-up design.

Nomenclature

- A_0 Catchment area of distributor, defined as cross sectional area divided by number of holes
- A_b Cross sectional area of reactor
- a_b Transport area of bubble phase
- $C_{i,b}$ Concentration of species i in the bubble phase
- $C_{i,d}$ Concentration of species i in the dense phase
- C_i, C_{pi} Heat Capacity of species i
- C_0 Mass of coke deposited on sand particle in the pyrolysis bed
- D_b Diameter of reactor
- d_b Bubble diameter
- $d_i, d_{p,i}$ Sand-particle diameter
- $\bar{d}_p$ Average Particle diameter
- $E(t)$ Residence time distribution function
- f_{cc} Mass fraction of solid feed to combustion zone that is coke
- g Gravitational acceleration
- K_1 Constant defined in equation (26)
- $k_{q,i}$ Mass-transfer coefficient for species i
- L Height of fluidized bed
- M_{cs} Mass feed rate of coked sand to combustion zone

M_H Molecular weight of hydrogen

m_H Mass fraction of coke composed of hydrogen

r_A^I Coke-combustion rate in second-stage combustion bed

$r_{i,b}$ Rate of production of species i by chemical reaction in the bubble phase

$r_{i,d}$ Rate of production of species i by chemical reaction in the dense phase

T Temperature

T_i Inlet temperature of fluidizing gas

T_0 Standard temperature of reaction

T_{ij} Time required in second-stage combustion bed for completion of coke oxidation reaction for a particle of size d_i that stayed in first-stage combustion bed for time t_j

t Time

t_j The time spent in the first-stage combustion bed

$\bar{t}$ Mean particle residence time in a fluidized bed

u, u_0 Superficial gas velocity in a fluidized bed

u_{mf} Minimum gas velocity required for fluidization condition

w_i Weight fraction of sand that is size d_i

x Coke conversion

$\bar{x}_i$ Mean coke conversion over time of particle size d_i

x_{ij} Coke conversion in second-stage combustion bed on a particle of size d_i that resided in first-stage combustion bed for t_j

$\bar{x}$ Mean coke conversion leaving bed

x_{O_2} Conversion of oxygen in a fluidized

y_i Mole fraction

z Axial position in bed

GREEK

Δh° Heat of coke-oxidation at T_0

ΔP Pressure drop across fluidized bed

$\bar{\Delta}P$ Average pressure drop across fluid bed

$\delta, \delta^+, \delta^-$ Ratio of pressure fluctuations

ϵ_b Volume fraction of bed occupied by bubbles

τ_i Time required in bed for completion of coke oxidation on a sand particle of size d_i

ξ_i Fraction of particles of size d_i in bed with unburned coke

Subscript

A Second-stage combustion bed

b Bubble phase

C First-stage combustion bed

d Dense phase

i Chemical species i or particle size i

j Time spent in first-stage combustion bed

mf Minimum fluidization condition

ms Minimum slugging condition

P Pyrolysis bed

LARGE-DIAMETER FLUIDIZED BED REACTOR STUDIES

Principal Investigator:
Graduate Student:

F.V. Hanson
J.V. Fletcher

Several major operating problems associated with the large-diameter fluidized bed system have been identified previously ^[178]. Correction of the feeder problem was described in the 1989-1990 annual report ^[179] and the remaining corrections were projected for this year. Included in the year's activities was the design, fabrication, installation and start up of a new 6 inch fluidized bed reactor. Associated with the new reactor are new subsystems for product recovery, byproduct removal, and reactor heating.

Reevaluation of Tar Sand Feeder

As described in the previous annual report^[179], the Acrison BDF-1.5/E2 feeder showed a marked decrease in feed rate when the feedstock was shifted from coked sand to tar sand. Since the tar sand rate was only 40% of the expected feed rate, a new faster pitch auger was required. An H/2 auger was selected and specified with a water jacket for cooling. Evaluation of this new auger under temperature controlled conditions led to the discovery that the moisture content of the tar sand has a significant influence on its behavior in a screw feeder. When tar sand of unknown moisture content was used in the Acrison feeder. Feed rate studies produced confusing results. The disparity in feed rates is illustrated in Table 32.

A series of calibration runs was made based on moisture content at constant feed rate. As shown in Figure 71, the average

TABLE 32

Mass of Whiterocks Oil Sand
(WRWN) Delivered in 8.0
minutes at 5% of Maximum Speed
(Acrison BDF1.5/H/2 Feeder)

Date	Mass (kg)
11/26/90	3.0
1/3/91	3.7
	3.5
	3.3
	3.4
	3.6
1/4/91	2.3
1/8/91	2.9
	3.3
1/15/91	3.9

rate of feed can be directly related to the moisture content of the tar sand. For purposes of this study we defined 0% moisture to be an air dry sample at laboratory conditions. Additionally, it was found that tar sand is somehow altered by the shear forces of the auger and always feeds at a slower rate the second time through the feeder. This is a phenomena of importance only if very long screw augers were needed in a commercial application.

At the slower rate of the H/2 auger, the water jacket appears to be very effective in keeping the tar sand cool. With supply water at 10C and tar sand at 20C in the hopper, tar sand can be delivered to the reactor at 12C after 12 minutes of operation using the 5% feed rate.

Figure 71. Oil Sand Mass Delivered vs. moisture content

Design and Evaluation of Coked Sand Withdrawal System

Both Sung^[178] and Shun^[179] described the problems associated with the valves used to withdraw the sand that accumulates in the reactor due to the pyrolytic removal of bitumen from the feed tar sand. In order to solve this problem, it was decided to try a nonmechanical L-valve system as described by Knowlton^[181] (Figure 72). As stated by Knowlton, L-valve design must be determined from test rig data, so a test rig was set up for this work.

A Knowlton-style L-valve was eventually abandoned as being too insensitive at the flow rates required. It would either flow too fast or plug. The broad size distribution of product sand, which includes 4% by weight in excess of 2 mm (Figure 73) appears to complicate the idealized L valve performance characteristics. Such a valve would be useable for narrow size distribution sands.

A functional, controllable, modified L valve design was eventually developed. In addition to determining the critical internal dimensions, the aeration requirement to produce the necessary solids flow was determined. A schematic of the new metering L valve is shown in Figure 74. A thorough study of this valve's flow characteristics remains for future work.

Design of Gas Distributor

As described above, a coked sand withdrawal system was designed to remove sand at rates from less than 300g/min to several kg/min. This system was designed to interface on a 1" inch stand pipe feeding sand by gravity from the lower part of the fluidized sand bed. The large diameter ensures that sand will not cavitate

L - VALVE

Figure 72. Diagram of L-Valve

Figure 73. **Size distribution of Whiterocks spent sand**

MODIFIED L - VALVE

Figure 74. Diagram of modified L-valve

at the standpipe entrance. This combination also suggested the use of a conical base distributor section with radial holes on one level^[181]. The distributor/metering L-valve combination is shown in Figure 75 with aeration points A and B.

Design Installation and Ambient Testing of Reactor

A 6 inch (15.24 cm) diameter fluidized bed reactor was designed, fabricated, and finally delivered to the laboratory in May 1990. Installation of the feeder was accomplished before delivery so that placement of the reactor would be correct. Reactor installation proceeded rapidly after delivery and included insulation, thermocouple and pressure monitoring systems, metering L-valve controls and a propane heater system.

Preliminary fluidization tests with air and coked sand showed leaks to be an especially difficult problem to find. A design error in the Acrison feeder was eventually found, corrected, and proved to be the largest leak. Data for fluidization tests suggested a channel was forming which meant the distributor section was not seated properly. Correction of that problem allowed a series of gas fluidization tests to be run resulting in a calibration curve of maximum bed pressure drop vs. bed height (Figure 76). This curve can be used to effectively "measure" bed holdups using the differential pressure gauge.

Measured and Predicted Minimum Fluidization Velocity

Fletcher et al.^[182] reported on a simplified method for

Figure 75. Diagram of spent sand removal system with standpipe and modified L-valve

Figure 76. Bed pressure drop vs. settled bed height

predicting minimum fluidization velocities for coked sands produced through tar sand pyrolysis. For coked sands studied by previous University of Utah investigators^[178, 183, 184].

$$Re_{mf} = \frac{Ar}{790 + 7\sqrt{Ar}} \quad (36)$$

from which U_{mf} can be calculated. The Archimedes number is calculated from

$$Ar = d_p^3 g \rho_g \frac{(\rho_s - \rho_g)}{\mu_g^2} \quad (37)$$

and U_{mf} from

$$U_{mf} = \frac{\mu_g Re_{mf}}{d_p \rho_g} \quad (38)$$

Using air as the fluidizing gas, and $d_p = 196 \text{ } \mu\text{m}$, one calculates $Ar = 326$ at the temperature and pressure of our lab. (29°C, 645mm Hg). This leads to a U_{mf} prediction of 3.8 cm/s using equation 1. Figure 77 shows a graph of a series of net bed pressure drops vs. gas velocity for the conditions above. Net pressure includes a correction for the gas distributor. Interpretation of this graph using the methods of Rowe and Nienow^[185] yields a notational $U_{mf} = 1.6 \text{ cm/s}$.

Inspection of Figure 77 reveals that although "notational U_{mf} "

Figure 77. Bed pressure drop vs. superficial gas velocity for four bed heights

values are acceptably consistent, there is a phenomena occurring at higher velocities which suggests the bed is not fully fluidized at $U = 1.6 \text{ cm/s}$ (37 SCFH). Even though the data for Figure 77 was taken in the customary defluidization mode, an excess pressure is consistently seen. Further, 1.6 cm/s is much lower than the U_{mf} predicted by any known correlation.

Fluidization of multicomponent materials is reviewed by Nienow and Chiba^[186] wherein they point out that a "special definition must be adopted" in the interpretation of defluidizing data for multicomponent beds. A "Notational U_{mf} " is therefore defined as the point where the bed has developed a steady 99% or more of its maximum pressure based on the bed mass/unit area. Using this criteria, the U_{mf} from Figure 77 would be 3.0 cm/s , a value that is still much lower than predicted using equation 36 but reasonably close to the 3.1 cm/s predicted using

$$Re_{mf} = \frac{Ar}{1170 + 7\sqrt{Ar}} \quad (39)$$

as described by Fletcher et al.^[182].

Using the above approach, preliminary U_{mf} vs temperature data was interpreted for air as the fluidizing gas. As reported previously^[179] the relationship

$$U_{mf} T^{0.27} = k_f \quad (40)$$

is believed to be valid for the sands being studied. A k_f was calculated for four experiments at different temperatures. A k_f of 13.8 was found with a standard deviation of 0.2 which is a relative error of less than 2%. If this k_f is valid, U_{mf} at 800K should be 2.3cm/s (53 SCFH).

SUMMARY AND CONCLUSIONS

The acrison feeder has been tested and shown to be a suitable device for feeding undiluted oil sands to a fluidized bed reactor. In the course of testing, several important feeding variables were identified and a set of best conditions for feeding was found. The conditions to successfully feed oil sands should be:

- a. low auger speeds (<20 RPM)
- b. a water jacketed auger cylinder to maintain approximately 15°C feed
- c. oil sand feed moisture of <1% on an air dry basis

Ambient testing of the new 6 inch I D reactor confirmed the suitability of a modified L-valve for solids withdrawal. This solves a long-standing mechanical problem with fluidized bed reactors. Fluidization testing confirmed the U_{mf} predictive methodology previously reported and the existence of a U_{mf} and temperature relationship.

FUTURE ACTIVITIES

The assembled 6 inch fluidized bed reactor system will be tested at pyrolysis temperatures and residence times of less than 20 minutes. A set point controller for propane heating will also be installed and tested.

Pyrolysis of tar sands at previously studied conditions will be used to gauge the performance of the new system before new studies are undertaken. Residence times of less than 10 minutes have never been studied in the fluidized bed and will be a primary objective once the new product recovery system has been thoroughly tested.

ROTARY KILN PYROLYSIS OF OIL SAND

Principal Investigator:
Graduate Student:

F.V. Hanson
S.M. Cha

INTRODUCTION

The rotary kiln has found wide industrial application in process schemes where large quantities of solid material must be contacted with gases. These applications include ore roasting, solids drying, calcining, incineration of hazardous wastes, reduction of solids and nodulization. However, the rotary kilns not been extensively used for the pyrolysis of tar sands with the exception of the process development and pilot plant studies conducted by Tacuik^[187, 188] with the Athabasca tar sands. Berg^[189], Kramer and Meresz^[190], Boyer et al^[191] and Zimmermann^[192] have patented processes which use a rotary kiln reactor to coke oil sands and/or oil shale; however, none of the inventors discussed the influence of process operating variables on the product distribution and yields. Cha and Guffy^[193] have developed a Recycle Oil Pyrolysis and Extraction (ROPE) process for the recovery of hydrocarbon liquids from the Utah and Athabasca oil sands. The ROPE process utilized a two-inch-diameter screw pyrolysis reactor system which consisted of a screw feeder, a horizontal screw pyrolysis reactor and an inclined screw pyrolysis reactor in series. The process consisted of two sequential pyrolysis steps: (1) retorting the oil sand at a low temperature ($T < 693$ K) in the presence of the recycled product oil; and (2) retorting the carbonaceous residue at a higher temperature ($T > 693$ K) in the

absence of recycled product oil. The authors reported that liquid yields from the ROPE process were greater than those obtained from conventional pyrolysis processes. The optimum pyrolysis temperature and solids residence time in the horizontal screw pyrolysis reactor were reported^[193] to be 673 K and 40 minutes, respectively. A maximum liquid yield of 89.4 weight percent was obtained at the optimum conditions.

The pyrolysis of Utah's tar sands in fluidized-bed reactors has been studied [178, 180, 184, 194, 195] to determine the influence of process operating variables on the product distribution and yields and on the total liquid product quality. The C₅ plus liquid product yield decreased as the reactor temperature increased at constant sand retention time and fluidization gas flow rate for all tar sand deposits investigated. The C₅ plus liquid product yield increased as the feed sand retention time decreased at constant reactor temperature and fluidization gas flow rate. The reactor pressure and the feed sand particle size distribution were the same in all experiments. The product distribution and yields were independent of the fluidization gas flow-rate. Cha et al^[196] reported on a preliminary process study in which the pyrolysis of the Whiterocks tar sand was carried out in a rotary kiln reactor. The total liquid product (C₅ plus) decreased with increased feed sand retention time at fixed pyrolysis zone temperature and sweep gas flow-rate. The total liquid products produced in both the fluidized bed and rotary kiln reactors were significantly upgraded relative to the native bitumens for all the Uinta Basin tar

sands^[178, 184, 194-195].

The objective of the rotary kiln process variable study was to confirm the trends observed in the preliminary, sand retention time process study^[196] and to determine the influence of the pyrolysis zone temperature and the sweep gas flow rate on the product distribution and yields.

EXPERIMENTAL

The rotary kiln apparatus consisted of three distinct sections: the tar sand feed system; the kiln-furnace assembly and the gas, liquid and solids recovery systems. The pyrolysis zone of the kiln was capable of nearly isothermal operation and the material balances, based on bitumen fed to the reactor were in excess of 94 weight percent. The rotary kiln apparatus, the solids and liquid product recovery systems and the operating procedures and the analytical test procedures have been described in detail by Cha^[197].

The mined and crushed ore from the Whiterocks tar sand deposit was used in all experiments. The mined ore was obtained from an active mine/pit located in Sections 18 and 19, Township 2 North, Range 1 East. The ore used in the process study was mined from the south end of the pit (WR-WS); however, the extracted bitumen was virtually the same as that mined from the north (WR-WN) and central (WR-WC) regions of the pit and was only slightly different than that used for the preliminary feed sand retention time study (WR-WO) discussed by Cha et al.^[196]. The physical and chemical properties of the native bitumens from the Whiterocks tar sand

deposit are presented in Table 33.

RESULTS AND DISCUSSION

The correlation of product distribution and yield data and total liquid product quality with process operating variables and the determination of optimum operating conditions requires that the experimental results are reproducible.

Reproducibility of Rotary Kiln Pyrolysis Experiments

A series of experiments were conducted at a reactor temperature of 798 K and a solids retention time of 21 minutes to specifically evaluate the re-productibility of the operating procedures and results with the rotary kiln. The normalized product distribution and yields are presented in Table 34. The produced hydrocarbon liquid, the light gas and the carbonaceous residue yields for these experiments were in good agreement. Reproducibility of the liquid product quality was also evaluated in this series of experiments. The results are presented in Table 35. The 'API gravity, the Conradson carbon residue, the viscosity, the pour point, the asphaltene and maltene contents were in good agreement. The H/C atomic ratios of the total liquid products were nearly identical. The differences in physical and chemical properties of the total liquid products were attributed to variations in the operation of the product recovery train. These experiments, along with a third experiment at 798 K and 24 minutes, were used to refine the operating and material balance procedures.

Table 33
Physical and Chemical Properties of Native Bitumens
- Whiterocks Oil Sand -

Source	WR-WO	WR-WN	WR-WC	WR-WS
Bitumen Content, wt%	7.2	7.6	6.0	7.3
Specific Gravity (298 K/ 298 K)	0.987	0.981	0.976	0.990
API Gravity, °API	11.9	12.7	13.5	11.4
Viscosity, cps (@ 333 K)	2665*	7897	7616	9979
Net Heat of Combustion BTU/lb	17688	17630	17599	17638
Conradson Carbon Residue, wt%	8.1	8.8	9.5	9.9
Ash Content, wt%	1.3	0.2	0.2	0.2
Pour Point, K	330	313	311	307
Asphaltenes, wt%	16.9	11.9	8.5	11.4
Maltenes, wt%	83.1	88.1	91.5	88.6
<u>Elemental Analysis</u>				
C, wt%	83.3	86.4	86.4	85.2
H, wt%	11.0	11.6	11.5	11.6
N, wt%	1.3	1.4	1.1	1.2
S, wt%	0.3	0.6	0.4	0.4
O, wt%	4.1	N/A	0.5	1.7
H/C Atomic Ratio	1.58	1.61	1.60	1.63
Molecular Weight, g/mol	402	561	500	678
Ni, ppm	67	78	81	77
V, ppm	<5	3.6	2.0	1.3
As, ppm	N/A	2.3	2.2	2.3
<u>Simulated Distillation</u>				
Volatility (<811 K), wt%	40.5	47.7	49.3	42.1
IBP, 477 K, wt%	0.0	0.0	0.1	0.3
477 - 616 K, wt%	4.9	6.3	7.4	6.6
616 - 811 K wt%	35.6	41.4	41.8	35.2
> 811 K, wt%	59.5	52.3	50.7	57.9
<u>Boiling Point Distribution</u>				
IBP, K	526.	525.	496.	485.
5 wt.% K	616.	608.	584.	585.
10 wt.% K	668.	658.	641.	649.
15 wt.% K	707.	697.	677.	695.
20 wt.% K	727.	723.	708.	724.
25 wt.% K	746.	739.	729.	744.
30 wt.% K	769.	754.	747.	765.
40 wt.% K	810.	787.	776.	798

* Viscosity measured at 358 K.

Table 34

Reproducibility of Product Distribution
and Yields with the Rotary Kiln

Feed Sand: Whiterocks WR-WS
Reactor Temperature: 798 K
Solids Retention Time: 21 minutes
Sweep Gas Flow Rate: 45 SCFH

Run I.D.:	RK-WR-7	RK-WR-14
Solids Retention Time, min.:	21	21
<u>Normalized Product Yields</u>		
Liquid, Wt.%	65.9	65.0
Gas, Wt.%	16.2	17.8
Coke, Wt.%	17.9	17.2
<u>Gas Product Distribution</u>		
H ₂ , Wt%	0.10	0.11
CH ₄ , Wt%	1.94	2.09
CO ₂ , Wt%	1.01	1.03
C ₂ H ₄ , Wt%	1.04	1.20
C ₂ H ₆ , Wt%	1.23	1.42
C ₃ H ₆ , Wt%	4.48	5.27
C ₃ H ₈ , Wt%	1.39	1.62
i-C ₄ , Wt%	0.11	0.16
n-C ₄ , Wt%	1.84	2.17
n-C ₄ , Wt%	0.82	1.10
i-C ₄ , Wt%	0.21	0.23
C ₅ , Wt%	1.54	1.88
C ₆ , Wt%	0.36	0.72

Table 35

Reproducibility of the Liquid Product Quality

Feed Sand: Whiterocks WR-WS
 Reactor Temperature: 798 K
 Solids Retention Time: 21 minutes
 Sweep Gas Flow Rate: 45 SCFH

Run I.D.	RK-WR-7	RK-WR-14
Solids Retention Time, min.:	21	21
<u>Properties</u>		
Specific Gravity (289 K/ 289 K)	0.913	0.28
Gravity, °API	23.5	21.0
Conradson Carbon Residue, Wt%	0.8	1.7
Ash Content, Wt%	0.05	0.05
Viscosity, cp @ 298 K	36	67
Pour Point, K	237	245
Asphaltenes, Wt%	2.7	3.2
Maltenes, Wt%	97.3	96.8
<u>Elemental Analysis</u>		
C, Wt%	87.2	86.4
H, wt%	11.7	11.5
N, wt%	0.7	0.8
S, wt%	0.3	0.3
H/C Atomic Ratio	1.61	1.60

¹⁾ Oxygen-free basis

ROTARY KILN PROCESS VARIABLE STUDY

Effect of Reactor Temperature on Product Yields

It is well known that the pyrolysis temperature is the most significant reaction parameter which affects the product distribution and yields in thermal cracking processes. Therefore, the influence of the rotary-kiln reactor temperature on the pyrolysis product distribution and yields was investigated with the crushed and sized Whiterocks oil sand ore. Two series of reactor temperature experiments were conducted with the WR-WS oil sand while the solids retention time and the sweep gas flow rate were held constant. The reactor pressure was the ambient pressure in each experiment.

In the first series of reactor temperature experiments, the pyrolysis reaction product distribution and yields were determined in the rotary kiln at a solids retention time of 21 minutes and a sweep gas flow rate of 45 standard cubic feet per hour (SCFH). The reactor temperature was varied from 748 to 848 K. In these experiments, the feed sand was prepared by mixing the fresh oil sand ore (minus 1/2 inch particle size) with coked sand in a weight ratio of 3:1. The results from this series of reactor temperature experiments are presented in Table 36. All yield data are reported as weight percent of total bitumen fed to the rotary kiln.

The pyrolysis liquid yield increased as the reactor temperature increased from 748 to 773 K. The maximum liquid yield was 65.5 wt% based on bitumen fed to the reactor at a temperature of 773 K. The liquid yield decreased slightly as the temperature

Table 36

Effect of Reactor Temperature on Product
Distribution and Yields

Feed Sand: Whiterocks WR-WS
Solids Retention Time: 21 Minutes
Sweep Gas Flow Rate: 45 SCFH

Run I.D.	RK-WR-23	RK-WR-15	RK-WR-14	RK-WR-16	RK-WR-17
Solids Retention Time, min.:	22	20	21	21	22
Reactor Temperature, K:	748	773	798	823	848
<u>Product Yields¹⁾</u>					
Liquid, Wt.%	63.4	65.5	65.0	56.3	45.0
Gas, Wt.%	14.3	13.0	17.8	26.0	38.6
Coke, Wt.%	22.3	21.6	17.2	17.7	16.4

¹⁾Normalized to 100 wt% based on bitumen fed.

increased from 773 to 798 K and then decreased significantly with further increase in temperature. The light gas ($C_1 - C_4$) yield was relatively stable up to 773 K; however, it increased significantly when the reactor temperature was increased from 773 to 848 K. This change is related to the increased thermal cracking of the bitumen and the bitumen-derived liquid. Above 773 K, thermal cracking was progressively more severe compared to the direct volatilization of the low molecular weight components of the bitumen from the sand.^[180, 198] The increase in the gas yield was accompanied by significant variations in the gas composition. This resulted in the sharp increase in the gas yield. The main gas products produced in the rotary kiln reactor were C_3 and C_4 hydrocarbon gases. The increase in the C_3 and C_4 gas yields beyond 773 K was related to an increase in propylene and n-butylene at the higher reactor temperatures.

The amount of bitumen converted to a carbonaceous residue deposited on the sand particles, was high (22.3 wt%) at 748 K, and decreased as the temperature increased to 848 K. At higher temperatures (798 - 848 K) the coke yield was insensitive to changes in reactor temperature; that is, the coke yield was stable at 16 to 17 wt% at temperatures above 798 K. Similar observations were reported by Dorius^[195] for the fluidized bed pyrolysis of the PR Spring oil sand.

In the second series of experiments, the reactor temperature was varied from 773 to 848 K while the solids retention time and the sweep gas flow rate were held constant at 10 minutes and 45

SCFH, respectively. The effect of reactor temperature on product distribution and yields is presented in Table 37. The trends in product distribution for this series of experiments were similar to those observed for the first series of experiments which were carried out at a longer solids retention time (21 minutes).

In this series of experiments, the maximum liquid yield of 68.7 wt. % was obtained at a temperature of 798 K. As the temperature increased from 798 to 848 K, the liquid yield decreased. The light gas ($C_1 - C_4$) yield increased significantly with increasing temperature from 798 to 848 K. The increase in the gas yield was always accompanied by a decrease in the liquid yield. The shift in the product selectivity toward light gases was due to increase in the rate of cracking at higher temperatures. The carbonaceous residue yield was high (29.9 wt%) at 773 K, and decreased with increased reactor temperature from 773 to 848 K.

The overall pyrolysis reaction is quite complex; however, two basic reactions modes have been proposed to account for the conversion of the bitumen to products: vaporization and thermal cracking^[195, 198, 199]. Recently Lin,^[199] studied the pyrolysis reaction mechanism by thermogravimetric techniques for Utah oil sands. He reported that the differential thermogram exhibited two major peaks, implying that the bitumen pyrolysis involved at least two separate reaction modes. The first peak was related to low temperature "devolatilization" in the conversion range from 10 to 50 wt%. The second peak was related to thermal decomposition reactions which commenced before devolatilization ceased.

Table 37

Effect of Reactor Temperature on Product
Yields with Whiterocks Oil Sand

Feed Sand: Whiterocks WR-WS
Solids Retention Time: 10 Minutes
Sweep Gas Flow Rate: 45 SCFH

Run I.D.:	RK-WR-22	RK-WR-18	RK-WR-21	RK-WR-20
Solids Retention Time, min.:	11	10	10	10
Temperature, K:	773	798	823	848
<u>Product Yields¹⁾</u>				
Liquid, Wt%	64.5	68.7	58.7	53.2
Gas, Wt%	13.6	12.4	22.7	33.0
Coke, Wt%	21.9	18.9	18.6	13.8

¹⁾ Normalized to 100 wt% based on bitumen feed.

Therefore, a simplified pyrolysis reaction mechanism was assumed to explain the observed trends in product distribution with respect to temperature. The reaction network consists of a sequence of physical and chemical processes: vaporization and thermal cracking. The simplified reaction scheme can be represented as follows:

Low MW Bitumen Fraction - - - -> Oil Vapor [Vaporization]

High MW Bitumen Fraction - - - -> Cracked Oil + Light Gas + Coke
[Thermal Cracking]

where MW represents molecular weight.

As the feed oil sand entered the reactor and was heated, low molecular weight saturates, naphthenes and aromatics were vaporized from the sand surface [vaporization] and were transported out of this reactor by the sweep gas. In the thermal cracking of the heavy bitumen fraction, high molecular weight saturates, naphthenes and a portion of the asphaltenes were thermally cracked in the liquid phase on the sand surface to lower molecular weight species. Concomitantly, a portion of the aromatics and asphaltenes present in the liquid phase on the sand surface underwent polymerization and condensation reactions to form the carbonaceous residue which remained on the sand surface.

The observed trends in product distribution with respect to reactor temperature can be explained on the basis of this reaction scheme. The rate of thermal cracking is more sensitive to changes in temperature than is the vaporization of light components from the sand surface. At reactor temperatures below 773 K for the

first series of experiments (798 K for the second series of experiments), the liquid yield increased with increasing temperature because of an increase in the rate of cracking of high molecular weight components along with an increase in vaporization of light components. As the temperature increased further, the rate of cracking continued to increase, resulting in an increase in the light gas yield and a decrease in the liquid yield.

Secondary cracking of the initial liquid product might occur in the liquid phase on the sand surface and/or in the vapor phase in the rotary kiln. As previously mentioned, the rotary kiln reactor had a preheat or cold zone in the product vapor exit region. A portion of the heavier hydrocarbon vapors may have condensed on the fresh feed sand when hydrocarbon vapors moved through the preheat zone after vaporization. These condensed hydrocarbons were carried back into the hot zone where secondary cracking in the liquid phase could occur.

Furthermore, as the hydrocarbon vapors were transported out of the reactor, vapor-phase secondary cracking might have taken place due to the relatively long gas retention time (40-70 seconds) in the reactor. The degree of mixing in the vapor space within the kiln also affects vapor phase secondary cracking. At low sweep gas flow rates (<45 SCFH) and high sand feed rates, stratification of the sweep gas (nitrogen) and vapor-phase hydrocarbons was observed^[196, 197]. Thus, a small portion of the heavier vapor-phase hydrocarbons moved co-currently with the solid phase rather than moving counter-currently to the product recovery section. This

resulted in a longer effective vapor retention time in the reactor, which led to increased secondary cracking in the vapor phase at a fixed pyrolysis zone temperature.

At lower temperatures, the rate of thermal cracking is suppressed. Thus, the carbonaceous residue produced at low reactor temperatures consisted of unconverted toluene soluble high molecular weight species ("soft" coke^[194]) which were not vaporized in addition to the insoluble carbonaceous residue. It was presumed that these species were primarily asphaltenes. At the higher temperatures, the decomposition rate of high molecular weight asphaltene in the bitumen increased and the cracked products vaporized, resulting in a decrease in the carbonaceous residue yield.

Effect of Solids Retention Time on Product Yields

In this investigation, the solids retention time in the heated zone, θ , was defined as follows:

$$\theta = W / 2 F \quad (41)$$

where W is the weight of sand held up in the kiln and F is the fresh oil sand free rate. The reactor heating system was designed and constructed to heat the center section (one-half the length of the tube) of the barrel. Thus, the reaction or pyrolysis zone was confined to one-half the length of the tube and the bed-holdup weight used in calculation of the solids retention time was the total weight of solids in the reactor divided by two. In this investigation, the solids retention time was not directly proportional to the screw feeder rate. The solids dwell time, θ_d ,

in a rotary kiln has been defined as follows:^[200]

$$\theta_d = 0.19 L / D N S \quad (42)$$

where L is the hot zone length, D is a diameter of the kiln barrel, N is the kiln rotational speed (rpm), and S is the slope of the kiln (deg.). Thus, the solids retention time was varied in this investigation by adjusting the rotational speed and the angle of inclination of the kiln, which, in turn, changed the rate of solids movement through the kiln, and thus, the sand holdup time.

In the previous section, it was pointed out that the product yields from the first series of reactor temperature experiments, conducted at a solids retention time of 21 minutes, were different from those obtained from the second series of experiments which were run at a solids retention time of 10 minutes. This suggests that there is an effect of solids retention time on product yields in rotary kiln pyrolysis. Thus, the influence of the solids retention time on product distribution and yields was investigated with the Whiterocks WR-WS oil sand.

In the retention time experiments with the Whiterocks WR-WS oil sand, the solids retention time was varied from 10 to 27 minutes at a reactor temperature of 798 K and a sweep gas flow rate of 45 SCFH. The effect of solids retention time on product distribution and yields for this series of experiments is presented in Table 38. The liquid yield decreased and the gas yield increased with increasing retention time thus confirming the trend observed with Whiterocks WR-WO ore in the preliminary study^[196].

The reported trends are related to the fact that the solid-

Table 38

**Effect of Solids Retention Time on Product
Distribution and Yields**

**Feed Sand: Whiterocks WR-WS
Reactor Temperature: 798 K
Sweep Gas Flow Rate: 45 SCFH**

Run I.D.:	RK-WR-18	RK-WR-11	RK-WR-14	RK-WR-19
Solids Retention Time, min.:	10	15	21	27
<u>Product Yields¹⁾</u>				
Liquid, Wt%	68.7	67.9	65.0	59.7
Gas, Wt%	12.4	14.5	17.8	22.8
Coke, Wt%	12.9	17.6	17.2	17.5

¹⁾ Normalized to 100 wt% based on bitumen fed.

vapor contact time affects the rate of thermal cracking of bitumen and also the rate of vapor-phase secondary cracking of the initial liquid product because the solid-vapor contact time is directly proportional to the solids retention time. As the solid-vapor contact time increases, the rates of primary thermal cracking and secondary cracking increase. This results in a decrease in liquid yield along with an increase in gas yields as the solids retention time increases.

Effect of Sweep Gas Flow Rate on Product Yields

The effect of the sweep gas flow rate on the pyrolysis product distribution and yields was investigated with the Whiterocks WR-WS oil sand. Three experiments were conducted at a reactor temperature of 798 K and an average solids retention time of 11 minutes. The sweep gas flow rate was varied from 45 to 100 SCFH. The results of these experiments are presented in Table 39. Slightly lower gas yields were obtained at higher sweep gas flow rates; however, no definitive trend was observed. Thus, it was concluded that the hydrocarbon liquid yield was independent of the sweep gas flow rate over the range of sweep gas flow rate studied.

The coke yield was relatively unchanged (18 - 20 wt%) with respect to the sweep gas flow rate. These observations were consistent with the conclusions drawn by Dorius ^[195] for the fluidized-bed pyrolysis of the Whiterocks and PR Spring oil sands.

Effect of Reactor Temperature on the Quality of the Liquid Products

The quality of the hydrocarbon liquid produced in the rotary

Table 39

**Effect of Sweep Gas Flow Rate on Product
Distribution and Yields**

**Feed Sand: Whiterocks WR-WS
Reactor Temperature: 798 K
Solids Retention Time: 11 minutes**

Run I.D.:	RK-WR-18	RK-WR-25	RK-WR-24
Solids Retention Time, min.:	10	12	11
Sweep Gas Flow Rate, SCFH:	45	75	100
<u>Product Yields¹⁾</u>			
Liquid, Wt%	68.7	70.3	70.1
Gas, Wt%	12.4	9.6	11.6
Coke, Wt%	18.9	20.1	18.3

¹⁾ Normalized to 100 weight percent based on bitumen fed.

kiln pyrolysis process was dependent upon the operating conditions.

A knowledge of the liquid product quality has an impact on the selection of the subsequent processing steps for the upgrading and/or refining of bitumen-derived hydrocarbon liquids.

Selected physical and chemical analyses of the liquids produced in the rotary kiln pyrolysis of the Whiterocks WR-WS oil sand were performed. The physical and chemical properties of the liquid products produced in the reactor temperature experiments conducted at solids retention times of 21 and 10 minutes are presented in Tables 40 and 41, respectively.

The API gravities of the total liquid product decreased at a constant solids retention time as the reactor temperature increased for both series of experiments. The decrease in API gravity at higher temperatures was related to the severity of thermal cracking. As the reactor temperature increased, the severity of thermal cracking increased. The increased severity of thermal cracking caused an increase in the aromaticity of the product liquids due to dealkylation reactions, resulting in increased density or decreased API gravity.

The atomic H/C ratio of the liquid products was dependent on reactor temperature. A lower H/C ratio was indicative of a more aromatic total liquid product; thus, an increase in the aromaticity of the product liquids with increased temperature caused a decrease in the H/C ratio of the product liquids. This trend is consistent with the decrease in API gravity as the temperature increased.

The Conradson carbon residues of the liquid products increased

Table 40

Effect of Reactor Temperature on the
Quality of the Liquid Product

Feed Sand: Whiterocks WR-WS
Solids Retention Time: 21 minute
Sweep Gas Flow Rate: 45 SCFH

Run I.D.:	RK-WR-23	RK-WR-15	RK-WR-14	RK-WR-16	RK-WR-17
Solids Retention Time, min.:	22	20	21	21	22
Temperature, K:	748	773	798	823	848
<u>Properties</u>					
Sp. Gravity [60°F/60°F]	0.908	0.924	0.928	0.938	0.943
Gravity, °API	24.4	21.6	21.0	19.3	18.5
Conradson Carbon Residue, Wt.%	0.5	1.3	1.7	1.9	3.8
Ash Content, Wt.%	0.08	0.02	0.05	0.02	0.04
Viscosity, cp @298 K	29	76	67	52	22
Pour Point, K	251	251	245	243	234
Asphaltenes, Wt.%	1.9	3.3	3.2	3.8	4.8
Maltenes, Wt.%	98.1	96.7	96.8	96.2	95.2
<u>Elemental Analysis¹⁾</u>					
C, Wt.%	87.1	87.2	87.3	87.5	88.0
H, Wt.%	12.2	11.9	11.6	11.5	10.9
N, Wt.%	0.4	0.6	0.8	0.7	0.8
S, Wt.%	0.3	0.3	0.3	0.3	0.3
H/C Atomic Ratio	1.68	1.64	1.60	1.58	1.48
Molecular Weight, g/mol	265	290	290	274	247
<u>Simulated Distillation</u>					
Volatility, Wt.%	100	100	100	100	100
IBP - 477 K, Wt.%	11.5	7.7	7.2	9.3	15.5
477 - 617 K, Wt.%	31.5	24.3	27.0	29.3	31.9
617 - 811 K, Wt.%	57.0	68.0	65.8	61.4	52.6
> 811 K, Wt.%	0.0	0.0	0.0	0.0	0.0
IBP, K	394	400	402	396	387

¹⁾ Oxygen free basis

Table 41

Effect of Reactor Temperature on the
Quality of the Liquid Product

Feed Sand: Whiterocks WR-WS
Solids Retention Time: 10 minutes
Sweep Gas Flow Rate: 45 SCFH

Run I.D.:	RK-WR-22	RK-WR-18	RK-WR-21	RK-WR-20
Retention Time, min.:	11	10	10	10
Temperature, K:	773	798	823	848
<u>Properties</u>				
Specific Gravity [60°F/60°F]	0.925	0.929	0.936	0.945
Gravity, °API	21.4	20.8	19.6	18.2
Conradson Carbon Residue, Wt.%	1.5	2.6	3.8	5.4
Ash Content, Wt.%	0.01	0.01	0.01	0.07
Viscosity, cp @298 K	57	57	30	24
Pour Point, K	258	252	234	230
Net Heat of Combustion BTU/lbs	17,900	17,800	17,450	17,480
Asphaltenes, Wt.%	2.6	2.6	3.4	4.2
Maltenes, Wt.%	97.4	97.4	96.6	95.8
<u>Elemental Analysis¹⁾</u>				
C, Wt.%	86.6	86.8	87.5	87.8
H, Wt.%	12.3	12.1	11.3	10.8
N, Wt.%	0.9	0.9	1.0	1.1
S, Wt.%	0.2	0.3	0.2	0.3
H/C Atomic Ratio	1.71	1.67	1.56	1.48
Molecular Wt., g/mol	280	288	263	253
Ni, ppm	14	9	22	22
V, ppm	< 0.5	< 0.5	< 0.5	< 0.5
As, ppm	1.7	<1	1.6	1.7
<u>Simulated Distillation</u>				
Volatility, Wt.%	100	100	100	100
IBP - 477 K, Wt.%	6.8	6.7	8.2	12.5
477 - 617 K, Wt.%	23.4	25.7	26.8	29.2
617 - 811 K, Wt.%	0.0	0.0	0.0	0.0
IBP, K	405	403	398	396

¹⁾ Oxygen free basis

as temperature increased. This is consistent with the trends in the other properties with respect to reactor temperature. As the reactor temperature increased, the aromaticity of the product liquids increased and the increased aromatics concentration resulted in an increase in the Conradson carbon residue.

The viscosity of the liquid product increased as the reactor temperature increased from 748 to 773 K. As the temperature increased further from 773 to 848 K, the viscosity of the liquid product decreased. The trend in the viscosity with increasing temperature is also related to the severity of thermal cracking. As the reactor temperature was increased, the severity of thermal cracking increased. Under these conditions, the alkyl side chains were cracked from the polynuclear aromatic (PNA) groups and the linkages between the PNA clusters were broken. The alkyl groups were cracked further to smaller (lower molecular weight) groups which volatilized and passed from the reactor in the light gas. Thus, at reactor temperatures below 773 K in the first series of experiments, the viscosity of the liquid product increased with increasing temperature. This was due to an increase in the rate of cracking of the alkyl side chains from PNA groups along with a relatively low rate of cracking of long-chain paraffinic groups to smaller groups. As the temperature increased further from 773 to 848 K, the rate of cracking of long-chain alkyl groups to smaller groups increased, resulting in a decrease in the viscosity of the liquid product (Tables 40 and 41).

The pour point of the liquid product decreased as the reactor

temperature increased. The decrease in the pour point is consistent with a decrease in the viscosity of the liquid product. As the reactor temperature increased, the rate of cracking of the alkyl side chains from the PNA groups increased, resulting in an increase in the aromaticity of the liquid products. Also, the rate of cracking of the alkyl groups to smaller groups which volatilized and passed from the reactor in the light gas increased with increasing temperature, resulting in lower paraffin concentrations in the liquid product. An increase in the aromaticity and a decrease in the paraffins resulted in a decrease in the pour point of the total liquid product.

The gasoline (< 477 K) and middle distillate ($477 - 617$ K) fraction decreased and the heavy ends ($617 - 811$ K fraction increased as the reactor temperature increased from 748 to 773 K. The gasoline (< 477 K) and middle distillate ($477 - 617$ K) fractions increased with further increase in reactor temperature, while the heavy ends ($617 - 811$ K) decreased. An increase in the light oil fraction along with a decrease in the heavy oil fraction with increasing temperature was due to the increased severity of thermal cracking.

The effect of reactor temperature on the distillation data for the liquid products obtained from the first series of experiments (at a solids retention time of 21 minutes) is presented in Table 42. The distillation curves were slightly different as a function retention time; however, no significant trends were observed. The distillation data for the liquid products obtained in the second

Table 42

**Effect of Reactor Temperature of Distillation
Fractions of the Liquid Product**

Feed Sand: Whiterocks WR-WS
Solids Retention Time: 21 Minutes
Sweep Gas Flow Rate: 45 SCFH

Run I.D.	RK-WR-23	RK-WR-15	RK-WR-14	RK-WR-16	RK-WR-17
Solids Retention Time, min.	22	20	21	21	24
Temperature, K:	748	773	798	823	848
Cumulative Wt.% Distilled					
IBP, K	394	400	402	396	387
10 Wt.%, K	468	496	497	485	448
20 Wt.%, K	515	558	549	537	499
30 Wt.%, K	558	607	598	583	541
40 Wt.%, K	603	647	639	622	586
50 Wt.%, K	646	681	673	658	627
60 Wt.%, K	685	711	703	692	663
70 Wt.%, K	721	733	731	722	699
80 Wt.%, K	745	756	752	747	734
90 Wt.%, K	774	783	780	776	765
100 Wt.%, K	807	810	809	809	805
Volatility, Wt.%	100	100	100	100	100
IBP - 477 K, Wt.%	11.5	7.7	7.2	9.3	15.5
477 - 617 K, Wt.%	31.5	24.3	27.0	29.3	31.9
617 - 811 K, Wt.%	57.0	68.0	65.8	61.4	52.6
> 811 K, Wt.%	0.0	0.0	0.0	0.0	0.0

series of experiments (at a solids retention time of 10 minutes) with respect to reactor temperature are presented in Table 43. The distillation curves for this series of experiments did not change significantly with changes in reactor temperature. However, at higher reactor temperatures, slightly more distillate liquid product was obtained at the same boiling point. This was due to the increased rate of thermal cracking at higher reactor temperatures.

Effect of Solids Retention Time on the Quality of the Liquid Products

The effect of the solids retention time on the physical and chemical properties of liquid products from Whiterocks WR-WS oil sands was investigated. Selected physical and chemical properties of the liquid products produced at various solids retention times are presented in Table 44.

No clearly established trend was observed for the API gravity, the Conradson carbon residue or viscosity of the liquid product with respect to solids retention time. The pour point of the liquid product decreased as a solids retention time increased. The decrease in the pour point is related to the increased rate of cracking of the alkyl groups to smaller groups as mentioned previously. This is consistent with an increase in the aromaticity of the liquid products.

The effect of solids retention time on the simulated distillation data for the liquid product is presented in Table 44. The light (< 617 K) fraction increased slightly and the heavy (617

Table 43
Effect of Reactor Temperature on Distillation
Fractions of the Liquid Product

Feed Sand: Whiterocks WR-WS
Solids Retention Time: 10 Minutes
Sweep Gas Flow Rate: 45 SCFH

Run I.D.:	RK-WR-22	RK-WR-18	RK-WR-21	RK-WR-20
Retention Time, min.:	11	10	10	10
Temperature, K:	773	798	823	848
<u>Cumulative Wt.% Distilled</u>				
IBP, K	404	403	398	396
10 Wt.%, K	501	503	494	480
20 Wt.%, K	561	557	551	524
30 Wt.%, K	612	605	597	567
40 Wt.%, K	648	645	634	618
50 Wt.%, K	684	680	671	658
60 Wt.%, K	716	713	705	692
70 Wt.%, K	745	740	731	714
80 Wt.%, K	768	761	754	742
90 Wt.%, K	788	768	781	773
100 Wt.%, K	810	811	809	807
Volatility, Wt.%	100	100	100	100
IBP - 477 K, Wt.%	6.8	6.7	8.2	12.5
477 - 617 K, Wt.%	23.4	25.7	26.8	29.2
617 - 811 K, Wt.%	69.8	67.5	65.0	58.3
> 811 K, Wt.%	0.0	0.0	0.0	0.0

Table 44

Effect of Solids Retention Time on
the Quality of the Liquid Product

Feed Sand: Whiterocks WR-WS
Reactor temperature: 798 K
Sweep Gas Flow Rate: 45 SCFH

Run I.D.:	RK-WR-18	RK-WR-11	RK-WR-14	RK-WR-19
Solids Retention Time, Min.:	10	15	21	27
<u>Properties</u>				
Specific Gravity [60°F/60°F]	0.929	0.934	0.928	0.927
Gravity, °API	20.8	20.1	21.0	21.2
Conradson Carbon Residue, Wt.%	2.6	2.4	1.7	2.5
Ash Content, Wt.%	0.01	0.00	0.05	0.01
Viscosity, cp @ 298 K	57	67	67	40
Pour Point, K	252	261	245	237
Asphaltenes, Wt.%	2.6	2.8	3.2	4.0
Maltenes, Wt.%	97.4	97.2	96.8	96.0
<u>Elemental Analysis</u> ¹⁾				
C, Wt.%	86.8	87.3	87.3	87.4
H, Wt.%	12.1	11.5	11.6	11.5
N, Wt.%	0.9	0.9	0.8	0.9
S, Wt.%	0.2	0.3	0.3	0.2
H/C Atomic Ratio	1.67	1.59	1.60	1.58
Molecular Weight, g/mol	288	286	290	289
<u>Simulated Distillation</u>				
Volatility, Wt.%	100	100	100	100
IBP - 477 K, Wt.%	6.7	6.5	7.2	8.0
477 - 617 K, Wt.%	25.8	27.0	27.0	28.2
617 - 811 K, Wt.%	67.5	66.6	65.8	63.8
> 811 K, Wt.%	0.0	0.0	0.0	0.0
IBP, K	403	412	402	408

¹⁾ Oxygen free basis

- 811 K) fraction of the total liquid product decreased with increasing solids retention time. This was due to the increased severity of thermal cracking related to longer solids retention times, as was discussed previously.

Extent of Upgrading of Liquid Products

It is important to determine the extent of upgrading of the total liquid product relative to the native bitumen product. Properties of the liquid product from the pyrolysis of Whiterocks WR-WO and WR-WS oil sands are compared to the properties of the native bitumen in Tables 45 and 46 respectively. The API gravity increased from 11.4°API for the WR-WS native bitumen to 20.8°API for the liquid product produced at a reactor temperature of 798 K. The viscosity of the bitumen decreased by several orders of magnitude when compared to the native bitumen at the same temperature. The pour point was reduced by 50 to 55°C, and the Conradson carbon residue and the asphaltene content of the liquid product were significantly lower than that of the native bitumen. The volatility (< 811 K) of the liquid product increased substantially relative to the native bitumen. In all rotary kiln pyrolysis experiments, it was apparent that the API gravity and volatility of the total liquid products increased relative to the native bitumen while the viscosity, Conradson carbon residue, pour point and asphaltene content markedly decreased.

In addition, the amount of heteroatoms (N and S) and trace metals (Ni, V and As) was substantially reduced in the liquid products, indicating that most of the heteroatoms and trace metals

Table 45

Comparison of the Liquid Product with Native Bitumen

Feed Sand: Whiterocks WR-WO
 Reactor Temperature: 798 K
 Solids Retention Time: 9 Minutes
 Sweep Gas Flow Rate: 77.5 SCFH

<u>Properties</u>	<u>Liquid Product (RK-WR-4)</u>	<u>WR-WO Native Bitumen</u>
Gravity, °API	20.3	11.9
Conradson Carbon Residue, Wt.%	1.3	8.1
Ash Content, Wt.%	0.0	1.3
Viscosity, cp	381 (@ 288 K)	2665 (@ 358 K)
Pour Point, K	276	330
<u>Elemental Analysis</u> ¹⁾		
C, Wt.%	87.4	86.9
H, Wt.%	11.6	11.4
N, Wt.%	0.8	1.4
S, Wt.%	0.2	0.3
H/C Atomic Ratio	1.59	1.58
<u>Simulated Distillation</u>		
Volatility, Wt.%	88.2	40.5
IBP - 477 K, Wt.%	0.0	0.0
477 - 617 K, Wt.%	24.4	4.9
617 - 811 K, Wt.%	63.8	35.6
> 811 K, Wt.%	11.8	59.5
<u>Gradient Elution Chromatography</u>		
Saturates, Wt.%	15.5	18.3
MNA/DNA Oil, Wt.%	39.7	5.5
PNA Oil, Wt.%	11.5	11.3
Soft Resin, Wt.%	13.3	13.8
Hard Resin, Wt.%	1.3	3.0
Polar Resign, Wt.%	1.3	1.6
Asphaltenes, Wt.%	9.5	29.6
Noneluted Asphaltenes, Wt.%	7.9	16.9

¹⁾ Oxygen-free basis

Table 46

Comparison of the Liquid Product with Native Bitumen

Feed Sand: Whiterocks WR-WS
 Reactor Temperature: 798 K
 Solids Retention Time: 10 Minutes
 Sweep Gas Flow Rate: 45 SCFH

<u>Properties</u>	<u>Liquid Product</u>	<u>WR-WS Native</u> <u>(RK-WR-18)</u>	<u>Bitumen</u>
Gravity, °API		20.8	11.4
Conradson Carbon			
Residue, Wt.%		2.6	9.9
Ash Content, Wt.%		0.0	0.0
Viscosity, cp	57 (@ 298 K)		9979 (@ 333 K)
Pour Point, K		252	307
Asphaltenes, Wt.%		2.6	11.4
Maltenes, Wt.%		97.4	88.6
<u>Elemental Analysis</u> ¹⁾			
C, Wt.%		86.8	86.6
H, Wt.%		12.1	11.8
N, Wt.%		0.9	1.2
S, Wt.%		0.2	0.4
H/C Atomic Ratio		1.67	1.63
Molecular Weight, g/mol		288	678
Ni, ppm		9	77
V, ppm		< 1	1.3
As, ppm		< 1	2.3
<u>Simulated Distillation</u>			
Volatility, Wt.%		100	42.1
IBP - 477 K, Wt.%		6.7	0.3
477 K - 617 K, Wt.%		25.7	6.6
616 K - 811 K, Wt.%		67.5	35.2
> 811 K, Wt.%		0.0	57.9

¹⁾ Oxygen-free basis

were deposited with the carbonaceous residue during the pyrolysis process. Moreover, the total asphaltene content as determined by gradient elution chromatography (Table 45) and pentane insolubles (Table 46) was greatly reduced.

Consequently, it was concluded that the rotary kiln pyrolysis process results in a significant upgrading of the liquid products relative to the native bitumen. The high quality of the liquid products is one distinct advantage of a thermal processing scheme over alternative bitumen-sand separation technologies.

Preliminary Process Kinetics of Rotary Kiln Pyrolysis of Tar Sands

A comprehensive mathematical model of a rotary kiln pyrolysis process is complicated because the geometry is three dimensional and includes coupled fluid mechanics, heat transfer, mass transfer and chemical kinetic phenomena. In this preliminary modeling attempt, it was assumed that the overall rate of thermal cracking of oil sand was primarily controlled by chemical kinetics rather than by other processes. Thus, the effects of diffusion, heat transfer and fluid mechanics were assumed to be negligible as a first approximation.

A simplified lumped kinetic model for the pyrolysis of oil sands was developed to account for the effect of process variables on the product distribution and yield in a rotary kiln reactor. Several reactions involving lumped components such as asphaltenes, maltenes, heavy oils, light oils, coke and light gas were used in an attempt to reproduce the observed experimental trends. The following simplified reaction scheme was considered:

$$\text{Asphaltenes } (C_{\text{NB}}) \xrightarrow{k_1} \text{A Coke } (C_{\text{CK}}) + \text{B Gas } (C_{\text{G}}) \quad (43)$$

$$\text{Maltenes } (C_{\text{LB}}) \xrightarrow{k_2} \text{C Heavy Oil } (C_{\text{NL}}) + \text{D Gas } (C_{\text{G}}) \quad (44)$$

$$\text{Heavy Oil } (C_{\text{NL}}) \xrightarrow{k_3} \text{E Light Oil } (C_{\text{LL}}) + \text{F Gas } (C_{\text{G}}) \quad (45)$$

In this model, the bitumen (asphaltenes and maltenes fractions) and the carbonaceous residue on the sand grains were assumed to be immobile on the surface of the sand. All the reactions in this network were assumed to be first-order and the reactions were written as mass reactions rather than mole reactions. The differential rate equations for all species were expressed as follows:

$$dC_{\text{NB}}/dt = -k_1 C_{\text{NB}} \quad (46)$$

$$dC_{\text{LB}}/dt = -k_2 C_{\text{LB}} \quad (47)$$

$$dC_{\text{NL}}/dt = C k_2 C_{\text{LB}} - k_3 C_{\text{NL}} \quad (48)$$

$$dC_{\text{LL}}/dt = E k_3 C_{\text{NL}} \quad (49)$$

$$dC_{\text{CK}}/dt = A k_1 C_{\text{NB}} \quad (50)$$

$$dC_{\text{G}}/dt = B k_1 C_{\text{NB}} + D k_2 C_{\text{LB}} + F k_3 C_{\text{NL}} \quad (51)$$

and the integrated expression for these rate equations are:

$$C_{\text{NB}} = C_{\text{NB0}} \exp (-k_1 t) \quad (52)$$

$$C_{\text{LB}} = C_{\text{LB0}} \exp (-k_2 t) \quad (53)$$

$$C_{NL} = \frac{C k_2 C_{L80}}{k_2 - k_3} [\exp(-k_3 t) - \exp(-k_2 t)] \quad (54)$$

$$C_{LL} = \frac{C E C_{L80}}{k_2 - k_3} [k_2 \exp(-k_3 t) - k_3 \exp(-k_2 t)] \quad (55)$$

$$C_{CX} = A C_{N80} [1 - \exp(-k_1 t)] \quad (56)$$

$$C_G = B C_{N80} [1 - \exp(-k_1 t)] + D C_{L80} [1 - \exp(-k_2 t)] + \frac{CFC_{L80}}{k_2 - k_3} [k_2 \exp(-k_3 t) - k_3 \exp(-k_2 t)] \quad (57)$$

In this preliminary model, the kinetic parameters were selected from the literature on kinetic models for the thermal cracking of oil sand bitumen^[201-203].

The choice of the reaction constants was based on kinetic parameters, but was, to a certain degree, arbitrary. The kinetic parameters and the stoichiometric coefficients used in this reaction network are presented in Table 47.

The purpose of this effort was to determine if the experimental trends could be reproduced qualitatively using a simple kinetic model. Product distributions as functions of temperature and solids retention time were computed from the integrated expression for each species. The total mass balances obtained from this computation were normalized to 100 weight percent of bitumen fed to the reactor. Thus, all the calculated yield data were normalized by adding the remaining weight percent

Table 47

Kinetic Parameters and Stoichiometric Coefficients
Rotary Kiln Bitumen Pyrolysis Model

$$k_1 = 1.16 \times 10^{10} \exp(-178,000/RT), \text{ hr}^{-1}$$

$$k_2 = 8.85 \times 10^7 \exp(-104,000/RT), \text{ hr}^{-1}$$

$$k_3 = 2.27 \times 10^{11} \exp(-171,000/RT), \text{ hr}^{-1}$$

$$A = 0.95$$

$$B = 0.05$$

$$C = 0.80$$

$$D = 0.20$$

$$E = 0.85$$

$$F = 0.15$$

to the liquid, gas and coke yields in proportion to their calculated yields. Product distributions as a function of temperature are plotted in Figure 78 and 79. The trends observed in these plots are similar to the experimental trends obtained in the rotary kiln pyrolysis experiments. It is observed from these plots that the temperature at which the maximum liquid yield is obtained decreased with increasing solids retention time.

Product distributions are plotted as a function of solids retention time for the WR-WS and the WR-WO ores in Figure 80 and 81, and in Figure 82, respectively. The same reaction rate constants and stoichiometric coefficients were used as were used for the plots of the temperature effect on product distribution. Qualitatively, the trends observed in these plots are similar to the experimental trends observed in the rotary kiln reactor. It is observed (Figures 80 and 81) that the retention time at which the maximum liquid yield was obtained decreased with increasing temperature.

This kinetic model for the pyrolysis of oil sand reproduced the experimental trends observed in the rotary kiln pyrolysis; however, the experimental product yields were not accurately predicted for the Whiterocks oil sand. This model should be considered a first step in the development of a comprehensive process model for the pyrolysis of oil sands in a rotary kiln reactor.

Figure 78.

Effect of Temperature on Product Distribution:
Rotary Kiln Kinetic Model

Feed Sand: Whiterocks WR-WS
Solids Retention Time: 10 minutes
Sweep Gas Flow Rate: 45 SCFH

Figure 79.

Effect of Temperature on Product Distribution:
Rotary Kiln Kinetic Model

Feed Sand: Whiterocks WR-WS
Solids Retention Time: 21 minutes
Sweep Gas Flow Rate: 45 SCFH

Figure 80.

Effect of Solids Retention Time on Product Distribution:
Rotary Kiln Kinetic Model

Feed Sand: Whiterocks WR-WS
Temperature: 798 K
Sweep Gas Flow Rate: 45 SCFH

Figure 81.

Effect of Solids Retention Time on Product Distribution:
Rotary Kiln Kinetic Model

Feed Sand: Whiterocks WR-WS
Temperature: 823 K
Sweep Gas Flow Rate: 45 SCFH

Figure 82.

Effect of Solids Retention Time on Product Distribution:
Rotary Kiln Kinetic Model

Feed Sand: Whiterocks WR-WO
Temperature: 798 K
Sweep Gas Flow Rate: 77.5 SCFH

SUMMARY AND CONCLUSIONS

The recovery of hydrocarbon values from the oil sands of Utah can be accomplished by any of several mining-surface recovery techniques. These processing strategies include aqueous separation, diluent-assisted aqueous separation and solvent extraction of the bitumen from the sand, and pyrolysis of the oil sand to produce a bitumen-derived hydrocarbon liquid. The rotary kiln process was evaluated as a possible option for the thermal processing of mined Utah oil sands, and a series of continuous-flow pyrolysis experiments were successfully conducted in a rotary-kiln reactor. The rotary-kiln reactor utilized is a semi-pilot scale, continuous-flow pyrolysis reactor. The process variables investigated included the pyrolysis reactor temperature, the solids retention time in the pyrolysis zone, the sweep gas flow rate, and the bitumen content of the feed sand. The experimental results indicated that the pyrolysis temperature, and the solids retention time in the pyrolysis zone were the two most important variables affecting the hydrocarbon liquid and gas yields in the rotary kiln. The liquid product (C_3) yield generally decreased with increasing reactor temperature. Concomitant with this decline in the liquid yield, there was an increase in the light gas (C_1 - C_4) yield. The liquid product yield increased with decreasing the solids retention time while the light gas yield decreased. No significant effect of the sweep gas flow rate on the product distribution and yields was observed. The quality of the bitumen-derived liquids was significantly better than that of the native bitumen. A

preliminary process kinetics model which conforms to the observed trends has been developed.

In this investigation, an effort has been made to determine the feasibility of a rotary-kiln pyrolysis for the recovery of hydrocarbon values from Utah oil sands. Four different oil sand samples from the west side of the Whiterocks deposit were evaluated as potential feed for this process. The following conclusions were drawn from this investigation:

1. The process variable data obtained in this exploratory investigation indicated that a rotary kiln pyrolysis process could be a feasible alternative to a fluidized-bed thermal process for the production of an upgraded bitumen-derived hydrocarbon liquid from Utah oil sands.
2. The pyrolysis temperature and the solids retention time in the pyrolysis zone were the two most important variables affecting the produced hydrocarbon liquid from gas yields in rotary kiln pyrolysis. The maximum C_3 plus hydrocarbon liquid yield, 68.7 wt%, was obtained at a reactor temperature of 798 K and a solids retention time of 10 minutes with the Whiterocks west-south oil sand sample.
3. The liquid product (C_3 plus) yield generally decreased with increasing reactor temperature at a fixed solids retention time while the light gas ($C_1 - C_4$) yield increased and the coke yield decreased slightly. The quality of the liquid product generally declined as reactor temperature increased.
4. The liquid product (C_3 plus) yield increased with decreased

solids retention time at constant temperature while the light gas ($C_1 - C_4$) yield decreased. The coke yield was relatively insensitive to the solids retention time.

5. The product distribution and yields and total liquid properties were independent of the sweep gas flow rate.

6. The bitumen-derived hydrocarbon liquid produced in the rotary kiln reactor was significantly upgraded relative to the native bitumen. It would be an excellent hydrogen refinery feedstock.

7. The lumped kinetic model used in the preliminary mathematical modelling study predicted the product distribution trends observed experimentally in the rotary kiln reactor with respect to both temperature and solids retention time.

FUTURE ACTIVITIES

Redesign product recovery system, evaluate the new components and test the assembled system. Design and evaluate a gas pump to pull the sweep gas through the kiln to minimize pressure drop across the kiln-barrel seals. Redesign the feeder-auger system and the barrel inlet-dike to permit continuous feeding of undiluted oil sands.

NOMENCLATURE

D	diameter of the kiln barrel, cm
F	fresh oil sand feed rate, g/min
k_1	apparent first-order rate constant for the decomposition of the asphaltene fraction, s^{-1}
k_2	apparent first-order rate constant for the decomposition of the maltene fraction, s^{-1}
k_3	apparent first-order rate constant for the decomposition

of the heavy oil fraction, s^{-1}

L length of the kiln pyrolysis zone, cm

N rotational speed of the kiln, rpm

s slope of the kiln barrel, deg

w weight of tar sand ore in the kiln barrel, g

θ solids retention time in the pyrolysis zone, min $^{-1}$

θ_d dwell time in the rotary kiln, min $^{-1}$

CATALYTIC UPGRADING OF BITUMEN AND BITUMEN DERIVED LIQUIDS

Principal Investigator

F.V. Hanson

HYDROTREATING THE BITUMEN-DERIVED HYDROCARBON LIQUID PRODUCED IN A FLUIDIZED-BED PYROLYSIS REACTOR

Post Doctoral Fellow
Graduate Students

C.H. Tsai
D.C. Longstaff
S.K. Kwak

INTRODUCTION

The recovery of hydrocarbon values from Utah's oil sands will occur by a combination of in-situ thermal EOR and mining-surface recovery techniques. The potential mining-surface recovery processes include aqueous separation,^[136, 204] pyrolysis,^[8, 197] and solvent extraction^[205-207]. The separation and extraction processes produce the native bitumen whereas the pyrolysis processes produce a bitumen-derived hydrocarbon liquid. The integration of the produced bitumens and/or bitumen-derived hydrocarbon liquids into the economy would likely be accomplished by using the native bitumens as asphalt base stocks^[41, 208] and/or as refinery feedstocks and by using the bitumen-derived liquids as refinery feedstocks. The high nitrogen content of the Uinta basin bitumens and the bitumen-derived liquids, 0.8-1.2 wt%, indicated that hydrotreating would be required as a primary upgrading process. The bitumen-derived hydrocarbon liquid produced during the fluidized bed pyrolysis of the mined ore from the Whiterocks tar sand deposit^[208] was used as the hydrotreater feedstock in this study.

The Whiterocks tar sand deposit is located in Sections 17-20 Township 2 North, Range 1 East in the Uinta Basin of northeastern

Utah. The Whiterocks tar sand was obtained from the Fausett mine/pit on the Western flank of the deposit in Sections 18 and 19. The ore was mined from the surface of the pit after removal of the first 15 or 25 feet of the ore body. Drum quantities were obtained by hand loading higher grade, unweathered material. The ore was crushed and screened prior to being used as feed sand in the fluidized bed pyrolysis production run. The physical and chemical properties of the native bitumen and the produced bitumen-derived hydrocarbon liquid are presented in Table 48⁽²¹⁰⁾.

The objective of this investigation was to conduct a process variable study related to the hydrotreating of the bitumen-derived liquid product. The process variables studied included the reactor temperature, the total reactor pressure, the liquid hourly space velocity and the hydrogen partial pressure.

EXPERIMENTAL METHODS AND MEANS

Fluidized Bed Pyrolysis System

The bitumen-derived liquid used in the hydrotreating studies was produced from the Whiterocks tar sand ore in a large diameter fluidized bed pyrolysis reactor which was operated continuously over a 25 day period. The reactor temperature ranged from 773 to 813 K, and the average feed sand retention time was 17.2 minutes during the course of the production run. The bitumen-derived liquid was significantly upgraded relative to the native bitumen (Table 48): 18.5 °API versus 11.9°API; a viscosity of 85.4 cps @ 289 K, versus 2665 cps @ 358 K; a volatility (<811 K [<1000°F]) of 82.2 wt.% versus 40.5 wt.%; a Conradson carbon residue of 4.6 wt%

Table 48
Analysis of the Native Bitumen and the
Bitumen-Derived Liquid from the Whiterocks
Oil Sand Deposit

Source	Native Bitumen	Bitumen-Derived Liquid Product
Bitumen content wt%	8.5	--
Product Yields, wt%		
C ₁ - C ₄ Gas	--	29.3
C ₅ Liquid	--	44.7
Carbonaceous Residue	--	25.0
Gravity, API	11.9	18.5
Density (60°F), g/cm ³	0.985	0.943
Heat of Combustion, BTU/lb	19692.	18750.
Viscosity, cps	2665. @ 358 K	85.4@ 289 K
Pour point, K (°F)	338. (149)	253. (-5)
Conradson carbon residue wt%	8.1	4.6
Simulated Distillation		
Volatility, wt%	40.5	82.2
IBP, K	489	414
IBP-417 K, wt%	0.0	4.7
477-617 K, wt%	4.9	18.5
617-811 K, wt%	35.6	59.0
> 811 K, wt%	59.9	17.8
Elemental Analysis		
C, wt%	85.1	86.0
H, wt%	12.3	11.1
O, wt%	1.1	1.5
N, wt%	1.2	1.12
S, wt%	0.3	0.32
Atomic H/C Ratio	1.73	1.55

versus 8.1 wt%; etc., respectively. The atomic hydrogen-to-carbon (H/C) ratio of the bitumen-derived liquid was lower than that of the native bitumen. This reduction was related to dealkylation and hydroaromatic dehydrogenation reactions during pyrolysis which resulted in the production of a more aromatic hydrocarbon liquid and consequently a lower H/C ratio. Furthermore, the asphaltene fraction in the native bitumen was assumed to be the primary precursor of the carbonaceous residue deposited on the spent sand. Thus the coking tendency of the bitumen-derived liquid during hydrotreating was expected to be less than that of the native bitumen. The production of the bitumen-derived hydrocarbon liquid from the Whiterocks tar sand has been described in detail by Sung^[178].

Hydrotreater Process Unit

Process studies were conducted in a fixed bed reactor which operated in the upflow mode to minimize thermal gradients in the catalyst bed and to ensure complete wetting of the catalyst. Constant withdrawal of the liquid product from the high pressure separator permitted continuous operation of the system. Operating problems associated with the high pressure separator and liquid level controller required that both liquid and gaseous products be withdrawn from the system through the back pressure control valve. A schematic of the hydrotreater system is presented in Figure 83. A schematic of the reactor is presented in Figure 84. The reactor was machined from 316 stainless steel and was designed for operation at a maximum pressure of 34.5 MPa at 773 K; however, the

Figure 83.

Flow Diagram of the Hydrotreating Catalyst Testing Unit

CATALYST BED
 LENGTH = 30.5 cm
 INSIDE DIAMETER = 2.54 cm
 CENTRAL THERMOWELL = 0.32 cm O.D.

Figure 84. Reactor Schematic

maximum operating pressure was limited to 20.7 MPa at 773 K. Manifold valves on the inlet and outlet lines from the reactor permitted operation in either the upflow or downflow mode. An exotherm was observed in the inlet region of the catalyst bed where the highly reactive olefins in the bitumen-derived liquid hydrogenated. The catalyst was diluted with quartz sand (50% by volume) in the inlet region of the bed (~20%) to trim the exotherm. A typical reactor temperature profile is presented in Figure 85. The denitrogenation and desulfurization data were correlated using the kinetic average temperature, T_k , which was, defined as follows:

$$T_k = \int_a^b \exp\left[\frac{-E_a}{RT(x)}\right] dx \quad (58)$$

where E_a is the apparent activation energy and $T(x)$ is an appropriate function which describes the variation of the catalyst bed temperature as a function of axial distance, x , in the bed. The kinetic average temperature calculated from Equation 58 for the temperature profile presented in Figure 85 was 663 K. The arithmetic average temperature was also 663 K. The kinetic average temperature and the arithmetic average temperature never differed by more than 0.5°C due to the dilution of the catalyst bed and to operation in the upflow mode.

The base case operating conditions for the hydrotreating study were as follows: reaction temperature, 619 K (653 °F); liquid hourly space velocity (LHSV), 0.5 h⁻¹; total reactor-pressure, 13.7 MPa (1980 psia) and hydrogen-to-hydrocarbon feed ratio, 890 m³/m³

Figure 85. Reactor Temperature Profile for Upflow Operation

(5000 scf/bbl). The API gravity of the total liquid product was constant at 23.2 °API after the reactor had been on-stream for 94 hours at the base case conditions. At this point, it was assumed that the catalyst had attained a stationary state and that 95% of the coke deposition had occurred. Once the reactor system had attained the stationary state, it was allowed to operate on automatic control overnight. A series of experiments were conducted in which the system was operated in a cyclic mode (base case condition/desired reaction condition/base case condition) for approximately 800 hours. The total liquid product from each experiment was collected for analyses. The analytical test procedures conformed to those outlined in the ASTM manuals.

Mass balances were taken for approximately 3 hours at the end of a 16-hour line-out period after the system had attained a stationary state at the new reaction conditions. The mass balances were conducted by monitoring the liquid fed to the reactor system for discrete time periods. Liquid samples were collected at room temperature and gas samples were collected at 76 K (in a container immersed in a liquid nitrogen bath) during the material balance. At the conclusion of each mass balance the gas condensate and liquid samples were weighed and the gas condensate was weathered into a vapor collector and analyzed by gas chromatography. All the mass balances were greater than 97.5 wt%. The design, construction and operation of the hydrotreater system has been discussed in detail by Longstaff^[209].

The extent of nitrogen removal was the key reactivity

parameter followed during the course of the study; however, the key operating parameter followed on the catalyst testing unit during the run was the specific and/or API gravity of the total liquid product. The nitrogen content of the total liquid product is plotted as a function of API gravity in Figure 86. The nitrogen-gravity data reported by Sullivan and Stangeland^[210] for shale oil hydrodenitrogenation is also plotted in Figure 86. The similarity between the trends indicated that the nitrogen-gravity correlation for the hydrodenitrogenation of the bitumen-derived liquid could be used with confidence. Thus, the nitrogen-gravity correlation was presumed to be acceptable as an on-line guide to estimate the real time influence of changes in operating variables during the course of the study.

Catalyst and Catalyst Activation

A total of 136 cm³ of a UNOCAL 1/16" quadralobe Ni/Mo/Al₂O₃ hydrodenitrogenation (HDN) catalyst was placed in the middle section (30.5 cm long) of the reactor. The catalyst was mixed with Ottawa sand in the inlet region of catalyst bed to dissipate the global heat of reaction generated by the olefin hydrogenation reactions. The catalyst contained 3.3 wt.% NiO, 12.8 wt.% MoO₃, and 0.8 wt.% P₂O₅. It had a surface area of 241 m²/g and a pore volume (Hg porosimetry) of 0.55 cm³/g. The sulfiding conditions were specified by the catalyst manufacturer. A solution of dimethyl disulfide in kerosene (~ 2 wt.% sulfur) was used to sulfide the catalyst at a LHSV of 1.0 h⁻¹. The hydrogen-to-sulfiding solution ratio was 890 m³/m³ (5000 scf/bbl). The catalyst was contacted with

Figure 86. Nitrogen Concentration - API Gravity Correlation

the sulfiding solution at the ambient temperature and the temperature was increased to 505 K (450°F) at a rate of 28°C per hour. The catalyst was held at 505 K for 2 hours or until sulfur breakthrough was observed. The temperature was then raised to 644 K (700°F) at a rate of 28°C per hour. The catalyst was held an additional 2 hours at 644 K to complete the sulfiding step. The sulfiding solution was discontinued and the reactor temperature was adjusted to the initial run temperature.

RESULTS AND DISCUSSION

Process Variable Study

The primary process variables investigated were the reaction temperature, the total reactor pressure and the liquid hourly space velocity. The operating conditions at which the process variable data were obtained are presented in Figure 87 and are summarized as a function of time on-stream in Table 49. Each experiment was conducted by changing one variable at a time from the base case conditions. Three sets of experimental data were obtained at the following conditions: 1) the reaction temperature was varied at constant pressure (13.7 MPa [1980 psig]) and LHSV (0.5 h⁻¹); 2) the LHSV was varied at constant temperature (663 K [733°F]); and pressure (13.7 MPa) and 3) the total pressure was varied at constant temperature (663 K) and LHSV (0.5 h⁻¹). The hydrogen-to-bitumen-derived liquid ratio was the same in all experiments (890 m³/m³ [5000 scf/bbl]). The experiments were conducted in a random manner to avoid systematic errors. After the stationary state was attained and a material balance was completed a second experiment

Figure 87. Reaction Conditions

Table 49

Run Conditions Employed to Hydrotreat
Bitumen-Derived Liquid from Whiterocks
Tar Sand Formation

Run Number	Time On Stream (h)	Reaction ^{a)} Temperature (K)	LHSV (h ⁻¹)	Reactor ^{b)} Pressure (MPa)
6	96	617.	0.50	13.7
7	117	681.	0.51	13.7
8	145	617.	0.54	13.6
9	170	663.	0.50	13.7
10	188	618.	0.49	13.7
11	262	663.	0.20	13.7
12	285	619.	0.48	13.8
13	309	664.	0.48	17.1
14	334	618.	0.51	13.5
15	359	665.	0.50	11.0
16	383	619.	0.50	13.7
17	429	663.	0.35	13.7
18	454	664.	0.37	13.6
19	477	618.	0.52	13.7
20	505	662.	0.50	15.5
21	524	617.	0.49	13.6
22	548	644.	0.49	13.6
23	581	618.	0.49	13.7
24	601	663.	0.77	13.8
25	623	618.	0.52	13.6
26	648	680.	0.19	13.5

^a Average catalyst bed temperature

^b Reactor outlet pressure

was conducted at the base case conditions listed in Table 50.

The API gravity of the total liquid product produced at the base case operating conditions is plotted as a function of time on-stream in Figure 88. The reactor was operated continuously at the base case conditions for the first 100 hours on-stream. The API gravity of the liquid produced in the initial deactivation period (~ 100 hours on-stream) was monitored; however, those points were not plotted so that the change in API gravity at the base case conditions during the course of the process variable study could be clearly discerned. It should be noted that the spread of the points above and below the least squares fit is accentuated by the expansion of the y-axis to a range of 0.7 of a degree of API. The difficulty associated with exact reproduction of the temperature and space velocity in the base case experiments also contributed to the scatter of the data. The deactivation or aging rate was estimated to be 0.25°F/day over approximately 800 hours on-stream. The deactivation rate was somewhat higher than expected; however, this was likely due to the nature of the feedstock. Furthermore, it should be noted that the study was not intended to precisely determine the aging rate of the catalyst. A portion of the accelerated deactivation was attributed to the variation in operating conditions from experiment to experiment.

Effect of Reaction Temperature

The effect of reaction temperature at a fixed pressure and space velocity on the product distribution and yields is presented in Figures 89 and 90 and in Table 51 and on denitrogenation in

Table 50

Operating Conditions for Hydrotreating
the Bitumen-Derived Liquid from the Whiterocks
Tar Sand Deposit

Process Variables

Operating Ranges

Temperature, K (°F)	616-680 (650-765)
LHSV, h ⁻¹	0.185-0.77
Pressure, MPa (psia)	11.0-16.9 (1600-2450)
H ₂ /Oil Ratio, m ³ /m ³ (SCF/B)	890 (5000)
Catalyst ^{a)}	
Loading, cm ³	136
Surface Area, m ² /g	241
Pore Volume ^{b)} , cm ³ /g	0.55
Composition	
NiO, wt%	3.3
MoO ₃ , wt%	12.8
P ₂ O ₅ , wt%	0.8
Base Process Conditions	
Temperature, K (°F)	616 (653)
Reactor Pressure, MPa (psia)	13.6 (1980)
LHSV, h ⁻¹	0.50
H ₂ /Oil Ratio, m ³ /m ³ (SCF/B)	890 (5000)

^{a)} UNOCAL 1/16 "Quadralobe HDN Catalyst

^{b)} Hg porosimetry

Figure 88. API Gravity vs Time On-Stream for Base Case Runs

Figure 89. Effect of Reactor Temperature on Light Gas and Naphtha Yields

Figure 90. Effect of Reactor Temperature on Middle Distillate, Gas Oil and Resid Yields

Table 51

Effect of Temperature on the Product Properties of the
Hydrotreated Bitumen-Derived Liquid from
Whiterocks Tar Sand Formation

Run Number	16	22	9	7
<u>Process Operating Conditions</u>				
Temperature, K	619	644	663	681
LHSV, h ⁻¹	0.5	0.5	0.5	0.5
Residence Time, h	2.0	2.0	2.0	2.0
Pressure, MPa	13.7	13.6	13.7	13.7
API Gravity	23.2	24.9	26.9	29.8
Specific Gravity	0.915	0.905	0.893	0.878
H ₂ Cons., m ³ /m ³ (SCF/bbl)	147 (825)	166 (933)	182 (1019)	195 (1097)
<u>Elemental Analysis</u>				
C, wt%	87.5	87.6	87.3	87.2
H, wt%	12.2	12.2	12.6	12.8
Nitrogen, ppm	3070	1631	748	202
Sulfur, ppm	271	65	45	16
H/C Atomic Ratio	1.66	1.66	1.72	1.76
<u>Product Yields, wt%</u>				
C ₁	0.2	0.2	0.5	0.9
C ₂	0.3	0.3	0.6	0.8
C ₃	0.4	0.4	0.8	1.3
i-Butane	0.2	0.2	0.3	0.4
n-Butane	0.4	0.4	0.6	0.8
C ₅ Liquid Product	97.8	98.3	96.3	94.8
Liquid Yield Vol.%	99.3	101.4	100.8	100.9
<u>Simulated Distillation of Total Liquid Product</u>				
Volatility, wt%	87.5	87.7	92.3	92.8
IBP, K	423	429	396	395
IBP-477 K	3.7	3.2	7.1	8.8
477-617 K	20.9	19.0	27.4	32.8
617-811 K	59.2	62.8	53.3	45.1
>811 K	12.5	12.3	7.7	7.2

Table 51. All experiments were conducted at a reactor pressure of 13.7 MPa, a space velocity of 0.5 h^{-1} and a H_2 -to-hydrocarbon ratio of $890 \text{ m}^3/\text{m}^3$. As the average catalyst temperature increased, a significant increase in the API gravity of the total liquid product relative to the bitumen-derived liquid was observed; that is, 29.8 °API and 18.5 °API, respectively, at a reaction temperature of 681 K. The API gravity of the total liquid product increased from 23.2 to 29.8 °API as the reaction temperature increased from 619 to 681 K. The increase in API gravity as a function of temperature was accompanied by an increase in H_2 consumption and in the atomic H/C ratio of the total liquid product as expected. The physical and chemical properties of the total liquid product did not change significantly as the temperature increased from 619 to 644 K; however, there was a substantial reduction in the nitrogen and sulfur concentrations. The nitrogen content decreased by 47% and the sulfur content decreased by 76%. Above 644 K the decrease in sulfur and nitrogen contents were accompanied by significant changes in the physical and chemical properties of the total liquid product (Table 51). These changes were presumed to be related to the conversion of more refractory heteroatom species. This speculation was confirmed by the product distribution data plotted in Figures 89 and 90. The resid ($> 811 \text{ K}$) and gas oil (617-811 K) yields declined as the temperature increased while the middle distillate, (477-617 K), naphtha (IBP - 477 K) and C_1 - C_4 gas yields increased. The shifts in boiling range and molecular weight were related to the conversion of more refractory compounds at higher

temperatures. Although higher temperatures would have led to higher denitrogenation activity, 681 K was selected as the upper reaction temperature limit to suppress thermal cracking and excessive coke deposition.

Effect of LHSV

The effect of LHSV on product distribution and yields at a fixed reaction temperature and pressure is presented in Figures 91 and 92 and in Table 52 and on denitrogenation in Table 52. The space velocity experiments were conducted at a reactor pressure of 13.7 MPa, a temperature of 663 K, and a H_2 -to-hydrocarbon ratio of $890 \text{ m}^3 / \text{m}^3$.

As the liquid hourly space velocity decreased the API gravity of the hydrotreated total liquid product relative to the bitumen-derived liquid increased: 30.2 °API and 18.5 °API, respectively, at a LHSV of 0.2 h^{-1} . The API gravity of the total liquid product increased from 25.7 to 30.2 °API as the space velocity decreased from 0.77 to 0.2 h^{-1} . The increase in API gravity as space velocity decreased was accompanied by an increase in the hydrogen consumption and in the atomic H/C ratio of the total liquid product. The space velocity appeared to have a greater influence on hydrogen consumption than reaction temperature and was related to the higher C_1 - C_4 yields as the space velocity decreased. The sulfur and nitrogen contents both decreased significantly as the space velocity decreased from 0.77 to 0.2 h^{-1} . The sulfur content, 77 ppm, at a space velocity of 0.37 h^{-1} (Table 52) may have been high due to inefficient stripping of dissolved H_2S prior to

Figure 91. Effect of Space Velocity on Light Gas and Naphtha Yields

Figure 92.

Effect of Space Velocity on Middle Distillate, Gas Oil and Resid Yield

Table 52

Effect of LHSV on the Product Properties of the
Hydrotreated Bitumen-Derived Liquid from
Whiterocks Tar Sand Formation

Run Number	24	9	18	11
<u>Process Operating Conditions</u>				
LHSV, h ⁻¹	0.77	0.5	0.37	0.2
τ , h	1.3	2.0	2.7	5.1
Temperature, K	663	663	664	663
Pressure, MPa	13.8	13.7	13.6	13.7
API Gravity	25.7	26.9	27.8	30.2
Specific Gravity	0.900	0.893	0.888	0.875
H ₂ Cons., m ³ /m ³ (SCF/bbl)	147 (825)	182 (1019)	239 (1343)	277 (1554)
<u>Elemental Analysis</u>				
C, wt%	87.4	87.3	87.2	87.0
H, wt%	12.4	12.6	12.7	13.0
Nitrogen, ppm	1434	748	686	186
Sulfur, ppm	349	45	77	18
H/C Atomic Ratio	1.69	1.72	1.75	1.78
<u>Product Yields, wt%</u>				
C ₁	0.6	0.5	0.6	1.1
C ₂	0.5	0.6	0.6	1.1
C ₃	1.0	0.8	0.9	1.7
i-Butane	0.4	0.3	0.4	0.5
n-Butane	0.8	0.6	0.8	0.9
C ₅ Liquid Product	95.6	96.3	96.3	94.5
Liquid Yield, Vol.%	98.5	100.8	100.2	100.5
<u>Simulated Distillation of Total Liquid Product</u>				
Volatility, wt%	89.1	92.3	92.2	95.0
IBP, K	417	396	400	380
IBP, 477 K	3.9	7.1	6.1	8.6
477-617 K	23.3	27.4	27.3	34.3
617-811 K	56.0	53.3	53.1	45.4
> 811 K	10.9	7.7	7.8	5.0

analysis.

The simulated distillation data (Table 52) indicated that more refractory, asphaltic compounds were converted at lower space velocities; that is, the residual and gas-oil fractions (>811 K and $617-811$ K, respectively) decreased whereas, the middle distillate ($477-617$ K), naphtha (IBP- 477 K) and C_1-C_4 gas yields increased (Figures 91 and 92). The heavy gas oil and residual fractions represented less than 50 % of the total liquid product produced at the lowest space velocity. This would translate to a reduced demand on the hydrocracker in downstream processing of this total liquid product or of its heavier fractions.

Effect of Reactor Pressure

The effect of reactor pressure at fixed space velocity and reaction temperature on product distribution and yields is presented in Table 53. The effect of pressure on hydrogen consumption is presented in Figure 93. The reaction temperature and LHSV were maintained at 663 K, and 0.5 h^{-1} , respectively, while the pressure varied from 11 to 17.1 MPa. The reactor pressure did not appear to exert a significant influence on the product distribution and yields nor on the physical and chemical properties of the total liquid product (Table 53). The API gravity of the total liquid product increased from 26.6 to 27.7°API as the pressure increased from 11 to 17.1 MPa. The product distribution, as indicated by simulated distillation data, appeared to be independent of the reactor pressure in the range 11 to 17.1 MPa (Table 53). The nitrogen content of the total liquid product

Table 53

Effect of System Pressure on the Product Properties of the
Hydrotreated Bitumen-Derived Liquid From
Whiterocks Tar Sands Formation

Run Number	15	9	20	13
<u>Process Operating Conditions</u>				
Pressure, MPa	11.0	13.7	15.5	17.1
Temperature, K	665	663	662	664
LHSV, h ⁻¹	0.5	0.5	0.5	0.48
τ , h	2.0	2.0	2.0	2.1
API Gravity	26.6	26.9	27.1	27.7
Specific Gravity	0.895	0.893	0.892	0.889
H ₂ Con., m ³ /m ³ (SCF/bbl)	135 (755)	182 (1019)	244 (1370)	287 (1611)
<u>Elemental Analysis</u>				
C, wt%	87.4	87.3	87.2	87.3
H, wt%	12.4	12.6	12.7	12.6
Nitrogen, ppm	1260	748	942	727
Sulfur, ppm	28	45	213	57
H/C Atomic Ratio	1.69	1.72	1.74	1.72
<u>Product Yields, wt%</u>				
C ₁	1.0	0.5	0.8	1.0
C ₂	1.1	0.6	0.9	1.0
C ₃	1.6	0.8	1.2	1.1
i-Butane	0.3	0.3	0.4	0.3
n-Butane	0.5	0.6	0.8	0.6
C ₅ Liquid Product	94.1	96.3	95.6	95.7
Liquid Yield, Vol.%	98.2	100.8	99.6	100.8
<u>Simulated Distillation of Total Liquid Product</u>				
Volatility, wt%	95.1	92.3	90.9	90.8
IBP, K	412	396	412	403
IBP-477 K	4.9	7.1	4.9	5.8
477-617 K	25.9	27.4	25.9	26.4
617-811 K	54.2	53.3	54.3	53.6
>811 K	8.2	7.7	9.1	9.2

Figure 93. Hydrogen Consumption versus Pressure

decreased with increased reactor pressure. The sulfur content did not vary significantly as the pressure increased from 11 to 17.1 MPa; however, the fractional sulfur conversion exceeded 0.69 over the entire range of pressures studied. The total liquid product produced at 15.5 MPa contained dissolved H_2S and NH_3 , which had not been completely stripped from the sample prior to analysis. Thus, the reported nitrogen and sulfur contents were suspect. Pressure appeared to exert a significant influence on hydrogen consumption (Figure 93). Small increases in the total reactor pressure increased hydrogen consumption to a much greater extent than increasing the temperature or decreasing the LHSV.

The nitrogen content of the total liquid product versus hydrogen consumption is presented in Figure 94 for three series of experiments in which the catalyst activity was adjusted by: 1) increasing the reaction temperature at fixed space velocity and reactor pressure; 2) by decreasing LHSV at fixed reaction temperature and reactor pressure; and 3) by increasing reactor pressure at fixed reaction temperature and space velocity. The relative effects of temperature, LHSV and pressure on hydrogen consumption are summarized in this figure. The nitrogen content- H_2 consumption curve obtained when temperature was varied had the steepest slope. Thus, large decreases in nitrogen content were accompanied by small increases in hydrogen consumption. The opposite was observed for the nitrogen content- H_2 consumption curve obtained when pressure was varied: small decreases in product nitrogen content were accompanied by large increases in hydrogen

Figure 94. Product Nitrogen vs. H₂ Consumption

consumption. The influence of LHSV on the slope of the nitrogen content-H₂ consumption curve was intermediate between the temperature and pressure trends.

If nitrogen removal were the sole objective in hydrotreating then nitrogen conversion could be accomplished at the lowest hydrogen consumption by operating at high temperatures. However, nitrogen removal is rarely the only objective in hydrotreating. For example, the aromatic contents of the jet fuel and diesel fractions must meet specifications; thus, a specific level of hydrogen consumption is required to saturate aromatic moieties. Even though high operating temperatures removed more nitrogen than operating at high hydrogen pressure, high operating temperatures led to greater gas yields and more rapid catalyst deactivation.

It was interesting to note that significant conversion of the resid fraction was accomplished at high temperatures and fixed space velocity and/or at long reactor residence times and fixed reaction temperature. The feed contained 18 wt.% resid (defined as material boiling above >811 K.) and the liquid produced at the highest temperature (681 K, 0.5 LHSV, 13.7 Mpa.) contained 6 wt.% resid. This represented 65% conversion of the residual fraction to lower boiling materials.

Statistical Analysis

The reaction conditions, product properties and yield structure of each run were analyzed by multivariate statistical analysis to determine the effect of temperature, LHSV and pressure on the product properties. It was found that the yields were most

significantly affected by the reactor temperature. LHSV was also important, but to a lesser extent than temperature. Reactor pressure had only a minor influence on product yields and conversions.

Pyrolysis-Hydrotreating Process Sequence

The changes which occurred in the processing sequence tar sand pyrolysis followed by hydrotreating of the bitumen-derived liquid are illustrated in Table 54 in which selected physical and chemical properties of the native bitumen, the bitumen-derived liquid and the hydrotreated total liquid product are presented. The bitumen-derived liquid was produced at ambient pressure, a feed sand retention time of 17.2 minutes and a sweep gas flow rate of 2.2 SCMH. The pyrolysis zone temperature ranged from 773 to 813 K. The hydrotreated total liquid product was produced at a reactor pressure of 13.7 MPa (1980 psia), an average catalyst bed temperature of 680 K (764 F) a liquid hourly space velocity of 0.19 h^{-1} and a H_2 -to-hydrocarbon feed ratio of $890 \text{ m}^3/\text{m}^3$ (5000 scf/bbl).

The pyrolysis or coking step resulted in three important changes that had an impact on the hydrotreater: a reduction in the Conradson carbon residue; 8.1 to 4.7 wt %; a reduction in the metals content of the total liquid product relative to the native bitumen, 67 ppm Ni to 9 ppm Ni; and a decrease in the residual fraction (>811 K) from 59.5 wt% to 17.8 wt%. These changes led to the selection of a hydrodenitrogenation (HDN) catalyst for the hydrotreater studies rather than a hydrodemetallation (HDM) catalyst. The reduction in boiling range did not lead to a

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Table 54

Properties of Bitumen and Bitumen-Derived Liquids
from the Whiterocks Deposit Tar Sand

	Native Bitumen	Bitumen-Derived Liquid	Hydrotreated Bitumen-Derived Liquid
<u>Operating Conditions</u>			
Temperature, K	--	773-813	680
Pressure, MPa	--	0.088	13.7
Feed Sand Retention Time, min	--	17.2	--
LHSV, h ⁻¹	--	--	0.185
H ₂ -to-Hydrocarbon Ratio, m ³ /m ³	--	--	890.
API Gravity	11.9	18.5	35
Conradson Carbon, Residue wt%	8.1	4.7	NA
Pour Point, K	338	279	259
<u>Simulated Distillation</u>			
Volatility, wt.%	40.5	82.2	97.4
IBP K	489	414	370
IPB - 477 K, wt%	0.0	4.7	12.5
477 - 617 K, wt%	4.9	18.5	40.
617 - 811 K, wt%	35.6	59.0	34.9
>811 K, wt %	59.5	17.8	2.6
<u>Elemental Analysis</u>			
C, wt%	85.1	86.0	86.7
H, wt%	12.3	11.1	13.3
N, wt%/ppm	1.2	1.1	43 ppm
S, wt%/ppm	0.4	0.3	16 ppm
O, wt%	1.1	1.5	0.
Ni, ppm	67	9	NA
V, ppm	<5	<1	NA
Atomic H/C Ratio	1.73	1.55	1.84

concomitant reduction in the nitrogen and sulfur contents of the bitumen-derived liquid relative to the native bitumen; however, there was a reduction in the hydrogen content.

The hydrotreating step resulted in a reduction of the nitrogen content from 1.1 wt% for the bitumen-derived liquid to 43 ppm for the hydrotreated total liquid product. A similar reduction in the sulfur content was observed: 0.32 wt% to 16 ppm, respectively. These reductions were accompanied by a significant increase in hydrogen content: 11.1 wt% to 13.3 wt%. The boiling range and molecular weight reductions were significant in that 40% of the total liquid product was in the high density, high energy aviation turbine fuel boiling range, 477-617 K (400-650°F). Fractional distillation of the total liquid product produced a water-white aviation turbine fuel fraction. The 617 K plus hydrotreated liquid product would make an excellent fluid catalytic cracker or fuels hydrocracker feedstock.

Preliminary Process Kinetics

A secondary objective of this study was to determine the apparent kinetic parameters for the following rate expressions:

$$r_H = k_{HDN} C_H^a P_{H_2}^b \quad (59)$$

$$r_S = k_{HDS} C_H^c P_{H_2}^d \quad (60)$$

where k_{HDN} is the apparent rate constant for hydrodenitrogenation, k_{HDS} is the apparent rate constant for hydrodesulfurization; P_{H_2} is the partial pressure of hydrogen; C_H is the concentration of

organic nitrogen; and C_s is the concentration of organic sulfur. The kinetics of nitrogen and sulfur removal were lumped due to the complexity of the feed; that is, the bitumen-derived liquid contained a broad range of nitrogen and sulfur compounds which differed in the ease of conversion and/or heteroatom removal. Neither the denitrogenation nor the desulfurization data could be successfully organized according to a first order dependence in nitrogen or sulfur heteroatom concentration. That is, the plots of the logarithms of the fraction unconverted as a function of inverse space velocity were non-linear.

The integrated kinetic equation for hydrodenitrogenation was given by

$$k_N \tau = f(x_N) \quad (61)$$

The function $f(x_N)$ was given by

$$f(x_N) = \frac{1}{C_{N_0}^{(n-1)}} \frac{1}{(n-1)} [(1-x_N)^{(1-n)} - 1] \quad (62)$$

where τ is the contact time or reciprocal of the space velocity, h ; x_N is the conversion of nitrogen, and C_{N_0} is the initial concentration of nitrogen, wt%. The rate constant, k_N , incorporated the hydrogen concentration term which was assumed to be approximately constant at high H_2 -to-hydrocarbon ratios; that is,

$$k_N = k_{NN} P_H^b \quad (63)$$

A plot of the function $f(x_n)$ versus the inverse of the space velocity should give a straight line of slope k_n ; however, this procedure required a value for the order with respect to nitrogen removal, n . Various values of n , the order for nitrogen removal, were chosen and $f(x_n)$ was plotted as a function of the reciprocal of the LHSV to obtain a family of curves. The value of n which gave the best fit of the data to a straight line was the apparent reaction rate order for nitrogen removal. The denitrogenation order for the bitumen-derived liquid was determined to be 1.55 from the slope of the plot in Figure 95.

Kinetic studies of model nitrogen compounds have shown that hydro-denitrogenation is first order with respect to nitrogen^[211]. The 1.55 order reported here was explained on the basis of the broad spectrum of nitrogen containing species present in the bitumen-derived liquid. It was presumed that nitrogen removal proceeded by a set of competitive parallel, first order reactions. The overall order for a reaction network of this type was expected to be between 1 and 2^[212]. The greater than first order dependence on the fraction of unconverted nitrogen was contrary to the first order dependence reported for Paraho shale oil^[210] and for an atmospheric residuum (>514 K (> 465°F))^[212]. The difference is of interest in that the Safaniya residuum and the whole shale oil contained 0.24 and 2.18 wt.% nitrogen, respectively, whereas the bitumen-derived liquid contained 1.1 wt.%. Thus, it was expected that denitrogenation of the bitumen-derived liquid would also have been first order in nitrogen concentration. We presumed that the

Figure 95. Integrated Rate Expression, $f(x_n)$, as a Function of Residence Time

difference in order was related to the differences in the nature of the nitrogen compounds in the bitumen-derived liquid relative to the shale oil and the Safaniya residuum.

The same procedure was used to determine the order for sulfur removal which was 1.5. The sulfur order is consistent with that reported by Riley ^[212] for hydrodesulfurization of the Safaniya atmospheric residuum. The greater than first order dependence for hydrosulfurization has previously been explained by considering the overall kinetics as a sum of competing, parallel first order reactions ^[212-214].

The activation energy for nitrogen removal was obtained from the slope of the Arrhenius plot for denitrogenation (Figure 96). There appeared to be a distinct break in the curve and two values for the apparent activation energy. At low temperatures where less refractory nitrogen compounds reacted the activation energy was 75.3 kJ/mol (18 kcal/mol). At high temperatures where the more refractory nitrogen compounds were expected to react the activation energy was 184.1 kJ/mol (44 kcal/mol). It was presumed that the change in the apparent activation energy was also related to the complex nature of the collection of nitrogen compounds in the bitumen-derived liquid. The Arrhenius plot for hydrodesulfurization is presented in Figure 97. The activation energy calculated from the slope was 92.1 kJ/mol (22 kcal/mol) and was constant throughout the range of temperatures studied.

The effect of reactor pressure on denitrogenation and desulfurization was examined; however, the scatter in the data when

Figure 96. Arrhenius Plot for Denitrogenation of Bitumen-Derived Liquid

Figure 97. Arrhenius Plot for Desulfurization of Bitumen-Derived Liquid

$\ln(k \cdot p_{\text{Total}}^n)$ was plotted versus $\ln(p_{\text{Total}})$ was quite large, thus, it was not possible to organize the data in a satisfactory manner. The effect of hydrogen consumption on nitrogen conversion for the bitumen-derived liquid at fixed space velocity and pressure as the temperature varied from 619 to 681 K is presented in Figure 98. The data reported by Sullivan and Stangeland^[210] for hydrodenitrogenation of shale oil is also presented in Figure 98 for comparison. The hydrogen consumption during hydrodenitrogenation of the bitumen-derived liquid was about half the hydrogen consumption for hydrodenitrogenation of shale oil. This difference was presumed to be related to the lower nitrogen content of the bitumen-derived liquid, 1.12 wt%, which was half the concentration of shale oil; however, the slopes of the plots were quite similar.

Derivation of the Integrated form of the Rate Equations

The rates of hydrodenitrogenation and/or hydrodesulfurization reactions were given by equations of the form

$$r_i = k_i C_H^n C_i^m \quad (64)$$

where k_i is the intrinsic rate constant for denitrogenation or desulfurization and C_i the concentration of the nitrogen or sulfur heteroatomic species. If the H_2 -to-hydrocarbon ratio was sufficiently high and the reaction temperature was sufficiently low then C_H was assumed to be constant such that

$$k_{app,i} = k_i C_H^n \quad (65)$$

Thus, the rate expression reduced to a pseudo nth order equation in

Figure 98. Denitrogenation vs. H₂ Consumption for Shale Oil and bitumen-Derived Liquid

C_1 ; that is

$$r_1 = k_{APP,1} C_1^2 \quad (66)$$

If we restrict consideration to denitrogenation then the equation was given by

$$r_N = k_{APP,N} C_N^2 \quad (67)$$

If the rate of denitrogenation is expressed as

$$r_N = -\frac{dC_N}{d\tau} \quad (68)$$

where τ is the liquid phase residence time (1/LHSV) and the concentration, C_N , is expressed as

$$C_N = C_{N,0} (1 - X_N) \quad (69)$$

Upon substitution into the rate expression we obtain the following equation

$$C_{N,0} \frac{d(1 - X_N)}{d\tau} = k_{APP,N} C_{N,0}^2 (1 - X_N)^2 \quad (70)$$

Upon rearrangement the following equation was obtained

$$\int \frac{dX_N}{(1 - X_N)^2} = \int k_{APP,N} C_{N,0}^2 d\tau \quad (71)$$

The integrated kinetic equation was

$$k_{APP,N} \tau = \frac{1}{C_{H,O}^{n-1}} \frac{1}{n-1} [(1-x_H)^{(1-n)} - 1] \quad (72)$$

SUMMARY AND CONCLUSIONS

The pyrolysis of bitumen-impregnated sandstone produces three primary product streams: C_1 - C_4 hydrocarbon gases, a C_5^+ total liquid product, and a carbonaceous residue on the spent sand. The bitumen-derived hydrocarbon liquid was significantly upgraded relative to the native bitumen: it had a higher API gravity, lower Conradson carbon residue, asphaltene content, pour point and viscosity and a reduced distillation endpoint relative to the native bitumen. The elemental composition was little different from that of the native bitumen except for the hydrogen content which was lower. Thus, integration of the bitumen-derived liquid into a refinery feedstock slate would require that it be hydrotreated to reduce the nitrogen and sulfur heteroatom concentrations and to raise the atomic hydrogen-to-carbon ratio.

The bitumen-derived liquid produced in a 4-inch diameter fluidized-bed reactor from the Whiterocks tar sand deposit has been hydrotreated in a fixed-bed reactor to determine the extent of upgrading as a function of process operating variables. The process variables investigated included total reactor pressure (11.0-17.2 MPa (1600-2500 psig)); reactor temperature (617-680 K (650-765°F)) and liquid hourly space velocity (0.18-0.77 LHSV). The hydrogen/oil ratio was fixed in all experiments at 890 m^3/m^3 (5000 SCF H_2 /bbl). A sulfided Ni-Mo on alumina hydrodenitrogenation catalyst was used in these studies.

The extent of denitrogenation and desulfurization of the bitumen-derived liquid was used to monitor catalyst activity as a function of process operating variables and to estimate the extent of catalyst deactivation as a function of time on-stream. The apparent kinetics for the nitrogen and sulfur removal reactions were determined. Product distribution and yield data were also obtained.

The processing sequence tar sand pyrolysis followed by hydrotreating appeared to be a viable concept by which the Whiterocks tar sand resource could be exploited. The 477-617 K (400-650°F) boiling range fraction of the hydrotreated bitumen-derived liquid would be an excellent candidate for high-density aviation turbine fuels. Catalyst activity during the hydrotreating of Whiterocks bitumen-derived liquid remained stable during 800 hours of operation and should remain reasonably stable for longer periods. The catalyst deactivation rate was 0.14°C/day (0.25°F/day). The reactivity of the bitumen-derived liquid was similar to the reactivity of shale oil.

The apparent reaction orders were 1.55 and 1.5 for nitrogen and sulfur removal, respectively. These fractional orders suggested the occurrence of many parallel first order reactions, each with a different first order rate constant. The activation energy for denitrogenation was 75.3 kJ/mol (18 kcal/mol) at lower conversions and temperatures where less refractory nitrogen-contained species reacted. At higher temperatures and conversions where the more refractory species reacted the activation energy was

184.1 kJ/mol (44 kcal/mol). The activation energy for desulfurization was 92.1 kJ/mol (22 kcal/mol) over the range of temperatures studied.

FUTURE ACTIVITIES

Conduct hydrotreating process variable study with the Whiterock bitumen over a commercial HDN catalyst.

EBULLIATED BED HYDROTREATING AND HYDROCRACKING

Principal Investigator
Graduate Student

F.V. Hanson
D.A. Deshpande

As discussed in the previous project report, one of the objectives of the upgrading studies is to set-up a laboratory system to study the hydrotreating and hydrocracking process applied to bitumens and bitumen-derived liquids. The concept of the laboratory system will be similar to the H-oil process used by City Services, Inc. to upgrade the bitumen obtained from Athabasca oil sands. Since the three-phase ebulliated reactor is the most important component of that system, the initial efforts were concentrated on studying the hydrodynamics of the ebulliated bed and developing a scale-down procedure for the reactor. The initial studies were carried out in the following stages:

Hydrodynamic studies of three-phase ebulliated beds

A detailed literature survey on the hydrodynamics of three-phase ebulliated beds was conducted with a focus on aspects such as phase holdups, bed expansion, particle disengaging height, bubble rise velocity and bubble formation at the grid. Amongst the various mathematical models available in the literature for the calculation of phase holdups, the generalized wake model proposed by Bhatia and Epstein ^[215] was selected because of its wide applicability. The model calculates the phase holdups in the bed from the values of basic system parameters and values for the bubble rise velocity u_{br} , the ratio of the solid holdup in the bubble wake to the solid holdup in the liquid-solid region and the ratio of the wake volume

to bubble volume, k . After a detailed study, methods were selected to calculate U_{br} , n and k . A computer program was then developed which calculates the phase holdup and the particle disengaging height for the bed. The stagewise partition model proposed by El-Temtany and Epstein^[216] was used to calculate the particle disengaging height.

Need and philosophy for scale down

Initial calculations using the computer program indicated that the length of the laboratory reactor, using a 1/8" pelleted catalyst, and with a bed expansion of 80% and a weight hourly space velocity of 1.0 would be nearly 70 feet. Since such a long reactor is impractical for laboratory-scale studies, it was imperative to develop a procedure to reduce the length of the reactor subject to the following constraints.

- The same space velocity in both the laboratory and the commercial reactors.
- The same gas, liquid and solid holdups in both the laboratory and commercial reactors.
- Reduce reactor length to a reasonable scale.

The procedure used to achieve the above objectives was

- Reduce particle size
- Reduce ebullition liquid velocity
- Reduce catalyst charge

The change in particle size and ebullition velocity has to be achieved in such a way that the constraints mentioned above are satisfied.

Similarity criteria and practical scale-down procedure

Through extensive similitude studies, involving fourteen parameters, similarity criteria that would satisfy the constraints were identified. The criteria required the equality of six dimensionless numbers. The criteria were validated by the computer program mentioned earlier. It was found that it was impractical to establish all the parameters in the set of dimensionless numbers at the desired values. Therefore, a practice scale-down procedure to achieve similarity by varying a minimum number of parameters, such as liquid and gas velocities and particle size was developed. This resulted in a set of two conditions which when satisfied yielded practically equal holdup in the two reactors.

Predictions of bubble rise velocity

One of the conditions identified to equalize the phase holdups in the commercial and the laboratory reactors, was that the bubble rise velocity in both the reactors should be the same. Therefore, a reliable and widely applicable method for calculating bubble rise velocity should be available. A literature search indicated that the existing methods were either highly approximate or had limited application. The development of a method for calculating bubble rise velocity was therefore undertaken using two approaches.

- Single bubble
- Effective bubble rise velocity

Each method has its individual advantages and disadvantages which are briefly mentioned below.

Single Bubble Approach:

- Potential for incorporating bed pressure effects
- No consideration for back mixing and phase interactions
- Estimate of bubble size required.

Effective bubble rise velocity approach:

- Considers back mixing and phase interaction
- Includes effect of
 - bed pressure
 - liquid velocity
 - gas velocity
 - surface tension
 - particle diameter

Single bubble approach

It has been observed that in high pressure fluidized and/or ebulliated beds, the bubble flow is in a discrete bubble regime and the bubble coalescence is minimal. This indicates that the size of the bubble formed at the grid orifice may remain almost unchanged as the bubble rises through the bed. A method of predicting the size of the bubble at the orifice could therefore be useful for predicting the bubble rise velocity.

As a first approximation, a new model for the prediction of volumes of bubbles generated from a single orifice in a two phase gas-liquid system was developed based on a rigorous bubble closure mechanism. The interactions between the primary bubble and subsequent bubbles formed at the orifice were incorporated into the model to account for bubble formation at high gas flow rates. The

distance travelled by the bubble from the orifice before it detaches was also calculated by the model. The model was validated, through an elaborate computer program, by comparison with the available experimental data and it was found that the model represents an improvement over previous models.

The advantages of the proposed model over the existing models are as follows:

- No assumption for detachment distances of the bubble from the orifice
- Applicable for both viscous and inviscid liquids
- Flexibility for incorporating high pressure effect of the bed

Effective bubble rise velocity approach

The equations in the generalized wake model were manipulated to give the best value of bubble rise velocity, which when substituted back in the model, yielded values of phase holdups close to the experimentally observed values. These values of the effective rise velocity were, fitted in correlations with the liquid superficial velocity, the gas superficial velocity, the liquid viscosity, the surface tension and the solid particle size as the variables.

The forms of the correlations were in agreement with the previously reported hydrodynamic behavior of three-phase ebulliated beds. This agreement included bubble flow behavior, flow regimes and their transition, flow transition liquid velocity, effects of solid wettability, effects of apparent bed viscosity, effects of

solid particles and effects of surface tension. This helped to gain a further understanding of the hydrodynamics phenomena involved in three phase ebulliated beds.

The three-phase systems considered by the correlations consist of a wide variety of materials, such as glass beads or cylindrical catalyst pellets as the solid phases, water or kerosene as the liquid phases and air, nitrogen and helium as the gas phases. The flow regimes were of industrial potential. Solid particles ranged in size from 1.0 - 5.0 mm. The extensive experimental data generated by Armstrong ^[217] and Vasalos ^[218] was used.

The new correlations are categorized as per

- the three-phase system (type of solid, liquid and gas)
- the solid particle size
- the superficial liquid velocity
- the superficial gas velocity
- solid wettability

Based on the above information following an overall scale-down procedure was proposed:

- Calculate bubble rise velocity for commercial reactor
- Calculate phase holdups
- Assume solid particle size for the laboratory reactor
- Use the practical scale-down procedure to determine liquid and gas superficial velocity for the laboratory reactor.
- Calculate particle disengaging height for the laboratory reactor

- For a known space velocity, calculate the stagnant bed height
- Calculate the laboratory reactor length
- If the reactor length is excessive, reduce the diameter of the solid particles and repeat the above steps (all the time ensuring that the solid disengaging height is not excessive).

SUMMARY AND CONCLUSIONS

The conceptual methodology has been developed by which commercial scale ebulliated bed reactors can be scaled down to laboratory size for process development studies.

FUTURE ACTIVITIES

The laboratory scale reactor will be designed based on a scale-down procedure developed at the University of Utah.

SUPERCRITICAL FLUID EXTRACTION

Principal Investigator	F.V. Hanson
Co-Principal Investigator	M.D. Deo
Graduate Student	J. Hwang

INTRODUCTION

Supercritical fluid extraction (SFE) has found application in solvent extraction, separation processes and in the upgrading of petroleum feedstocks^[219-221]. The SFE concept is also of interest in enhanced oil recovery processes in oil reservoirs since the performance of these processes depends on the extraction of oil components by a solvent that is typically in a supercritical state. There are several potential SFE applications related to oil sands production, bitumen upgrading and bitumen analysis. 1) Upgrading bitumens and bitumen-derived liquids by rejecting asphaltenes using techniques similar to the ROSE^[219-221] process. 2) Recovering bitumen using SFE in mining - surface recovery schemes. 3) Using dense gases as recovery agents and/or as additives in the production of heavy oils by in-situ recovery methods^[222]. 4) Using SFE as an analytical tool to develop an understanding of the nature and thermodynamic behavior of oil sand bitumen. Two phases, the lighter extract phase and the heavier oleic phase usually result when the feedstock is contacted with the solvent. In a continuous SFE process, the extracted phase is removed continuously as fresh solvent is introduced into the system. Thus, the nature of the solute and the compositions and phase properties of all the relevant phases change continuously. The process operates at thermodynamic equilibrium in a well-mixed system and as the phase

compositions of the extracted phases are analyzed, the system provides a vast amount of information related to SFE phenomena.

In this work, extractions of three different feedstocks; a paraffinic crude oil, a bitumen-derived liquid produced in a fluidized-bed pyrolysis reactor from the Whiterocks oil sands and the native Whiterocks bitumen, with two typical SFE solvents, carbon dioxide (CO_2) and propane (C_3H_8), were conducted with the intention of studying the extraction process as a function of the density of the feedstock and its chemical makeup.

EXPERIMENTAL

The SFE system was custom-built for the University of Utah by Autoclave Engineers, Inc. A schematic of the apparatus is presented in Figure 99. Central to the system was a temperature controlled extractor with a capacity of 300 cc and rated to a pressure of 37.2 MPa at 616 K. The extractor was equipped with a magnetic-drive packerless stirring device. Solvent (CO_2 or propane) was charged into the extractor and the system was brought to the desired pressure using a high-pressure liquid pump. Pressure control was achieved by incorporating a back pressure regulator in a loop with the pump. The pump-head was cooled by a circulating cooling bath to ensure that the solvent was maintained in the liquid state at the pump-head.

Once the initial equilibrium state was attained in the extractor, solvent was continuously pumped through the extractor. Commercial grade propane which contained about 9% propane and 4% C_1 , C_2 and C_4 hydrocarbon gases was used in this work. A heated

Figure 99. Schematic of the supercritical fluid extraction system.

metering valve was used to displace the extracted phase from the extractor to the separator which was at the room pressure. The solvent separated from the extracted phase at the separator was vented through a flow totalizer which measured the cumulative volume of solvent. The oil in the separator was collected, weighed and analyzed.

In all the experiments, a weighed amount of oil was charged to the extractor and the extraction process was begun. After about 25 liters of solvent (at room temperature) had flowed through the totalizer, the oil in the separator was collected and weighed. When the amounts of oil extracted were less than 5% relative to the initial amount extracted, the extraction was stopped, the extractor was depressurized, and the residue was weighed and analyzed. In each extraction sequence, seven to eight extract samples were collected. Each sample corresponded to an extraction window of 25 liters of solvent vented through the totalizer or about to 20 minutes of extraction time.

Feedstock Characterization

Properties of the feedstocks used in this study are listed in Table 55. The hexadecane used was 99% pure. The bitumen-derived liquid was produced from the Whiterocks oil sands in a fluidized-bed pyrolysis reactor. The reactor temperature ranged from 773 to 813 K at a retention time of 17.2 minutes during the production run. The bitumen was toluene-extracted from the Whiterocks oil sands. The API gravities in Table 55 indicate that the bitumen-derived liquid is heavier than the crude oil and that

TABLE 55

Selected Properties of the Feedstocks

	Crude Oil	Bitumen-derived Liquid	Bitumen
Specific Gravity (288 K)	0.81	0.95	0.98
Conradson Carbon (wt%)	0.02	3.2	9.5
Pour Point, K	293	277	327
Asphaltenes, Wt%	0.1	3.0	5.9
Maltenes, Wt%	99.9	97.0	94.1
Elemental Analysis			
C, Wt%	86.1	87.1	87.0
H, Wt%	13.7	11.4	11.3
N, Wt%	0.2	0.2	1.4
S, Wt%	0.0	0.3	0.4
H/C Atomic Ratio	1.9	1.6	1.6
Simulated Distillation			
Volatility, Wt%	100	76.9	32.5
IBP, K	309	417	520
IBP-477 K, Wt%	35.5	4.5	0
478-616 K, Wt%	37.6	24.4	5.6
617-811 K, Wt%	26.9	48.0	26.9
>811 K, wt%	0	23.1	67.5

Notes:

Asphaltenes are defined as pentane insolubles

C,H,N and S analyses are normalized to 100%

the bitumen is the heaviest of the feedstocks. The carbon number distributions of the three materials presented in Figure 100, give an indication of the size-range of the compounds in the three materials. Gas chromatographic - mass spectrometric analyses conducted as part of the present and previous investigations^[41,223] indicated that the crude oil was predominantly paraffinic, that the bitumen-derived liquid contained olefins and significant amounts of aromatics and that the native bitumen was mainly comprised of naphthenes and naphtheno-aromatics with long alkyl side chains. Thus, the feed materials used in this study were diverse with respect to both the size and type of compounds present in them.

RESULTS AND DISCUSSION

Mass recoveries in excess of 95% of the material initially charged to the extractor were obtained in all experiments. The losses were attributed to material trapped in dead spaces. Two sets of experiments were performed at identical conditions to assess the experimental reproducibility and to confirm that the experiments were reproducible. The results of the reproducibility tests for the four different materials used in this work are presented in Figure 101. It can be observed from this figure that the experiments with all the feedstocks were reproducible.

Initial experiments performed with hexadecane and CO₂ demonstrated that the system operated at thermodynamic equilibrium. Results of hexadecane experiments with CO₂ at a temperature of 311 K and pressures of 10.3 Mpa and 17.2 Mpa are presented in Figure

Figure 100. Carbon number distributions for the crude oil, the bitumen-derived liquid and the bitumen determined by simulated distillation (SIMDIS).

Figure 101. Experimental reproducibility for all the feedstocks used in the study.

Figure 102. Results of hexadecane extractions with CO₂; the straight-line extraction yields demonstrate thermodynamic equilibrium.

102. It is expected that the phase compositions for the binary CO₂-hexadecane system remain invariant as a function of the system overall composition. This fact is clearly demonstrated by the straight-line extraction yields at both 10.3 Mpa and 17.2 MPa. The phase compositions of the extracted phases are compared to those obtained by Larson et al.^[224] and to those predicted by the Peng-Robinson equation of state^[225] in Table 56. The close agreement between all the values demonstrates that the system is capable of producing reliable thermodynamic information.

Extraction of the Paraffinic Crude Oil with CO₂

Extractions were performed at a series of temperatures and pressures. The initial oil charge to the extractor was 80 g in all the experiments. It is well-known that the extraction of complex hydrocarbon mixtures such as crude oil by CO₂ is governed by the density of pure CO₂ at extraction conditions^[226,227]. In fact, it has been observed^[228] that to a first approximation, the solvent power of a supercritical fluid can be related to the solvent density in the critical region. The reduced densities of CO₂ at the experimental conditions are listed in Table 57. Analysis of the crude oil extraction data revealed that at a constant temperature of 311 K ($T_r = 1.02$), the extraction yields increased as the pressure was increased from 7.6 MPa to 17.2 MPa. The pure CO₂ reduced density increased from 0.67 to 2.19 corresponding to the pressure increase. Thus, in the vicinity of the critical temperature of CO₂, the extraction yields increased when the CO₂ density increased. This observation is consistent with the earlier

Table 56

Extract Phase Compositions for
the CO₂-Hexadecane System

	Hexadecane, Mole%		
	Literature	SFE	PR EOS
10.3 MPa/311 K	1.1	1.2	1.3
17.2 MPa/311 K	4.1	4.4	4.2

Notes:

Literature values were obtained from Larson et al.²²⁴ in this paper, the phase compositions were determined at 10.2 MPa and 305 K and 17.1 MPa and 305 K, respectively.

Table 57

Reduced Density of CO₂ at Experimental Conditions

Temperature T_r	297 K	304 K	311 K	339 K	366 K
	0.98	1.00	1.02	1.11	1.20
Pressure					
5.5 MPa	--	--	0.36	--	--
7.6 MPa	--	--	0.68	--	--
10.3 MPa	2.22	2.03	1.77	0.75	0.56
17.2 MPa	--	--	2.19	--	1.11
24.0 MPa	--	--	2.35	--	1.54
30.9 MPa	--	--	--	--	1.82

Notes:

Reduced density was calculated based on a density of 0.37 g/cm₃ at the critical point of carbon dioxide ($P_c = 7.38$ MPa; $T_c = 304$ K).

All the densities were obtained by a two-dimensional interpolation of the data from Vargaftik²³¹.

observations for continuous crude oil extractions with CO_2 ^[226,227].

However, extraction yields as a function of temperature for a constant pressure (10.3 MPa) were practically identical for the three temperatures (297, 304 and 311 K; $T_r = 0.98, 1.0$ and 1.02) in the vicinity of the critical temperature of CO_2 , while the yield decreased significantly at a higher temperature (339 K; $T_r = 1.11$). Examination of Table 57 reveals that the reduced density of pure CO_2 decreases from 2.22 at $T_r = 0.98$ to 1.77 at $T_r = 1.02$. The enhanced solvating power of the solvent just above its critical temperature appears to have compensated for this decrease in pure solvent density. Thus, density of the pure solvent is not the only governing parameter in these extractions. This fact is clearly demonstrated in Figure 103, where the extractions at 297 K and 10.3 MPa and 311 K and 17.2 MPa are compared. It should be observed that at these two sets of conditions, the reduced densities of pure CO_2 are 2.22 and 2.19 respectively. It is seen from Figure 103 that at the lower reduced density, the extraction yield is higher. The decrease in yield at the higher temperature (339 K) is due to the phase behavior transition from liquid-liquid (L-L)-like system to a liquid-vapor (L-V)-like system. It is known that the L-L system exhibits considerably greater oil extraction capability than the L-V system^[226,227]. The behavior is also consistent with a marked drop in the reduced density of CO_2 at the higher temperature (0.75 at 10.3 MPa and 339 K). This significant reduction in solubility of oil in the solvent phase is also the technical basis for solvent recovery in the ROSE process^[219-221,228].

Figure 103. Demonstration of enhanced extraction in the vicinity of the solvent critical temperature for the CO₂ extractions of crude oil; higher yields are observed for the lower reduced CO₂ density.

Compositional information for the extract phases was obtained using simulated distillation (SIMDIS). The earlier extracts contained lighter components and the later extracts contained progressively heavier compounds in all the experiments. Comparison of the carbon number distributions of the middle extracts at three different pressures and constant temperature (Figure 104) illustrates extraction of heavier hydrocarbons at higher pressure. These observations are consistent with continuous extraction crude oil - CO₂ experiments reported by Orr, et al.^[227]. Examination of the carbon number distributions of the middle extracts obtained at three temperatures close to the CO₂ critical temperature showed practically no discrimination between these fractions. This compositional nondiscrimination despite a considerable density change is consistent with the observations related to extraction yields. Despite a lower reduced density, the extracts at 311 K, 17.2 MPa contained relatively heavier compounds compared to the extracts at 297 K, 10.3 MPa. Thus, the observation that the reduced density is not the only governing parameter appears to be valid when considering the quality of the extracted material as well. The middle extract at the higher temperature, 339 K, contained considerably more light components due to the L-L to L-V transition.

Extraction of the Bitumen-Derived Liquid

In all the experiments, 94 g of the bitumen-derived liquid was initially charged to the extractor. The extraction yields for propane were considerably higher than for CO₂ due to the greater

Figure 104. Carbon number distributions of the middle extracts for the CO_2 extractions of the crude oil showing the extraction of heavier compounds at higher pressures.

affinity of propane for the hydrocarbon components of the feedstock. The cumulative yields for CO_2 increased linearly in a manner analogous to the extraction of a pure hydrocarbon component (such as hexadecane) exhibiting L-L phase behavior with CO_2 .

Extractions of the bitumen-derived liquid with propane were conducted at a temperature of 311 K and three different pressures (5.5 MPa, 10.3 MPa and 17.2 MPa) and at a pressure of 10.3 MPa and three different temperatures (311 K, 380 K and 408 K). The critical temperature for propane is 369.7 K and its critical pressure is 4.25 MPa. In general, as the pressure was increased at constant temperature, the extraction yields increased. For the propane extractions, an explanation for the extraction trends was attempted based on the density of pure propane at the extraction conditions (Table 58). The pure propane reduced densities in Table 58 were calculated using the Peng-Robinson equation of state. The increase in extraction yields as a function of pressure can be related to a corresponding increase in reduced densities. The enhanced solvating power of the solvent near the pure solvent critical temperature was evident when the extraction yields with respect to temperature were evaluated. It was observed that the highest yields were obtained in the vicinity of the propane critical temperature. The yields at 10.3 MPa and two different temperatures (311 K and 380 K) are presented in Figure 105. At this constant pressure, the propane reduced density decreases from 2.92 at 311 K ($T_r = 0.84$) to 2.11 at 380 K ($T_r = 1.03$). Despite this decrease, the extraction yield at 380 K is higher than at 311

Table 58

Reduced Density of Propane at Experimental Conditions

Temperature	311 K	339 K	380 K	408 K	422 K
T_r	0.84	0.92	1.03	1.10	1.14
Pressure					
5.5 MPa	2.81	--	1.43	--	--
10.3 MPa	2.92	2.64	2.11	1.69	1.48
17.2 MPa	3.04	--	2.44	--	--

Notes:

Reduced density was calculated based on a density of 0.18 g/cm₃ at the critical point of propane (P_c = 4.25 MPa; T_c = 370 K).

All the densities were calculated using the Peng-Robinson equation of state.^[225]

Figure 105. Demonstration of enhanced extraction in the vicinity of the solvent critical temperature for the propane extractions of bitumen-derived liquid; higher yields are observed for the lower reduced propane density.

K demonstrating the enhanced oil solubility in the propane phase near the pure-propane critical temperature. This again leads to the conclusion that density is not the only parameter that controls the extractions of complex hydrocarbon mixtures by dense gases.

Examination of the compositional variation of the extracts as functions of time, temperature and pressure for the extractions of bitumen-derived liquid with both CO₂ and propane revealed essentially no compositional variation relative to any of these variables. An example of this trend for the propane extracts is presented in Figure 106. There is essentially no preferential extraction of the bitumen-derived liquid unlike that which was observed for the crude oil. The bitumen-derived liquid behaves effectively like a single component in these extractions, except that the composition of the extracted phases is different from the original composition of the bitumen-derived liquid. The nondiscriminatory extractions of the bitumen-derived liquid by propane and by CO₂ clearly demonstrate that these compositional trends are features of the chemical nature of the bitumen-derived liquid. This behavior can be attributed to the presence of olefins and aromatics which were formed during the pyrolysis process. The bitumen contained naphthenic and naphtheno-aromatic compounds with long alkyl side chains. The cleavage of these side chains could have led to the formation of similar-sized compounds whose cosolubilizing effect caused the bitumen-derived liquid to act as an integrated unit. Despite the lack of compositional differences in the extracts, the cumulative extraction curves for the

Figure 106. Carbon number distributions of the middle extracts for the propane extractions of the bitumen-derived liquid showing essentially nondiscriminatory extraction.

bitumen-derived liquid were not linear. This was attributed to changes in extract phase densities as a function of time and extraction conditions. The fact that heavier compounds were found in the propane extracts was consistent with the greater extraction yields with propane than with CO₂.

Extraction of the Native Bitumen

For CO₂ extractions, 99 g of native bitumen was charged to the extractor. Extractions were performed at 367 K and pressures of 10.3 MPa, 17.2 MPa, 24.0 MPa and 30.9 MPa. At the highest extraction pressure (30.9 MPa), a total of 2 wt% of the material was extracted. At the other three pressures, practically no oil was extracted.

For the propane experiments, 50 g of the native bitumen was initially charged to the extractor. The absolute yields of bitumen extractions, compared to the propane extractions of the bitumen-derived liquid, were lower; however, the extraction trends were similar. The extraction yields increased as a function of pressure and the extraction appeared most effective when the extraction temperature was in the vicinity of the critical temperature of propane. The increased solvency of the native bitumen in the vicinity of the propane critical point is demonstrated in Figure 107, where the yields at 10.3 MPa and 339 K (propane reduced density = 2.64) are compared to the yields at 17.2 MPa and 380 K (propane reduced density = 2.44). The yields at 380 K are higher despite a lower propane reduced density.

The compositional variations as a function of time were

Figure 107. Demonstration of enhanced extraction in the vicinity of the solvent critical temperature for the propane extractions of bitumen; higher yields are observed for the lower reduced propane density.

evaluated by reviewing the carbon number distributions of the first, middle and the last extracts for the experiments at various temperatures and pressures. The latter extracts contained heavier compounds than the earlier ones. The carbon number distributions as a function of pressure (Figure 108) indicate that heavier compounds are extracted at higher pressure. No significant compositional changes were observed as a function of temperature. This trend was similar to the CO₂ - crude oil extractions and highlighted the unusual, nondiscriminatory extractions of the bitumen-derived liquid.

Modeling of the Extraction Process

Equations of state (EOS) have been a popular choice for the representation of the phase behavior of complex hydrocarbon mixtures. Preliminary phase behavior calculations were performed using the Peng-Robinson EOS^[225] and the component lumping approach.

The 35-component crude oil system determined by SIMDIS was lumped into six pseudocomponents using Whitson's^[229] lumping procedure. Four fractions of the bitumen-derived liquid generated by the SIMDIS analysis were adopted directly as pseudocomponents in the phase behavior calculations. Approximately 35% of the native bitumen boils below 811 K. Based on the boiling point curve up to 811 K, an extrapolated curve extending to 1100 K was generated. This extrapolated curve was divided into five pseudocomponents with each pseudocomponent corresponding to 20 wt% of the bitumen. The pseudocomponent representations of each of the three materials are presented in Table 59. Once the pseudocomponents were assigned,

Figure 108. Carbon number distributions of the middle extracts for the propane extractions of the bitumen showing the extraction of heavier compounds at higher pressures.

Table 59

Pseudocomponent Representation for the Feedstocks

	Boiling Point Range (K)	Wt%
Crude Oil		
Pseudocomponent 1	309-447	24.3
Pseudocomponent 2	448-468	5.0
Pseudocomponent 3	469-489	4.6
Pseudocomponent 4	490-508	4.1
Pseudocomponent 5	509-575	20.6
Pseudocomponent 6	>575	41.4
Bitumen-derived-Liquid		
Pseudocomponent 1	417-477	4.5
Pseudocomponent 2	478-616	24.4
Pseudocomponent 3	617-811	48.0
Pseudocomponent 4	>811	23.1
Bitumen		
Pseudocomponent 1	520-689	20.0
Pseudocomponent 2	690-786	20.0
Pseudocomponent 3	787-857	20.0
Pseudocomponent 4	858-931	20.0
Pseudocomponent 5	>931	20.0

the pseudocritical properties of each pseudocomponent were computed. Mean boiling point and molecular weight of each of the components were used for the estimation of critical properties for the crude oil. A Watson characterization factor of 11 was used for all the fractions to estimate pseudocomponent specific gravity for the bitumen-derived liquid and the bitumen. Kesler-Lee^[230] correlations were used to calculate the critical properties in all cases. For the CO₂ system, the interaction parameters between CO₂ and the hydrocarbon components that decreased with carbon number were used. In the propane case, interaction parameters between propane and the pseudocomponents of the feedstock that increased with carbon number were used. The choice of these interaction parameters was arbitrary and they were adjusted until the most reasonable agreement was found between calculated and experimental results.

The initial extractor charge was used to calculate the overall feed compositions and a flash calculation was performed at the system conditions. It was assumed that for the first extraction window, the extract phase composition was given by this initial flash. The amount of solvent exiting the system and the amount of oil extracted during the first extraction window were determined experimentally. These amounts, along with the composition of the extracted oil, determined by SIMDIS, were used to reconstruct the extract phase composition inside the extractor at the given extraction conditions. This provided the comparison between the calculated and experimental extract phase compositions. The phase

density of the extract phase was calculated by the Peng-Robinson EOS. The amount of material withdrawn during the first extraction window and the density of the extract phase were used to compute the volume of the extract phase withdrawn during the first stage. It was assumed that this volume was replaced by fresh solvent at the system conditions for the next window. A material balance on the solvent and the oil components yielded the overall mixture composition for the flash calculation for the next extraction stage. This procedure was repeated for all the extraction stages.

A comparison of the experimental and calculated extract phase compositions for the crude oil - CO₂ extraction at 10.3 MPa and 311 K is presented in Table 60. The agreement between the calculated and experimental results is reasonable considering the uncertainties of modeling such a complex process. Phase behavior calculations for the propane - bitumen-derived liquid system at 10.3 MPa and 380 K are compared to the experimental values in Table 61. The EOS model predicts a complete depletion of lighter components from the bitumen-derived liquid by the time of the last extraction. However, experimentally, it was observed that heavier components are extracted with equal efficiency from the bitumen-derived liquid. The current phase behavior models do not have the sophistication of predicting the unusual extraction behavior of the bitumen-derived liquid. Examination of the experimental and calculated values for the native bitumen - propane extractions at 10.3 MPa and 380 K (Table 62) indicates reasonable

Table 60

Comparison of Experiments and PR EOS Calculations:
Crude Oil-CO₂ System at 10.3 MPa and 311 K

(Unit) Mole %	Extract Phase First Window		Extract Phase Middle Window		Extract Phase Last Window		Residual Phase After Extraction	
	Expt.	PR EOS	Expt.	PR EOS	Expt.	PR EOS	Expt.	PR EOS
CO ₂	95.7	96.1	97.6	97.2	98.8	97.7	--	--
F ₁ Oil	1.9	2.4	0.8	1.5	0.4	1.1	33.3	27.8
F ₂ Oil	0.3	0.3	0.2	0.2	0.1	0.2	5.6	5.8
F ₃ Oil	0.3	0.2	0.2	0.2	0.1	0.1	4.7	5.1
F ₄ Oil	0.2	0.2	0.2	0.1	0.1	0.1	4.3	4.6
F ₅ Oil	0.9	0.5	0.6	0.4	0.4	0.4	17.5	22.2
F ₆ Oil	0.7	0.4	0.4	0.4	0.2	0.4	34.7	34.6

Notes:

The oil fractions are the pseudocomponents used to represent the crude oil.

Table 61

**Comparison of Experiments and PR EOS Calculations:
Bitumen-Derived-Liquid - Propane System 10.3 MPa and 380 K**

(Unit) (Mole%)	Initial Overall Composition	Extract Phase First Window		Extract Phase Middle Window		Extract Phase Last Window	
		Expt.	PR EOS	Expt.	PR EOS	Expt.	PR EOS
Propane	82.7	90.2	94.3	95.1	99.6	97.7	99.7
F ₁ Oil	3.3	1.1	2.5	0.5	0.0	0.2	0.0
F ₂ Oil	5.2	3.7	2.4	1.9	0.0	0.9	0.0
F ₃ Oil	7.1	4.7	0.7	2.4	0.3	1.1	0.2
F ₄ Oil	1.7	0.3	0.1	0.1	0.1	0.1	0.1

Notes:

The oil fractions are the pseudocomponents used to represent the bitumen-derived liquid.

Table 62

**Comparison of Experiments and PR EOS Calculations:
Bitumen-Propane System 10.3 MPa and 380 K**

(Unit) (Mole%)	Initial Overall Composition	Extract Phase First Window		Extract Phase Middle Window		Extract Phase Last Window	
		Expt.	PR EOS	Expt.	PR EOS	Expt.	PR EOS
Propane	95.0	98.9	98.4	99.2	99.3	99.6	99.7
F ₁ Oil	1.6	0.6	1.2	0.4	0.4	0.1	0.1
F ₂ Oil	1.1	0.4	0.3	0.3	0.2	0.2	0.1
F ₃ Oil	0.9	0.1	0.1	0.1	0.1	0.1	0.1
F ₄ Oil	0.8	0.0	0.0	0.0	0.0	0.0	0.0
F ₅ Oil	0.6	0.0	0.0	0.0	0.0	0.0	0.0

Notes:

The oil fractions are the pseudocomponents used to represent the bitumen.

agreement between the two values. Thus, the EOS models with component-lumping perform reasonably well for typical extraction predictions; however, the models breakdown when dealing with unusual behavior like that of the bitumen-derived liquid.

SUMMARY AND CONCLUSIONS

Supercritical fluid extraction of complex hydrocarbon mixtures is important in separation processes, petroleum upgrading and enhanced oil recovery. In this work, extractions of a crude oil, a bitumen-derived liquid and bitumen were conducted at several temperatures and pressures with carbon dioxide and propane in order to assess the effect of the size and type of compounds that comprise the feedstocks on the extraction process.

It was observed that the pure solvent density at the extraction conditions was not the only variable governing extraction and that the proximity of the extraction conditions to the pure solvent critical temperature affected the extraction yields and the compositions of the extract phases. In fact, higher oil yields were obtained at lower solvent reduced densities when the extraction temperatures were in the vicinity of the pure solvent critical temperature.

In the crude oil and native bitumen extractions, it was observed that as the extraction time and/or the extraction pressure increased, heavier compounds were found in the extract phases. This preferential extraction was not observed with the bitumen-derived liquid. The nondiscriminatory extraction behavior of the bitumen-derived liquid was attributed to its thermal history

and to the presence of olefins and significant amounts of aromatics.

Phase behavior calculations using the Peng-Robinson equation of state and component lumping procedures provided reasonable agreement between calculated and experimental results for the crude oil and bitumen extractions, but failed in the prediction of the bitumen-derived liquid extractions.

The specific conclusions drawn from this study are as follows:

1) Pure solvent density is not the only parameter that controls extraction efficiency. Factors such as the vicinity of the extraction temperature to the critical temperature of the pure solvent also appear to affect the extraction yields. Both the solvents, CO₂ and propane, exhibit enhanced extraction in the vicinity of their respective critical temperatures for feedstocks ranging from a light paraffinic crude to a heavy naphthenic oil. Higher extraction yields can be obtained at lower reduced solvent densities when the extraction temperatures are in the vicinity of pure solvent critical temperature.

2) Heavier compounds are extracted as extraction time and extraction pressure increase for the extractions of naturally occurring petroleum materials such as crude oil and native bitumen. However, no preferential extraction can be expected for the extractions of thermally processed oils such as the bitumen-derived liquid. This can be attributed to the presence of olefins and aromatics in the bitumen-derived liquid and to its thermal history.

3) EOS models and component-lumping methods can be used to

describe a typical extraction sequence. However, this approach is incapable of handling unusual extraction behavior like that exhibited by the bitumen-derived liquid.

FUTURE ACTIVITIES

A series of propane supercritical extraction experiments will be conducted with a high asphaltene content bitumen from the PR Spring oil sand deposit.

BITUMEN UPGRADING

Principal Investigator
Graduate Student

J.W. Bunger
J. Pu

The upgrading process options include the following:

- o Visbreaking
- o Coking
- o Hydropyrolysis
- o Hydrocracking
- o Catalytic cracking
- o Steam cracking
- o Catalytic hydrotreating

Comparison Criterion

The comparison criterion is economics. It is because every engineering structure, with few exceptions, is first suggested by economic requirements; and the design of every component, with few exceptions, and of the whole are finally evaluated from the economic standpoint.^[232]

In general, the preferred economic evaluation methods are net present value (NPV) and internal rate of return (IRR).

Net present value discounts all the future cash flows at the chosen discount rate in order to reduce them to their net cumulative values at the start of the project. If this single cumulative present value is positive, then the project is expected to earn more than the company's required minimum rate of return. A higher NPV is indicative of the preferred investment from among the alternative projects competing at any one time. This assumes

the same discount rate is used and all the projects are discounted to the same point in time.

Internal rate of return determines the highest interest rate that hypothetically could be paid on money borrowed for a project, based on the project's cash-flow schedule, and still allows the project to break even over its economic life. This breakeven discount rate then can be compared to the company's minimum acceptable rate of return to see if it meets or exceeds that standard. The project having higher IRR would be selected from among the alternative competing projects.

Process Details

Except for hydrocracking, all the process options listed in part 1 have been studied as a part of the University of Utah tar sands program. With the experimental data, several computer software, such as ASPEN, PROCESS, can be used for this purpose. So, how detail of the process should be considered. Since this work is a comparative study not a process design and/or optimization, simplified process schemes will be used. The block diagrams are presented in Figures 109 and 110.

Based on the simulation results, the economic criteria can be calculated.

FUTURE ACTIVITIES

Looking for the kinetics data of hydrocracking since the University of Utah did not do the experiments of upgrading bitumen by this process before.

Kinetics models of all the processes involved.

Figure 109. Simplified Thermal Process Scheme

Figure 110. Simplified Hydroprocessing Scheme

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